University of Belgrade, Technical Faculty in Bor

29th International Conference Ecological Truth
& Environmental Research

EcoTER'22

Proceedings

Editor
Prof. Dr Snežana Šerbula

21-24 June 2022, Hotel Sunce, Sokobanja, Serbia

University of Belgrade, Technical Faculty in Bor

29th International Conference Ecological Truth
& Environmental Research

EcoTER’22

Proceedings

Editor
Prof. Dr Snežana Šerbula

21-24 June 2022, Hotel Sunce, Sokobanja, Serbia

PROCEEDINGS

29th INTERNATIONAL CONFERENCE

ECOLOGICAL TRUTH AND ENVIRONMENTAL RESEARCH – EcoTER'22

Editor:

Prof. Dr Snežana Šerbula

University of Belgrade, Technical Faculty in Bor

Technical Editors:

Dr Jelena Milosavljević

University of Belgrade, Technical Faculty in Bor

Asst. Prof. Dr Ana Radojević

University of Belgrade, Technical Faculty in Bor

Dr Jelena Kalinović

University of Belgrade, Technical Faculty in Bor

Asst. Prof. Dr Tanja Kalinović

University of Belgrade, Technical Faculty in Bor

Asst. Prof. Dr Žaklina Tasić

University of Belgrade, Technical Faculty in Bor

Publisher: University of Belgrade, Technical Faculty in Bor

For the Publisher: Prof. Dr Nada Štrbac, Dean

Printed: GRAFIK CENTAR DOO Beograd, 120 copies

Year of publication: 2022

ISBN 978-86-6305-123-2

CIP - Каталогизација у публикацији
Народна библиотека Србије, Београд

502/504(082)(0.034.2)
574(082)(0.034.2)

INTERNATIONAL Conference Ecological Truth & Environmental Research (29 ; 2022 ; Sokobanja)
Proceedings [Elektronski izvor] / 29th International Conference Ecological Truth and Environmental Research - EcoTER'22, 21-24 June 2022, Sokobanja, Serbia ; [organized by University of Belgrade, Technical faculty in Bor (Serbia)] ; [co-organizers University of Banja Luka, Faculty of Technology – Banja Luka (B&H) ... [et al.]] ; editor Snežana Šerbula. - Bor : University of Belgrade, Technical faculty, 2022 (Beograd : Grafik centar). - 1 USB fleš memorija ; 5 x 5 x 1 cm

Sistemski zahtevi: Nisu navedeni. - Nasl. sa naslovne strane dokumenta. - Tiraž 120. - Bibliografija uz svaki rad. - Registar.

ISBN 978-86-6305-123-2

а) Животна средина -- Зборници б) Екологија -- Зборници

COBISS.SR-ID 69053705

29th International Conference Ecological Truth and Environmental Research 2022

is organized by:

UNIVERSITY OF BELGRADE, TECHNICAL FACULTY IN BOR (SERBIA)

Co-organizers of the Conference:

University of Banja Luka, Faculty of Technology
– Banja Luka (B&H)

University of Montenegro, Faculty of Metallurgy and Technology
– Podgorica (Montenegro)

University of Zagreb, Faculty of Metallurgy
– Sisak (Croatia)

University of Pristina, Faculty of Technical Sciences
– Kosovska Mitrovica

Association of Young Researchers – Bor (Serbia)

The Conference is financially supported by

the Ministry of Education, Science and Technological

Development of the Republic of Serbia

Platinum Donor of the Conference

HONORARY COMMITTEE

Dr Petar Paunović, Zaječar (Serbia)
Prof. Dr Stevan Stanković, Bor (Serbia)
Prof. Dr Zvonimir Stanković, Bor (Serbia)
Prof. Dr Velizar Stanković, Bor (Serbia)
Dragan Ranđelović, Society of Young Researchers – Bor (Serbia)
Toplica Marjanović, Society of Young Researchers – Bor (Serbia)
Mihajlo Stanković, Special Nature Reservation of Zasavica, Sremska Mitrovica (Serbia)

SCIENTIFIC COMMITTEE

Prof. Dr Snežana Šerbula, ***President***

Prof. Dr Alok Mittal
(India)
Prof. Dr Jan Bogaert
(Belgium)
Prof. Dr Aleksandra Nadgórska-Socha
(Poland)
Prof. Dr Luis A. Cisternas
(Chile)
Prof. Dr Wenhong Fan
(China)
Prof. Dr Martin Brtnický
(Czech Republic)
Prof. Dr Isabel Maria De Oliveira Abrantes
(Portugal)
Prof. Dr Shengguo Xue
(China)
Prof. Dr Tomáš Lošák
(Czech Republic)
Prof. Dr Maurice Millet
(France)
Prof. Dr Murray T. Brown
(New Zealand)
Prof. Dr Xiaosan Luo
(China)
Prof. Dr Daniel J. Bain
(United States of America)
Prof. Dr Che Fauziah Binti Ishak
(Malaysia)
Prof. Dr Richard Thornton Baker
(United Kingdom)
Prof. Dr Mohamed Damak
(Tunisia)
Prof. Dr Jyoti Mittal
(India)
Prof. Dr Miriam Balaban
(United States of America)
Prof. Dr Fernando Carrillo-Navarrete
(Spain)
Prof. Dr Pablo L. Higueras
(Spain)
Prof. Dr Mustafa Cetin
(Turkey)
Prof. Dr Mauro Masiol
(Italy)
Prof. Dr George Z. Kyzas
(Greece)
Prof. Dr Mustafa Imamoğlu
(Turkey)
Prof. Dr Petr Solzhenkin (Russia)

Prof. Dr Yeomin Yoon
(United States of America)
Prof. Dr Chang-min Park
(South Korea)
Prof. Dr Faramarz Doulati Ardejani
(Iran)
Prof. Dr Ladislav Lazić
(Croatia)
Prof. Dr Natalija Dolić
(Croatia)
Prof. Dr Milutin Milosavljević
(Kosovska Mitrovica)
Prof. Dr Nenad Stavretović
(Serbia)
Prof. Dr Ivan Mihajlović
(Serbia)
Prof. Dr Milovan Vuković
(Serbia)
Prof. Dr Nada Blagojević
(Montenegro)
Prof. Dr Darko Vuksanović
(Montenegro)
Prof. Dr Irena Nikolić
(Montenegro)
Prof. Dr Šefket Goletić
(B&H)
Prof. Dr Džafer Dautbegović
(B&H)
Prof. Dr Borislav Malinović
(B&H)
Prof. Dr Slavica Sladojević
(B&H)
Prof. Dr Nada Šumatić
(B&H)
Prof. Dr Mirjana Rajčić Vujasinović
(Serbia)
Prof. Dr Snežana Milić
(Serbia)
Prof. Dr Dejan Tanikić
(Serbia)
Prof. Dr Milan Trumić
(Serbia)
Dr Jasmina Stevanović
(Serbia)
Dr Dragana Đorđević
(Serbia)
Dr Jelena Milojković
(Serbia)

ORGANIZING COMMITTEE

Prof. Dr Snežana Šerbula, *President*
Prof. Dr Snežana Milić, *Vice President*
Prof. Dr Đorđe Nikolić, *Vice President*
Prof. Dr Milica Veličković (Serbia)
Prof. Dr Danijela Voza (Serbia)
Prof. Dr Maja Nujkić (Serbia)
Dr Ana Simonović (Serbia)
Dr Tanja Kalinović (Serbia)
Dr Ana Radojević (Serbia)
Dr Žaklina Tasić (Serbia)
Dr Jelena Kalinović (Serbia)
Dr Jelena Milosavljević (Serbia)
Dr Dragana Medić (Serbia)
Aleksandra Papludis, MSc (Serbia)
Sonja Stanković, MSc (Serbia)
Vladan Nedelkovski, MSc (Serbia)
Mara Manzalović, English language teacher (Serbia)
Enisa Nikolić, English language teacher (Serbia)

PREFACE

In today’s world, the environment has been endangered by the use of outdated technology, fossil fuels and environmental law violations. Therefore, environmental and many other scientists all over the world have been concerned about finding sustainable technology in resolving these issues. That is why environmental research and ecological truth are at the focus of the 29th International Conference Ecological Truth & Environmental Research 2022 (EcoTER’22), which will be held in Sokobanja, Serbia, 21–24 June 2022. On behalf of the Organizing Committee, it is a great honor and pleasure to wish all the participants a warm welcome to the Conference.

We hope to convey the message of the conference, which is that a transformation of attitudes and behavior would bring the necessary changes. This is also an opportunity for the participants who are experts in this field to exchange their experiences, expertise and ideas, and also to consider the possibilities for their collaborative research.

The 29th International Conference Ecological Truth & Environmental Research 2022 is organized by the University of Belgrade, Technical Faculty in Bor, and co-organized by the University of Banja Luka, Faculty of Technology, the University of Montenegro, Faculty of Metallurgy and Technology – Podgorica, the University of Zagreb, Faculty of Metallurgy – Sisak, the University of Pristina, Faculty of Technical Sciences – Kosovska Mitrovica and the Association of Young Researchers, Bor.

These proceedings include 85 papers from the authors coming from the universities, research institutes and industries in 6 countries: Bulgaria, Italia, Albania, Bosnia and Herzegovina, Montenegro and Serbia.

As a part of this year's conference, the 4th Student section – EcoTERS’22 is being held. We appreciate the contribution of the students and their mentors who have also participated in the Conference.

Financial assistance provided by the Ministry of Education, Science and Technological Development of the Republic of Serbia is gratefully acknowledged by the Organizing Committee of the EcoTER’22 conference.

The support of the Platinum donor and their willingness and ability to cooperate have been of great importance for the success of EcoTER’22. The Organizing Committee would like to extend their appreciation and gratitude to the Platinum donor of the Conference for their donation and support.

We appreciate the effort of all the authors who have contributed to these Proceedings. We would also like to express our gratitude to the members of the scientific and organizing committees, reviewers, speakers, chairpersons and all the Conference participants for their support to EcoTER’22. Sincere thanks go to all the people who have contributed to the successful organization of EcoTER’22.

Prof. Snežana Šerbula,

President of the Organizing Committee

TABLE OF CONTENTS

Plenary Lectures

Conference Papers

Plenary Lectures

EcoTER'22
29th International Conference Ecological Truth
& Environmental Research
21 - 24 June 2022, Hotel Sunce, Sokobanja, Serbia
www.eco.tfbor.bg.ac.rs

PURINES AS GREEN CORROSION INHIBITORS

Marija Petrović Mihajlović[1*], **Milan Antonijević**[1]
[1]University of Belgrade, Technical Faculty in Bor, V.J. 12, 19210 Bor, SERBIA
[*]*mpetrovic@tfbor.bg.ac.rs*

Abstract

Metals present one of the major groups of materials used for all kinds of different applications in various environments. Often those environments pose a threat regarding the stability and preservation of metals and they undergo corrosion. Corrosion processes lead to several consequences that can have a detrimental effect on the environment such as metals release due to dissolution, leakage of various chemicals that are stored in reservoirs or transported via pipelines. These processes should be diminished, and one of the ways of metals protection is the application of corrosion inhibitors. There is a great number of the potential inhibitors tested, however, some of them have undesired effects on the environment and health. Purines present bioorganic compounds that show a tendency to interact with metals and form complexes that can adsorb on the surface of metal and that characteristic indicates that potentially they can efficiently inhibit corrosion. This is confirmed within numerous studies and those results are presented and discussed. Most of them are done using copper with the addition of purine or adenine, however, other derivatives are studied as well. Common conclusion is that the increase in the number of heteroatoms and molecular size leads to inhibition efficiency increase.

Keywords: corrosion inhibitors, environmentally friendly, purine

INTRODUCTION

Wide world applications of metal materials in various environments, that present media of different degree of corrosiveness, might account for significant release of metals. Exposure of metals to different chemical agents, such as solutions of acids, salts or alkalis, in industrial applications might lead to their corrosion. On the other hand, natural surroundings can also cause similar effects. For instance marine environment is considered to be very corrosive [1,2]. However, having in mind some examples such as offshore wind farms [3], antifouling coatings based on metal oxides [4] etc., the need for metal exploitation in sea water becomes obvious. Moreover, the unintentional depositions of metals in the form of shipwrecks contribute to the metal content as well [5]. Atmospheric corrosion in coastal areas is also significant [6]. Rain water in the urban environment induces release of metals, also the behavior of metals differs in the cases when they are present in bulk and in alloys and that has to be considered when the effects on the environment and health are studied [7]. According to Bertling *et al*. [8] most of the copper that is released to runoff water from patinated copper roofs is retained on solid surfaces and soil [8]. Similar findings are reported by Wallinder *et al*. [9] regarding stainless steel. Consideration of all the above mentioned data points to the fact that the cycle of metals in the environment is very important to study and understand in order to have a clear picture of the amounts of metals that can be found in the environment and the effect that they can have. High amounts of metals due to dissipative releases can have a significant adverse effects on the environment quality, and on the other hand present the loss of resources. Detailed study regarding copper is presented by Lifset *et al*. [10].

On the other hand, as seen in the paper published by Kirchgeorg *et al*. [3], the corrosion protection systems can also be a source of metals and organic compounds. Already mentioned marine environment requires efficient corrosion protection, however, it should be carefully designed in order to protect environment from polluting releases, and Rossini [4] pointed out the need for more environmentally friendly coatings. When corrosion inhibitor reaches the environment, water, soil etc. it can also have an effect on the growth and development of the living organisms such as plants, and on the uptake of the other present elements. This is clearly presented in the study published by Liu *et al*. [11] regarding the effect of widely used corrosion inhibitor benzotriazole. Hence, numerous eco-friendly corrosion inhibitors are studied by now [12–16].

One of the groups of compounds that can be considered as bioorganic compounds and have a potential to be used as green environmentally friendly corrosion inhibitors is group of purines. Purines are components of various biochemical compounds, among others, they are found in DNA and RNA, so they are present in human body and involved in very important metabolic processes. On the other hand purine and adenine and their derivatives have a tendency to react with metal ions and form complexes. Structures and the atoms that are involved in coordination between metal and organic part of the complexes differ depending on the form of organic molecule since it can be in the form of neutral molecule, anion and cation [17,18]. Based on the possibility to react and form bonds with metals purine and derivatives are considered to have a potential to inhibit corrosion of metals. Another very specific area of metals application is the area of biomaterials. Hence, back from the 80s [19], the metals release from dental biomaterials became an important topic which importance just grow during time [20]. Pourbaix [21] started studying the appearance of corrosion of metals used as biomaterials in 1984, and the research still continues nowadays [22]. One of the applications of copper as biomaterial is in the construction of intrauterine devices (IUD) [23–26]. Due to their origin and characteristics, since some purine and adenine derivatives may be used in various medical treatments [27,28], these compounds are considered as the potential inhibitors of corrosion of metallic biomaterials in real or simulated body fluids, as well [29–32]. The broad area of possible applications and characterization of these compounds as environmentally friendly and non-toxic indicate that they should receive adequate attention.

DISCUSSION

The most often studied compounds belonging to this group are purine and adenine. Their structure is presented in figure 1. They contain imidazole and pyrimidine ring, whereas adenine also has amino group in its molecule. Purine and adenine as copper and brass corrosion inhibitors were studied in several different media such as chloride [33,34], sulfate [35–38] and nitrate [39] solutions. The results can be seen in Table 1 and the mechanism of their action is described as formation of adsorbed protective layer, $[\mathrm{Cu\text{-}INH}]_{ads}$, on metal surface.

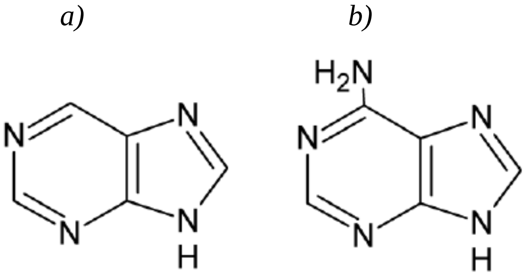


***Figure 1** Molecular structure of a) purine; b) adenine*

In chloride solution reaction mechanism is proposed as follows, depending on the starting form of copper [33,34]:

$CuCl_{ads} + INH \leftrightarrow [Cu\text{-}INH]_{ads} + Cl^{-} + H^{+}$ (1)

$Cu + INH - e^{-} \leftrightarrow [Cu\text{-}INH]_{ads} + H^{+}$ (2)

$nCuCl_{2}^{-} + nINH \leftrightarrow (Cu\text{-}INH)_{n} + nH^{+} + 2nCl^{-}$ (3)

$[Cu\text{-}INH]_{ads} + (Cu\text{-}INH)_{n} \leftrightarrow [(Cu\text{-}INH)_{m}]_{ads}$, where $m = n+1$. (4)

The proposed model of inhibitor action includes adsorption via Cu-N bond or interaction of π electrons of aromatic ring with Cu or electrostatic interactions enhanced by adsorption of negatively charged chloride ions. More detailed adsorption mechanism is provided later based on new theoretical findings.

***Table 1** Copper and brass corrosion inhibition efficiency obtained using purine and adenine*

Inhibitor	Concentration, M	Medium	Inhibition efficiency, %	Reference
Purine	$1\cdot10^{-2}$	1 M NaCl	76^{a}	[33]
Adenine	$1\cdot10^{-2}$	1 M NaCl	92^{a}	[34]
Purine	$1\cdot10^{-2}$	0.5 M $NaNO_3$	$90^{a}/91^{b}$	[39]
Adenine			$91^{a}/96^{b}$	
Purine	$1\cdot10^{-2}$	0.5 M Na_2SO_4 pH 6.8	91^{b}	[35]
Adenine			94^{b}	
Purine		0.5 M Na_2SO_4 pH 1.0	78.6^{b}	
Adenine			88.1^{b}	
Purine	$1\cdot10^{-2}$	0.5 M Na_2SO_4 pH 6.8	76^{a}	[36]
Adenine			91^{a}	
Purine	$1\cdot10^{-2}$	0.5 M Na_2SO_4 pH 7.0	91.08^{a}	[37]
		0.5 M Na_2SO_4 pH 9.0	88.88^{a}	
Purine	$1\cdot10^{-2}$	0.5 M Na_2SO_4 pH 7.0	85.2^{a}	[38]
		0.5 M Na_2SO_4 pH 9.2	91.0^{a}	

Inhibition efficiency values obtained using: [a] potentiodynamic polarization, [b] weight loss.

Petrovic *et al.* [40] studied purine (PU), adenine (AD) and 6-benzylaminopurine (BAP) as copper corrosion inhibitors in weakly alkaline solution containing chloride ions (0.1 mol dm^{-3} $Na_2B_4O_7$, 0.05 mol dm^{-3} NaCl). The experimental results, presented in the Table 2, indicated that the increase in molecular size and weight leads to the increase of the inhibition efficiency. Since the molecules studied may have different forms depending on the pH value of the media it has to be considered when the mechanism of the interaction with metals surface is proposed. According to Scendo [33], in weakly alkaline media PU is in the form of neutral molecule, whereas AD and BAP can also be found in anion form [34,39,41]. In that case adenine tends to react with Cu(I) ions and complex Cu(I)-adenine can be formed [42]. Hence, the proposed mechanism can be one of the following:

$$Cu^{+} + INH_{(ads)} \leftrightarrow [Cu(I)\text{-}INH]^{+} \quad (5)$$

$$Cu^{+} + INH^{-}_{(ads)} \leftrightarrow Cu(I)\text{-}INH \quad (6)$$

Analysis of the data regarding sulfate solutions presented in Table 1 confirms the conclusion that inhibition efficiency depends on the pH value. Purine and adenine show superior protection in neutral media, however they can be efficiently used also in acidic [35] or weakly alkaline solutions [37]. The mode of adsorption can be described by Langmuir adsorption isotherm [34–39]. In this media reaction mechanism can be proposed as follows [37]:

$$4Cu + 4PU_{(ads)} + O_2 \leftrightarrow 4Cu(I)\text{-}PU + 2H_2O \quad (7)$$

Both inhibitors influence cathodic and anodic reactions so they are considered to be mixed type inhibitors. The look of the brass surface, Figure 2, after polarization without and with the addition of purine can elucidate the need for inhibitor application and proper choice of inhibitor.

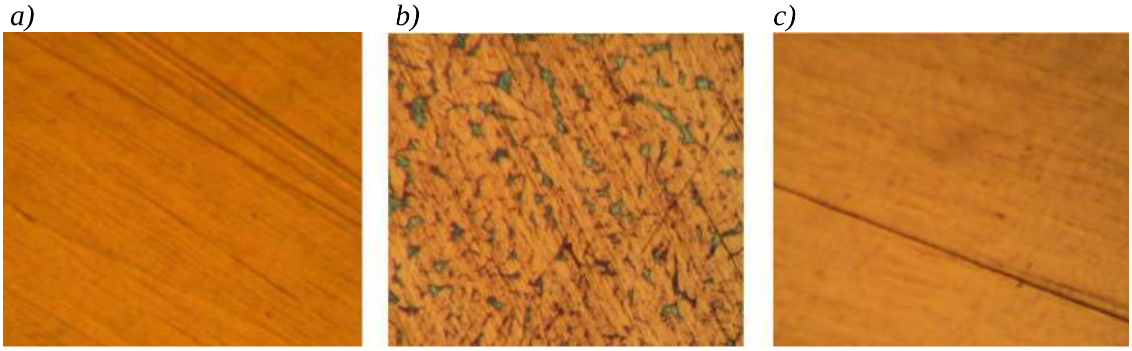


Figure 2 *Brass surface after polishing a) after chronoamperometric measurements at 0V vs. SCE in weakly alkaline 0.5 mol/dm^3 Na_2SO_4 solution, b) and after chronoamperometric measurements at 0V vs. SCE in weakly alkaline 0.5mol/dm^3 Na_2SO_4 solution with $1\cdot10^{-2}$ mol/dm^3 purine c) (magnified 200x) [38]*

The possibility to enhance the effect of adenine by the addition of cetyltrimethylammonium bromide (CTAB) is studied in synthetic sea water [43]. As can be seen from the data, Table 2, beneficial effect of CTAB is confirmed by the experimental results.

Based on the all of the results mentioned above, it was logical to broaden the research and provide some more insight into how the molecular structure influences the inhibition efficiency values and guidance for adequate inhibitor choice. Petrović Mihajlović *et al*. [44] applied imidazole, purine, adenine and 6-benzylaminopurine as corrosion inhibitors, and the expected trend was confirmed since the inhibition efficiency increased as following: imidazole < purine < adenine < 6-benzylaminopurine. Electrochemical experiments were substantiated by quantum chemical calculations and correlation of some parameters with inhibition efficiency is noticed. When structurally similar compounds are studied lower value of ΔE ($\Delta E = E_{LUMO} - E_{HOMO}$) and decrease of global hardness (η) or increase of dipole moment (μ) indicate that it can be expected that compound can perform as better corrosion inhibitor.

***Table 2** Copper corrosion inhibition efficiency obtained using purine and derivatives*

Inhibitor	Concentration, M	Medium	Inhibition efficiency, %	Reference
Adenine	$1\cdot10^{-3}$	Synthetic seawater	84.35[a]	[43]
	$5\cdot10^{-3}$		92.17[a]	
CTAB	15 ppm		68.70[a]	
Adenine + CTAB	$1\cdot10^{-3}$ M + 15 ppm		91.30[a]	
Purine	$1\cdot10^{-3}$	0.1 M $Na_2B_4O_7$ + 0.05 M NaCl	78.38[a]	[40]
Adenine	$1\cdot10^{-3}$		78.65[a]	
6-benzylaminopurine	$1\cdot10^{-3}$		83.78[a]	
Purine	$5\cdot10^{-3}$	Synthetic seawater	91.91[a]	[44]
Adenine	$5\cdot10^{-3}$		92.17[a]	
6-benzylaminopurine	$5\cdot10^{-3}$		94.43[a]	
Purine	$1\cdot10^{-2}$ in NaCl 3h	SUF	85[b]	[30]
Adenine	$1\cdot10^{-2}$	BM3	88.10[a]/89.69[c]	[32]
2,6-diaminopurine	$1\cdot10^{-2}$		87.18[a]/90.10[c]	
Adenine + potassium sorbate	$1\cdot10^{-2}$ M + 0.01%		91.17[a]	
2,6-diaminopurine + potassium sorbate	$1\cdot10^{-2}$ M + 0.01%		93.02[a]	
			IE% at -0.1 V vs SCE	
Purine	$1\cdot10^{-3}$, 1 h	SUF	61.20[a]	[29]
	$1\cdot10^{-3}$, 3 h		98.61[a]	
	$1\cdot10^{-2}$, 1 h		98.10[a]	
	$1\cdot10^{-2}$, 3 h		99.18[a]	

Inhibition efficiency values obtained using: [a]potentiodynamic polarization, [b]polarization resistance, [c]electrochemical impedance spectroscopy.

However, quantum chemical calculations are considered to be insufficient to provide dipper understanding of metal-inhibitor interactions so corrosion inhibition mechanism of these compounds was further studied by Kumar *et al*. [45] using density functional theory (DFT) and reactive force fields (ReaxFF). They studied the adsorption of imidazole, purine, adenine and 6-benzylaminopurine on Cu (111) surface and the interactions that occur between the surface and inhibitor molecules. The results of quantum chemical calculations were in accordance with our calculations and experimental findings. Adsorption studies indicated that all of the tested compounds do adsorb on Cu surface while the interaction energy increases from imidazole towards 6-benzylaminopurine, whereas higher values are obtained for parallel orientation of adenine and perpendicular orientation for all other compounds. Charge distribution indicates that adenine and Cu (111) surface interact via electrostatic and van der Waals interactions, whereas adsorption of imidazole, purine and BAP occurs via, one or in the case of BAP two, Cu-N covalent bond formation and weak van der Waal's and H-Cu interactions.

Purine and adenine also have the ability to inhibit copper corrosion in the hydrocarbon medium [46] and under the high temperature are humidity conditions that can be found in the production of chips and LSI devices [47]. In both cases thin protective inhibitor film is formed on copper surface.

Non-toxic characteristics inspired some other investigations as potential inhibitors for applications in human organisms. Alvarez *et al.* [29,31] studied the effect of purine [29], 6-mercaptopurine (6-MP) [31] and pterin (PT) [31] on corrosion of copper in simulated uterine fluid (SUF). This could find its application for the treatment of intrauterine devices IUDs that are used for birth control. In both cases inhibitor was applied as pretreatment before testing in SUF. The desired effect of reduction of burst release and providing of continual release of small dose that enables contraception effect is achieved by a complex mechanism including adsorption of inhibitor and chloride ions described by the following reactions [31]:

$$\mathrm{Cu(6\text{-}MP)_{ad}+Cl^{-}\rightarrow Cu(Cl)_{ad}+6\text{-}MP+e^{-}} \quad (8)$$

$$\mathrm{Cu+H_2O\leftrightarrow Cu(OH)_{ad}+H^{+}+e^{-}} \quad (9)$$

$$\mathrm{Cu+Cl^{-}\leftrightarrow Cu(Cl)_{ad}+e^{-}} \quad (10)$$

Purine pretreatment and its adsorption on copper surface in aqueous and NaCl media was studied in more detail by Alonso *et al.* [30]. Quartz crystal microbalance (QCM) was applied in order to directly monitor mass change due to purine adsorption. Interestingly greater increase of mass is noticed in chloride solution and in the presence of lower concentration of purine. However, an explanation is also proposed. In the presence of high purine concentration it adsorbs on the pure Cu surface, whereas in the presence of lower purine concentration and chloride ions, chloride compounds of copper are formed that further react with purine and form Cu(I)-purine complex. X-ray photoelectron spectroscopy (XPS) measurements confirmed these assumptions since there is a difference in the composition of products on copper surface. In the presence of high $1\cdot10^{-2}$ mol dm^{-3} - $1\cdot10^{-3}$ mol dm^{-3} purine concentration purine chemisorption on pure copper surface occurs and $(\mathrm{Cu(0)\text{-}PU})_{ads}$ forms. When purine concentration is lower such as $1\cdot10^{-4}$ mol dm^{-3} there are compounds of copper and chlorine beside the $[\mathrm{Cu(I)\text{-}PU}]_{ads}$ compound.

Petrovic Mihajlovic *et al.* [32] studied the possibility to apply purine compounds, adenine and 2,6-diaminopurine (DAP), as copper corrosion inhibitors in simulated blood plasma (BM3). This medium is complex regarding its composition, however dominant ions and molecules that interact with copper are oxygen, hydrogen and chloride, so the products are copper ions, oxides, hydroxides and chlorides. When adenine or 2,6-diaminopurine are present in the solution peaks that correspond to copper oxidation are either shifted towards more positive potentials or disappear if the concentration is high enough. Reason for such behavior can be found in the reaction and formation of complexes Cu(I)-AD/Cu(I)-DAP at lower potentials, and Cu(II)-AD/Cu(II)-DAP at higher potentials due to oxidation of Cu(I) to Cu(II) [44,48]. Higher concentration of AD or DAP enables better surface coverage by adsorbed molecules and thus the oxidation of copper is hindered [30,34,44]. The adsorption of inhibitor molecules on copper surface was also confirmed by scanning electron microscope coupled with energy dispersive spectroscopy (SEM-EDS), Figure 3. As already seen before, further improvement of inhibition efficiency can be provided if the mixture of inhibitors that show synergistic effect is used. In this case potassium sorbate was used since it is safe compound regarding health and is frequently used as food additive and preservative [49,50].

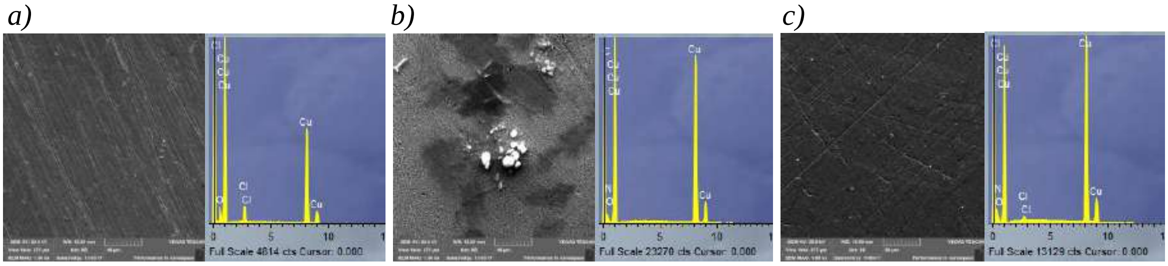


***Figure 3** SEM images and EDS spectrum of copper surface obtained after 7 days immersion in a) BM3 solution and with the addition of b) $1 \cdot 10^{-2}$ M adenine, c) $1 \cdot 10^{-2}$ M 2,6-diaminopurine [32]*

CONCLUSION

Purine compounds, including purine, adenine, 6-mercaptopurine, 2,6-diaminopurine and 6-benzylaminopurine, showed good properties as inhibitors of corrosion of copper and its alloy, brass. They are efficient in numerous media such as chloride, sulfate, nitrate solutions, synthetic seawater, and synthetic body fluids such as blood plasma and uterine fluid. The obtained inhibition efficiency depends among other conditions on the pH value of the test media. Their influence is a results of interaction with metal surface via adsorption and complex formation. The adsorption is confirmed using surface analysis methods such as SEM and the mode of adsorption and most probable orientations and places for interaction are proposed using theoretical calculations. Inhibition efficiency rises as the molecular size and number of heteroatoms increase. The values of inhibition efficiency can be further improved by the addition of compounds providing synergistic effect such as CTAB and potassium sorbate. These inhibitors can be used as the addition to the corrosive media or as a pretreatment.

ACKNOWLEDGEMENT

The authors are grateful to the Ministry of Education, Science and Technological development of the Republic of Serbia for financial support (451-03-68/2022-14/200131).

REFERENCES

[1] N.W. Farro, L. Veleva, P. Aguilar, Open Corros. J; 2 (2009) 130–138.

[2] L. Núñez, E. Reguera, F. Corvo, *et al*., Corros. Sci; 47 (2005) 461–484.

[3] T. Kirchgeorg, I. Weinberg, M. Hörnig, *et al*., Mar. Pollut. Bull; 136 (2018) 257–268.

[4] P. Rossini, L. Napolano, G. Matteucci, Chemosphere; 237 (2019) 124475.

[5] J.N. Hahladakis, M. Stylianos, E. Gidarakos, J. Hazard. Mater; 250–251 (2013) 256–264.

[6] I.O. Wallinder, X. Zhang, S. Goidanich, *et al*., Sci. Total Environ; 472 (2014) 681–694.

[7] G. Herting, S. Goidanich, I. O. Wallinder, *et al.*, Environ. Monit. Assess; 144 (2008) 455–461.

[8] S. Bertling, I.O. Wallinder, D.B. Kleja, *et al.*, Environ. Toxicol. Chem; 25 (2006) 891–898.

[9] I.O. Wallinder, S. Bertling, D.B. Kleja, *et al.*, Water Air Soil Pollut; 170 (2006) 17–35.

[10] R.J. Lifset, M.J. Eckelman, E.M. Harper, *et al.*, Sci. Total Environ; 417–418 (2012) 138–147.

[11] Z. Liu, L. Wang, C. Wang, *et al.*, Chemosphere; 186 (2017) 24–30.

[12] M. Shahid, Adv. Nat. Sci: Nanosci. Nanotechnol; 2 (2011) 043001.

[13] M.M. Antonijević, M.B. Petrović, Int. J. Electrochem. Sci; 3 (2008) 1–28.

[14] M.B. Petrović Mihajlović, M.M. Antonijević, Int. J. Electrochem. Sci; 10 (2) (2015) 1027–1053.

[15] Ž.Z. Tasić, M.B. Petrović Mihajlović, M.B. Radovanović, *et al.*, Chem. Pap; 73 (2019) 2103–2132.

[16] M.A. Quraishi, D.S. Chauhan, V.S. Saji, J. Mol. Liq; 341 (2021) 117265.

[17] A. Domínguez-Martín, M. del Pilar Brandi-Blanco, A. Matilla-Hernández, *et al.*, Coord. Chem. Rev; 257 (19–20) (2013) 2814–2838.

[18] D. Choquesillo-Lazarte, M. del Pilar Brandi-Blanco, I. García-Santos, *et al.*, Coord. Chem. Rev; 252 (10–11) (2008) 1241–1256.

[19] D. Brune, Biomaterials; 7 (1986) 163–175.

[20] A. Martín-Cameán, Á. Jos, P. Mellado-García, *et al.*, Environ. Toxicol. Pharmacol; 40 (2015) 86–113.

[21] M. Pourbaix, Biomaterials; 5 (1984) 122–134.

[22] C. Zhang, J. Liu, W. Yu, *et al.*, Mater. Sci. Eng. C; 55 (2015) 267–271.

[23] S. Benjamín Valdez, G. Navor Rosas, B. Mónica Carrillo, *et al.*, Anti-Corrosion Methods Mater; 50 (2003) 129–135.

[24] X.X. Xu, F.L. Nie, J.X. Zhang, *et al.*, Mater. Lett; 64 (2010) 524–527.

[25] X.X. Xu, F.L. Nie, Y.B. Wang, *et al.*, Acta Biomater; 8 (2012) 886–896.

[26] D. Wildemeersch, P.J. Sabbe, M.G. Dowsett, *et al.*, Contraception; 90 (2014) 454–459.

[27] J.R. Bertino, W.R. Waud, W.B. Parker, *et al.*, Cancer Biol. Ther; 11 (2011) 627–632.

[28] E. De Clercq, Antiviral Res; 75 (2007) 1–13.

[29] F. Alvarez, P.L. Schilardi, M.F.L. De Mele, Contraception; 85 (2012) 91–98.

[30] C. Alonso, E. Casero, E. Román, *et al.*, Electrochim. Acta; 189 (2016) 54–63.

[31] F. Alvarez, C. Grillo, P. Schilardi, *et al.*, ACS Appl. Mater. Interfaces; 5 (2013) 249–255.

[32] M.B. Petrović Mihajlović, M.B. Radovanović, A.T. Simonović, *et al.*, Results Phys; 14 (2019) 102357.

[33] M. Scendo, Corros. Sci; 49 (2) (2007a) 373–390.

[34] M. Scendo, Corros. Sci; 50 (7) (2008a) 2070–2077.

[35] M. Scendo, Corros. Sci; 49 (2007b) 3953–3968.

[36] M. Scendo, Corros. Sci; 49 (7) (2007c) 2985–3000.

[37] M.B. Petrović, A.T. Simonović, M.B. Radovanović, *et al.*, Chem. Pap; 66 (2012) 664–676.

[38] M.B. Radovanović, A.T. Simonović, M.B. Petrović, *et al.*, Int. J. Electrochem. Sci; 7 (2012) 11796–11810.

[39] M. Scendo, Corros. Sci; 50 (6) (2008b) 1584–1592.

[40] M. Petrović, M. Radovanović, A. Simonović, *et al.*, 6. Simpozijum Hemija i zaštita životne sredine EnviroChem 2013 sa međunarodnim učešćem, Vršac, Serbia (2013) 182.

[41] P Barták, D. Pěchova, P. Tarkowski, *et al.*, Anal. Chim. Acta; 421 (2000) 221–229.

[42] F. Jelen, A. Kourilova, S. Hason, *et al.*, Electroanal; 21 (2009) 439–444.

[43] M. Petrović, M. Radovanović, A. Simonović, *et al.*, 16. YuCorr, Tara, Serbia (2014) 204.

[44] M.B. Petrović Mihajlović, M.B. Radovanović, Ž.Z. Tasić, *et al.*, J. Mol. Liq; 225 (2017) 127–136.

[45] D. Kumar, V. Jain, B. Rai, Corros. Sci; 171 (2020) 108724.

[46] M. Levin, P. Wiklund, C. Leygraf, Corros. Sci; 58 (2012) 104–114.

[47] M. Hara, D. Watanabe, C. Kimura, *et al.*, Jpn. J. Appl. Phys; 48 (2009) 04C016.

[48] N. Aladag, L. Trnkova, A. Kourilova, *et al.*, Electroanalysis; 22 (2010) 1675–1681.

[49] A.A. Ghoneim, R.S. El-Kamel, A.M. Fekry, Int. J. Hydrogen Energy; 45 (46) (2020) 24370–24382.

[50] Z.Z. Tasic, M.M. Antonijevic, M.B. Petrovic Mihajlovic, *et al.*, J. Mol. Liq; 219 (2016) 463–473.

ENVIRONMENTALLY SAFE CORROSION INHIBITORS: AMINO ACIDS

Milan Radovanović[1*], Milan Antonijević[1]
[1]University of Belgrade, Technical faculty in Bor, V. J. 12, 19210 Bor, SERBIA
[*]*mradovanovic@tfbor.bg.ac.rs*

Abstract

Copper, brass, aluminum and steel are considerably used in many industries due to their good electrical and mechanical properties. Most industrial environments are highly aggressive and corrosive for metals and alloys which leads to their decay during use. This further leads to operating problems which can cause a partial or total shutdown of the process. Stoppage of the process for even a short time causes economic and financial losses. Due to high economic losses, protection from corrosion is the focus of many industries as well as scientific research. The use of different compounds which possess characteristics of the inhibitor is extensively examined over the years. Most compounds that show good inhibition efficiency are toxic and considered environmental pollutants. In recent years demands for environmental protection are high which lead to needing for finding new environmentally safe inhibitors of corrosion of metals and alloys. Amino acids are cheap for production, highly soluble in water, and can be produced in high purity. Amino acids also contain heteroatoms in their structure which makes them almost ideal candidates for green corrosion inhibitors in different aggressive solutions. Different amino acids were tested as corrosion inhibitors in many aggressive mediums and showed good results in inhibition efficiency. The action mechanism of amino acids is based on the adsorption of molecules of amino acids on the metal surface and the formation of the protective film which prevents further dissolution of metals. Often, amino acids react with metal ions through coordinative bonds and form complexes that protect the surface of the metal. Also, amino acids in combination with other compounds manifest a synergistic effect. The synergistic effect is detected in the combination of two amino acids and in the combination of amino acids and surfactants. Surfactants provide better adsorption of the molecules of the amino acids on the metal surface and lead to higher inhibition efficiency.

Keywords: amino acid, corrosion, inhibition, copper, steel

INTRODUCTION

Corrosion of metals and alloys are one of the biggest sources of accidents in a number of industries which lead to huge material and economic losses [1]. According to the available literature data, annual losses caused by corrosion of metals and alloys in the USA achieved 4.2 % of GDP [2,3]. Implementation of available methods for the protection of metals from corrosion leads to the reduction of annual costs originated by corrosion up to 35 %. This is one of the main reasons for constant effort for finding new and more efficient methods for inhibiting corrosion [4]. The cause of corrosion of metals and alloys are chemical and/or electrochemical interaction between the metal surface and corrosive medium which as results have the formation of stable products or fatigue of metals. The electrochemical corrosion encompasses processes with release of electrons (anodic dissolution of metals) and processes that accept electrons (cathodic processes). Oxygen, oxidizing agents and hydrogen are usually used as substances which accept electrons in cathodic processes [5]. The inhibition of the corrosion of metals and alloys may be achieved in many ways. One of the most represented method for inhibition of corrosion is use of protective coatings. Moreover, the usage of inorganic and organic compounds as corrosion inhibitors in different solutions is a very promising method for metals protection. The data collected from research done up to now, reveals that the inhibition action of organic compounds is based on adsorption of organic molecules or/and formation of protective film onto metal surface. The inhibitors effect on corrosion rate by decreasing the anodic or/and cathodic reactions, by decreasing diffusion of reactants to the metal's surface and by decreasing electrical resistance of the surface of the metal. The organic compounds which are used as corrosion inhibitors block active sites on a metal's surface. Blocking of the active sites is the result of adsorption of inhibitor molecules on the metal's surface. Four types of adsorption of inhibitors are [6]:

- Electrostatic interaction between inhibitors molecules and metal
- Interaction between lone electron pair in inhibitors structure and metal
- Interaction between metal and π-electron in inhibitor structure
- Simultaneous electrostatic interaction and interaction between metal and π-electron in inhibitor structure

Existence of the heteroatoms (oxygen, nitrogen, sulfur, phosphorus) or double bond in the inhibitor structure are necessary for interaction between inhibitors and metals.

Inhibition efficiency of a tested compound depends on the presence of heteroatoms in the molecular structure. The dependence of the inhibitor efficacy on the heteroatoms present increases in the following order: $O < N < S < P$ [7]. Numerous compounds that show high value of inhibition efficiency are toxic and have a negative impact on the environment which limits their usage. The effect of this is that research groups all around the world have focused on finding corrosion inhibitors that are environmentally safe and nontoxic. Years of research confirms that a large number of organic compounds which belong to „green" inhibitors have acceptable inhibition efficiency. Amino acids, pharmaceutical products and plant extracts are one of the most prominent compounds which belong to „green" inhibitors with confirmed high protection ability for corrosion of copper, brass, steel, aluminum and other metals and alloys in different solutions [8–16].The cost of inhibitors is an important factor during the selection of adequate inhibitor in a tested system. Besides that, inhibitor must be readily available when considering its applicability. Accordingly, amino acids are one of the most interesting groups of compounds which achieve these demands. Also, amino acids are an integral part of proteins and thus a part of the human body, which makes them suitable choice for the inhibitors of corrosion in body solutions. Further, amino acids are well soluble in water solutions, relatively inexpensive and can be easily obtained with a high degree of purity [17].

INHIBITION MECHANISM OF AMINO ACIDS

According to the available literature data, amino acids were intensively investigated as environmentally friendly corrosion inhibitors for different metals and alloys [17–20]. Many studies have been performed on mild steel and copper in HCl and H_2SO_4 solutions [21–24]. Cysteine and methionine are the most tested amino acids in these solutions as corrosion inhibitors [25–27]. Other amino acids were sporadically tested. Amino acids are compounds that were investigated as potential inhibitors for preventing corrosion of biomaterials. It is well known that amino acids are bio compounds present in the human body. The understanding of the influence of amino acids on the corrosion of biomaterials is of huge significance for further implementation. Due to that, corrosion properties of biomaterials such as stainless steel were examined in different artificial physiological solutions [28,29]. Lysine and threonine are amino acids that were tested as stainless steel corrosion inhibitors in BM - 3 solution [30]. Threonine differs from other amino acids because it is a polar amino acid with heteroatoms and aliphatic hydroxyl groups in structure and electron pairs available for bonding with metals. Lysine is more interesting as a potential corrosion inhibitor. First, lysine is a basic amino acid with two N atoms in structure which provide more active centers for bonding with metals. Also, lysine is an amino acid with a chain longer than a chain in most amino acids, which can provide better surface coverage and better inhibition efficiency [30].

Six amino acids were tested as potential corrosion inhibitors for copper and carbon steel in H_2SO_4 solution by Mendonca *et al.* [18]. Inhibition efficiency of tested amino acids ranks in order: Arg > Gln > Asn > Met > Cys > Ser for copper and Met > Cys > Ser > Arg > Gln > Asn for steel. Asparagine (Asn), Glutamine (Gln), and Arginine (Arg) are long-chain amino acids with a different number of amino groups (more than one) in their structure which make them suitable for corrosion inhibitors in aggressive solutions. Cysteine (Cys), Methionine (Met), and Serine (Ser) are interesting because of differences in structure and the influence of various groups on the forming bond between the metal surface and inhibitor molecules. Electrochemical tests reveal that all tested amino acids act like mixed-type corrosion inhibitors in aerated H_2SO_4. In an acidic medium in the presence of amino acids, cathodic reactions stay unchanged and can be shown as follows [31,32]:

$$H^+_{(aq)} + e^- = \frac{1}{2}H_{2(g)}$$

$$O_{2(g)} + 4H^+_{(aq)} + 4e^- = 2H_2O_{(l)}$$

Cathodic current density decreases due to the adsorption of an amino acid's molecule on the metal surface blocking cathodic active sites. Anodic dissolution of steel in acidic solutions starts with the exchange of the water molecules adsorbed on the metal surface with the amino acid’s molecule [18]:

$$Inh_{(solution)} + xH_2O_{(adsorbed)} = Inh_{(adsorbed)} + xH_2O_{(solution)}$$

During the reactive dissolution of steel, Fe^{2+} ions are generated according to the equation [18]:

$$Fe_{(s)} = Fe^{2+}_{(aq)} + 2e^-$$

Generated Fe^{2+} ions react with adsorbed inhibitor molecules and form the Fe(II)-Inh complex with protective ability on the metal surface [18]:

$$Fe^{2+}_{(aq)} + (Inh)_{(adsorbed)} = Fe(Inh)^{2+}_{(adsorbed)}$$

On the other hand, during the corrosion of copper in the H_2SO_4 solution, the cathodic process was under the control of the diffusion of the dissolved oxygen. In this system, oxygen reduction is a dominant cathodic reaction that can be inhibited by the adsorption of amino acids molecules on the cathodic active sites. Anodic dissolution of copper in acidic solutions includes two steps. In the first step, the Cu^+ ions adsorb on the metal surface [18]:

$$Cu = Cu^{+}_{(adsorbed)} + e^{-}$$

The second step is actually oxidation of the Cu^+ to the Cu^{2+} [18]:

$$Cu^{+}_{(adsorbed)} = Cu^{2+}_{(adsorbed)} + e^{-}$$

In the presence of amino acids such as cysteine and methionine, Cu(I)-Cys and Cu(I)-Met complex were formed which have protective characteristics and prevent metal from further dissolution.

The methionine was examined as a potential corrosion inhibitor of stainless steel in 1 M H_2SO_4 and shows that it successfully inhibits anodic and cathodic corrosion processes. In the concentration higher than 50 ppm methionine reduces anodic dissolution of iron and postpone the hydrogen evolution reaction [26]. Tafel slopes indicate the influence of tested inhibitors on the corrosion mechanism. If the addition of inhibitor has no influence on the shift of Tafel slopes, it means that corrosion reactions are under the control of the activation process. Also, this indicates that with the addition of an inhibitor, the corrosion mechanism stays unchanged. The shift of the corrosion potential (E_{corr}) in the presence of an inhibitor points to the class of the inhibitor type. If the shift of the E_{corr} is lower than 85 mV in the presence of an inhibitor that indicates that the tested inhibitor is the mixed-type inhibitor. The shift of the E_{corr} higher than 85 mV in the presence of an inhibitor indicates examined inhibitor is an anodic or cathodic type of the inhibitor [33–36]. Methionine and valine show inhibition activity on corrosion of carbon steel in phase change materials solution. The best results were achieved in solution with the molar ratio of amino acids 1/1. The inhibition mechanism is associated with the adsorption of methionine and valine molecules on the steel surface through heteroatoms (N and S) and –COOH group as main active sites [27].

Loto [17] examined influence of L-Leucine on the steel corrosion in HCl solution. L-leucine is a weak acid and during the electrochemical reaction the carboxylic acid functional group deprotonates and becomes negative $–CO_2^-$ group, while the amino functional group protonates and becomes a positive ammonium group. At low concentration, the ammonium group is dominant while at high concentration, the carboxylate group becomes dominant. The nitrogen atom from the ammonium group and the oxygen atom from carboxylate consist lone pair of electrons that are involved in the reaction between the amino acid molecule and metal which as a result has adsorption of leucine on the metal surface. The inhibition activity of leucine strongly depends on concentration. At the lower concentration of the leucine adsorption occurs dominantly on cathodic active sites and determines that leucine inhibits cathodic corrosion process. With the increase of the leucine concentration, molecules of the inhibitor start to adsorb on the entire surface of metal, increasing the impedance of the metal. Adsorption on the entire surface of the metal means that the inhibitor adsorbs equally on cathodic and anodic active sites, inhibiting cathodic and anodic corrosion processes. This suggests that at the higher concentration, leucine acts like a mixed-type inhibitor in hydrochloric solution [17].

Also, the visible-light illumination can affects the adsorption of cysteine on low-alloy steel surfaces in sodium chloride solution. The illumination of a steel surface according to the existing photovoltaic effect comes to the adsorption of the photons in the visible-light range and to the formation of an electron-hole pair. This leads to the intensive relocation of chloride ions that cause more intensive corrosion as a result. However, in the presence of cysteine, formation of holes in the process of photon adsorption is difficult, which leads to a decrease in the relocation of chloride ions. The result is a decrease in corrosion of the steel surface [37]. The inhibition efficiency of tested amino acids in different aggressive solutions was present in Table 1.

Table 1 *Inhibition efficiency of amino acids as corrosion inhibitor*

Amino acid	Material	Concentration	Solution	IE [%]	References
Arginine	Copper	$1\cdot10^{-2}$ M	0.5 M H_2SO_4	93.7^{EIS}	[18]
Glutamine				88.5^{EIS}	
Asparagine				74.91^{EIS}	
Methionine				60.03^{EIS}	
Cysteine				58.98^{EIS}	
Serine				42.82^{EIS}	
Cysteine	Copper	$1\cdot10^{-2}$ M	0.5 M Na_2SO_4	82.73^{PP}	[20]
Cysteine	Carbon steel	50 mg/dm^3	3.5 % NaCl	74.7^{EIS}	[25]
Methionine	Stainless steel	700 ppm	1 M H_2SO_4	97^{EIS}	[26]
Methionine	Carbon steel	0.05 M	Phase change materials	79.43^{EIS}	[27]
Valine		0.05 M		59.51^{EIS}	
Methionine + Valine		0.05 M		95.09^{EIS}	
Lysine	Stainless steel	0.1 M	BM - 3	71.1^{PP}	[30]
Threonine				88.4^{PP}	
Lysine + SDS		0.1 M + $1\cdot10^{-2}$ M		93.8^{PP}	
Cysteine	Copper	$1\cdot10^{-2}$ M	0.5 M Na_2SO_4	75.68^{PP}	[33]
			0.5 M Na_2SO_4 + NaOH	88.16^{PP}	
Cysteine	Brass	$1\cdot10^{-3}$ M	0.5 M Na_2SO_4	85.1^{PP}	[34]
Cysteine	Steel	5 mM	1 M HCl	54^{PP}	[38]
Arginine	Steel	900 mg/dm^3	1 M HCl	70.53^{EIS}	[39]
Arginine			3.5 % NaCl	88.20^{EIS}	[40]
Cysteine	Brass	$1\cdot10^{-2}$ M	0.05 M HCl	88.9^{PP}	[41]
Methionine	Copper	10 mM	1 M NaOH	90.8^{PP}	[42]
Cysteine	Copper	200 ppm	1 M H_2SO_4	84.60^{EIS}	[43]
Alanine		200 ppm		82.40^{EIS}	
Cysteine + Alanine		150 ppm + 50 ppm		95.59^{EIS}	
Methionine	Copper-Nickel alloy	40 ppm	3.5 % NaCl	68^{PP}	[44]
Methionine + sodium silicate		20 ppm + 20 ppm		92^{PP}	
Cysteine	Copper	$1\cdot10^{-2}$ M	3.5 % NaCl	97.08^{PP}	[45]

***Table 1** continued*

Proline	Copper	$1\cdot10^{-3}$ M	8 M H_3PO_4	39.6^{PP}	[46]
Cysteine				52.17^{PP}	
Alanine				36^{PP}	
Histidine				54.34^{PP}	
Glycine				32.9^{PP}	
Glycine	Copper	15 mM	0.5 M HCl	60^{EIS}	[47]
Cysteine		15 mM		92.9^{EIS}	

ADSORPTION ISOTHERM (THERMODYNAMICS OF THE INHIBITION MECHANISM OF AMINO ACIDS)

The inhibition efficiency of amino acids is connected with the strength of adsorption of amino acid's molecules on the metal surface. The adsorption of the inhibitor on the metal surface is one of the most important steps in the inhibition mechanism [34]. Adsorption of amino acids on the metal surface depends on many parameters but the most important are: orientation of the inhibitor molecule, ionization and polarization of the amino acid molecules [48]. Besides, the adsorption of inhibitors depends on several more factors, such as the nature of the metal surface, the distribution of charge in the inhibitor molecule, the chemical structure of the inhibitor, and the type of interaction between the inhibitor and metal surface [49]. An illustration of amino acids adsorption on the metal surfaces is shown in Figure 1. Inhibitory effect can be associated with physical adsorption or with chemisorption of the inhibitor [8,50]. Metal surface must be electrically charged in physical adsorption process and charged species should be present in the bulk of the solution. Nonetheless, chemical adsorption requires existence of vacantlow-energy electron orbital in metal structure and inhibitors with relatively loosely bonded electrons in molecules or heteroatom with lone pair electrons [51].

Langmuir, Freundlich, Tempkin and Frumkin adsorption isotherms are the most frequently used for fitting results of the amino acids adsorption on metal surface in different solutions [20,30]. According to the Langmuir adsorption isotherm on the metal surface exists a certain number of sites are available for the adsorption of inhibitor molecules. This leads to the definitive number of inhibitor molecules which can be adsorbed on the metal surface without lateral interaction between adsorbed molecules.

Literature data reveals that the Langmuir adsorption isotherm is the most often used isotherm in thermodynamically investigation of the adsorption of amino acids on the metal surface [38,52,53]. The Frumkin adsorption isotherm was used in systems where metal surface was heterogeneous. This adsorption isotherm describes the interaction between adsorbed inhibitor molecules. The Freundlich isotherm describes the relationship between adsorbed molecules, their interaction and influence on the adsorption process [17]. The Gibbs free energy, an important thermodynamic parameter, is calculated from a Langmuir adsorption isotherm according to the equation [17,53]:

$$-\Delta G = \left(lnK - ln\left(\frac{1}{55.5}\right)\right) \cdot R \cdot T$$

Where R stands for universal gas constant, T is the thermodynamic temperature and 55.5 represents the molar concentration of water in solution. The value of Gibbs free energy lower than 20 kJ/mol indicates the physisorption of inhibitor molecules on the metal surface. Chemisorption of inhibitor molecules is determined by the value of Gibbs free energy higher than 40 kJ/mol. At these values charge sharing or a transfer from the inhibitor molecules to the metal surface to form a coordinate type of bond occurs. Values between 20 and 40 kJ/mol indicate mixed adsorption of inhibitor molecules.

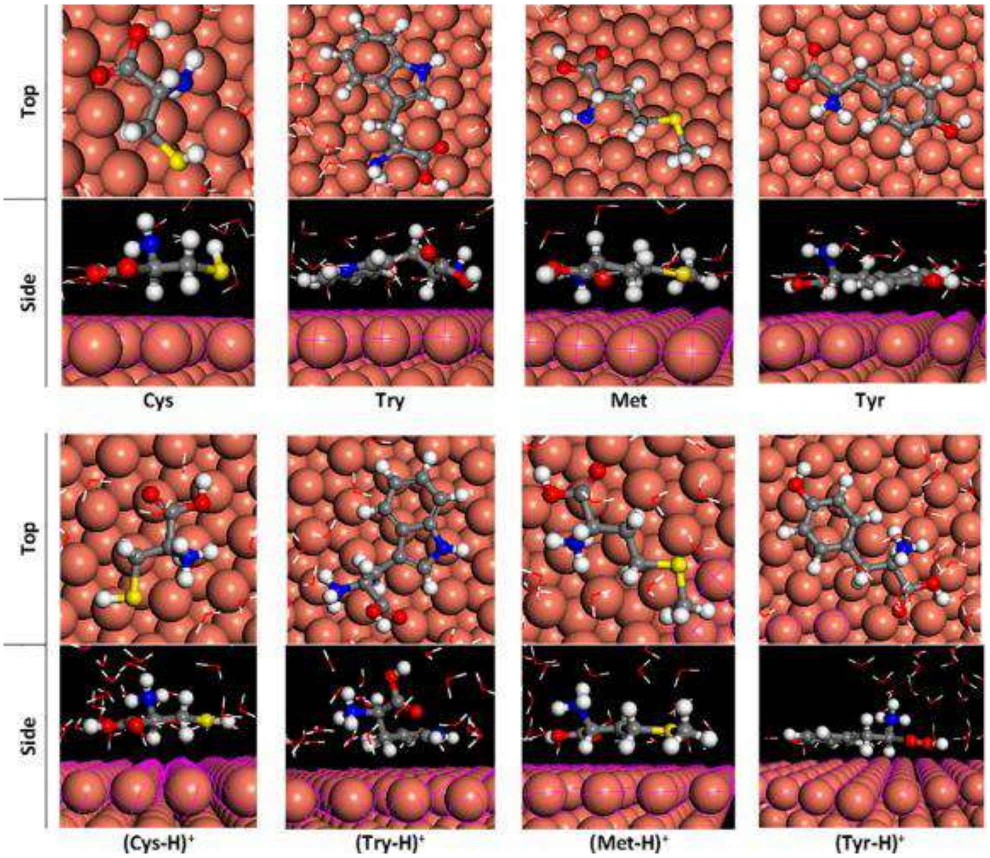


Figure 1 *Optimized systems of some amino acids in neutral and protonated forms on Cu (111) in aqueous phase. Reprinted from B. El Ibrahimi et al. (2020) published in accordance with the principles of open access under CC BY-NC-ND 4.0 (B. El Ibrahimi et al. Journal of King Saud University – Science 32 (1) (2020) 163)*

QUANTUM CHEMICAL CALCULATIONS

In order to study the influence of electronic properties and molecular structure on the corrosion inhibition efficiency of amino acids and to prove that the inhibitor molecules can adsorb on the metal surface, quantum chemical calculation was used [27,35,54]. The quantum chemical calculation enable the determination of parameters such as: energy of the highest occupied molecular orbital (E_{HOMO}), energy of th elowest unoccupied molecular orbital (E_{LUMO}), energy gap (ΔE), dipole moment (μ), ionization potential (I), electron affinity (A), electronegativity (χ), global hardness (η) and number of transferred electrons (ΔN). Equations used for calculations are [30]:

$I = -E_{HOMO}$

$A = -E_{LUMO}$

$\chi = 0.5 \cdot (I + A)$

$\eta = 0.5 \cdot (I - A)$

$\Delta N = (\chi_{Fe} - \chi_{inh})/[2 \cdot (\eta_{Fe} + \eta_{inh})]$

Donor-acceptor interaction explains the adsorption mechanism of inhibitor molecules on the metal surface. E_{LUMO} represents the ability of a molecule to accept charge from the donor pair of electrons. E_{HOMO} is the capacity of the molecules to donate electrons to the metal with vacant d-orbitals. In the structure of amino acids, HOMO is usually located in the vicinity of the heteroatoms, making it a reaction center for interaction with metal. The values of E_{HOMO} and E_{LUMO} indicate inhibition efficiency of tested compounds. Published data reveal that a higher value of E_{HOMO} and a lower value of E_{LUMO} point to stronger inhibition efficiency of tested amino acids as corrosion inhibitors in different solutions [30]. The energy gap is a useful parameter that indicates the inhibition efficiency of the tested compounds. The minor difference in E_{HOMO} and E_{LUMO} values suggests the higher inhibition efficiency due to the lower energy necessary to remove electrons from the last occupied orbital [55]. Also, the lower value of electronegativity points to better inhibition efficiency due to easier electron transfer between reaction center in inhibitor structure and vacant d-orbitals in metal structure [56]. Global hardness is also parameter which can point out to the efficiency of tested amino acids as corrosion inhibitor in tested solution. A lower value of η implies higher polarizability and indicates better inhibition efficiency [30]. The dipole moment is used for determining the polarity of a molecule and it is a parameter that was used for the prediction of inhibition efficiency of the examined compounds [57]. The number of transferred electrons describes the intensity and direction of the electron transfer. The value of ΔN below 3.6 indicates the tendency of a molecule to donate electrons to the metal. In that case, stronger inhibition efficiency was determined by the higher value of ΔN [30].

SYNERGISTIC EFFECT

The inhibition efficiency of amino acids used as corrosion inhibitors in aggressive solutions was enlarged through a synergistic effect with other compounds [30,41,44,58]. For the estimation of the synergistic inhibition effect of two used inhibitors, the synergistic parameter was utilized [27,59]. The synergistic parameter was calculated according to the equation [60]:

$$S = \frac{1 - \theta_{1+2}}{1 - \theta'_{1+2}}$$

$$\theta_{1+2} = (\theta_1 + \theta_2) - (\theta_1 \cdot \theta_2)$$

θ_1 – surface coverage by the first inhibitor

θ_2 – surface coverage by the second inhibitor

θ'_{1+2} – surface coverage by binary inhibitor composition

The synergistic parameter’s value higher than 1 reveals a synergistic effect due to cooperative adsorption. In the case when S is lower than 1, an antagonistic effect is observed as a result of competitive adsorption. Finally, if the synergistic parameter’s value is 1, it indicates no interaction between inhibitors.

The synergistic effect of cysteine and alanine was investigated in a 1 M H_2SO_4 solution and it was observed due to the co-adsorption mechanism. The combination of cysteine and alanine in an acidic environment suppresses anodic and cathodic corrosion processes [43]. The concentration of tested inhibitors has a great influence on the synergistic effect. In the phase change materials solution, methionine and valine show synergistic adsorption at concentrations higher than 0.04 M. However, at concentrations lower than 0.03 M competitive adsorption was achieved leading to the antagonistic effect [27].

Surfactants are used often as corrosion inhibitors in combination with other tested compounds [25,38]. Radovanović *et al.* [30,41] examined influence of sodium dodecyl sulfate (SDS) on the protection ability of cysteine and lysine in HCl and BM – 3 solutions. SDS molecules adsorb on the electrode surface through electrostatic forces and hydrogen bonding, leading to the enhanced adsorption of amino acid molecules. Improved adsorption of amino acids leads to the decrease of the anodic and cathodic current density [30]. SEM-EDS and AFM investigations confirmed the formation of protective film in aggressive solution in the presence of amino acids and sodium dodecyl sulfate (Figure 2 and 3).

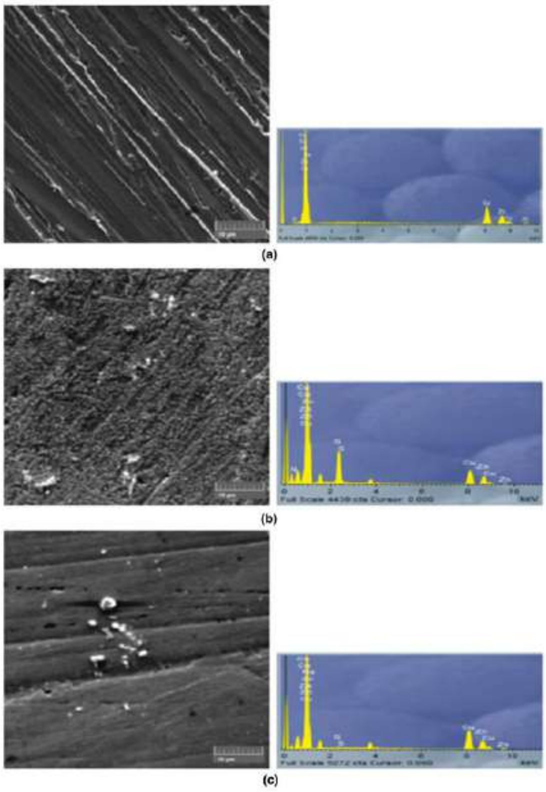


***Figure 2** SEM and EDS analysis of a) the polished brass surface without any treatment; b) brass surface after immersion of the electrode for 1140 min in $1 \cdot 10^{-2}$ M cysteine solution and c) brass surface after immersion of the electrode for 4080 min in $1 \cdot 10^{-3}$ M SDS solution. Reprinted from M. B. Radovanović et al. (2018) published under Creative Commons Attribution License CC BY 4.0 (M. B. Radovanovic et al. Advances in Materials Science and Engineering (2018) 9152183)*

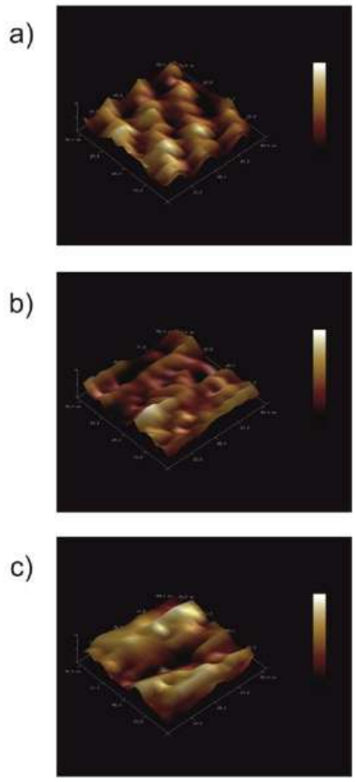


Figure 3 *3D AFM images of stainless steel surface after immersion in a) BM – 3 solution (5 days); b) 0.1 M L-Lysine (5 days) and c) 0.01 M SDS (24h) + 0.1 M L-Lysine (5 days). Reprinted from M. B. Radovanović et al. (2021) with permission of Elsevier (M. B. Radovanovic et al. Journal of Molecular Liquids 342 (2021) 116939)*

CONCLUSION

Corrosion of metals leads to great loss. One of the main achievements is to find an adequate method to prevent and inhibit the corrosion of metals and alloys. Some of that methods are the use of inorganic and organic compounds which act as corrosion inhibitors in different media. Today, scientists around the globe always have in mind that compounds which can be used as corrosion inhibitors must be environmentally friendly. Different groups of compounds meet that condition such as amino acids, plant extracts, purines etc.

Amino acids are one of the most prominent classes of compounds that are tested as corrosion inhibitors in different solutions. The low cost, easy production, and existence of different heteroatoms in their structure provide wide application in the protection of metals and alloys. Some amino acids have numerous active centers in their structure or some others have a longer chain or electron pairs that are available for bonding with metals. All of these provide better inhibition efficiency in aggressive solutions. Tested amino acids act, in numerous solutions, like mixed-type inhibitors. The inhibition action of amino acids is linked with the adsorption of amino acids molecules on the cathodic and anodic active sites.

The formation of a protective complex is also observed in the presence of amino acids. Langmuir, Freundlich, Tempkin, and Frumkin adsorption isotherms are used for fitting results of the amino acids adsorption on metal surfaces in different solutions and Langmuir adsorption isotherm is the most often used isotherm in thermodynamically investigation of the adsorption of amino acids on the metal surface. The synergistic effect of amino acids with other compounds was confirmed.

The synergistic effect was observed between two different amino acids and between amino acids and surfactants. Surfactants enhance the adsorption of amino acids on the metal surface and improve inhibition efficiency in tested solutions.

The quantum chemical calculation in recent years was extensively used for the examination of the influence of electronic properties and molecular structure on the corrosion inhibition efficiency of amino acids. This calculation provides an abundance of information on compounds that may be used for further experimental investigation.

In further years, the main focus of the researchers can be an increase in the inhibition efficiency mentioned compounds as well as the synthesis of new compounds which are derivatives of purines, amino acids, and others, which can achieve better inhibition efficiency in aggressive solutions.

ACKNOWLEDGEMENT

The authors would like to acknowledge financial support from the Ministry of Education, Science and Technological Development of the Republic of Serbia (Agreement No 451-03-68/2022-14/200131).

REFERENCES

[1] D.A. Winkler, Metals; 7 (2017) 553.

[2] C. Verma, D.K. Verma, E.E. Ebenso, *et al.*, Heteroatom. Chem; 29 (2019) e21437.

[3] M. Goyal, S. Kumar, I. Bahadur, *et al.*, J. Mol. Liq; 256 (2018) 565.

[4] C. Verma, E.E. Ebenso, I. Bahadur, *et al.*, J. Mol. Liq; 266 (2018) 577.

[5] P.B. Raja, M.G. Sethuraman, Mater. Lett; 62 (2008) 113.

[6] H. Ju, Y. Ju, Y. Li, J. Mater. Sci. Technol; 28 (9) (2012) 809.

[7] O. Ghasemi, I. Danaee, G.R. Rashed, *et al.*, J. Mater. Eng. Perform; 22 (2013) 1054.

[8] Ž.Z. Tasić, M.B. Petrović Mihajlović, M.B. Radovanović, *et al.*, J. Mol. Struc; 1159 (2018) 46.

[9] Ž.Z. Tasić, M.B. Petrović Mihajlović, M.B. Radovanović, *et al.*, J. Mol. Liq; 265 (2018) 687.

[10] R. Padash, G.S. Sajadi, A.H. Jafari, *et al.*, Mater. Chem. Phys; 244 (2020) 122681.

[11] Q.H. Zhang, B.S. Hou, Y.Y. Li, *et al.*, Corros. Sci; 164 (2020) 108346.

[12] M.B. Harb, S. Abubshait, N. Etteyeb, *et al.*, Arab. J. Chem; 13 (3) (2020) 4846.

[13] E.E. Oguzie, Pigm. Res. Technol; 34 (6) (2005) 321.

[14] M.G. Sethuraman, P.B. Raja, Pigm. Res. Technol; 34 (6) (2005) 327.

[15] G.O. Avwiri, F.O. Igho, Mater. Lett; 57 (2003) 3705.

[16] G. Gunasekaran, L.R. Chauhan, Electrochim. Acta; 49 (2004) 4387.

[17] R.T. Loto, J. Mater. Res. Technol; 8 (2019) 484.

[18] G.L.F. Mendonca, S.N. Costa, V.N. Freire, *et al.*, Corros. Sci; 115 (2017) 41.

[19] D. Kumar, Appl. Surf. Sci; 514 (2020) 145905.

[20] A.T. Simonović, M.B. Petrović, M.B. Radovanović, *et al.*, Chem. Pap; 68 (3) (2014) 362.

[21] A.M. Abuelela, M.A. Bedair, W.M. Zoghaib, *et al.*, J. Mol. Struct; 1230 (2021) 129647.

[22] P.K. Paul, M. Yadev, J. Electroanal. Chem; 877 (2020) 114599.

[23] A. Deghani, G. Bahlakeh, B. Ramezanzadeh, *et al.*, J. Mol. Liq; 279 (2019) 603.

[24] H. Kumar, T. Dhanda, J. Mol. Liq; 327 (2021) 114847.

[25] Y. Zhu, Q. Sun, Y. Wang, *et al.*, Corros. Sci; 185 (2021) 109414.

[26] M. Yeganeh, I. Khosravi-Bigdeli, M. Eskandari, *et al.*, J. Mater. Eng. Perform; 29 (2020) 3983.

[27] Z. Zhang, W. Li, W. Zhang, *et al.*, J. Mol. Liq; 272 (2018) 528.

[28] S. Kaur, S. Sharma, N. Bala, Mater. Chem. Phys; 238 (2019) 121923.

[29] E.W.F. Sabara, V. Pereira, A.L. Molisani, Mater. Res. Express; 7 (2020) 10.

[30] M. Radovanović, M. Petrović Mihajlović, Ž. Tasić, J. Mol. Liq; 342 (2021) 116939.

[31] E. Kowsari, S.Y. Arman, M.H. Shahini, *et al.*, Corros. Sci; 112 (2016) 73.

[32] M. Dehdab, M. Shahraki, S.M. Habibi-Khorassani, Amino Acids; 48 (2016) 291.

[33] M.B. Petrović, M.B. Radovanović, A.T. Simonović, *et al.*, Int. J. Electrochem. Sc; 7 (2012) 9043.

[34] M.B. Radovanović, M.B. Petrović, A.T. Simonović, *et al.*, Environ. Sci. Pollut. R; 20 (2013) 4370.

[35] M.B. Radovanović, Ž.Z. Tasić, M.B. Petrović, *et al.*, Sci. Rep - UK; 9 (1) (2019) 16081.

[36] M.B. Radovanović, Ž.Z. Tasić, A.T. Simonović, *et al.*, ACS Omega; 5 (22) (2020) 12768.

[37] P. Qiu, H.F. Yang, L.J. Yang, *et al.*, Mater. Corros; 68 (9) (2017) 1004.

[38] R. Farahati, S.M. Mousavi–Khoshdel, A. Ghaffarinejad, *et al.*, Prog. Org. Coat; 142 (2020) 105567.

[39] M. Zefraoui, H. Oudda, B. Hammouti, *et al.*, Prog. Org. Coat; 51 (2) (2004) 134.

[40] M.A. Amin, S.S. Abd El Rehim, M.M. El-Naggar, *et al.*, J. Mater. Sci; 44 (2009) 6258.

[41] M.B. Radovanovic, Z.Z. Tasic, M.B. Petrovic Mihajlovic, *et al.*, Adv. Mater. Sci. Eng; (2018) 9152183.

[42] J. Wu, X. Zheng, W. Li, *et al.*, Res. Chem. Intermed; 41 (2015) 8557.

[43] M. Kuruvilla, A.R. Prasad, S. John, *et al.*, J. Bio. Tribo. Corros; 3 (2017) 5.

[44] X. Li, W. Li, S. Yang, *et al.*, Mater. Express; 7 (6) (2017) 480.

[45] G. Kilinççeker, H. Demir, Anti - Corros. Method. M; 60 (3) (2013) 134.

[46] H.H. Abdel Rahman, A.H.E. Moustafa, M.K. Awad, Int. J. Electrochem. Sc; 7 (2012) 1266.

[47] D.Q. Zhang, B. Xie, L.X. Gao, *et al.*, Thin Solid Films; 520 (2011) 356.

[48] S.A.M. Refaey, F. Taha, A.M. Abd El-Malak, Int. J. Electrochem. Sc; 1 (2006) 80.
[49] O. Olivares, N.V. Likhanova, B. Gómez, *et al.*, Appl. Surf. Sci; 252 (2006) 2894.
[50] H. Li, S. Zhang, B. Tan, *et al.*, J. Mol. Liq; 305 (2020) 112789.
[51] M.B. Radovanović, M.M. Antonijević, J. Adhes. Sci. Technol; 31 (4) (2017) 369.
[52] K.W. Shinato, F.F. Huang, Y.P. Xue, *et al.*, Rare Metals; 40 (5) (2021) 1317.
[53] M. Oubaaqa, M. Ouakki, M. Rbaa, *et al.*, J. Mol. Liq; 331 (2021) 116520.
[54] Y. Xu, S. Zhang, W. Li, *et al.*, Appl. Surf. Sci; 459 (2018) 612.
[55] N. Yilmaz, A. Fitoz, Y. Ergun, *et al.*, Corros. Sci; 111 (2016) 110.
[56] K.F. Khaled, Electrochim. Acta; 55 (2010) 6523.
[57] M. Mahdavian, S. Ashhari, Electrochim. Acta; 55 (2010) 1720.
[58] M. Mobin, M. Parveen, M.Z.A. Rafiquee, Arab. J. Chem; 10 (2017) S1364.
[59] Z.Z. Tasic, M.M. Antonijevic, M.B. Petrovic, *et al.*, J. Mol. Liq; 219 (2016) 463.
[60] K. Haruna, I.B. Obot, N.K. Ankah, *et al.*, J. Mol. Liq; 264 (2018) 515.

BIO-ELECTROCHEMICAL SYSTEMS – STATE OF THE ART: BIOLOGY, ELECTROCHEMISTRY AND APPLICATION IN WASTEWATER MANAGEMENT

Hyusein Yemendzhiev[1*], **Yana Mersinkova**[1], **Ralitza Koleva**[1], **Gergana Peeva**[1], **Valentin Nenov**[1]

“Prof. Asen Zlatarov” University, Y. Yakimov Blvd. No1, 8010 Burgas, BULGARIA

[*]*hyemendzhiev@btu.bg*

Abstract

Several options in applying the bio-electrochemical systems (BES) in water treatment are under discussion. Recently many studies reported that this type of reactors are capable to simultaneously remove contaminants form wastewater and recover energy in form of electricity by the specific biology and electrochemistry of the processes involved. The potential applications include COD/BOD removal, precipitation of metal ions such as Cu^{2+} *in industrial effluents, production of hydrogen form organic waste, etc. The microbial fuel cell (MFC) type reactors could be used even for sensing toxic compounds in water based on the biological response of the so called electrogenic microorganisms presented in the anode biofilms. In this paper, some of the biological, electrochemical and technological characteristics of the BES are presented in sense of their application in wastewater treatment and management.*

Keywords: wastewater treatment, bio-electrochemical systems, microbial fuel cell

INTRODUCTION

One of the challenges related to the wastewater management is to develop technologies with lower footprint in terms of energy consumption and secondary emissions. The conventionally applied activated sludge process is efficient in COD and nutrients removal but creates huge amounts of residual sludge with high organic content and potentially pathogenic microorganisms. Also, the aerobic nature of this process requires aeration and this particular operation contributes to nearly half of the wastewater treatment cost (due to the electrical energy used) [1]. It is well known that the organic matter in wastewater could be a source of energy. Recent study estimated that the usual energy value of domestic wastewater could reach 7.4 kJ per litre (based on the typical COD of 500 mg O_2 dm^{-3}) and in specific cases this value could be even higher [2]. Anaerobic digestion is one of the commonly used alternatives in this sense. Applied mainly toward concentrated waste streams, during the anaerobic digestion some of the energy could be recovered as methane containing biogas. However, anaerobic digestion has drawbacks such as low level of substrate mineralization, temperature requirements and involvement of additional technological stages (combustion, cogeneration, etc.) for energy harvesting.

Bio-electrochemical systems (BES) are technology recently attracted attention for their ability to directly convert chemical energy of organic compounds into electricity. This is a result of the specific metabolic activity of electrochemically active microorganisms. They are capable to use the electrode of the bio-electrochemical reactor as a terminal electron acceptor during biological oxidation of substrates and this characteristic creates diverse applications including wastewater treatment [3]. The most known BES is the microbial fuel cell (MFC) in which the electron flow generated during the microbial decomposition of organic matter at anode compartment is directed to the cathode by external circuit. On the cathode surface the delivered electrons are involved in reduction of a soluble chemical acceptor at higher potential - usually dissolved oxygen or ferricyanide (Figure 1). Variety of chemical compounds and species could be used as electron acceptors in the cathodic semi-reactions, such as manganese, copper and iron ions, nitrates, sulphate, etc., resulting in their chemical reduction and transformation into a preferable form [4].

The process has specific biochemical and molecular factor - specific redox-active proteins, soluble metabolic mediators and even conductive cellular structures (often called nanowires in the literature). All of them playing crucial role in the extracellular transfer of electrons from the cell respiratory chains to the electrode surface [5].

Important detail is that the anodic processes in MFC are anaerobic and driven by anaerobic (obligate and facultative) bacterial communities. From the biochemical point of view, there is fundamental difference between the conventional anaerobic digestion and bio-electrochemical processes even though both processes are anaerobic. The Anaerobic digestion is predominantly fermentative transformation of the substrates without involvement of any complex electron transport mechanisms for ATP synthesis. On the contrary, on the anode surface of the microbial fuel cell, a respiratory type of metabolism is implemented with all the typical energy benefits for the bacterial cell. Beside the bio-electrochemical systems, anaerobic respiration is a part of the biochemical mechanisms behind the global nitrogen, iron, sulphur, and carbon cycles and it is a quite common metabolic activity in variety of environments [6].

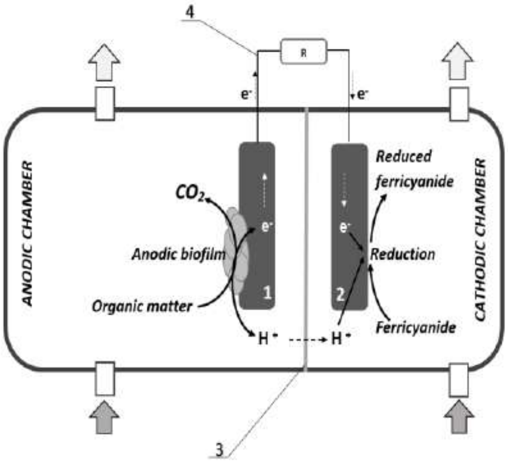


***Figure 1** Typical two chamber MFC. 1—anode, 2—cathode, 3 – Proton exchange membrane, 4—external circuit and resistor*

Summarizing the above, it is clear that the bio-electrochemical processes offer a promising alternative of the conventional processes for wastewater treatment. As a part of the anodic processes the organic content of the wastewater could be removed by microbial degradation resulting in elimination of COD/BOD and on the other hand - the cathodic reduction could be use as alternative to chemical precipitation of metal ions, nitrate reduction or even more sophisticated processes beyond the boundaries of the wastewater treatment. In this article, the current state of development of the bio-electrochemical systems achieved in the *Water Technology Laboratory* at the *"Prof. Asen Zlatarov" University* in Burgas, Bulgaria is presented in the context of their application in wastewater management and treatment.

MATERIALS AND METHODS

MFC configuration and operation

The MFC used in this study was designed as a cylindrical plastic reactor consists of two chambers separated by Nafion® 424 perfluorinted proton exchange membrane. The cell segments were equipped with the respective sampling and gas/liquid transport ports. The electrodes were 30 mm in diameter made of carbon cloth with stainless steel current collectors. The tipical electric resistance applied in the external circuit is 1 kΩ. The volumes of cathode and anode chambers are 45 dm^3. The anode compartment is fed by 10 gdm^{-3} Luria–Bertani (LB) nutrient medium with 2 gdm^{-3} glucose (initial pH 7.5 and organic load COD equivalent to 9558 mgO_2dm^{-3}) and mixed culture of electrochemically active bacteria isolated from lake bottom sediments [7] with initial cell density of 10^6 CFU per millilitre. 2% solution of potassium ferricyanide was used as catholyte and terminal electron acceptor by permanent recirculation in order to maintain the concentration and the state of the cathode reactions. The MFC experiment were carried out in controlled ambient temperature of 18–20°C.

Analytical methods

The biomass growth was measured by KERN DAB100-3 Moisture and dry weight and expressed as a concentration of dry biomass. The yield and the specific yield of residual sludge were calculated by the difference in the amount of the final and initial biomass measured and then the values were related to the COD removed during the time of process.

The COD and the organic acids content substrate in the anode compartment were measured by HACH Lange cuvette tests on Lange DR 3900 spectrophotometer.

Electrochemical Analyses

Metrohm Autolab PGSTAT101 apparatus and NOVA 2.1 software were used fir cyclic voltammetry in potentiostatic mode with the anode and cathode connected as working and counter electrode respectively. The electrical parameters (open circuit voltage, current and resistance) of the MFC were measured by auto ranging digital multimeter Model MY-66.

Scanning electron microscopy

For inspection of the anode biofilm growth scanning electron microscopy was performed. The apparatus used is Inovenso IEM11. The samples were collected form working MFC reactors and prepared for scanning by drying under vacuum at low temperature.

16s rRNA gene sequencing and taxonomic affiliation

16s rRNA gen amplification and sequencing were performed for identification of the bacterial species populating the anode biofilm. Isolation of the cultures, DNA extraction, PCR amplification of 16s rRNA gene and sequencing were performed according to procedure described in earlier publication [8]. The sequences obtained were analysed by BLAST algorithm service of the NCBI Gene Bank database for taxonomic affiliation of the studied strains.

RESULTS AND DISCUSSION

Electrochemical and degradation characteristics of the anode biofilm in MFC

In our preliminary studies a lake sediment samples were analysed in terms of the conditions supporting anaerobic respiration. The results obtained demonstrated that the specific physical and chemical parameters of the environmental niches associated with this type of metabolism are usually available in lake and river sediments with high concentration of organic matter, presence of iron and manganese ions and low concentration of dissolved oxygen [7]. Following this conclusion, mixed anaerobic bacterial culture was isolated form the sediment samples collected in different spots of “Poda” wetland near city of Burgas, Bulgaria (42°26'42.2"N 7°27'56.0"E). Later, this enriched culture was used as inoculum in the anode chamber of the lab-scale MFC in order to examine the electrochemical activity of the microbial isolates. The biofilm formation and its electrochemical activity was monitored by the so-called “anode current values” (result of the electron flow from the bacterial cell to the anode surface) which are measured by potentiostatic cyclic voltammetry with specific data processing. The higher the value, better the biofilm performs (Figure 2).

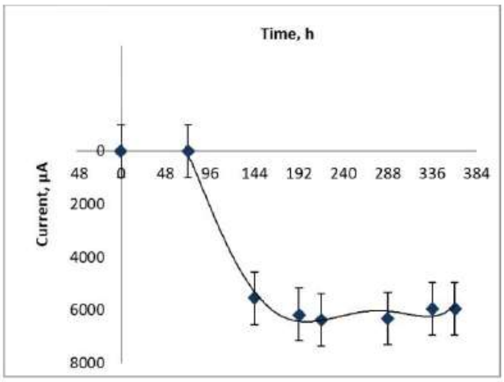


***Figure 2** Biofilm development expressed as anodic current measured by the cyclic voltammetry [7]*

Starting from zero and after 48 hours of lag phase, the anode current started increasing significantly after the third day of cultivation in the MFC. This indicates a change in electrochemistry of the anode, probably due to the electrode colonization and biofilm growth. Reaching a plateau after a certain period is associated with the electrochemical stabilization of the system after the biofilm reached a “working” state of development. This conclusion was supported by the SEM images of the biomass collected on the anode surface (Figure 3).

The MFC operation was evaluated by the electrical performance and COD removal rate. The open circuit voltage reached its maximal value of 277 mV after one week of cultivation, which correlates with the data for the biofilm formation. During this period, the power density reached 3.5 W/m^2 (based on the anode surface) and the average COD removal rate observed was 172 mgO_2dm^{-3} per day.

The 16s rRNA gene sequencing data showed that at biofilm is dominated by two bacterial species – *Pseudomonas lutea* and *Bacillus cereus* which could be considered as most electrogenic among the species presented in the initial consortia. Different Bacillus and Pseudomonas genera representatives are reporter to be discovered in anodic biofilms previously [8].

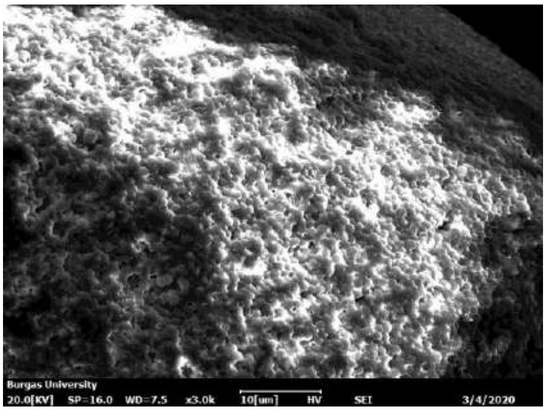


Figure 3 *SEM images of the anode biofilm after one week of cultivation in MFC*

Toxicity detection and water quality monitoring

The detection of hazardous materials in water is crucial part of the water management and monitoring. However, analysing the entire diversity toxic compounds, potentially presented in the water is not an easy, nor economical task and sometimes it is impossible, as well. This group of chemicals varies from heavy metals ions to complex organic molecules and bio-toxins. Finding a general indicator for the toxicity presented in water and aquatic environments could be an important step toward the development of early warning systems to support decision making in water monitoring.

In this study, bio-electrochemical reactor is used as a sensor to evaluate the specific biological response to the toxic compounds presented in water. Phenol was used as a model toxic compound in two different scenarios, namely freshwater and wastewater pollution. The tested concentrations varied from 0 to 40 mg dm^{-3}. In order to evaluate the bio-toxicity the effect of the phenol on the electrochemically active bacteria in MFC was evaluated based on the fluctuations of the electric signal observed. The theoretical expectation was to observe signal drop after introduction of the phenol in the tested water samples due to the inhibition of the anode respiration systems of the microbial culture. The data obtained are presented in Figures 4.

From this initial data it is obvious that there is a certain amount of correlation between the status of the tested water and the electrical output of the MFC in both cases – freshwater and wastewater. Overall voltage of the system in the experiments with wastewater is higher due to the higher concentration of organic substrates compared to the freshwater. When freshwater is monitored, the MFC sensor device demonstrates very high sensitivity detecting even the lowest concentration of 0.5 mg dm^{-3} phenol.

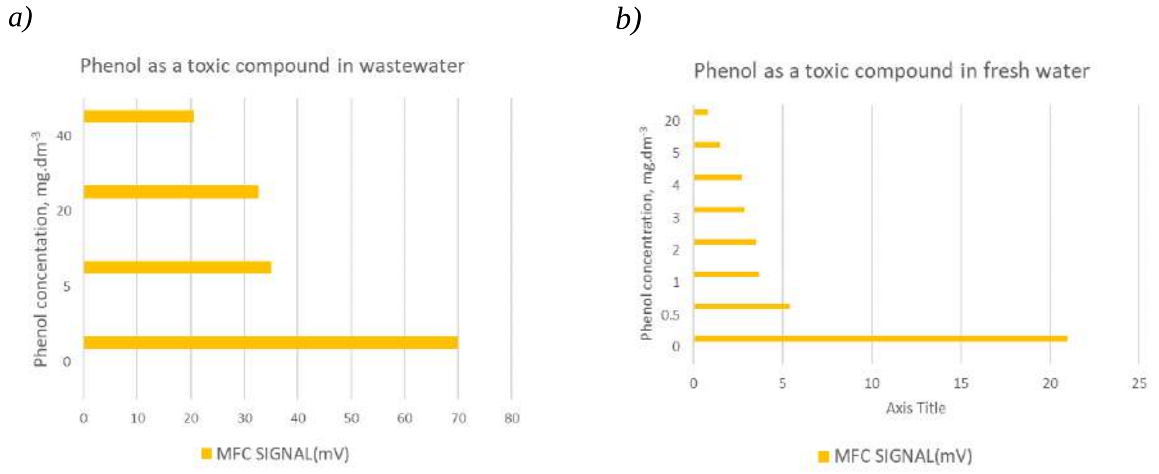


Figure 4 *Effect of different concentrations of phenol in wastewater (a) and freshwater (b) on the electric output of MFC*

CONCLUSION

Recently, in the *Water Technology Laboratory* of Burgas “Prof. Asen Zlatarov” University, variety of applications of BES in wastewater treatment and management were studied. The results obtained demonstrated the potential of this emerging technology. Mani factors affecting the performance of the reactors such as biology of the anode biofilm, type of the wastewater, electrochemical conditions and reactor design are already clarified. However, the future implementation and commercialization of this technology needs interdisciplinary approach to the topic since the complex nature of the bio-electrochemistry. Mathematical modelling, optimization and scale-up studies are crucial step in this direction and good example are already available in the scientific literature.

ACKNOWLEDGEMENT

This work was supported by Operational program “Science and Education for Smart Growth” 2014–2020 of Ministry of Education and Science, Republic of Bulgaria under the BG05M2OP001-1.002-0019 Clean & Circle and BG05M2OP001-1.002-0011MIRACLe projects.

REFERENCES

[1] K. Hussey and J. Pittock, Ecol. Soc; 17 (2012) 31–39.

[2] E.S. Heidrich, T.P. Curtis, J. Dolfing, Environ. Sci. Technol; 45 (2001) 827–832.

[3] B. Logan, K. Rabaey, Science; 337 (6095) (2012) 686–690.

[4] S. Đorđievski, H. Yemendzhiev, R. Koleva, *et al.*, J. Serbian Chem. Soc; 87 (2022) 1–10.

[5] D.R. Lovley Nat. Rev. Microbiol; 4 (7) (2006) 497–508.

[6] W. Zhi, Z. Ge, Z. He, *et al.*, Biores. Technol; 171 (2014) 461–468.

[7] Y. Mersinkova, H. Yemendzhiev, J. Adv. Biol. Biotechnol; 23 (2020) 19–25.

[8] Y. Mersinkova, H. Yemendzhiev, V. Nenov, Biotechnol. Biotechnol. Eq; 36 (1) (2022) 141–146.

GREEN ORGANIC CHEMISTRY: A FRAMEWORK FOR SUSTAINABLE ENVIRONMENTAL PROTECTION

Aleksandar Marinković[1*]

[1]University of Belgrade, Faculty of Technology and Metallurgy, Karnegijeva 4,
11120 Belgrade, SERBIA

marinko@tmf.bg.ac.rs

Abstract

Lignin based microspheres adsorbent, LBM, obtained via inverse suspension copolymerization of methacryloyl modified Kraft lignin and trimethylolpropane triacrylate (TMPTA) cross-linker was used for Carminic acid (CA) and Sudan Orange G (SOG) dyes removal from water. Structural and morphological characterization of developed porous LBM was performed using BET, SEM and FTIR spectroscopy. The diameter of the LBM was 780 ± 88 µm, while surface area and porosity was 3.81 m^2 g^{-1} *and 56%, respectively. Effect of the initial dye concentration, pH, temperature, and adsorption time on efficiency of CA and SOG dyes removal was studied. High potential of LBM for removal of CA and SOG dyes from waste water was noticed. Determined adsorption capacities were 121.20 mg* g^{-1} *for CA and 62.86 mg* g^{-1} *for SOG removal from model water solution. Favourable and spontaneous process was deduced from thermodynamic data. Adsorption performances of LBM were additionally proved by kinetic and diffusional kinetic data confirming that intra-particle diffusion is a main rate controlling step.*

Keywords: lignin methacrylate, kinetic, adsorption isotherm, thermodynamic

INTRODUCTION

Using synthetic organic dyes to color products is widely presented in most of the industries, especially paper, textile, leather, printing, food, cosmetics, plastics, and rubber. Widespread industrial application of dyes, *e.g.* over 100000 commercial dyes exist today [1], causes pollution from effluents which disturb human health and ecological equilibrium [2]. The treatment/purification of the wastewater which contains organic dyes is recognized as crucial need before its discharge in surface water considering both the environmental and health effects (toxic and potentially carcinogenic) [3].

There are different physico-chemical processes for removal of dyes from wastewater such as coagulation, chemical oxidation/degradation, separation using porous membrane, electrochemical process, and adsorption. Synthetic organic dyes are visible pollutants and can hardly be removed from the effluents by most conventional wastewater treatment methods [4]. However, among them the adsorption represents an attractive and promising method due to low cost, high efficiency, and ability of the adsorbent regeneration [5,6]. In recent years, an increased interest in development of bio-based adsorbents for removal of synthetic organic dyes from wastewater was due to their abundance and eco-friendliness [5,7].

The cellulose, hemicelluloses and lignin are main bio polymers in woody biomass [5,7,8]. Even the significant progress is being made in the research areas for applicability of the woody biomass there are still needs to be explored for utilization of its full potential [5,7].

Lignin is a waste by-product from the pulp and paper industry or biomass pretreatment processes. Moreover, lignin represents the main renewable source of aromatic structures, and due to its 3-D structure and chemical functionality it has a high capacity to adsorb organic/inorganic pollutants, e.g. dyes and pharmaceutics and heavy metal ions [5,7].

In this work, the main focus is development and research of adsorption potential of porous spherical adsorbent synthesized from methacryloyl functionalized kraft lignin for a removal of common synthetic organic dyes, Carminic acid (CA) and Sudan orange G (SOG), which are used in a wide variety of food and textile processing. These dyes are mutagenic for microorganisms especially bacteria and yeast, toxic to female reproductive system and can cause dermatitis to sensitive skin [8]. The spherical lignin-based adsorbent (**LBM**) is synthesized *via* suspension copolymerization method which provides an adsorbent with low surface area and better diffusion, dispersion, and mass transfer behaviour, in comparison to traditional adsorbents.

MATERIALS AND METHODS

Materials

Kraft lignin purchased from Sigma-Aldrich, Germany; TMPTA produced by BSF, Germany; triethylamine from Merck, Germany; dimethyl sulfoxide (DMSO), methacryloyl chloride (MAC), tetradecanol, azobisisobutyronitrile (AIBN) and toluene are from Sigma-Aldrich, Germany. Setacin 103 Spezial (disodium laureth sulfosuccinate) was supplied by Zschimmer & Schwarz, Germany. CA was supplied by Kemika Croatia, and SOG was supplied by Carl Roth Gmbh, Germany.

Chemical modification of lignin

Methacryloyl derivative of kraft lignin was prepared thorough the modified procedure proposed by Podkoscielna *et al.* [9]. In a 100 mL round-bottomed laboratory flask equipped with a mechanical stirrer, a thermometer and a dropping funnel, 1.0 g of kraft lignin and 30 mL of DMSO solvent were placed with 1 mL of triethylamine in an ice bath and stirred for 30 min. Next, 0.8 mL of methacryloyl chloride was added for 1 h at a temperature range of 3–5 °C. Subsequently, the reaction mixture was stirred for 1 h at 5 °C and for 1 h at room temperature. After the reaction, isopropyl alcohol was added to the filtrate and the resulting precipitate was filtered off. Obtained product was vacuum dried at 50 °C for 12 h.

Synthesis of LBM

In a 250 mL three-necked laboratory flask equipped with a stirrer, condenser and a thermometer, 32 mL of deionized water and 0.35 g of Setacin 103 surfactant were stirred for 30 min at 80 °C. Then, TMPTA (2.4 g) and vinyl functionalized lignin (0.5 g), the AIBN initiator (1 wt. %) and the mixture of pore-forming agents (tetradecanol and toluene; 1.8 g) were added and the reaction mixture was stirred at 350 rpm for 18 h at 80 °C. After centrifugation, the SLA was washed with hot deionized water (1.5–2 L), extracted in a Soxhlet apparatus with boiling acetone. After vacuum drying at 40 °C for 10 h, product,

LBM, was further characterized. Wetting of the **LBM** was performed by soaking in deionized water, treating at vacuum until no air bubbles was observed.

Batch adsorption experiments

Adsorption experiments were performed by addition of 1, 2, 3, 4, 5, 7.5 and 10 mg of adsorbent in vials of 20 mL containing 20.0 mg dm^{-3} of CA solutions and 5.0 mg dm^{-3} of SOG solution at pH 6. Adsorption equilibrium and thermodynamic parameters were evaluated at three temperatures: 298, 308 and 318 K. The adsorption kinetics were studied by varying the contact time in the range 5–90 minutes at Ci = 20.0, mg dm^{-3} for CA and 5–60 minutes at C_i = 5 mg dm^{-3} for SOG, pH$_i$ 6, at 298, 308 and 318 K.

RESULTS AND DISCUSSION

Adsorbent characterization

Results of determination of textural properties of **LBM**, performed using BET method (Micromeritics ASAP 2020), gave 3.81 m^2 g^{-1} of surface area, 0.0228 cm^3 g^{-1} of total pore volume and 10.95 nm of mean pore diameter. Also, volumetric titration was used for determination of hydroxyl, phenolic and carboxylic groups according to the standard methods ISO 4326:1992, (ASTM D3644) and [10], respectively.

FTIR technique, performed using Nicolet™ iS™ 10 FT-IR Spectrometer (ThermoFisher SCIENTIFIC), was used for analysis of the surface functionalities before and after adsorption (Figure 1a). Spectra of **LBM** before and after dyes adsorption show a broad absorption band in region 3500 to 3200 cm^{-1} due to aliphatic and phenolic OH-groups of kraft lignin. Other peaks are assigned to C=C aromatic skeletal and C-H deformation vibration (1611, 1510, and 1462 cm^{-1}), C=O stretching (1731 cm^{-1}) and aliphatic C–H stretching (2920, 2850 cm^{-1}) which correspond mostly to the lignin and TMPTA structure as well. From the spectra of **LBM** after adsorption it could be clearly observed that significant amount of both dyes are adsorbed at outer surface. This is clearly visible by appearance of the absorption bands in FTIR spectra of **LBM/CA** and **LBM/SOG** that originates from adsorbed dyes. SEM micrographs, obtained using Tescan Mira 3 XMU FEG, was used for observation of **LBM** morphology as well as determination of mean particle diameter: 780 ± 88 µm. Non-uniform spherical geometry indicate necessity of the development of production technology which will gave mostly spherical product (Figure 1b).

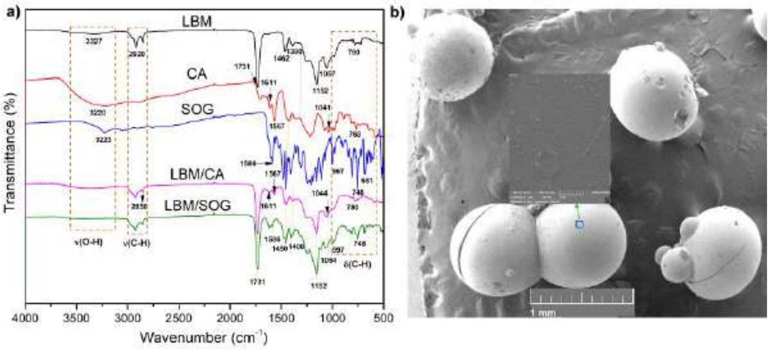


Figure 1 *a) FTIR spectra of* ***LBM****, CA and SOG, and after adsorption,* ***LBM****/CA and* ***LBM****/SOG; b) SEM micrograph of synthesized* ***LBM***

Content of phenol, hydroxyl and carboxyl groups in Kraft lignin was: 4.4 mmol g^{-1}, 2.3 mmol g^{-1} and <25 μmol g^{-1}, respectively. Phenol and hydroxyl groups, due to their nucleophilic character, are able to react with methacryloyl chloride, at different extent, to produce modified Kraft lignin. After reaction of modified lignin with TMPTA and **LBM** adsorbent synthesis appropriate number of residual functionalities: 2.2 mmol g^{-1} of phenol and 1.6 mmol g^{-1} of hydroxyl, could create multiple electrostatic and hydrogen-bonding interactions with dyes functionalities providing their effective removal from water.

Adsorption and kinetic study

Adsorption data were fitted to four adsorption models: Langmuir, Freundlich, Temkin and Dubinin-Radushkevich (D-R) models, and obtained results are given in Tables 1 and 2.

Table 1 *The results of Langmuir model fitting for CA and SOG adsorption onto* ***LBM*** *($C_{i[CA]}$ =20.0 mg dm^{-3}; $C_{i[SOG]}$ =5.00 mg dm^{-3}; m/V= 50–500 mg dm^{-3}, pH=6)*

	T **(K)**	q_m **(mg g^{-1})**	K_L **(dm^3 g^{-1})**	R^2
CA	298	107.92	0.78496	0.985
	308	114.58	0.77426	0.988
	318	121.20	0.76828	0.991
SOG	298	56.65	1.74358	0.944
	308	59.83	1.74520	0.947
	318	62.86	1.75483	0.951

Table 2 *Freundlich, Temkin and Dubinin-Radushkevich isotherm parameters for CA and SOG adsorption onto LBM*

Isotherm model	**Isotherm parameters/ correlation coefficient**	**CA**			**SOG**		
		298 K	**308 K**	**318 K**	**298 K**	**308 K**	**318 K**
Freundlich isotherm	K_F (mg g^{-1})(dm^3 mg^{-1})$^{1/n}$	50.21	51.73	53.34	31.16	33.14	35.21
	$1/n$	0.266	0.283	0.298	0.451	0.468	0.484
	R^2	0.990	0.994	0.993	0.996	0.996	0.993
Temkin isotherm	A_T (dm^3 g^{-1})	24.32	20.33	17.66	26.03	25.17	24.48
	b_T	16.45	18.09	19.72	10.19	10.89	11.60
	B (J mol^{-1})	150.65	141.62	134.15	243.38	235.17	228.02
	R^2	0.976	0.981	0.982	0.919	0.924	0.930
Dubinin-Radushkevich isotherm	q_m (mg g^{-1})	75.02	78.39	81.76	33.04	34.86	36.74
	K_{ad} (mol^2 KJ^{-2})	8.37	8.32	8.28	8.78	8.72	8.67
	E_a (KJ mol^{-1})	7.731	7.751	7.771	7.547	7.571	7.594
	R^2	0.790	0.783	0.778	0.858	0.868	0.877

The adsorption capacity, q_m, and affinity, K_L, calculated using Langmuir equation are the most important for analysis of adsorption process. The K_L constant, can be used to calculate a dimensionless equilibrium parameter (R_L) by the following equation: $R_L = \frac{1}{1+K_L \cdot C_i}$, where C_i is the initial CA and SOG concentration. The value of R_L indicates the adsorption nature to be either unfavourable ($R_L > 1$), linear ($R_L = 1$), favourable ($0 < R_L < 1$) or irreversible ($R_L = 0$). R_L values are in the range 0.059–0.394 and 0.102–0.534 for CA and SOG, respectively, indicate favourable adsorption.

Adsorption data, obtained at 298, 308 and 318 K, was used for calculation of thermodynamic data, and obtained results are given in Table 3.

***Table 3** Calculated Gibbs free energy, enthalpy and entropy for CA and SOG adsorption onto **LBM** adsorbent*

	ΔG^{Θ} (kJ mol^{-1})			ΔH^{Θ} (kJ mol^{-1})	ΔS^{Θ} (J mol^{-1} K^{-1})	R^2
	298 K	308 K	318 K			
CA	-40.80	-42.13	-43.48	-0.85	133.97	0.980
SOG	-41.76	-43.16	-44.58	0.25	140.90	0.942

Thermodynamic data indicate feasible and spontaneous process with increased randomness at adsorbent surface. Additionally, kinetic study performed at different temperature shows that the PSO kinetic model provides the best correlation of the experimental data (Table 4), and also obtained results (Tables 4 and 5) indicate that the rate-determining step is a intra-particular diffusion of the dyes through **LBM** adsorbent pore.

***Table 4** Pseudo-first, PSO and second order model parameters for the adsorption of CA and SOG on **LBM** ($C_{i[CA]}$ =20.0 mg dm^{-3}; $C_{i[SOG]}$ =5.0 mg dm^{-3}; m/V=50 mg dm^{-3}, pH=6, T=298 K)*

Pollutant	**Eq. parameter**	**Pseudo-first**	**PSO**	**Second order**	***Ea* (kJ mol^{-1})**
CA	q_e	108.87	128.79	128.79	12.67
	k (k_1, k_2)	0.051	0.00039	0.00016	
	R^2	0.987	0.996	0.853	
SOG	q_e	32.561	55.173	55.173	7.19
	k (k_1, k_2)	0.0825	0.00401	0.00209	
	R^2	0.986	0.998	0.829	

***Table 5** Kinetic parameters of the D-W, Elovich, HSDM and UT models for the adsorption of SY and SOG onto **LBM** ($C_{i[CA]}$ =20.0 mg dm^{-3}; $C_{i[SOG]}$ =5.00 mg dm^{-3}; m/V=50 mg dm^{-3}, pH=6, T=298 K)*

Model	**Eq. parameters**	**CA**	**SOG**
Dunwald-Wagner (D-W)	$K^{***}\times10^{-2}$	0.01223	0.02936
	R^2	0.938	0.914
Elovich	α^{*}(mg g^{-1} min^{-1})	13.607	68.82
	β^{**}(mg g^{-1})	0.0348	0.1168
	R^2	0.989	0.962
Homogenous Solid Diffusion Model (HSDM)	$Ds^{****}\times 10^{-11}$	1.68	3.32
	R^2	0.912	0.903
Urano and Tachukawa Model (UT)	$Di \times 10^{-4}$	3.334	5.715
	q_e	104.0	51.3
	R^2	0.980	0.985

CONCLUSION

Multifunctional microsphere adsorbent **LBM**, was characterized using BET, FTIR and SEM techniques as well as volumetric methods. Even **LBM** have low active surface it showed high adsorption potential and exceptional kinetic with respect to dyes removal as a result of the presence of wealth of surface functionalities such as phenolic and hydroxyl groups. Due to numbers of dyes proton-donating/proton-accepting sites a different adsorbate/adsorbent interaction could be achieved with dominating electrostatic and hydrogen-bonding interactions. Significance of these surface groups was confirmed by high adsorption performances of **LBM**, *i.e.* increased adsorption capacity of 525.66 mg g^{-1} obtained for highly contaminated solution ($C_{i[CA]}$ =150 mg dm^{-3}). This could not be applied for SOG due to low solubility of this dye. Kinetic study, using PSO equation, and diffusional models indicate pore diffusional transport as limiting step. In general, presented results indicate necessity of the future development and optimization of adsorbent, similar to **LBM** microsphere, which would have uniform spherical shape, higher porosity and increased surface functionalities. Except of this the most significant intention would be directed to use of mostly bio-based raw materials in the synthesis of microsphere precursors and porogen as well. In that manner use of bio-renewable materials for production of biodegradable adsorbent with potential applicability in a real water purification would be a comprehensive approach in a creation of circular economy system.

ACKNOWLEDGEMENT

This work was supported by the Ministry of Education, Science and Technological Development of the Republic of Serbia (Contract No.451-03-68/2022-14/200135).

REFERENCES

[1] Z.A. Alothman, Y.E. Unsal, M. Habila, *et al.*, Food Chem. Toxicol; 50 (8) (2012) 2709–2713.

[2] S. Sahnoun, M. Boutahala, A. Kahoul, *et al.*, Comptes. Rendus. Chimie; 21 (3–4) (2018) 391–398.

[3] M. Wawrzkiewicz, B. Podko, T. Jesionowski, *et al.*, Ind. Crops. Prod; 180 (2022) 114785.

[4] M. Wawrzkiewicz, Z. Hubicki, J. Haz. Mat; 164 (2–3) (2009) 502–509.

[5] A.L. Popović, J.D. Rusmirović, Z. Veličković, *et al.*, Int. J. Biol. Macromol; 156 (2020) 1160–1173.

[6] K.A. Taleb, J.D. Rusmirović, M.P. Rančić, *et al.*, J. Serb. Chem. Soc; 81 (10) (2016) 1199–1213.

[7] A. Popović, J. Rusmirović, S. Lević, *et al.*, 31st Int. Congr. Process Ind., 6–8.6.2018. Bajina Bašta, Serbia (2018) 235–239.

[8] J. Iqbal, F. H. Wattoo, M.H.S. Wattoo, *et al.*, Arab. J. Chem; 4 (4) (2011) 389–395.

[9] M. Sobiesiak, B. Podkościelna, O. Sevastyanova, J. Anal. Appl. Pyrolysis; 123 (2017) 364–375.J.

[10] L. Serrano, E.S. Esakkimuthu, N. Marlin, *et al.*, Energy Fuels; 32 (5) (2018) 5969–5977.

Conference Papers

SO_2 POLLUTION IN ŠABAC (2009–2020)

Sanja Mrazovac Kurilić[1*], Ana Ćirišan[1], Zorica Podraščanin[2],
Ljiljana Nikolić Bujanović[1]

[1]Faculty of Ecology and Environmental Protection, Union-Nikola Tesla University,
Belgrade, SERBIA

[2]Faculty of Science and Mathematics, University of Novi Sad, Novi Sad, SERBIA

[*]*mrazovac@gmail.com*

Abstract

The paper presents the results of measuring the concentration of SO_2 in the territory of Šabac for the period 2009–2020. Mean values per hours of day, per days of the week and months of the year for the total time period are shown. Also, the average annual values calculated by days, months and years are shown. Significant deviation and markedly high values of SO_2 for 2012 and 2015 can be noticed. The result can be interpreted by increasing the volume of industry in the observed territory in that period.

Keywords: air, SO_2, pollution

INTRODUCTION

Due to the increasingly rigorous regulations, air quality in Europe is slowly improving, but pollutants in particular continue to have a serious impact on human health. SO_2 is one of the most important precursors of secondary aerosols in the atmosphere. It has a significant role in air pollution, leading to degraded visibility, changes in the radiation budget, and acid rain [1–4]. Many studies have shown a dependence of SO_2 concentrations in the ambient air on meteorological parameters, particularly the wind speed and direction, air temperature, humidity, and atmospheric pressure. SO_2 is the most widely distributed and important air pollutant originating from industrial and domestic emissions. This substance is formed upon the combustion of sulfur-containing fuels, e.g., coal, oil, and diesel. In the chemical industry, this gas is produced in the contact process for the production of sulfuric acid and occurs in the form of residual SO_2 [5]. SO_2 as an air pollution indicator is a gas of strong smell, colorless, suffocating, irritating, and its toxicity increases with humidity, adversely affecting the health of people, animals, and plants [6,7]. It may cause increased respiratory diseases, reduced pulmonary function, low birth weight, and mortality [8]. The varying coefficient models illustrated that the temporal (yearly) variation of SO_2 concentration was more influenced by human-related factors, especially by secondary industry share. The sulfur oxides are among the most common pollutants because sulfur can be found in various forms in most fuels and ores. The spatial variation of such concentration was more affected by meteorological indicators, especially by wind speed [9].

MATERIALS AND METHODS

The urban monitoring stations monitor the influence of urban and suburban settlements over air quality [5]. Monitoring station in Šabac was selected for this study. Radius of the monitoring area varies approximately between 1 and 7 km. Sampling of gaseous pollutants (SO_2) is carried out by absorbing the contaminant from the known volume of air in the appropriate absorption solution, using the apparatus for air sampling (the manufacturer PROEKOS Belgrade, type AT-801X-PE-07-12/10). The method of testing sulfur dioxide is determination of the acidic gaseous pollutants index in the air (titrimetry) SRPS ISO 4220:1997.

RESULTS AND DISCUSSION

Figures 1–6 show the SO_2 concentrations in air on the territory of the Republic of Serbia for the period from 2009 to 2020. The SO_2 limit value according to the Regulation on air monitoring is 50 μg/m^3 at the annual average level.

Figure 1 shows the values by days of the week for the observed period. It can be concluded that there is no significant deviations by days, and average daily values are between 50 and 60 μg/m^3.

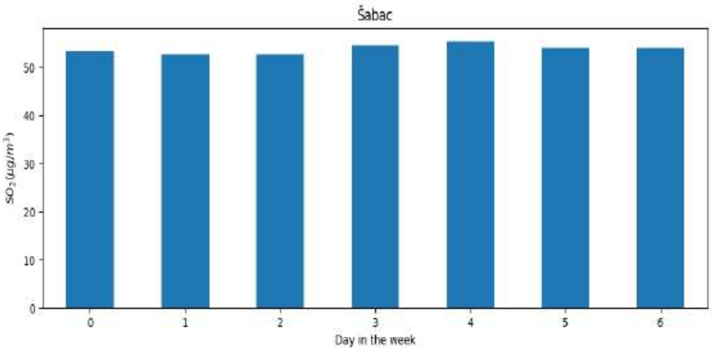


Figure 1 *SO_2 average concentration in air by days of the week (Šabac, 2009–2020)*

Figure 2 shows the mean hourly values over 24 hours for the observed period. They are also between 50 and 60 μg/m^3. The graph shows an increase in value in the period from 7 am to evening (around 6 pm), which coincides with the working hours during the day.

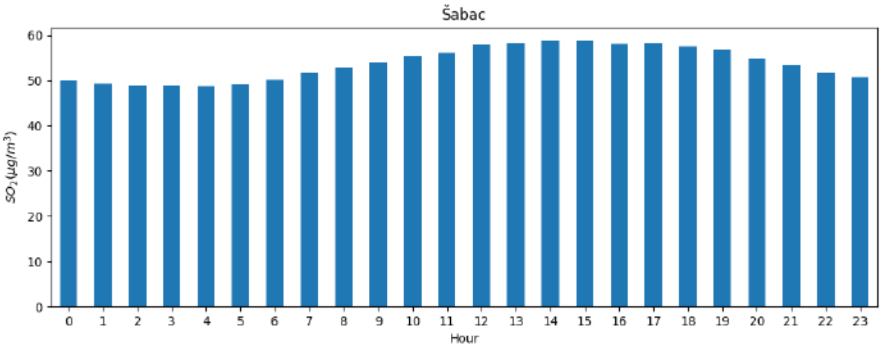


Figure 2 *SO_2 average concentration in air by hours of day (Šabac, 2009–2020)*

Figure 3 shows the mean monthly values over 12 months of the year for the observed period. They are between 20 and 90 μg/m^3. The graph shows an increase in value in the period of autumn and winter due heating season.

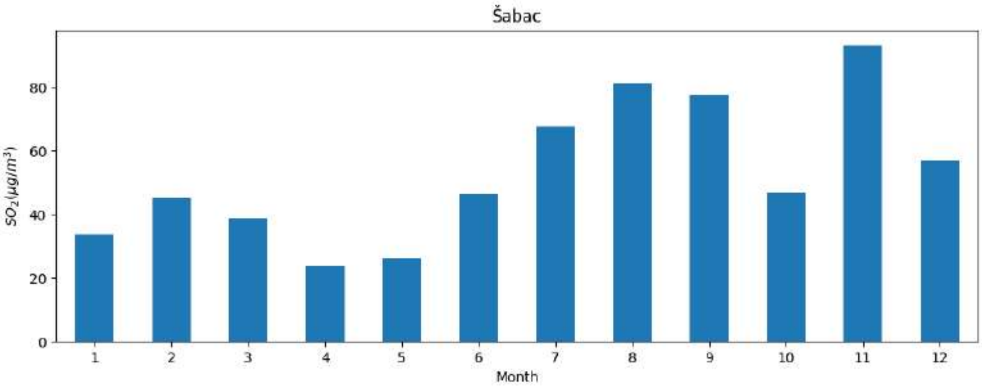


Figure 3 *SO_2 average concentration in air by months (Šabac, 2009–2020)*

Figures 3–6 show the values of concentrations in the period from 2009 to 2020, based on hourly, daily and monthly mean values. From the graphics (Figures 4–6), it can be seen that the measured concentrations of SO_2 extremely exceed the limit value in 2012 and 2015.

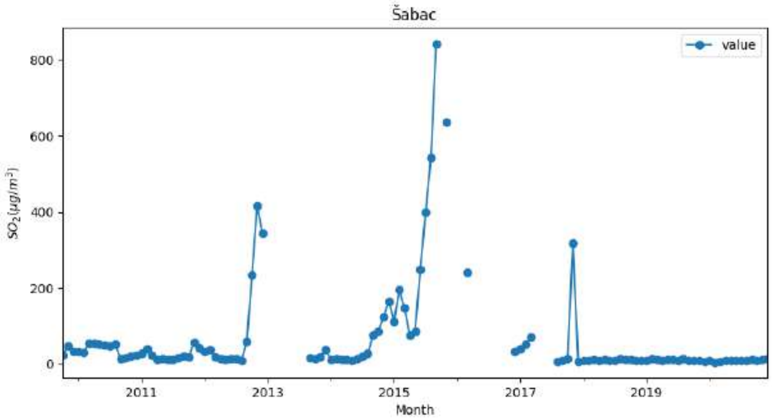


Figure 4 *SO_2 average concentration in air, monthly values (Šabac)*

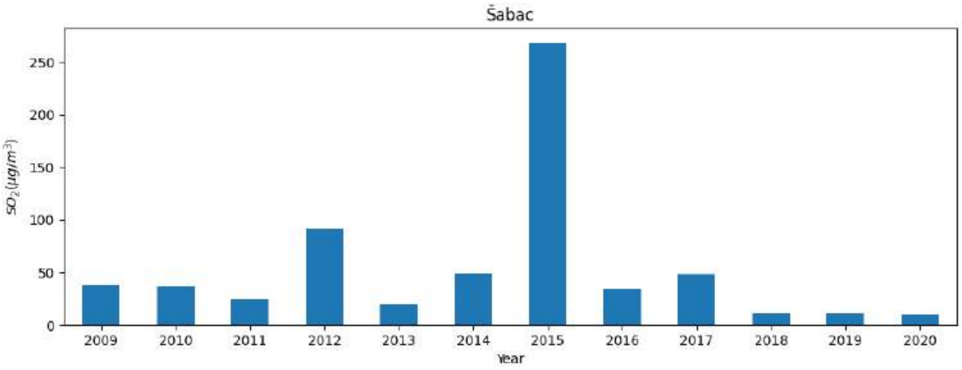


Figure 5 *SO_2 average concentration in air, yearly values (Šabac)*

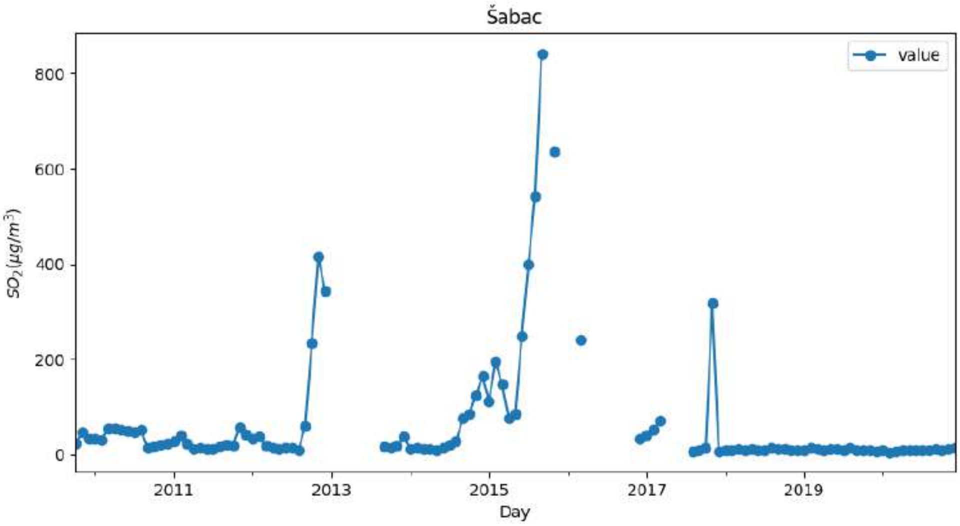


Figure 6 *SO_2 average concentration in air, daily values (Šabac)*

CONCLUSION

Based on the presented results, it can be concluded that during the observed period 2009–2020 there are high values of sulfur dioxide concentration, and markedly high values, up to 800 μg/m^3, based on hourly and daily data, are in 2012 and 2015. Such results can be explained by the increase in industrial production on the territory of Šabac.

ACKNOWLEDGEMENT

Authors appreciate that this work was financed from project 3949/1 supported by the Faculty of Ecology and Environmental Protection, Union-Nikola Tesla University, Belgrade, Serbia.

REFERENCES

[1] C. Oprea, D.M. Grigore, E. Bogan *et al.*, Proceedings air and water: Components of the environment, “World Water Day“, March 7–19, Cluj-Napoca, Romania (2017) 289–296.

[2] V. Ramanathan, P.J. Crutzen, Atmos. Environ; 37 (2003) 4033–4035.

[3] L. Wang, Z. Guo, X. Xiao *et al.*, Geogr. Sci; 18 (3) (2008) 353–362.

[4] M.G. Zhang, I. Uno, Y. Yoshida *et al.*, Atmos. Environ; 38 (2004) 6947–6959.

[5] S.K. Bhargava. Practical methods for water and air pollution monitoring, New Delhi: New age international (P) limited, New Delhi (2009), p.149, ISBN: 8122429211 9788122429213.

[6] B. Brunekreef, S.T. Holgate, Lancet; 360 (9431) (2002) 1233–1242.

[7] M. Wang, T. Zhu, J.P. Zhang *et al.*, Atmos. Chem. Phys; 11 (2011) 11631–11645.

[8] X.P. Xu, L.H. Wang, T.H. Niu, Ecosyst. Health; 4 (1998) 199–209.

[9] X. Yang, S. Wang, W. Zhang *et al.*, J. Clean Prod; 167 (2017) 824–836.

THE DISTRIBUTION OF THE MASS CONCENTRATIONS OF K, Th AND U IN THE SOILS OF THE TEKIJA REGION, THE NP ĐERDAP

Ana Čučulović[1*], Jelena Stanojković[1], Rodoljub Čučulović[2], Saša Nestorović[3], Nenad Radaković[3]

[1]University of Belgrade, Institute for the Application of Nuclear Energy – INEP,
Banatska 31b, 11080 Zemun, SERBIA
[2]University of MB, Faculty of Business and Low, Teodora Drajzera 21,
11000 Belgrade, SERBIA
[3]Public Company Đerdap Nationalni Park, Kralja Petra I 14a,
19220 Donji Milanovac, SERBIA
anas@inep.co.rs

Abstract

Soil samples (27) were collected in June in the period from 2018 to 2020 on the territory of the National park Đerdap (Tekija region, from 4 governing units). Mass concentrations of potassium, thorium and uranium calculated based on measured gamma spectrometric radionuclide activity are shown in this work. The mean value of mass concentration of the analyzed elements in soil samples in the investigated three year period were 1.84% potassium, 3.17 mg kg^{-1} uranium and 10.15 mg kg^{-1} thorium. The strength of the absorbed gamma radiation dose originating from radionuclide activity was calculated. The total and also annual effective doses were in the range of average values determined in the World.

Keywords: NP Đerdap, mass concentration, potassium, thorium, uranium

INTRODUCTION

A National Park (NP) is a protected region with large numbers of diverse natural ecosystems of national significance, landscape features and cultural heritage where man lives in accordance with nature [1]. The first NP in the World was founded in 1872 in the Yellowstone region (USA), while in Europe the first NP was founded in 1909 (Sarek, Sweden). The first NP was founded in 1924 on the territory of former Yugoslavia in the Triglav lake valley. In 1948 the United Nations formed the International Union for Conservation of Nature (IUCN). Since the XIV century Serbia has worked on environmental protection (Dušan’s Code, article 123). The oldest NP in Serbia was founded in 1960 (Fruška gora), followed by: Đerdap (1974), Kopaonik (1981), Tara (1981) and Šar-planina (1986). The procedure for protecting Stara Planina and Kučaj-Beljanice as a NP started in 2022. All NPs in Serbia cooperate with the independent non-governmental organization EUROPARC – Federation of Nature and National Parks of Europe [2]. NP Đerdap is located in the North-Eastern part of Serbia and covers part of the area of the Đerdap gorge (Iron Gate) in the middle flow of the Danube. It includes parts of the Severni Kučaj, Miroč and Štrbac massive 2-10 km wide, and also parts of the Danube belonging to the Republic of Serbia [1]. The very complex relief in NP Đerdap, specific climate, large number of relic species and phytocenosis, and also a great variety in the lithological composition of rocks, genetic affiliation and geological age have caused the formation of a variety of soil types with different properties and production potential [2,3]. Land is a dynamic system in which different physico-chemical and biological processes occur. It is composed of two components: mineral and organic. Rocks that are part of the Earth crust contain a certain concentration of natural radionuclides (uranium, radium, thorium and potassium) that are also present in the soil formed when they decompose and their contribution to natural radioactivity in the environment is the highest [4]. According to the UNSCEAR report (United Nations Scientific Committee on the Effects of Atomic Radiation) average mass concentrations (concentration range) (mg kg^{-1}) of uranium, radium, thorium, and potassium (%) in soil in the World are: 2.82 (1.29–8.87); 3.18 (1.53—5.45); 7.32 (2.68–15.61) and 1.54 (0.54–3.28), respectively [5]. The behavior of radionuclides depends on interactions with other soil components and their interrelations can be used to evaluate different processes in soil. Knowledge of their distribution and concentration plays a significant role in radiation protection.

External radiation of the population mainly originates from gamma radiation formed after the decay in radioactive series of uranium, thorium and potassium. Other radionuclides of natural origin are present in small amounts and to not contribute very much to population radiation [6].

Continual measurement and monitoring of basic activity levels of samples from the environment has a fundamental significance from the aspect of ecosystem protection, as this is the basis for building criteria of radiological security of the biosphere. In order to obtain a realistic picture of soil radioactivity, the most significant and sensitive component of the environment, soils samples were collected in NP Đerdap, in the Tekija region in the period 2018-2020 and the obtained results are presented in this work.

MATERIAL AND METHODS

Soil samples (27) were collected in the Tekija region, NP Đerdap, from 4 management units (MU) (Faca Tekija, Dafin, Đerdap and Štrbačko korito), up to the depth of 10 cm, in June 2018–2020. Localities were carefully chosen based on the results obtained for bioindicator radioactivity in previous years [7–9]. After arrival to the laboratory, the samples were cleaned by removing visible impurities, dried, mechanically chopped, homogenized and packed into Marinelli vessels with a volume of 0.5 L, hermetically sealed with paraffin and left to sit for 40 days in order to establish a radioactive stability of post-radon series members ^{238}U, prior to gamma spectrometric analysis. The sample mass was up to 600g. A semiconducting germanium high purity detector of the n-type, ORTEC – AMETEK, USA, with 8192 channels, resolution 1.65 keV and relative efficiency of 34% at 1.33 MeV for ^{60}Co. Spectra were analyzed using the Gamma Vision 32 software package [10].

Specific activity of ^{40}K, ^{238}U and ^{232}Th were converted into mass concentrations of potassium, uranium and thorium elements [11], respectively using the equation (1):

$$F_E = \frac{M_E \times C}{\lambda_{E,i} \times N_A \times f_{E,i} \times A_{E,i}} \tag{1}$$

where: F_E – participation of element E in the sample, M_E – atomic weight (kg mol^{-1}), $\lambda_{E,i}$ – constant of the radioactive decay of isotope i of element E (s^{-1}), $f_{E,i}$ – representation of isotope i in the nature, $A_{E,i}$ – measured specific activity (Bq kg^{-1}) of radionuclides (^{40}K, ^{238}U, ^{232}Th), N_A – Avogadro number (6.023 × 10^{23} atom/mol) and C – constant with values in 10^{6} for U and Th (mass concentration mg kg^{-1}) or 100 for K (mass concentration in %).

According to the recommendation of UNSCEAR [5], the absorbed dose strength (D) at 1 m above ground can be calculated based on measured activity levels ($A_{U,Th,K}$) (Bq kg^{-1}) of natural radionuclides in investigated soil samples according to equation (2) with the assumption that all progeny are in equilibrium with their precursors and that radionuclides insignificantly contribute to the total dosage due to external exposition, using the conversion factors for ^{238}U, ^{232}Th and ^{40}K 0.462; 0.604 and 0.042 (nGyh^{-1}/(Bq kg^{-1}) respectively:

$$\text{D (nGyh}^{-1}\text{)} = 0.462A_{U}+0.604A_{Th}+0.042A_{K} \tag{2}$$

If the total absorbed radiation dose strength (D) is known then equation (3) can be used to calculate the yearly effective radiation dose for an adult H (mSv):

$$\text{H (mSv)} = \text{D}\times 0.7\times 0.2\times 8760 \tag{3}$$

where: 0.7 (SvGy^{-1}) is the conversion coefficient (ratio between the yearly effective dose received by the population and the absorbed dose in air); 0.2 – is the exposition factor for external irradiation (it is assumed that on average the population spends about 20% time outside in the open); 8760 – number of hours in a year [5].

RESULTS AND DISCUSSION

The natural radioactivity of soil depends on the type of radiation and geological structure of the area. Table 1 shows mass concentrations of potassium (%), uranium and thorium (mg kg^{-1}) in soil, minimal and maximal values, collected from 2018 to 2020 in the Tekija region.

Analysis of data shown in Table 1 enabled calculation of average values of mass concentrations of potassium present in soil collected in 2018 of 1.96%, 2019 2.02% and 2020 of 1.55%. These values are somewhat higher compared to our research conducted in previous years [7–9], but in the range of values determined in the World [5]. The average value of the mass concentration of uranium in soil was: 2018 3.24 mg kg^{-1}, 2019 3.35 mg kg^{-1} and 2020 2.92 mg kg^{-1}. These values are in the range of values obtained in our previous research [7–9] and in the World [5]. The average value of mass concentration of thorium in soil was: 2018 9.68 mg kg^{-1}, 2019 10.68 mg kg^{-1} and 2020 9.97 mg kg^{-1} and they are somewhat higher compared to our previous research and in the range determined in the World [5,7–9]. The values of the Pearson coefficient among radionuclides in soil are similar: for U–Th 0.499; K–U (0.537) and K–Th (0.503) indicating their moderate linkage.

Table 1 *Mass concentrations, average, minimal and maximal values of potassium, uranium and thorium in soil collected in the period 2018–2020 in the Tekija region*

MU* (samples)	**Year**	**K (%)**		**U (mg kg^{-1})**		**Th (mg kg^{-1})**	
		A**	**Min–max**	**A****	**Min–max**	**A****	**Min–max**
Faca Tekija (2)	2018	1.82	1.72–1.91	2.99	2.16–3.81	9.92	9.85–9.98
Dafin (2)		1.63	1.58–1.68	3.22	2.84–3.60	10.25	9.90–10.59
Đerdap (4)		2.20	1.89–2.64	3.38	2.56–4.38	9.29	8.17–10.00
Đerdap (7)	2019	2.18	1.32–2.97	3.56	2.60–4.20	11.08	8.46–13.12
Š.korito (3)		1.65	1.48–1.88	2.87	2.58–3.17	9.75	9.17–10.49
Đerdap (6)	2020	1.49	1.00–1.88	2.84	2.06–3.15	9.07	5.41–10.59
Š. Korito (3)		1.67	1.45–1.98	3.08	2.52–3.40	11.77	9.34–13.73

*MU-management unit, A**-average value

The absorbed radiation dose strength per radionuclide and in total D (nGyh^{-1}) was calculated based on equation (2) as shown in Table 2. The average value of the radiation dose strength of potassium, uranium and thorium (nGyh^{-1}) in soil collected in the territory of the Tekija region was: in 2018 it was 25.73, 18.57 and 23.98, in 2019 26.52, 19.19 and 26.46, and in 2020 20.38, 16.71 and 24.69, respectively. The average value of the total absorbed dose strength (nGyh^{-1}) in soil collected in the period 2018-2020 was 68.27, 72.17 and 61.78. Knowing D (nGyh^{-1}), and based on equation (3) the average annual effective radiation doses in the Tekija region were calculated as: in 2018 0.084 mSv, in 2019 0.088 mSv, and in 2020 0.088 mSv. These values were higher than the average value determined in the World (0.070 mSv), but within the measurement range.

Table 2 *Absorbed radiation dose strength per radionuclide and in total (nGyh^{-1}), annual effective radiation dose (nGy h^{-1}) in the Tekija region in the period 2018–2020*

MU*	**Year**	**Absorbed dose strength per radionuclide and in total**				**H**
		K	**U**	**Th**	**D**	**(mSv)**
		(nGy h^{-1})				
Faca Tekija	2018	23.81	17.12	24.55	65.48	0.080
Dafin		21.36	18.46	25.37	65.19	0.080
Đerdap		28.87	19.35	23.00	71.22	0.087
Đerdap	2019	28.58	20.38	27.45	76.41	0.097
Š.korito		21.70	16.42	24.14	62.26	0.076
Đerdap	2020	19.58	16.26	22.46	58.30	0.071
Š. Korito		21.98	17.62	29.15	68.75	0.084

*MU-management unit

Based on the Guidelines [6] the annual effective dose for the population is increased if it is higher than 1 mSv for a year. The calculated average values show that the effective dose for the population in Tekija region is low.

CONCLUSION

The average mass concentration of potassium in soil samples collected from 2018 to 2020 in the Tekija region was 1.84%, while the uranium concentration was 3.17 mg kg^{-1}, and the thorium concentration was 10.15 mg kg^{-1}.

The values of Pearson coefficients between radionuclides in soil were similar: for U–Th (0.499); K–U (0.537) and K–Th (0.503) indicating moderate linkage.

The absorbed gamma radiation dose strength originating from radionuclide activity in soil was calculated. Total and also annual effective doses were also calculated and they were in the range of average values in the World.

ACKNOWLEDGEMENT

The research presented in this work was performed with the financial backing of the Ministry for Education, Science and Technological development of the Republic of Serbia, as part of financing scientific research at the Institute for the Application of Nuclear Energy – INEP, contract number 451-03-68/2022-14/200019.

REFERENCES

[1] Zakon o zaštitu životne sredine Srbije, Službeni glasnik Republike Srbije br. 66/91, 83/92, 53/93, 67/93, 48/94, 53/95, 84/15 i 95/18.

[2] M. Medarević, Šume Đerdapa, JP Nacionalni park Đerdap - Donji Milanovac i IP Ecolibri, Beograd (2001), ISBN: 86-7905-037-7 (in Serbian).

[3] M. Knežević, R. Milošević, O. Košanin, Glasnik šumarskog fakulteta; 102 (2010) 57–68.

[4] A. Dangić, Geohemijski procesi u prirodi i radionuklidi, Jonizujuća zračenje iz prirode, Jugoslovensko društvo za zaštitu od zračenja, Institut za nuklearne nauke Vinča. Jugoslovensko društvo za zaštitu od zračenja, Beograd, Srbija (1995) 41–56.

[5] UNSCEAR (2000), United Nations Scientific Committee on the Effects of Atomic Radiation. *Sources and Effects of Ionizing Radiation. UNSCEAR 2000 Report to the General Assembly, with Scientific Annexes*, New York (2000).

[6] Pravilnik o granicama izlaganja jonizujućim zračenjima i merenjima radi procene nivoa izlaganja jonizujućim zračenjima, Službeni glasnik RS, 86/2011 i 50/2018.

[7] A. Čučulović, R. Čučulović, M. Sabovljević, *et al.*, Arh. Hig. Rada Toksikol; 67 (2016) 31–37.

[8] A. Čučulović, R. Čučulović, S. Nestorović, *et al.*, 26th International Conference Ecological Truth & Environmental Research EcoTER'18, Proceedings, 12–15 June, Bor Lake, Serbia (2018) 140–145.

[9] A. Čučulović, R. Čučulović, S. Nestorović, *et al*., 14th International Conference on Fundamental and Applied Aspects of Physical Chemistry, Proceedings, Volume II, 24–28 September, Belgrade, Serbia (2018) K-14-P, 821–824.

[10] ORTEC, Gamma Vision 32, Gamma-Raz Spectrum Analzsis and MCA Emulation, ORTEC, Oak Ridge, Version 5.3 (2001).

[11] IAEA, Construction and use of calibration facilities for radiometric field equipment, Technical Report Series 309. International Atomic Energy Agency (IAEA), Vienna (1989).

APPLICATION OF NANO- MnO_2 MODIFIED LIGNIN – BASED ADSORBENT FOR REMOVAL OF DICHROMATE IONS AND DICLOFENAC FROM WATER

Jovana Bošnjaković[1*], Mladen Bugarčić[2], Milena Milošević[3], Nevena Prlainović[4], Rabab Salih[4], Petar Batinić[5], Ana Popović[6], Maja Đolić[4]**

[1]Research and Development institute Lola Ltd., Kneza Višeslava 70a,
11030 Belgrade, SERBIA

[2]Institute for Technology of Nuclear and Other Mineral Raw Materials,
Bulevar Franš d'Eperea Street 86, 11000 Belgrade, SERBIA

[3]University of Belgrade - Institute of Chemistry, Technology and Metallurgy - National institute of the Republic of Serbia, Department of Ecology and Technoeconomics,
Njegoševa 12, 11001 Belgrade, SERBIA

[4]University of Belgrade, Faculty of Technology and Metallurgy, Karnegijeva 4,
11060 Belgrade, SERBIA

[5]Institute for Medicinal Plant Research "Dr. Josif Pančić", Department of Agricultural Research and Development, Tadeuša Koščuška 1, 11000 Belgrade, SERBIA

[6]The Academy of Applied Technical Studies Belgrade, 3 Katarine Ambrozic Str.,
11000 Belgrade, SERBIA

[*]*jovana.bosnjakovic@li.rs*

[**]*apopovic@politehnika.edu.rs*

Abstract

The aim of this paper is to investigate the application of modified lignin-based adsorbent for successful removal of dichromate ions and sodium diclofenac (DCF) from aqueous solutions by adsorption. Modification of lignin-based adsorbent (LBA) was performed by inverse suspension copolymerization with branched poly (ethylene-imine) using epichlorohydrin as a crosslinker. After that, the functionalization of LBA was performed by chemical binding of amino modified nanoparticles of manganese (IV) oxide, in order to improve the adsorption properties. Characterization of LBA-MnO_2 *microspheres was performed using FT-IR spectrometer, Scanning electron microscopy, BET/BJH analysis. The adsorption process was performed in a batch adsorption system. The results were obtained with the help of kinetic and corresponding equilibrium adsorption isotherms. The maximum adsorption capacity for the removal of* $Cr_2O_7^{2-}$ *ions and DCF was obtained using the Langmuir model and amounts to 88.4 mg* g^{-1} *and 52.8 mg* g^{-1} *at 45 °C, respectively. Adsorption kinetics was described using a second-order pseudo model. Based on thermodynamic parameters, it was concluded that the adsorption process is an endothermic and spontaneous. Based on the obtained results, LBA-*MnO_2 *material possess very good adsorption properties.*

Keywords: sodium diclofenac, dichromate ions, adsorption, lignin-based adsorbent

INTRODUCTION

Rapid industrial development and increased number of inhabitants are continuously causing an increased amount of generated waste, which easily reaches water recipients. Heavy metals, widely spread in water, belong to the group of the most dominant pollutants [1]. Heavy metals accumulate in human body due to the consumption of contaminated water, which can lead to various diseases [2]. They are toxic, even at low concentrations, and not biodegradable [2]. Also, there is an increasing concentration of pharmaceuticals in drinking water and wastewater, which can pose a great danger to human life [3,4]. In recent years, sorbents based on natural materials, originating from renewable or waste sources, have been used for removing heavy metal ions and pharmaceuticals [5]. The adsorption process is mostly used because of its simplicity and efficiency. Economy, distribution and beneficial impact on the environment are the main reasons for using sorbents based on natural materials for removing heavy metals ions and pharmaceuticals from aqueous systems [6,7]. Lignin can be obtained by processing biomass, as a by-product in the pulp and paper industry [8–11]. In this study, the modified craft lignin has been used as a bio-sorbent for removing inorganic (dichromate ions) and organic pollutants (sodium diclofenac, DCF). In order to characterize bio-sorbent Fourier transform infrared spectroscopy (FT-IR), scanning electron microscopy (SEM) and BET/BJH were performed. Variation of adsorption efficiency and concentration of heavy metals ions were determined varying temperature, mass of the adsorbent, pH value of the solution and contact time duration in the scoring system. Langmuir, Freundlich and similar isotherm models were applied to determine the maximum adsorption capacities for the removal of heavy metal ions and DCF. Adsorption kinetics was calculated using first, second and pseudo second order.

The aim of this paper is to investigate the possibility of using MnO_2-modified lignin-based adsorbent to remove cations of dichromate and sodium diclofenac from aqueous solutions by adsorption process.

MATERIALS AND METHODS

A modified process based on the inverse suspension copolymerization [1] of kraft lignin with branched poly (ethylene-imine), PEI, to obtain an amino functional adsorbent and with the help of epichlorohydrin as a crosslinking agent, the synthesis of lignin bio-sorbent was performed. 10 mL of deionized water and 0.5 g of lignin were added to the three-necked balloon. Further, 2.0 g of PEI, 0.1 g of sodium dodecyl benzene sulfonate, as well as 10 mL of sodium alginate emulsifier solution, were added with stirring. Stirring was continued for 30 minutes at 60°C. In order to obtain a suspension, 80 mL of liquid paraffin was added to the flask. The copolymerization process was completed by adding dropwise 2.0 mL of crosslinker, epichlorohydrin, with the constant stirring for 120 minutes. The obtained copolymerized LBA, was centrifuged, washed with ethanol, ether and finally with water. The process of lyophilization was performed by drying LBA for 24 hours at 40°C. The synthesis of manganese (IV) oxide nanoparticles was performed by the reaction between potassium permanganate ($KMnO_4$) and ethyl alcohol (C_2H_5OH). 0.5 g of $KMnO_4$ was dissolved in 300 mL of distilled water. With constant stirring, 10 mL of C_2H_5OH was added dropwise to the mixture. A dark brown precipitate was formed, which was filtered and washed. Amino-functionalization resulted in the formation of nanoparticles, with the use of (3-aminopropyl) triethoxysilane (APTES) and the formation of amino-modified nanoparticles of manganese (IV) oxide (NP-OA-MnO_2). The LBA adsorbent was modified with the help of synthesized MnO_2 nanomaterial. Adsorbate solutions of sodium diclofenac and potassium dichromate (initial concentration 10 mg L^{-1}, both) were prepared by dilution of standard solutions (1000 mg L^{-1}).

RESULTS AND DISCUSSION

The textural properties of the LBA-MnO_2 adsorbent, determined by BET/BJH analysis, are presented in Table 1. Specific surface area (S_{BET}), pore volume (V_{tot}) and intermediate pore (V_{meso}), and mean pore diameter (D_m) were determined. The specific surface area of samples was calculated according to the Brunauer, Emmett, Teller (BET) method from the linear part of the nitrogen adsorption isotherms. The total pore volume (V_{tot}) was given at $p/p_0 = 0.98$. The volume of the mesopores was calculated according to the Barrett, Joyner and Halenda (BJH) method from the desorption branch of isotherm.

Table 1 *Textural properties of LBA-MnO_2 adsorbent*

Samples	**S_{BET}, m^2/g**	**V_{tot}, cm^3/g**	**V_{meso}, cm^3/g**	**D_m, nm**
LBA-MnO_2	188.4	0.3256	0.3045	5.12

SEM micrographs of the LBA-MnO_2 sample are shown in Figure 1. As can be seen, small particles of irregular shape were observed, in which the agglomeration process can be noticed. The reason for this is the low concentration of emulsifiers (≤1.0 wt. %).

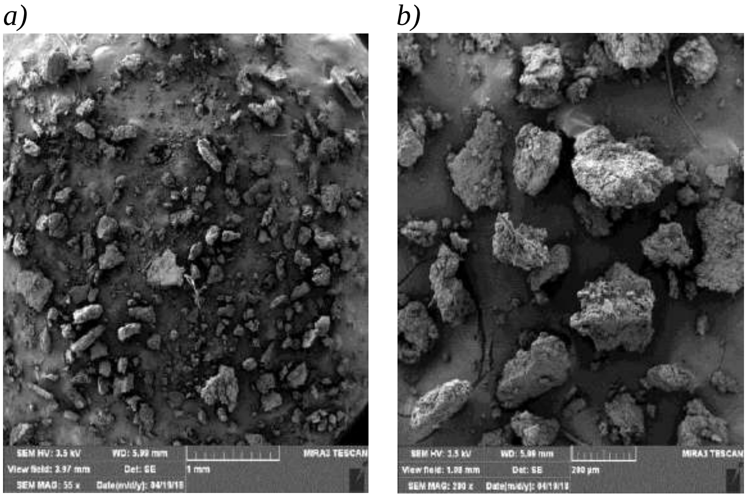


Figure 1 *SEM image of LBA-MnO_2 sample*

Figure 2 represents the FT-IR spectrum of the LBA-MnO_2 sample. The peak at 3329 cm^{-1} of the LBA-MnO_2 sample corresponds to the phenolic and hydroxyl vibrations of the O-H bond elongation [12,13]. Bands at 1593 cm^{-1}, as well as in the range of 1400–1470 cm^{-1}, indicate the presence of an aromatic structure from lignin [12,13]. The peaks at 2849 and 2917 cm^{-1} refer to the symmetric and asymmetric C-H tensile vibrations of the methylene group [14].

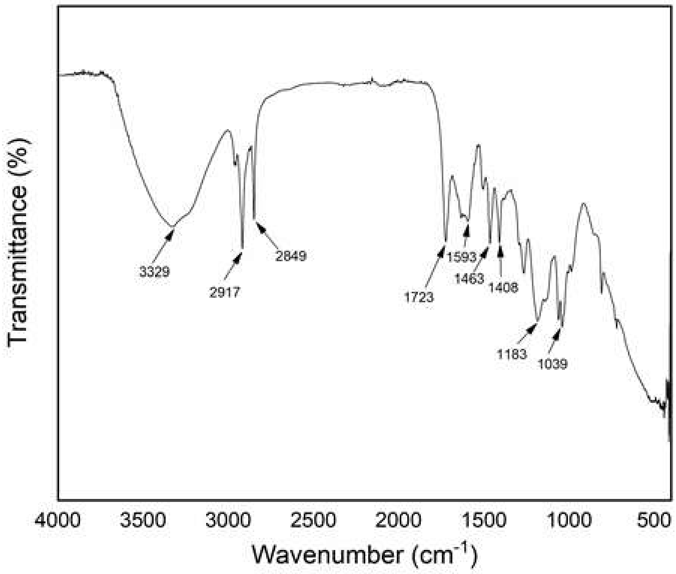


***Figure 2** FT-IR spectrum of the LBA-MnO_2 sample*

Nonlinear models of Langmuir, Freundlich, Temkin and Dubinin–Radushkevich adsorption isotherms are presented in Tables 2 and 3. Based on the results from Table 2, obtained with the help of Langmuir adsorption model, the adsorption capacity (q_e) increases with increasing temperature. Also, with increasing temperature there is an increase in Langmuir constant (K), which shows that at higher temperatures there is higher affinity of LBA-MnO_2 adsorbent. The maximum adsorption capacity (q_e) during the adsorption of $Cr_2O_7^{2-}$ ions and DCF is 88.4 and 52.8 at 45°C, respectively.

***Table 2** Results of Langmuir adsorption model when removing* $Cr_2O_7^{2-}$ *and DCF at 25, 35 and 45°C*

Lengmuir isotherm		q_m **(mg g^{-1})**	K_L**(L mg^{-1})**	**R^2**
LBA-MnO_2- $Cr_2O_7^{2-}$	25°C	78.653	0.14833	0.99091
	35°C	83.639	0.15172	0.99679
	45°C	88.434	0.15620	0.99748
LBA-MnO_2-DCF	25°C	43.498	0.54497	0.97590
	35°C	48.086	0.48902	0.97190
	45°C	52.831	0.44583	0.96781

Freundlich parameter (1/n) is less than 1 for both DCF and $Cr_2O_7^{2-}$ adsorption, indicating heterogeneity of the surface. A slight increase of 1/n value with increasing temperature due to subsequential heterogenization of the surface may be observed in Table 3. Also, from the same table, 1/n values for adsorption of sodium diclofenac and dichromate noticeably differ. It may be concluded that the surface is more homogenized after sodium diclofenac sorption, which may be explained as similiraty in structure of sodium diclofenac and lignine.

With the help of Dubinin – Radushkevich and Temkin's model, significant data on the adsorption process were obtained. Based on the values of energy adsorption (E) for the adsorption of $Cr_2O_7^{2-}$ and DCF obtained on the basis of the Dubinin – Radushkevich model, it can be concluded that the ion exchange mechanism is dominant and its value ranges around 8 kJ mol^{-1}. Also, based on the value of E, it is concluded that adsorption bonding is physisorption ($E<8$ kJ mol^{-1}) [15]. The bond constant, A, based on the Temkin model, represents the maximum binding energy ($dm^3\ g^{-1}$). The maximum binding energy, for $Cr_2O_7^{2-}$ adsorption is reached at a temperature of 45°C, while for sodium diclofenac adsorption is reached at 25°C. The value of the mean index, B, for both types of pollutants also confirm conclusion made by comparison of energy activation that adsorbate bonding occurs *via* physical adsorption [16].

Table 3 *Results of Freundlich, Dubinin Radushkevich and Tempkin adsorption model when removing* $Cr_2O_7^{2-}$ *and DCF at 25, 35 and 45°C*

Isotherm models and parameters			**Temperature**		
			25°C	**35°C**	**45°C**
Freundlich isotherm	K_F ($mg\ g^{-1}$)($dm^3\ mg^{-1}$)$^{1/n}$	LBA-MnO_2-$Cr_2O_7^{2-}$	9.915232	10.70843	11.56561
	1/n		0.77341	0.77612	0.77780
	R^2		0.99286	0.99407	0.99457
	K_F ($mg\ g^{-1}$)($dm^3\ mg^{-1}$)$^{1/n}$	LBA-MnO_2-DCF	17.79673	18.23528	18.08722
	1/n		0.29308	0.31726	0.34001
	R^2		0.99421	0.99491	0.99422
Dubinin Radushkevich	q_m ($mg\ g^{-1}$)	LBA-MnO_2-$Cr_2O_7^{2-}$	25.16	2.638	27.59
	E ($KJ\ mol^{-1}$)		8.09316	8.11841	8.14253
	B		7.63	7.59	7.54
	R^2		0.87000	0.86472	0.85912
	q_m ($mg\ g^{-1}$)	LBA-MnO_2-DCF	28.20	719.34	29.71
	E ($KJ\ mol^{-1}$)		7.34852	8.60338	7.36927
	B		9.26	6.76	9.21
	R^2		0.69894	0.99711	0.68413
Tempkin isotherm	A ($dm^3\ g^{-1}$)	LBA-MnO_2-$Cr_2O_7^{2-}$	2.492848	2.586535	2.693991
	b		197.03	193.19	189.92
	B ($mg\ g^{-1}$)		12.58	13.26	13.93
	R^2		0.95123	0.95045	0.94929
	A ($dm^3\ g^{-1}$)	LBA-MnO_2-DCF	12.359	9.667758	7.98153
	b		346.34	314.28	288.71
	B ($mg\ g^{-1}$)		7.16	8.15	9.16
	R^2		0.95185	0.94362	0.93564

CONCLUSION

The subject of this paper refers to the application of sorbents based on natural polymer, kraft lignin, which is further modified by manganese dioxide nanoparticles, to remove heavy metal ions, such as $Cr_2O_7^{2-}$ and sodium diclofenac from aqueous solutions by adsorption. According to Langmuir's adsorption model, the highest adsorption capacity of 88.3 mg g^{-1} for removal of $Cr_2O_7^{2-}$ ions was reached at 45°C. When removing sodium diclofenac from water, the maximum adsorption capacity was 52.8 mg g^{-1} at 45°C. The mechanism of adsorption was subjected to Freundlich's model (chemisorption process), with a great contribution of Temkin's model. Based on the value of the mean free adsorption energy, it was determined that an overall removal process is a physisorption. Based on the presented results, it can be concluded that nano-modified, porous lignin-based adsorbent, LBA-MnO_2, can be used to remove heavy metal ions and sodium diclofenac from the aqueous solutions.

ACKNOWLEDGEMENT

This work was supported by the Ministry of Education, Science and Technological Development of the Republic of Serbia (Contract Nos. 451-03-68/2022-14/200066; 451-03-68/2022-14/200023; 451-03-68/2022-14/200135; 213-1/21-08-03-2021; 451-03-68/2022-14/200003; 451-03-68/2022-14/200026).

REFERENCES

[1] Y. Ge, L. Qin, Z. Li, Mater. Design; 95 (2016) 141–147.

[2] A.E. Burakov, E.V. Galunin, I.V. Burakova, *et al.*, Ecotox. Environ. Safe; 148 (2018) 702–712.

[3] V. Geissen, H. Mol, E. Klumpp, *et al.*, Int. Soil Water Conse. Res; 3 (2015) 57–65.

[4] S. Zhang, Y. Dong, Z. Yang, *et al.*, Chem. Eng. J; 304 (2016) 325–334.

[5] L. Ramrakhiani, A. Halder, A. Majumder, *et al.*, Chem. Eng. J; 308 (2017) 1048–1064.

[6] G. Gellerstedt, Ind. Crop. Prod; 77 (2015) 845–854.

[7] F.G. Calvo-Flores, J.A. Dobado, Chem. Sus. Chem; 3 (2010) 1227–1235.

[8] A. Duval, M. Lawoko, React. Funct. Polym; 85 (2014) 78–96.

[9] G. Huang, D. Wang, S. Ma, *et al.*, J. Colloid Interf. Sci; 445 (2015) 294–302.

[10] A.J. Ragauskas, G.T. Beckham, M.J. Biddy, *et al.*, Science; 344 (2014).

[11] S. Gillet, M. Aguedo, L. Petitjean, *et al.*, Green Chem; 19 (2017) 4200–4233.

[12] I. Bykov, Characterization of Natural and Technical Lignins using FTIR Spectroscopy, Master Thesis, Luleå University of Technology (2008).

[13] R.J.A. Gosselink, Lignin as a renewable aromatic resource for the chemical industry (2011).

[14] Y. Ge, Z. Li, D. Xiao, *et al.*, J. Ind. Eng. Chem; 20 (2014) 1765–1771.

[15] J. Perendija, Z.S. Veličković, I. Cvijetić, *et al.*, Process Saf. Environ. Protection; 147 (2021) 609–625.

[16] J. Perendija, Z.S. Veličković, I. Cvijetić, *et al.*, Cellulose; 27 (2020) 8215–8235.

MAPPING HEALTH RISKS OF CRITERIA CHEMICAL(S) TO DEMONSTRATE BENEFITS OF RISK ASSESSMENT FOR DECISION-MAKERS

Branislava Matić[1*], Snežana Živković Perišić[1], Dragana Jovanović[1], Snežana Dejanović[1], Dragan Miljuš[1], Lana Kukobat[2]

[1]Institute of Public Health of Serbia, Dr Subotića 5, 11000 Belgrade, SERBIA

[2]University of Belgrade, Faculty of Biology, Studentski trg 16, 11000 Belgrade, SERBIA

[*]*brankicam@batut.org.rs*

Abstract

Exposures to chemicals (and physical agents) are typically unevenly distributed geographically as well as temporally. Disease occurrence also shows geographically varying patterns. Geographic information systems (GIS) may be used to produce maps of exposure and/or disease to reveal spatial patterns. Supported by the World Health Organization (WHO) and the Ministry of Health, Institute of Public Health of Serbia (IPHS) has conducted a project "Strengthening of national capacities for assessment of chemicals risks for guiding risk reduction decisions". Basic task of the project was to prioritize chemicals for further risk assessment, according to the "10 criteria pollutants" defined by the WHO, among which expert team depicted arsenic and phthalates as chemicals of highest public health concern for the population of Serbia. Being abundant in environmental media, as a consequence of anthropogenic activities, As distribution was mapped for its presence in soil and PM10 in the vicinity of industrially contaminated sites. As arsenic is often following other heavy metals (Cd, Pb, Hg), a justified need for the systematic inclusion of human biomonitoring in regular health care practice is imposed. Also, a serious cross-sectional study on the extent of human exposure to such chemicals in the vicinity of ICSs should be performed, especially targeting the children.

Keywords: mapping, health risk, arsenic, soil, air

INTRODUCTION

The World Health Organisation has identified 10 (group of) chemicals of major public health concern and for each of them has provided risk management recommendations: Air pollution, Arsenic, Asbestos, Benzene, Cadmium, Dioxin and dioxin-like substances, Inadequate or excess fluoride, Lead, Mercury, Highly hazardous pesticides [1]. Chemicals risk assessment (RA) is addressed as a priority in strategic documents in areas of chemical safety and environmental health, in particular, the WHO Chemical Road Map, World Health Assembly (WHA) resolutions (67.11, 69.4), the International Health Regulation, the SAICM, and Ostrava Declaration on Environment and Health [2–6]. National road map for strengthening engagement of the health sector in chemicals management was developed recently, in 2021. It identified RA of chemical emergencies, organization trainings and education in the field of risk assessment, contribution to development of globally harmonized methods and new tools and approaches for RA, making available health-related data incl. risk assessment results as priority at national level [7].

The project "Strengthening of national capacities for assessment of chemicals risks for guiding risk reduction decisions" was implemented in 2021 by the Institute of Public Health of Serbia (IPHS), supported by the World Health Organization (WHO) and the Ministry of Health at the national level. This project was a continuation of involving health sector into the complacent process of managing chemicals, beginning with the project "Strengthening Serbian national capacities and inter-sectorial synergies for safe management of contaminated sites and related hazardous substances to prevent negative impact on human health and the environment" in 2018, through the project "Development of a national road map to enhance health sector engagement-contribution to sound chemicals management in Serbia till 2030", both of which were supported by the WHO as activities of Ostrava Declaration implementation [6,8]. Project's first objective was "Prioritization of chemicals for further assessment of risks" at the national level, according to the "WHO 10 chemicals of public health concern" list [1]. After an in depth analysis of different kinds of exposures to chemicals at the national level, the team has chosen arsenic as the most abundant element in the environmental media in Serbia and phthalates as a group of persistent organic pollutants (POPs) broadly present in a myriad of items of general use, whose ability to act as endocrine disrupting compounds and carcinogens seriously undermines national demographic status and general health [9].

Arsenic is extremely poisonous. International Agency for Research on Cancer (IARC) has classified arsenic as a human carcinogenic substance, group 1. Long-term intake of drinking water with elevated arsenic concentrations can cause the development of arsenicosis, the collective term for diseases caused by chronic exposure to arsenic. It includes several kinds of skin lesions and cancers, like hyper-pigmentation, hyperkeratosis, gangrene, skin cancer, lung cancer and bladder cancer [10,11].

Figure 1 *Arsenic-affected countries of the world [12]*

Key objective of this paper is to present results of the final project task "Mapping health risks of chemical(s) of concern to demonstrate benefits of RA for decision-makers", according to the available environmental data for the presence of arsenic. The key aim of this task was to demonstrate the scope of dissemination of the chosen prioritized chemical, arsenic (As), in different environmental media, in order to emphasize the severity of the public health hazard it poses to the exposed population in Serbia.

MATERIALS AND METHODS

Data for the Project mapping task were obtained from the publicly available data sources, such as:

- regular Annual Report on drinking water quality from public water supply systems for 2018 in the municipalities of Kikinda, Čoka, Novi Kneževac, Ada, Senta and Kanjiža, generated by the local IPH Kikinda [13];
- scientific article targeting ten municipalities in AP Vojvodina, on the issue of As in drinking water, including the Town of Zrenjanin, as well, not included in the previous document [14];
- UNEP–SEPA project on the status of heavily contaminated soil in Serbia, implemented in 2017 [15];
- distribution of As concentration in PM_{10} for the period 2010–2020, from the regular monitoring of ambient air quality, performed by both the SEPA and a number of local IPHs, presented in the regular "Annual Report on the Scope of Monitoring of Urban Ambient Air Quality performed within the Network of IPHs in Serbia", published on-line by the Institute of Public Health of Serbia [16].

The tables prepared in this way are georeferenced and with the data contained in them are imported into the ArCGiS tool for processing. During the processing, the type of data being processed was taken into account in order to select the most optimal display on the map.

RESULTS AND DISCUSSION

Maps chosen for this article will present As presence in soil and ambient air in the vicinity of industrially contaminated sites, as direct consequence of continuous anthropogenic activity. As in drinking water and aquifers in the north are, also mapped for the project is a result of natural occurrence in geological strata of the Panonian plane, providing different intake patterns [14].

According to the WHO, *contaminated sites*, following the public health perspective, are "areas hosting or having hosted human activities which have produced or might produce environmental contamination of soil, surface or groundwater, air, and food chain, resulting or being able to result in human health impacts" [17]. At the national level, the Law on Soil Protection specifies that contaminated soils are those in which concentrations of hazardous and harmful substances are confirmed to be above the limit values, whereas in the case of potentially contaminated soils there is only a presumption of possible contamination [18]. In November 2010, the Government of the Republic of Serbia adopted the Regulation on the program of systematic monitoring of soil quality via indicators for assessment of soil degradation risk and methodology for creation of remediation programmes [19]. This Regulation defines the term "*contaminated sites*" as those locations where the presence of hazardous and harmful substances caused by human activity is confirmed, in concentrations that can cause a significant risk to human health and the environment [15].

Figure 2 presents spatial distribution of the scope of soil contamination by As deriving from industrial and mining processes in the vicinity of sampling sites in Serbia: Šabac chemical industry complex, Zajača antimony mining site, Kraljevo metal-processing and constructing plants, Bor copper mining-smelting complex. These findings correspond to similar cases of oil contamination worldwide [20].

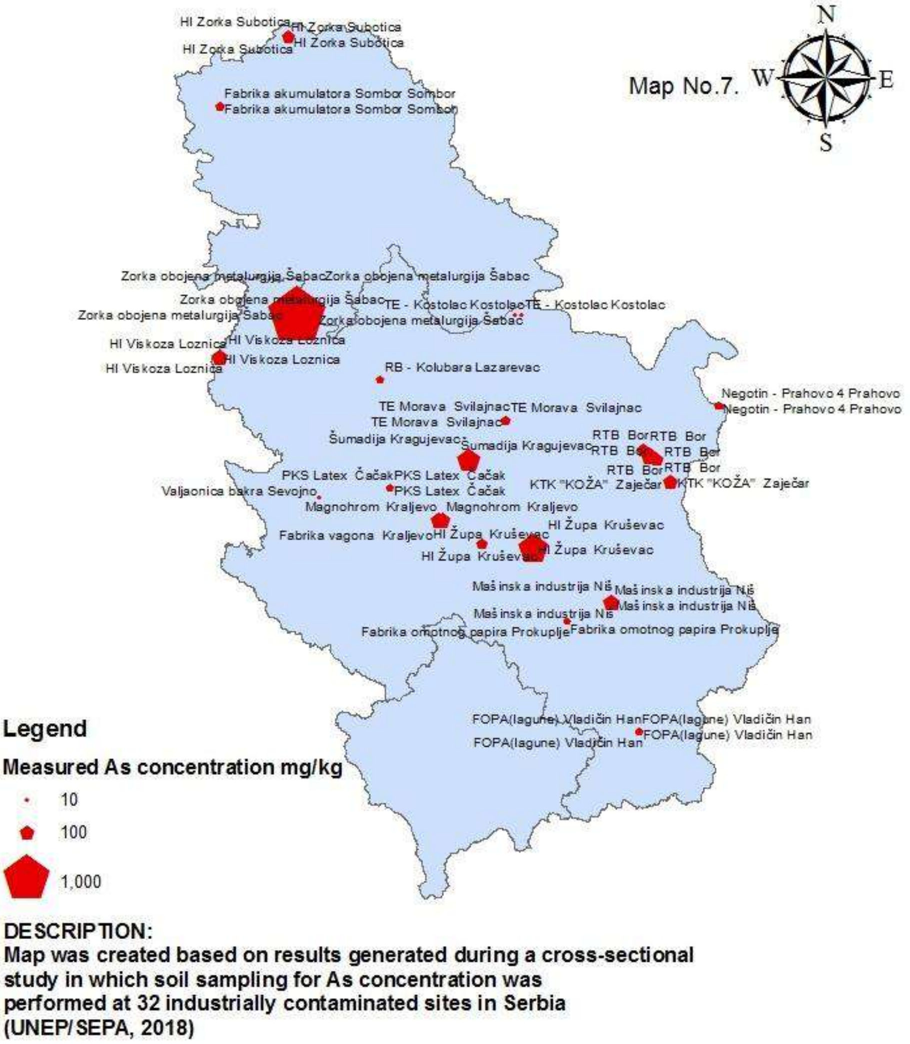
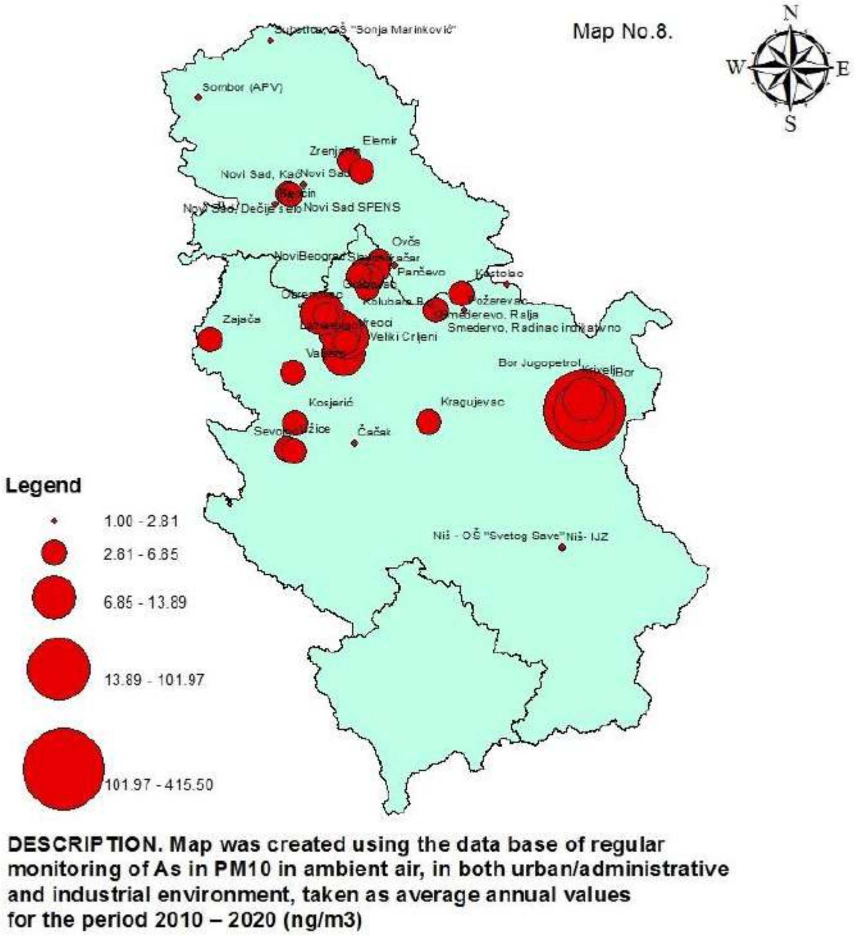


Figure 2 *Arsenic in soil in the vicinity of industrially contaminated sites (Project, 2021)*

Distribution of As in PM_{10}, measured continuously during a 10-year period (2010–2020), as presented in Figure 3 depicts that arsenic emissions to ambient air mostly generate from: lignite coal-firing power plants (Veliki Crljeni, Vreoci, Kostolac), copper milling (Sevojno), copper mining and smelting (Bor), steel production (Smederevo), battery recycling plant and secondary lead smelter (Zajača), chemical plants (Subotica, Kruševac, Šabac).



DESCRIPTION. Map was created using the data base of regular monitoring of As in PM10 in ambient air, in both urban/administrative and industrial environment, taken as average annual values for the period 2010 – 2020 (ng/m3)

Figure 3 *Distribution of arsenic in PM_{10} (ng/m^3) measured during 2010–2020 in Serbia (Project, 2021)*

CONCLUSION

After analyzing the data presented on the maps, our conclusion is that the choice of arsenic as a chemical of high public health concern is completely justified. Knowing that environmental arsenic is often followed by heavy metals, such as cadmium, lead, mercury, imposes a justified need for the systematic inclusion of human biomonitoring in regular health care practice. In order to obtain this goal, a serious cross-sectional study on the extent of human exposure to such chemicals in the vicinity of industrially contaminated sites should be performed, especially targeting the population group of exposed children.

REFERENCES

[1] WHO 10 Chemicals of public health concern, *Available on the following link*: www.who.int/news-room/photo-story/photo-story-detail/10-chemicals-of-public-health-concern

[2] WHO Chemicals Road Map, Road map to enhance health sector engagement in the Strategic Approach to International Chemicals Management towards the 2020 goal and beyond, *Available on the following link*: www.who.int/publications/i/item/WHO-FWC-PHE-EPE-17.03

[3] WHA 67.11. Resolution, Public health impacts of exposure to mercury and mercury compounds, The role of WHO and ministries of public health in the implementation of the Minamata Convention, *Available on the following link*: www.who.int/publications/i/item/resolution-wha67.11.-public-health-impacts-of-exposure-to-mercury-and-mercury-compounds-the-role-of-who-and-ministries-of-public-health-in-the-implementation-of-the-minamata-convention

[4] WHA 69.4. Resolution, The role of the health sector in the Strategic Approach to International Chemicals Management towards the 2020 goals and beyond, *Available on the following link*: www.apps.who.int/iris/handle/10665/328534

[5] International Health Regulations (2005), 3rd Edition, World Health Organization, *Available on the following link*: www.who.int/publications/i/item/9789241580496

[6] Declaration of the sixth ministerial conference on environment and health, 6th Ministerial Conference on Environment and Health, Euro/Ostrava 2017/6, Ostrava, Czech Republic, 13–15 June 2017, *Available on the following link*: www.euro.who.int/__data/assets/pdf_file/0007/341944/OstravaDeclaration_SIGNED.pdf

[7] Case study: Development of the national road map for enhancing health sector engagement/contribution to sound management of chemicals in Serbia till 2030, *Available on the following link*: www.who.int/publications/i/item/9789240035881

[8] Improving Contaminated Sites Management in Serbia; Institute of Public Health of Serbia "Dr Milan Jovanovic Batut", Belgrade (2020), ISBN: 978-86-7358-106-4.

[9] Endocrine Disrupting Chemicals 2012; United Nations Environment Programme, World Health Organization (2013), *Available on the following link*: www.apps.who.int/iris/bitstream/handle/10665/78102/WHO_HSE_PHE_IHE_2013.1_eng.pdf

[10] International Agency for Research on Cancer: Some drinking-water disinfectants and contaminants, including arsenic, IARC Monographs on the evaluation of carcinogenic risks to humans, Vol. 84, 2004.

[11] World Health Organization: Guidelines for drinking-water quality, 1st Addendum to 3rd Edition, Vol. 1, Recommendations, Geneva (2006).

[12] IARC Monographs, Arsenic, metals, fibres and dusts; 2012, ISBN:978 92 832 1320 8 https://monographs.iarc.fr/wp-content/uploads/2018/06/mono100C.pdf

[13] "Analysis of the hygienic quality of drinking water for the period from January to December 2018 in the municipalities of Kikinda, Čoka, Novi Kneževac, Ada, Senta and Kanjiža" IPH Kikinda, *Available on the following link*: https://zavodki.org.rs/wp-content/uploads/2019/09/kvalitet-vode-kikinda-godisnji-2018.pdf

[14] D. Jovanovic, B. Jakovljevic, Z. Rašić-Milutinović, *et al.*, Environ. Res; 111 (2) (2011) 315–8.

[15] Towards Soil Decontamination in the Republic of Serbia (2018); Ministry of Environmental Protection – Environmental Protection Agency, Belgrade, ISBN: 978-86-87159-20-4, *Available on the following link:* www.sepa.gov.rs/download/zemljiste/TowardsSoilDecontamination.pdf

[16] Annual Report on the Scope of Monitoring of Urban Ambient Air Quality Performed within the Network of IPHs in Serbia in 2020, *Available on the following link:* www.batut.org.rs/download/izvestaji/higijena/Godisnji%20izvestaj%20vazduh%202020.pdf

[17] WHO (2012), Contaminated sites and health. Report of two WHO workshops: Syracuse, Italy, 18 November 2011, Catania, Italy, 21–22 June 2012. Copenhagen: WHO Regional Office for Europe, *Available on the following link:* https://apps.who.int/iris/bitstream/handle/10665/108623/e96843.pdf?sequence=1&isAllowed=y

[18] Law on the Soil Protection, "*Off. Gazette of the Republic of Serbia*", No. 112/2015 (in Serbian), *Available on the following link:* www.paragraf.rs/propisi/zakon-o-zastiti-zemljista-republike-srbije.html

[19] Regulation on systematic monitoring of the condition and quality of soil, "Off. Gazette of the Republic of Serbia", No. 73/2019 (in Serbian).

[20] Kim Y.-D., Eom S.-Y., Yim D.-H. *et al.*, J. Korean Med. Sci; 31(4) (2016) 489–496.

CHARACTERISTCS OF WINTER TEMPERATURE REGIME IN SPRUCE FOREST ON KOPAONIK

Violeta Babić[1*], Branko Kanjevac[1], Milan Milenković[2], Snežana Stajić[3], Marina Vukin[4], Nenad Stavretović[1], Miloš Račić[3]

[1]University of Belgrade, Faculty of Forestry, Kneza Višeslava 1, 11000 Belgrade, SERBIA
[2]Geographical Institute "Jovan Cvijić", Đure Jakšića 9, 11000 Belgrade, SERBIA
[3]Institute of Forestry, Kneza Višeslava 3, 11000 Belgrade, SERBIA
[4]University Metropolitan, Faculty for Applied Ecology – Futura, Požeška 83a, 11000 Belgrade, SERBIA
[*]*violeta.babic@sfb.bg.ac.rs*

Abstract

The paper presents the characteristics of the winter temperature regime (December, January and February) in the spruce forest on Kopaonik. In addition, a comparative analysis of temperature conditions during the winter in spruce forest and open space was performed. The average, minimum and maximum temperatures during the winter in the period 2012-2018 at two meteorological stations in the Kopaonik National Park were studied: an automatic weather station in a spruce stand (ICP Forests - International Cooperative Programme on Forest Condition Monitoring in Europe - Level II sample plot) and the main meteorological station Kopaonik, which is located in the open space. Average monthly, average minimum, as well as average maximum temperatures are significantly higher in the spruce forest in all winter months compared to the open space. The obtained results indicate that higher temperatures occur in the spruce forest during the winter period, as well as that the forest canopy has the potential to alleviate temperature extremes during the winter months.

Keywords: winter temperature regime, spruce forests, NP Kopaonik, Serbia

INTRODUCTION

Climate change is one of the biggest environmental problems facing the world in modern circumstances. Reports of the Intergovernmental Panel on Climate Change (IPCC) indicate that, according to all possible scenarios, air temperatures will rise during the 21st century, and that there is a high probability that heat waves will occur more frequently and last longer, and that extreme climatic events when it comes to precipitation will become more intense and frequent in many regions [1]. In order to actively adapt to climate change, forest management measures should be adapted to changing environmental conditions - new knowledge and strategies in forest management are needed; the formation of new climate zones would affect the formation of new forest ecosystems, which implies significant changes in the composition of forests; it will be necessary to define new areas of species distribution, etc. [2]. Adaptation, i.e., adaptation to climate change in a broader sense implies adaptation of ecological, social and economic systems in response to the effects of climate change [3–5].

Occurrence and survival of vegetation in a specified area, its distribution, zonal distribution and height differentiation, together with other ecological factors (edaphic, orographic, biotic), are mostly conditioned, i.e., dependent on the climatic characteristics of the region [6–8]. Transitional zones between neighboring ecosystems, such as ecotones along altitude and continental gradients, where contrasting vegetation types and biomes meet, are particularly hard hit by climate change [9,10].

In addition, the world's forests affect the climate through physical, chemical and biological processes that affect planetary energy, the hydrological cycle and the composition of the atmosphere [11]. Forests respond to climate change in different ways caused by local site conditions and the adaptive potential of trees [12]. In general, forest ecosystems are characterized by high resilience and many species and ecosystems have historically adapted to changing conditions. Consequently, future changes are potentially of such magnitude or will occur at rates that are beyond the natural capacity of forest species or ecosystems to adapt, leading to local extinction and loss of important functions and services, including reduced forest carbon stocks and sequestration capacity [13].

It can be expected that the increase in global temperature and the higher frequency of climate extremes due to current climate change will affect the microclimate in forests with the potential to shape future structures of forest ecosystems, especially where natural regeneration is common practice [14,15]. This indicates the importance of studying the microclimatic characteristics of forests, especially when it comes to studying habitat conditions, bioecological characteristics of tree species, as well as the process of natural regeneration in forests [16,17].

This paper aims to indicate the climatic conditions during the winter period in the belt of spruce forests, determine whether there are temperature differences in forest conditions and the open space, as well as to indicate the importance of microclimatic measurements in the context of global climate change.

MATERIALS AND METHODS

Since 2003, the ICP Program has been running continuously in the Republic of Serbia (International Cooperative Programme on Forest Condition Monitoring in Europe). Within Level 1 of this program, a network of approximately 6000 plots (bioindication points) has been established in Europe to monitor the health status of forests and their spatial and temporal changes on a broad basis, and over the necessary period.

By establishing experimental plots in NP Fruška gora, NP Kopaonik, Odžaci, Crni vrh and Mokra Gora in the period 2009–2013, Serbia joined the European network of over 800 level 2 bioindication points where intensive monitoring of the impact of transboundary air pollution on forest ecosystems in Serbia is performed [18,19].

Experimental plot for intensive monitoring - bioindication point of level 2 on the mountain Kopaonik was established in 2010. The experimental field is located in the 74th department of the management unit "Samokovska reka" in the Kopaonik National Park in a pure spruce stand (*Picea abies* (L.) Karst.). The area of the experimental field is 0.5 ha (100x50 m).

On the experimental field in Kopaonik National Park, in addition to other parameters included in the monitoring, meteorological data are collected from the automatic meteorological station, based on which the analysis of microclimatic conditions in the context of current global climate change is performed.

For the purposes of this paper, climate data from the automatic meteorological station “WS-GP1” located on the experimental field in a pure spruce stand in NP Kopaonik, as well as data from the main meteorological station Kopaonik which is located in an open space for the period 2012-2018 were used. These meteorological stations are located in the immediate vicinity.

The paper presents a comparative analysis of temperature conditions in the mentioned period, during which the average, minimum and maximum air temperatures during the winter months (December, January and February) were analyzed.

RESULTS AND DISCUSSION

The influence of the forest canopy on the microclimatic conditions in the forest is, directly and indirectly, related to the degree of the forest canopy and the number of trees. Branches, leaves and needles reflect and absorb some of the sun's radiation during the day, allowing less energy to reach the ground below the forest canopy [20]. In addition, it is generally known that the degree of absorption largely depends on the structural characteristics of the forest, as well as on the composition of the species in the forest. Accordingly, one of the main characteristics of forest areas, when it comes to microclimatic conditions, is that they cool less during the night and limit the daily heating of the air, i.e., the temperature amplitude is lower in relation to the open space. Characteristically, this effect of equalizing the daily temperature amplitude is most pronounced on warm sunny days, and especially in stands characterized by a large number of trees [15].

Figure 1 shows the average monthly temperatures in the winter months at the meteorological station Kopaonik, as well as at the meteorological station in the spruce stand in the period 2012–2018.

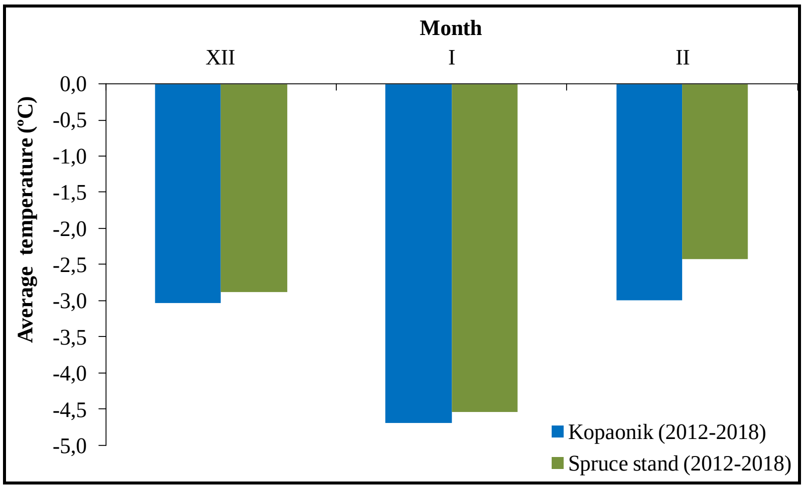


Figure 1 *Average monthly air temperatures at the meteorological station Kopaonik and meteorological station "WS-GP1" in the spruce stand in the analyzed period*

In the analyzed period 2012–2018, the average monthly temperatures in the winter months have higher values in the spruce forest compared to the meteorological station Kopaonik, which is located in the open space (Figure 1).

The average temperature in the winter in the spruce forest is -3.3ºC, while in the open space the value of this parameter is lower and amounts to -3.6ºC. The largest difference occurs in February when the average monthly temperature in the spruce forest is higher by 0.6ºC, while the smallest difference is recorded in December when the average monthly temperature is also higher in the spruce forest by 0.1ºC.

Figure 2 shows the average minimum monthly temperatures in the winter months at the meteorological station Kopaonik, as well as at the meteorological station in the spruce stand in the period 2012–2018.

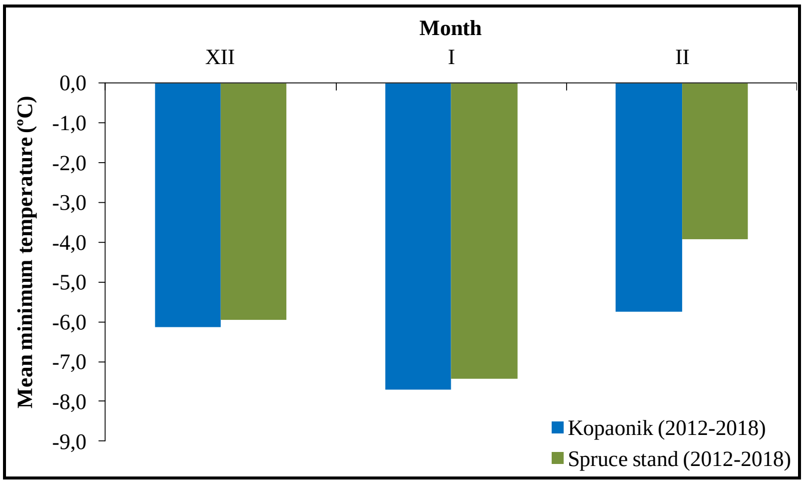


Figure 2 *Average minimum monthly air temperatures at the meteorological station Kopaonik and meteorological station "WS-GP1" in the spruce stand in the analyzed period*

The average minimum monthly air temperatures in the analyzed period 2012–2018 in the winter months are also characterized by higher values in the spruce forest compared to the meteorological station Kopaonik, which is located in the open space (Figure 2).

The average minimum temperature in the winter period in the spruce forest is -5.8ºC, while in the open space the value of this parameter is lower and amounts to -6.5ºC. The largest difference occurs in February when the average monthly temperature in the spruce forest is higher by 1.8ºC, while the smallest difference is recorded in December when the average monthly temperature is also higher in the spruce forest by 0.2ºC.

Figure 3 shows the average maximum monthly temperatures in the winter months at the meteorological station Kopaonik, as well as at the meteorological station in the spruce stand in the period 2012–2018.

The average maximum monthly air temperatures in the analyzed period 2012–2018 in the winter months are also characterized by higher values in the spruce forest compared to the meteorological station Kopaonik (Figure 3).

The average maximum temperature in the winter period in the spruce forest is 0.6°C, while in the open space the value of this parameter is lower and is -0.1°C. The largest difference occurs in February when the average monthly temperature in the spruce forest is higher by 1.5°C, while the difference in December and January is identical, i.e., in both months the average monthly temperature in the spruce forest is higher by 0.2°C.

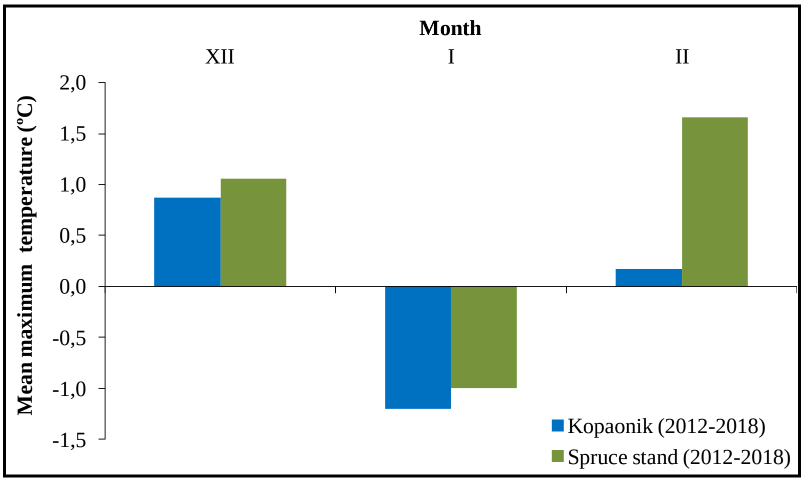


Figure 3 *Average maximum monthly air temperatures at the meteorological station Kopaonik and meteorological station "WS-GP1" in the spruce stand in the analyzed period*

The obtained results confirm the previous statements of the author that the forest canopy has the potential to alleviate temperature extremes that occur, especially during the winter and summer months [15].

CONCLUSION

The paper presents the results of a comparative analysis of temperature conditions from two meteorological stations in the Kopaonik National Park for the period 2012–2018: meteorological station "WS-GP1" which is located in a pure spruce stand and the main meteorological station of the Republic Hydrometeorological Service of Serbia on Kopaonik which is located in the open space.

For the analyzed period, a comparative analysis for 2 meteorological stations determined that in all three months of the winter season there are significantly higher average monthly, average minimum, as well as average maximum temperatures in the spruce forest compared to the open space. The largest differences were recorded in February, while the smallest differences in the analyzed parameters occur in December.

The obtained results in the paper indicate that spruce forest has higher temperatures during the winter period, as well as that the spruce forest canopy has the potential to alleviate temperature extremes during the winter months.

REFERENCES

[1] IPCC, Climate Change 2014: Synthesis Report, (2014), *Available on the following link*: https://www.ipcc.ch/report/ar5/syr/

[2] V. Babić, M. Krstić, M. Milenković, *et al.*, Proceedings of the XI International Scientific Agricultural Symposium “Agrosym 2020”, October 8–9, Jahorina, Bosnia and Herzegovina (2020) 1103–1113.

[3] D.L. Spittlehouse, R.B. Stewart, BC Journal of Ecosystems and Management; 4 (1) (2003) 1–11.

[4] B. Smit, I. Burton, R.J.T. Klein, *et al.*, Clim. Change; 45 (2000) 223–251.

[5] B. Smit, O. Pilifosova, In: Climatic Change, Cambridge University Press, New York, N.Y. (2001) 876–912.

[6] M. Krstić, V. Babić, B. Kanjevac, Šumarstvo; 3–4 (2013) 113–124.

[7] V. Babić, M. Krstić, Šumarstvo; 3–4 (2014) 49–62.

[8] V. Babić, M. Krstić, Šumarstvo; 1–2 (2021) 7–23.

[9] J.F. Fernández-Manjarrés, P. Ruiz-Benito, M.A. Zavala, *et al.*, Sustainability; 10 (3065) (2018) 1–18.

[10] P. Evans, C.D. Brown, Environ. Rev; 25 (4) (2017) 423–431.

[11] G.B. Bonan, Science; 320 (5882) (2008) 1444–1449.

[12] R. Jandl, P. Spathelf, A. Bolte, *et al.*, Ann. For. Sci; 76 (2019) 48.

[13] R. Seppälä, A. Buck, P. Katila, Adaptation of forests and people to climate change: a global assessment report, (2009), *Available on the following link*: https://gec.cr.usgs.gov/outgoing/dhester/ClimateChange/IUFRO_Forests_ClimateChange.pdf

[14] R. Bertrand, J. Lenoir, C. Piedallu, *et al.*, Nature; 479 (7374) (2011) 517–520.

[15] G. von Arx, M. Dobbertin, M. Rebetez, Agric. For. Meteorol; 166–167 (2012) 144–145.

[16] V. Babić, M. Krstić, Šumarstvo; 1–2 (2016) 79–89.

[17] V. Babić, M. Krstić, Z. Govedar, *et al.*, Therm. Sci; 19 (2) (2015) 415–425.

[18] NFC - National Focal Centre for monitoring the condition - vitality of forests in the Republic of Serbia, Monitoring and assessment of air pollution and its effects on forest ecosystems in Serbia - Forest condition monitoring - Level I and Level II - Report, (2017), *Available on the following link*: https://www.forest.org.rs/

[19] NFC - National Focal Centre for monitoring the condition - vitality of forests in the Republic of Serbia, Monitoring and assessment of air pollution and its effects on forest ecosystems in Serbia - Forest condition monitoring - Level I and Level II - Report, (2018), *Available on the following link*: https://www.forest.org.rs/

[20] R. Geiger, R.H. Aron, P. Todhunter, The Climate Near the Ground, Rowman & Littlefield, Lanham (2009), p.623.

ENVIRONMENTAL RISK ASSESSMENT OF PTES IN AGRICULTURAL SOILS AFFECTED BY INDUSTRIAL ACTIVITIES IN BELGRADE

Dragana Pavlović[1*], Dragan Čakmak[1], Veljko Perović[1], Marija Matić[1], Milica Marković[1], Miroslava Mitrović[1], Pavle Pavlović[1]

[1]Department of Ecology, Institute for Biological Research 'Siniša Stanković' - National Institute of the Republic of Serbia, University of Belgrade, Bulevar Despota Stefana 142, 11060 Belgrade, SERBIA

[*]*dragana.pavlovic@ibiss.bg.ac.rs*

Abstract

This study investigated the effects of proximity to different contamination sources, such as a coal mine, thermal power plants and fly ash disposal sites, in three Belgrade municipalities (Obrenovac, Lazarevac and Surčin) on agricultural soil contamination with As, Cd, Cr, Cu, Fe, Hg, Mn, Ni, Pb, and Zn. Concentrations of As, Cr, Cu, Ni, Pb and Zn were within the reference range for European soils and did not exceed the limit thresholds set by national legislation, except for Cr in Lazarevac and Ni at all the examined sites. The highest concentrations of As, Cr, Cu and Ni were measured in soil from Lazarevac, with the largest differences determined for As, Cr, and particularly Ni. The high Ni content in soil samples in Lazarevac indicates potential risk from the toxic effects of this element in the soil, close to the mine, the Kolubara-A thermal power plant and the ash dump. However, overall, values obtained for ecological risk indices were low, meaning that there is negligible enrichment and contamination of soil with the tested elements at the study sites and, therefore, no potential ecological risk to the environment or agricultural crop production.

Keywords: industrial pollution, potentially toxic elements, agricultural soils, pollution indices

INTRODUCTION

Soil contamination is one of the greatest issues in terms of threats to soil resources both in Europe and globally [1]. Although the distribution of contamination sources varies from country to country, industrial activities are responsible for the contamination of more than 60% of European soils and, in terms of contamination from local sources, data from the European Environment Agency indicate that today there are more than 650,000 registered sites where polluting activities occur in national and regional inventories [2]. In Serbia, the latest update to the Cadastre database shows that 709 contaminated sites have been recorded [3].

Anthropogenic activities, such as mineral resource exploitation, energy production, metal processing and smelting, and industrial waste disposal, have been proven to be the primary sources of pollution from potentially toxic elements (PTEs) [4,5]. These activities contribute considerably to polluting metal levels in soils, in particular agricultural soils in the vicinity of industrial facilities, resulting in contamination and a decrease in soil quality [6]. Pollution from PTEs has become a critical issue as they can accumulate and be retained in soils for a long time. Once the content of elements exceeds environmental quality standards, they pose potential ecotoxic risks [7]. Hence, soil pollution indices can provide information on soil quality and degree of contamination for each soil sample, based on individual PTE levels [8–10].

Previous research indicates the geochemical origin of PTEs in Serbian soils [11], as is the case with most soils in the world [7]. However, soil contamination with PTEs is becoming more serious and widespread, particularly in industrial centres. In Belgrade, the problem of pollution is mainly related to anthropogenic activities. Namely, on the territory of the City of Belgrade, there are three thermal power plants (‘Nikola Tesla-A’ and ‘Nikola Tesla-B’ in Obrenovac and ‘Kolubara-A’ in Lazarevac), opencast coal mines, and large areas of ash deposit sites, which pose a risk to the environment, food production, and the health of residents.

This study aimed to quantify As, Cd, Cr, Cu, Fe, Hg, Mn, Ni, Pb and Zn concentrations in agricultural soils and to estimate the potential environmental risks from soil pollution in three Belgrade municipalities. Contamination levels and the potential ecological risk to the environment were assessed using the contamination factor (Cf), degree of contamination (Cdeg), potential ecological risk (Er^i), and the potential ecological risk index (RI).

MATERIALS AND METHODS

Site description and soil sampling

Soil sampling was conducted in three Belgrade municipalities: in fields close to the fly ash disposal site at the ‘Nikola Tesla-A’ thermal power plant, located in the municipality of Obrenovac (Krtinska village, 44030 ’N, 19058’ E; average altitude 80 m), in the municipality of Lazarevac (Sokolovo village 20019’7’’ E, 44028’32’’ N, average altitude 93 m), and in the municipality of Surčin (Jakovo village, 20015’45’’ E, 44044’35’’ N, average altitude 75 m). Soil at each sampling site was sampled from six individual sampling points from a depth of 0-10 cm. The samples were dried to a constant weight, ground, and sieved through a 2 mm sieve.

Soil sample preparation and measurement

To determine total PTE content, soil samples were digested in a microwave oven (CEM, 39 MDS-2000), using the USEPA 3052 method [12]. PTE concentrations in soil were measured using optical emission spectrometry for simultaneous multi-element analysis (ICP - OES, Spectro Genesis). The content of chemical elements was expressed in mg kg^{-1} of the dry sample. The analytical procedure was validated using standard reference material (Loam soil - ERM - CC141), which underwent standard digestion procedures to control the quality of the laboratory protocol, and an accuracy of 100±15% was achieved. All samples were prepared in three repetitions and standard deviation was less than 10%. The detection limits were: As-0.007, Cd-0.001, Cr-0.001, Cu-0.014, Fe-0.018, Hg-0.002, Mn-0.009, Ni-0.018, Pb-0.004, and Zn-0.001.

Contamination and ecological risk assessment

Contamination factor (Cf)

An assessment of soil contamination can be conducted using the contamination factor (Cf). Cf is the ratio of the concentrations of the tested element (C_i) and its pre-industrial values, i.e., background (C_b). Background values of PTEs in the study area were proposed by Mrvić *et al.* [11,13] and Knežević [14]. Cf is calculated using Equation (2):

$$\mathrm{Cf} = \mathrm{C_i}/\mathrm{C_b} \tag{2}$$

Degree of contamination (Cdeg)

The degree of contamination (Cdeg) represents the sum of the contamination factors and is calculated using Equation (3):

$$\mathrm{C_{deg}} = \sum_{i=1}^{n} \mathrm{Cf} \tag{3}$$

Potential ecological risk (E_r^i)

The potential ecological risk (E_r^i) of a particular PTE is the product of the Cf and the toxic response factor (T_r^i) of a particular PTE and is calculated using Equation (4):

$$\mathrm{E_r^i} = \mathrm{T_r^i} \times \mathrm{Cf} \tag{4}$$

T_r^i reflects the level of toxicity and biological sensitivity to contamination with a particular element. T_r^i values are as follows: As-10, Cr-2, Cu-5, Pb-5, Ni-5, and Zn-1 [15].

Potential Ecological Risk Index (RI)

The Potential Ecological Risk Index (RI) represents the sum of E_r^i and is calculated using Equation (5):

$$\mathrm{RI} = \sum_{i=1}^{n} \mathrm{E_r^i} \tag{5}$$

The recommended classifications for all factors and indices are described in Pavlović *et al.* [10].

RESULTS AND DISCUSSION

The combustion of coal in power plants results in the emission of a wide range of pollutants including PTEs, which, once released, reach the surrounding soil, where they are deposited and remain for years [5,16,17]. The results of this study showed that Cd and Hg content in the studied soils were below the detection limit. The highest average concentrations of the tested PTEs were measured in soil from Lazarevac, with the largest differences determined for As and Cr, and in particular Ni. Concentrations of As, Cu, Pb and Zn, were at background levels for European soils [18] and did not exceed maximum allowable concentrations (MAC) as set by national legislation [19] (Table 1). Somewhat higher concentrations of Cr were measured in soil from Lazarevac, where the content was above background and MAC values (Table 1). These elevated Cr concentrations may be due to the thermal power plant, i.e., the dispersion of ash particles from ash dumps to agricultural fields, with this ash characterized by increased levels of various PTEs [20]. A similar study in

Kostolac (Serbia) also revealed Ni, Cu and Cr concentrations above the prescribed limits [17]. It was further found that average Ni concentrations at all the sites exceeded background values for European soils and MAC, with concentrations of this element in soil from Lazarevac significantly higher (up to 134.82 mg kg^{-1}), which indicates a potential risk from the toxic effects of this element. However, such high Ni concentrations do not necessarily indicate that it is of predominantly anthropogenic origin. Namely, previous studies by Mrvić *et al.* [11,13] have shown that Ni and Cr in Serbian soils are mainly of geochemical origin, i.e., they are naturally found in these soils in elevated concentrations. Numerous soil surveys conducted in central parts of Serbia, including Belgrade, have concluded that the origin of Ni and Cr in soil is determined to a great extent by the geological substrate [21–23]. However, the proximity of open pit mines, coal combustion plants, and ash deposit sites can also contribute significantly to an increase in Ni content in surrounding agricultural soils. Since Pb and Zn content in the tested soil samples was uniform and did not exceed the MAC, it can be concluded that these elements do not represent a limiting factor for the cultivation of agricultural crops on the examined soils.

The results show that there is generally no risk in terms of elevated PTE concentrations, except for Ni. In this sense, potential risk occurs in soils in the municipality of Lazarevac, where, due to the proximity of the mine, ash deposit site and ‘Kolubara-A’ thermal power plant, there is a risk of the accumulation of PTEs in surrounding agricultural soils.

***Table 1** Average content of PTEs (mg kg^{-1} d.w.) in agricultural soils in the municipalities of Obrenovac, Lazarevac and Surčin. Values are presented as mean and standard deviation*

Locality/PTEs	**As**	**Cr**	**Cu**	**Fe**	**Mn**	**Ni**	**Pb**	**Zn**
Surčin - Jakovo	7.093 (1.140)	68.278 (0.776)	34.106 (0.514)	47933.117 (617.654)	711.979 (14.924)	96.050 (4.465)	59.691 (2.637)	85.019 (3.080)
Lazarevac - Sokolovo	13.370 (0.903)	107.011 (17.517)	36.312 (1.251)	46526.27 (5362.197)	613.031 (44.228)	134.827 (7.643)	57.673 (12.557)	84.337 (5.512)
Obrenovac - Krtinska	5.264 (0.928)	61.932 (2.388)	31.743 (0.478)	42006.42 (573.636)	470.323 (5.606)	98.716 (1.071)	52.957 (1.762)	80.543 (4.222)
Background values in European soils[a]	/	75–100	50–100	/	/	50–70	70–100	150–200
MAC[b]	25	100	100	/	/	50	100	300
Background[c] **values**	10.4	61	30	24771	489.29	72	37	68

[a] Background values in European soils [20]; [b] Maximum allowable concentrations of PTEs [21]; [c] Background values of PTEs in the studied soils (method: Median + 2MAD) [12,14,15].

Contamination levels and ecological risk assessment

PTE pollution is a notable threat to agricultural production and, in soils, can cause potential ecological risks [24]. The results of Cf and Cdeg (Figure 1) indicate a low degree of contamination in the soils from Surčin and Lazarevac, although the potential risk from contamination is more pronounced in Lazarevac. Categorized according to E_r^i and RI, soils in the examined localities can be classified as soils with low potential ecological risk.

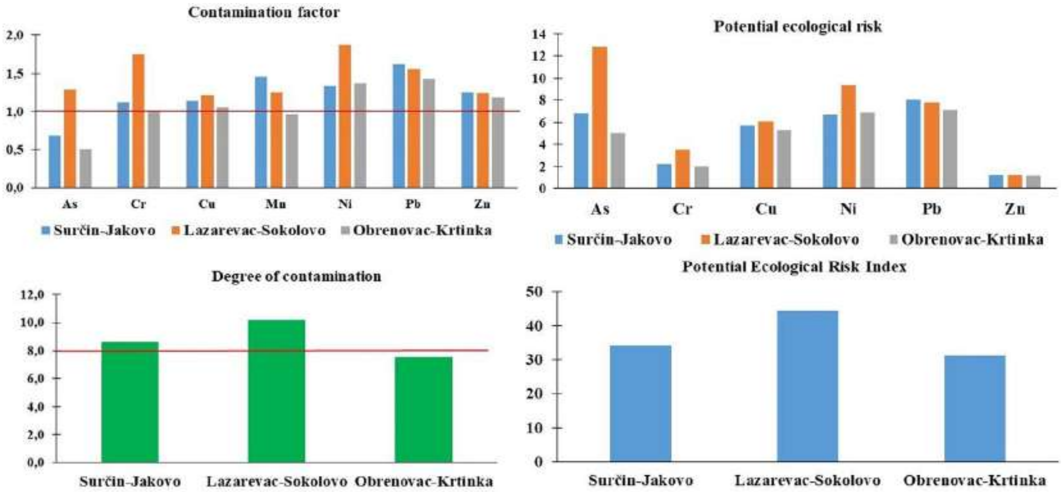


Figure 1 *Contamination level and ecological risk assessment of PTEs in the examined soils using the contamination factor (Cf), degree of contamination (Cdeg), ecological risk index (E_r^i), and potential ecological risk (RI)*

CONCLUSION

Concentrations of all the tested PTEs were within the range of background values for European soils and did not exceed the MAC set by national legislation, except Cr in Lazarevac and Ni at all the localities. In terms of localities, the highest As, Cr, Cu and Ni concentrations were measured in soil from Lazarevac, with the largest differences determined for As, Cr, and particularly Ni.

The elevated Ni content in all the tested samples, but particularly in Lazarevac, indicates the potential risk from the toxic effects of this element in soil, in the vicinity of the mine, the ‘Kolubara-A’ thermal power plant, and the ash deposit site in the municipality of Lazarevac. However, overall, the values obtained for ecological risk indices were low, meaning that there is negligible enrichment and contamination of soil with the tested elements at the study sites and, therefore, no potential ecological risk to the environment or agricultural crop production.

This study could contribute to knowledge on the accumulation of PTEs in soil, especially in agricultural soil. In the vicinity of industrial facilities in large urban and industrial areas, which require safe agricultural products, it is necessary to assess the environmental risk and form strategies for dealing with this risk.

ACKNOWLEDGEMENT

This work was supported by the Ministry of Education, Science and Technological Development of the Republic of Serbia, grant no. 451-03-68/2022-14/200007.

REFERENCES

[1] CEC (2006) Thematic Strategy for Soil Protection, Commission of the European Communities, Brussels, *Available on the following link*: https://ec.europa.eu/environment/archives/soil/pdf/SEC_2006_620.pdf

[2] EEA (2020) Soil contamination widespread in Europe. The European Environment Agency, Luxembourg, Publications Office of the European Union, *Available on the following link*: http://www.eea.europa.eu/highlights/soil-contamination-widespread-in-europe

[3] EPA RS (2018) Ministry of Environmental Protection - Environmental Protection Agency, Belgrade Towards soil decontamination in the Republic of Serbia. Project "Enhanced Cross-Sectoral Land Management through Land Use Pressure Reduction and Planning", Environmental Protection Agency, Republic of Serbia.

[4] S. Serbula, D. Miljkovic, R. Kovacevic, *et al.*, Ecotox. Environ. Safe; 76 (2012) 209–214.

[5] O. Kostić, S. Jaric, G. Gajić, *et al.*, Catena; 163 (2018) 78–88.

[6] B.J. Alloway, Sources of heavy metals and metalloids in soils, In: B.J. Alloway (ed.). Heavy metals in soils, Trace metals and metalloids in soil and their bioavailability, Springer Dordrecht Heidelberg New York London, (2013), p.11–50, ISBN: 978-94-007-4469-1.

[7] A. Kabata-Pendias, H. Pendias, Trace elements in soils and plants, CRC Press LLC, Boca Raton, London, New York, Washington, (2001), p.413, ISBN: 0-8493-1575-1.

[8] J.B. Kowalska, R. Mazurek, M. Gąsiorek, *et al.*, Environ. Geochem. Health; 40 (2018) 2395–2420.

[9] D. Čakmak, V. Perović, M. Kresović, *et al.*, Arch. Environ. Cont. Tox; 78 (2020) 190–205.

[10] D. Pavlović, M. Pavlović, V. Perović, *et al.*, Int. J. Env. Res. Pub. He; 18 (17) (2021) 9412.

[11] V. Mrvić, G. Antonović, Lj. Martinović, Fertility and content of hazardous and harmful substances in the soils of central Serbia. Institute of Land, Belgrade (2009) p.223, ISBN: 978-86-911273-1-1.

[12] US EPA (1996) Microwave Assisted Acid Digestion of Siliceous and Organically Based Matrices 3052 (A 20), SW-846 Ch 3.2, Method code 10136206, U.S. Environmental Protection Agency, Washington, DC.

[13] V. Mrvić, Lj. Kostić-Kravljanac, D. Čakmak, *et al.*, J. Geochem. Explor; 109 (2011) 18–25.

[14] M. Knežević, Determination of the state, degree of pollution and chemical degradation of the land of the industrial zones of Pancevo and Sabac and the fire on the mountain Tara, Project No. 401-00-00051/2014-02), Ministry of Agriculture and Environmental Protection, Belgrade (2014).

[15] L. Hakanson, Water Res; 14 (1980) 975–1001.

[16] P. Pavlović, M. Mitrović, L. Đurđević, Environ. Manage; 33 (5) (2004) 654–663.

[17] D. Savic, D. Nisic, N. Lunch, *et al.*, Minerals; 8 (54) (2018).

[18] B.W. Gawlik, G. Bidoglio (Eds.), Background Values in European Soils And Sewage Sludges PART III, Conclusions, Comments and Recommendations, European Commission, Directorate-General Joint Research Centre, Institute for Environment and Sustainability (2006).

[19] SG RS (1994) Rulebook on permitted quantities of hazardous and harmful substances in soil and irrigation water and methods of their testing, "Official Gazette of RS", no. 23/94, Ministry of Agriculture, Forestry and Water Management in agreement with the Ministry of Environmental Protection of the Republic of Serbia, Belgrade (in Serbian).

[20] J. Haynes, J. Environ. Manage; 90 (1) (2009) 43–53.

[21] D. Čakmak, V. Perović, S. Antic-Mladenović, *et al.*, J. Soil Sediment; 18 (2018) 1981–1993.

[22] M. Pavlović, D. Pavlović, O. Kostić, *et al.*, Int. J. Environ. Res; 11 (5–6) (2017) 625–639.

[23] M. Mitrović, T. Blanusa, M. Pavlović, *et al.*, 13 (17) (2021) 9784.

[24] M. Xiang, Y. Li, J. Yang, *et al.*, Environ. Poll; 78 (2021) 116911.

ANALYSIS OF As AND Pb ACCUMULATION IN GARDEN SOIL AND VEGETABLE CROPS IN THREE BELGRADE MUNICIPALITIES

Olga Kostić[1*], Gordana Gajić[1], Snežana Jarić[1], Zorana Mataruga[1], Dimitrije Sekulić[1], Natalija Radulović[1], Miroslava Mitrović[1], Pavle Pavlović[1]

[1]Department of Ecology, Institute for Biological Research 'Siniša Stanković' - National Institute of the Republic of Serbia, University of Belgrade, Bulevar Despota Stefana 142, 11060 Belgrade, SERBIA

[*]*olgak@ibiss.bg.ac.rs*

Abstract

This study evaluated concentrations of arsenic (As) and lead (Pb) in vegetable crops (carrots and cabbage) and garden soil in three municipalities in the City of Belgrade (Lazarevac, Obrenovac and Surčin) to assess soil contamination levels and the affinity of the crops to absorb these heavy metal(loid)s. Elevated levels of As and Pb were measured in garden soil in Lazarevac, which indicates a potential risk for growing vegetable crops in this municipality. Although bioconcentration factor values for both elements in both cultures indicated the low affinity of the examined species to accumulate these elements in those organs used in the human diet (BCF<1), As concentrations were found to be above the normal range for plants and higher than the permitted levels for dried vegetables in both vegetable cultures at all the sampling sites, while Pb content was higher in carrots than the permitted levels for dried vegetables as set out by national legislation, which requires further investigation.

Keywords: arsenic, lead, garden soil, vegetable crops, bioaccumulation

INTRODUCTION

Rapid industrial activity and the scale of exploitation in developing countries has led to many mining areas and industrial regions being contaminated to such an extent that the risk to human health is a matter of great concern [1,2]. A large number of heavy metal(loid)s from mining waste, tailings, thermal power plant emissions, fly ash, etc., are transferred to soil and affect plant performance [3,4]. In addition, mining and coal combustion residues are subjected to erosion and weathering processes, which release these contaminants into surrounding agricultural areas [5]. Heavy metal(loid)s are the most hazardous contaminants due to their build-up in crops and the consumption of contaminated crops can pose a serious risk to human health [6]. Potential risks from metal(loid)s can be assessed using the bioconcentration factor (BCF) to estimate the ability of crops to accumulate elements from soil. Bearing in mind the fact that vegetable crops are one of the essential foodstuffs in the human diet, understanding their ability to accumulate toxic concentrations of hazardous elements can help to reduce potential human health risks [7].

In this regard, this study focusses on an evaluation of concentrations of arsenic (As) and lead (Pb) in vegetable crops (carrots and cabbage) and garden soil in the vicinity of an open pit mine, thermal power plants, and fly ash disposal sites in three Belgrade municipalities (Lazarevac, Obrenovac and Surčin) and an assessment of the affinity of the examined plant cultures to absorb these chemical elements.

MATERIALS AND METHODS

Study areas

To determine As and Pb content in soil and plant material, as well as assess vegetable crop efficiency to accumulate these elements from the soil, soil and plant material sampling was conducted in three municipalities in the City of Belgrade - Lazarevac, Obrenovac and Surčin. Sampling was carried out in gardens located in the vicinity of the fly ash disposal site at the ‘Nikola Tesla-A’ thermal power plant in the municipality of Obrenovac (Krtinska village, lat. 44°30’ N long. 19°58’ E, average altitude 80 m), in the municipality of Lazarevac (Sokolovo village, lat. 20°19’7’’ E, long. 44°28’32’’ N, average altitude 93 m), and in the municipality of Surčin (Jakovo village, lat. 20°15’45’’ E, long.44°44’35’’ N, average altitude 75 m). The research area is characterized by a moderate continental climate with a mean annual temperature of 12.5 °C and mean annual precipitation of 690.1 mm.

At each of the three sampling sites, five sampling points (gardens) were randomly selected for plant and associated soil sampling. At each sampling point, one paired soil and plant sample was collected (soil samples from the surface layer at 0–10 cm, plant samples from individuals, 30 g).

Analysis of the content of the tested chemical elements in soil and vegetables from vegetable gardens

Pseudo-total heavy metal(loid) As and Pb concentrations in soil and total concentrations in the edible parts of carrots and cabbage were determined after wet digestion in a microwave oven (CEM, Mars 6 Microwave Acceleration Reaction System, Matthews, NC, USA) [8,9]. Certified reference materials were analysed to test the accuracy of the analytical procedures: soil (Clay ERM – CC141) and plant material (Beech leaves BCR – 100), provided by the Institute for Reference Materials and Measurements (Geel, Belgium), certified by the European Commission - Joint Research Centre. Concentrations of arsenic and lead (mg/kg) in the examined samples were determined using inductively coupled plasma optical emission spectrometry (ICP-OES, Spectro Genesis, Spectro-Analytical Instruments GmbH, Kleve, Germany). Detection limits for As and Pb were 0.005 mg/kg and 0.004 mg/kg, respectively. The average recovery values for the elements in the standard reference materials were in the range of 100 ± 20%. The efficiency of the investigated vegetables to absorb As and Pb from soil was compared by assessing the bioconcentration factor (BCF), which was calculated according to the formula: BCF = Element concentration in edible parts of vegetables/Element concentration in soil [10].

Statistical analysis

All values in Tables 1 and 2 are presented as the mean (M) with the standard deviation (SD) of 6 replicates (n=6). The data from this study was analysed using statistical analysis (ANOVA) and means were separated with a Bonferroni test at a level of significance of $p<0.05$, using the Statistica software package (StatSoft In., Tulsa, USA, 2007). Correlations between the levels of the tested elements in soil and the roots and edible parts of vegetables were obtained using the non-parametric Spearman rank-order correlation coefficient at a level of significance of $p<0.05$.

RESULTS AND DISCUSSION

The highest content of As and Pb in the soil was measured at the sampling site in Lazarevac (Table 1). Arsenic concentrations above the average range for world soils (4.4–8.4 mg/kg) [11] were measured in Lazarevac, while higher levels than average background concentrations in world soils (5 mg/kg) [12] were measured at all the sampling sites. At the same time, As concentrations at all the localities were lower than the maximum acceptable limits for agricultural soil recommended by the European Community (20.0 mg/kg) [13], and lower than the MAC as prescribed by the National Regulations on Permitted Quantities of Hazardous and Harmful Substances in Soil (25 mg/kg) [14]. Lead concentrations in all samples were also higher than the average concentration range for world soils (22–28 mg/kg) [11], but lower than the maximum permissible concentrations in soils for agricultural purposes (375 mg/kg) [15], and also lower than concentrations posing an ecological risk (200 mg/kg) [16] and the MAC (100 mg/kg) [14].

Table 1 *Content of As and Pb in soil from vegetable gardens at the study sites*

Study site	**As**	**Pb**
	M(SD) mg/kg	
Surčin	5.55±0.78 b	43.83±5.93 b
Lazarevac	19.83±0.04 a	63.50±0.84 a
Obrenovac	5.43±1.11 b	50.83±8.08 b

These non-essential and toxic elements are generally poorly mobile in soil and are most common in the surface layer thanks to their being adsorbed on fine soil particles, organic matter and amorphous oxides [11]. Additionally, their elevated levels in agricultural soils may be the result of the earlier use of lead-arsenate pesticides. In conditions of low organic matter, phosphates and low pH, plants easily absorb these elements from such soils [17].

A very low correlation was found between As and Pb concentrations in soil and concentrations in carrots and cabbage ($r=0.1952$, $p<0.05$; $r=0.1055$, $p<0.05$, respectively), which can be explained by the effect of the different physical and chemical soil characteristics on their bioavailability, as well as the impact of different types and sources of pollution at the study sites. In agricultural soils, these pesticide-derived elements are more available and phytotoxic than those originating from thermal power plant emissions and mining activities [18].

In both vegetable crops at the study sites, no significant differences were found in As concentrations (Table 2).

Table 2 *Content of As and Pb in carrot and cabbage samples*

Study site	As	Pb
	Carrot M(SD) mg/kg	
Surčin	2.49±0.75 a	3.29±0.32 a
Lazarevac	3.35±1.06 a	4.90±0.23 a
Obrenovac	2.77±0.77 a	3.84±0.43 a
	Cabbage M(SD) mg/kg	
Surčin	3.64±0.79 a	<0.004
Lazarevac	3.32±0.52 a	<0.004
Obrenovac	3.10±0.64 a	<0.004

Although carrots and cabbage did not accumulate As (BCF<1; Figure 1), its concentrations were above the normal range for plants (1–1.7 mg/kg) [11] and higher than the permitted levels for dried vegetables under national legislation (1 mg/kg) [19]. Namely, the relatively high solubility of As in water contributes to the greater potential for its uptake in the tissues of the roots and leaves of vegetable crops, especially root vegetables [17,20]. Likewise, some *Brassicaceae* species showed high potential for the uptake and translocation of As [21].

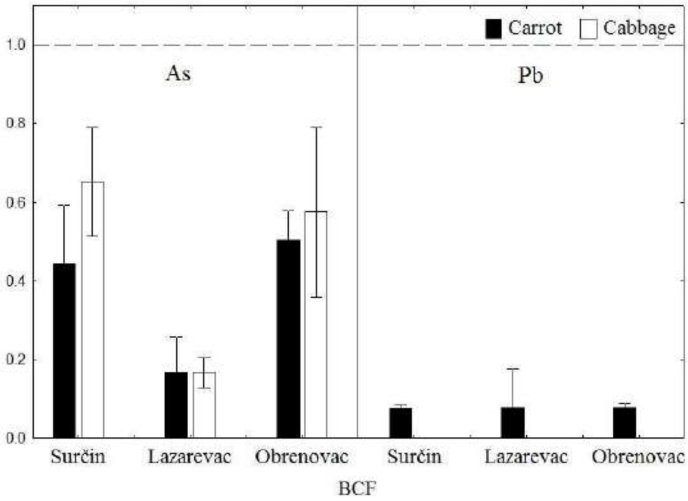


Figure 1 *Affinity of carrots and cabbage to accumulate the tested chemical elements in vegetable gardens at the study sites based on the bioconcentration factor (BCF)*

The studied cultures also did not accumulate Pb (BCF<1; Figure 1), but the content of this element in carrots from all localities was still higher than the permitted levels for dried vegetables (3 mg/kg) [19]. In previous research, in soils with elevated As and Pb content, similar concentration ranges were found in carrots for As (0.38–1.64 mg/kg) and for Pb (2.67–7.3 mg/kg) [22]. In general, the lower transfer of Pb compared to As previously determined in leafy vegetables [17] was also confirmed in this study with the example of cabbage, where the Pb content was below the detection level. The lower accumulation of Pb in leafy vegetables can also be the result of its predominantly airborne transportation and deposition on aboveground parts, from where it can easily be removed by atmospheric precipitation [23,24].

CONCLUSION

All the findings revealed elevated levels of As and Pb in garden soil in Lazarevac in comparison to the other two sampling sites, which indicates a potential risk for growing vegetable crops in this municipality. In regard to the reference values for concentrations of As and Pb in world soils, higher concentrations of these potentially toxic elements were measured at all the sampling sites. However, they are still lower than the maximum acceptable limits for agricultural soils as recommended by the European Community and the maximum concentrations allowed by Serbian legislation.

At the same time, As concentrations were found to be above the normal range for plants and higher than the permitted levels for dried vegetables in both vegetable cultures at all the sampling sites, while Pb content in carrots was higher than the permitted levels for dried vegetables as set out by national legislation. This was despite bioconcentration factor values for both elements in both crops (BCF<1) indicating the poor affinity of the investigated species to accumulate these elements in those plant organs used in the human diet.

Bearing in mind the fact that the bioavailability of these toxic elements is conditioned by different physical and chemical soil characteristics, the forms of the elements, and the influence of different types and sources of pollution at the study sites, it is necessary to investigate the fractions of these elements available to plants further, as well as different species-specific factors of plants related to the uptake, accumulation and transfer of heavy metal(loid)s. This will contribute to a better understanding of contamination risks for vegetable crop cultivation in the vicinity of urban and industrial zones.

ACKNOWLEDGEMENT

This work was supported by the Ministry of Education, Science and Technological Development of the Republic of Serbia, grant no. 451-03-68/2022-14/200007.

REFERENCES

[1] S.M. Serbula, J.S. Milosavljevic, J.V. Kalinovic, *et al.*, Sci. Total Environ; 777 (2021) 145981.

[2] L. Chen, S. Zhou, Y. Shi, *et al.*, Sci. Total Environ; 615 (2018) 141–149.

[3] P. Pavlović, M. Mitrović, D. Đorđević, *et al.*, Sci. Total Environ; 540 (2016) 396–409.

[4] M. Mitrović, P. Pavlović, D. Lakušić, *et al.*, Sci. Total Environ; 407 (2008) 338–347.

[5] O. Kostić, S. Jarić, G. Gajić, *et al.*, Catena; 163 (2018) 78–88.

[6] J. Zhang, H. Li, Y. Zhou, *et al.*, Environ. Pollut; 235 (2018) 710–719.

[7] X. Luo, B. Ren, A.S. Hursthouse, *et al.*, Environ. Geochem. Health; 42 (2020) 1965–1976.

[8] US Environmental Protection Agency, (1998) Microwave assisted acid digestion of sediments, sludges and oils (3051), Washington, DC, *Available on the following link:* https://settek.com/documents/EPA-Methods/PDF/EPA-Method-3051.pdf

[9] US Environmental Protection Agency, (1996) Microwave Assisted Acid Digestion of Siliceous and Organically Based Matrices (3052), Washington, DC, *Available on the following link:* https://www.epa.gov/sites/default/files/2015-12/documents/3052.pdf

[10] A.J.M. Baker, J. Plant Nutr; 3 (1981) 643–654.

[11] A, Kabata-Pendias, H. Pendias, Trace Elements in Soils and Plants, CRC Press LLC, Boca Raton, FL, USA, (2001), p.413, ISBN: 0-8493-1575-1.

[12] A. Gomez-Caminero, P. Howe, M. Hughes, *et al.*, Environmental Health Criteria 224, Arsenic and arsenic compounds, World Health Organization, Geneva, (2001).

[13] M.A. Rahman, H. Hasegawa, M.M. Rahman, *et al.*, Chemosphere; 69 (6) (2007) 942–948.

[14] Pravilnik o dozvoljenim količinama opasnih i štetnih materija u zemljištu i vodi za navodnjavanje i metodama njihovog ispitivanja (Službeni Glasnik RS, br. 23/94) (National Regulations on Permitted Quantities of Hazardous and Harmful Substances in Soil (Official Gazette of the Republic of Serbia, no. 23/94)).

[15] OECD (1993) Risk reduction, monograph No. 1: LEAD–background and national experience with reducing risk. OECD/GD(93)67 Environment directorate, Environmental health and safety division, Paris, Accessed 17 Dec 2019.

[16] G. Tóth, T. Hermann, M.R. Da Silva, *et al.*, Environ. Int; 88 (2016) 299–309.

[17] M.B. McBride, Appl. Environ. Soil Sci; (2013) Article ID 283472.

[18] G.P. Warren, B.J. Alloway, N.W. Lepp, *et al.*, Sci. Total Environ; 311 (2003) 19–33.

[19] Pravilnik o količinama pesticida, metala, metaloida i drugih otrovnih supstancija, hemioterapeutika, anabolika i drugih supstancija koje se mogu nalaziti u namirnicama: SRJ 5/1992-67, 11/1992-151 (ispravka), 32/2002-2, RS 25/2010-16 (dr. pravilnik), RS 28/2011-9 (dr. pravilnik) Službeni Glasnik RS, br. 23/94 (National Regulations on the quantities of pesticides, metals, metalloids and other toxic substances, chemotherapy drugs, anabolics and other substances that can be found in foodstuffs: FRY 5/1992-67, 11/1992-151 (amend.), 32/2002-2, RS 25/2010-16 (other regulations), RS 28/2011-9 (other regulations) Official Gazette RS, no. 23/94).

[20] P. Nathanail, C. McCaffrey, R. Ogden, *et al.*, Land Contamination and Reclamation; 12 (3) (2004) 219–238.

[21] A. Raab, P.N. Williams, A. Meharg, *et al.*, Environ. Chem; 4 (2007) 197–203.

[22] E.E. Codling, R.L. Chaney, C.E. Green, J. Plant Nutr; 38 (2015) 509–525.

[23] R.L. Hough, N. Breward, S.D. Young, *et al.*, Environ. Health Perspect; 112 (2004) 215–221.

[24] F. Douay, H. Roussel, C. Pruvot, *et al.*, Sci. Total Environ; 401 (2008) 29–38.

NEW STRATEGIES FOR DEVELOPMENT OF HIGHLY SELECTIVE MATERIALS FOR CARBON DIOXIDE CAPTURE

Marija Ječmenica Dučić[1], Dragana Vasić Anićijević[1], Branislava Savić[1*], Danka Aćimović[1], Marija Simić[1], Danijela Maksin[2], Tanja Brdarić[1]

[1]University of Belgrade, VINČA Institute of Nuclear Sciences – National Institute of the Republic of Serbia, Department of Physical Chemistry, Mike Petrovića Alasa 12–14, 11000 Belgrade, SERBIA

[2]University of Belgrade, VINČA Institute of Nuclear Sciences – National Institute of the Republic of Serbia, Department of Chemical Dynamics & Permanent Education, Mike Petrovića Alasa 12–14, 11000 Belgrade, SERBIA

[*]*branislava@vin.bg.ac.rs*

Abstract

Selective separation of CO_2 *is a field of intensive research due to emerging emissions from fire coaled and natural gas power plants. In the focus of development efforts is a design of regenerable* CO_2 *capture material where adsorption technologies and advanced solid adsorbents are again in the centre of interest. Short screening of composite zeolite/activated carbon material in the terms of its selectivity for* CO_2 *towards water is presented in this research. Adsorption rate of* CO_2 *and* H_2O *is determined and analysed at two different temperatures and equilibrium pressure of 3.5 kPa which corresponds to flue gases contents. The results imply the water should be removed from treated gas before* CO_2 *separation and capture. Design of advanced materials can be facilitated by implementation of DFT calculations. A preview of DFT analysed materials with higher affinity for* CO_2 *than for water adsorption is presented within this research. It underscores the possibility of defining future strategies for the design of novel carbon dioxide capture materials more resistant to water compared to currently used zeolites.*

Keywords: CO_2 capture, adsorption, DFT theory

INTRODUCTION

Emerging emission of CO_2 implies a need for urgent implementation of CO_2 capturing technologies. Development efforts are significant, especially in field of separation from power and sour natural gas plants flue streams and from syngas [1]. Having in mind that any chemical employed to capture CO_2 will rapidly exhaust its global supplies if it is used in a once-through manner, and that any chemical produced from CO_2 as a reactant will rapidly saturate global markets for that chemical [2], the necessity of development of regenerable capture material is underlined.

Within CO_2 capture technologies by adsorption, advanced solid zeolite-based adsorbents with high capacity towards CO_2 represent an acceptable alternative [3]. In this case, where energy input for regeneration is the main criterion for evaluating the cost-effectiveness of CO_2 capture technology [4], current strategies include composites based on commercial zeolites

[5] and carbons [6]. Carbon component decreases the overall adsorbent capacity towards CO2, but as a conductive material it enables short and efficient regeneration by Joule effect using electric power [7,8].

One of the problems when capture the CO_2 with zeolite-based adsorbents is water content of 10–15 vol.% in flue gases of fire coaled and natural gas power plants [9]. Namely, zeolite-based materials have high affinity for water and efficient carbon capturing requires highly selective adsorption of CO_2 [10], with little or no adsorption of other combustion gas components (N_2, H_2O).

Within this research the adsorption rate of CO_2 and H_2O on zeolite/carbon composite material was analysed with the main goal to develop a strategy for a design of highly selective material for CO_2 capture. Design of novel, sophisticated materials can be facilitated by implementation of DFT calculations.

MATERIALS AND METHODS

Adsorption rates of pure gases (CO_2 and H_2O) were measured in automatic volumetric unit BELsorp-max II (Verder Scientific, Germany).

The composite material was prepared mixing the commercially available zeolite X13 (Chemiewerk Bad Köstriz, Germany) with acetylene carbon black (AlfaAesar, Heysham, UK) in ratio 80 wt.% : 20 wt.%. Prior to the experiments, the material was degassed at 150°C under vacuum for a period of 15 hours (heating ramp of 2°C/min).

Adsorption rates for both gases were measured at two temperatures, 30°C and 150°C, and equilibrium pressure of 3.5 kPa. The mass of adsorbent used in the water experiments was smaller to reduce the time of measurement (0.2851 g for CO_2 and 0.0804 g for H_2O).

RESULTS AND DISCUSSION

CO_2 and H_2O adsorption rate on zeolite/carbon composite

The adsorption rate of pure CO_2 and H_2O is determined at 30°C and 150°C. The first temperature (30°C) was chosen as the highest expectable during adsorption, and the second (150°C) as an acceptable limit for material thermo-stability. The results are presented in Figure 1, where C, C_{eq} and C_0 represent actual, equilibrium and initial concentration [kPa] of gas.

Higher adsorption rate of water is obvious at 30°C: H_2O reaches the equilibrium after approximately 100 s, while CO_2 is not in equilibrium even after 300 s. Very fast decrease of water concentration implies the binding on adsorption sites is strong and that water would first occupy available adsorption sites in the case of competitive adsorption (such as the separation of flue gases).

At 150°C adsorption rate of CO_2 and H_2O is approximately equal, which implies the adsorbent regeneration could be difficult in the case of competitive adsorption.

Water adsorption on zeolite involves chemisorption on multiple adsorption sites. For this reason, it is difficult to describe the adsorption rate by any of the simple kinetics models, and the same should be expected for the adsorption isotherm.

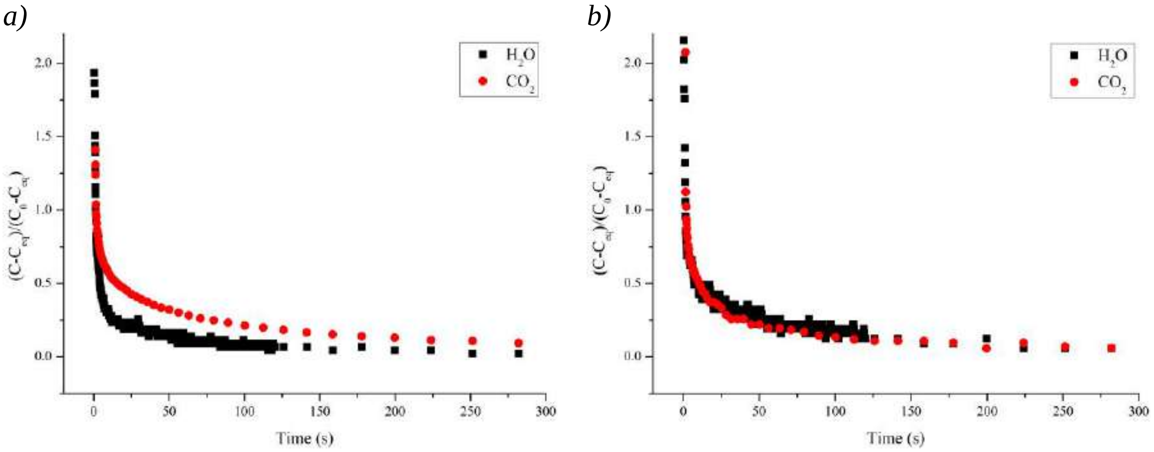


__Figure 1__ Adsorption rate of CO_2 and H_2O on zeolite/carbon composite a) at temperature 30°C; b) at temperature 150°C

Overview of DFT calculated adsorption energies of CO_2 and H_2O on various materials

Plenty of literature data on co-adsorption of water and CO_2 on various materials are already available. There are numerous materials with considerably higher affinity for CO_2 than for water adsorption. Some of them are presented in Table 1.

__Table 1__ DFT calculated adsorption energies (E_{DFT}) of CO_2 and H_2O on various materials

Material	**$E_{DFT,CO2}$**	**$E_{DFT,H2O}$**	**Reference**
As_2O_3	-52 kJ/mol	-144 kJ/mol	[11]
graphene	-17.9 kJ/mol	-20.2 kJ/mol	[12]
graphite	-16.5 kJ/mol	-14.9 kJ/mol	[13]
zeolite (faujasite) [a]	-21–36 kJ/mol	-58–88 kJ/mol	[14]
CaO	-243 kJ/mol	-146 kJ/mol	[15]

[a] multiple adsorption sites.

As can be seen from Table 1, it is possible to find existing materials with lower affinity for water adsorption compared to CO_2 adsorption. Initial design and preparation of the novel materials with controlled H_2O and CO_2 adsorption properties can be guided by DFT calculations. Besides the selectivity, the novel materials should also meet the requirements for CO_2 capture, such as good adsorption capacity or good conductivity.

CONCLUSION

Strong physical and chemical binding of water on zeolite 13X reduces adsorbent capacity for CO_2 and efficiency of regeneration on low temperatures (up to 150°C) that significantly affect the overall cost-effectiveness of separation process (i.e. CO_2 capture). It is possible to define future strategies for the design of novel carbon capture materials, more resistant to water compared to currently used zeolites. DFT theory can contribute to the prediction of adsorption properties and guide the sophisticated design of the materials.

ACKNOWLEDGEMENT

This work was supported by the Ministry of Education, Science and Technological Development of Republic of Serbia; grant number 451-03-68/2022-14/200017.

REFERENCES

[1] P. Madejski, K. Chmiel, N. Subramanian, *et al.*, Energies; 15 (3) (2022) 887.

[2] D.M. D'Alessandro, B. Smit, J.R. Long, Angew. Chem., Int. Ed. Engl; 49 (35) (2010) 6058–6082.

[3] J.Y. Lai, L.H. Ngu, S.S. Hashim, Greenh. Gases: Sci. Technol; 11 (5) (2021) 1076–1117.

[4] A. Cousins, P. Feron, J. Hayward, *et al.*, IEAGHG Technical Report, April 11th, Melbourne, Australia (2019).

[5] E. Khoramzadeh, M. Mofarahi, C.H. Lee, J. Chem. Eng. Data; 64 (12) (2019) 5648–5664.

[6] J. Wang, Q. Pu, P. Ning, *et al.*, Greenh. Gases: Sci. Technol; 11 (2) (2021) 377–393.

[7] J.S. Lee, J.H. Kim, J.T. Kim, *et al.*, J. Chem. Eng. Data; 47 (5) (2022) 1237–1242.

[8] M.J. Regufe, A.F.P. Ferreira, J.M. Loureiro, *et al.*, Adsorption; 24 (3) (2018) 249–265.

[9] J.H. Copen, T.B. Sullivan, B.C. Folkedahl, *et al.*, Proceedings of the International Symposium POWER-GEN, December 6–8th, Las Vegas, Nevada (2005) 13.

[10] O. Cheung, Z. Bacsik, N. Fil, *et al.*, ACS Omega; 5 (39) (2020) 25371–25380.

[11] P. Hu, Q. Weng, D. Li, *et al.*, J. Hazard. Mater; 403 (2021) 123866.

[12] Z. Gao, Y. Ding, J. Mol. Model; 23 (6) (2017) 187.

[13] M. Rubeš, J. Kysilka, P. Nachtigall, *et al.*, Phys. Chem. Chem. Phys; 12 (24) (2010) 6438.

[14] E.P. Hessou, W.G. Kanhounnon, D. Rocca, *et al.*, Theor. Chem. Acc; 137 (12) (2018) 161.

[15] X. Ma, Y. Li, W. Zhang, *et al.*, Chem. Eng. J; 370 (2019) 10–18.

EcoTER'22
29th International Conference Ecological Truth
& Environmental Research
21 - 24 June 2022, Hotel Sunce, Sokobanja, Serbia
www.eco.tfbor.bg.ac.rs

CHARACTERISTIC, SOURCE AND ECOLOGICAL RISK OF PAHs IN AGRICULTURAL SOILS PLJEVLJA MUNICIPALITY (MONTENEGRO)

Miljan Bigović[1], Dijana Đurović[2,3*], Irena Nikolić[4], Ljubica Ivanović[2], Borko Bajić[2]

[1]University of Montenegro, Faculty of Sciences and Mathematic, Džordža Vašingtona bb,
Podgorica, MONTENEGRO

[2]Institute of Public Health of Montenegro, Džona Džeksona bb, 81000 Podgorica,
MONTENEGRO

[3]University Donja Gorica, Faculty for Food Technology, Food Safety and Ecology, Oktoih 1,
81000 Podgorica, MONTENEGRO

[4]University of Montenegro, Faculty of Metallurgy and Technology, Džordža Vašingtona bb,
Podgorica, MONTENEGRO

*dijana.djurovic@ijzcg.me

Abstract

The content source of PAHs in agricultural soil in Pljevlja municipality (Montenegro) along with potential ecological risk were evaluated in this study. Mean concentrations of ΣPAHs was calculated to be 271.49 $\mu g\ kg^{-1}$. PAHs content in agricultural soli follow descending order: Ace > Fl > IcdP > Flu > BghiP > Cry > Pyr >Np > Phe > BbF > DahA > BaA > BaP > BkF > Ant. Based on the PAHs diagnostic ratios coal/wood combustion and traffic emissions were identified as the main PAHs sources in soil. Content of Np, Ace, Fl, Phe, Ant, Pyr, BaA, BbF, BaP and DahA in soil samples implies moderate ecological risk.

Keywords: agricultural soil, PAHs, source apportionment, ecological risk

INTRODUCTION

Polycyclic (polynuclear) aromatic hydrocarbons (PAHs) or polyarenes are a large group of organic aromatic compounds that are composed of two or more condensed rings. This group is included about 10 000 substances, with widely varying toxic features. Depending on ways of rings connection, they can be linear or angular. The division was also made according to the number of rings – hydrocarbons containing up to six rings are classified as small PAHs, and those containing more than six are large PAHs [1]. The general physical characteristics od PAHs are high melting points and very low solubility in water, because they are lipophylic supstances [2].

PAHs are very strong environmental pollutants and they are always emitted as a mixture. They are highlighted as specific pollutants worldwide and in this sense their properties, quantities and distribution have been closely monitored since the 1970 [3]. They can occur either during biological processes or through human activities. Natural sources of PAHs are forest or brush fires, volcanic activity, hydrothermal processes, hydrocarbon bearing rock formation, burning of organic materials. Anthropogenic sources are automobile emissions or cigarette smoke, thermal processing of food (roasting, frying, grilling) or drying or smoking food. PAHs are formed during incomplete combustion of organic matter (wood of fossil fuels).

PAHs are strongly adsorbed to the organic fraction of soils and therefore they do not usually penetrate deeper in soil layers. Once they reach the soil, the PAHs there remain because they are, as very non-polar, insoluble in water and thus cannot be further mobilized through the soil. High hydrophobicity and stable chemical structure of PAHs cause their poor solubility, so they are easily adsorbed primarily on organic components from the soil. After deposition in the soil, they can further accumulate in plants, and thus through the food chain they can reach the human body.

According to United States Environmental Protection Agency (USEPA), sixteen PAHs have been listed as priority pollutants (among them, seven have been confirmed to be carcinogenic substances). On the other side, according to International Agency for Research on Cancer, eight of PAHs are considered as possible carcinogenic agents for humans. Given the fact that both the environment and humans are highly exposed to and exposed to pollutants, it is very important to assess the ecological risks of polycyclic aromatic hydrocarbons of soil, which was the goal of our paper.

So, the aim of this study was to assess content of PAHs content in agricultural soil in Pljevlja municipality and to establish the source of PAHs and ecological risk as well.

MATERIALS AND METHODS

A top soil samples were collected from a maximum of 20 cm of depth from agricultural fields in the vicinity of coal fired power station (43°20'09.1" N, 19°19'34.6" E) during the period of August to November, 2019. Sampling points were selected in a way that reflects the impact of anthropogenic activities, coal combustion in coal-fired power plants, wood combustion for heating residential buildings as well as the impact of traffic exhaust.

PAHs extraction was carried out according modified standard method EPA 3550C. PAHs quantification was performed using an SHIMADZU LC-20AB liquid chromatograph, equipped LC-20AT binary pump, a DGU-20A on-line degasser, a SIL-20A autosampler, a CTO-20A column oven, a RF-10-AXL fluorescence detector and a CBM-20A lite system controller.

Ecological risk posed by the presence of individual PAHs in agricultural soil was evaluated on the basis risk quotients (RQ_{NCs}) and (RQ_{NCs}) (Equations 1 and 2).

$$RQ_{NCs} = \frac{C_{PAHs}}{C_{QV_{(NCs)}}} \qquad (1)$$

$$RQ_{MPCs} = \frac{C_{PAHs}}{C_{QV_{(MPCs)}}} \qquad (2)$$

where, C_{PAHs} is the concentration of certain PAHs in the soil and C_{QV} is the corresponding quality values of PAHs in the soil [4,5]. $C_{QV(NCs)}$ and $C_{QV(MPCs)}$ are the quality values of the negligible concentrations (NCs) and the maximum permissible concentrations (MPCs) in the soil. Ecological risk classification of individual PAHs is given in Table 1.

Table 1 *Ecological risk classification of individual PAHs*

Individual PAH		**Ecological risk**
RQ$_{NCs}$	**RQ$_{MPCs}$**	
0	-	Risk free
≥1	<1	Moderate risk
-	≥1	High risk

RESULTS AND DISCUSSION

Main concentrations of PAHs detected in agricultural soils in Pljevlja municipality are given in Figure 1. Fifteen PAHs were detected soil samples: naphthalene (Np), acenaphthene (Ace), fluorene (Fl), phenanthrene (Phe), anthracene (Ant), fluoranthene (Flu), pyrene (Pyr), benz[a]anthracene (BaA), chrysene (Cry), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[a]pyrene (BaP), dibenz[a,h]anthracene (DahA), benzo[ghi]perylene (BghiP) and indeno[1,2,3-cd]pyrene (IcdP). The average value of ΣPAHs was found to be 271.49 μg kg^{-1}. PAHs concentrations in soil follow descending order: Ace > Fl > IcdP > Flu > BghiP > Cry > Pyr >Np > Phe > BbF > DahA > BaA > BaP > BkF > Ant. Average concentration of seven carcinogenic PAHs was 99.53 μg kg^{-1} contributing 33.48% of Σ PAHs. Results obtained in this study were compared to Montenegrin guidelines for permeable concentration of toxic components in soil. The target values of the acceptable PAHs concentrations for agricultural use soils according the Montenegrin legislation is 600 (μg·kg^{-1}) [6]. The results obtained in this study indicated unpolluted agricultural soils in Pljevlja municipality with respect to PAHs content.

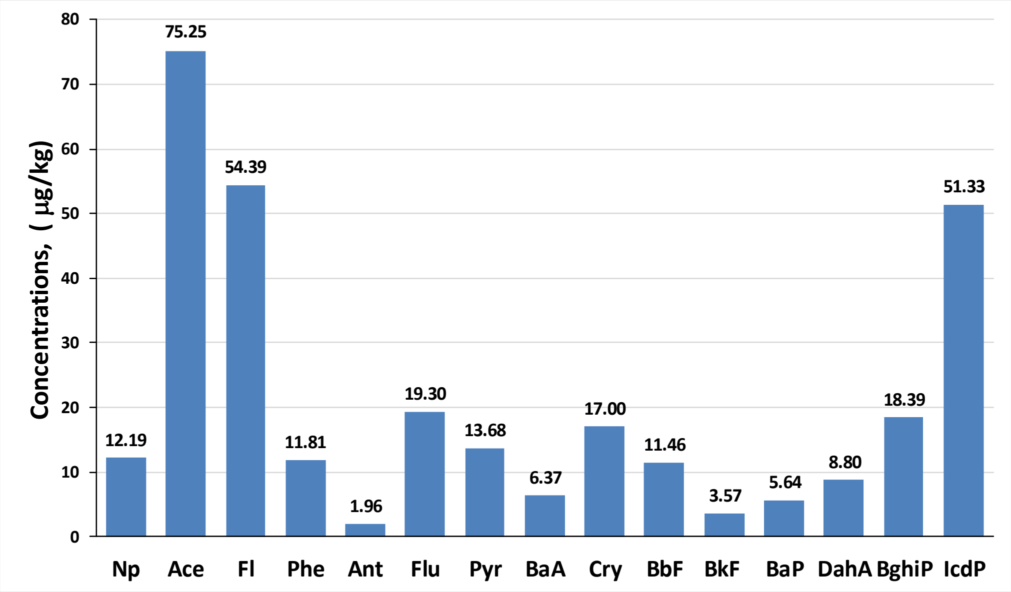


Figure 1 *PAHs concentration in agricultural soil in Pljevlja municipality*

Diagnostic ratio is useful tool for identification of PAHs source. Several diagnostic ratios was used in this study: IcdP/(IcdP + BghiP), Fl/(Fl+Pyr), BaA/(BaA+Cry) and BaP/BghiP. The results are given in Figure 2. The three values of IcdP/(IcdP+BghiP) ratio were used to identify the source of PAHs. Ratio values <0.2 indicate petrogenic source, values between 0.2 and 0.5 indicate petroleum combustion as a PAHs source while ratio values >0.5 indicate that PAHs in soil originate from the grass, wood and coal combustion [7]. The values of Flu/(Flu+Pyr) <0.4 indicates petroleum input sources; values between 0.4 and 0.5 indicates petroleum combustion (especially liquid fossil fuel, vehicle, and crude oil), and values >0.5 implies combustion of biomass and coal. The values of BaA/(BaA+Cry) below 0.2 imply petrogenic source while values above 0.35 suggest combustion source. The values between 0.2 and 0.35 indicate the mixed (petrogenic/combustion) source of PAHs [6]. In addition, values of BaP/BghiP ratio below 0.6 suggest non-traffic source while values above 0.6 implies traffic source of PAHs [8].

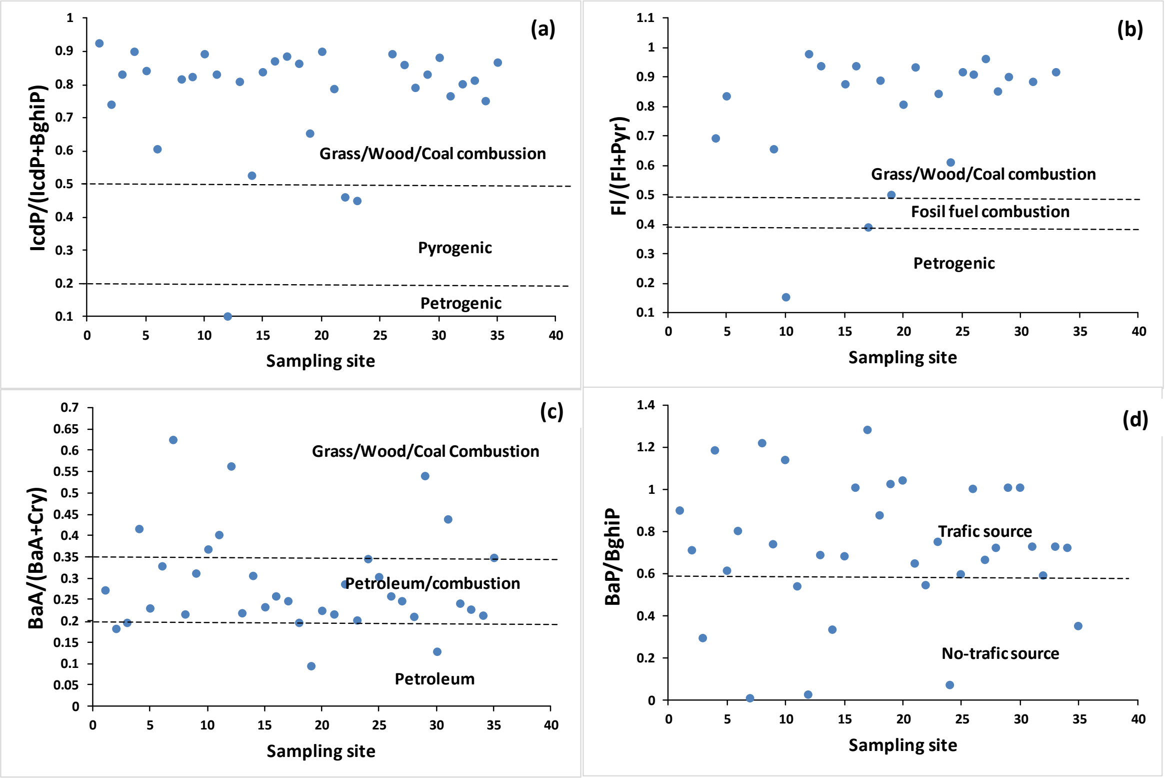


Figure 2 *Diagnostic ratio charts: (a) – IcdP/(IcdP + BghiP), (b) – Fl/(Fl+Pyr), (c) – BaA/(BaA+Cry) and (d) – BaP/BghiP*

The results obtained in this study indicate combined influence of traffic and grass/wood/coal combustion. The results presented in Figure 4(a) and showed that 68.7% of soil samples had a IcdP/(IcdP + BghiP) values above 0.5 and values of BaA/(BaA+Cry) between 0.2 and 0.35 suggesting mixed source of PAHs in soil samples (combustion/petroleum). Moreover, results presented in Figure 4(b) indicted the 80% of soil samples had a IcdP/(IcdP + BghiP) ratio values above 0.5 and BaA/(BghiP) values above 0.6 suggesting combined traffic and grass/wood/coal combustion sources of PAHs in soils.

Evaluation of IcdP/(IcdP + BghiP) ratio indicated that 93.75% of sampling site had the ratio values above 0.5 which implies grass/wood/coal combustion sources of PAHs in soils. The same conclusion is derived by the evaluation of Fl/(Fl+Pyr). Namely, 90.90% of sampling sites had a values of this ratio above 0.5 which also indicates grass/wood/coal combustion sources of PAHs in soils. However, evaluation of BaA/(BaA+Cry) ratio indicated the mixed source of PAHs, petroleum/combustion since majority of ratio values (62.86%) fall in the range between 0.2 and 0.35. Traffic source of PAHs was also identified since 77.14% of sampling sites had a ratio of BaP/BghiP were higher than 0.6.

Potential ecosystem risk of PAHs in agricultural soil in Pljevlja municipality was evaluated on the basis of mean values of $RQ_{(NCs)}$) since $RQ_{(MPCs)}$ values were below 1. The values of $RQ_{(NC)}$ for Np, Ace, Fl, Phe, Ant, Pyr, BaA, BbF, BaP and DahA were higher than one indicating that these PAHs showed moderate level of ecological risk and some control and prevention be measure must be taken. On the other hand, mean values of $RQ_{(NC)}$ for Flu, Cry, BghiP and IcdP were bellow one suggesting no ecological risk.

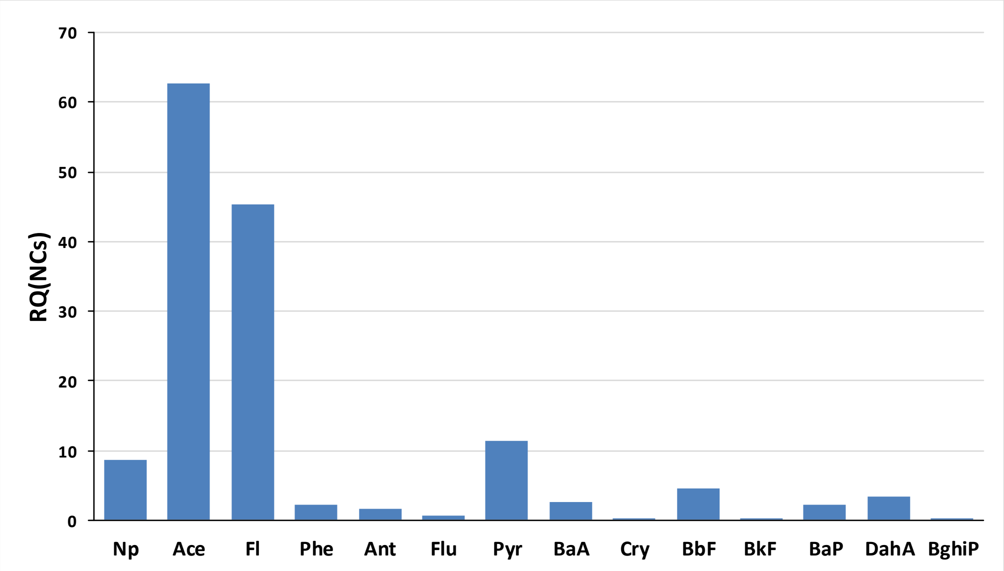


Figure 3 *Values of RQ(NCs) for individual PAHs*

CONCLUSION

Content and source of PAHs in agricultural soils around the thermal plant in Pljevlja municipality was evaluated in this study. Ecological risk assessment was also evaluated. The most dominant PAHs present in soil were Ace, Fl and IcdP. Comparison of Σ7PAHs obtained in this study with the Montenegrin legislation indicated unpolluted agricultural soil with respect to PAH content. Evaluation of PAHs source indicated that coal/wood combustion and traffic emissions could be primary sources in agricultural soils from the Pljevlja municipality. Ecological risk assessment indicated moderate level with respect to content of Np, Ace, Fl, Phe, Ant, Pyr, BaA, BbF, BaP and DahA while there is no ecological risk with respect to the content of Flu, Cry, BghiP and IcdP.

ACKNOWLEDGEMENT

This work was supported by the Montenegrin Ministry of Science under grant No. 01-779/2.

REFERENCES

[1] H.M. Abdel-Shafy, A. Mansour, Egypt J. Petroleum; 25 (2016) 107–123.

[2] J. Masih, R. Singhvi, K. Kumar, *et al*., Aerosol Air Qual. Res; 12 (2012) 515–525.

[3] G. Grimmer, Toxicol. Environ. Chem; 10 (1985) 171–181.

[4] D.F. Kalf, T. Crommentuijn, E.J. van de Plassche, Ecotoxicol. Environ. Saf; 36 (1997) 89–97.

[5] Z. Cao, J. Liu, Y. Luan, *et al*., Ecotoxicology; 19 (2010) 827–837.

[6] Rulebook of Allowed Concentrations of Hazardous and Dangerous Substances in Soil and Methods for Determination; Official Gazette of Republic of Montenegro 18/97: Podgorica, Republic of Montenegro (1997).

[7] M.B. Yunker, R.W. Macdonald, R.Vingarzan, *et al*., Org. Geochem; 33 (2002) 489–515.

[8] P.K Pandey, K.S. Patel, J. Lenicek, Environ. Monit. Assess; 59 (1999) 287–319.

EFFECT OF DIFFERENT ENVIRONMENTAL CONDITIONS ON LIPID PEROXIDATION LEVEL IN *Rutilus rutilus* (ACTINOPTERYGII: CYPRINIDAE)

Jelena Vranković[1*], Katarina Jovičić[1], Vesna Đikanović[1]

[1]Department of Hydroecology and Water Protection, Institute for Biological Research
"Siniša Stanković", National Institute of Republic of Serbia, University of Belgrade,
Despot Stefan Blvd 142, 11060 Belgrade, SERBIA

[*]*jeca.s@ibiss.bg.ac.rs*

Abstract

The present study aimed to assess the lipid peroxidation (LPO) level under the different environmental conditions on the common roach (Rutilus rutilus). Lipid peroxides were measured in fish collected within the Danube River at two points: Veliko Ratno ostrvo (P1), which was considered a reference point, and Višnjica (P2), the point with compromised water quality. A significant difference is revealed between the points suggesting signs of stress in fish from the Višnjica point. Concerning that Višnjica experiences intense environmental pressure, we noticed an increased concentration of lipid peroxides in the fish liver, compared to those individuals from the P1 ($p < 0.05$). A significantly increased level of LPO in fish from P2 can be the indication of the presence of pro-oxidant stressors that through oxidative stress lead to oxidation of cell lipids in fish. These results give a good base for R. rutilus to be a bioindicator of a disturbed environment.

Keywords: Danube River, lipid peroxidation, *Rutilus rutilus*

INTRODUCTION

Fish are an important bioindicator species and play an increasingly important role in the monitoring of water pollution because they respond with great sensitivity to changes in the aquatic environment [1]. The effects of fish exposure to sub-lethal levels of pollutants can be measured in terms of their biochemical, physiological, or histological responses. Environmental contaminants that are accumulated in the tissues of fish may catalyze reactions that generate reactive oxygen species (ROS). When the production and accumulation of ROS are beyond the organism's capacity to deal with these reactive species oxidative stress occurs [2]. This can damage lipids, proteins, and deoxyribonucleic acid (DNA). Some ROS can initiate lipid peroxidation, a self-propagating process in which a peroxyl radical is formed when a ROS has sufficient reactivity to abstract a hydrogen atom from an intact lipid which may generate DNA alterations and peroxidation of membrane lipids initiating the cellular degenerative process [3].

In the aquatic environment, biota can be subjected to a multipollutant state in the presence of a mixture of pollutants. Chemical analyses of pollutants are expensive and it is not feasible to measure all classes of chemicals likely to be found in an aquatic environment given the complex mixture. Biomarkers represent toxicant-induced changes in biological systems and serve as links between environmental contamination and its effects, providing relevant data about the possible pathological process in fish [4].

The liver is an organ that is widely used in biomarker approach studies on fish health assessment and is associated with detoxification processes, due to its function, position, and blood supply. It is also one of the most affected organs in contaminated waters but also plays an important role in fish physiology. In addition, the parenchymal liver tissue in fish has important physiological functions, such as the detoxification of chemical contaminants [5]. Lipid peroxidation (LPO) is one of the main manifestations of oxidative damage induced by various compounds, including metals hence, it has been used as a biomarker of pollution [6].

This study aimed to explore whether the untreated wastewaters of Belgrade city could induce oxidative stress and damage to aquatic organisms in the Danube River. To evaluate the effects of environmental pressure, levels of malondialdehyde (MDA) in the liver tissue of the *Rutilus rutilus* collected from Veliko Ratno ostrvo and Višnjica points were analyzed.

MATERIALS AND METHODS

Sampling points

Fish samples were caught from two points at the Serbian part of the Danube River in the April of 2021. The first point Veliko Ratno ostrvo (P1, Lat. 44.8289559, Long. 20.4297724), devoid of any industrial facilities that could cause pollution, is considered a reference point. The second point, Višnjica (P2, Lat. 44.8295251, Long. 20.5498088) suffers anthropogenic pressure resulting from the presence of a marina for recreational boats (Figure 1).

Figure 1 *The geographical position of the sampling points on the Danube River: Veliko Ratno ostrvo and Višnjica*

At the time of sampling, environmental parameters, including water temperature, pH, and dissolved oxygen were measured *in situ* at both points (Table 1).

***Table 1** Values of physicochemical parameters at Veliko Ratno ostrvo (P1), and Višnjica (P2) in situ on the day of fish collection*

Physicochemical parameters	P1	P2
Temperature (°C)	9.3	10
pH	8.1	8.3
Dissolved O_2 (mg^{-1})	9.7	9.8

The adult fish (n = 10 per sampling point) were transported to the laboratory in ice-cold containers (0–4 °C) on the same day. The fishes were dissected and the livers were quickly removed and stored at -80 °C until further analysis.

Determination of malondialdehyde (MDA)

Lipid peroxidation was determined as described by Rehncrona *et al*. [7]. Tissue (100 mg from each liver) was minced and homogenized in 10 volumes of 0.05 M TRIS-EDTA buffer (pH 7.4) using a Janke & Kunkel IKA-Werk Ultra-Turrax homogenizer and then sonicated for 15 s at 10 kHz on ice [8]. The lipid peroxides concentration was measured as the absorbance change at 532 nm in the reaction of sample malondialdehyde (MDA) with the thiobarbituric acid as the reagent. Malondialdehyde was quantitated by using $\Sigma = 1.56 \times 10^5\ M^{-1}\ cm^{-1}$.

Statistical analyses

All variables were tested for normal distribution using the Kolmogorov-Smirnov test and for homogeneity of variance among groups using Levene's test. Significant differences were analyzed using one-way ANOVA and post-hoc Tukey honest significant difference (HSD) multiple-comparison test. $p < 0.05$ was considered significant. All the statistics were carried out in SAS 9.1.3 software (SAS Institute Inc., Cary, NC).

RESULTS AND DISCUSSION

Aquatic systems are the main recipients of almost all anthropogenic discharges. Metals are major pollutants of aquatic ecosystems due to disposal of industrial effluents, or via direct dumping in the river of waste material such as sewage sludge [9]. They are usually toxic at high levels, may accumulate in the aquatic organisms, and trigger a range of oxidative damages [10]. Malondialdehyde is one of the LPO products deriving from an oxidative attack on cell membrane phospholipids and circulating lipids, and its level directly reflects the degree of oxidative damage induced by contaminants [11]. Several studies have already shown enhanced LPO in aquatic organisms exposed to high concentrations of inorganic contaminants [12–14].

The MDA levels (an index of LPO) in the liver of *Rutilus rutilus* samples from P1 and P2 are shown in Figure 2. MDA was significantly higher in the fish liver (~ 60%) caught at P2 than in fish from the reference point P1. Fish inhabiting the Višnjica region of the Danube River are exposed to a complex of different mixtures of pollutants. A marina for recreational boats sited at the Višnjica location is occasionally subjected to accidental spillage of fuel/oil into the surrounding water. Diesel fuel is considered to be highly toxic due to its high content of polycyclic aromatic hydrocarbons, the most toxic component of petroleum hydrocarbons.

Because of its widespread use in recreational vessels, diesel fuel represents a potentially significant contaminant to aquatic environments [15]. Dramatically increased utilization of Cu-based antifouling coatings on vessel hulls has led to elevated Cu concentrations in those marinas and harbors where substantial numbers of small craft or large vessels are berthed [16]. Most antifouling paints prevent the attachment and growth of aquatic organisms by continually leaching biocides such as Cu into the water [17]. In addition, abiotic factors may influence biomarker responses to pollutants, but in our study physicochemical parameters varied in a narrow range between two sampling points (Table 1).

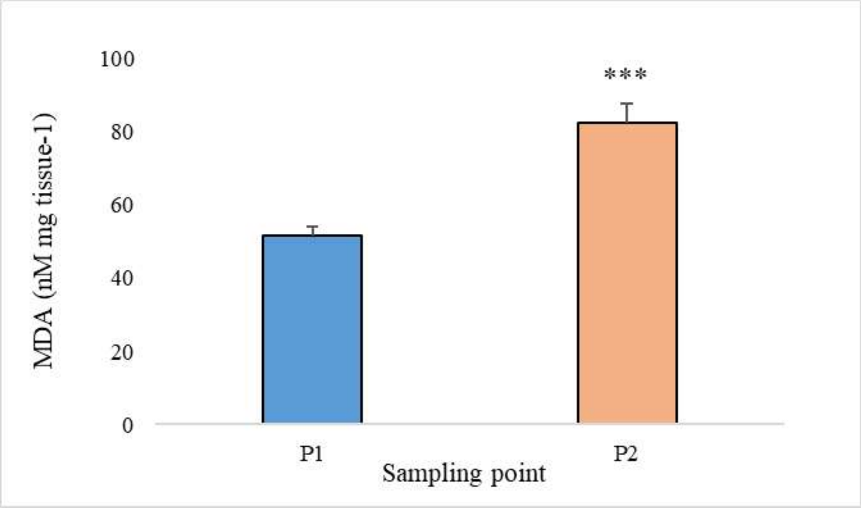


Figure 2 *The levels of malondialdehyde (MDA) in the liver of Rutilus rutilus from the Veliko Ratno ostrvo (P1) and Višnjica (P2). Values are mean + SE of 10 fishes. The significant difference between P1 and P2 were calculated by one-way ANOVA and marked with an asterisk,*** p < 0.001*

Our results suggest that the elevated MDA level could be considered a result of oxidative stress from xenobiotics at Višnjica point. Similar results were obtained for the specimen of freshwater fish (Cyprinidae), as demonstrated by other authors [18,19]. These researchers reported that the MDA level was increased in the liver of fish collected from polluted areas. As measurement of MDA content provides a relative measure of the potential for pollutants to cause oxidative injury [20,21], significantly elevated levels of MDA in the liver tissue of *R. rutilus* in response to toxicants indicate that some cell damage might have occurred.

CONCLUSION

The present study confirmed that the aquatic environment at Višnjica point with its current environmental pressure is responsible for oxidative stress in the liver tissue of *Rutilus rutilus*. This state of oxidative stress fish reflects through drastically increase in MDA levels. The findings of the present investigation suggest that the presence of certain prooxidative pollutants that can lead to oxidative stress in the fish at the Višnjica point and oxidative stress biomarkers may be important to evaluate the effects of untreated waste on living organisms in the Danube River.

ACKNOWLEDGEMENT

This work was supported by the Serbian Ministry of Education, Science and Technological Development (contract number 451-03-68/2022-14/ 200007).

REFERENCES

[1] M.M. Authman, M.S. Zaki, E.A. Khallaf, *et al*., J. Aquac. Res. Dev; 6 (2015) 328–340.

[2] D.R. Livingstone, Rev. Med. Vet; 154 (2003) 427–430.

[3] B. Halliwell, J.M. Gutteridge, Free Radicals in Biology and Medicine, 4th edition, Oxford University Press, USA (2015), ISBN-13: 9780198717478.

[4] V.L. Maria, I. Ahmad, M. Oliveira, *et al*., Ecotoxicol. Environ. Safe; 72 (2009) 1861–1870.

[5] S. Stoyanova, E. Georgieva, I. Velcheva, *et al*., Water; 12 (2020) 1837.

[6] B.C. Almroth, J. Sturve, A. Berglund, *et al*., Aquat. Toxicol; 73 (2005) 171–80.

[7] S. Rehncrona, D.S. Smith, B. Akesson, *et al*., J. Neurochem; 34 (1980) 1630–1638.

[8] M.A. Rossi, G. Cecchini, M.U. Dianzani, Med. Sci-Biochem; 11 (1983) 805–806.

[9] C.S. Carvalho, V.A. Bernusso, H.S.S. Araújo, *et al*., Chemosphere; 89 (2012) 60–69.

[10] W. Sanchez, O. Palluel, L. Meunier, *et al*., Environ. Toxicol. Phar; 19 (2005) 177–183.

[11] B.D. Banerjee, V. Seth, A. Bhattacharya, Toxicol. Lett; 107 (1999) 33–47.

[12] I. Ahmad, T. Hamid, M. Fatima, *et al*., Bioch. Biophys. Acta; 1523 (2000) 37–48.

[13] S. Pandey, S. Parvez, R.A. Ansari, *et al*., Chem-Biol. Interact; 174 (2008) 183–192.

[14] D.A. Monteiro, F.T. Rantin, A.L. Kalinin, Ecotoxicology; 19 (2010) 105–123.

[15] M. Martins, P.M. Costa, A.M. Ferreira, *et al*., Aquat. Toxicol; 142–143 (2013) 85–95.

[16] I.K. Konstantinou, T.A. Albanis, Environ. Int; 30 (2004) 235–248.

[17] M. Srinivasan, G.W. Swain, Environ. Manage; 39 (2007) 423–441.

[18] Ş. Gül, E.B. Kurutaş, E. Yıldız, *et al*., Environ. Int; 30 (2004) 605–609.

[19] C.S. Carvalho, V.A. Bernusso, H.S.S. Araújo, *et al*., Chemosphere; 89 (2012) 60–69.

[20] T. Vlahogianni, M. Dassenakis, M.J. Scoullos, *et al*., Mar. Pol. Bul; 54 (2007) 1361–1371.

[21] M.A. Radwan, K.S. El-Gendy, A.F. Gad, Arch. Environ. Contam. Toxicol; 58 (2010) 828–835.

EVALUATION OF MICROBIAL ENVIRONMENT ON THE BEACH SAND

Aurora Bakaj (Çizmja)[1], Mirela Lika (Çekani)[2]

[1]University of Vlora, Faculty of Technic and Natural Sciences, Department of Biology,
L. Pavaresia, 9400 Vlore, ALBANIA

[2]University of Tirana, Faculty of Natural Sciences, Department of Biology,
Boulevard ZOG I, no. 25/1, 1001 Tirana, ALBANIA

**mirela.lika@fshn.edu.al*

Abstract

The growth of microorganisms in the sand is limited by the lack of nutrients and competition with the native microbial flora. However, enterococci typically show tolerance to pH, extreme temperatures and salinity, and detergents. The study showed that there are some factors that affect their concentration in the sand. Humidity, temperature, UV rays or a decomposed organic carbon concentration are some of the factors that affect the viability of microorganisms. Some researchers say there is a difference in reducing the ratio of indicator microorganisms to 20 ºC compared to 10 ºC, with a faster decrease in their concentration to 20 ºC. The beaches represent unconsolidated sediments which lie on the border between water and land and are usually composed of sand, clay, or pebbles. Microorganisms serve as reservoirs or infection vectors and are an important component of sand. Bacteria, fungi, parasites, and viruses have all been isolated from beach sand. Some microorganisms that can be encountered through contact with sand, are potentially pathogenic and can easily meet humans through sand. Fecal indicators are non-pathogenic microorganisms which are used to indicate the degree of fecal contamination. They are generally present in a larger number than pathogenic microorganisms and are easily isolated, identified, and counted. Fecal indicators include coliforms (thermotolerant and Escherichia coli coliforms) and intestinal enterococci. E. coli was observed in 59% of the samples and the enterococci exceeded the coliforms. A statistically significant correlation was found between yeasts and fungi, E. coli and enterococci in an investigation on wet sand and dry sand. Fungi that are often found in the environment as saprophytes can behave like opportunistic pathogens, especially in individuals with weakened immunity. The study in the coastal area shows dermatophytes in 39% of the sand samples of the beaches analyzed. The most common were Trichophyton mentagrophytes and Microsporum nanum, all isolated from sandy areas, unbroken, and with organic residues. These types are all related to skin infections. The saprophytic fungi were isolated in the flooded area and the wet sand during the tides, most species belonged to the genus Aspergillus.

Keywords: faecal pollution, sand, pathogens, bacteria, yeasts, moulds

INTRODUCTION

In recent years, special attention has been to the care and cleaning of the shores, as many microorganisms have been isolated from the sand of the beaches. Several genera and species of these microorganisms that can be encountered through contact with sand are potentially pathogenic. As a result, concerns have been raised that beach sand or similar materials may act as reservoirs or infection vectors [1].

The beaches represent unconsolidated sediments which lie on the border between water and land and are usually composed of sand, clay, or pebbles. A significant percentage of time is spent on the beach than on the water. Microorganisms are an important component of beach sand. Bacteria, fungi, parasites, and viruses have all been isolated from beach sand. Some genera and species that can be encountered through contact with sand are potentially pathogenic. As a result, there is concern that beach sand or similar materials may act as reservoirs or infection vectors [2,3].

Studies have shown that there are some factors that affect the concentration of microorganisms in the sand. Thus, humidity, temperature, UV rays or a decomposition of dissolved organic carbon are some of the factors that affect the viability of microorganisms [4]. Some researchers say there is a difference in reducing the ratio of indicator microorganisms to 20 ºC compared to 10 ºC, with a faster decrease in their concentration to 20 ºC, while other researchers do not find such a correlation [5,6].

Fungi which are often found in the environment as saprophytic can behave like opportunistic pathogens, especially in individuals with weakened immunity [7]. Buck [8] studies in the coastal area have shown dermatophytes in 42% of the sand samples of the beaches analyzed. The most common were *Trichophyton mentagrophytes*, *T. rubrum*, and *Microsporum nanum*, all isolated from sandy areas, unbroken, and with organic residues. These types are all related to skin infections, where *T. mentagrophytes* is the most common agent of dermatomycosis in Europe and *T. rubrum* the most common agent worldwide [9]. Saprophytic fungi (*Aspergillus candidus*, *A. ochraceus*, and *A. fumigatus*) were isolated in the flooded area and wet sand during the tides [1,10].

The main microbial risk to human health encountered on the beach and in similar areas is that which comes from contact with animal feces, especially those of dogs.

In some states, mechanical sand cleaning is a common practice that can eliminate visible debris in the sand, reducing the amount of organic matter and thus reducing the further development of microorganisms [8,11]. The use of clean towels on the beach, good personal hygiene, animal restraint and mechanical cleaning have been considered, by some authorities, as important.

The growth of microorganisms in the sand is limited by the lack of nutrients and competition with the native microbial flora. However, enterococci typically show tolerance to pH, extreme temperatures and salinity, and detergents.

MATERIALS AND METHODS

This study was conducted using modern methods for coastal sand, based on the guidelines of the World Health Organization and the European Community. For a better assessment of the quality of the monitored beach environments, a hygienic-sanitary inspection was carried out to determine the sources of pollution and to determine the microbial load of sand.

Based on the European Community Directive 2006/7/EC, sand samples were protected from exposure to sunlight [12]. Samples were stored at a temperature of approximately 4 ºC, in the thermos until arrival at the laboratory. Samples were analyzed on sampling day.

Hygienic-sanitary inspection was carried out to determine the sources of pollution at the selected points for monitoring (determination of urban discharges and used waters that flow directly or indirectly into the beaches). Of great importance, in addition to determining the microbial load as the main indicator in assessing the degree of cleanliness of beaches, there is also the assessment of the state of the environment, urban discharges (quantity and composition), surface water discharges on each beach, as and all hygienic-sanitary factors affecting the level of microbiological pollution of beaches.

The sampling was conducted in accordance with the World Health Organization Manual for bathing water and monitoring and quality assessment of beaches [12]. The frequency of sampling was once a month. 100 ml sterile plastic bottles were used for bacteriological analysis of sand samples.

In our study to assess the sand quality of selected beaches, some important microorganisms were identified and identified. Such are coliforms, intestinal enterococci, salmonella, shigella, yeast and fungi.

Ten grams of sand samples were inoculated into 90 ml of Selenite-F broth and incubated at 37 ºC for 24 h, after which the colonies were switched to DC terrain. Suspicious colonies from the Hajna and KIA terrains were identified by the respective serums [1] at the Institute of Public Health, Tirana.

A 10-1 w/v suspension of sand samples based on wet weight was prepared in the field 0.1% buffer peptone water. The enumeration was performed using the Dichloran Rose Bengal Chloramphenicol (DRBC) Agar field method. The dishes were incubated at 25 ºC. The examination for the growth of yeasts and molds was done after 3, 4, and 5 days of incubation. Peak colonies appear pink by absorption of Rose Bengal. For the identification of *Candida albicans* the suspicious colonies were transferred to the Sabouraud Dextrose Agar field. The identification of the main molds was done through macroscopic and microscopic observation as well as the use of appropriate atlases. Results are reported as forming colony units (CFU) per gram or milliliter sample.

RESULTS AND DISCUSSION

For sand samples the quality assessment was based on the concentration of intestinal enterococci as they have a longer lifespan than fecal coliforms in marine environments. Also, this concentration is higher in wet sand than in dry sand. The mean value of intestinal enterococci during the monitoring period at sampling points was 753 CFU /100 g. During the measurement period the number of intestinal enterococci ranged from 10 to 4100 CFU /100 g.

The mean value of intestinal dry sand sample enterococci during the monitoring period at sampling points was 676 CFU /100 g. During the measurement period the number of intestinal enterococci ranged from 8 to 5000 CFU /100 g.

The mean value of water sample fungi during the monitoring period at sampling points was 62 CFU /100 ml. During this period, the number of yeasts and fungi ranged from 0 to 500 CFU /100 ml.

Since intestinal enterococci survive for a longer time in marine environments than fecal coliforms, they were selected as the most suitable indicator for the evaluation of sand samples based on the recommendations of the [12]. Summary data for intestinal enterococci in wet sand samples are presented in Table 2. During the monitoring period the bacterial concentration ranged from 10 CFU /100 g to 4050 CFU /100 g.

In the Table 1 we have shown the isolated bacteria from beach sand. We have isolated *E. coli*, *Enteroccoccus* spp, *Staphylococcus* spp, *Pseudomonas aeruginosa*, *Salmonella* spp, *Campylobacter* spp. and *Shigella* spp.

Table 1 *Isolated bacteria from beach sand*

Bacteria	Origins
Escherichia coli	Microorganism of enteric flora humans and animals. Humidity, temperature, UV rays and the concentration of organic carbon disintegrate affect the longevity of microorganism.
Enterococcus spp.	Microorganism of enteric flora humans and animals. *Enterococcus* spp. resistant strains are often isolated in the sand of the beach.
Staphylococcus spp.	Microorganism of the normal flora of humans and animals. They dominate the sand.
Pseudomonas aeruginosa	Environmental microorganism. It was isolated in all sand samples.
Salmonella spp. *Campylobacter* spp. *Shigella* spp.	They are discharged from human feces. Although isolated from samples of and animals, except *Shigella* which sand, it is determined that they do not has human origins pose a significant risk to beachgoers.

The highest levels of intestinal enterococci were observed at the second station, where the average was 1373 (SD = 1522), while IE 95% was 4000. The average value of intestinal enterococci at the first station was 498 (SD = 484), while IE 95% was 1707. The mean in the Station 3 was 983 (SD = 1106), while IE 95% 3465.

Table 2 *Intestinal enterococci in wet sand samples according to monitoring stations*

	Location	No. of samples	Avr	SD	Min	Max	IE 95%
1	Station 1	20	498	484	90	2030	1707
2	Station 2	20	1373	1522	60	4100	4000
3	Station 3	20	983	1106	50	3600	3465

Avr – Average; SD – Standard deviation; Min – Minimum; Max – Maximum; IE 95% – Percentile 95.

Summary data on intestinal enterococci in dry sand samples according to sampling points are presented in Table 3. Intestinal enterococci were isolated at all sampling points. During the monitoring period the bacterial concentration ranged from 10 to 5000 CFU /100 g, where the highest value of indicative bacteria (5000 CFU /100 ml) was found in Station 1. The average sample value of this beach was 848 (SD = 1400), while IE 95% was 4550. The average intestinal enterococci at the second station were 963 (SD = 784), while IE 95% was 2100. The average sample at the Station 3 resulted in 439 (SD = 476), while IE 95% 1450.

Table 3 *Intestinal enterococci in dry sand samples according to monitoring stations*

	Location	No. of samples	SD	Min	Max	IE 95%
1	Station 1	20	1400	10	5000	4550
2	Station 2	20	784	50	2000	2077
3	Station 3	20	439	10	1400	1450

SD – Standard deviation; Min – Mminimum; Max – Maximum; IE 95% – Percentile 95.

Based on Table 2 it turns out that the concentration of intestinal enterococci is in accordance with the norms and sand of these beaches turns out to have a suitable quality for attendance. Also, if we compare the concentration of intestinal enterococci in the sand environment, it is noticed that this concentration is higher in wet sand than in dry sand. It is noted that in Station 1 the concentration of intestinal enterococci is higher in dry sand than in wet sand. This fact may indicate that seawater is not the only cause of pollution, but pets, wild birds and even rainfall can cause pollution in the sand of the beach.

Table 4 below presents the results of yeasts and molds found at each sampling point in water samples, wet sand, and dry sand. From the table it is seen that the samples of dry sand have a higher concentration of yeasts and molds than the samples of wet sand. Thus [4] reported a statistically significant correlation between yeasts and fungi and *E. coli* in an investigation on wet sand and dry sand in Italy. The most common genus of isolated yeast was *Candida* sp. During the monitoring period the concentration of *Candida* sp. ranged from 0 to 4500 CFU /100 g, and the highest value (4500 CFU /100 g) was presented by dry sand samples at the Station 2. This value is four times higher than the allowable rate.

Table 4 *Yeast and mold in water samples, wet sand, and dry sand*

	Location	n	*Candida* ssp. (%)	Avr of *Candida* spp.	Amplitude of yeast (CFU /100 g)	Fungi (%)	Avr of Fungi	Amplitude of Fungi (CFU /100g)
1	**Station 1**							
	Wet sand	15	15	20.0	$0 – 1.0·10^2$	25	40.0	$0 – 2.0·10^2$
	Dry sand	15	35	150	$0 – 6.0·10^2$	65	4000	$0 – 15.5·10^3$
2	**Station 2**							
	Wet sand	15	25	40.0	$0 – 2.0·10^2$	35	400	$0 – 3.6·10^3$
	Dry sand	15	25	500	$0 – 4.0·10^3$	60	300	$0 – 1.3·10^3$
3	**Station 3**							
	Wet sand	15	35	30.0	$0 – 1.0·10^2$	20	40.0	$0 – 2.0·10^2$
	Dry sand	15	35	60.0	$0 – 3.0·10^2$	30	220	$0 – 1.5·10^3$

n – Number of samples analyzed; Percentage of positive samples (%); Mean and amplitude density of microorganisms.

The growth of microorganisms in the sand is limited by the lack of nutrients and competition with the native microbial flora. However, enterococci typically show tolerance to pH, temperatures, extreme salinity, and detergents.

Table 5 *Parasites and fungi isolated from beaches*

Microorganisms	Source
Parasites:	
Toxocara spp. *Ankylostoma* spp. *Nocardioles*	Many parasites have been isolated from the beach sand. Microorganisms which are discharged from the gastrointestinal tract of humans and animals.
Fungi:	
Trichosporon spp. *Candida* spp. *Trichophyton* spp. *Microsporum* spp. *Penicillium* spp. *Aspergillus* spp.	Fungi are often found in the sand and survive longer long compared to other microorganisms Fungi are classified as anthrophilic, zoophilic and geophile.

In terms of fungi, the most common isolated species were Aspergillus sp (especially *A. niger*, *A. fumigatus*) and *Penicillium sp*. In Figure 1, are shown the dermatofites. Mold concentrations ranged from 0 to 16000 CFU /100 g and the highest values were observed in dry sand samples, especially in Station 1 which also has the highest average for molds. This high concentration of yeasts and molds can result in numerous infections such as skin, and especially vaginal infections in women during the summer season.

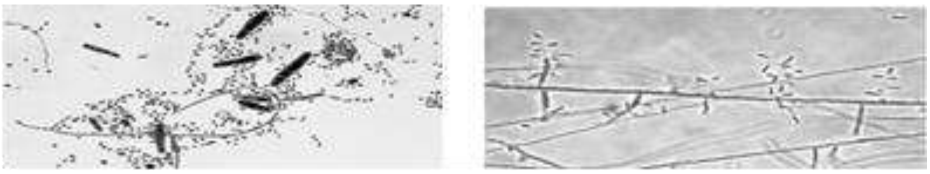


Figure 1 *Morphology of common dermatophytes in sand*

The mean and amplitude of yeasts and molds in water and sand samples according to the seasons is presented in Table 6. From the analysis of the results, it is noticed that there is no significant increase of values from season to season. In contrast the environment is a significant factor, where dry sand samples have a higher concentration of yeasts and molds compared to wet sand samples and water samples.

Candida albicans and *Candida* spp. others have been isolated from the sand of beaches in the south of France [8]. In the same study, 8 keratinophilic fungi and 11 non-keratinophilic species, all potential pathogens, were isolated. Were isolated 16 species of fungi from beach sand along the northeastern Mediterranean coast of Spain, some of which were potentially pathogenic strains.

Table 6 *Concentration of yeasts and fungi at sampling points according to the seasons*

Parameter	Season	Environment	Average	Amplitude
Yeasts and fungi	Spring	Wet sand	30.2	0–300
		Dry sand	164	0–100
	Summer	Wet sand	400	0–4000
		Dry sand	380	0–3500
	Autumn	Wet sand	100	0–300
		Dry sand	3000	0–16000

Candida species may be present in high numbers in immunocompromised, diabetic, or operative beachgoers. Candida species may be responsible for fecal contamination in both wet and dry sand [3]. Also, yeasts and molds generally show tolerance to salt. Vogel [9] showed that, while reproduction of yeasts and molds in sand was not intensive, intestinal yeasts could survive in saline environments and 250 species of Candida were found in soil in warm areas.

CONCLUSION

The beaches of Vlora Bay are easily basic and do not pose a risk to the health of visitors, also the turbidity of these beaches is low. This study also showed that the bacterial concentration is higher in wet sand than in dry sand.

In terms of peaks and molds, the situation is particularly difficult in Station 1, where untreated urban waters flow, which penetrate the sand and end up in the sea. Compared to previous studies in our study, there was a decrease in the values of fecal indicators, but again these beaches are classified as beaches of poor quality.

REFERENCES

[1] E.J. Baron, S.M. Finegold. Diagnostic Microbiology, 8th Ed, The C.V. Mosby Company, Philadeiphia, (1990).

[2] S.C. Clarke, Diagn. Microbiol. Infec. Dis; 41 (2001) 9–98.

[3] T.R. Desmarias, H.M. Solo-Gabriele, C.J. Palmer, Appl. Environ. Microbiol; 68 (3) (2002) 1165–1172.

[4] K.M. Yamahara, S.P. Walters, A.B. Boehem, App. Environ. Microbiol; 75 (2009) 151–1524.

[5] A.H. Shah, A.M. Abdelzaher, M. Phillips *et al*., J Applied Microb; 110 (2011) 1571–158.

[6] L. Volterra, L. Bonadonna, F.A. Aulicino, Water Air Soil Pollut; 29 (1986) 403–413.

[7] T.B. Kuntz, S.T. Kuntz, Prim. Care Update Ob. Gyns; 6 (6) (1999) 192–195.

[8] J.D. Buck, Microb. Ecolog; 9 (1983) 171–176.

[9] C. Vogel, A. Rogerson, S. Schatz *et al*., Water Res; 41 (5) (2007) 1915–1920.

[10] M.L.R. Soussa, Fungi. Lisbon, National Institute of Health (INSA), Centre of Epidemiologic Surveillance of Transmissible Diseases (Epidemiology Bulletin No. 5) (1990).

[11] J.C. Gentles, C.J. LaTouche, Yeasts as human and animal pathogens In: The Yeasts, Vol. 1, Academic Press, New York (1969) 107–182.

[12] World Health Organization WHO (1995), Manual for recreational water and beach quality monitoring and assessment.

IMPACT OF THE MINING ACTIVITIES IN THE GOLIJA NATURE PARK AREAS SITUATED ON THE TERRITORY OF RAŠKA MUNICIPALITY

Dragana Ranđelović[1*], **Radoje Pantović**[2]
[1]Institute for Technology of Nuclear and Other Mineral Raw Materials,
Franchet d'Esperey Boulevard 86, 11000 Belgrade, SERBIA
[2]University of Belgrade, Technical Faculty in Bor, V.J. 12, 19210 Bor, SERBIA
[*]*d.randjelovic@itnms.ac.rs*

Abstract

Traces of present or former mining activity in the Golija Nature Park areas situated on the territory of Raška Municipality are assessed and analyzed in terms of their impact on the environment and possibilities for remediation and reclamation. Active dolomite quarry "Lokve", closed magnesite mine „Trnava",tunnel Brvenica – Trnava, scheelite deposit and undermining excavation site Jurija and other exploitation sites have left consequences to the environment, including localized pollution, altered hydrological regime and landscape degradation and fragmentation. Remediation scope, activities and types differ depending upon the exploitation and exploration methods, and include biotechnological approaches as well as contemporary category of mining geoheritage preservation.

Keywords: exploitation; reclamation; environmental impact

INTRODUCTION

Mining activities cause diverse environmental consequences, which are even more pronounced if the exploitation is undertaken within the protected area or in its immediate surrounding. Main types of such impact, according to [1] are: a) land and biota loss resulting from direct mining or associated impacts; b) pollution of environmental mediums, including water, soil and air; c) impact connected with infrastructure necessary for mine activities (roads, pipelines, transport tracks, power stations etc.) that are causing noise or habitat fragmentation; d) secondary effects on livelihood opportunities (migration of residents, shortage of water supplies, alien invasions etc.); e) Visual impairment due to mining and following activities (deposition of mine waste, transportation, habitat degradation or loss).

The area of Mt Golija was designated as a natural asset of exceptional importance [2], as well as a protected area of international, national or exceptional importance, with an established three-level protection regime [3]. Within this area, in 2001, the first biosphere reserve in Serbia "Golija-Studenica" was declared by the act of the UNESCO MAB programme. Due to the presence of numerous plant and animal species of national and international importance, and in order to protect priority habitat types, Golija has been identified as the international ecological network Emerald site, and internationally important area for plants (IPA), birds (IBA) and butterflies (PBA). It is considered as a center of genetic, species and ecosystem diversity in the Balkans and Europe. According to the landscape typization, Golija Nature Park is classified as a cultural landscape, a subtype of cultural landscape close to nature, within which several biotope complexes with distinct representatives of species can be singled out [4]. Being poorly inhabited, distinct demographic aging is taking place within this area of broking type settlements, with cattle breeding as the main activity [5]. As cultural landscapes are hosting diverse traces of humans and nature interactions, that often includes historical or active mining sites, as is the case with Golija Natural Park.

The quality of water, soil and air in the Nature Park has been largely preserved, primarily due to the poor utilization of natural resources [6]. The land is endangered by erosion [4], and a certain degree of degradation is also present in the zones of mineral exploitation. Air pollution is considered to be mostly local; however, there are no measuring stations for monitoring of air quality in the area of the Nature Park. Pollution of water in this area originates both from uncontrolled waste disposal near watercourses and from the consequences of mining activities [7].

Golija Nature Park includes parts of municipalities Ivanjica, Sjenica, Kraljevo, Novi Pazar and Raška, out of which Raška municipality covers 12 623 ha (17% of the total territory). Within this area, two natural assets of the first degree of protection (sites Plakaonica and Ravnine) and two natural assets of the second degree of protection (sites Plakaonica 2 and Retko Bučje) are registered. Regarding the exploitation, coal, dolomite and construction stone are currently exploited in this territory or in its immediate vicinity (e.g. in quarries Biniće, Zvečarica, Binićko Polje and Luke). The consequences of mining works are still visible, most often in the form of landscape transformation or degradation. This paper analyses the current state, impact and possibilities of remediation of the consequences of former or current mine deposits as well as areas of exploitation of mineral resources within the investigated part of protected area.

OVERVIEW AND CHARACTERISTIS OF EXPLOITATION AND MINING SITES IN THE INVESTIGATED AREA

During the field activities carried out in August 2021 for the needs of "Zeleni putokazi Golije" project (https://www.village.org.rs/zeleni-putokazi-golije/), the terrain was reconnoitred and localities of present or former mining activities and their traces were identified (Figure 1).

***Figure 1** Locations of current and former mining activities in the area of the Golija Nature Park situated on the territory of Raška Municipality*

Presentation of their main characteristics, dominant environmental hazards conditioned by their presence and adequate remediation measures were proposed for each case.

Dolomite quarry “Lokve”

Active exploitation of the dolomite stone in quarry ‘Lokve’ takes place within the third protection zone of the Golija Nature Park. Locality is surrounded by natural and artificial forests, as well as the degraded forest communities [8]. The consequences of the exploitation of dolomite on the environment are of local character. In addition to the destruction of landscapes in the area of exploitation and the devastation of the surrounding terrain, environmental disturbances are present in the form of dust and noise that impacts nearby areas and accompanying flora and fauna. Floating particles from the process of exploitation and preparation of raw materials and exhaust gases of machinery used in this process reduce air quality, while dust particles settle on plant leaves, interfering with the process of photosynthesis and physiological functions. These dust particles are also a source of soil pollution in the immediate vicinity of the place of exploitation. After the original ecosystems have been destroyed or devastated, they are replaced by other, initial communities and species or early vegetation stages. This can cause the emergence of invasive species, but also the emergence of potentially endangered species such as *Epilobium dodonaei* that, due to the threat to their natural rocky habitats, began to inhabit these anthropogenic areas, as the natural competition of other species is reduced. The described conditions of environmental disturbance are also present, to a lesser or greater extent, on the other querry sites located in the study area, depending on whether is the case of active exploitation or an abandoned site.

Rehabilitation measures of the dolomite mine "Lokve" would imply the reclamation of the area, which is obligatory after the end of the exploitation period [9]. The project should include a plan which envisages stabilization and revegetation of the final terraces and plateaus, as well as the removal of ancillary facilities. The goal of reclamation in protected areas would be to integrate the area into the natural surroundings, striving to reach the state as close to the natural as possible. Modern trends in the reclamation of quarries include the use of targeted blasting of the final terraces to create cracks that would accelerate the development of the root system [10] and biological systems with high terrain coverage and initiation of pedological and biological processes are coming into use [11]. Additionally, it is possible to perform reclamation of the space for the recreational uses and tourism development [12].

Closed magnesite mine “Trnava”

In the peridotite massif located between Raška and the village of Trnava there are occurences of magnesite deposits concentrated in several smaller units. The main and side ditches were opened at the location of the "Trnava" magnesite for the purpose of exploitation of the magnesite ore. Mining activities ended in early 1990s, and nowadays anthropogenic relief forms –partially exposed or totally exposed halds – are visible in the area. Halds are predominantly colonized by individual black pine trees (*P. nigra*) originating from nearby natural and antropogenically raised stands.

Traces of the forest fires are present in the immediate vicinity of the excavation sites. The whole landscape has undergone a certain degree of anthropogenic change. Presence of surrounding forest ecosystems represents a favorable moment for the natural revitalization of the mining activities remnants in the area. On the other hand, the thinning of forest ecosystems, either by felling or due to natural disasters such as fires, reduces the degree of connectivity in the landscape and slows down the natural processes of colonization. Afforestation of halds with *P. nigra* trees would be a way for anthropogenically assisted rehabilitation of this area that would return the landscape to state close to the natural. In contrast, treating and protecting this part of the area as a kind of mining geoheritage that is a transitional category between geoheritage (natural) and industrial (cultural) heritage of an area [13], could represent potential for developing base for research, education and geotourism in in the municipality of Raška.

Tunnel Brvenica – Trnava

Right next to the river Brvenica, the most important water source for the municipality of Raška, there is deposited material from a tunnel built during the 70s of the last century in order to shorten the transport of magnesite from the Trnava mine to the processing plant in Bela Stena – Baljevac. Due to the collapse of water-tight layer of rocks in the tunnel Trnava, there was a gradual violation of the natural hydrogeological balance, i.e. drainage of surface and groundwater from the area of Zimovnik, Poljane and Breza in the tunnel Brvenica - Trnava. Due to the easier transport of ore by wagons, the tunnel was made with a slope towards Brvenica. For this reason, nowadays the water from the area of the Trnava mine flows through a tunnel towards Brvenica. That water is used to supply part of the Raška municipality with drinking water. On the other hand, due to the change of the hydrological regime, the wells and springs in Zimovnik have dried up.

The impact of deposited embankment made from the excavated material during formation of tunnel on the environment is relatively localized, but the place of disposal on the banks of the river Brvenica, between the zone of water sources and agricultural areas represents a potential risk to the quality of surrounding waters and soils, primarily due to the natural enrichment of serpentinite elements such as Ni, Cr, Co and others.

The process of primary and secondary colonization of embankment is underway (with predominant species being *Pinus nigra* and *Achnatherum calamagrostis*) and may represent a form of spontaneous reclamation which would eventually help to reach the state close to the surrounding area. On the other hand, the possibility of using crushed stone from the embankment for industrial or other purposes after examining its suitability would also be an adequate way to rehabilitate the terrain and remove these remnants of former mining activities in the municipality of Raška.

Scheelite deposit and undermining excavation site Jurija

The Golija ore region is located directly along the contact between the Dinarides and the Vardar zone. Within that region, there is significant ore field “Lisa - Crni Vrh”. Two basic associations of minerals are known in this ore field, with the dominant distribution of scheelite mineralization: (I) Skarns scheelite paragenesis that includes, in addition to scheelite, magnetite, quartz and calcite (II) High-temperature associations of scheelite with sulphides are much more common in this ore field, and larger than scheelite mineralization in skarns [14]. The Jurija deposit is the only tungsten / sheelite deposit that was explored in more detail on Golija, during the 1950s. The location is placed near to the Ravnina site that is under the I level of protection within the Golija Nature Park.

Jurija site includes the former undermine excavation site and the hald, which consists of the deposits from excavation works. Hald is located on a slope at a height of about 100 m above Klisurski potok, and is completely bare as vegetation cover is missing. The entrance to the former trench is noticeable in the vicinity of halda, but also the water that flows out of the trench and flows down to the Klisura stream. This way, Klisura stream becomes a recipient of both water that flows out of the former undermining excavation site, and material that is washed out from the halda directly into the stream.

Preliminary water quality tests have not been performed at this location that would provide a basic insight into the extent of the impact of this former mining facility on the environment. It is necessary to perform sampling and analysis of waters that flow from the former undermining excavation site in order to determine their composition and quality, but also of the water from the Klisura stream at the locations before and after the inflow, in order to assess the possible environmental impact. Additional information about the long-term impact of these activities on the water quality would be provided by the study of biological parameters, such as the analysis of the status of aquatic biota. Partial remediation of this site is feasible by removing the material of the halda, after its mineral and chemical composition, the category of waste to which it belongs according to its characteristics, as well as the appropriate method of disposal have been determined.

CONCLUSION

The paper presents an analysis of the state of locations with former or ongoing mining activities within the Golija Nature Park in the municipality of Raška. Exploitation of mineral raw materials and mining explorations left several categories of consequences to the environment: a) Pollution of water, air and soil of predominantly local character; b) Change of groundwater regime in wider area c) Landscape change and landscape fragmentation. These activities disrupt the character and function of the Golija Nature Park landscape. Remediation types differ depending upon the exploitation and exploration methods, and include technical and biological reclamation, spontaneous and assisted recolonization of mine waste sites, potential use of waste as raw material in the construction industry, relocation of waste outside the Nature Park, but also the preservation of visible traces of mining activities as an inseparable part of cultural and geological heritage, in order to develop geotourism in this area.

ACKNOWLEDGEMENT

The authors thank those who helped in the realization of this analysis, including people from Municipality of Raška, Forest management unit „Raška“, village Plešin and from CSO „Association of Young Researchers of Bor“. We are also grateful to the Ministry of Education, Science and Technological development of the Republic of Serbia for financial support (451-03-68/2022-14/200023 and 451-03-68/2022-14/200131).

REFERENCES

[1] A. Phillips, Mining and Protected Areas, International Institute for Environment and Development, UK (2002).

[2] Decree on the protection of the Golija Nature Park, “Official Gazette of the RS”, no. 45/2001.

[3] Rulebook on Criteria for Evaluation and Categorization of Protected Areas “Official Gazette of the RS”, no. 97/15.

[4] Center for Urban Development, Spatial plan of the Area of special purpose Golija Nature Park, Strategy of Protection and Development, Belgrade (2004) (in Serbian).

[5] G. Vojković, B. Stojadinović, Stanovništvo; 2 (2006) 35–64.

[6] D. Miljanović, Glasnik Srpskog geografskog društva; 85 (1) (2005) 249–264.

[7] Lj. Grujičić-Tešić, Geonasleđe Golije i Peštera, Doktorska disertacija, Rudarsko-geološki fakultet Univerziteta u Beogradu, Beograd (2017).

[8] Forest management plan for MU “Divan-Lokva-Breze” (2019-2028), FM Raška, Bureau for forestry planning, Serbia Forests (2018) (in Serbian).

[9] Law on Mining and Geological Research, "Official Gazette of the RS", no. 101/2015, 95/2018 and 40/2021 (in Serbian).

[10] D.K. Norman, P.J. Wampler, A.H. Throop, *et al*., Best Management Practices for Reclaiming Surface Mines in Washington and Oregon, Washington Department of Natural Resources, USA (1997).

[11] N. Era, T. Verasscina, Environmental restoration with deep roots herbaceous species, In: M. Manassero, A. Dominijanni, S. Foti, *et al*., (eds.) Coupled Phenomena in Environmental Geotechnics, Taylor & Frencis Group, London, (2013) 401–506, ISBN: 9781138000605

[12] T. Kalybekov, M. Sandibekov, *et al*., Substantiation of ways to reclaim the space of the previously mined-out quarries for the recreational purposes, E3S Web of Conferences, 123 (2019) 01004, doi:10.1051/e3sconf/201912301004.

[13] M. Mesarić, N. Buzjak, Stanje i ugroženost rudarske geobaštine Međimurja, Acta Geographica Croatica; 45/46 (2018/2019) (2020) 85–94.

[14] B. Stajević, Metalogenija rudnog rejona Golije, doktorska disertacija, Rudarsko-geološki fakultet, Beograd (1980).

INDICATIVE ECOLOGICAL STATUS ASSESSMENT OF SELECTED STREAMS ON ROGOZNA MOUNTAIN BASED ON AQUATIC MACROINVERTEBRATES

Bojana Tubić[1*], Katarina Zorić[1], Nataša Popović[1], Maja Raković[1], Nikola Marinković[1], Momir Paunović[1]

[1]University of Belgrade, Institute for Biological Research "Siniša Stanković", National Institute of the Republic of Serbia, Bulevar despota Stefana 142, Belgrade, SERBIA

[*]*bojana@ibiss.bg.ac.rs*

Abstract

This paper presented indicative ecological status assessment of four investigated streams of Rogozna Mountain based on aquatic macroinvertebrate community. A total number of 116 taxa from 16 taxa groups were identified at 9 selected localities within the study area. The aquatic insects were the most dominant group in the benthic community in respect to taxa richness, while the rest of the community consisted of taxa groups with lower participation. General conclusion is that the degree of organic pollution of the surveyed streams is low and indicative ecological status of streams in the study area, based on aquatic macroinvertebrates community, could be assessed as good to moderate.

Keywords: aquatic macroinvertebrates, Rogozna Mountain, streams, ecological status assessment

INTRODUCTION

Rogozna is a mountain in the southwest part of Serbia, situated in a triangle composed of the river flows of the upper and central flow of the Ibar River and the Raška River, 12 km from Novi Pazar [1]. Aquatic ecosystems in this area are poorly investigated.

The area is recognized as the potentially significant for ore extraction, thus it is a subject of potential investigations on the cost effectiveness, social aspects, but also biodiversity. The study area (=23.63 km^2) is under the potential impact of exploration drilling activities of Au, Cu, Pb, Zn and Ag [2].

The aim of this study is to assess the state of ecological status and baseline aquatic macroinvertebrates diversity of target area with the idea of continuing further research because of investigative geological works and potential mining activities could cause substantial damage to environment, including aquatic ecosystems of target area.

MATERIALS AND METHODS

Aquatic macroinvertebrates are the most frequently used for the integrated quality assessment of rivers based on the requirements of the Water Framework Directive [3].

Samples have been collected using Kick and Sweep (K&S) method (adapted [4]), from all microhabitat types and the procedure was standardized according to time which was spent for sampling and it was proportional to the evaluated habitat percentage and the sampling section [5]. Biological indices calculation was done using the ASTERICS 4.04 software package.

Data were collected during the period of April and September 2021 at 9 localities as detailed in Figure 1: two from the Barska reka, two from the Karavansalijska reka, three from the Kašaljska reka, one from ephemeral pond near Kašaljska reka and one on the Netvički potok. Selected sampling sites Karavansalijska and Kašaljska reka are draining to Ibar through Banjska and Barska reka, while Netvički potok drains to Raška through the Tranavska reka.

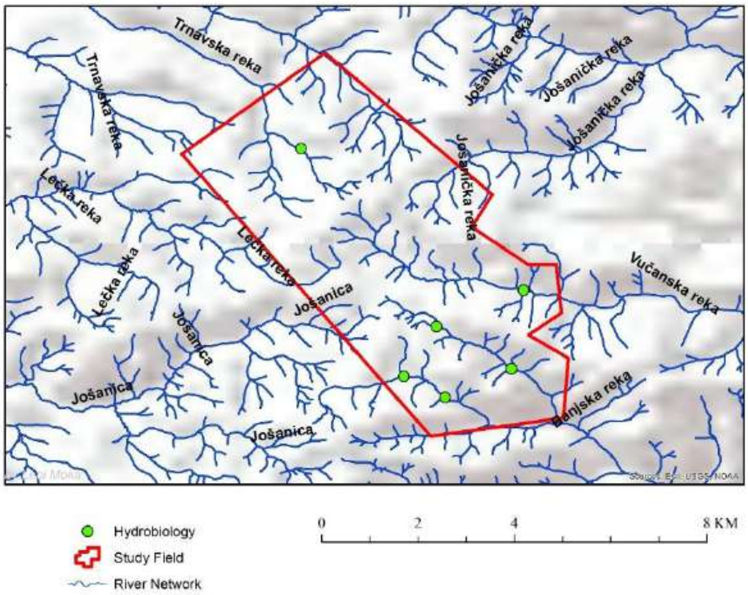


***Figure 1** Sampling locations within the study area*

RESULTS AND DISCUSSION

A total number of 116 taxa from 16 taxa groups were identified within the area of investigation.

The highest number of taxa (48) was recorded at site Kašaljska reka 1, while the lowest number of taxa (21 taxa) was recorded at site Kašaljska reka 3. A significant taxa richness was also detected at locality Karavansalijska reka 2 (39 taxa), on both sites in Barska reka (35), followed by Kašaljska reka 2 (34), while a smaller number of taxa were registered on sites Karavansalijska reka 1 (26) and Netvički potok (25). The number of recorded taxa per site presented at Figure 2.

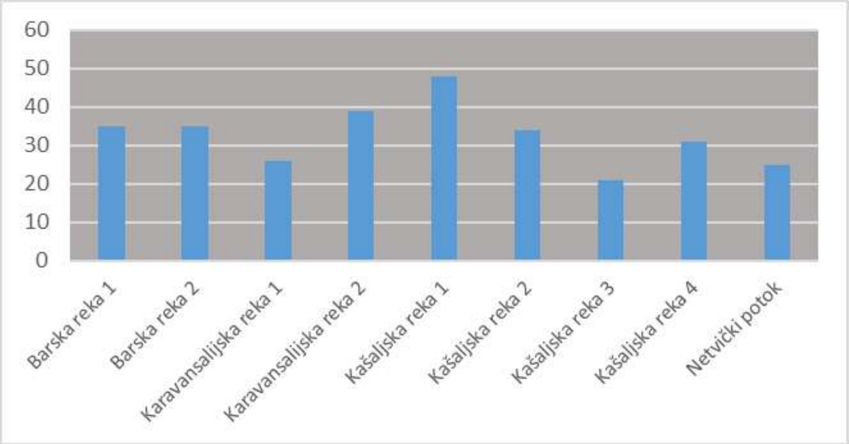


Figure 2 *Number of taxa per sampling sites*

The aquatic insects were the most dominant group in the community in respect to taxa richness (78.64%), while the rest of the community consisted of Crustacea (family Gammaridae) (17.41%) and Oligochaeta (3.37%). Other taxa groups had lower percentage participation in the benthic community (Figure 3). Insect orders, Diptera (31.06% - almost 90% belonged to the Chironomidae family) and Plecoptera (29.73%) were present with the highest percentages in the total community. Ephemeroptera (9.87%) and Trichoptera (6.87%) constituted an important component of the community, but had lower percentage participation.

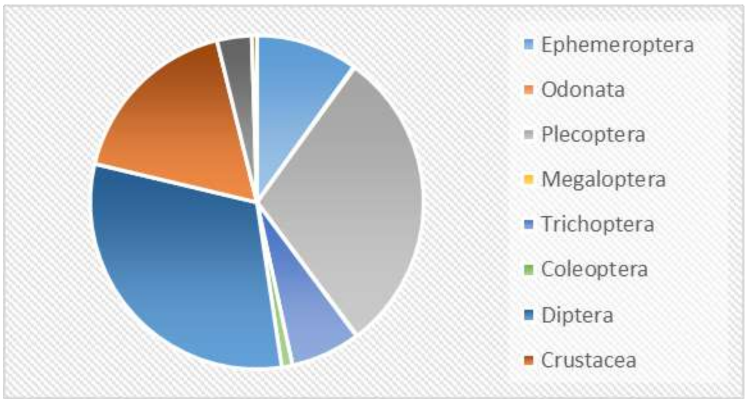


Figure 3 *Proportions of different aquatic invertebrate taxa, expressed as a percentage of the overall aquatic macroinvertebrate community*

Regarding the tolerance to organic pollution, the majority of detected species within the area could be considered as sensitive. Thus, according to the ecological classification of the taxa, with regard to saprobic conditions (saprobic valence) of Moog [6], 20.45% species were tolerant to moderate organic load (beta-mesosaprobic). 14.79% of the identified species belong to the oligosaprobic group (tolerant of low rates of organic matter loading), 8.6% of the taxa could be characterized as alpha-mesosaprobic (tolerant of high organic matter loading), while 5.54% belong to the xenosaprobic group (tolerant to only the very lowest rate of organic matter loading). 0.9% recorded species were adapted to high organic load (polysaprobic). For almost half of the community (49.73%) there is no data for classification with regard to saprobic tolerance.

Surveyed localities belong to river Type 6, based on national legislature [7,8]. For this type of river, the following metrics were used to evaluate the ecological status of the investigated streams: Zelinka and Marvan Saprobic Index SI [9], total number of taxa per site, percentage participation of subfamily Tubificinae (Oligochaeta), EPT index (number of Ephemeroptera, Plecoptera and Trichoptera) and number of sensitive taxa. Indicative status assessment was performed according to the procedure proposed by Paunović *et al*. [10], based on the class boundaries shown in Tables 2 and 3**.**

The values of SI indices varied per sampling location. Low values on Barska reka 2 (1.247) and Karavansalijska reka 2 (1.154) indicated high status (I class), which indicate low level of organic pollution. Higher values of SI on sites Karavansalijska reka 1 indicate to a higher level of organic pollution and moderate ecological status (III class). Registered values for the rest of sampling sites indicate good ecological status (II class) (Table 3).

Number of present groups of organisms in the macrozoobenthic community (Number of taxa) indicates to the overall diversity. Higher scores indicating high status (I class) for the all investigated streams (Table 3).

Status assessment according to percentage participation of the subfamily Tubificinae (Oligochaeta) in the macroinvertebrate community revealed good status (II class) for most localities, except Barska reka 1 and Karavansalijska reka 1. Good status is not reached at these two sites, which means higher level of organic pollution present and moderate ecological status.

EPT Index (Ephemeroptera, Trichoptera and Plecoptera Index) is based on the premise that high-quality streams usually have the greatest species richness of these groups. The greater the pollution, the lower the species richness is expected which is the most obvious among three aquatic insects orders - Ephemeroptera (mayflies), Plecoptera (stoneflies), and Trichoptera (caddisflies), since majority of the species belonging to mentioned insects are sensitive to environmental stress - pollution, habitat degradation and change in hydrology of streams. Thus, the higher values of EPT index are associated with non-impacted or slightly impacted streams, while decline of index indicates increasing of environmental stress.

The number of EPT taxa per locality varied in range from 8 to 18 (Table 2). The highest value of the EPT index was recorded at sites Barska reka 2 and Karavansalijska reka 2 (18 taxa), while number of EPT taxa at localities Netvički potok (8 taxa) and Karavansalijska reka 1 (9 taxa) were lower. Water quality according to EPT index at all investigated locality characterised good status assessment (II class).

According to the number of sensitive taxa on all investigated localities were reached good status (II class) (Table 3).

Table 2 *Values of calculated macroinvertebrate metrics*

Metric/Locality	**Barska reka 1**	**Barska reka 2**	**Karavansa-lijska reka 1**	**Karavansa-lijska reka 2**	**Kašaljska reka 1**	**Kašaljska reka 2**	**Kašaljska reka 3**	**Kašaljska reka 4**	**Netvički potok**
Saprobic Index (Zelinka & Marvan)	1.514	1.247	2.222	1.154	1.715	1.567	1.99	2.075	1.974
Number of Taxa	35	35	26	39	48	34	21	31	25
Tubificinae (Oligochaeta) [%]	7.45	0	6.88	0.25	1.82	2.67	0	1.09	0.33
EPT taxa	18	14	9	18	17	15	12	10	8
Number of sensitive taxa	7	7	5	9	11	8	5	4	7

Table 3 *Assessment of ecological status based on macroinvertebrate metrics*

Metrics/Locality	**Barska reka 1**	**Barska reka 2**	**Karavansa-lijska reka 1**	**Karavansa-lijska reka 2**	**Kašaljska reka 1**	**Kašaljska reka 2**	**Kašaljska reka 3**	**Kašaljska reka 4**	**Netvički potok**
Saprobic Index (Zelinka & Marvan)	II	I	III	I	II	II	II	III	II
Number of Taxa	I	I	I	I	I	I	I	I	I
Tubificinae (Oligochaeta) [%]	−	+	−	+	+	+	+	+	+
EPT taxa	+	+	+	+	+	+	+	+	+
Number of sensitive taxa	+	+	+	+	+	+	+	+	+
Indicative ecological status	**III**	**II**	**III**	**II**	**II**	**II**	**II**	**III**	**II**

+ Good status; − Good status not reached.

CONCLUSION

The overall status of rivers in the Study area could be assessed as good to moderate. Based on used community indices, the general conclusion is that the degree of organic pollution of surveyed streams is low. This is also confirmed by the taxa richness (characteristic number of species for small streams of hilly-mountainous regions of ecoregion 5 and 6 [10]) and community structure (appearance of taxa characteristic for small streams of hilly-mountainous regions of ecoregion 5 and 6 [10]).

ACKNOWLEDGEMENT

Publication of manuscript was supported by Ministry of Education, Science and Technological Development of Republic of Serbia (contract number: 451-03-68/2022-14/ 200007). We would like to thank to Zlatna Reka d.o.o. for collaboration during the realization of this investigation.

REFERENCES

[1] G. Tomović, Kosovo and Metohija on old maps from the XV to the XVIII century, Source: Kosovo and Metohija- past, present, future, Papers presented at the International Scholarly Meeting held at the Serbian Academy of Science and Arts, Belgrade (2007) 49– 60.

[2] Zlatna Reka Resource Announcement, Drilling Returns 69.5m @ 2.0g/t Au, 0.3% Cu, 0.5% Pb, 0.8% Zn and 18g/t Ag at Zlatna Reka’s Rogozna Gold Project (2021).

[3] WFD, Water Framework Directive- Directive of the European Parliament and of the Council 2000/60/EC - Establishing a Framework for Community Action in the Field of Water Policy (2000).

[4] AQEM, Manual for the application of the AQEM system: A comprehensive method to assess European streams using benthic macroinvertebrates, developed for the purpose of the Water Framework Directive, Contract No: EVK1-CT1999- 00027 (2002).

[5] EN 27828: 1994, Water quality - Methods of biological sampling, Guidance on handnet sampling of aquatic benthic macro-invertebrates - ISO 7828:1985.

[6] O. Moog, Fauna Aquatica Austriaca, Wasserwirtschaftskataster, Bundesministerium für Land- und Forstwirtschaft, Umwelt und Wasserwirtschaft (2002).

[7] Official Gazette of the Republic of Serbia 74/2011, Regulation on the parameters of ecological and chemical status of surface waters and parameters of chemical status and quantitative status of ground waters (in Serbian).

[8] Official Gazette of the Republic of Serbia 96/2010, Regulation on establishment of surface and groundwater bodies (in Serbian).

[9] M. Zelinka, P. Marvan, Zur Präzisierung der biologischen Klassifikation der Reinheit fliessender Gewässer. – Arch. Für Hydrobiol., Stuttgart, 57 (1961) 389–407.

[10] M. Paunović, V. Simić, P. Simonović, *et al.*, Biological Quality Elements in WFD implementation in Serbia – typology, reference conditions and ecological status class boundaries, Technical Report, Institute for Biological Research “Siniša Stanković”, Beograd (2009).

INDICATIVE ECOLOGICAL STATUS ASSESSMENT BASED ON EPILITHIC DIATOMS OF SMALL RIVERS AT ROGOZNA MOUNTAIN

Božica Vasiljević[1*], Jelena Tomović[1], Ana Atanacković[1], Rastko Petrović[2]
[1]University of Belgrade, Institute for Biological Research “Siniša Stanković”, National Institute of the Republic of Serbia, Bulevar despota Stefana 142, Belgrade, SERBIA
[2]Zlatna Reka Resources doo, Bulevar kralja Aleksandra 24, Belgrade, SERBIA
[*]*bozica@ibiss.bg.ac.rs*

Abstract

Epilithic diatom community investigation of small rivers at Rogozna Mountain was conducted in order to create baseline for future surveys, since hydrobiological data are lacking. Diatom sampling and analysis was performed according to the guidance of national standards and regulations. Indicative ecological status was determined by the IPS diatom index. At investigated area a total number of 49 diatom taxa were identified. The most frequent and abundant taxa, such as Achnanthidium minutissimum, Meridion circulare and Navicula lanceolata are common for the hilly-mountain watercourses. Qualitative and quantitative analysis of diatom samples have shown excellent and good indicative ecological status of small rivers of Rogozna Mountain.

Keywords: epilithic diatoms, hilly-mountain river, ecological status

INTRODUCTION

Benthic diatoms are well known as bioindicators of changes in water quality: they have short generation time, well studied ecological preferences, broad distribution, they are present in heterogeneous microhabitats, and sampling and analysis methods are standardized [1]. Diatom based bioassesment in Serbia is regulated by the national laws and covers all river types [2,3].

Rogozna Mountain in south-western Serbia has at all times been known for its natural ores, forests and thermo-mineral springs [4]. This mountain follows a north-western to south-eastern orientation, with the highest peak Crni Vrh with altitude of 1504 m. Its geological structure is largely represented by serpentine and eruptive stones [5]. Rogozna Mountain is surrounded by the Ibar River on the south, east and northeast, and the Raška and Jošanica Rivers on the northwest. Considering diversity and water quality of streams at Rogozna Mountain, there is no data. Conducted investigation of epilithic diatom community included small rivers the Barska reka, Karavansalijska reka, Kašaljska reka (the Ibar River basin) and the Netvički potok (the Raška River basin). Study area was selected in order to estimate indicative ecological status of watercourses, and to support hydrobiological reference point data due to potential mining activities.

MATERIALS AND METHODS

Benthic diatoms were sampled during April and September 2021 from the eight localities at surveyed watercourses: two at the Barska reka, two at the Karavansalijska reka, three at the Kašaljska reka, and one at the Netvički potok. Samples were collected from cobbles and stones that were submerged in the water, according to standard SRPS EN 13946: 2015 [6]. Material was preserved with formaldehyde to the final concentration of 4%. In laboratory, phytobenthos samples were exposed to a hot acid method, afterwards permanent diatom slides were made by using Naphrax® mounting medium [6]. Diatom slides were observed and photographed with microscope Zeiss Axio Lab1 with Axiocam ERc 5s camera and ZEN software. Qualitative and quantitative analysis, and interpretation of results were performed according to the SRPS EN 14407: 2015 [7]. Identification was done by standard algological literature, and relative abundance of diatom taxa was determined by counting 400 valves at each slide. OMNIDIA software [8] was used to calculate diatom indices. Ecological status classes based on IPS index [9] were determined by national regulations [2,3].

RESULTS AND DISCUSSION

At investigated area of Rogozna Mountain, altogether 49 diatom taxa were identified, belonging to 26 genera. Diatom taxa richness was the greatest in the river Kašaljska reka (31 taxa), while in the rivers Barska reka, Karavansalijska reka and Netvički potok was uniform (22, 20 and 22, respectively). The most frequent species in the diatom communities of investigated rivers were *Achnanthidium minutissimum* (Kützing) Czarnecki, *A. subatomoides* (Hustedt) Monnier, Lange-Bertalot et Ector, *Adlafia minuscula* (Grunow) Lange-Bertalot, *Gomphonema micropus* Kützing, *Meridion circulare* (Greville) C.A. Agardh, *Navicula lanceolata* (Agardh) Ehrenberg, *Nitzschia dissipata* (Kützing) Grunow, *N. palea* (Kützing) W.Smith and *Planothidium lanceolatum* (Brébisson ex Kützing) Lange-Bertalot.

In analysed material, 12 diatom taxa had relative abundance higher than 5% per sample (Table 1). Some of the most frequent taxa of studied watercourses were also dominant and/or subdominant in the significant number of samples, such as *A. minutissimum*, *M. circulare* and *N. lanceolata* (Table 1). *A. minutissimum* is cosmopolitan diatom, usually reported in small hilly-mountain watercourses, in wide trophy spectrum [10]. *M. circulare* is also very common in running waters, and prefers lower trophic levels. *N. lanceolata* has wide ecological amplitude, from oligo- to α-mesosaprobic waters, and favours higher trophic levels. Both *M. circulare* and *N. lanceolata* are characteristic for lower temperature waters, and can be very abundant in the spring months [11,12], when the most samples from rivers of Rogozna Mountain were collected.

Table 1 *Diatom taxa with relative abundance higher than 5% per sample*

Taxa / Locality	**Barska reka 1**	**Barska reka 2**	**Karavans. reka 1**	**Karavans. reka 2**	**Kašaljska reka 1**	**Kašaljska reka 2**	**Kašaljska reka 3**	**Netvički potok**
Achnanthidium minutissimum	28.01	6.86	8.36	43.53		18.14	13.05	19.41
Fragilaria capucina	16.9	9.69						
Gomphonema micropus	9.26	14.18		16.52	11.41	5.39		
Meridion circulare	19.44	12.29	18.02	26.56	5.58	9.07		9.34
Navicula lanceolata	5.56	11.82	7.83		30.83	19.85	50.35	
Achnanthidium subatomoides		10.87		6.25				
Nitzschia dissipata		6.86	7.57		11.89	6.62		
Odontidium mesodon			23.5					
Nitzschia palea					14.32	6.86		
Planothidium frequentissimum								19.41
Planothidium lanceolatum								11.3
Rhoicosphenia abbreviata							8.86	12.53

Watercourses in the study area at Rogozna Mountain belong to the river type 6, according to national typology [2,3], thus indicative ecological status classes are determined by the IPS index values (Figure 1, Table 2).

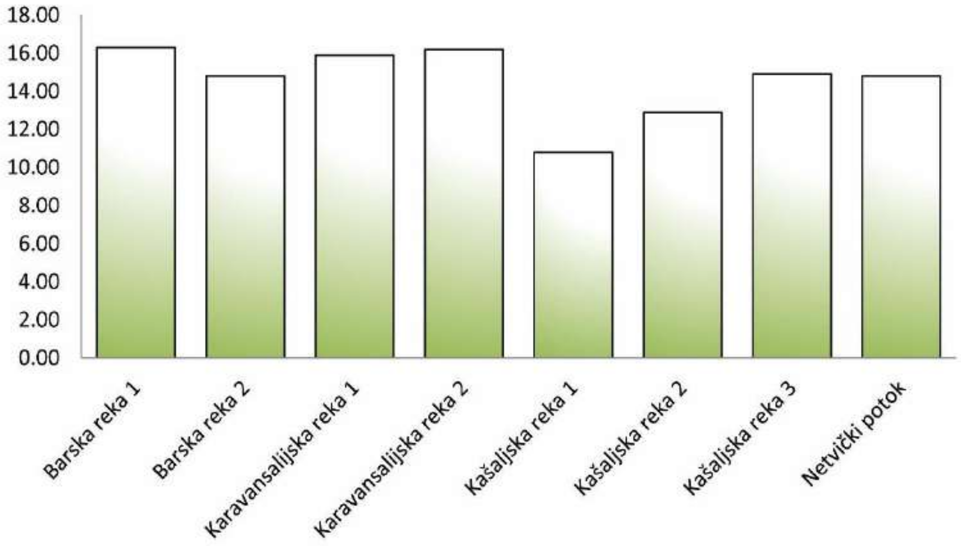


Figure 1 *Values of IPS index at surveyed localities*

Values of IPS index at localities on rivers the Barska reka, Karavansalijska reka, Netvički potok, and at the third locality at the Kašaljska reka ranged from 14.8 to 16.3, denoting the first class of indicative ecological status, while values of IPS index at remaining localities at the Kašaljska reka were 10.8 and 12.9, showing the second class of indicative ecological status.

Table 2 *Indicative ecological status classes of surveyed localities based on IPS index*

Locality	**Barska reka 1**	**Barska reka 2**	**Karavans. reka 1**	**Karavans. reka 2**	**Kašalj-ska reka 1**	**Kašalj-ska reka 2**	**Kašalj-ska reka 3**	**Netvički potok**
Indicative ecological status class	**I**	**I**	**I**	**I**	**II**	**II**	**I**	**I**

CONCLUSION

Taxa richness and diatom community structure of the investigated watercourses at Rogozna Mountain are common for spring months at small hilly-mountain rivers, with a prevalence of larger fractions of rock substrates and direct current. Diatom community is dominated by taxa with preference to oligosaprobic and mesosaprobic waters. Qualitative and quantitative analysis of diatom samples according to the national regulations have shown excellent and good indicative ecological status of small rivers of Rogozna Mountain.

ACKNOWLEDGEMENT

Work on this paper was supported by Ministry of Education, Science and Technological Development of Republic of Serbia (contract number: 451-03-68/2022-14/ 200007). We would like to thank to Zlatna Reka d.o.o. for cooperation during the survey.

REFERENCES

[1] A. Masouras, I. Karaouzas, E. Dimitriou, *et al.*, Water; 13 (4) (2021) 478.

[2] Službeni glasnik Republike Srbije 96/2010, Pravilnik o utvrđivanju vodnih tela površinskih i podzemnih voda.

[3] Službeni glasnik Republike Srbije 74/2011, Pravilnik o parametrima ekološkog i hemijskog statusa površinskih voda i parametrima hemijskog i kvantitativnog statusa podzemnih voda.

[4] D.R. Ivanović, D.A. Valjarević, R.D. Srećković-Batoćanin, *et al.*, Open Geosci; 11 (1) (2019) 1071–1083.

[5] O. Papović, M. Miljković, N. Ranđelović, *et al.*, Biol. Nyssana; 5 (1) (2014) 17–30.

[6] SRPS EN 13946:2015, Kvalitet vode – Uputstvo za rutinsko uzimanje uzoraka i pripremu preparata bentosnih silikatnih algi reka i jezera.

[7] SRPS EN 14407:2015, Kvalitet vode – Uputstvo za identifikaciju i utvrđivanje brojnosti bentosnih silikatnih algi iz reka i jezera.

[8] C. Lecointe, M. Coste, J. Prygiel, Hydrobiologia; 269/270 (1993) 509–513.

[9] Cemagref, Etude des methods biologiques d'appré-ciation quantitative de la qualitédes eaux, Rapport Q.E. Lyon, Agence de l'eau Rhöne-Méditerranée-Corse-Cemagref, Lyon, France (1982).

[10] D. Vidaković, J. Krizmanić, S.I. Šovran, *et al*., Zb. Matice Srp. prir. nauke; (128) (2015) 29–40.

[11] S. Simić, A. Petrović, N. Đorđević, *et al*., Kragujevac J. Sci; 40 (2018) 227–242.

[12] O. Jakovljević, S. Popović, I. Živić, *et al*., Biol. Serb; (2022), in press.

ARSENITE–SOIL HUMIC ACID BINDING BY ISOTHERMAL TITRATION CALORIMETRY: THERMODYNAMICS AND MNIS MODEL

Đuro Čokeša[1*], Mirjana Marković[1], Nebojša Potkonjak[1], Branka Kaluđerović[1], Svjetlana Radmanović[2], Snežana Šerbula[3]

[1]University of Belgrade, VINČA Institute of Nuclear Sciences, National Institute of the Republic of Serbia, Mike Petrovica Alasa 12–14, 11000 Belgrade, SERBIA

[2]University of Belgrade, Faculty of Agriculture, Nemanjina 6, 11080 Belgrade, SERBIA

[3]University of Belgrade, Technical Faculty in Bor, V.J. 12, 19210 Bor, SERBIA

**cokesadj@vinca.rs*

Abstract

Arsenite–humic acid-binding process was investigated using the Isothermal Titration Calorimetry (ITC). The ITC data were successfully (R^2=0.996-0.936) interpreted by applying the MNIS model, enabling thermodynamic parameters to be determined. The MNIS model was adjusted to the arsenite–HA binding process assuming hydrogen bonding as the dominant type of interaction in the system. Negative enthalpy change values indicated the arsenite–HAs binding as an exothermic process. Negative ΔG values (-(27.85-26.83) kJ mol^{-1}) pointed out to spontaneous binding reaction, leading to the formation of the arsenite–HA complexes. High binding constants values ((7.57-5.02)10^5 M^{-1}) clearly demonstrated pronounced binding affinity. As ΔS values (0.041-0.027) kJ mol^{-1} K^{-1}) were apparently positive, but close to zero, and $\Delta H>\Delta S$, the reaction could be considered enthalpy driven. Reaction heats and ΔH values (-(18.96-15.64) kJ mol^{-1}) confirmed hydrogen bonds as the most ascendant interaction type in the arsenite–HA complex. Thermodynamic and reaction parameters clearly indicated that arsenite–HA complexes are formed at common soil pH values, confirming the possible influence of humic acids on increased As mobility, and its reduced bioavailability.

Keywords: humic acid, arsenate, enthalpy, reaction coefficient

INTRODUCTION

Arsenic (As) as one of the inorganic contaminants is an extremely toxic metalloid that reaches soil and water as a result of anthropogenic activities or mobilization from natural sources [1]. Arsenic toxicity toxicity is directly related to its chemical form. The inorganic species are generally more toxic than the organic ones. Considering the inorganic forms, arsenate (As(III)) is more toxic in comparison to arsenite (As(V)) [2]. Arsenic toxicity is highly dependent on its speciation, which could be influenced by various environmental conditions such as pH, redox potential and the presence of organic and inorganic compounds and microorganisms [3]. Natural organic matter (NOM) plays a significant role in regulating As speciation, reactivity, mobility, bioavailability, and related toxicity [2,3].

Humic substances, including humic acids (HAs), are the most abundant fractions of NOM. HAs are the most reactive compounds in soil having the capacity for various chemical and physical reactions in the environment. HAs have a complex structure and contain active functional groups, such as carboxyl and hydroxyl, having an important impact on transformation and migration of metal and metalloids in soil [4]. Thus, toxic metalloid arsenic interacts with HAs and forms As–HA complexes, further influencing As adsorption on the mineral solid phase surfaces, its solubility, and mobility [5].

The isothermal titration calorimetry (ITC) is a physical technique used to determine the thermodynamic parameters of interactions in solution. ITC has been widely used to study the binding of both organic and inorganic compounds to humic acids [6–8]. To the authors' knowledge, there are no literature data on As-HA binding process using ITC technique. Martin *et al.*, [9] are the only ones using ITC to inspect the thermodynamics and kinetics of arsenic adsorption on ferrihydrite-kaolinite as influenced by the presence of humic acid coverage.

To better understand arsenic-soil HA binding process, in this study the system containing arsenite solution and soil humic acid suspension only was investigated by ITC technique. Row ITC data were interpreted by Multiple Non-Interacting Sites (MNIS) theoretical model adjusted for binding of charge-neutral molecular species to humic acid. Applying this model, thermodynamic parameters of arsenite–HA interaction were determined.

MATERIALS AND METHODS

Three soil humic acids (LPHA, TCHA and ESHA) of different origin were investigated. LPHA was isolated from Leptosol, originating from Negotin, E Serbia; TCHA was isolated from Technosol originating from Serbia ZiJin Bor Copper mine, formed on reclaimed copper post-flotation tailings; ESHA is the IHSS standard humic acid isolated from Elliott Soil [10]. LPHA and TCHA samples were isolated using a modified IHSS method [10] (HA gel was dried at 35 °C, powdered, and sieved using a 0.05 mm sieve).

Stock humic acid suspensions of LPHA, TCHA and ESHA (2 g dm^{-3}) were prepared in 0.01 M KOH and stored at 4 °C. Working HA suspensions (0.8 g dm^{-3}) were prepared before each titration by mixing stock suspensions and 0.1 M KNO_3 solution (1:1.5). Initial pH of working HA suspensions was adjusted to 5. Arsenate solution (5 mM) was prepared using sodiumhydroxoarsenate (III) ($NaAsO_2$) (Merck, Darmstadt, Germany) in 0.1 M KNO_3.

Thermal events were monitored by the Thermal Activity Monitor (227, LKB Bromma, Sweden) using a perfusion cell (227-401/402, Sweden) as a measuring device. Titrations were performed using Radiometer Automatic Titrator (ABU 80, Denmark). Prior to titration experiments, the measuring cell of the perfusion system was filled with 2.5 ml of HA suspension, thermally equilibrated in four steps and calibrated (10 µW range) using both static and dynamic calibration procedures. The working temperature was 298.15 K. Titration experiments started after the stable baseline was obtained.

Titrant (5 mM arsenite solution) was added in 30 µl portions at every 30 minutes with titration speed and mixing rate of 50 µl/min and 120 min^{-1}, respectively. For each titration, the output signal, power (µW) versus time (min), was recorded by the TAM assistant software and thermograms were obtained. Software used for titration control and data acquisition, as well as software for thermogram peak area determination, was developed in the laboratory.

Under the experimental conditions used for ITC titrations, pH-metric titration was performed as well. The HA suspension (10 ml) was titrated by 120 µl of 5 mM arsenite solution using Radiometer TTT85 titrator at 298 K. Titration speed was 12.5 µl min^{-1}. The next titration step was started after the pH value was stable for 7 s with pH units drift not exceeding ±0.001.

The plot of the heat of exchange (dQ/dn) as a function of the molar charge ratio Z ([As]m/[HA]m), where [As]m and [HA]m are the arsenate and humic acid molar charge concentrations, respectively, is fitted with the MNIS model [8,11]. The MNIS model is chosen because neutral arsenite species ($As(OH)_3$ and $HAsO_2$) were the only ones present in the titration range. The MNIS constant fitting parameters for carboxyl and phenolic HA functional groups (maximum charge densities, dissociation constants, and empirical parameters) were adopted from Ritchie and Perdue [12]. The MNIS model was adjusted assuming hydrogen bonds as dominant in the arsenate–HA interaction. Arsenite–HA binding enthalphy change (ΔH [kJ mol^{-1}]), affinity constant (K [M^{-1}]) and reaction stoichiometry (n) were obtained from the MNIS fit. K and ΔH values obtained by the fitting procedure applied were used to calculate binding Gibbs free energy ΔG [KJ mol^{-1}] and entrophy ΔS [kJ K^{-1} mol^{-1}] change.

RESULTS AND DISCUSSION

Thermograms generated by the ITC measurements are illustrated in Fig. 1a. The respective integrated heat data (dQ/d[As]) as a function of molar charge ratio ($[As]_m/[HA]_m$) fitted by the MNIS model are presented in Fig. 1b. By inspecting R^2 values, which ranged from 0.996 to 0.936, it is obvious that the MNIS model can be used to successfully interpret the arsenite–HAs binding process. As a result of the fitting procedure performed, ΔH, K and n were obtained and reported in Table 1. Also, ΔG and ΔS values are calculated and given in Table 1.

Table 1 *ΔH, K, and n values obtained by the MNIS fit of row ITC data and calculated ΔG and ΔS values*

	LPHA	**TCHA**	**ESHA**
ΔH (kJ mol^{-1})	-(16.25±0.26)	-(15.64±0.36)	-(18.96±0.19)
K10^{5} (M^{-1})	5.02±0.85	7.57±212	5.36±0.51
n	0.629±0.005	0.586±0.006	0.448±0.002
ΔG (kJ mol^{-1})	-26.83	-27.85	-27.00
ΔS (kJ mol^{-1} K^{-1})	0.035	0.041	0.027

Negative peaks in the ITC thermograms and negative enthalpy change values indicate the arsenite–HAs binding as an exothermic process. Regarding negative ΔG values, it can be concluded that the binding reaction is spontaneous, leading to the formation of arsenite–HA complexes. High binding constants values ((7.57–5.02)10^{5} M^{-1}) clearly demonstrated pronounced binding affinity. As ΔS values ((0.041–0.027) kJ mol^{-1} K^{-1}) were apparently positive, but close to zero, and ΔH>ΔS, the reaction could be considered enthalpy driven.

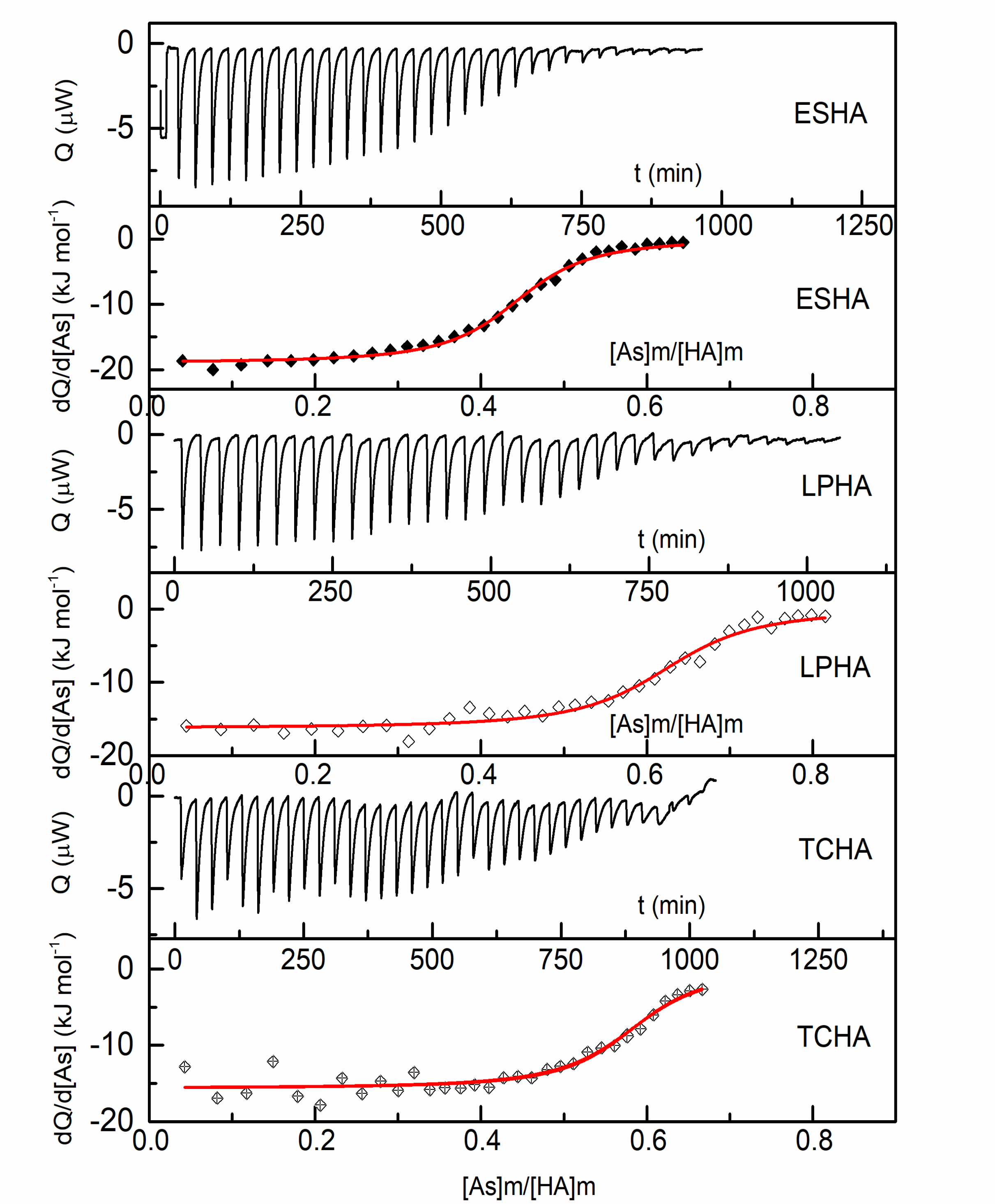


Figure 1 *(a) ITC thermograms; (b) integrated heat data (dQ/d[As]) as a function of molar charge ratio ([As]$_m$/[HA]$_m$) for LPHA, TCHA and ESHA; solid lines - the MNIS fit*

In this study, initial pH at the titration start was 5, not exceeding 8 for LPHA and 9 for ESHA and TCHA at the end of titration. Since As(III) forms stable neutral hydroxo complexes ($As(OH)_3$ and $HAsO_2$) at pH under 8 [13], these compounds are the only ones present in the sample solution. At pH above 8, anions AsO_2^- are formed and one can expect that an ionic exchange reaction exists, causing the MNIS model not fit the data obtained in this pH range. Over the reaction stoichiometry range (0.629–0.448), where titration can be considered as completed, the MNIS model obviously fitted the experimental points successfully (Figure 1b), suggesting arsenate–HA hydrogen bonds remain as the dominant reaction type.

Previously reported data [3,14,15] did not include reaction heat measurements. Considering the results of this study, reaction heats measured by ITC and ΔH values (-(18.96–15.64) kJ mol^{-1}) obtained by the MNIS fit, confirm hydrogen bonds (typical bond strength from 10 to 40 kJ mol^{-1}) as the only interaction type in the arsenate–HA complex for both carboxyl and phenolic functional groups.

Due to the extensive presence of toxic arsenic species in the environment, their interaction with NOM is comprehensively studied in the literature. HA as a NOM fraction, binding arsenic species present in soils and sediments, enhance their mobilization and release into the soil solution. Increased As mobility can lead to groundwater contamination, but it can also be useful in soil remediation processes [5]. Besides the HA role in As mobility increases, forming the HA-As complexes can have a positive impact on the environment by reducing the bioavailability of toxic arsenic species [2]. Thermodynamic and reaction parameters obtained in this study clearly indicate that arsenite–HA complexes are formed at common soil pH values, confirming the possible influence of humic acids on increased As mobility, as well as reduced bioavailability.

CONCLUSION

The arsenate-humic acid binding process was investigated using the ITC technique. The ITC data were successfully interpreted applying the MNIS model, enabling thermodynamic parameters of the arsenite–HA interaction to be determined. Negative enthalpy change values (-(18.96–15.64) kJ mol^{-1}) indicated the arsenite–HAs binding as an exothermic process. Negative ΔG values (-(27.85–26.83) kJ mol^{-1}) pointed out to spontaneous binding reaction, leading to the formation of the arsenite–HA complexes. High binding constants values ((7.57–5.02)10^{5} M^{-1}) clearly demonstrated pronounced binding affinity. As ΔS values (0.041–0.027) kJ mol^{-1} K^{-1}) were apparently positive, but close to zero, and ΔH>ΔS, the reaction could be considered enthalpy driven.

The MNIS model applied was adjusted to the arsenate–HA binding process assuming that hydrogen bonding is the dominant type of interaction in the system. Reaction heats measured by ITC and ΔH values (-(18.96–15.64) kJ mol^{-1}) obtained by the MNIS fit, confirm hydrogen bonds (typical bond strength from 10 to 40 kJ mol^{-1}) as the most ascendant interaction type in the arsenate–HA complex for both carboxyl and phenolic functional groups. The assumption validity was confirmed by good MNIS fit (R^2 = 0.996–0.936) as well.

Thermodynamic and reaction parameters obtained in this study clearly indicate that arsenite–HA complexes are formed at common soil pH values, confirming possible influence of humic acids on increased As mobility, as well as reduced its bioavailability.

ACKNOWLEDGEMENT

This work was partially supported by the Ministry of Education, Science and Technological Development of the Republic of Serbia (Grants no. 451-03-68/2022-14/200017 and 451-03-68/2022-14/200116).

REFERENCES

[1] C. Catrouillet, M. Davranche, A. Dia, *et al*., J. Colloid Interface Sci; 470 (2016) 153–161.

[2] A. Costa, A. Nascimento, W. Botero, *et al*., Sci. Total Environ; 802 (2022) 149779.

[3] J. Ren, W. Fan, X. Wang, *et al*., Water Res; 108 (2017) 68–77.

[4] Y. Liu, L. Zhi, S. Zhou, *et al*., Environ. Sci. Pollut. Res; 27 (15) (2020) 18650–18660.

[5] G. Qian, L. Xu, N. Li, *et al*., Chemosphere; 286 (2022) 131784.

[6] S. Liu, J. Zhou, J. Guo, *et al*., Environ. Pollut; 293 (2022) 118604.

[7] J. Xu, L. Koopal, L. Fang, *et al*., Environ. Sci. Technol; 52 (2018) 4099−4107.

[8] F. Loosli, L. Vitorazi, J-F. Berret, *et al*., Environ. Sci.: Nano; 2 (2015) 541.

[9] M. Martin, L. Celi, E. Barberis, *et al*., Can. J. Soil Sci; 89 (2009) 421–434.

[10] IHSS, Source Materials for IHSS Samples, Standard samples, *Available on the following link*: http://humic-substances.org/source-materials-for-ihss-samples

[11] J. Courtois, J.F. Berret, Langmuir; 26 (2010) 11750–11758.

[12] J.D. Ritchie, E.M. Perdue, Geochim. Cosmochim. Acta; 67 (2003) 85–96.

[13] P. Warwick, E. Inam, N. Evans, Environ. Chem; 2 (2) (2005) 119–124.

[14] J. Buschmann, U. Kappeler, U. Lindauer, *et al*., Environ. Sci. Technol; 40 (2006) 6015–6020.

[15] G. Liu, Y. Cai, J. Hazard. Mater; 262 (2013) 1223–1229.

Cu(II) ACCUMULATION POTENTIAL OF AQUATIC MACROPHYTE *PISTIA STRATIOTES*

Tatjana Anđelković[1*], Ivana Kostić Kokić[1], Bojan Zlatković[2], Darko Anđelković[3]
[1]University of Niš, Faculty of Science and Mathematics, Department of Chemistry,
Višegradska 33, 18000 Niš, SERBIA
[2]University of Niš, Faculty of Science and Mathematics, Department of Biology and Ecology,
Višegradska 33, 18000 Niš, SERBIA
[3]University of Niš, Faculty of Agriculture, Kosančićeva 4, 37000 Kruševac, SERBIA
[*]*tatjana.andjelkovic@outlook.com*

Abstract

The accumulation potential of selected macrophyte for copper uptake was studied in terms of bioconcentration factor, translocation factor, and aerial tissue and root concentration factor, as enrichment factors. Study was performed in two different growing conditions, only nutrients and with addition of organic matter, as fulvo and humic acid. Results of bioaccumulation study indicate that presence of organic matter increase bioaccumulation potential of plant. Obtained values for bioaccumulation factor and enrichment factor show that Pistia stratiotes have a potential to accumulate Cu. Favourable transport of Cu ions from the root zone to other parts of the plant, expressed as translocation factor (TF), was also established.

Keywords: heavy metal, plant, bioaccumulation, translocation, enrichment

INTRODUCTION

As a result of industrialization, contamination of the aquatic environment increases. This contamination effects the life of aquatic environment, *i.e.* plants, animals, and microorganisms [1]. Common contaminants of aquatic systems are waste waters that contains inorganic and organic chemical compounds. These contaminants are usually heavy metals and wide range of pesticides [2].

Heavy metals are recognized as some of the major causes of cancer, asthma, skin diseases and cardiovascular problems and because of that developing of strategies for water purification is an important topic [3]. Among numerous strategies the most preferable are those that include phytoremediation using aquatic plants. The effectiveness of using plants to reduce or eliminate toxic chemicals depends on capability of selected plants to grow and accumulate metals under specific conditions [4]. Among various species, some free-floating aquatic species such as *Pistia stratiotes* could be useful plant in phytoremediation technology to restore water quality as potential accumulator of heavy metals [5].

Bioconcentration factor (BF) is indication of the accumulation of contaminants in the plant tissues and represents the ratio between metal concentration in plant and the metal concentration in the water. BF is used as a measure of metal accumulation efficiency and if

BF value is higher than 1, plant has phytoremediation or phytoextraction potential. Enrichment factor (EF) represents the ratio of mean metal concentration in sample to metal concentration in reference (*i.e.* mean metal concentration in leaves to metal concentration in water). Translocation factor (TF) represents ability of a plant to translocate metals from its roots to aerial parts. TF is important factor in process of screening potential of plant for phytoextraction and value higher than 1 indicate translocation to the aerial parts of plant [6,7].

Although copper is reported as widespread heavy metal pollutant in natural and wastewaters as result of industrial and agriculture activities, copper is an essential micronutrient and a component of several enzymes which mainly participating in electron flow and catalyzing the redox reactions [8]. The aim of this study was determination of Cu (II) accumulation potential of *Pistia stratiotes* in different growing conditions.

MATERIALS AND METHODS

Sampling and experimental setup

Plant materials

Healthy, well-developed plants of *P. stratiotes* of uniform size, mass and root length and with similar growth stage were collected from a thermal spring in locality Ostrovica (Niš, Serbia, 43.32680, 22.11117). Selected plants were firstly washed thoroughly in a running tap water and then with distilled water to remove the impurities.

Preparation of chemicals

Stock solutions of all used salts were prepared by dissolving of appropriate amount of these salts in ultra-deionized water. Precise measurement was performed with an accuracy of 0.00001 using an analytical balance (Kern, Germany). Concentrations of these solutions were the following: 0.0916 M $CuCl_2 \cdot 2H_2O$; 0.1 M KH_2PO_4 and 0.7601 M NH_4NO_3. Also, solutions of HCl, HNO_3 and NaOH, all in concentration of 0.1 M, used for pH adjusting were prepared by dissolving in ultra-deionized water. All used chemicals were purchased from Merck (Germany) and Sigma Aldrich (Germany). Ultra-deionized water was obtained using Smart2Pure system (Thermo Scientific, SAD).

Accumulation potential study

To the accumulation study, 10 specimens of species *P. stratiotes* were used. They were divided into two groups (treatments), each group consisting of 5 individuals, all grown in separate, plastic transparent containers (10 L). The first (I) container contended water, nutrients and Cu ions (10 µmol L^{-1}), while the second container (II) container were filled in with water, nutrients, Cu ions, humic acid (HA) and fulvic acid (FA). Experiment was established in the period of 56 days (8 weeks).

Preparation of plant material for analysis

After 56 of growth in plastic tanks, samples of *Pistia stratiotes* were washed out of excessive substrate solution with fresh water and left to dry indoor at ambient temperature until complete dryness. Afterwards, to remove possible residual humidity, plants were additionally dried in a laboratory oven, at 100°C for 30 minutes, prior to weighing. Each part of plant specimen (leaves and root) was cut in small pieces and pulverized. Then a particular weight of each plant sample was digested with 15 mL of a mixture (v/v 3:1) of concentrated 63% nitric acid and 30% hydrogen peroxide and solution was evaporated until dryness. The solid residue was redissolved in 13 mL of 0.1 M nitric acid, filtered through filter paper, then through micro-filter (0.45 pm), after which the mineralized plant material was ready for instrumental analysis. Metal content in plant material were determined by atomic absorption spectroscopy (AAS) using VARIAN AAnalyst 300 with acetylene/air flame (Perkin Elmer).

Calculations

The bioaccumulation factor is calculated as ratio between the mean concentration of metal in whole plant (μg g^{-1}) and the mean metal concentration in solution (μg g^{-1}). The plant could be considered as hyperaccumulator if the BCF is higher than 1 [6–10].

Translocation factor (TF) is calculated as ratio of the metal concentration in aerial parts of the plants to those in the roots (μg g^{-1}). The TF>1 indicates that the plant translocations metals effectively from the roots to its aerial parts [11].

Enrichment factor (EF) is calculated as ratio of the metal concentration in aerial parts of the plants (μg g^{-1}) to the mean metal concentration in solution (μg g^{-1}) [12].

RESULTS AND DISCUSSION

Results obtained during investigation of accumulation potential of *Pistia stratiotes* to Cu(II) ion as well as influence of organic matter presence on bioconcentration potential are presented in Table 1 and 2.

Table 1 *Content of Cu(II) ions (μg/g) in part of Pistia stratiotes plants grown in two different environments*

Treatment	Root	Leaves	Whole plant
I	33.93	0.74	7.48
II	36.97	2.62	9.64

Obtained results indicate that presence of organic matter (fulvic and humic acid in this case) increases bioconcentration potential of plant. Plants from treatment II contained higher concentration of Cu(II) than plants from treatment I, that contained only nutrients and Cu(II) ions. Also, concentration of Cu(II) in leaf rosette from plants that were grown in treatment II is about 3.5 times higher than from plants grown in treatment I. Difference between concentrations in roots is slightly higher in favour plants from treatment II than in plants from treatment I.

Table 2 *Enrichment factor (EF), bioaccumulation factor (BCF) and translocation factor (TF) of Pistia stratiotes corelated to Cu ion in plants grown in two different environments*

Treatment	EF (root)	EF (leaves)	BCF	TF
I	53.39	1.16	11.77	3.23
II	58.18	4.12	15.17	8.17

Based on these results, bioconcentration factor (BCF), enrichment factor (EF) and translocation factor (TF) were calculated and obtained results are presented in Table 2. The values of bioaccumulation factor (BCF>1) indicate that *P. stratiotes* shows a tendency to accumulate copper from the environment. As previous, these results showed that accumulation capacity for Cu ion was registered higher in treatment II than in treatment I. These results indicate that presence of fulvo and humic acid affects the increase of Cu accumulation. In both treatments, there was a significant accumulation level of Cu ions in the root tissues compared to aerial parts of the plant. However, favourable transport of Cu ions from the root zone to other parts of the plant, expressed as translocation factor (TF), was also established. The lowest value of copper content was determined in areal parts of plants from treatment I.

CONCLUSION

The presence of accumulated copper in plants is evident, both in the root and in the rosettes in individuals from I and II treatments in which the concentration of copper ions in the solution is initially increased. Based on obtained values of bioconcentration factor (BCF) for the mentioned two treatments, can be concluded that *P. stratiotes* show a tendency to accumulate heavy metals from the environment, at the level of the root and leaf rosette. Also, obtained values of the translocation factor (TF) and enrichment factor (EF) indicate that there is hyperaccumulation and translocation of copper from the root into the upper plant parts.

ACKNOWLEDGEMENT

This study was supported by the Ministry of Education, Science and Technological Development, Republic of Serbia (Contract Number 451-03-68/2022-14/200124).

REFERENCES

[1] A.A. Ansari, M. Naaem, S. S. Gill, *et al*., Egypt. J. Aquat. Res; 46 (2020) 371–376.

[2] A.W. Verla, E.N. Verla, C.E. Amaobi, *et al*., Int. J. Sci. Res; 3 (2018) 40–46.

[3] M.E. Eid, T.M. Gala, N.A. Sewelam, *et al*., Environ. Sci. Pollut. Res; 27 (2020) 12138–12151.

[4] S.K. Prajapati, N. Meravi, S. Singh, Proc. Int. Acad; 2 (2) (2012) 136–138.

[5] V.J. Odjegba, I.O. Fasidi, Ecotoxicology; 13 (2004) 637–646.

[6] N.K. Singh, A.S. Raghubanshi, A.K. Upadhyay, Ecotoxicol. Environ. Saf; 130 (2016) 224–233.

[7] V. Kumar, J. Singh, A.K. Chopra, Int. J. Phytoremediation; 20 (5) (2018) 507–521.

[8] S. Kumar, S. Nand, B. Pratap, *et al*., J. Clean. Prod; 327 (2021) 129468–129475.

[9] S. Rezania, S. M. Taib, M.F.M. Din, *et al*., J. Hazard. Mater; 318 (2016) 587–599.

[10] T. Mishra, V.C. Pandey, Phytomanagement of Polluted Sites Market Opportunities in Sustainable Phytoremediation, Chapter 16 - Phytoremediation of Red Mud Deposits Through Natural Succession, Elsevier, Amsterdam (2019) p.409, ISBN: 9780128139127.

[11] T. Jayampathi, T. Atugoda, C. Jayasinghe, Pharmaceuticals and Personal Care Products: Waste Management and Treatment Technology, Elsevier, Amsterdam (2019) p.87, ISBN: 9780128161890.

[12] R. Dragović, B. Gajić, S. Dragović, *et al*., J. Clean. Prod; 84 (1) (2014) 550–562.

PHTHALATES MIGRATION FROM ABSORABLE SURGICAL SUTURES INTO MODEL SOLUTION

Tatjana Anđelković[1*], Danica Bogdanović[1], Ivana Kostić Kokić[1], Hristina Kocić[2], Gordana Kocić[2]

[1]University of Niš, Faculty of Science and Mathematics, Department of Chemistry, Višegradska 33, 18000 Niš, SERBIA

[2]University of Niš, Faculty of Medicine, Department of Biochemistry, Bulevar dr Zorana Đinđića 81, 18000 Niš, SERBIA

[*]*tatjana.andjelkovic@outlook.com*

Abstract

The aim of this work was to quantitative determine five phthalates – dimethy phthalate (DMP), di-n-butyl phthalate (DBP), benzyl butyl phthalate (BBP), di-n-octyl phthaate (DOP) and di-2-ethylhexyl phthalate (DEHP) in absorable surgical sutures using gas chromatography-mass spectrometry (GC/MS). Quantitative determination is based on the fact that phthalates migrate almost 100% after appropriate time to a non-polar environment such as the n-hexane as recipient model solution. The ion of base peak m/z 149 for DBP, BBP, DEHP and DOP and the ion of base peak m/z 163 for DMP were selected for the screening studies. The acquisition was performed at the selected ion monitoring mode (SIM). The mass-selective detector (MSD) response for GC/MS calibration standards was linear between 0.25 and 2.50 μg mL^{-1}. The study showed that DMP, BBP and DOP were not detected in the test surgical sutures, while DBP and DEHP were present in certain amounts. The amounts of DBP and DEHP present in surgical sutures are expressed as the percentage of migrated phthalates to the n-hexane as model recipient after 30 days of migration and the amounts from 0.00043 to 0.01271 % for DBP, and from 0 to 0.02065 % for DEHP.

Keywords: DBP, DEHP, surgical sutures, GC-MS

INTRODUCTION

Phthalates are compounds that are most often used in the form of plasticizers, in order to soften plastics, which nature is rigid and become more flexible and convenient to use. Phthalates are most often added to poly vinyl chloride (PVC), but they can also be found in other types of plastics, such as polypropilene (PP), polyetilen (PE) and polystirene (PS), because phthalates are used as part of the catalyst (Ziegler-Natta catalyst) during the polymerization process of noted plastics [1]. Research shows that phthalates are found in a large number of plastic products intended for home use as well as items intended for medical use [2]. Phthalates are endocrine disruptors, which means that they negatively affect the work of glands that secrete hormones, and thus cause harmful consequences for human health: they affect infertility, cause testicular cancer, etc. [3]. This reflects the importance of determining phthalates in various articles, especially in medical equipment. A surgical sutures are medical equipment that have direct contact with human tissue and can be adsorbed into the tissue, they may also contain phthalate coatings [4].

Surgical sutures are sterile filaments used in surgical procedures to close wounds. They can be made of absorbable or non-absorbable materials. The requirements for surgical wound closure are to establish a sterile environment, stimulate the healing process and avoid any negative reactions - all of which lead to an ideal suture. The difference between absorbable and non-absorbable sutures is that the absorbable suture is biodegradable in body tissues to soluble products and disappears within 2 to 6 months, while the non-absorbable suture is resistant to biodegradation and must be surgically removed after some time as a foreign body.

Absorbable sutures are synthetic sutures made of a material with a chemical structure that is susceptible to hydrolytic and enzymatic degradation. These are materials based on proteins, polyesters, polysaccharides, etc. [5]. The absorbable sutures are listed below. Polyester sutures made from lower α-hydroxy acids are used as absorbable sutures. This type of sutures includes poly (glycolic acid) (poly (GA)) sutures. Another type of sutures are copolymer sutures, which are obtained by copolymerizing lactic acid with glycolic acid, to obtain polymers that are more easily absorbed in tissues, since pure polylactic acid is slowly degraded to lactic acid. Such a suture is L(-)lactide-co-glycolide, and it is usually plasticized with bis(2-methoxy methyl) phthalate or acetoxy triethyl citrate to obtain more flexible filaments. Also, sutures made of absorbable material polyglactin (vicryl) are used in surgery and these sutures provide minimal complications and proved to be stronger compared to other sutures. Also, sutures composed of polyglyton, a material that represents the composition of glycolide, caprolactone, trimethylene carbonate and lactide, are used in surgery. This structure of the material enables faster recovery of patients due to fast absorption in the tissue and reduced possibility of infection.

The presence of phthalates in the surgical sutures would mean further phthalates migration into the blood and a negative effect on human health, because phthalates are non-polar compounds and are not chemically bound to the polymer, wherefor they can easily migrate under appropriate conditions to the non-polar environment that surrounds them [3].

The aim of this paper is to investigate the migration of five phthalates DMP, DBP, BBP, DOP and DEHP from absorable surgical sutures into a *n*-hexane, as solution model, in order to determine whether the analyzed absorable surgical sutures contain analyzed phthalates. Quantitative phthalates determination was performed using gas chromatography-mass spectrometry analysis (GC-MS), which is the most commonly used method for this analyse [6].

MATERIALS AND METHODS

Reagents and materials

The *n*-hexane (HPLC grade) was purchased from Carlo Erba (France). DMP, DBP, BBP, DEHP and DOP were purchased (99.7 % purity) from Sigma–Aldrich (USA). Dibutyl adipate (DBA) was purchased from Fluka (Switzerland) and used as an internal standard.

Plastic materials

To determine phthalates in surgical sutures using the GC-MS technique, 6 surgical sutures purchased from a Clinical center Niš (Serbia) with a clearly stated declaration of composition were analysed. Six surgical sutures are absorbable in human tissue. These surgical sutures are further marked with numbers from 1 to 6. The surgical suture number 1 is made of polyglyton, the surgical sutures number 2 and 3 are made of polyglactin, the surgical suture number 4 is made of L(-)lactide-co-glycolide, the surgical suture number 5 and 6 are made of glycolic acid.

Apparatures and equipment

Gas chromatographic analysis was performed by Gas Chromatograph 6890 (Hewlett-Packard, USA) equipped with a mass selective detector (MSD) 5973 (Hewlett-Packard, USA), Auto sampler 7683 (Agilent, USA) and SGE 25QC2/BPX5 0.25 capillary column (25 m × 0.22 mm × 0.25 µm, non-polar). The analytical balance (Kern, CA) with accuracy of ± 0.00001 g for gravimetric measurements was used.

GC-MS technique

The gas chromatograph was operated in the split less injection mode. The oven temperature was programmed from initial temperature 90 °C (hold time 0 min) to 280 °C at a rate of 20 °C per min with hold time of 4 min, and post run 300 °C (2 min). Helium was the carrier gas (flow rate of 1.0 mL min^{-1}). The operating temperature of the MSD was 280 °C with the electron impact ionization (EI) voltage of 70 eV. The dwell time was 100 ms. The MSD was used in the single ion-monitoring mode (SIM), the quantification ion is *m/z* 149 for DBP, BBP, DEHP and DOP, *m/z* 163 for DMP and ion *m/z* 185 was chosen as representative ion of DBA. Analyte response was normalized to DBA as internal standard. The identification and quantification of target compound was based on the relative retention time, the presence of target ions and its relative abundance. Both data acquisition and processing were accomplished by Agilent MSD ChemStation® D.02.00.275 software.

Calibration standards

To obtain calibration curves for investigated five phthalates and calibrate GC-MS instrument, standard solutions of the tested phthalates (DMP, DBP, BBP, DEHP, DOP) were prepared in *n*-hexane so that their concentration amounts to 0.25, 0.50, 1.00, 1.50 and 2.50 µg mL^{-1} with addition of DBA as an internal standard at a concentration of 1 µg mL^{-1}.

Sample preparation

n-Hexane was selected as phthalate model recipient to obtain the maximum degree of phthalate migration from surgical sutures, since *n*-hexane is nonpolar solvent. The weight of each surgical sutures for analysis was from 0.02 to 0.10 g whereby the measurement was performed with an accuracy of ± 0.00001 g.

Migration experiment

Monitoring the migration of phthalates from six surgical sutures was performed by setting migration tests. The measured surgical sutures, numbered from 1 to 6, were poured with 5 mL of *n*-hexane, after which the procedure of monitoring the migration of phthalate from surgical sutures into the *n*-hexane was performed for 6, 15 and 30 days. After 6 days the recipient volume was pipetted (900 µL) and added DBA so that its concentration was 1 µg mL^{-1}. The prepared solution was analyzed by GC-MS technique. The analysis was repeated after the migration tests were performed for 15 and 30 days. To obtain reliable results with a certain standard deviation, the analysis of each item was performed three times.

RESULTS AND DISCUSSION

GC-MS acquisition

The obtained GC-MS chromatograms of standard solutions show good separation of five investigated phthalates and DBA with retention times 4.728, 7.375, 9.289, 9.842, 10.044 and 6.275 min for DMP, DBP, BBP, DEHP, DOP and DBA, respectively. Figure 1 shows the linear analytical curve obtained for DBP and DEHP within concentration range 0.25–2.5 µg mL^{-1} with correlation coefficient of $R^2 = 0.993$ and linear equation (1) for DBP and $R^2 = 0.993$ and linear equation (2) for DEHP.

$$y = (382947 \pm 16602)x - (38722 \pm 23258) \tag{1}$$

$$y = (178435 \pm 7429)x - (24253 \pm 10408) \tag{2}$$

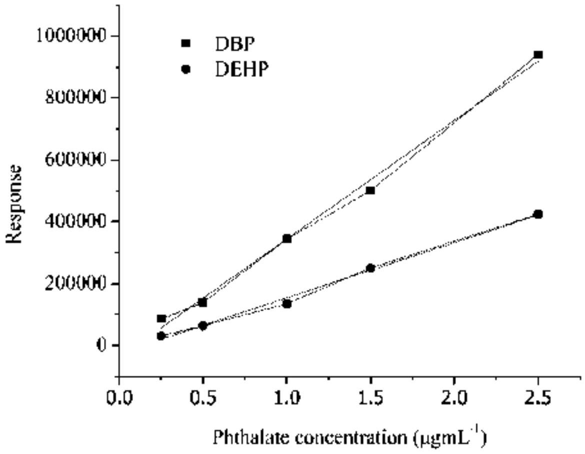


Figure 1 *The analytical curves for DBP and DEHP within concentration range 0.25–2.5 µg mL^{-1}*

Phthalate migration into the recipient model

After appropriate sample preparation and performed phthalates migration tests for 5, 15 and 30 days, quantitative phthalate determination was performed using the GC-MS technique and the results of this analysis are shown as a percentage of phthalates migration relative to the mass of investigated absorbable surgical sutures. The obtained results show that of the five phthalates tested, only DBP and DEHP are detected in *n*-hexane as recipient model, while DMP, BBP and DOP are absent, even after 30 days of the migration test. The value of the migration estimates of these two phthalates are given in Table 1 and amounts from 0.00043 to 0.01271% for DBP, and from 0 to 0.02065% for DEHP. The surgical suture number 2, made from polyglactin, contain the largest amounts of these two phthalates. The results show that the surgical suture number 3, also made from polyglactin, contain only DBP.

Considering that the migration percentage for these two phthalates from the examined surgical suture is very low and the fact that the TDI value for DEHP and DBP 0.05 mg kg^{-1} and 0.01 mg kg^{-1} body weight [7], there is no risk of contamination of the body with phthalates due to their migration from the sutures during the time of their decomposition.

Table 1 *Percentage of phthalate migration after 30 days of migration test*

Surgical suture	**Mass of surgical suture**	**Mass of migrated phthalates after 30 days**		**Migration percentage**	
		DBP	**DEHP**	**DBP**	**DEHP**
1	0.09324	1.77778	2.88889	0.00191	0.00310
2	0.01399	1.77778	2.88889	0.01271	0.02065
3	0.07346	0.64000	0	0.00087	0
4	0.09353	1.77778	2.88889	0.00190	0.00309
5	0.07395	0.32000	2.32333	0.00043	0.00314
6	0.08112	1.45778	2.88889	0.00180	0.00356

CONCLUSION

After 30 days of the migration test only DBP and DEHP of the five tested phthalates were detected in the recipient model. From the fact that 30 days of migration test is required for 100% migration of all present phthalates in plastic into a recipient model such as *n*-hexane, the amount of phthalates present in the surgical suture, expressed as a percentage of migration, was established. Values of migration percentages estimate range from 0.00043 to 0.01271% for DBP, and from 0 to 0.02065% for DEHP, and these amounts do not depend on the type of material from which the surgical suture are made, because at the same time the surgical suture containing the most and least phthalate is the thread made of polyglactin.

ACKNOWLEDGEMENT

This study was performed within the research program – Contract No. 451-03-68/2022-14/200124.

REFERENCES

[1] Y. Kissin, X. Liu, J. David, *et al*., J. Mol. Catal. A: Chem; 287 (1–2) (2008) 45–52.

[2] R. Rudel, L. Perovich, Atmos. Environ; 43 (1) (2009) 170–181.

[3] S. Benjamin, E. Masai, N. Kamimura, *et al*., J. Hazard. Mater; 340 (2017) 360–383.

[4] K. Syamala Devi, P. Vasudevan, J. Macromol. Sci. Part C; 25 (3) (1985) 315–324.

[5] F. Jummaat, E. B. Yahya, A.H.P.S. Khalil, *et al*., Polymers; 13 (2021) 633–651.

[6] S. Qian, H. Ji, X.X. Wu, *et al*., Plos One; 13 (12) (2018) e0208467.

[7] V. Silano, J.M.B. Baviera, C. Bolognesu, *et al*., Efsa J; 17 (12) (2019) 5838–5923.

THE CONTENT OF DANGEROUS CONTAMINANTS PAHs IN THE SOIL AND ROOTS OF *HEDERA HELIX* IN SLATINA (BOR'S MUNICIPALITY)

Aleksandra Papludis[1*], Slađana Alagić[1], Snežana Milić[1], Ivana Zlatanović[2], Milica Filipović[3], Jelena Nikolić[2], Vesna Stankov Jovanović[2]

[1]University of Belgrade, Technical Faculty in Bor, V.J. 12, 19210 Bor, SERBIA

[2] University of Nis, Faculty of Sciences and Mathematics, Department of Chemistry, Višegradska 33, 18000 Niš, SERBIA

[3]Hemofarm A.D., Beogradski put bb, 26300 Vršac, SERBIA

[*]*apapludis@tfbor.bg.ac.rs*

Abstract

The samples of roots and soil from the rooting zone of poison ivy (Hedera helix) were collected from the rural settlement of Slatina, near Bor town, with the aim to determine the content of 16 priority polycyclic aromatic hydrocarbons (PAHs); they were analyzed by gas chromatographic-mass spectrometric method. Generally, the concentrations of 16 PAHs in the sample of roots (from n.d. to 491.06 μg/kg) were much higher than in the soil (from n.d. to 98.88 μg/kg). The accumulation rates in the roots of the investigated plant species were determined using bio-concentration factor (BCF). The highest accumulation rates for 16 PAHs were found in the cases of acenaphthene, fluorene, fluoranthene and pyrene. For these compounds the investigated plant may be useful in the root phytoacumulation, practically in the soil phytostabilization. Also, Hedera helix can be successfully used in phytostabilization of the compounds such as anthracene, dibenzo(a,h)anthracene, and the sum of benzo(k)fluoranthene and benzo(b)fluoranthene, because it accumulated these compounds very efficiently (the extraction from the soil was maximal). However more research in the future is needed for the formulation of more safe conclusions about the accumulation capacities of Hedera helix.

Keywords: GC/MS, *Hedera helix*, BCF, PAHs

INTRODUCTION

The Copper Mining and Smelting Complex Bor more then 100 years has had strong impact on the environment pollution of Bor's municipality by heavy metals [1].

The aim of this research was to determine the content of specific and dangerous organic pollutants such as 16 polycyclic aromatic hydrocarbons (PAHs) in the soil and roots of *Hedera helix* in the rural settlement of Slatina, which is located 6.5 km away from the Bor town and from the heating plant and the copper smelter, as possible sources of PAH pollution. Also, according to Alagić *et al.* [2], one of the main sources of pollution in the rural area is domestic heating based on wood combustion. Additionally, it was important to determine the level of soil pollution according to the classification given in Table 1, and to establish the related accumulation rates (which is important for phytoremediation).

In the United States Environmental Protection Agency (USEPA), 16 PAHs have been included in the list of pollutants of highest priority. It includes the following compounds:

naphthalene (Nap), acenaphthylene (Acy), acenaphthene (Ace), fluorene (Flr), anthracene (Ant), phenanthrene (Phe), fluoranthene (Flt), pyrene (Pyr), benzo(a)anthracene (BaA), chrysene (CHR), benzo(a)pyrene (BaP), benzo(k)fluoranthene (BkF), benzo(b)fluoranthene (BbF), indeno(1,2,3-c,d)pyrene (IcP), benzo(g,h,i)perylene (BgP), and dibenzo(a,h)anthracene (DhA). USEPA classified 7 PAHs as possible carcinogens: BaA, CHR, BaP, BbF, BkF, IcP and DhA [2–6].

Table 1 *The level of soil pollution depending on the Σ16 PAHs (μg/kg) [7]*

Class of soil contamination	16 PAHs
Non-contaminated	<200
Weakly contaminated	200–600
Contaminated	600–1000
Heavily contaminated	>1000

MATERIALS AND METHODS

Sample collection, preparation and analyses

The samples of soils and roots of *Hedera helix* were collected from the chosen location at the end of September 2020. From the investigated site, 3 plants were taken; these samples were pooled to obtain a representative sample for roots and for the soil. All samples were placed into paper bags and transported to the laboratory. The roots were carefully cleaned from soil particles, and after that, they were washed with tap and distilled water. All samples were air-dried until constant weight, over a period of couple of months. In a laboratory mill were homogenized all dried samples. The samples of soils and roots were placed in sealed bags and stored at the fridge at 4°C until PAHs determination by gas chromatographic-mass spectrometric (GC/MS) method (before GC/MS analysis PAHs were extracted from the prepared samples using mixture water/acetonitrile and then all samples were purified).

The prepared samples of the soil and roots were analyzed on 7890/7000B GC-MS/MS triple quadripole device equipped with a Combi PAL auto sampler and HP-5MS capillary column.

The bio-concentration factor (BCF) was used to estimate the accumulation rates of 16 PAHs in *Hedera helix* roots [2,3]. BCF was determined according to the equation (1):

$$BCF = \frac{C_{root}}{C_{soil}} \tag{1}$$

where C_{root} and C_{soil} are the concentrations (μg/kg, dry weight) of the compound in the root and in the corresponding soil. Namely, BCF values represent a first sign that the investigated plant may be useful for application in the root phytoextraction/phytoaccumulation.

RESULTS AND DISCUSSION

The total concentrations of 16 priority PAHs in the soil and root samples at the investigated site ranged from 4.27–98.88 μg/kg and from 1.74–491.06 μg/kg, respectively

(Table 2). The concentrations of 16 PAHs for the soil from the sampling site S decreased in the order as follows: 98.88 µg/kg (Phe), 72.43 µg/kg (Nap), 36.96 (Flt), 32.17 (BaA), 19.54 (Flr), 10.15 (Pyr), 10.09 (BaP), 9.78 (Acy), 4.27 (Ace). Anthracene was not registered in the soil, as well as heavier compounds such as: CHR, Bkf+BbF, IcP, BgP and DhA.

The concentrations of 16 PAHs in the roots of poison ivy decreased in the order as follows: 491.06 µg/kg (Flr), 190.26 (Flt), 94.31 (DhA), 91.31 (Phe), 83.97 (Pyr), 30.77 (Nap), 16.39 (Ant), and 1.74 (BkF+BbF). The concentrations of Acy, BaA, CHR, BaP, IcP and BgP, were not registered in the roots.

The results of the obtained analyses clearly showed that the sum of 16 PAHs was significantly higher in the roots than in the soil.

***Table 2** The concentrations of 16 priority PAHs (µg/kg, dw) in the soil and root samples of Hedera helix together with the calculated BCFs*

PAHs/Sample	Soil	Root	BCF
Nap[a]	72.43 ± 1.31	30.77 ± 0.36	0.4
Acy	9.78 ± 0.55	nd	nc
Ace	4.27 ± 0.62	75.60 ± 9.21	**17.7**
Flr	19.54 ± 1.39	491.06 ± 45.56	**25.1**
Ant[a]	nd	16.39 ± 1.91	nc
Phe[a]	98.88 ± 5.88	91.31 ± 5.70	0.9
Flt[a]	36.96 ± 2.15	190.26 ± 19.24	**5.1**
Pyr	10.15 ± 0.90	83.97 ± 3.58	**8.3**
BaA[a,b]	32.17 ± 1.09	nd	nc
CHR[a,b]	nd	nd	nc
BaP[a,b]	10.09 ± 0.13	nd	nc
Bkf+Bbf[a,b]	nd	1.74 ± 0.45	nc
IcP[a,b]	nd	nd	nc
BgP[a]	nd	nd	nc
DhA[b]	nd	94.31 ± 3.79	nc
Σ 16 PAHs	294.28	1075.4	
Σ 10 PAHs	250.54	330.46	
Σ 7 PAHs	42.26	0.0	

nd – not detectable; nc – not calculable

[a] – Σ10 PAHs (Nap, Ant, Phe, Flt, BaA, CHR, BaP, BkF, IcP and BgP)

[b] – Σ7 carcinogenic PAHs (USEPA) (BaA, CHR, BaP, BbF, BkF, IcP and DhA)

PAHs such as CHR, IcP and BgP were not registered in the samples of soil and roots of *Hedera helix*. The most abundant PAH in the soil sample was Phe (98.88 µg/kg), while in the root sample the most abundant was Flr (491.06 µg/kg). The dominant compounds among all 16 PAHs in soil were Phe, Nap, Flt, and BaA, but in roots were as follows: Flr, Flt, DhA and Phe.

As mentioned, the total concentration of 16 PAHs in the soil sample was 294.28 µg/kg; based on the level of soil pollution (Table 1) this soil can be classified as weakly contaminated.

The concentrations for Σ10 PAHs (Nap, Ant, Phe, Flt, BaA, CHR, BaP, BkF, IcP and BgP) and Σ7 cancerogenic PAHs (BaA, CHR, BaP, BbF, BkF, IcP and DhA) were not exceeding the defined maximum allowed concentrations (MAC) of 1000 µg/kg [8–12] and 300 µg/kg [9,10,13], respectively.

The values of BCFs for 16 PAHs are also given in Table 2. The highest accumulation rates for all investigated PAHs were found in the cases of Flr (25.1), Ace (17.7), Pyr (8.3) and Flt (5.1). The very high values of BCFs for these compounds were a safe sign that the investigated plant may be very useful for the application in the root phytoextraction/phytoacumulation; the compounds such as Ant, BkF+BbF and DhA were totally extracted from the soil and accumulated in the roots, so, it can be concluded that *Hedera helix* can be successfully used in their phytostabilization too; obviously, it can keep large quantities of many PAHs in its roots.

The concentrations for Nap and Phe were higher in the soil sample than in the roots; therefore BCF values were less than 1. In the cases of Acy, BaA and BaP the concentrations were higher in the soil sample - in fact, they were not registered in the roots and BCF values were not calculable.

CONCLUSION

Observing all the tested compounds (16 PAHs), the results in this study showed that the concentrations of CHR, IcP and BgP were not detected in both investigated samples. The highest concentrations were detected in the roots for Flr (491.06 µg/kg), Flt (190.26 µg/kg) and DhA (94.31 µg/kg), while in the soil, the highest concentration was for Phe (98.88 µg/kg). Based on the calculated BCFs, it was clear that the highest values were for Ace, Flr, Flt and Pyr (17.7, 25.1, 5.1 and 8.3, respectively) which means that the investigated plant may be useful in the root accumulation for these compounds, practically in the soil phytostabilization. For the compounds such as Ant, Bkf+BbF, and Dha, BCF values were not calculable, because their soil concentrations were practically totally extracted, which signalize that *Hedera helix* is able to keep large quantities of these compounds in the roots and can be also successfully used in their phytostabilization. However, more research is needed for the formulation of more safe conclusions about PAH accumulation capacities of *Hedera helix*.

ACKNOWLEDGEMENT

The research presented in this paper was done with the financial support of the Ministry of Education, Science and Technological Development of the Republic of Serbia, within the funding of the scientific research work at the University of Belgrade, Technical Faculty in Bor (contract number 451-03-68/2022-14/200131), and at the University of Nis, Faculty of Science and Mathematics in Nis (contract number 451-03-68/2022-14/200124).

REFERENCES

[1] A. Papludis, M. Nujkić, S. Milić, *et. al.*, XIV International mineral processing and recycling conference, 12–14 May 2021, Belgrade, Serbia (2021) 430–435.

[2] S. Alagić, V. Stankov Jovanović, V. Mitić, *et. al*., Sci. Total Environ; 562 (2016) 561–570.

[3] S. Alagić, V. Stankov Jovanović, V. Mitić, *et. al*., Environ. Sci. Pollut. Res; 24 (18) (2017) 15609–15621.

[4] E. Morillo, A. Romero, C. Maqueda, *et. al*., J. Environ. Monit; 9 (9) (2007) 1001–1008.

[5] J. Simon, J. Sobieraj, Remed. J; 16 (3) (2006) 25–35.

[6] http://www.epa.gov/osw/hazard/wastemin/priority.htm

[7] B. Maliszewska-Kordybach, J. Appl. Geochem; 11 (1–2) (1996) 121–127.

[8] A. Adeyi, P. Oyeleke, J. Health Pollut; 7 (15) (2017) 71–84.

[9] A. Leung, Z. Wei Cai, M. Huang Wong, J. Mater. Cycles Waste Manag; 8 (2006) 21–33.

[10] C. Shen, Y. Chen, S. Huang, *et.al*., Environ. Int; 35 (1) (2009) 50–55.

[11] A. Melnyk, A. Dettlaff, K. Kuklińska *et. al*., Sci. Total Environ; 530–531 (2015) 18–27.

[12] The Official Gazette of Republic of Serbia, No. 30/2018 and 64/2019.

[13] M. He, S. Yang, J. Zhao, *et. al*., Environ. Int; 133 (2019) 105136.

TOXIC METALS BIOACCUMULATION IN *Plantago lanceolata* FROM ANTHROPOGENICALLY DISRUPTED AREA

Jelena Milosavljević[1*], Snežana Šerbula[1], Ana Radojević[1], Tanja Kalinović[1],
Jelena Kalinović[1], Boban Spalović[1]
[1]University of Belgrade, Technical Faculty in Bor, V.J. 12, 19210 Bor, SERBIA
[*]*jmilosavljevic@tfbor.bg.ac.rs*

Abstract

The study was carried out on Plantago lanceolata, sampled in the anthropogenically endangered area due to the long-term copper mining-metallurgical activities. The purpose of this paper was to analyze the concentrations of toxic metals (Al, Cu, Fe, Mn, Ni, Pb and Zn) in roots, leaves, stems and flowers of P. lanceolata. Toxic metals accumulation abilities in plant parts were assessed using the metal accumulation index (MAI). The MAI values ranged between 77.19 and 158.58 for roots, 63.64–101.24 for leaves, 60.17–146.57 for stalks and 52.86–118.96 for flowers. Relative deviations in toxic metal content from the corresponding values given for the "reference plant" were also calculated. The positive deviations were denoted for Cu, Ni and Pb in all parts at the site 1, which could indicate high bioavailability of these metals as well as good adaptation abilities to the extreeme environmental pollution. Positive deviations were denoted for all the analyzed toxic metals (except Mn) in the roots from all the sampling sites, which was particularly noticeable for Cu and Pb at the site 1 in the immediate vicinity of the copper smelter. The relative deviations for the aboveground parts were positive and negative depending on the sampling site.

Keywords: copper smelter, *Plantago lanceolata*, toxic metals, metal accumulation index

INTRODUCTION

Metal mining and smelting are regarded as one of the most environmentally destructive anthropogenic activities. Extremely high content of hazardous substances (i.e. toxic metals) originates from the metal production activities, as well as from the ore processing wastes, such as mine tailings. Toxic metals are extremely persistent and may be present in high concentrations for decades and even centuries in the environment. This poses a serious problem not only in the areas in the immediate vicinity of the pollution sources, but also in the adjacent areas to which toxic metals are subsequently transported [1–4].

Accumulation of different hazardous substances in the environment, and particularly their bioaccumulation, is a worldwide problem. Plants transfer toxic metals from abiotic to biotic environment, while avoiding their detrimental effects, thus posing a risk of metal transfer to higher food chain strata [1,5,6].

The areas impaired with anthropogenic activities could be observed as reservoirs of plants with different accumulation abilities. The analysis of biological material in the environmental quality monitoring is recognized as a distinctive approach to acquire information regarding toxic metal contamination [5]. *Plantago lanceolata* has been shown to have the abilities to accumulate toxic metals from different anthropogenically polluted environments [1,5,7].

The aim of this paper is to analyze toxic metals accumulation in the parts of *P. lanceolata* sampled in the area endangered by the long-term copper mining-metallurgical activities.

MATERIALS AND METHODS

Sampling and analysis of the plant material

Plant material was sampled at the most endangered sites in the Bor area in regard to the vicinity of the primary pollution source (i.e. copper smelter), secondary pollution sources (i.e. the city heating plant, flotation tailing ponds, traffic and individual home heating) and the prevailing wind directions. Sampling was performed at the following sites: site 1 (Town Park, 0.5 km SW from the copper smelter), site 2 (Brezonik, 2.5 km NW), site 3 (Oštrelj, 4.5 km ESE), site 4 (Slatina, 6.5 km SE) and site 5 (Gornjane, 17 km N, represented the control site).

Microwave digestion was performed by adding 7 mL 65% HNO_3 and 1 mL 30% H_2O_2 to 0.5 g of washed, air dried and grinded plant material (separated into roots, leaves, stalks and flowers). The concentrations of Al, Cu, Fe, Mn, Ni, Pb and Zn in plant parts were determined by the Inductively Coupled Plasma Optic Emission Spectroscopy (ICP–OES, Model Optima 8300).

Toxic metals analysis

Accumulation of toxic metals in the plant parts was assessed by calculating the metal accumulation index (MAI), according to the following expressions [8]:

$$\mathrm{MAI} = \left(\frac{1}{N}\right)\sum_{j=1}^{N} Ij \qquad (1)$$

where N represents the total number of toxic metals analyzed, and Ij is a sub-index for variable j which is defined as:

$$Ij = \frac{x}{\delta x} \qquad (2)$$

where x represents toxic metal concentration, and δx represents its standard deviation.

Data visualization

Data visualization was performed in the R statistical environment (v 4.1.0) [9] with different packages [10,11].

RESULTS AND DISCUSSION

The MAI values for each individual plant part of *P. lanceolata* at selected sampling sites are given in Table 1. The highest MAI value was observed in the roots sampled at the control site 5, while the lowest was noted in the flowers sampled at the site 1. Taking into account different plant parts, the MAI values were in the following ranges: 77.19–158.58 (in the roots); 63.64–101.24 (leaves); 60.17–146.57 (stalks); 52.86–118.96 (flowers). In the study by Nadgórska-Socha *et al.* [7] the MAI values for Cd, Cu, Pb, Mn, Fe and Zn in *P. lanceolata* leaves sampled from the urban environment (i.e. around industrial plants, main roads, city parks and green areas) ranged between 4.71 and 23.1 and were far lower than for the samples from Bor and the surroundings.

The MAI values obtained for *P. lanceolata* sampled in the Bor area were higher compared to the data for different tree and shrub species sampled in the anthropogenically polluted areas [6,12–14]. Various factors, such as local atmospheric conditions and meteorological parameters, sampling time and plant features, could influence the MAI value [14]. Hu *et al*. [12] denoted that low-growing plants were more exposed to soil splash compared to the high-growing plants (i.e. trees). Plants with high MAI values should be used as barriers between polluted and non-polluted areas [12].

Table 1 *Metal accumulation index (MAI) of P. lanceolata sampled at different sites in the Bor area*

Plant part	**Sampling sites**				
	Site 1	**Site 2**	**Site 3**	**Site 4**	**Site 5**
Roots	77.19	82.72	120.59	129.10	158.58
Leaves	101.24	64.70	71.31	93.89	63.64
Stems	109.67	65.91	146.57	60.17	94.27
Flowers	52.86	118.96	78.30	68.86	79.74

The expression “Reference plant”, proposed by Markert [15], includes typical content of toxic metals in plants, which are: 80 mg kg^{-1} (Al), 10 mg kg^{-1} (Cu), 150 mg kg^{-1} (Fe), 200 mg kg^{-1} (Mn), 1.5 mg kg^{-1} (Ni), 1 mg kg^{-1} (Pb) and 50 mg kg^{-1} (Zn). In respect to the values for the “reference plant”, toxic metals content in the plant parts of *P. lanceolata* sampled in the Bor area were 0.06–14.43 (for Al), 0.62–46.29 (Cu), 0.15–6.80 (Fe), 0.04–0.71 (Mn), 0.44–3.87 (Ni), 13.90–37.99 (Pb) and 0.48–6.11 (Zn) times higher.

The reference values given by Markert [15] could be used to establish the baseline of the “chemical fingerprint”. The illustration of this approach is presented as the relative deviations in toxic metal content in comparison to the contents defined for the “reference plant” [16]. Figure 1 represents “chemical fingerprints” of *P. lanceolata* sampled in the anthropogenically disrupted Bor area.

Toxic metal content in the plant samples varied from the “reference plant” with relative deviations between: -93.71 and +1343.13 for Al (Figure 1a), -37.69 and +4529.07 for Cu (Figure 1b), -85.06 and +580.18 for Fe (Figure 1c), -96.47 and -28.69 for Mn (Figure 1d), -55.71 and +286.66 for Ni (Figure 1e), +1289.61 and +3698.61 for Pb (Figure 1f), -51.57 and +510.90 for Zn (Figure 1g).

With respect to the “reference plant” the relative deviations were predominantly positive for the analyzed toxic metals (except for Mn) in the plant samples from the site 1. This was particularly denoted for Cu and Pb whose relative deviations in roots were 4529.07% and 3698.61%, respectively, in respect to the “reference plant”. According to Remon *et al*. [16], high positive relative deviation from the “reference plant” could be explained with higher metal bioavailability at the given sampling site.

The positive relative deviations for Al in the roots from all the sampling sites were noticed, while negative relative deviations were calculated for almost all the aboveground plant parts (except sites 1 and 4).

The positive values of the relative deviations for Cu in all the analyzed plant parts from the site 1 could be an indication of high metal bioavailability at the given sampling site [16], in the conditions of the extreme environmental pollution. Positive relative deviations for Cu in the roots from the all sampling sites were noticed. The relative deviations of Cu content in the aboveground plant parts were positive, except in the stalks (sites 2, 3, 4 and 5) and in the leaves (site 5). Such regularities pointed out the good adaptation abilities to the environmental pollution with Cu.

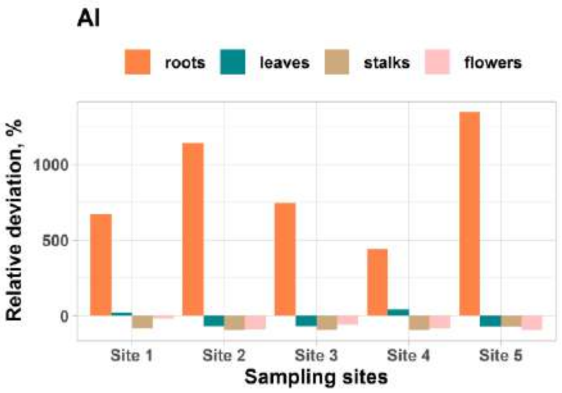
The relative deviations of Fe in the roots from all the sampling sites were positive, while negative deviations were calculated for Fe in the aboveground plant parts except in the leaves and flowers from the sites 1 and 4.

The negative relative deviations of Mn in all the plant parts from all the sampling sites. These results could indicate low Mn bioavailability in the study area.

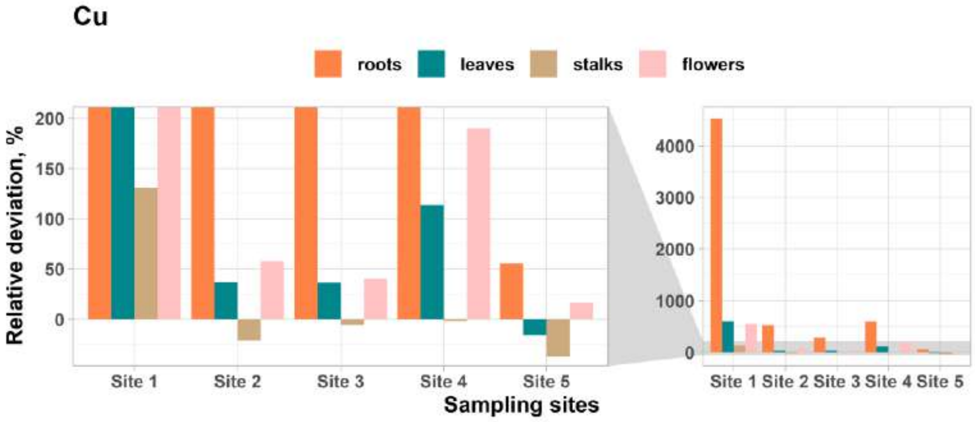
The relative deviations of Ni were positive in all plant parts from the analysed sampling sites except the sites 2 and 5, where deviations in the aboveground parts were negative depending on the part.

Unlike Mn, all relative deviations calculated for Pb were positive, which could indicate high bioavailability of this toxic metal [16], as well as good adaptation ability to Pb.

a)



b)



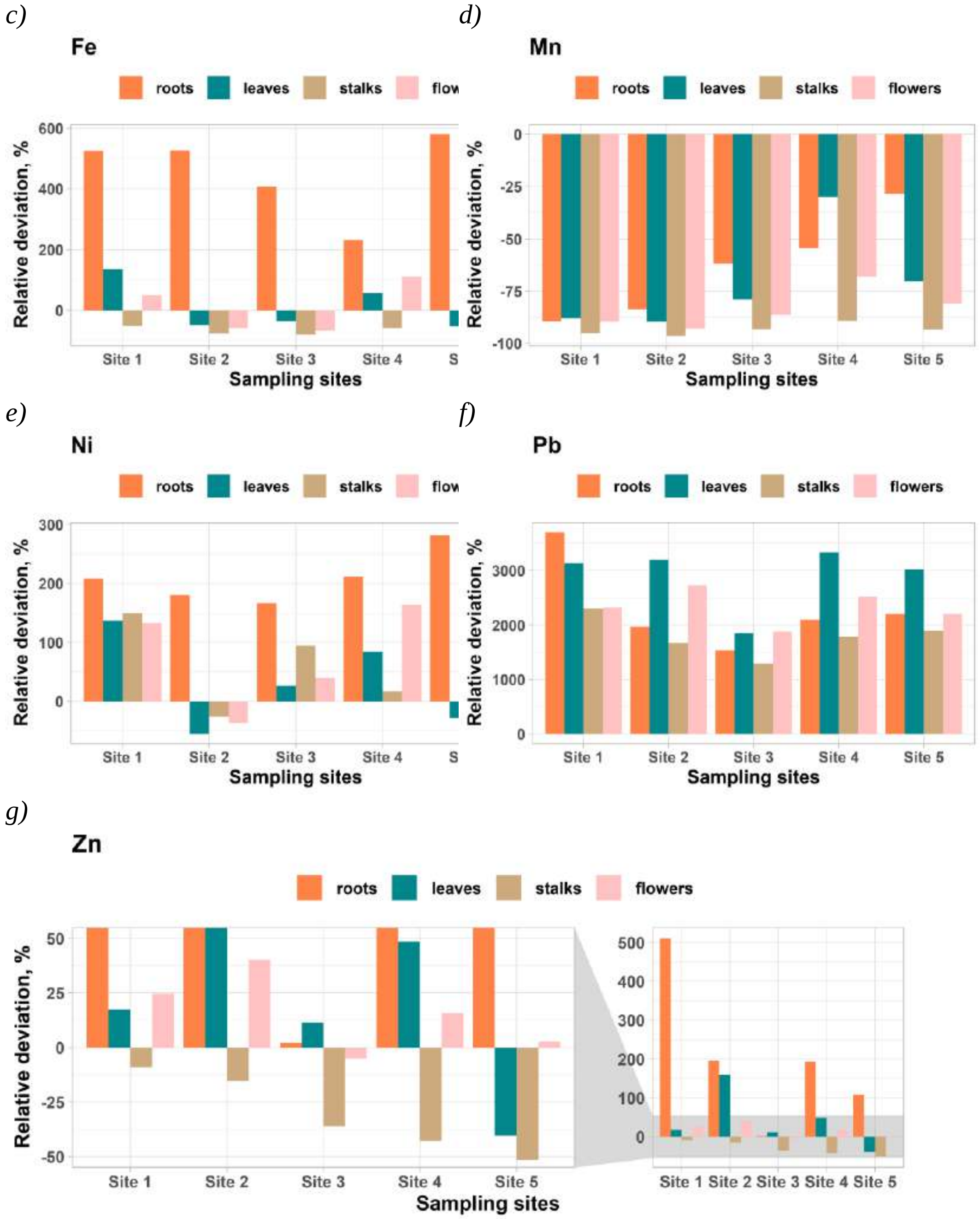


Figure 1 *Chemical fingerprints of toxic metal content in parts of P. lanceolata, sampled from the anthropogenically disrupted Bor area, expressed as relative deviations from the "reference plant"*

It was characteristic that relative deviations for Zn were positive in the roots at all the sampling sites, while for stalks they were negative. The relative deviations for the leaves were negative only for samples from the control site 5, which was probably because of the low Zn environmental concentration at this unpolluted site. Taking into account Zn concentrations in the flowers, regularities concerning relative deviations calculated for the samples from the study area were not observed.

CONCLUSION

The content of toxic metals (Al, Cu, Fe, Mn, Ni, Pb and Zn) was determined in the plant parts (roots, leaves, stalks and flowers) of *P. lanceolata* sampled in the Bor area endangered by the mining-metallurgical activities. Sampling of the plant material was performed at the most imperilled sites due to their location in the vicinity of the copper smelter, as well as the other pollution sources (i.e. the city heating plant, flotation tailing ponds, traffic and individual home heating) and in the prevailing wind directions. The analyzes of the toxic metal concentrations in the plant samples were performed using metal accumulation index (MAI). Taking into account the investigated plant parts, the roots were characterized with the highest MAI values, which indicated higher accumulation efficiencies in roots, compared to the other parts. Moreover, comparisons of toxic metals content obtained in the investigated plant parts to the corresponding contents given for the “reference plant” allowed establishing chemical fingerprints. The results indicated positive deviations for Cu, Ni and Pb in all plant parts at the site 1, which could be an indication of the good adaptation abilities of *P. lanceolata* to the environmental pollution with these toxic metals. The relative deviations for all the studied toxic metals in the roots (except Mn) were positive. The highest positive deviations were denoted for Cu and Pb in the roots samples from the site 1, which was the most anthropogenically endangered. The obtained negative relative deviations of Mn in the plant material from all the sampling sites, and positive deviations of Pb in the plant material from all the sampling sites could indicate the environmental load with these elements.

ACKNOWLEDGEMENT

The authors are grateful to the Ministry of Education, Science and Technological development of the Republic of Serbia for financial support, within the funding of the scientific research work at the University of Belgrade, Technical Faculty in Bor, according to the contract with registration number 451-03-68/2022-14/200131. Our thanks go to English language teacher Mara Manzalović from the Technical Faculty in Bor (University of Belgrade) for providing language assistance.

REFERENCES

[1] A.M. Stefanowicz, M. Stanek, M.W. Woch, *et al.*, Environ. Sci. Pollut. Res; 23 (2016) 6524–6534.

[2] M. Pająk, E. Blonska, M. Szostak, *et al.*, Water Air Soil Pollut; 229 (2018) 392.

[3] J. Álvarez-Rogel, A. Peñalver-Alcalá, F.J. Jiménez-Cárceles, *et al.*, Catena; 201 (2021) 105191.

[4] B. Wu, S. Luo, H. Luo, *et al.*, Sci. Total Env; 808 (2022) 151995.

[5] A. Nadgórska-Socha, B. Ptasiński, A. Kita, Ecotoxicology; 22 (2013) 1422–1434.

[6] A. Roy, T. Bhattacharya, M. Kumari, Sci. Total Env; 722 (2020) 137622.

[7] A. Nadgórska-Socha, M. Kandziora-Ciupa, M. Trzęsicki, Chemosphere; 183 (2017) 471–482.

[8] Y.J. Liu, Y.-G. Zhu, H. Ding, Environ. Poll; 145 (2007) 387–390.

[9] R Core Team (2018) R: A language and environment for statistical computing. R Foundation for Statistical Computing, Vienna, Austria, *Available on the following link:* https://www.R-project.org/

[10] H. Wickham, (2016) ggplot2: Elegant Graphics for Data Analysis. Springer-Verlag New York, *Available on the following link:* https://ggplot2.tidyverse.org/

[11] T.L. Pedersen, (2020) ggforce: Accelerating 'ggplot2'. R package version 0.3.1., *Available on the following link:* https://cran.r-project.org/web/packages/ggforce/index.html

[12] Y. Hu, D. Wang, L. Wei, *et al*., Ecotoxicol. Environ. Saf; 110 (2014) 82–88.

[13] A. Nadgórska-Socha, M. Kandziora-Ciupa, R. Ciepał, *et al*., Int. J. Environ. Sci. Technol; 13 (2016) 1741–1752.

[14] T. Fang, T. Jiang, K. Yang, *et al*., Environ. Monit. Assess; 193 (2021) 151.

[15] B. Markert, Water, Air, and Soil Pollut; 64 (1992) 533–538.

[16] E. Remon, J.-L. Bouchardon, M. Le Guédard, *et al*., Environ. Pollut; 175 (2013) 1–7.

ECOLOGICAL AND AESTHETIC CHARACTERISTICS OF TREES IN “BELGRADE WATERFRONT” PARKING LOTS

Mirjana Ocokoljić[1*], **Djurdja Petrov**[1], **Nevenka Galečić**[1], **Mitar Miodrag**[1]
[1]University of Belgrade - Faculty of Forestry, Kneza Višeslava 1, 11030 Belgrade, SERBIA
[*]*mirjana.ocokoljic@sfb.bg.ac.rs*

Abstract

Having in mind that public parking lots have important influence to road traffic and an element of green infrastructure in urban areas, the paper analyses the ecological and aesthetic characteristics of trees in “Belgrade Waterfront” parking lots. The results of this paper are the starting point for future planning, and are also important as a corrective factor for already green parking lots in “Belgrade Waterfront” and similar environmental conditions.

Keywords: exotic plants, focal point, ecological functionality of the city

INTRODUCTION

According to the project of the Russian architect Grigory Pavlovich Kovalevsky in 1923, the area of future “Belgrade Waterfront” was included in the General Urban Plan for Belgrade under the name "Sava Amphitheatre" which included the construction of residential and commercial buildings in the areas near the railway station and along the Sava River [1]. The examined area is characterized by anthropogenic terrain, construction land formed by embankment but also by fluvial deposits of the Sava River and Mokroluški Stream [2]. “Belgrade Waterfront” is located on degraded chernozem in disarray [3]. Belgrade's climate is temperate continental. For the reference period from the year 1991 to 2020 the average annual air temperature is 13.2 °C, the average number of ice days during the year is 13.9, the average annual rainfall is 698.8 mm, the average annual relative humidity is 67.8%, the average number of days with snow cover during the year is 35.2, and the most frequent wind is Koshava wind (SE).

Today's “Belgrade Waterfront” is a residential and commercial type settlement, in which 60% of the area is planned to be residential, 30% with commercial facilities and 10% under vegetation (45,584 m^2, of which 23,463 m^2 are park areas). The plan is to allocate 14,245 m^2 for parking spaces. According to the Spatial plan from November 2021, green areas were reduced by 20 to 25% [4].

Therefore, surveying inventory and analysis of the impact of trees in the historic centre of Belgrade, parking lots in “Belgrade Waterfront” on the transformation of the space and today's appearance of the city image have been performed. The aim is exploring the possibilities of improvement, enrichment, expansion and increasing green spaces as the most important elements for environmental functionality of the city.

MATERIAL AND METHOD

The subject of the paper are trees in parking lots in “Belgrade Waterfront”, ecological and aesthetic characteristics of trees that bring dynamics to shapes, dimensions and colours, connect different contents and stand out in the image of the city. For the purposes of this paper, the locations bordered by Karadjordje Boulevard (from the north and northeast), Savski Boulevard (from the east) and Vojvode Mišića Boulevard (from the south and southeast) and the Sava River (from the west) on a total area of 808,000 m^2 were investigated.

The method of work consists of the analysis of collected data from the available scientific and professional literature and field research conducted during 2021 and 2022. For the assessment of visual-aesthetic characteristics, the VTA (visual tree assessment) method of observation, recognition and diagnosis was applied [5].

The research also included photographing trees in order to show the aesthetic and functional aspect to the observers. For each selected area, the angle of observation that will best represent it, was chosen. Then the images were processed in such a way that the trees stand out. This visual presentation is the basis for the analysis of aesthetic and functional characteristics of trees. The analysis included the examination of the basic compositional elements and the principles according to which the plants are arranged. The texture and colour of vegetation and its different perception depending on the position of the observer have been singled out as important aesthetic characteristics [6]. The overall aesthetic impression is presented as a result of these and other factors because it is an important aspect of the functionality of green spaces and the image of the city.

RESULTS AND DISCUSSION

There are a total of 616 parking spaces in public streets and off-street parking lots in the investigated area, with the exception of parking spaces for commercial, residential and other facilities (underground parking lots). Out-of-street parking is based on three parking lots with a total of 428 parking spaces: "Sava Promenade", "BW Sava Play" and "BW Vista". All three parking lots have main entrances from Hercegovacka Street. The largest parking lot (6,300 m^2) is "Sava Promenade", with 234 parking spaces. The streets along which there is street parking are: Brisel, Vozd Djordje Stratimirovic, Railway, Queen Draga Obrenovic and Herzegovina streets. There are a total of 188 street parking spaces along these streets. The largest parking space is along Brisel Street (880 m^2), with 80 parking spaces. There is no street parking on Woodrow Wilson Boulevard, which is the main street in “Belgrade Waterfront” area. The Sava promenade is the most important element of the green infrastructure of the settlement, but also of the city of Belgrade.

The surveying inventory determined that in the off-street parking lots: Sava promenade has 53 trees, common hornbeam cultivar with pyramidal habit *Carpinus betulus* 'Fastigiata' and black locust cultivar with pink flowers *Robinia pseudoacacia* 'Casque-Rouge', BW Sava Play has seven trees of *Celtis occidentalis* L. and on BW Vista four specimen of *Photinia serrulata* 'Red Robin' as lollipop topiary tree. Only Norway maple trees (*Acer platanoides* L.) were recorded in the street parking spaces, in: 19 trees on Brisel Street, 13 trees on Vožda Đorđa Stratimirovića Street and 43 trees on Hercegovačka Street. The total number of trees is 142, of which only one is an evergreen taxon while the rest are deciduous. Also, it was stated that only one species is autochthonous and one allochthonous, while other taxa are from the order of cultivars of special ornamental values.

By comparative analysis of photographs of parking spaces in the area of "Belgrade Waterfront", it can be concluded that vegetation is of key importance for the city. Apart from the ecological and importance in environmental protection, the presence of vegetation in the city is necessary and has great aesthetic value [7]. The research confirmed that special attention was paid to the selection of trees and that their adequate selection was made in relation to climatic and other environmental conditions, given that they have maximum ratings of vitality and decorativeness confirmed by the VTA method. By researching the basic compositional elements, linear elements different in texture, colour and perception were selected. It is evident that without the vegetation, "Belgrade Waterfront" would not have the picture it has today. From Figures 1–3 it can be seen that the trees, in addition to the indisputable ecological significance, significantly affect the visual identity of the space and that it is an important constitutive element of the image of the city.

Figure 1 *a) Photinia serrulata 'Red Robin'; b) Robinia pseudoacacia 'Casque-Rouge';*
c) Acer platanoides L. *in Hercegovacka street*

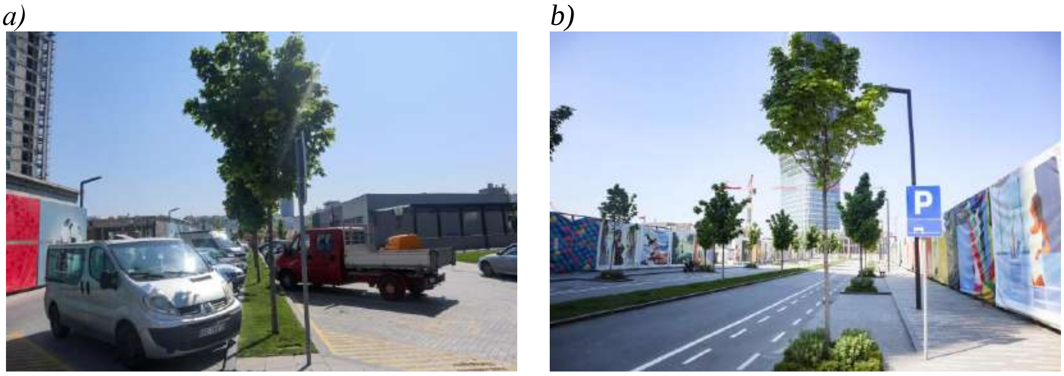


Figure 2 *a) Acer platanoides* L. *in Brisel street; b) Acer platanoides* L. *in Vozd Djordje Stratimirovic street*

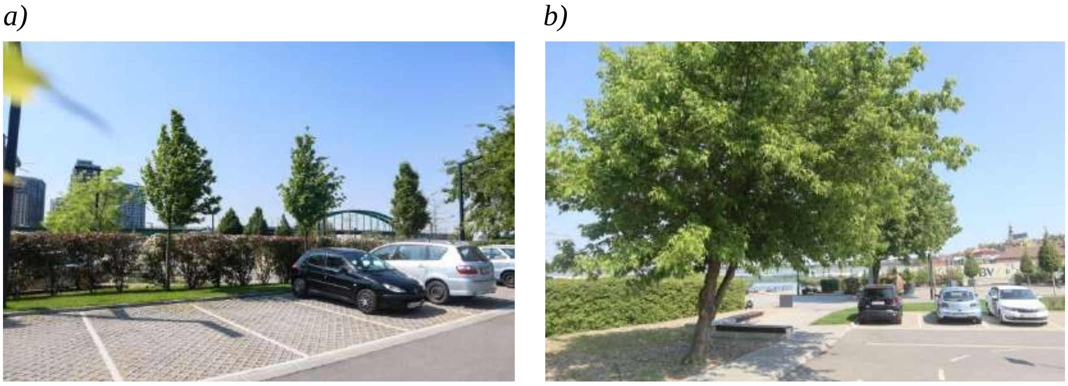


Figure 3 *a) Carpinus betulus 'Fastigiata'; b) Celtis occidentalis* L.

CONCLUSION

Trees on the analysed surfaces, with their shape, colours and dimensions, significantly influence the appearance and composition of the parking spaces, and the area structures are defined according to them. Therefore, the analysis of trees in the parking lots of “Belgrade Waterfront” area was of great importance. In a total of 616 parking spaces 142 trees were recorded. The following were recorded: common hornbeam cultivar with pyramidal habit *Carpinus betulus* 'Fastigiata', black locust cultivar with pink flowers *Robinia pseudoacacia* 'Casque-Rouge', *Celtis occidentalis* L., *Photinia serrulata* 'Red Robin' as lollipop topiary tree and Norway maple trees (*Acer platanoides* L.). With the right choice of trees, elements of nature are introduced into the urban landscape. Each tree is in the function of reducing global warming, air pollution, saving energy, identity of places, habitat for birds and insects, preserving biodiversity, but also inspiration, that is, trees can be viewed as a collection of art sculptures.

ACKNOWLEDGEMENT

The Ministry of Education, Science and Technological Development is financing the scientific research work of the University of Belgrade - Faculty of Forestry in 2022 on the basis of the Agreement on the realisation number: 451-03-9 / 2022-14 / 200169.

REFERENCES

[1] S. Gavrilović, Savski amfiteatar – od ideje do realizacije (2007).

[2] Z. Vuksanović Macura, Bara Venecija i Savamala: Železnica i grad, Nasledje; XVI, (2015) 9−26, doi:10.5937/nasledje1516009V.

[3] A. Škorić, Pedološka karta Jugoslavije, Jugoslovensko društvo za proučavanje zemljišta, Beograd (1961).

[4] Urbanistički zavod Beograda, Prostorni plan područja posebne namene uređenja dela priobalja grada Beograda- područje priobalja reke Save za projekat „Beograd na vodi”, (2021).

[5] N. Anastasijević, V. Anastasijević, Funkcionalnost zelenih površina Beograda, Monografija, Šumarski fakultet, Beograd (2012).

[6] K. Lynch, The Image of the City, United States of America (1960).

[7] T. Simonds, The Benefit of Trees in Parking Lots: Analysis of Six New England Cities and Recommendations for Better Development, Plymouth State University, Plymouth, New Hampshire (2018).

STATE, FUNCTIONS AND PERSPECTIVES OF DENDROFLORA IN THE SCHOOLYARD OF THE MEDICAL SCHOOL IN BELGRADE

Mirjana Ocokoljić [1*], Djurdja Petrov[1], Andreja Tutundzić[1], Dragana Skočajić[1], Smiljana Petrović[1]

[1]University of Belgrade, Faculty of Forestry, Kneza Višeslava 1, 11000 Belgrade, SERBIA

[*]*mirjana.ocokoljic@sfb.bg.ac.rs*

Abstract

Schoolyards are a special type of public green spaces, with a special purpose. It is very important that the environment in which students spend time is pleasant and healthy. In addition to improving environmental conditions, greenery and vegetation have a positive effect on mental and physical health. The choice of plant material for schoolyards is also very important due to the sanitary-hygienic and aesthetic functions that greenery provides. However, it is necessary that the schoolyard plants are chosen for educational reasons. Therefore, the bioecological analysis of woody plants in the area of the Medical School in Zvezdara was performed, because of the importance of the educational role of greenery. A total of 214 tree individuals and 2 groups of shrubs, of 26 woody taxa from the subclass Pinidae and subclass Magnoliidae, were recorded. The research confirmed the small diversity of the dendroflora in the area of the Medical School in Zvezdara, Belgrade, and the need to enrich the dendrofond of the schoolyard in order to be in the function of an outdoor classroom that activates all the senses.

Keywords: landscape architecture, garden of educational institutions, education

INTRODUCTION

According to the Decision on the arrangement and maintenance of green and recreational areas [1], schoolyards are public green areas for special purposes. They must fulfil sanitary, engineering-technical, architectural-urbanistic, psychological, aesthetic and cultural-educational functions. Plants, especially dendroflora, are of great importance in terms of structure, shape and characteristics because they affect the microclimate (increase humidity and reduce temperature and wind speed), reduce air pollutants, protect soil from erosion, mitigate reflection, etc.

The urban role of the green infrastructure is especially emphasized in the structure and improvement of modern cities, where the right choice of plant material is very important [2,3]. Having in mind the above, the paper analyses the dendroflora of the schoolyard of the first medical school in the Balkans, founded in 1921 – the Medical School on the territory of the municipality of Zvezdara in Belgrade.

MATERIAL AND METHOD

In the schoolyard of the Medical School (44°80"41" north latitude and 20°49'97" east longitude), dendroflora was analysed using the method of bioecological analysis [4]. The aim was to record the existing dendrofond, spatial distribution and presence of individual taxa, analyse their quantity, but also identify proposals for improving the existing situation, maintenance and their protection as well as the management process.

The research included the collection of data on environmental conditions, as well as field recording and mapping of individuals. With regard to the observed dendrofond, the paper specifically points out the climatic parameters for the reference period 1991–2020 [5]. The climate that prevails in Belgrade is temperate-continental with large deformations of climatic parameters due to the high percentage of urban areas. In the last 30 years, the average annual air temperature was 13.2°C. The average number of ice days with temperatures below 0°C was 13.9 days. When analyzing the average annual precipitation in the period from 1991 to 2020, their amount was 698.8 mm, while the average number of days with snow cover during the year was 35.2. The mean annual relative humidity for the reference period was 67.8%. The most common wind that has appeared in Belgrade for the last thirty years is the south-east wind, Košava. The schoolyard of the Medical School in Zvezdara is located at an altitude of 175.5 to 179.5 m. The total area of the yard is 19579 m^2, of which greenery and grass occupies 13068 m^2, while the paths and plateaus occupy 6511 m^2.

The adaptability of the dendroflora was analysed on the basis of the following parameters: tree height, trunk diameter at breast height, trunk height without branches and crown diameter. The state of vitality and decorative value were also assessed. The character of growth was determined by measuring tree heights by the altimeter (Haglof Vertex IV) and measuring the trunk diameters at breast height with a standard tree calliper (Mantax), while the crown diameter was measured by tape as field projection of crown. The height and width were measured for shrubs. Decorative value and vitality were rated on a scale of 1 to 5 (1 - a tree without aesthetic values, and 5 - a tree with distinct aesthetic qualities and good health). The collected data on dendrometric characteristics, as well as health and aesthetic values of the observed individuals were statistically processed.

RESULTS AND DISCUSSION

There are a total of 214 trees and 2 groups of shrub taxa in the school yard. Overall, 26 woody taxa were recorded. Seven tree taxa were recorded and analysed from the subclass Pinidae Cronquist, Takht. & Zimmerm.: *Abies concolor* (Gordon & Glend.) Lindl. ex Hildebr., *Calocedrus decurrens* (Torr.) Florin, *Chamaecyparis lawsoniana* (A. Murraybis) Parl., *Picea omorika* (Pancic) Purk., *Platycladus orientalis* (L.) Franco, *Pseudotsuga menziesii* (Mirb.) Franco and *Thuja occidentalis* L.; and one shrub: *Juniperus chinensis* ’Grey Owl’.

There were 17 tree taxa recorded and analysed from subclass Magnoliidae Takhtajan: *Acer negundo* L., *Acer platanoides* L., *Acer psudoplatanus* L., *Betula pendula* Roth, *Fraxinus ornus* L., *Fraxinus pennsylvanica* Marshall, *Juglans regia* L., *Malus sylvestris* (L.) Mill., *Morus alba* L., *Prunus avium* (L.), *Prunus cerasifera* Ehrh., *Prunus cerasifera* ’Atropurpurea’, *Robinia pseudoacacia* L., *Sambucus nigra* L., *Styphnolobium japonicum* (L.) Schott, *Scandosorbus intermedia* (Ehrh.) Sennikov, *Tilia tomentosa* Moench; and one shrub: *Berberis thunbergii* ’Atropurpurea’.

From the schoolyards' 26 taxa, 10 autochthonous, 13 allochthonous species and 3 cultivars were recorded. One endemic species was recorded – *P. omorika* (Pancic) Purk. (7 trees). Medically important plants are represented with 4 taxa (*A. concolor* (Gordon & Glend.) Lindl. ex Hildebr., *P. avium* (L.), *S. nigra* L. and *T. tomentosa* Moench). A total of 6 taxa are honey-bearing (*M. sylvestris* (L.) Mill., *P. cerasifera* Ehrh., *P. cerasifera* 'Atropurpurea', *R. pseudoacacia* L., *S. japonicum* (L.) Schott and *T. tomentosa* Moench). Useful fruit taxa are also found in the schoolyard (6): *J. regia* L., *M. sylvestris* (L.) Mill., *M. alba* L., *P. avium* (L.), *P. cerasifera* Ehrh. and *P. cerasifera* 'Atropurpurea'. There are also two invasive species in the study area: *A. negundo* L. (10 specimens) and *F. pennsylvanica* Marshall (2 specimens), which are proposed for removal. Three taxa of less poisonous plants have been recorded (*P. orientalis* (L.) Franco, *T. occidentalis* L. and *J. chinensis* 'Grey Owl').

When it comes to the percentage of use of deciduous and evergreen individuals, the presence of deciduous use prevails with 68.3% (144 individuals), while 32.7% (70 individuals) of evergreens. The ratio of the application of deciduous and evergreen taxa corresponds to the recommendations in landscape architecture that 1/3 of the species in the green area should be evergreen [6].

Comparative analysis of tree heights at the individual level reveals the species *P. menziesii* (Mirb.) Franco (12.5 m) with the highest height, while with the lowest height (2 m) is of the taxon: *Ch. lawsoniana* (A.Murraybis) Parl. At the population level, the highest average tree height was achieved by the species *P. menziesii* (Mirb.) Franco (9.8 m), and the lowest average height by the species *P. cerasifera* Ehrh. (3.4 m).

The analysis of the diameter at breast height (DBH) of trunk at the individual level highlights the species *A. platanoides* L. (48 cm) with maximum DBH, while the species *Ch. lawsoniana* (A. Murraybis) Parl. stands out with minimum DBH (4 cm). At the population level, *A. platanoides* L. (29.3 cm) had also maximum average DBH, and *S. nigra* L. (4.5 cm) had minimum average DBH (Table 1).

The analysis of decorative value and vitality, at the individual level, selects as many as 18 taxa with the highest marks (5). The lowest grade (1) for decorative value was given to 15 trees of 9 taxa, and to 19 trees of 12 taxa for vitality. At the population level, the species *P. menziesii* (Mirb.) Franco has the highest average values of vitality and decorativeness with a score of 4.7 and 4.6, respectively. The taxon of the least vitality and decorativeness, which has not adapted to environmental conditions, is *Ch. lawsoniana* (A. Murraybis) Parl. (Table 1). Both shrubs, *B. thunbergii* 'Atropurpurea' and *J. chinensis* 'Gray Owl'. have the highest grades (5) of both vitality and decorative value.

Table 1 *Recorded parameters of the analysed dendroflora in the schoolyard of the Medical School in Zvezdara*

Taxa	**Number of specimens**	**Tree height (m)**	**Tree height without branches (m)**	**Trunk diameter at breast height DBH (cm)**	**Crown diameter (m)**	**Decorative value (1–5)**	**Vitality (1—5)**
A. concolor (Gordon & Glend.) Lindl. ex Hildebr.	13	7.6	3.1	22.3	3.3	3.1	2.8
A. negundo L.	10	5.9	0.93	15.7	4	3	4.8
A. platanoides L.	41	9.7	2.1	29.3	5.9	4.4	4.0
A. psudoplatanus L.	1	5.5	0.5	10	2	5	5
B. thunbergii ’Atropurpurea’	1 group	2	/	/	18 m^2	5	5
Betula pendula Roth	12	9.1	2.4	24.1	4.1	4.6	3.4
C. decurrens (Torr.) Florin	1	8.5	1.6	45	6	5	5
Ch. lawsoniana (A.Murraybis) Parl.	2	5.2	1.3	11	1.5	1	1
F. ornus L.	1	10	1.9	35	6	5	5
F. pennsylvanica Marshall	2	3.25	0	9.5	3	1	4.5
J. regia L.	35	5.6	1.7	10.7	2.9	3.5	4.5
J. chinensis ’Grey Owl’	1 group	2.2	/	/	6.3 m^2	5	5
M. sylvestris (L.) Mill.	2	3.7	1.2	12.5	3.2	2	1.5
M. alba L.	7	6.6	0.5	15.7	5.8	3.9	4.4
P. omorika (Pancic) Purk.	7	4.5	1.7	11.8	2.3	3.7	3.7
P. orientalis (L.) Franco	11	5.5	1.0	13.4	3.1	2.6	2.4
P. avium (L.)	4	5.5	0.9	9	2.2	3.5	3.7
P. cerasifera Ehrh.	4	3.4	0	12	2.6	4	4.2
P. cerasifera ’Atropurpurea’	5	7.8	1.2	20	5	4.6	3.2
P. menziesii (Mirb.) Franco	31	9.8	3.0	25.3	4.2	4.7	4.6
R. pseudoacacia L.	10	9.2	2.7	16.6	3.9	4.1	4.3
S. nigra L.	2	3	0.1	4.5	1.7	2.5	2
S. japonicum (L.) Schott	2	3.7	0.5	9.5	3.2	4.5	4
S. intermedia (Ehrh.) Sennikov	4	6.9	1.2	21.7	3.5	4.5	3.2
T. occidentalis L.	5	4.5	0	9.6	1.5	3	2.8
T. tomentosa Moench	2	6.5	1.1	18.5	4.5	5	4.5

CONCLUSION

The use of proper plant material in schoolyards is very important not only because of environmental and social functions, but also because of education and raising students' awareness of the importance of preserving, maintaining and benefiting from medicinal plants and fruit trees.

The presence of 26 different woody taxa, 22 tree taxa and 2 shrub taxa was recorded in the schoolyard of the Medical School in Zvezdara. The values of dendroflora in schoolyards are higher if their vitality and decorativeness are at the highest level. The analysis of vitality and decorative value concluded that the average state of vitality was 3.6, and decorativeness 3.7. Taxa from the subclass Magnoliidae, showed greater adaptability compared to taxa from the subclass Pinidae. Based on the analysed characteristics of dendroflora, 9 taxa with substantial adaptability and high average decorative value over 4.5 are distinguished: *A. psudoplatanus* L., *B. pendula* Roth, *C. decurrens* (Torr.) Florin, *F. ornus* L., *P. cerasifera* ’Atropurpurea’, *P. menziesii* (Mirb.) Franco, *S. japonicum* (L.) Schott, *S. intermedia* (Ehrh.) Sennikov and *T. tomentosa* Moench. Ten autochthonous taxa are present on the investigated area, so the diversity of autochthonous dendroflora needs to be supplemented with woody species specific to Serbia. In order to enrich the dendroflora, it is proposed to increase the number of endemic and relict species (*Forsythia europaea* Degen & Bald., *Pinus heldreichii* Christ and *Pinus peuce* Griseb.), but also exotic plants (*Magnolia grandiflora* L. and *Sequoiadendron giganteum* (Lindl.) J. Buchholz), which have an educational function. Plant material can also be used as a didactic tool, so it is recommended to increase the use of medicinal and other useful taxa. A proposal was made to remove a large number of *A. negundo* L. taxa (10 specimens) and *F. pennsylvanica* Marshall (2 specimens) which are invasive and belong to the category of weed species.

It is also proposed to increase the use of shrub taxa, which are represented by only 7.7%, as well as the establishment of shaped and free-growing hedges of *Ligustrum ovalifolium* Hassk., *Prunus laurocerasus* L., *Hibiscus syriacus* L. and *Kerria japonica* (L.) DC. to visually isolate, separate the schoolyard from the street and guide the walking routes.

ACKNOWLEDGEMENT

The Ministry of Education, Science and Technological Development is financing the scientific research work of the University of Belgrade - Faculty of Forestry in 2022 on the basis of the Agreement on the realisation number: 451-03-9 / 2022-14 / 200169.

REFERENCES

[1] "Službeni list grada Beograda", br. 12/2001, 15/2001, 11/2005, 23/2005, 29/2007, 2/2011, Skupština grada Beograda (in Serbian).

[2] C. Hastie, A summary of the benefits of urban trees accompanied by a selection of research papers and pamphlets, Warwick District Council (2003).

[3] H. Graham, D.L. Beall, M. Lussier, *et al.*, J. Nutr. Educ. Behav; 37 (2005) 147–151.

[4] N. Anastasijević, V. Anastasijević, Funkcionalnost zelenih površina Beograda, Monografija, Šumarski fakultet, Beograd (2012).

[5] Republički hidrometeorološki zavod Republike Srbije: Meteorološki godišnjaci-klimatološki podaci, *Available on the following link:* https://www.hidmet.gov.rs/latin/meteorologija/klimatologija_godisnjaci.php

[6] L. Miller, W. Brown, R. Mercer, *et al.*, Landscape Design - A Student Handbook, Teacher Education Series 9 (3) (1968).

TRACHYCARPUS FORTUNEI (HOOK.) H. WENDL. IN THE CONDITIONS OF CHANGED TEMPERATE CONTINENTAL CLIMATE IN BELGRADE

Mirjana Ocokoljić[1*], Djurdja Petrov[1]

[1]University of Belgrade, Faculty of Forestry, KnezaVišeslava 1, 11000 Belgrade, SERBIA

[*]*mirjana.ocokoljic@sfb.bg.ac.rs*

Abstract

The presence, survival and distribution of plant communities are dependent on various environmental factors-altitude, terrain, exposition, soil type but also climate conditions. Thermophilic plants require a mild climate, without low air temperatures. Due to climate change and suitable temperature conditions in Belgrade, it is increasingly possible to grow certain species of Mediterranean floral element, which have shown exceptional adaptability. This paper presents the species of palm Trachycarpus fortunei (Hook.) H. Wendl. originally from Asia, which has been successfully growing in the municipality of Stari grad in Belgrade for three years.

Keywords: windmill palm, palms, exotic plants, cold-hardy

INTRODUCTION

Serbia has a very rich flora, due to its geographical position. The territory of Serbia is located at the borders of the Pontic-South Siberian, Central European and Mediterranean regions which makes Serbian vegetation particularly diverse. The prevailing climate in Serbia is moderately continental, but there are also influences of the Continental and Mediterranean climates. Exotic plants are often grown in the Belgrade climate, due to their decorative character and diversity. The dendrofond of Belgrade is enriched with the introduced woody species. In recent years, in the capital of Serbia, thermophilic woody species such as crepe-myrtle, laurel, kiwi, loquat, chinaberry, southern magnolia, banana and others can be noticed more often [1–3]. Thus, three years ago, dioecious palm trees-windmill palm *Trachycarpus fortunei* (Hook.) H. Wendl, were planted in Belgrade. This species is native to China and Myanmar (the slopes of the Himalayas). In order to determine the adaptability of this new species in Belgrade, canopy condition, vitality and decorativeness of the recorded specimen of windmill palm were analysed.

MATERIAL AND METHOD

This paper analyzes the effects of climate change on the presence and adaptability of *Trachycarpus fortunei* (Hook.) H. Wendl. on the green area in Belgrade, in the conditions of changed temperate continental climate. Climate conditions comparison was performed between the period from 2019 to 2021 (2022) and the thirty-year period from 1991 until 2020. The analysis of meteorological data is based on the data from the Republic Hydrometeorological Service of Serbia. Throughout the three-year period from 2019 to 2021, the average annual air temperature in Belgrade was 14.1°C, which is 1°C higher than the reference thirty-year period 1991–2020, when the annual air temperature averaged 13.2°C. Also, the average annual minimum air temperature was higher during the period from 2019 to 2021 (9.9°C) compared to the thirty-year period, when it was 9.1°C. Based on the data for monthly absolute minimum air temperatures in the three-year period, there is an increase in absolute minimum air temperatures compared to the previous thirty-year period. The lowest absolute minimum air temperature was -8.8°C in January 2022, and in the previous thirty-year period (1999–2020) it was -14.6°C.The average annual maximum air temperature also increased by 1°C, in the period from 1991 to 2020. It was 18.0°C, while in the period from 2019 to 2021 it was 19.0°C. The maximum daily precipitation at the annual level in the period from 2019 to 2021 in Belgrade was in the month of June (64.9 mm), while in the previous thirty-year period (1991–2020) it was in the month of May (109.8 mm). The most abundant precipitation occurs in late spring and early summer, which is very favourable for vegetation. Snow falls less often in Belgrade and does not last long. The monthly absolute maximum snow cover height for the period from 2019 to 2021 in Belgrade was 32 cm, while in the last thirty-year period, it was 52 cm.

Six windmill palms *Trachycarpus fortunei* (Hook.) H. Wendl were noted in the municipality of Stari grad, in the Kalemegdan Park, near the art pavilion of Cvijeta Zuzorić. The specimens were imported from Spain by JKP Zelenilo Beograd and planted in two rows of three. The studied individuals of windmill palm were located at coordinates 44°82"16" north latitude and 20°45'41" east longitude, on a sunny open area, at an altitude of about 111 m. Field research included recording and mapping the individuals of *Trachycarpus fortunei* (Hook.) H. Wendl. in the Kalemegdan Park. The height of the tree without leaves (measured by the altimeter Haglof Vertex IV), and the trunk diameter at breast height (measured by tree calliper Mantax) were analysed, while the decorative value and vitality were evaluated by scoring from 1 to 5; where 1 is an individual without aesthetic values, low vitality, and 5-an individual with distinct aesthetic qualities, good vitality. The number and quality of compound leaves were also recorded.

RESULTS AND DISCUSSION

Family *Arecaceae* Bercht. & J. Presl, which is in the order of Arecales Bromhead, contains 182 genera, among which is the genus *Trachycarpus* H. Wendl. Genus *Trachycarpus* H. Wendl. includes 10 species of palms, low or medium height, with fan-shaped leaves, built out of dense fibres from which ropes and nets are made. Native range of the genus *Trachycarpus* H. Wendl. is Asia, from the Himalayas to China. Species *Trachycarpus fortunei* (Hook.) H. Wendl., from this genus, is one of the most tolerant and cold-hardy palms [4–6].

The windmill palm (*Trachycarpus fortunei* (Hook.) H. Wendl.) tolerates up to -15°C (-20°C), but young individuals can die at -8°C. In its natural habitat it can grow at an altitude of 100 to 2,400 m. This palm is a dioecious, evergreen palm. It usually reaches a height of 12 m, although specimens that can reach 20 m have been recorded. A diameter at breast height can be 15 to 30 cm. A crown, whose diameter can be about 3 m, is formed by 40 to 50 leaves gathered at the top of the stem. The leaves are compound, fan-shaped and 1.9 m long [7–9].

Table 1 *Recorded parameters of the analysed Trachycarpus fortunei (Hook.) H. Wendl. individuals in Belgrade*

Specimen number	Tree height without leaves (m)	Trunk diameter at breast height (cm)	Number of leaves	Vitality (1–5)	Decorative value (1–5)	Remarks
1.	2.38	28	34	5	5	-
2.	2.51	24	28	5	5	6 inflorescences
3.	2.46	23	23	3	3	1 dry leaf
4.	2.52	27	24	4	4	-
5.	2.45	26	26	5	5	1 dry leaf
6.	2.53	29	28	4	5	-

In the study area, six specimens of *Trachycarpus fortunei* (Hook.) H. Wendl were recorded (Figure 1).

Figure 1 *Trachycarpus fortunei (Hook) H. Wendl. specimen a) No.1; b) No.2; c) No.3; d) No.4; e) No.5; f) No.6 in Belgrade*

The average height of a stem without leaves of analysed individuals is 2.47 m. The lowest height is 2.38 m (Individual No.1), and the highest is 2.53 m (Individual No.6). Since the analysed individuals were planted three years ago, they are still not expected to reach the heights stated for the species in the literature. It takes 10 to 20 years for the species to reach its maximum height. The mean value of the trunk diameters for all 6 individuals is 26.2 cm. The individual with the largest diameter at breast height is No.6 (29 cm), while the individual No.3 is with the smallest trunk diameter (23 cm). However, to determine their adaptability and growth rate, it is necessary to continue monitoring these specimens in the future.

The phenophase of flowering and the formation of male inflorescences were observed on individual No.2. The average number of leaves for all six individuals is 27.8. Individual No.1 has 38 leaves, which is approximate to the literature data, and this is also the largest number of leaves compared to other specimens.

The top and the edge of the leaflets in the compound leaves are brown, which indicates the freezing of the top at low temperatures. Unfavourable meteorological conditions in December 2021, heavy rain showers, followed by a sudden drop in air temperature and heavy, wet snow, probably led to leaf damage. Therefore, the question arises whether the specimens are sufficiently protected with reeds and nylon during the winter months (Figure 2a and b).

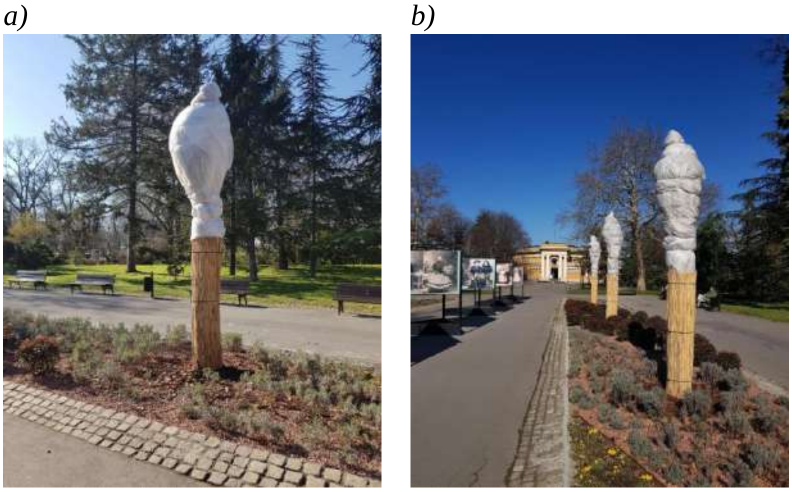


Figure 2 *Winter protection of Trachycarpus fortunei (Hook.) H. Wendl. specimen a) No.1; b) No.4, No.5, No.6 in Belgrade*

Vitality and decorative value assessments were conducted using comparative analysis (Table 1). The investigated specimens of windmill palm have a very good average rating of vitality: 4.3, while the average rating of decorativeness is excellent: 4.5. Individuals No.1 and No.6 (Figure 1a and f) are singled out with the highest marks for both vitality and decorativeness, and on the basis of appearance they stand out from other individuals. Specimen No.3 (Figure 1c) stands out as the tree with the lowest grades for vitality and decorativeness, with grades 3 and 3. This specimen has also one dry leaf, as well as the smallest number of leaves in the group, so it looks the least representative.

Based on the results obtained in the paper, six individuals of windmill palm showed good acclimatisation in a period of three years in the conditions of climate change in Belgrade. However, it is necessary to continue with the research of hardiness and monitoring of leaf damage, as well as the reactions of windmill palm to air temperatures in the winter, but also the appearance of early and late freeze.

CONCLUSION

Due to climate change and global warming, many plant species have changed their distribution. With the increase of air temperature, plant species expand their habitat, but they are also introduced by humans because of their ornamental values. Thus, new exotic plant species are grown in areas non specific to them, where many of them will be acclimatised, while others will fail to survive in the new environment.

Six specimens of palm species, *Trachycarpus fortunei* (Hook.) H. Wendl, were recorded in the Kalemegdan Park, Belgrade. Individuals have very good and excellent grades of vitality and decorative value. Individual No.1 and No.6 stand out as the most representative. On all specimens, a change in the colour of the top and edges of the leaflets was noticed, due to low air winter temperatures. Due to all of the above, it is necessary to continue the research and determine will the windmill palm continue to grow successfully after a longer period of years, in the main Belgrade park with maintenance and protection measures during the winter.

ACKNOWLEDGEMENT

The Ministry of Education, Science and Technological Development is financing the scientific research work of the University of Belgrade - Faculty of Forestry in 2022 on the basis of the Agreement on the realisation number: 451-03-9 / 2022-14 / 200169.

REFERENCES

[1] E. Vukićević, K. Žujović, Šumarstvo, XXIV (11–12), Beograd (1971) (9–14).

[2] O. Purić–Daskalović, Glasnik Šumarskog fakulteta br. 71, 72. Beograd (1989/90) 171–190 (in Serbian).

[3] Đ. Stojičić, M. Ocokoljić, D. Obratov-Petković, Book of Abstracts of XIII OPTIMA Meeting, March 22–26, Antalya, Turkey (2010) 91.

[4] APG IV (2016): Angiosperm Philogeny Group IV - APG IV.

[5] POWO (2022): The International Plant Names Index and World Checklist of Selected Plant Families 2022, *Available on the following link*: http://apps.kew.org/wcsp/

[6] FOC (2022): "Trachycarpus fortunei". 23. Flora of China: 145, *Available on the following link*: www.efloras.org

[7] C.J. Chen, Y. Zhang, *et al.*, Kem. Ind; 64 (2015) 467–472.

[8] T. Reichgelt, C.K. West, D.R. Greenwood, Sci. Rep; 8 (1) (2018) 4721.

[9] J. Zhu, J. Li, C. Wang, H. Wang, Forests; 10 (2019) 1130, DOI: 10.3390/f10121130.

GREEN OASIS EFFECT ON URBAN ENVIRONMENT

Marija Perkunić[1,2], Stefan Vukić[1], Zlata Živković[2], Vladanka Stupar[2], Markola Saulić[2*]
[1]Environmental Association “Friends of Čačalica”, Moše Pijade bb,
12000 Požarevac, SERBIA
[2]Academy of Applied Technical Studies Belgrade, College of Applied Engineering Sciences,
Nemanjina 2, 12000 Požarevac, SERBIA
[*]*markola.saulic@vts-pozarevac.edu.rs*

Abstract

Air pollution is a topic that has been attracting a lot of the public attention in the recent few years. One of the most important tasks of urban policy makers is planned creating of green oases and infrastructure which would contribute to healthier and better quality life of inhabitants. The city of Požarevac has its own urban lungs. Memorial Park Čačalica, which was originally planned and designed in memory of patriots who laid their lives for the people of Braničevo District during the WWI and WWII, has become a green oasis over time. In the last few decades Čačalica with 26.6 ha of green areas and with over 28,000 of trees and undergrowth and a few hundred species of wild plants has been providing the inhabitants of Požarevac with clean air and at the same time it has been preserving plant and animal diversity.

Keywords: green oasis, Požarevac city, memorial park Čačalica, urban lungs

INTRODUCTION

Air pollution is one of the greatest environmental health hazards. In 2019, 99% of the world population was living in places where the WHO (World Health Organization) air quality guidelines levels were not met. Air pollution is now the leading environmental cause of mortality, causing premature deaths twice the number of deaths due to road traffic accidents a year [1]. As evidence of its devastating impacts of air pollution on human health air pollution continues to increase, improving urban air quality has become one of the most pressing tasks which policy makers are facing world-wide. The introduction of green infrastructure is seen as a win–win solution to urban air pollution, reducing ground-level concentrations without imposing restrictions on traffic and other polluting activities [2]. The interest in air pollution topic has increased drastically with the research and mass measuring of air pollution in cities all over Serbia. Knowledge particulate matter, ozone, nitrogen dioxide and sulfur dioxide including particulate matter (PM), ozone (O_3), nitrogen dioxide (NO_2) and sulfur dioxide (SO_2) are essential step for the quality life of the people in urban areas. The city of Požarevac (44°30′ and 44°48′ north latitude and between 21°03′ and 22°00′ east longitude), as an urban representative with approximately 60,000 inhabitants is famous for its industrial settlement Kostolac with the thermal (coal-fired) power plant Kostolac (TE Kostolac or TE-KO). Eight out of 4 European thermal power plants with the greatest SO_2 emission are situated in the Western Balkans, while four of them are in Serbia. On average, thermal power plants in the Western Balkans emit 20 times more SO_2 and 16 times more PM particles than thermal power plants in the European Union [3]. For these reasons, at the end of 2020, a flue gas desulphurization system was built and put into operation at TE Kostolac B, which brought SO_2 and NO_2 emissions within the framework of EU standards. Also, the installation of electrostatic precipitators has reduced emissions of powdered substances in flue gases below 20 mg m^3. However, the city is threatened by a high level of air pollution due to the proximity of the thermal power plant (14.87 km) and intensive individual fireboxes, thanks to Memorial Park Čačalica air quality is better than expected (Figure 1) [4]. The green oasis Čačalica, hill with on area of 26.6 ha (203 m above the sea level), is located on the southeast outskirts of the city [5].

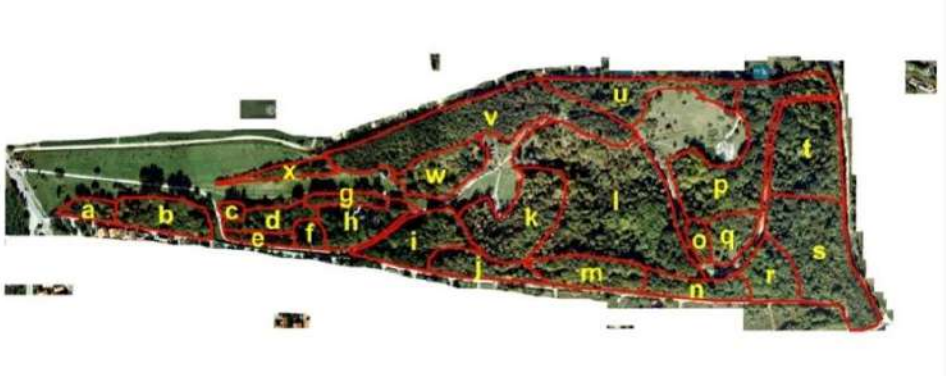


***Figure 1** Topographic view of the Čačalica Memorial Park*

THE HISTORY OF THE MEMORIAL PARK ČAČALICA

The first data on Čačalica date back from the Turkish documents more than 300 years ago, where it is described as a neglected village pasture overgrown with elm trees (*Ulmus minor*), hawthorn woods (*Crataegus monogyna*), elder trees (*Sambucus nigra*), blackthorn (*Prunus spinosa*), rosehip (*Rosa canina*), bramble (*Rubus fruticosus*). Black locust (*Robinia pseudoacacia*) and English oak (*Quercus robur*) grew sporadically on the outer edge of the hill and wetland soil with its unpleasant odor of decay was a real mosquito breeding place. During WWI the hill of Čačalica with its trees and undergrowth was an obstacle to the aggressors and for the occupying forces in the WWII the dense forest was a threat and a constant cause of fear. But at that war period all the trees were cut down just within 48 hours. Deforested Čačalica was as a shooting place and gravesite for soldiers and patriots. Since then it has become the symbol of heroism, an eternal resting place and a memorial park to the unknown heroes [6]. As a tribute to those who laid their lives for the well-being of people in Braničevo District several monuments were built in Čačalica (1953, 1955, 1962, 1963, 1986) [7].

ČAČALICA DIVERSITY

Records show that “the smell of gunpowder was still lingering” when the Forestry Department of People’s liberation committee in Požarevac took into consideration the possibility of planned reforestation. The first reforestation with 1,300 tree seedlings was started on 8 March in 1946 by 350 students from Požarevac Gymnasium and in the same year over 20,000 tree seedlings of a black locust (*Robinia pseudoacacia*) and 150 kg of English oak acorns (*Quercus robur*) were planted [5].

Although trees have been planted on Čačalica every year since the whole process began the results were really poor because the trees failed to establish themselves and flourish. It used to be said that even "Romans have given up on" the specific soil of Čačalica due to its sticky loamy clay and wetland soil. Forest Engineer Žika Stokić initiated the planned reforestation with ten-year-old tree seedling of black pine (*Pinus nigra*), by founding an environmental movement "Pokret Gorana" which covered the swampy land with a huge amount of soil and planted thousands of tree seedlings the forest has been revived [6]. There was an intensive work concerning the drainage of surface waters by constructing 500 m long open concrete canals, the mass planting of trees was done from the autumn 1962–1964 and during that period Čačalica was transformed the way it looks now [7].

The most difficult action was organized by as many as 3,000 "Pokret Goran's" activists in the fall of 1967, when 482 Siberian birches (*Betula verrucossa* (*pendula*)) from the Soviet Union were planted on 3.5 ha. It was stated that Siberian birches, unlike domestic ones, are late with vegetation for about twenty days. Their number dropped to 70, presumably due different habitat from the natural one. Since the beginning of planned afforestation, a total of 91,342 seedlings have been planted on 15 ha, and the census between 1970s and 1980s determined that there were 28,763 seedlings of various species [6].

From 2010 until today, the Ecological Society "Friends of Čačalica", originated from the "Pokret Gorana", has taken care of the memorial park with its initiatives and volunteer actions. Today, Čačalica is known for its enviable plant diversity, which includes: 17 species of tall conifers, 6 species of low and ground cover conifers, 70 tall medium-sized deciduous trees, 24 deciduous shrubs, 3 evergreen shrubs and 3 roses [7]. If it is known that a 100-year-old tree with a well-developed crown can have an active leaf area of up to 1,600 m, so that in 1 hour it can absorb about 2.3 kg of carbon dioxide and produce 1.6 kg of carbohydrates and over 1.7 kg of oxygen [8], then Čačalica with its almost 30,000 seedlings is a real benefit for the city of Požarevac. In the oxygen production, the species that can be found in this locality are standing out in the world: Douglas fir (*Pseudotsuga taxifolia* (*menziesii*)), silver fir (*Abies alba*), common beech (*Fagus sylvatica*), sycamore maple (*Acer pseudoplatanus*), planetree (*Platanus aceriforlia*), oak (*Q. robur*, *Q. rubra*) and aspen (*Populus tremula*). Conifers absorb excess heat and they change the microclimate by lowering the air temperature by 2–8 °C, and help to reduce CO_2 and dust particles [9]. However, deciduous tree species are the most effective in protecting the environment when it comes to gaseous pollutants and dust particles characteristic for this area. Birch (*Betula verucossa* (*pendula*)) and yew (*Taxus baccata*) are the most important in the attachment of dust particles, while oak and horse chestnut (*Aesculus hippocastanum*) predominatein the absorption of CO_2 [10]. All these species can be found in large numbers on Čačalica.

Today, Čačalica is a real small arboretum because instead of going to Japan, sophora (*Styphnolobium japonicum*) can be seen right here, as well as the Australian giant redwood (*Sequoia dendrongiganteum*), Caucasian fir (*Abies nordmanniana*), Pančić spruce (*Picea omorika*). *S. japonicum* attracts attention with its attractive appearance and healing properties

[11]. *S. dendrongiganteum* is a natural wonder, a long living tree (3,000 years) and it is suitable for afforestation of waste hip in surface mines of mining basins [12] while *Abies nordmanniana* is a fast-growing decorative species that significantly contributes to oxygen production. Pančić spruce (*Picea omorika*) is an endemic of the Balkan Peninsula and a Tertiary relic which shows its importance in terms of global biodiversity preservation [13]. It is also known for the rare species of deciduous conifer taxodium or the swamp cypress (*Taxodium distichum*), an indigenous species of checker tree (*Sorbus torminalis*) and several American red oaks (*Quercus rubra*) [14].

The importance and value of tree forms of Čačalica plants for our flora, and at the same time for the biodiversity preservation on a global level, is shown by the fact that many of them are on the IUCN Red List of Endangered Species – giant sequoia (*Sequoia dendrongiganteum*) since 2011 [15], also in the “Red Book of Flora of Serbia 1” – Pančić spruce (*Picea omorika*), yew (*Taxus baccata*), as a very rare mugo pine (*Pinus mugo*) with only 3 seedlings. These species are considered as endangered and enjoy a high protection level [16].

It is believed that 57,792 m^2 Čačalica is under various grassy and wild species and that over a hundred medicinal plants grow there [7]. Among the very medicinal species are: periwinkle (*Vinca minor*), greater burdock (*Arctium lappa*), comfrey (*Symphytum officinale*), St. John's wort (*Hypericum perforatum*), common and red hawthorn (*Crataegus monogyna* and *C. oxyacantha* (*laevigata*)) [17]. The horticultural project from 2000 included a plan to expand afforestation on the left side of the entrance to Čačalica, where it is planned to plant 197 hardwood seedlings ha, 205 coniferous seedlings ha and 281 shrub seedlings.

CONCLUSION

Although Čačalica is primarily a memorial park, among the citizens it is intensively being raised ecological awareness that it is a real green oasis of the city. The ecological association “Friends of Čačalica” has big conceptual plans for its arrangement as a recreational center and observation point, drainage canals restoration, aquatic biotopes preservation and plant diversity protection. In March 2022 a Memorandum was signed between the City Government of Požarevac and the Ecological Association “Friends of Čačalica” with a joint mission of greening and protecting the city's lungs – Čačalica.

REFERENCES

[1] World Health Organization 2021, WHO Global Air Quality Guidelines: particulate matter ($PM_{2.5}$ and PM_{10}), ozone, nitrogen dioxide, sulfur dioxide and carbon monoxide (2021), p.273, *Available on the following link:* https://apps.who.int/iris/handle/10665/345329

[2] C.N. Hewitt, K. Ashoworth, A.R. MacKenzie, Ambio; 49 (2020) 62–73.

[3] Chronic Coal Pollution – EU action on the Western Balkans will improve health and economies across Europe, HEAL, CAN Europe, Sandbag, CEE Bankwatch Network and Europe Beyond Coal (2019) p.48, *Available on the following link:* www.env-health.org/wp-content/uploads/2019/02/Chronic-Coal-Pollution-report.pdf

[4] IQ*Air, Available on the following link*: www.iqair.com

[5] D. Marjanović, M. Marjanović, Međunarodno savetovanje "Održivi razvoj grada Požarevca i energetskog kompleksa Kostolac", Zbornik radova (2014) 247–256.

[6] D. Bogdanović-Bucić, Čačalica, Centar za kulturu Požarevac (1991).

[7] D. Bogdanović-Bucić, Čačalica, Požarevac (2007).

[8] R.A. Horne, The Chemistry of the Environment, John Wiley & Sons, New York (1978), ISBN10: 0471409448, ISBN13: 9780471409441.

[9] M. Matović, S. Bukvić, D. Jovićić, Zaštita životne sredine i biljni svet, Naučna knjiga, Beograd (1994).

[10] A. Beeby, A.M. Brennan, First Ecology – Ecological Principles And Environmental Issues, Oxford University Press, England (2003) p.386.

[11] M. Josifović, R.M. Sarić, Flora SR Srbije, SANU, Beograd (1986).

[12] M.R Ahuja, Euphitica; 165 (1) (2008) 5–19.

[13] E. Vukićević, Dekorativna dendrologija, Šumarski fakultet, Univerzitet u Beogradu (1996).

[14] B. Jovanović, Dendrologija, Šumarski fakultet, Univerzitet u Beogradu, Naučna knjiga (2007).

[15] The IUCN Red List of Threatened Species, *Available on the following link:* www.iucnredlist.org/

[16] V. Stevanović, Crvena knjiga flore Srbije 1, Ministarstvo zaštite prirodnih bogatstva I životne sredine Srbije, Biološki fakultet, Univerzitet u Beogradu (1999).

[17] S. Rakić, Samonikla flora spomen parka Čačalica Požarevac, Ekološko društvo Požarevac (2010).

APPLICATION OF GREEN AREAS AND GREEN ROOFS IN URBAN AREAS

Anđela Stojić[1*], Dejan Tanikić[1]
[1]University of Belgrade, Technical Faculty in Bor, V.J. 12, 19210 Bor, SERBIA
[*]*astojic@tfbor.bg.ac.rs*

Abstract

Modern city development a large number of cars and industrial plants have led to a dramatic decline in air quality, which in some cities around the world reaches alarming parameters, which are very harmful to public health. In larger cities, during most of the year, air quality is in a moderately harmful and harmful range. Modern urban development, which introduces various new materials and sources of pollution into the urban fabric, should require an increase in the percentage of green areas, in order to maintain air quality at a level estimated to be healthy for human life. Strategic afforestation of parts of cities could have the effect of reducing the amount of harmful particles in the air, planting tall plants would in some way lead to the filtration of city air. The construction of green, vegetation, roofs would mitigate the effect of the heat island, reduce the energy needed to cool buildings, effectively manage atmospheric water, improve air quality, increase biodiversity, reduce noise, etc.

Keywords: energy efficiency, air pollution, green roofs, ecology, green areas

INTRODUCTION

With the increase of the human population, the population density in urban areas also increases. This leads to the conversion of natural, undeveloped areas into construction land, which further causes the degradation of the quality of the environment, especially in urban centers, which is reflected in changing microclimatic conditions, air pollution, noise, etc. [1]. Typical pollutants are present in every environment and in the vicinity of thermal power plants. These include: sulfur dioxide, soot, nitrogen oxides, carbon monoxide and precipitates. Today, there is an increasing tendency to reduce these particles in the air. By building green roofs and increasing vegetation in cities, the negative impact of these particles could be mitigated and thus the quality of the environment improved.

Green roofs date back to 500 BC, when they are mentioned in the hanging gardens of Babylon and ziggurats in Mesopotamia [2,3]. The term green (vegetation) roof is used to describe a roof system whose structure is covered with vegetation located on the top floor of a building or at any elevation of the building and representing its final roof surface. In scientific research, the terms are also used: roof gardens, roof gardens, living roofs and eco roots.

GREEN ROOFS

The issue of green roofs in urban areas has become increasingly important in recent years. The basic question that their application raises is the chance to adapt urban environments to the newly emerging climate change. The application of green roofs brings multiple positive effects on a better quality of life in urban areas:

- Reduces the total energy consumption for heating and cooling facilities
- Contributes to increasing the area under vegetation in urban areas
- Reduces the effect of urban heat islands in summer
- Affects the quality and quantity of atmospheric water
- The impact of their application on air, soil and water pollution is significant
- The impact on reducing elevated noise levels in urban areas is not negligible
- Contributes to the environmental and aesthetic values of urban areas
- The use of green roofs increases vegetation in urban areas

In the long run, green roofs are economically viable and sustainable. Under the green roof, the internal temperature, without additional cooling, is 3–5 degrees Celsius lower than the external temperature. Installing a green roof on the observed building saves 1–15% of annual energy consumption. Planned erection of green roofs can reduce the increase in building temperature by up to 20 degrees Celsius and save up to 80% of the energy required for cooling or heating. By applying a green roof, its lifespan is extended almost three times, roofing materials are protected from mechanical damage, ultraviolet radiation, extreme temperatures, which results in reduced maintenance and repair costs.

Figure 1 *Green roofs in urban areas*

CLASSIFICATION OF GREEN ROOFS

The most commonly used green roof construction consists of a concrete construction, a layer of thermal insulation, a drainage layer, a final layer of soil, ie a medium for growth and planted greenery. The classification of green roofs can be done according to several criteria. The most general division is according to the method of landscaping and maintenance, into:

- intensive landscaping
- extensive landscaping

Intensive landscaping can also be defined as a "roof garden" and includes, in addition to planting trees, shrubs and grasslands, and the construction of water areas and the like. This approach requires constant maintenance in terms of irrigation, plant care, construction maintenance interventions, etc. The costs of such roofs are higher and more suitable for public and commercial buildings.

Extensive landscaping is reduced mainly to grassy areas and low vegetation, which does not require special care and tolerates dry conditions. This type of greening of roofs is more suitable for residential buildings, because maintenance costs are lower.

GREEN ROOFS AND REDUCING THE EFFECT OF URBAN HEAT ISLAND

Another common problem of densely built cities are heat islands, i.e. areas in the city that heat up and reach a higher temperature than their surroundings. The temperature in urban areas rises with the increase of absorbing surfaces that retain the heat they receive during the day and emit it into the environment during the night, which creates hot urban islands. The difference in temperature between the city center and the peripheral parts of the city in the summer months can be up to 10°C, which significantly affects the health and quality of life of residents. Greenery can absorb up to 80% of excess heat energy through soil moisture and vegetation. Green roofs can reduce heat, minimize the heat-absorbing surface, and thus reduce the effects of heat islands. The positive effect is proportional to the size of the surface that the plants occupy.

A study of the impact of the green roof on the thermal islands of Toronto indicates a decrease in temperature maximums during the day from 0.4 to 0.8°C and during the night from 1.1 to 2°C. In that way, they make the steamy summer nights, when the heated asphalt and concrete radiate heat, become a little more pleasant. Green roofs have been proposed as an energy saving solution in many countries with different climatic conditions, but their cooling and heating potential strongly depends on the climate, plant choices and building characteristics [5].

Measurements on the territory of the city of Nis showed that during the summer days, the temperature on the surface of the classic flat roof varied from 35 to 60°C. While for the same period the temperature on the surface of the green roof did not exceed 25°C. This significant difference is further reflected in the air temperature in the rooms under the roof. By reducing heat gains, we also reduce the need to cool the room [5].

Takebayashi and Moriyama [4] examined the characteristics of a green roof compared to conventional flat roofs with different finishes. Experimental research was conducted on the flat roof of the Kobe University building in Japan, which is divided into several sections for this purpose. Table 1 shows the values of solar reflection for each type of roof tested, from which it can be concluded that the lowest value for the green roof. For a complete analysis and final results, it is necessary to take into account all the factors from the external environment, which, according to the authors, have been met and the importance of green roofs from this aspect of construction has been confirmed.

Table 1 *Values of solar reflection for each type of roof tested [4]*

Observed area	Bare soil (substrate)	Vegetation	Concrete	Highly reflective gray paint	Highly reflective white paint
Solar reflection	0.17	0.15	0.37	0.36	0.74

GREEN ROOFS AND MITIGATION OF THE CONSEQUENCES OF EXTREME RAINFALL IN CITIES

Green roofs also help solve the problems that arise during events with an extreme amount of precipitation, which is increasing due to climate change. They are able to absorb a certain amount of water, as well as delay the moment when the largest amount of water reaches the street sewer system. This prevents flooding of the streets and blocking of traffic, both car and pedestrian.

Reduction of runoff during heavy rains is very important for countries like England, where studies are being done on the example of London on how to distribute green roofs around the city and achieve the best effect. Green roofs regulate the largest amount of water in the summer, when the plants are active and when the warm weather promotes evaporation. Green roofs not only retain water, but also act as natural filters for the water found on them, they reduce pollutants, which are transmitted to local drainage systems and eventually flow into surface waters [5].

INFLUENCE OF GREEN ROOF ON REDUCTION OF POLLUTANTS IN AIR

The vegetative layer of the green roof affects the air pollution in the largest percentage by absorbing gaseous pollutants. Inside the plant, these gases react with water to form acids and other chemical compounds. The vegetative layer also stops the spread of solid pollutants, ie PM particles with their contact surface. PM10 carries carcinogenic particles small enough to pass defense in lung tissue and reach deep into human lungs. Some of these particles can be absorbed by the plant while the rest can be easily adhered to the surface of the plant and thus prevent further spread.

A study in Beijing showed that green roofs of 1000 m^2 can capture 160–220 kg of dust per year, reducing the concentration of dust in the atmosphere by about 25 percent. An indirect effect on reducing pollution is achieved with the help of vegetation by modifying the microclimate. By lowering the ambient temperature, the use of vegetation slows down photochemical reactions and thus reduces secondary air pollution such as ozone [5].

LARGE INITIAL INVESTMENTS AND LACK OF INSTITUTIONAL SUPPORT ARE THE REASON FOR THE LACK OF GREEN ROOFS IN SERBIA

While in the rest of Europe, "Green Building" is developing at a dizzying speed, while finding mechanisms by which ecological design will be incorporated into everyday life through do-it-yourself design, in Serbia the situation is a little different. The reason for the small number of green vegetative roofs in our country is the large initial investments, primarily due to the import of materials, as well as the lack of relevant laws and strategies. The benefits are much higher at the level of society than the individual, which is not primarily for investors. All this has the consequence that we still see green roofs in Serbia much more on conceptual projects than in construction.

CONCLUSION

Disruption of the natural environment and degradation of the quality of the environment in urban centers can be reduced by building green roofs. By increasing the area under greenery, numerous advantages are realized, some of which are exposed in the paper, and they concern the ecological aspects of construction. Users of buildings with a green roof benefit from lower outdoor and indoor temperatures in the summer, better flow and cleaner air. This means better thermal comfort and energy savings. Also, less noise and the natural environment have a positive effect on mental health. Green oases in a concrete environment calm and reduce stress levels. By increasing the area under green roofs, positive effects can be achieved at the city level. Vegetative roofs respond to the problems of existing air pollution, reduce the concentration of pollutants in the air and prevent the spread of particles, allowing our cities to breathe better. They are fighting against floods in cities and against urban islands. If we make a comparison between an area completely covered with concrete or stone in the same environment as an identical area covered with vegetation, it can be concluded that there will be a large difference in temperature. When concrete and stone slabs heat up, they emit heat back, while the green surface "absorbs" it and does not return it to the environment. "Dressing" an object in greenery means at least partially compensating for negative influences, returning part of the space to nature, but also giving the built environment an aesthetic and microclimatically more acceptable form.

REFERENCES

[1] M. Stamenkovic, D. Gavrilovic, Proceedings of the 2nd International Scientific Meeting STATE AND TRENDS OF CIVIL ENGINEERING GTZ 2012, 07–09 June, Tuzla (2012) 1051–8.

[2] F. Pacheco-Torgal, J.A. Labrincha, L.F. Cabeza, *et al.*, Eco-efficient Materials for Mitigating Building Cooling Needs. Woodhead Publishing (2015).

[3] U. Berardi, A. Ghaffarian Hoseini, A. Ghaffarian Hoseini, Appl. Energy; 115 (2014) 411–428.

[4] H. Takebayashi, M. Moriyama, Build. Environ; 42 (2007) 2971–2979.

[5] D. Dimitrijević, Prednost zelenih krovova, *Available on the following link:* https://nationalgeographic.rs/ekologija/a38929/Prednost-zelenih-krovova.html

SOIL EROSION ASSESSMENT USING EPM: A CASE STUDY IN THE CATCHMENT AREA OF THE TURKISH BROOK, WESTERN SERBIA

Gordana Šekularac[1*], Tatjana Ratknić[2], Miroljub Aksić[3], Nebojša Gudžić[3], Milica Vranešević[4], Mihailo Ratknić[5]
[1]University of Kragujevac, Faculty of Agronomy,
Cara Dušana 34, 32000 Čačak, SERBIA
[2]Institute of Forestry, Kneza Višeslava 3, 11000 Belgrade, SERBIA
[3]University of Priština, Kosovska Mitrovica, Faculty of Agriculture,
Kopaonička nn, 38219 Lešak, SERBIA
[4]University of Novi Sad, Faculty of Agriculture, Department of Water Management,
Trg Dositeja Obradovića 8, 21000 Novi Sad, SERBIA
[5]Faculty of Applied Ecology - Futura, Požeška 83a, 11000 Belgrade, SERBIA
[*]*gordasek@kg.ac.rs*

Abstract

Soil erosion involves detachment and transport of soil particles from the upper parts of a slope and their deposition at its lower parts. Erosion causes soil degradation and reduces soil productivity. Soil eroded from the upland catchment causes depletion of fertile agricultural soil and the resulting sediment deposited at the river networks creates river morphological change and reservoir sedimentation problems. As regards the initiation of the wearing away of soil particles from the catchment slope, EPM - Erosion Potential Method were used to quantify soil erosion. The aim of this study was to evaluate erosion factors in the catchment area of the Turkish brook, classified as a dry valley and a smaller torrent. The annual erosion intensity is 94.33 m^3 km^{-2} *of soil. Based on natural and anthropogenic factors, the Turkish brook catchment area belongs to erosion category IV, weak intensity, mixed type, with the erosion coefficient of 0.25.*

Keywords: Gavrilović, analytical method, erosion intensity, catchment

INTRODUCTION

Soil is the basis of agricultural production, and thus for the survival of the human race. Formation of soil is a continuing process, but at the same time, there are processes of soil degradation. Process of soil regeneration is very slow. Soil erosion by water is the detachment and transport of soil particles by rainfall or runoff. Several mechanisms contribute to both processes [1]. The effects of different factors of erosion change the soil and geological substrate. Changes in soil can be slow or fast, as a result erosion characteristics are slow or fast. In Serbia more than 90% of the total soil area is affected by erosion of various types and intensity [2]. In the Republic of Serbia, it is registered that each year from an area of 21,000 ha layer of soil depth of 16.0 cm has been removed [3]. In the Republic of Serbia (Central Serbia) there is 1.221 million ha of eroded soil and 36,000 ha is steady now [4].

In the region of Čačak trends of increase in temperature and decrease in rainfall are evident [5]. That climatic changes cause deterioration of the physical characteristics of the soil, increasing its erodibility, reducing the role of protective vegetation, and aggravated its natural and artificial regeneration. All this affects intensification of the process of erosion, both surface and deep forms. Negative impact of the erosion endangers agriculture, forestry and water management, thus there is an increasing need for erosion protection and soil reclamation.

Quantitative amount of erosion and regarding how much sediment it causes, is shown on the part of the river basin Kamenica (part of the Western Morava river basin), its sub-basin, the area of which is its left tributary of the first order, Turkish brook.

MATERIALS AND METHODS

The Turkish brook is located near Čačak (43°53' N; 20°21' E), Western Serbia, and belongs to the catchment of the Western Morava river (Figure 1).

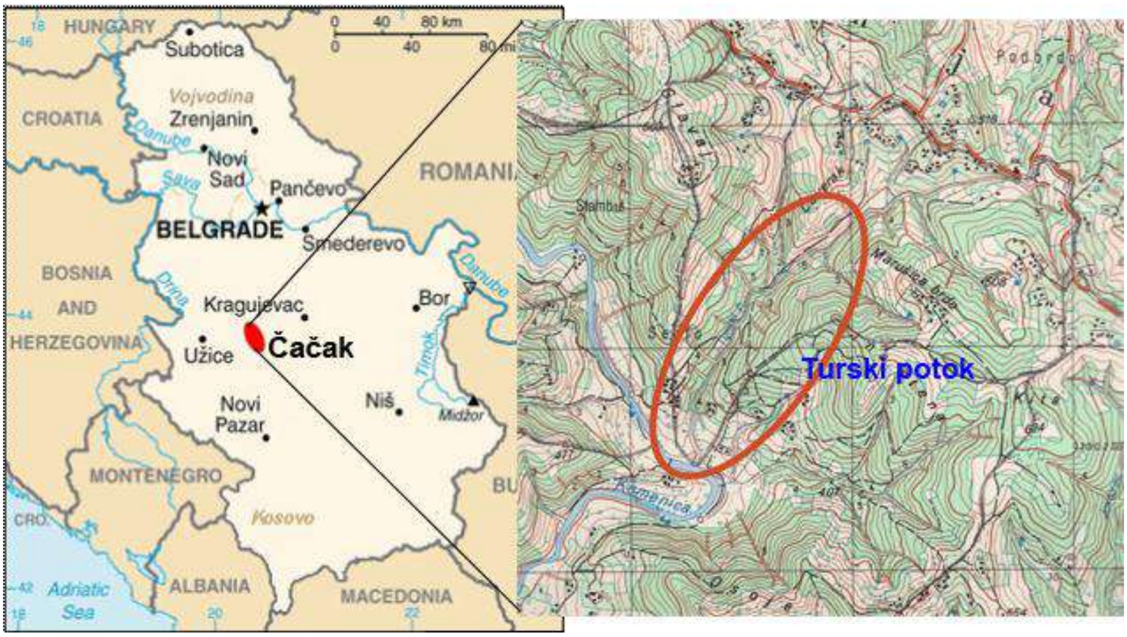


__Figure 1__ The Turkish brook catchment

Using the method of reconnaissance of the ground, the elements of the configuration of the basin were monitored and shown. This basic method is complemented by the use of topographic, geologic and soil maps of certain scales, allowing for defining the nature and impact of natural erosion agents in the studied basin. Using the method of rainfall interpolation by rain-gradient [6] and calculation of air temperature for any altitude [7], meteorological parameters were calculated for the basin. Quantitative indicators of soil erosion were calculated using the analytical method (Erosion Potential Method – EPM) [8], according to the equation (1):

$$G_{yr \times sp^{/1}} = T \times H_{yr} \times \pi \sqrt{Z^3} \times R_u \tag{1}$$

where: $G_{yr\ sp}^{-1}$ - specific annual total erosion-induced sediment yield reaching the confluence, $m^3\ yr^{-1}\ km^{-2}$; T - temperature coefficient of the catchment; H_{yr} - amount of rainfall, mm; π - 3.14; Z - coefficient of erosion; R_u - coefficient of retention of soil in the catchment.

The Erosion Potential Model (EPM), also known as Gavrilović method, is a widespread empirical model used for estimating sediment yield and soil erosion severity on catchment scale. The method considers six individual factors, depending on geology and soil properties, topographic features, climate, soil use and degree of erosion. It has been widely implemented in several countries (Serbia, Croatia, Slovenia, Italy etc), with Greece being one of them, providing reliable results [9].

RESULTS AND DISCUSSION

The basic elements of the basin, which are important for the occurrence of soil erosion, are size, length and its shape. The characteristics of the Turkish brook catchment: area (F) is 1.96 km^2, length (L) 1.87 km, circumference (C) 7.07 km. According to size, Turkish brook is classified as type I [10] as its bed branches mostly in the upper course. Soil and loose geological substrate are washed off this part of the catchment. The middle and lower course of such catchments have no tributaries and are hydrographically undeveloped.

The presented basic elements of Turkish brook catchment and the special features of its relief, the geological substrate, the distribution of soil, climate, and the soil use have contributed that the process of erosion of the basin has specific quantitative indicators.

The main parameters of the Turkish brook catchment relief, agents which have the primary responsibility for the occurrence of erosion, are shown in the Table 1.

Table 1 *The basic parameters of the Turkish brook catchment relief*

Catchment Name: The Turkish brook	
The lowest point of the main watercourse and catchment (B), m	359
The highest point of the main watercourse (C), m	465
The highest point of the catchment (E), m	603
Average slope of the main watercourse in the catchment (I_a), %	5.2
Mean catchment altitude (A_m), m	496.63
Mean catchment altitudinal difference (D), m	137.63
Mean catchment slope (I_m), %	26.1
Coefficient of catchment relief erosion energy (E_r), m $km^{-1/2}$	65.41

Table 1 presents the Turkish brook relief which plays a primary role in the occurrence of soil erosion. The mean altitude (A_m) of the Turkish brook is 496.63 m and the mean altitudinal difference (D) is 137.63 m. The mean slope (I_m) is 26.1%. Relief of a region can also be determined by the coefficient of relief erosion energy (E_r), the value thereof for the Turkish brook catchment being 65.41 m $km^{-1/2}$. An increase in relief parameter values results in increasing intensity of soil erosion in the catchment.

The following agents of erosion, geologic substrates, with their characteristics and diversity contributed to the emergence of the process of erosion in the Turkish brook catchment (Table 2).

Table 2 *Geological substrate of the Turkish brook catchment, coefficient of water permeability (S_1) and erosion resistance*

Catchment name: The Turkish brook	**km^2**	**%**
F_{ppr}- Poorly permeable rocks	1.96	100
• Serpentine	1.10	56.00
• Lake sediments of tertiary clay and loam	0.86	44.00
Coefficient of geological substrate water permeability (S_1)	1.00	
Resistance of geological substrate to erosion	Non-resistant	

The geological substrates of the Turkish brook catchment are: serpentine (1.10 km^2, i.e. 56.00%), lake sediments of tertiary clay and loam (0.86 km^2, i.e. 44.00%), characterized by properties that are poorly permeable rocks, which contributes to the nonresistance soil erosion process. Coefficient of geological substrate water permeability (S_1=1.00), indicates nonresistance of the Turkish brook catchment (Table 2).

The soil and their properties as an agent of erosion, to a lesser or greater extent, contributed to this process. In the area of the Turkish brook catchment, effects of pedogenetic factors are present as well as following soils: eroded vertisol and humus-silicate soils.

Eroded vertisol is profile type A_h–A_hC–C. Eroded vertisol belongs to the deep soil, in the Turkish brook catchment low level of process erosion is expressed. Group of shallow soil of the Turkish brook catchment belongs to humus-silicate soils, with the profile type of Ah-C. In this soil of the studied basin a strong degree process of erosion was represented [11].

The elements of climate which contribute to the occurrence of the process of soil erosion are rainfall, air temperature and soil temperature. The average annual rainfall (R) in the Turkish brook catchment is 751.1 mm, and the mean annual air temperature (t) is 9.3°C, which indicates thet these two elements of climate play an important role on soil erosion in study area.

Representation of the another factor of the process erosion, vegetation, both domestic as well as those of anthropogenic origin, and vegetation cover coefficient (S_2), are shown in Table 3.

The total area under forests and coppice of good spacing ($\sum F_f$) in the Turkish brook catchment is 0.79 km^2 (40.31%), the amount of grasses vegetation ($\sum F_g$) is 0.71 km^2 (36.22%), and the barren land ($\sum f_b$) is 0.46 km^2 (23.47%), so the study area is protected from the effects of erosion (coefficient of vegetative cover, S_2 = 0.77), Table 3.

Table 3 *The structure of the Turkish brook catchment according to type of land use and vegetative cover coefficient (S_2)*

Type of land use		Surface area	
		km^2	%
$\sum F_f$	Forests and coppice of good spacing	0.79	40.31
F_g	Orchards	0.30	15.31
	Meadows	0.16	8.16
	Pastures and devastated forests and coppices	0.25	12.75
	$\sum f_g$	0.71	36.22
F_b	Arable land	0.46	23.47
	Infertile soil	0.00	0.00
$\sum f_b$		0.46	23.47
Vegetation cover coefficient (S_2)		0.77	

In which scope the potential of Turkish brook catchment presents great destructive power and a factor of erosion, can be indicated by elements of hydrographic and hydrological characteristics of the study area. Characteristics of family of torrential flow (F_{tf}) of the Turkish brook catchment are: D; IV; Z=0.25 which means that Turkish brook as a dry valley and a smaller torrent is IV class with erosion coefficient (Z) of 0.25 (weak intensity of erosion processes, of the mixed type). Due to all these characteristic of the Turkish brook catchment a certain amount of sediment is produced and certain intensity of erosion is manifested. Size of process erosion of the the Turkish brook catchment is shown by mean annual erosion sediment (W_{year}=560.25 m^3 year^{-1}). Measured midterm total volume of sediment (G_{year}), which reachs the mouth of Turkish brook is 184.88 m^3 year^{-1}, and the total specific annual erosion sediment that reaches the mouth of the Kamenica ($G_{yr\ sp}{}^{-1}$), is 94.33 m^3 km^{-2} year^{-1}. These data indicate that from the Turkish brook areas disappear per year 0.28 ha of soil by the effect of erosion, the depth of 0.2 m, and 0.06 mm soil disappears from the basin area per year, i.e. 0.42 t ha^{-1} of soil. In Vojvodina, about 85% of agricultural land is affected by aeolian erosion, which causes an average annual loss of 0.9 t of soil per hectare [12].

CONCLUSION

Turkish brook a dry valley and a smaller torrent has its own specific features: IV class destructiveness, coefficient of erosion (Z) 0.25, which indicates the strength of weak erosion of the mixed type. The above, and other factors of erosion of the basin has contributed that annual erosion sediment was 184.88 m^3 year^{-1}, while the intensity of erosion was 94.33 m^3 km^{-2} year^{-1}.

ACKNOWLEDGEMENT

The authors are grateful to the Ministry of Education, Science and Technological development of the Republic of Serbia for financial support (451-03-68/2022-14/200088; 200189; 451-03-68/2022-14/200027) and Provincial Secretariat for Higher Education and Scientific Research of the Vojvodina for financial support (142-451-2578/2021-01/01).

REFERENCES

[1] K. Auerswald, Water erosion, Springer, Dordrecht, Berlin, Heidelberg, New York (2008), p.817, ISBN: 978-1-4020-3994-2.

[2] M. Djorović, R. Kadović, Proceedings of the Ninth Congress of the Yugoslav Association for the Study of land, June 23–27, Novi Sad, Serbia, (1997) 665–677.

[3] B. Spalević, Conservation of soil and water, Faculty of Agriculture, Belgrade-Zemun (1997), p.24.

[4] Statistical Yearbook, Data on eroded areas of soil, Republic Institute for Statistics, Belgrade (2008).

[5] G. Šekularac, Melioration and Agriculture, University of Novi Sad, Faculty of Agriculture, Department of Water Management, Novi Sad (2002), p.14, ISBN: 86-7520-014-5.

[6] O. Bonacci, Manual for hydraulic reclamation, Society for drainage and irrigation of Croatia, Zagreb, Croatia (1984), p.66.

[7] D. Dukić, Hidrology mainland, Science book, Belgrade, Serbia (1984), p.185.

[8] S. Gavrilović, Engineering of torrential flows and erosion, Building, Special Issue, Belgrade, Serbia (1984), p.110.

[9] N. Efthimiou, E. Lykoudi, Bull. Geol. Soc. Greece; 50 (1) (2016) 305–314.

[10] Б.А. Аполлов, Учние о реках, II изд., МГУ, Москва, Советский Союз (1963), p.124.

[11] G. Šekularac, The ratio of the intensity of erosion and degree erodibility of soil of the Kamenica River, Doctoral dissertation, University of Kragujevac, Faculty of Agronomy, Čačak, Serbia (2000).

[12] V. Ličina, Lj. Nešić, M. Belić, *et al.*, Field Veg. Crop Res; 48 (2011) 285–290.

MODIFIED LIGNIN-BASED MICROSPHERES AS A GREEN SORBENT FOR THE REMOVAL OF CHROMIUM IONS

Nataša Knežević[1*], Aleksandar Jovanović[1], Rabab Salih[1], Zlate Veličković[2], Ana Popović[3], Petar Batinić[4], Aleksandar Marinković[1], Jelena Gržetić[2,5]

[1]University of Belgrade, Faculty of Technology and Metallurgy, Karnegijeva 4,
11000 Belgrade, SERBIA

[2]University of Defense, Military Academy, General Pavla Jurišića Šturma 33,
11000 Belgrade, SERBIA

[3]The Academy of Applied Technical Studies, Katarine Ambrozić 3, 11000 Belgrade, SERBIA

[4]Institute for Medicinal Plant Research "Dr. Josif Pančić", Tadeuša Košćuška 1,
11000 Belgrade, SERBIA

[5]Military Technical Institute, Ratka Resanovića 1, 11000 Belgrade, SERBIA

natasaknezevic94@gmail.com

Abstract

The unique chemical structure of lignin shows the possibility of its application as a basic material for the sorption of various pollutants from water. In this paper, the newly synthesized porous lignin-based material was used to remove Cr(VI) ions. Modified lignin microspheres (LMS) were synthesized by the process of inverse copolymerization of kraft lignin with poly (ethylene-imine), and amino modified iron oxide (magnetite) using epoxy-functionalized cross-linker. The shape of obtained adsorption material was partially spherical to spherical. The functionalization was performed to improve the pollutant removal capacity. Structural and surface characteristics of the LMS microspheres were characterized by Brunauer-Emmett-Teller method (BET), Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM) and point of zero charge pH (pH_{PZC}). The maximum adsorption capacity for oxyanion Cr(VI) was 77.024 mg g^{-1}obtained by Langmuir adsorption isotherm at 35°C. Based on kinetic studies, the adsorption process follows a pseudo second-order model. Thermodynamic parameters have shown that the adsorption process is endothermic and spontaneous. LMS is an environmentally friendly, cost-effective and therefore promising adsorbent for the removal of Cr(VI) with efficient adsorption and reusability.

Keywords: lignin-based sorbent, heavy metal removal, adsorption, wastewater treatment

INTRODUCTION

In recent years, a large amount of scientific research has been based on the use of natural materials to remove contaminants from polluted water. In order to eliminate them, several methods have been discovered, among which adsorption stands out as a very flexible, efficient and reliable method [1]. Heavy metal ions are stable, highly toxic and non-biodegradable pollutants. In order to make their removal more efficient and economical, the naturally available materials and nanoparticles are most often used as adsorbents, because of the developed specific surface, higher porosity and larger number of functional groups.

Natural lignocellulosic materials, which are cellulose, lignin and hemicellulose, are very popular because of their structure. Lignin, the second most abundant natural polymer besides cellulose, includes various structural groups including carboxyl and phenolic units. It is continuously researched in order for lignin to reach its full potential as an ecological bio-adsorbent for the efficient removal of pollutants from wastewater [2]. Chemical modifications made to the structure of lignin strengthen its affinity, resulting in improved miscibility with other polymer matrices, whereby composites of improved performance can be obtained [3].

The subject of this study is the synthesis of adsorption materials from kraft lignin, using the procedure of suspension copolymerization, followed by additional modification of the obtained material with iron oxide nanoparticles (magnetite). Thus, synthesized and chemically modified material was used to remove chromium oxyanion from water in the batch system.

MATERIALS AND METHODS

Materials

The following materials were used to optimize LMS microspheres and adsorption processes: chloropropane epoxy (Merck Schuchardt), kraft lignin (KL), liquid paraffin oil and poly (ethylene imine) grafting agent (PEI) (Sigma-Aldrich), sodium alginate (medium viscosity) and sodium lauryl sulphate (Centrohem). Iron (II)-chloride and iron (III)-chloride (Merck) were used for the synthesis of magnetite. The chromium solution (10 ppm) was made using a standard manufactured by Carl Roth Gmbh.

Preparation of adsorbent and adsorption experiments

Lignin microspheres were synthesized by the copolymerisation of lignin with PEI, amino modified magnetite in liquid paraffin/water suspension using chloropropane epoxy cross-linker. Sodium dodecyl benzenesulfonate and sodium 5 wt% alginate solution was used as emulsifier. The synthesis procedure is developed by Popovic *et al.* [4].

Evaluation of adsorption efficiency of Cr(VI) oxyanions on LMS were performed at temperatures of 25 °C, 35 °C, 45 °C with variation in sample weight (1, 2.5, 5, 7.5 and 10 mg) and contact time (5, 10, 15, 30 and 60 min) with continuous stirring. A volume of 10 ml of Cr(VI) solution with a concentration of C_i=10 mg L^{-1} and pH value 6 was used in order to determine the efficiency and define the optimal conditions for adsorption on LMS materials. The calculation of adsorption capacities was performed using the appropriate equation [5].

Material characterization

The synthesized sorbent was recorded using Fourier transform infrared spectrometry (FTIR) in order to examine present functional groups in obtained material. Nitrogen adsorption-desorption isotherms were determined using a Micromeritics ASAP 2020 instrument, while the specific surface area and the volume of the mesopores of the samples was calculated according to the Brunauer, Emmett, Teller (BET) method and Barrett, Joyner and Halenda (BJH) method, respectively. Morphology and composition of the sample surface was examined using TESCAN MIRA3 FEG electron microscope (SEM). Adsorption properties were determined performing equilibrium adsorption, kinetic and thermodynamic studies in the batch system following the Taguchi model. Ion concentration after adsorption was analyzed by inductively coupled plasma mass spectrometry (ICP-MS).

RESULTS AND DISCUSSION

Material characterizations

As can be seen from Figure 1a, the LMS sample is spherical in shape with irregular edges which can be explained by additional functionalization with magnetite nanoparticles. Moreover, high porous structure was obtained via magnetite functionalization of LMS (Figure 1b, Table 1).

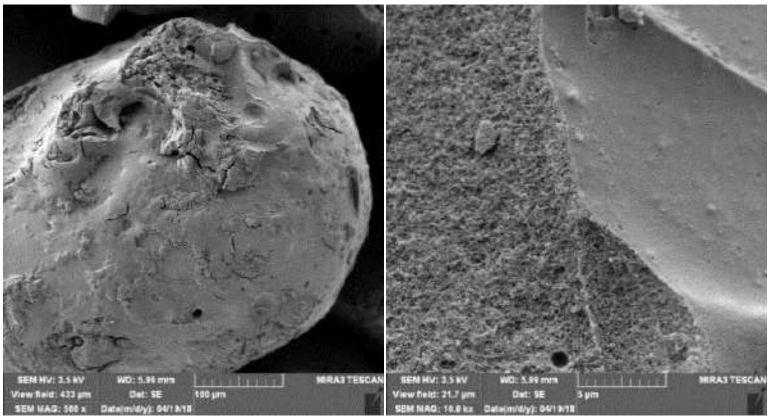


***Figure 1** SEM images of modified adsorbent at 100 and 10.000 magnifications*

***Table 1** Textural properties of modified LMS adsorbent*

Adsorbent	**S_{BET}, m^2/g**	**V_{total}, mL/g**	**$V_{mesopore}$, mL/g**	**$D_{avmesopore}$, nm**	**D_{max}, nm**
LMS	3.81	0.0228	0.0224	10.95	20.25

The values of 3.81 m^2 g^{-1} and 0.0228 mL g^{-1} for specific surface area and total pore volume, respectively, was determined while the mean pore diameter was 10.95 nm (Table 1). Results indicate that developed LMS represents a promising adsorbent for the removal of Cr(VI).

The FTIR spectra of modified lignin microspheres with magnetite are shown in Figure 2. The peaks recorded at 2930 and 2845 cm^{-1}, which is characteristic for symmetric and asymmetric C-H stretching vibrations of the methylene group [6]. Bands at wavelengths of 1728 cm^{-1} and 1459 cm^{-1} indicate the contribution of vibrations of the aromatic structure of lignin. The low-intensity peak at 1389 cm^{-1} can be attributed to the vibrations of the syringyl aromatic rings and the stretching C-O vibrations, while the vibration at 1250 cm^{-1} originates from the guaiacyl aromatic rings. The band at 1152 cm^{-1} originates from the deformation vibrations of C-O bonds in primary alcohol and phenolic groups [7] correspond to the successful copolymerization between lignin, PEI, amino functionalized magnetite and epoxy-chloropropane. Peaks at lower wavelengths are associated with deformation vibrations of C-H bonds in aromatic rings and bending vibrations of N-H bonds outside the plane (808 cm^{-1} and 781 cm^{-1}) [7,8]. The range between 530 and 781 cm^{-1} corresponds to the vibration of the Fe-O / Fe-OH magnetite phase [8].

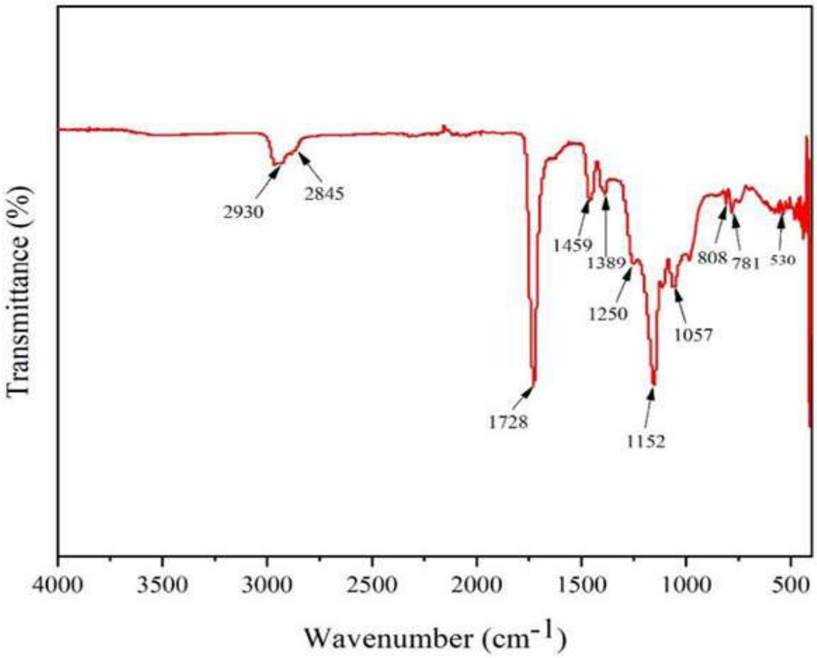


Figure 2 *FTIR spectrum of synthesized LMS-Fe_3O_4*

Adsorption kinetics

Pseudo-second-order (PSO) model was used to predict the law of kinetic rate. The results obtained by adjusting the experimental data with selected kinetic model show high match estimated according to the regression coefficient (R^2). The PSO model is given by equation (1) [9]:

$$q_t = \frac{t}{1/k_2 q_e^2 + 1/q_e} \tag{1}$$

Table 2 *The PSO kinetic parameters for Cr(VI) adsorption on LMS adsorbent*
($Ci=10.00$ mg L^{-1}, pH=6, m/V=125 mg L^{-1}, T=25 °C)

Adsorbent	Model parameters	Pseudo-second
LMS-Fe_3O_4	*k* (k_1, k_2) (g mg^{-1} min^{-1})	0.467
	R^2	0.998
	Ea	8.360

The results of the PSO model indicate the rapid mass transfer and the internal effect of diffusion within the particles on the total mass transport within the pore networks.

The state of interaction/binding of the adsorbate on the surface of the solution/adsorbent is described by adapting the experimental data to Langmuir and Freundlich adsorption isotherms. The rate constants from intra-particle diffusion model are given in Table 3. The adsorption capacities of LMS material increases with the temperature increase and the highest value was obtained at 35 °C (72.06 mg g^{-1}).

Table 3 *Results of isothermal models for the adsorption Cr(VI)*

Isotherm models and parameters		**Temperature**		
		25 °C	**35 °C**	**45 °C**
Langmuir isotherm	q_m (mg g^{-1})	64.72	68.49	72.06
	K_L(L mg^{-1})	0.14	0.15	0.16
	R^2	0.998	0.999	0.999
Freundlich isotherm	K_F (mg g^{-1}) (mL mg^{-1})$^{1/n}$	8.30	8.96	9.67
	1/n	0.65	0.71	0.71
	R^2	0.984	0.9844	0.983

Thermodynamic study

The influence of temperature on the adsorption process was investigated at three different temperatures. The obtained thermodynamic parameters are shown in Table 4.

Table 4 *Calculated thermodynamic parameters*

Adsorbent	**ΔG^{Θ} (kJ mol^{-1})**			**ΔH^{Θ} (kJ mol^{-1})**	**ΔS^{Θ} (J mol^{-1} K^{-1})**	**R^2**
	25 °C	**35 °C**	**45 °C**			
LMS-Fe_3O_4	-32.17	-33.12	-34.84	7.45	132.50	0.5371

Negative values of Gibbs free energy (ΔG°) at all temperatures indicate the spontaneity of the adsorption process which occurs via both physisorption and chemisorption mechanisms (32.17–34.84 kJ mol^{-1}). Positive values of enthalpy (ΔH°) and entropy change (ΔS°) indicate the endothermic nature of the sorption process, better stability of the complex and easier feasible adsorption process, as well.

CONCLUSION

In this paper, the lignin-based material was modified with amino-magnetite to improve the adsorption capacity of the spherical adsorbent to remove chromium oxyanions. The performed kinetic and thermodynamic studies have confirmed the high potential of this material as an adsorbent, as well as the nature of the adsorption process, spontaneity and endothermic binding of pollutants. FTIR and SEM analyses confirmed the structure of the modified LMS and provided information on the groups involved in chromium ion binding. The results of the PSO model indicate the rapid mass transfer and the internal effect of diffusion within the particles on the total mass transport within the pore networks. The presented methodology opens new guidelines in the field of environmental engineering, especially in the revaluation of industrial wastewater treatment.

ACKNOWLEDGEMENT

This work was supported by the Ministry of Education, Science and Technological Development of the Republic of Serbia (Contract Nos. 451-03-01330/2020-14/2685, 451-03-9/2021-14/200135, 451-03-68/2022-14/200325, 451-03-68/2022-14/200026, 451-03-68/2022-14/200003).

REFERENCES

[1] L. Ramrakhiani, A. Halder, A. Majumder, *et al.*, Chem. Eng. J; 308 (2017) 1048–1064.

[2] A.L. Popovic, J.D. Rusmirovic, Z. Velickovic, *et al.*, J. Ind. Eng. Chem; 93 (2021) 302–314.

[3] J. Perendija, Uklanjanje toksičnih jona iz vodenih rastvora primenom adsorbenata na bazi modifikovane celuloze, doktorska disertacija, Tehnološko-metalurškifakultet, Univerzitet u Beogradu, Beograd (2021).

[4] A.L. Popovic, J.D. Rusmirovic, Z. Velickovic, *et al.*, Int. J. Biol. Macromol; 156 (2020) 1160–1173.

[5] A. Pal, Y. He, M. Jekel, *et al.*, Environ. Int; 71 (2014) 46–62.

[6] Y. Ge, Z. Li, D. Xiao, *et al.*, J. Ind. Eng. Chem; 20 (2014) 1765–1771.

[7] I. Bykov, Characterization of Natural and Technical Lignins using FTIR Spectroscopy, Master Thesis, Lulea Univ. Technol. (2008).

[8] R.J.A. Gosselink, Lignin as a renewable aromatic resource for the chemical industry, PhD Thesis, Wageningen University, Wageningen, NL (2011), ISBN: 978-94-6173-100-5.

[9] H. Zhang, J. Deng, Y. Wu, ACS Sustain. Chem. Eng; 5 (2017) 658–666.

IMPROVED TECHNOLOGY FOR PRODUCTION OF PE AND PP REGRANULATES

Aleksandar Jovanović[1*], Nataša Knežević[1], Natalija Čutović[1], Maja Đolić[1], Nevena Prlainović[1], Zlate Veličković[2], Marija Vuksanović[3]

[1]University of Belgrade, Faculty of Technology and Metallurgy, Karnegijeva 4,
11070 Belgrade, SERBIA

[2]University of Defense, Military Academy, Veljka Lukića Kurjaka 33,
11042 Belgrade, SERBIA

[3]University of Belgrade, National Institute of the Republic of Serbia, Institute of Nuclear Sciences, Mike Petrovića Alasa 12–14, 11000 Belgrade, SERBIA

[*]*aleksandarjovanovic.tmf@gmail.com*

Abstract

Management of waste polymers (polyethylene - PE and polypropylene - PP) represents one of the major obstacles in the field of environmental protection, which demands a most efficient and eco-friendly technological solution. Due to the high use of various plastic materials, the amount of landfilled or dissipated plastic waste is continuously growing. Therefore, this paper examines the possibilities of recycling these polymers, alongside obtaining granules of similar or advanced physico-mechanical characteristics to the commercially available ones. The applied technology consists of several consecutive processes (collecting, grinding, washing and extruding) where the obtained materials can later be incorporated into widely applicable products, such as foils, bin liners, bags, among others. In this way, high-quality products with great market potential are obtained, which will consequently contribute to lower extraction and less depletion of natural resources. Thus major problems may be solved optimally, consolidating the efficiency of improved eco-friendly technologies which is in line with environmental protection and sustainable waste management.

Keywords: polyethylene, polypropylene, recycling technology, plastic processing

INTRODUCTION

The field of environmental engineering, in the first-place environmental prevention and protection, is daily gaining more public attention. A special place is occupied by waste management due to the possibility of using generated mass to obtain products that can easily be reused or incorporated into new products, improving their initial properties. The benefits of recycling are reflected in the following: conservation of natural resources, decreased consumption of electricity and water, reduction of gas emissions into the ecosystem, etc.

The global polyethylene market size was USD 107.43 billion in 2019, and it is projected to reach USD 130.26 billion by 2027, exhibiting a compound annual growth rate (CAGR) of 3.4%, whereas, the CAGR for polypropylene is 5.2%, due to the market growth from USD 75.12 billion to estimated USD 108.57 billion, within a period of eight years [1,2]. From the above data, it can be concluded that the development of recycling processes can achieve significant economic benefits. Polyethylene is popular in industry branches related to packaging and construction, due to its good physicochemical and mechanical characteristics. PE is a plastic material that is the most widely produced while having the simplest basic structure out of all polymers (a repetition of CH_2 units). PE's key advantages include its low cost, strong electrical insulation, excellent chemical resistance, good processability, toughness, flexibility, and transparency in thin films of certain grades [3]. Even today, many applications still rely on virgin material instead of PE regranulate, such as LDPE. Regranulates are less expensive than virgin material, especially since PE regranulates available on the market have shown high discrepancies in quality and high impurity of constituents.

However, conventional production still prefers virgin material to eco-friendly regranulate. This tendency has to be emergency changed. With high-quality PP regranulates, high-quality cleaner production may be established respecting environmental protection and promoting the new concept of the circular economy. PE as one of the lightest and most adaptable polymers available, may go through a wide range of manufacturing procedures. Commercial PE is often a blend of 75% isotactic and 25% atactic, even though it comes in three different tactic forms. PE demand is continuously increasing, making it one of the most frequent kinds of microplastic discovered in the marine environment [4].

The paper focuses on the development of a novel technology for the production of regranulates based on PE and/or PP in order to improve their commercial competitiveness. Waste polymer preparation consists of three process operations: sorting, washing, and grinding. The new technology will boost productivity and flexibility, reduce energy consumption, make labor easier, and produce fewer waste byproducts. This will result in higher-quality regranulates, as well as improved filtration, homogenization, and degassing, making recycling more efficient and profitable.

The products obtained in this way possess a wide range of applications, because of their advanced mechanical and physicochemical properties. They can be used in the automotive industry, for the production of various profiles by extrusion or coextrusion. On the other hand, it can be used for the making of brushes, brooms, various types of fibers, trash cans and doormats.

MATERIALS AND METHODS

Processing of waste PE and PP

The entire process of recycling waste PE and PP (Figure 1) is presented in a set of operations that effectively contribute to the productivity of the process. The process of recycling plastic films begins with inspection and selection (stage 1), in order to remove any foreign materials, contaminants, or other plastics. Some dirtier or cross-contaminated materials may require flotation separation, in which certain types of plastic rise to the top of the flotation tank while others sink due to their higher densities [5]. After collecting and controlling, PE and PP waste further go into mill 1 for coarse grinding (Shredder – stage 2), then to mill 2 for fine grinding. Finally, the raw materials are washed, and plastic grind is led across the conveyor belt to the extruder where it is melted by heat and friction (stage 3). The molten plastic is filtered through a screen so that the remaining contaminants are removed. The final product in form of little pellets are obtained and ready for the market.

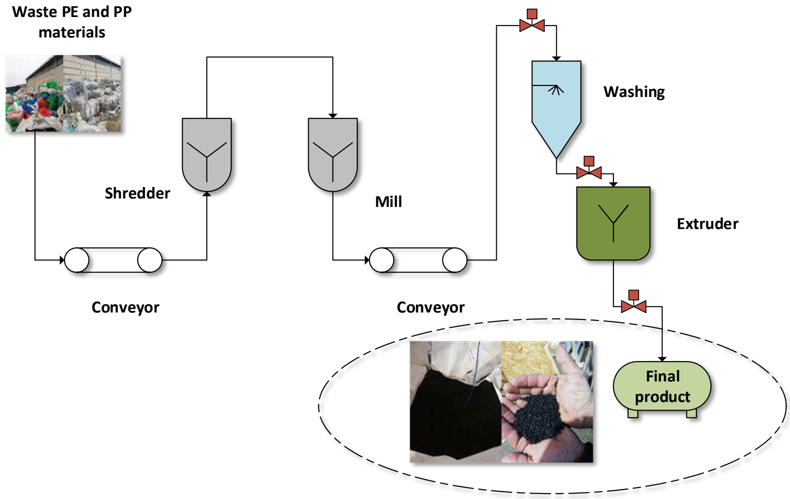


__Figure 1__ The scheme of PE and PP waste processing

RESULTS AND DISCUSSION

Tables 1 and 2 show results from mechanical and chemical examinations of commercial and recycled materials.

__Table 1__ The physico-mechanical properties of commercial PE and PP materials

Properties	PE	PP
Specific mass $\gamma_{s\,s}$	910–930 k N/m^3	900 k N/m^3
Glass Transition Temperature T_g	80 °C	100–120 °C
Thermal conductivity coefficient λ	0.13 W/m °C	0.88 W/m °C
Thermal coefficient of linear expansion αT	120–140 (x 10^{-60}C^{-1})	120 (x 10^{-60}C^{-1})
Tensile strength	7–15 (MPa)	33–35 (MPa)
Compressive strength	9–10 (MPa)	35 (MPa)
Elongation at break ε	300–700 (%)	20–300 (%)
Modulus of elasticity *E*	120–140 (MPa)	900–1400 (MPa)
The effect of ultraviolet rays *EUV:*	reduces its strength	without influence
Effect of chemical agents *ECA:*	it is dissolved by acids	it is dissolved by acids

__Table 2__ The physico-mechanical properties of recycled PE and PP materials obtained using process schema shown in Figure 1

Properties	PE	PP
Specific mass $\gamma_{s\,s}$	905–926 k N/m^3	870 k N/m^3
Glass Transition Temperature T_g	78 °C	93–114 °C
Thermal conductivity coefficient λ	0.10 W/m °C	0.82 W/m °C
Thermal coefficient of linear expansion αT	110–131 (x 10^{-60}C^{-1})	114 (x 10^{-60}C^{-1})
Tensile strength	5–11 (MPa)	26–29 (MPa)

Table 2 *– continued*

Compressive strength	6–9 (MPa)	30 (MPa)
Elongation at break ε	220–630 (%)	15–240 (%)
Modulus of elasticity *E*	110–127 (MPa)	800–1100 (MPa)
The effect of ultraviolet rays *EUV:*	reduces its strength	without influence
Effect of chemical agents *ECA:*	it is dissolved by acids	it is dissolved by acids

From the acquired data, it can be concluded that the obtained materials have the same characteristics as raw materials, thus showing that recycled regranulates can be used in their replacement. In this way, it is shown that recycling has just as a method for PE and PP waste processing with the final aim to protect natural resources.

CONCLUSION

This paper aimed to examine the physicochemical and mechanical characteristics of plastic materials acquired by recycling PE and PP waste, in order to produce their regranulates. The composition of the gained materials was examined by analyzing tensile strength, compressive strength, elongation at break, etc. Based on the presented results, it can be concluded that materials obtained by recycling PE and PP have shown good mechanical and chemical properties. In addition, due to the acceptable specific mass and glass transmission temperature, as well as good mechanical characteristics, regranulates obtained by recycling raw materials, will avoid numerous negative effects on the environment.

ACKNOWLEDGEMENT

This work was supported by the Ministry of Education, Science and Technological Development of the Republic of Serbia (Contract No. 451-03-68/2022-14/200135; 451-03-68/2022-14/200017).

REFERENCES

[1] Fortune business inside, Polyethylene market size, *Available on the following link*: https://www.fortunebusinessinsights.com/industry-reports/polyethylene-pe-market-101584

[2] Fortune business inside, Polypropylene market size, *Available on the following link*: https://www.fortunebusinessinsights.com/industry-reports/polypropylene-pp-market-101583

[3] S. Ronca, Brydson's Plastics Materials (Eighth Edition), Butterworth-Heinemann, Oxford (2017), p. 247–278, ISBN: 9780323358248.

[4] C.B. Crawford, B. Quinn, (First Edition), Elsevier, Amsterdam (2017), p. 57–100, ISBN: 978-0-12-809406-8.

[5] F. Pita, A. Castilho, Waste Manag; 60 (2017) 91–99.

A SHORT REVIEW OF TREPČA MINING WASTE IMPACT ON ENVIRONMENT

Jasmina Dedić[1], Miljan Mojsić[1], Dragan Lazarević[1], Bojan Stojčetović[2*], Živče Šarkoćević[1]

[1]Faculty of technical sciences, Knjaza Miloša 7, Kosovska Mitrovica, SERBIA

[2]Kosovo and Metohija academy of professional studies, Zvečan department, Nušićeva 6,
38227 Zvečan, SERBIA

[*]*bojan.stojcetovic@akademijakm.edu.rs*

Abstract

The development of today's economies is inconceivable without the participation of industry. At the same time, mining is of great importance and participation in development. Unfortunately, in addition to contributing to development, mining often has a negative impact on the environment. The contamination of soil, air and water with different pollutants is a complex long-term problem that impact our environmental and endangers human health. This paper gives a brief overview of the papers that investigated the impact of mining from Trepča company on the environment. Unfortunately, it can be concluded that there is an evident impact on water, air and land as a result of improper waste treatment.

Keywords: Trepča, mining, waste

INTRODUCTION

Mining is an important activity that provides critical raw materials for the development, and also, it is an important economic driver for many countries, especially for some developing [1]. However, mining brings large impacts on the environment and population. The mining process generates a large quantity of residues that must be strategically treated and managed to combine economic efficiency with demands for environmental sustainability [2]. Opencast mines are more pollution intensive as they generate much higher quantities of waste compared to the underground mines [3]. Open-pit mines produce 8 to 10 times as much waste as underground mines [4].

The mining and metallurgical production at Kosovo and Metohija province is well known from antic and medieval times. But, significant development of metallurgical activities at north has started in 1926 when Englishman bought concession and established “Trepča Mines Limited”. Result of that development is that in city of Mitrovica is situated the largest metallurgic and mining complex in Europe named “Trepča” [5]. The production in Trepča was not interrupted even within the Second World War. After 1945, the economic development has been intensified, especially in the field of mining, metallurgy and energetic. In the period from 1970–1990, processing industry was developed in Trepča and existing capacities enlarged [6]. Finally, due to environmental, economic and political reasons production completely stopped in 1999. For 60 years, in the period 1939–1999, 3.284.568 t of refined lead, 4.110 t of silver, 3.296 t of bismuth and other commercial products [7] have been produced. However, now the greatest danger to the environment is posed by industrial waste from Trepča.

In text that follows, a short review of papers that describe Trepča waste impact on water, air and soil are presented.

RESULTS AND DISCUSSION

Impact on air

According to Chaturvedi and Patra [8] the primary sources of air contamination at mine sites are fugitive dust from dry surfaces of dry tailings impoundments, as well as overburden, waste rock, and ore piles. With the help of the wind the dust reaches ground water, surface water, and soil.

There are few Trepča industrial landfills in Mitrovica and Zvečan and they are potential (and real) sources of air pollution. For that reason [9] implemented measurement in urban areas in Mitrovica in order to check air quality. Shala *et al.* [9], beside measurement of total suspended particulate material, fractions of particles with aerodynamic diameter of 10 µm and 2.5 µm, also conducted chemical analysis of dust for the four urban sites, the concentration of cadmium, lead and zinc in µg/m^3 in 24 hours and results are shown in Table 1.

Table 1 *Results from chemical analyses of collected dust [9]*

Measurement points	**Cd (µg/m^3)**	**Pb (µg/m^3)**	**Zn (µg/m^3)**
MIP – Faculty of Mining and Metallurgy	0.01266	1.196	1.116
Squer “Adem Jashari”	0.0034	0.373	0.0207
Primary school “Muharrem Bekteshi”	0.00866	0.7145	0.067
Bair, Camp and KFOR-it Greek	0.003	0.78	0.0437

Shala *et al.* [9] of above mentioned research concluded that “air pollution in Mitrovica exceeds the limit of allowed values, comparing with the norms of the European Union, doubtless this zone is classified as injurious for health of the people”.

Impact on water

Exposed ore, overburden piles, waste rock and ore piles, tailings impoundments, and other disturbed areas can contribute sediment and increase the total solids load to surface water bodies. Other potential sources of surface and groundwater contamination include fuel spills, flotation reagents, cleaning solutions, and other chemicals used or stored at the site [8].

Ferati *et al.* [10] conducted assessment of heavy metal contamination in water and sediments of Trepča and Sitnica rivers in six selected sampling sites. The result revealed that high levels of concentration for As, Cd, Pb, and Zn in the site marked P2 (industrial outfalls) originate primarily from anthropogenic sources such as discharge of industrial water from mining flotation, whereas the concentration of heavy metals in sites P4 (drain outfalls) and P5 (industrial outfalls) is originating from the mine waste eroded from the river banks. The water from the investigated sites is classified from II to III categories, except for the site P2 that is classified to category V [10].

Table 2 *Heavy metal concentrations in water samples from Trepča and Sitnica rivers and national limited values (mg/dm^3) [10]*

Sample	**Heavy metals**								**pH**
	As	**Cd**	**Co**	**Cr**	**Cu**	**Ni**	**Pb**	**Zn**	
P1	<MDL	<MDL	0.042±0.003	<MDL	0.046±0.007	<MDL	<MDL	<MDL	8.04±0.02
P2	0.076±0.002	0.071±0.004	0.046±0.004	0.035±0.001	0.054±0.002	<MDL	0.288±0.01	7.994±0.05	7.06±0.01
P3	<MDL	<MDL	0.044±0.01	<MDL	0.032±0.003	<MDL	<MDL	0.876±0.03	8.29±0.01
P4	0.046±0.01	0.045±0.002	0.044±0.06	<MDL	0.038±0.004	<MDL	<MDL	0.029±0.006	7.96±0.01
P5	0.084±0.009	0.081±0.002	0.042±0.003	0.054±0.03	0.034±0.003	0.058±0.003	0.488±0.028	0.260±0.01	7.93±0.06
P6	<MDL	0.017±0.001	0.044±0.003	0.051±0.028	0.050±0.002	<MDL	<MDL	0.336±0.04	8.07±0.01
MDLs	0.05	0.012	0.028	0.031	0.012	0.01	0.031	0.022	
UA 13/2008[a]	0.05	0.01	0.5	0.5	0.1	0.5	0.2	0.5	
75/440/EEC[b]	0.05	0.005	-	0.05	0.02	-	0.05	0.5	
BWA[c]	-	*0.3*	*7.1*	*90*	*45*	*68*	*20*	*95*	

MDL = $t_{(1-p,\, n-1)}s$ where s is standard deviation and t is the correct Student's t value;

MDL method detection limits;

[a] Republic of Kosovo/Ministry of Environmental and Spatial Planning (2008): Administrative instruction No. 13/2008;

[b] European Council Directive 75/440/EEC of 16 June 1975;

[c] BWA – Background World Average.

The pollution of river Trepča with heavy metals is also researched by Kadriu *et al.* [11]. According to results obtained in this research and comparing them with reference values arising from Directive 75/440/EEC as Kosovo and Administrative Instruction No.13/2008 authors concluded that exceeded the reference in the river Trepča with heavy metals, with the exception of Cd, have on all samples taken. Kadriu *et al*. [11] also concluded that the sources polluting the waters of the Trepča are untreated waters by underground galleries of combine “Trepča” and the untreated waters arising from the process of flotation ore located in the first tunnel.

Hoxha *et al.* [12] performed research and comparison of the potato samples that are irrigated in the land plots near Ibar river, compared with samples of potatoes that were cultivated with only atmospheric precipitation and those in greenhouses (protected from air impact and irrigated with clean water) in order to investigate is there heavy metals in water impact on potato. In first case, where potatoes were irrigated from Trepča river results show that the concentration of lead and other elements surpasses the international norms and it reaches up to 180 ppm above the allowed limits for potable water [12]. In second case potatoes were irrigated only by the atmospheric precipitations. Results show that the concentration of lead and other elements does not exceed the international norms, however they are increased up to maximum allowed level, compared to the standards for potable water [12]. It can be concluded that the air is polluted with heavy metals as a result of mining activities of Trepča and it reach the potatoes. In third case potatoes were isolated from air impact and only clean water is used for irrigation and concentration of lead and other heavy elements does not exceed the international norms [12].

Impact on soil

Stafilov *et al.* [13] investigated arsenic in surface soils affected by mining and metallurgical processing in Mitrovica region. Authors collected 159 soil surface samples (0 cm to 5 cm depth) from Mitrovica region (300 km^2) that was covered with a sampling grid of 1.4×1.4 km^2. The results of this study on distribution of arsenic in topsoil (0–5 cm) over the Mitrovica region, show that the average content of As in the topsoil for the entire study area is 30 mg/kg (with a range of 2.1–3,900 mg/kg), which exceeds the estimated European arsenic average by a factor of 4.3. It is evident that the content of arsenic is very high in topsoil from the areas closest to the lead and zinc smelter plant (Zvečan zone), as well as in topsoil in the city of Mitrovica [13].

CONCLUSION

Mining is a very important part of industry that contributes to development of economies worldwide. On the other hand, it is a type of industry that can have negative impact on people and environment. In this paper is presented several researches about Trepča mining waste impact on water, air and soil.

According papers presented it can be concluded that industrial waste from Trepča cause intense contamination of the water, soil and air in Mitrovica region. In order to protect future contamination it is necessary to take the necessary measures to protect environment and human health.

In future research, it is necessary to investigate in detail the impact of waste from Trepča and define measures to solve this problem.

REFERENCES

[1] L. Moreno, J. I. Ordóñez, L. A. Cisternas (2014) La industria salitrera y los recursos hídricos, In: L. A. Cisternas, L. Moreno (eds.) El Agua de Mar en la Minería: Fundamentos y Aplicaciones, RIL Editores, Santiago, Chile.

[2] J. Aznar-Sánchez, J.J. García-Gómez, J.F. Velasco-Muñoz, *et al*., Minerals; 8 (7) (2018) 284.

[3] C.M.G. Abiahu, V.I. Fagorite, I.C. Oli, *et al*., Intern. J. App. Sci; 5 (7) (2019) 1–12.

[4] Anon, Dirty Metal, Mining Communities and Environment, Earthworks, Oxfam America, Washington (2006) p.4.

[5] L. Prathumratana, R. Kim, K.W. Kim, Environ. Geochem. Health; 42 (2020) 1033–1044.

[6] B. Nikolić, Lj. Jakšić, J. Min. Metall. B; 41 B (2005) 135–140.

[7] B. Nikolić, Metalurgija; 5 (2) (1999) 141–156 (in Serbian).

[8] N. Chaturvedi, H.K. Patra, Int. J. Sci. Res. Metodol; 5 (1) (2016) 397–420.

[9] F. Shala, M. Sadiku, B. Rexha, *et al*., Recent Res. Environ. Energy Plan. Pollut; (2011) 37–42, ISBN: 978-1-61804-012-1.

[10] F. Ferati, M. Kerolli-Mustafa, A. Kraja-Ylli, Environ. Monit. Assess; 187 (2015) 338.

[11] S. Kadriu, M. Aliu, M. Sadiku, *et al.*, J. Int. Environ. Appl. Sci; 11 (2) (2016) 166–169.

[12] I. Hoxha, N. Shala, G. Xhabiri, Rasayan J. Chem; 11 (2) (2018) 682–687.

[13] T. Stafilov, M Aliu, R. Sajn, Int. J. Environ. Res. Public Health; 7 (2010) 4050–4061.

INFLUENCE OF UNDERGROUND MINING WORKS OF THE OMAZIĆI BROWN COAL MINE BANOVIĆI ON THE SURFACE TERRAIN

Senad Čergić[1*], Hamid Husić[1], Vahidin Aganović[1]
[1]Brown Coal Mines "Banovici", 75290 Banovici, BOSNIA AND HERZEGOVINA
[*]*senadcergic@hotmail.com*

Abstract

Underground exploitation of mineral resources due to its technological processes of extraction is one of the significant factors of disruption of the natural environment. This way of exploitation creates empty spaces within the mineral deposits and disturbs the state of natural balance in the rock massif. Empty spaces cause the process of moving the massif and collapsing the excavated part of the deposit, which is manifested on the surface of the terrain in the form of subsidence and folds. Taking into account the above, the obligation of the Mine is to regularly monitor the condition of the terrain surface above the active underground premises and work sites. Occasional control of the movement of the terrain surface above the old works that were excavated earlier is also obligatory.

Keywords: underground exploitation, subsidence, geodetic monitoring

INTRODUCTION

Exploitation of coal in Mine "Underground exploitation" has been carried out for many years in the immediate vicinity of the town of Banovići in the production plant of the Omazići Mine. Exploitation was previously carried out in the northern and central part of the deposit, and in the last 30 years it has been carried out in the western part of the deposit.

The movement of the rock mass and the surface of the terrain in the zone of mining works creates a risk of disturbing the hydrogeological conditions, flora and fauna, as well as material damage.

Due to the negative consequences of underground exploitation, it is necessary to collect information on the range of harmful effects of mining works before the exploitation and to define the area of expected displacements and deformations as well as their intensity.

Also, during the exploitation, the legal obligation is to determine the position of underground mining works in relation to facilities and surface water.

This paper will present the effects of underground coal mining on the terrain surface, as well as the measures taken by the mine in order to predict the impact of terrain shifting.

BASIC DATA ABOUT THE MINE "UNDERGROUND EXPLOITATION" BCM "BANOVIĆI"

Geological and engineering-geological description of the deposit of the Mine Omazići

The geology of the deposit treats a complex of younger rock deposits which, in terms of formation, form a geological whole and a common structural form, with stratigraphic units (bottom-main layer of coal-roof) standing out. The roof series of the main coal seam has a sharp transition in contrast to the gradual transition from the base to the coal series. The coal seam lies at an angle of 14°–25° at a depth of up to 350 m [1]. Geological characteristics of the working environment and the coal seam given in Figure 1.

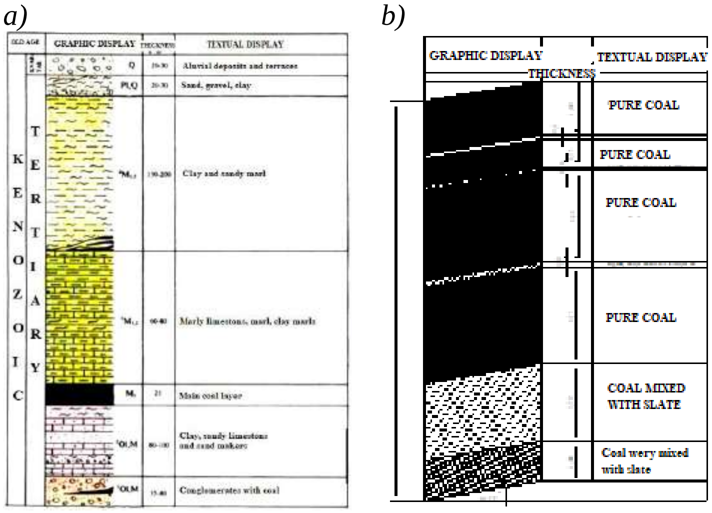


Figure 1 *a) Geological column on the coal deposit; b) Geological pillar of the coal seam*

Overview of coal exploitation in the area of the pit Omazići of the Brown Coal Mine Banovići

The exploitation of coal in the Omazići mine with a smaller capacity began in 1939 at the “Begov potok” site [2].

The intensification of production began after the second world war, more precisely in the period 1954–1970 in the northeastern part of the deposit. Coal mining was performed by the transverse method (Figure 2, Position 1) [2].

In the period 1975–1982, excavations were carried out in the central part of the deposit (between the two current lowlands 'jug-2' and 'jug-3'). The excavation was performed by the wide-mouthed method (Figure 2, Position 2) [2].

From 1981–1987 excavation was carried out in the eastern part of the deposit by excavation method (Figure 2, Position 3) [2].

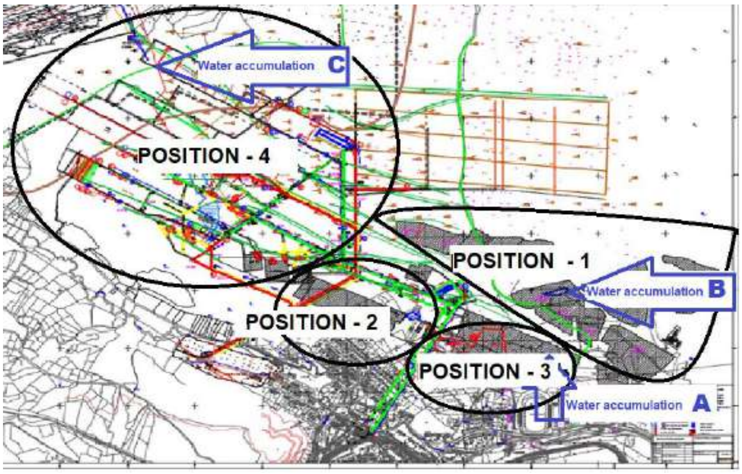


Figure 2 *Location of mine works underground mining pits Omazići*

Coal has been mined in the western part of the pit since 1989. until today (Figure 2, Position 4). In the western part of the Omazić mine, two digging methods are used:

- Wide front method of excavation in belts with roof destruction
- Wide front method of excavation with coal production above excavation.

The wide-front method of excavation with coal production above excavation means that coal is first obtained in the excavation part of the excavation field 2.5 m high, and then from the excavation part 5 to 7.5 m high, depending on the capacity of the coal seam [2]. Excavation fields are up to 100 m wide and 600 to 800 m long. Part of the field has already been excavated, so the remaining height for exploitation is variable for individual excavation fields and varies from 3.2 to 15 m [2].

From 2010–2012 year, coal mining was performed by semi-mechanized wide-mouthed method with an annual production of approximately 190,000 t excavation with two foreheads in spans of 2.5 m and advancing on the forehead approximately 23 m/month [2].

Since 2013, excavation has been carried out with a mechanized wide forehead with an average annual production of approximately 420,000 t (of flat coal) in a span of 3.4 m and an advance of approximately 75 m/month [2].

RESULTS OF GEODETIC MONITORING OF FIELD SURFACE SHIFT

In accordance with the legal obligation, the geodetic service of the Underground Exploitation Mine performed annual measurements in connection with determining the displacement in the zone of influence of excavation. As a basis for this research work, data from the Study were taken, where two groups of geodetic points are presented, which are grouped [3].

The first group consists of nine points, marked with numbers from 121 to 131, which were determined by position and height in three series of measurements. The first (zero) series of measurements was performed in December 2008, the second series was measured in September 2016, and the third series was measured in September 2017. Table 1 shows the values of the coordinates in the height of this group of points. In columns 10 and 14 of this table, the total vertical and horizontal displacements for each point are calculated [3].

***Table 1** Coordinates and heights for the first group of points*

Point	Y0_08	X0_08	H0_08	x1_ Se16	H1_ Se16	H2_ De16	H3_ Ap17	H4_ Se17	dHu (m)	dH_1 (m)	dy (m)	dx (m)	dd (m)
1	2	3	4	5	6	7	8	9	10	11	12	13	14
121	6541817.5	4919268.21	330.28	19268.21	330.28	330.28	330.28	330.28	0	0	0	0	0.00
122	6541728.3	4919307.06	330.55	19307.06	330.55	330.55	330.55	330.55	0	0	0	0	0.00
126	6541482.96	4919786.78	362.92	19787.12	362.69	362.92	362.69	362.64	-0.28	-0.05	0.16	0.34	0.38
127	6541413.75	4919892.38	362.18	19892.85	361.88	362.18	361.88	361.88	-0.3	0	0.01	0.47	0.47
128	6541289.01	4920006.64	367.61	20006.69	367.09	367.61	367.09	367.09	-0.52	0	0.12	0.05	0.13
129	6541137.94	4920193.45	373.02	20193.46	372.83	373.02	372.83	373.01	-0.01	0.18	-0.04	0.01	0.04
130	6541134.69	4920304.77	391	20304.71	390.87	391	390.87	390.87	-0.13	0	0.03	-0.06	0.07
131	6540973.61	4919934.27	340.83	19934.36	340.81	340.83	340.81	340,81	-0.02	0	-0.12	0.09	0.15

The second group consists of points marked with numbers 305 to 328, including point 212. These points in the first (zero) series are determined by position and height. In the next two series, only heights were determined. The first series of measurements was performed in December 2016, the second series is in April 2017, and the third series in September 2017. Table 2 shows the heights and coordinates of the second group of points, as well as the calculated total vertical displacements (column 5). This group of points is located north of OPZ1, i.e. near the borders of OPZ3, which was excavated in 2017 by mechanized excavation [3].

Table 2 *Coordinates and altitudes for the second group of points*

y	**x**	**H0_sept.2016**	**H1_Sept.2017**	**dH**	point
1	2	3	4	5	6
6542110	4919951	362.14	362.14	0.00	306
6541763	4920127	337.3	335.19	-2.11	310
6541659	4920162	343	341.83	-1.17	321
6541727	4920182	335.5	334.33	-1.17	316
6541965	4920240	381.62	381.51	-0.11	319
6541945	4920336	376.79	375.63	-1.16	212
6541506	4920461	348.56	347.6	-0.96	323
6542116	4919904	360.44	360.44	0.00	307
6541581	4919947	360	355.36	-4.64	312
6541545	4920393	345.3	344.2	-1.10	322
6541672	4920582	362.3	362.2	-0.10	328

Figure 3 shows the position of these points in relation to the excavation fields. In addition to the name/number of the point, the settlement determined from the geodetic survey data in the first/zero and last series of measurements is also entered [4].

With this method of excavation, the advance of the forehead is approximately 75 m/month, so it manifests itself on the surface much faster, which can be seen by the size of the registered subsidence at points that are in the zone of impact OPZ3 (Figure 3).

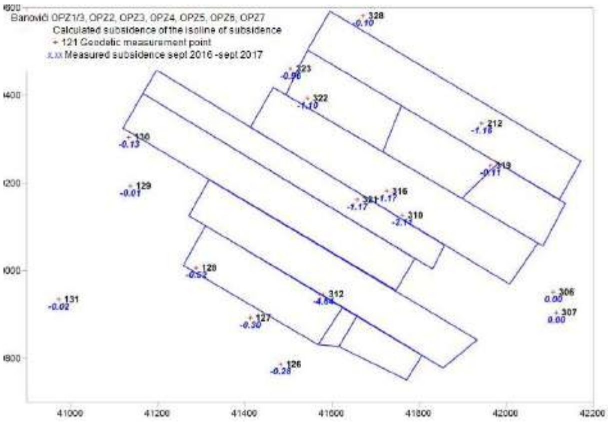


Figure 3 *Points of the geodetic network for monitoring the movement of the terrain surface above the current mining works (Position 4 from Figure 2)*

Table 3 shows the results of measurements of the displacement of the terrain above the old mining works in the period 2008 to 2022.

Table 3 *Coordinates of the points above the old works*

Point number	Y	X	H (2008)	H (2022)	ΔH
106	6543496.565	4919808.914	328.65	328.69	+0.04
107	6543471.796	4919522.224	321.58	328.50	-0.08
108	6543591.840	4919205.461	317.84	317.79	-0.05
109	6543417.425	4919091.072	345.59	345.40	-0.19
110	6542891.344	4919049.954	316.55	616.44	-0.11
116	6542249.164	4919326.019	342.44	342.38	-0.06

MANIFESTATION OF UNDERGROUND WORKS OF OMAZIĆI MINE ON THE FIELD

Based on the performed geodetic measurements, it can be concluded that the underground exploitation of coal in specific conditions causes manifestations on the surface of the terrain in the form of subsidence, sinkholes, folds and the like. Figure 4 shows subsidence and folds above the work zone.

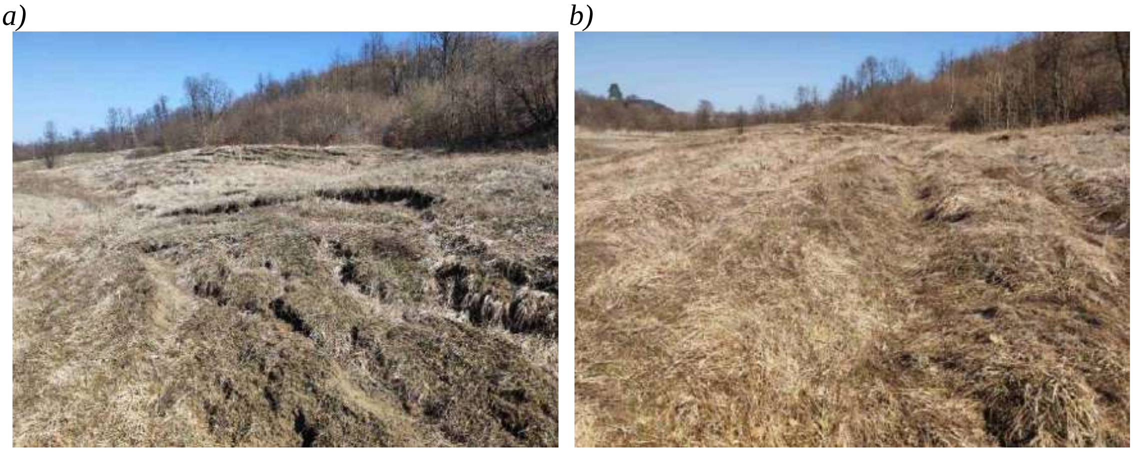


Figure 4 *Representation of the impact of underground works in the form of depressions and folds*

On such a deformed surface of the terrain, water accumulations of different shapes and depths are often formed. Figure 2 shows the water accumulations of positions A, B, and C. Figure 5 shows water accumulations above the work zone.

When it comes to water accumulations, they represent a danger to workers and machinery engaged in the production process. For that reason, water accumulations above active work sites are pumped out and buried. Water accumulations above the old mining works represent a potential danger and their level is regularly monitored and the condition is recorded in the appropriate books. The construction of residential and other buildings within the exploitation field is defined by a special study.

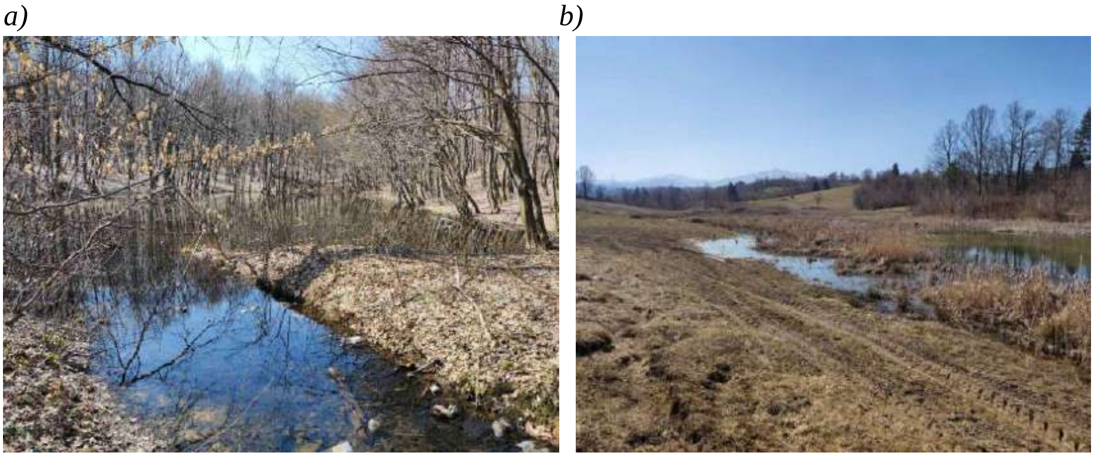


Figure 5 *Overview of the impact of underground works where water reservoirs were formed a) in the northern part; b) in the western part*

The study defines the zones of influence of underground mining works. Based on these influences, building permits are also defined: without restrictions, conditional construction and construction ban.

In this particular case, construction above the current underground mining works is prohibited. This refers to the area shown in Position 4 of Figure 2. Above the old underground mining works, conditional construction is allowed.

CONCLUSION

Every type of exploitation, regardless of whether it is surface or underground exploitation, leaves behind certain anomalies in the form of craters, landfill plenums, lakes, wrinkled areas, etc. Any of the types of exploitation directly reflects on the appearance and condition of natural resources that are in the sphere of influence of works.

Underground coal exploitation shows its manifestation of the impact on the environment in the way of deformation of the terrain surface in the form of subsidence, creation of water accumulations and folds.

The impact of the works on the surface is evident throughout the history of the Omazići mine. This influence is different and depends on the method of excavation, the speed of advance of the excavation front and the depth at which the excavation is performed.

Also, it is evident that mechanized excavation, whose excavation front has greater progress than other applied excavation methods in BCM “Banovići”, manifests faster and larger displacements on the surface of the terrain.

Data obtained from long-term monitoring of terrain subsidence indicate that the greatest displacements on the surface are in the first 5 years after exploitation. In that period, the process of consolidation and subsidence of the terrain is completed on about 95% of the surface. In the next 15 years, the process of consolidating the remaining 5% of the area will be completed. Of course, this statement is not general and depends on a number of factors. Ultimately, it can be said that in 20 years the terrain above the old underground mining works has been largely stabilized and its further displacements are minimal.

REFERENCES

[1] Study "Defining the possible limit of the influence of underground mining works of the western district on the surface of the field during the excavation of the entire designed part of the deposit in the mine "Underground exploitation" BMC Banovici d.d. Banovici, RGGF Tuzla, March 2018.

[2] Dopunski rudarski projekat priprema OPZ_2 revira zapad Rudnika “Podzemna eksploatacija uglja” RMU Banovići d.d. Banovići (2021).

[3] Study of the influence of underground mining works of the western district on the surface of the field by phases/stages of excavation in the mine "Underground exploitation" BMC Banovici d.d. Banovici, RGGF Tuzla, (2018).

[4] Č. Ruža, „Numerical model of surface surface as a basis for determination of vertical deformations of field surface“ XXIII Zbornik radova RGGF-a., 17–23, Tuzla (2001). ISSN: 1512-7044.

ARSENIC IN PARTICULATE MATTER ORIGINATED FROM MINING-METALLURGICAL PROCESSES

Snežana Šerbula[1*], Jelena Milosavljević[1], Tanja Kalinović[1], Ana Radojević[1], Jelena Kalinović[1]

[1]University of Belgrade, Technical Faculty in Bor, V.J. 12, 19210 Bor, SERBIA

ssherbula@tfbor.bg.ac.rs

Abstract

The air quality in Bor is determined at the measuring sites in the urban-industrial, suburban and rural area during the 2010–2022 period. High level of arsenic in suspended particulate matter (PM) is of a predominantly industrial origin. The major source of pollution is the copper smelter, which is situated in the close vicinity of the urban area of Bor. The ambient level of As in PM is influenced by meteorological parameters as well as the remoteness from the copper smelter. Continual exceedances of the annual limit value (LV) for As (6 ng m^{-3}) were recorded at the measuring sites in the urban-industrial and suburban areas. Maximum annual As concentration recorded at the site Jugopetrol (550 ng m^{-3}) in 2019, was more than 90 times higher compared to the LV. The daily concentration of arsenic in April 2022 also exceeded the limit value by more than 100 times in relation to the LV.

***Keywords**:* arsenic, particulate matter, air quality, mining-metallurgical processes

INTRODUCTION

Air pollution represents one of the most important environmental, as well as social problems, which poses multiple challenges in terms of managing and mitigation of harmful pollutants [1]. Weather patterns alter the transport, dispersion, deposition and formation of air pollutants in the atmosphere [2]. Air pollution can lead to the increase in the incidence of respiratory and cardiovascular diseases, as well as cancer, but it can also cause premature death [1]. Human health and the environment are undoubtedly influenced by the air quality, hence its monitoring is essential, especially in the regions affected by different industrial processes. Copper production based on pyrometallurgical processes is regarded as an important source which emits vast quantities of air pollutants such as sulphur dioxide (SO_2) and particulate matter (PM) with high content of toxic elements, i.e. arsenic (As) [3].

Particulate matter, air pollutant consisting of a mixture of suspended solid and liquid particles, can be either directly emitted (denoted as the primary PM) or be formed secondarily in the air from gaseous precursors (mainly SO_2, NO_x, NH_3 and non-methane volatile organic compounds). The most important chemical constituents of PM are sulphates, nitrates, ammonium, inorganic ions, organic and elemental carbon, particle-bound water and toxic elements. PM is generated by anthropogenic activities, such as transport, energy production, domestic heating and could be emitted from a wide range of industries [4]. PM poses high risk to human health due to its ability to enter the respiratory system. Both acute and chronic exposure to PM from the ambient air has been linked to different health outcomes, ranging from the modest transient changes in respiratory tract and impaired pulmonary function to the increased risk of death from cardiovascular and respiratory diseases or lung cancer. Since PM can be transported in the atmosphere for hundreds or even thousands of kilometres, it represents not only a serious local but also regional, as well as international environmental problem [4]. In terms of the potential to harm human health, besides NO_2 and ground-level O_3, PM is recognised as Europe's most serious air pollutant [3].

The primary pollution sources in the environment of the Bor city are the mining and metallurgical processes. They are a source of sulphur-dioxide emission, dust with high content of heavy metals (lead, arsenic, cadmium, copper, zinc, etc.), soot, carbon-dioxide and other pollutants [3].

One hundred and nineteen years of mining activities on the territory of Bor and its surroundings resulted in numerous ecological problems and enormous consequences as an inheritance. This kind of pollution endangers not only the biotope, but all the living organisms including humans [3].

Taking into account the long-term and extreme air pollution with substances originating from mining and metallurgical processes, this study aimed to determine the level of air quality when the smelter is operating and when it is under repair. In this paper, the level of arsenic air pollution in PM in the area of Bor is presented during the period 2010–2021 as well as on a daily basis during April 2022.

METHODOLOGY

The study area and measuring sites

The primary sources of environmental pollution in Bor (Serbia) are mining (surface mining of copper ore) and metallurgy (pyrometallurgical copper production from the following sulfide ores: chalcopyrite ($CuFeS_2$), chalcozine (Cu_2S) and covelline (CuS). Additional sources of air pollution in Bor and the surroundings are flotation tailings and open pits, from which particles are emitted with a high concentration of sulfates. The main pollutants are SO_2, particulate matter with a high content of As, Pb, Cu, Zn, Cd, and aero sediments, which also contain heavy metals and sulfates [3].

The monitoring of As concentrations in the air was performed by the Mining and Metallurgy Institute Bor [5]. A detailed description of experimental procedure was given in the paper of Serbula *et al*. 2013 [6]. In this study, the presented data of air quality monitoring data are from the following measuring sites (Figure 1a): Krivelj (KR), Town Park (TP), Institute (IN), Jugopetrol (JP), Brezonik (BR), Technical Faculty (TF), Oštrelj (OŠ) and Slatina (SL). Daily As concentrations in PM were measured at the sites: KR, JP, OŠ, BR, IN and TP during April 2022 [7]. A wind rose diagram for the study area of Bor is shown in Figure 1b [7]. The predominant winds in the study area were of WNW, NNW, SSW, SW and E directions. Less frequent winds were of S, NE, ESE and NNE directions. The measuring sites JP and SL were characterized by the high-frequency WNW winds. The surroundings of the sites TP and TF were characterized by the prevailing east wind directions, while the site IN was along the directions of prevailing north winds.

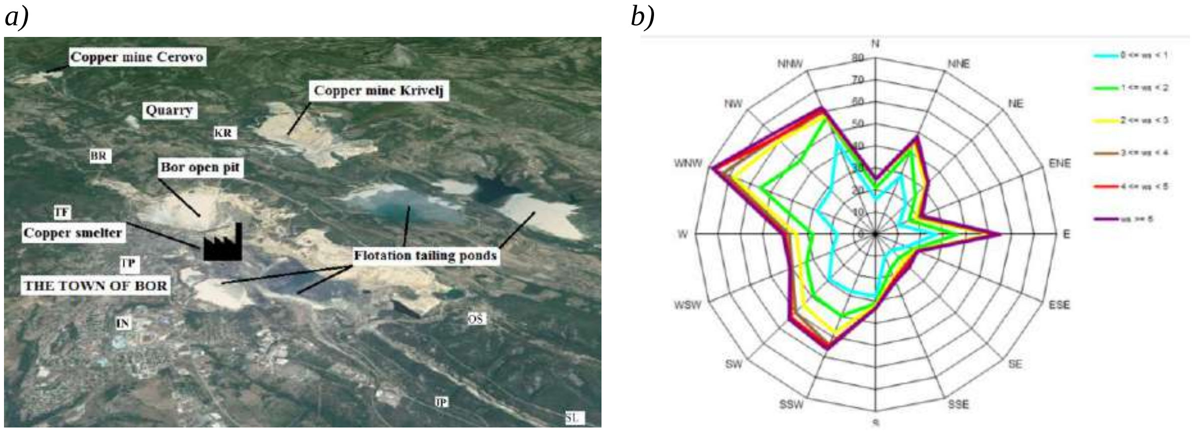


Figure 1 *a) Location of the measuring sites in Bor (KR – Krivelj, BR – Brezonik, TF – Technical Faculty, TP – Town Park, IN – Institute, JP – Jugopetrol, OŠ – Oštrelj and SL – Slatina) in respect of the copper smelter; b) Rose diagrams for different wind speeds for the period 01.04.2022–30.04.2022 at the measuring site IN in Bor [7]*

RESULTS AND DISCUSSION

From Figure 2 it can be seen that all the available annual As concentrations in the air of Bor and the surroundings exceeded the target value (TV) defined by the Serbian Regulation and the European Commission Regulation [8]. However, the exceedances of the annual TV for As in the period 2015–2021 were more pronounced than in the previous period 2010–2015, which is the period of application of the new smelter [3]. Maximum annual As concentrations measured at the site JP during 2019 was 550 ng m^{-3}, which is more than 90 times the allowable value.

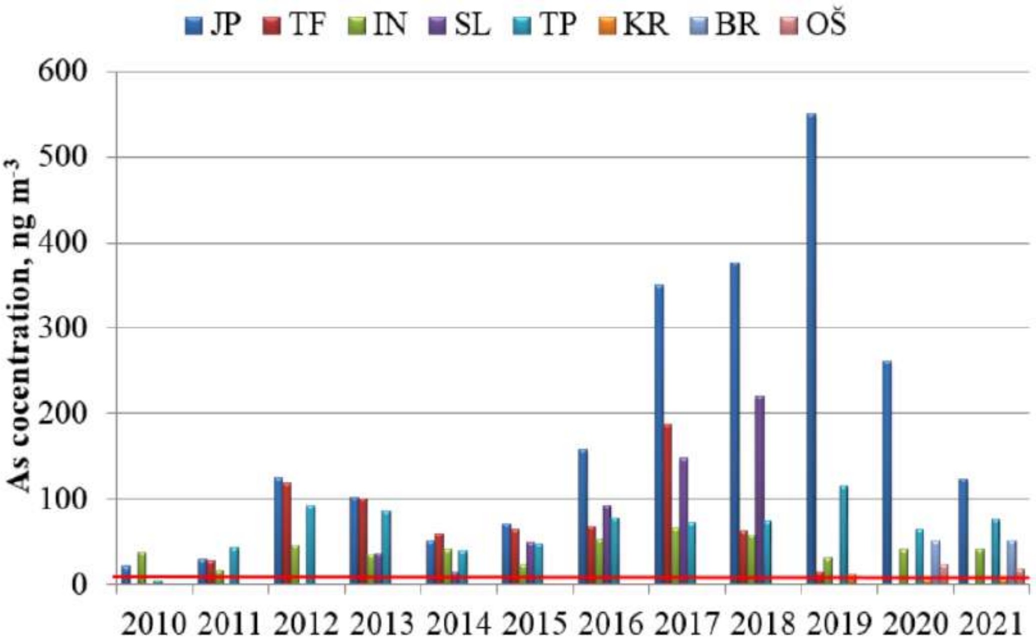


Figure 2 *Average annual As concentrations in PM at eight measuring sites in the Bor area during period 2010–2021; Target value (TV) (red horizontal line) is defined at 6 ng m*$^{-3}$ *[8]*

The influence of wind direction on pollutant distribution from industrial facilities to populated areas has been shown in many research results. According to the estimates of the World Health Organization (WHO) for Europe, arsenic concentrations range from 1 to 10 ng m^{-3} in rural areas to 30 ng m^{-3} in urban areas. Near emission sources, such as non-ferrous metal smelters and power plants in which arsenic-rich coal is burned, concentrations of airborne arsenic can exceed 1 μg m^{-3} [4]. According to the data presented in Figure 3, the average daily As concentrations in the rural area of Bor were within the WHO guideline values, whereas the As concentration at the measuring site Jugopetrol was higher than the WHO estimations due to influence of the unfavourable wind direction [9]. The average daily concentrations of arsenic were the highest at the measuring site Jugopetrol during April 2022. The production in the copper smelter in Bor was stopped on April 20, 2022, due to the scheduled maintenance and overhaul. At all the measuring sites, the average daily concentrations of arsenic were less than recorded on April 20, 2022, except on April 23/24 when was recorded one exceedance at the measuring site JP which amounted 120.1 ng m^{-3}. This confirms the influence of meteorological factors on arsenic concentrations in the ambient air, because the measuring site JP is located in the direction of the dominant winds. The higher the wind speed, the more the deposited PM particles rise from the ground. Resuspension is the second largest source of arsenic after the copper smelter. Large areas of mining and flotation tailings surrounding of Bor are also a source of resuspension particles of the smallest dimensions, which contain high concentrations of arsenic compounds. Over the 100 years of mining and metallurgy in Bor have had great consequences for the environment, which is desirable to be rehabilitate as soon as possible.

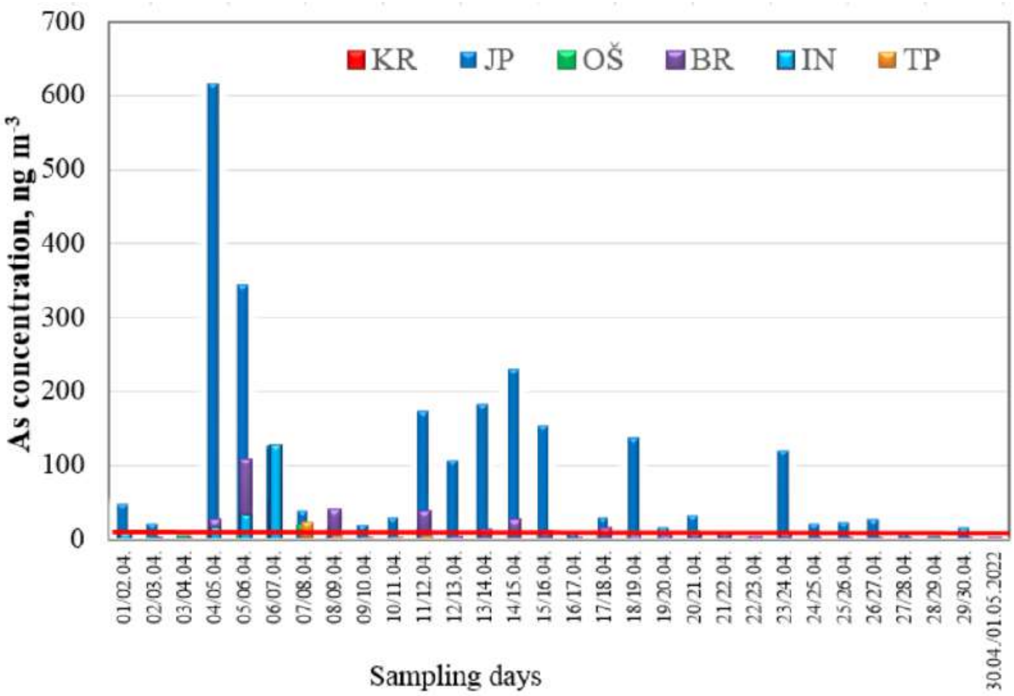


Figure 3 *Average daily As concentrations in PM at six measuring sites in the Bor area during April 2022; Target value (TV) (red horizontal line) is defined at annual level at 6 ng* m^{-3} *[8]*

CONCLUSION

Situated in the close vicinity of the urban zone of the town of Bor, the Mining and Smelting Complex is the major pollution source emitting particulate matter into the atmosphere of the city of Bor and its surroundings. Air quality measurements are conducted at the measuring sites in the urban-industrial, suburban and rural areas, from 2010 to 2021. Long-term monitoring of air-quality parameters in the Bor area, and scientific studies as well, prove that the mining-metallurgy complex, is the major pollution source emitting particulate matter into the atmosphere.

Airborne PM with high content of heavy metals, pollute not only the urban parts of the city in the close vicinity of the mining-metallurgical complex, but also the suburban and distant rural zones. Data analysis showed a direct influence of the wind direction on the pollutant transport to the particular measuring sites. Due to unfavourable meteorological conditions (e.g. wind directions), as well as the periods of calm weather conditions, the area around the measuring site Town Park is considered to be pollution risk area. As far as suburban settlements are concerned, the areas around the measuring sites Jugopetrol and Brezonik are endangered. Long-term measurements of the content of As in PM have shown permanent exceedance of the TV for As concentrations. The greatest danger for the environment and all the living organisms are the high concentrations of arsenic in PM. Over 50% of the measured arsenic concentrations at all the sites in the examined period by far exceeded the allowed values. Arsenic is a carcinogenic matter, so that this state of matter is troublesome. During the last eleven years not a single average annual As concentration has been within the annual limit value at the measuring sites Town Park, Institute and Jugopetrol in Bor. The maximum arsenic concentration in the period 2010–2021 was recorded in 2019 at the measuring site Jugopetrol which amounted 550 ng m^{-3}. The immediate vicinity of the measuring site Town Park to the pollution source, as well as the position of the measuring site Jugopetrol along the prevailing wind direction caused high pollution levels of As in the air.

The predominance of a particular wind direction determined the distribution of PM and As. A one-month analysis of data during April 2022 showed a direct influence of the wind direction on the pollutant transport to the particular measuring sites. Due to unfavourable wind conditions, the area around the measuring site Jugopetrol is considered to be pollution risk area. As far as suburban settlements are concerned, within the municipality of Bor, the rural settlement Oštrelj is most endangered with pollution. The rural settlement Krivelj is located in the direction of a less frequent S wind, which accounts for a lower pollution level in this area.

In toxicological risk assessment it should be taken into consideration that the inhabitants of Bor are simultaneously exposed to other types of pollutants, which also increases the health risk. High concentrations of sulfur dioxide, heavy metals and their compounds in suspended particles are constantly present in the atmosphere of Bor.

ACKNOWLEDGEMENT

The authors are grateful to the Ministry of Education, Science and Technological development of the Republic of Serbia for financial support, within the funding of the scientific research work at the

University of Belgrade, Technical Faculty in Bor, according to the contract with registration number 451-03-68/2022-14/200131. Our thanks go to professor Mara Ž. Manzalović, English language teacher at the Technical Faculty in Bor, University of Belgrade for providing language assistance.

REFERENCES

[1] EEA, 2017. Air quality in Europe – 2017 report. In: European Environment Agency (Ed.), EEA Report No 13/2017, *Available on the following link*: https://www.eea.europa.eu/publications/air-quality-in-europe-2017

[2] EEA, 2018. Air quality in Europe – 2018 report. In: European Environment Agency (Ed.), EEA Report No 12/2018, *Available on the following link*: https://www.eea.europa.eu/publications/air-quality-in-europe-2018

[3] S.M. Serbula, J.S. Milosavljevic, J.V. Kalinovic, *et al.*, Sci. Total Environ; 777 (2021) 145981.

[4] WHO (2006) Health Risks of Particulate Matter from Long-Range Transboundary Air Pollution, World Health Organization, European Centre for Environment and Health. Copenhagen, Denmark.

[5] Mining and Metallurgy Institute Bor, annual reports about quality of ambient air in Bor from 2010 to 2021, Sector for Measuring and Control of Gaseous and Dust Parameters. Department Chemical-Technical Control, Bor, Serbia (in Serbian).

[6] S.M. Serbula, T.S. Kalinovic, J.V. Kalinovic, *et al*., Environ. Earth Sci; 68 (2013) 1989–1998.

[7] Mining and Metallurgy Institute Bor, monthly report about quality of ambient air in Bor from April 2022, Sector for Measuring and Control of Gaseous and Dust Parameters. Department Chemical-Technical Control, Bor, Serbia (in Serbian).

[8] Official Gazette of Republic of Serbia (2013), Regulation on the conditions for monitoring and requirements of the air quality, No. 11/10, 75/10, 63/13 (in Serbian).

[9] S.M. Šerbula, M.M. Antonijević, N.M. Milošević, *et al*., J. Hazard. Mater; 181 (2010) 43–51.

THE ASSOCIATION BETWEEN SHORT-TERM EXPOSURE TO SO_2 AND EMERGENCY ROOM ADMISSIONS IN URBAN AREA. CASE STUDY SERBIA

Nevena Ristić[1], Milica Veličković[2*], Danijela Voza[2]
[1]Institute for Mining and Metallurgy, Zeleni bulevar 35, 19210 Bor, SERBIA
[2]University of Belgrade, Technical Faculty Bor, V.J. 12, 19210 Bor, SERBIA
[*]*mvelickovic@tfbor.bg.ac.rs*

Abstract

The aim of this study was to explore the risk effect of air pollution caused by SO_2 on the emergency room admissions for cardiovascular, respiratory diseases, schizophrenia, and pregnancy-related problems in Bor, Serbia. We collected data on some patients for each of these outcomes, including daily mean concentrations of SO_2 and daily mean temperature and relative humidity for 2014-2018. The generalized-additive model (GAM) was utilized to evaluate the associations between daily SO_2 and emergency room visits for each outcome. The results have shown that short-term exposure to high SO_2 concentration has a significant effect on citizens' health, especially vascular diseases, inflammation, schizophrenia, and pregnancy problems.

Keywords: SO_2, Generalized-Additive Model, health impact, urban area

INTRODUCTION

Air pollution is considered a great ecological problem [1] in urban areas, especially in developing countries. Monitoring of air quality [2] and the impact of local pollution sources [1] aim to improve overall environmental quality [3].

Besides PM particles, a high concentration of sulfur dioxide SO_2 is still the main air pollution source in urban and industrial areas of developing countries [4]. Sulfur dioxide SO_2 is a sharp-smell colorless gas that is heavier than air and water-soluble [5]. Sulfur is a component of oil derivates, coal, gas, and metal ores, whose processing results in significant emission of this gas into the atmosphere [6]. Also, the gas is being emitted during the refining of crude oil in refineries and cement production. Cars as a by-product and factory chimneys emit sulfur dioxide SO_2 into the air [1,4]. Air pollution has become a leading risk [7] for the global mortality and morbidity rate. In the last decades, the yearly level of sulfur dioxide concentration has been reduced under the limits. However, developing countries are still dealing with the problem of sulfur dioxide emission [4,8].

There are limited epidemiological studies whose aim was to investigate the correlations between mortality, morbidity, and air pollution [9], especially in areas with a high level of sulfur dioxide SO_2 concentration [4,7,10,11]. Air pollution from sulfur dioxide SO_2 causes disorders, health problems, hospitalization, and lower average life expectancy [9]. Sulfur dioxide SO_2 is a strong respiratory irritant [12] and bronch-opstructure [4], which irritates the mucous membranes and upper respiratory tract. People's reactions are different because the sensitivity to sulfur dioxide SO_2 is not the same. During normal breathing, a larger amount of inhaled sulfur dioxide SO_2 is retained in the nose and throat [4], while a smaller amount reaches the lungs [7]. In serious cases, inhalation of higher concentrations [3] causes excess fluid in the lungs, blood oxygen reduction, and death in a few minutes [4,13]. Symptoms of excess fluid in the lungs are coughing and shortness of breath which may occur several hours after exposure. It causes systemic inflammation and oxidative stress. [14,15] Short-term exposure to a higher concentration of SO_2 [16] correlates with the increases in mortality and morbidity rates [17].

Therefore, this time-series analysis aims to explore the impacts of short-term exposure to SO_2 on hospital admissions for respiratory, cardiovascular, mental diseases, and pregnancy-related problems and to point out how increased pollution impacts the population's health.

MATERIALS AND METHODS

Study area

Bor is a small city (44°05′N, 22°06′E, 350–400 m above sea level) of 45,000 inhabitants, located in the Eastern part of the Republic of Serbia. The city of Bor (Serbia) is a mining and industrial city with developed non-ferrous extractive metallurgy. The copper smelter is located near the city, and for decades the local population has been exposed to pollutants such as SO_2 and PM_{10} with a high percentage of heavy metals [18].

Data collection

Data on the number of patients were collected between April 2014 and December 2018 from the local emergency room in Bor, Serbia, and used to examine the risk of copper smelter pollution to human health in order to make recommendations on how the local population's quality of life could be improved. The daily average SO_2 concentrations were collected from the Bor Municipality's website. The daily mean temperature and relative humidity were collected from the Serbian Agency for Environmental Protection and the Mining and Metallurgy Institute in Bor. Patients with cardiovascular, respiratory, mental, and pregnancy-related disorders who sought care from the emergency room during the day were included in the study. The diagnoses are primary, classified according to the International Classification of Diseases (ICD-10).

Statistical analysis

Generalized Additive Model (GAM) was used to assess the relationship between the SO_2 variation (Lags 0, 1, 2 and 3) and the daily number of patients for each particular diagnosis. At lag 0, GAM was used to detect the connection between air pollution and disease on a given day. Similarly, the mean concentration of air pollution at lag 1, 2 and 3 refer to one, two or three days before and the number of patients on the current day. Overall cumulative exposure to SO_2 on the current day and the previous three days (lag 0:3) was also estimated.

GAM was used in this study with the quasi-Poisson distribution. Several covariates were adjusted with the penalized spline function. The generalized cross-validation (GCV) score was used to find the optimum degrees of freedom (df) [19]. For the calendar time, the optimal df was 7 per year. For the mean temperature, the optimal df was 3, and for the relative humidity, the optimal df was 3. Besides the single lag model, the distributed lag model, where the multiple lags (lag 0:3) of air pollution are simultaneously included in the model, was applied. So, the model can be expressed as follows:

$$\log(\mu_t) = \alpha + \beta_{t-l}(SO2_{t-l}) + s(\mathrm{Time}, df = 7) + s(T, df = 3) + s(RH, df = 3) \qquad (1)$$

where the $\log(\mu_t)$ referred to the daily number of the diseases, t was the first day, and l was the lag days. β_{t-l} was the regression coefficient and $SO_{2_{t-l}}$ was the mean concentration of SO_2 at different lag days. The time was the calendar time. T stood for temperature, and RH was relative humidity. α was an intercept, and s was the penalized cubic spline function.

The results were expressed as the percentage changes (PC (%)) in the daily subject visits for each outcome for a 10 μg/m^3 increment of the SO_2 concentrations and its 95% confidential intervals. Statistical analysis was performed using the R software (https://www.r-project.org). To fit the GAM model, the 'mgcv' package was used. $p<0.05$ was considered statistically significant.

RESULTS AND DISCUSSION

The distribution of the average daily SO_2 concentrations from 2014 to 2018 is presented in Figure 1 . Mean daily concentrations of SO_2 were exceeded 66 times during the observed period, with maximum daily average values above 2000 μg/m^3.

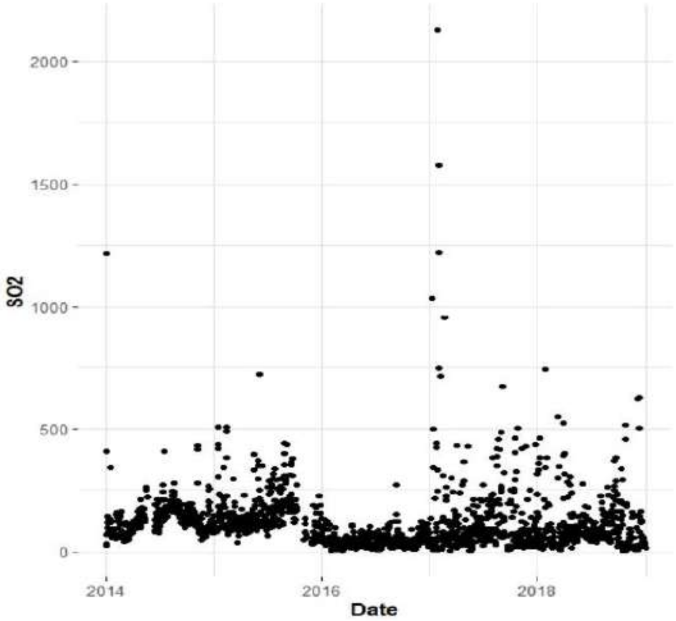


Figure 1 *Time-series plots of SO_2 concentrations between 2014 and 2018*

The estimates from the single pollution model are presented in Table 1.

According to the single pollutant model (Table 1), each 10 μg/m^3 increase in SO_2 (lag 3 and lag 0:3) is associated with the 0.78% (95% CI: (0.15, 1.35)) and 0.88% (95% CI: (0.32, 0.1.34)) increase in the output visits for the subjects with cerebrovascular diseases, respectively. Also, the increase in SO_2 (lag 0:3 - accumulative) is associated with the 0.29%

(95% CI: (0.12, 0.48)) increase in admission for upper respiratory tract infection. Besides, the increase in SO_2 (lag 3 and lag 0:3 - accumulative) is associated with the 0.19% (95% CI: (0.03, 0.36)) and 0.44% (95% CI: (0.11, 0.78)) increase in the subjects with psychotic disorders. The largest increase in the number of the subjects with pregnancy-related problems found for SO_2 on day 4 (Accumulative) was 0.25% (95% CI: (0.07, 0.38)).

Table 1 *The air pollution model*

	PC (%)	**95CI (%)**	**P value**
Model I: SO_2			
Vascular deseases, lag 3	0.78	(0.15; 1.35)	0.05
Vascular deseases, lag 0:3	0.88	(0.32, 1.34)	0.05
Upper respiratory tract infection, lag 2	0.53	(0.16; 0.91)	0.05
Upper respiratory tract infection, lag 3	0.78	(0.22; 1.36)	0.01
Upper respiratory tract infection, lag 0:3	0.29	(0.12; 0.48)	0.05
Chronic lung obstruction, lag 2	0.23	(0.04; 0.44)	0.03
Chronic lung obstruction, lag 3	0.41	(0.19; 0.62)	0.04
Chronic lung obstruction, lag 0:3	0.63	(0.13; 1.01)	0.05
Psychotic disorders, lag 3	0.19	(0.03; 0.36)	0.03
Psychotic disorders, lag 0:3	0.44	(0.11;0.78)	0.02
Pregnancy problems, lag 3	0.17	(0.01; 0.32)	0.03
Pregnancy problems, lag 0:3	0.25	(0.07; 0.38)	0.03

To assess the robustness of the main results obtained in this research study, a sensitivity analysis was performed. The df of the calendar time (5–8 df), the temperature (T) (3–5 df), and the relativity humidity (RH) (3–5 df) were changed. The results showed that when varying the degrees of freedom for time (5–8 df) no significant change in the effect was noticed, in the association between the SO_2 pollutant and the variables, as for the Temperature (T) (3–5 df) and the Relativity Humidity (RH) (3–5 df).

Similar results have been obtained in other studies. Increased oxidative stress and inflammation in the nervous system may be crucial biochemical mechanisms underlying the relationship between SO_2 and mental health [20]. Changes in synaptic plasticity in the hippocampus have been linked to SO_2 exposure [21]. Regarding the impact on pregnancy, in their study, Zhou *et al*. [22] found that SO_2 was one the largest contributor to an increased risk of preterm birth.

However, there has been a long debate on whether SO_2 has an independent effect on human health or serves as a proxy for combustion mixture [23]. Either way, further experimental or observational studies based on personal measurements and modeled residential concentrations are required to evaluate whether SO_2 has a causative health impact.

CONCLUSIONS

The present study confirmed that the daily emergency room admissions for vascular, respiratory, mental, and pregnancy diseases were significantly associated with exposure to

SO_2 in the city of Bor (Serbia). The study also revealed that risks of hospital admissions increased with the cumulative days of exposure to air pollution (lag 2, 3, and 0:3). Based on our findings, we would recommend certain categories of population, like pregnant women and chronic patients, to reduce their outdoor activities during elevated concentrations of pollutants. This study once again highlights the importance of monitoring and controlling the emission sources.

ACKNOWLEDGEMENT

The research presented in this paper was done with the financial support of the Ministry of Education, Science and Technological Development of the Republic of Serbia, within the funding of the scientific research work at the University of Belgrade, Technical Faculty in Bor, according to the contract with registration number 451-03-68/2022-14/200131.

REFERENCES

[1] A.L. Duarte, I.L. Schneider, P. Artaxo, *et al.*, Geosci. Front; 13 (1) (2022) 101168.

[2] A. Shilpa, P. Sindhu, Int. J. Innov. Res. Technol. Sci. Eng; 6 (5) (2017) 9261–9269.

[3] J.S. Kiurski, N.M. Ralević, S.D. Ignjatijević, *et al.*, Air Qual. Atmos. Health; 12 (8) (2019) 955–962.

[4] L. Wang, C. Liu, X. Meng, *et al.*, Environ. Int; 117 (2018) 33–39.

[5] M. Todorović, Određivanje porekla PM2,5 frakcije aerosola u graničnoj zoni urbanog područja Beograda primenom komplementarnih statističkih metoda – doctoral dissertation, Univerzitet u Beogradu, Fakultet za fizičku hemiju, Beograd, (2020) (in Serbian).

[6] A. Al-Hemoud, L. Al-Awadi, M. Al-Rashidi, *et al.*, Build. Environ; 122 (2017) 50–60.

[7] S.K. Dash, A.K. Dash, Indian J. Sci. Technol; 8 (35) (2015) 1–7.

[8] M. Greenstone, J. Environ. Econ. Manage; 47 (3) (2004) 585–611.

[9] A.M. Aenab, S.K. Singh, A.J. Lafta, Atmos. Environ; 71 (2013) 84–91.

[10] R. Chen, Y. Zhang, C. Yang, *et al.*, Stroke; 44 (4) (2013) 954–960.

[11] Q. Deng, C. Lu, Y. Li, *et al.*, Atmos. Environ; 157 (2017) 18–26.

[12] G.D. Thurston, H. Kipen, I. Annesi-Maesano, *et al.*, Eur. Respir. J; 49 (1) (2017) 1600419.

[13] N.M. Sofwan, W.R.W. Mahiyuddin, M.T. Latif, *et al.*, Sustain. Cities Soc; 75 (2021) 103390.

[14] H.C. Routledge, S. Manney, R.M. Harrison, *et al.*, Heart, 92 (2) (2006) 220–227.

[15] M. Zhu, J. Du, A.D. Liu, *et al.*, Histol Histopathol; 29 (2014) 1107–1111.

[16] H. Amini, N.T.T. Nhung, C. Schindler, *et al.*, Environ. Pollut; 254 (2019) 113121.

[17] H. Qiu, L. Wang, L. Luo, *et al.*, Environ. Res; 204 (2022) 111928.

[18] S.M. Serbula, J.S. Milosavljevic, J.V. Kalinovic, *et al.*, Sci. Total Environ; 777 (2021) 145981.

[19] M. Li, H. Dong, B. Wang, *et al.*, Sci. Total Environ; 754 (2021) 142110.

[20] Y. Ma, W. Wang, Z. Li, *et al*., J. Hazard. Mater; 424 (2022)127535.

[21] G. Yao, Y. Yun, N. Sang, Environ. Toxicol; 31 (2016) 820–829.

[22] G. Zhou, J. Wu, M. Yang, *et al*., Chemosphere; 286 (2022) 131833.

[23] WHO, WHO air quality guidelines for particulate matter, ozone, nitrogen dioxide and sulfur dioxide. In: Global Update 2006. Geneva.

ADSORPTION ISOTHERMS FOR COPPER IONS BIOSORPTION ONTO WALNUT SHELLS

Miljan Marković[1*], Milan Gorgievski[1], Nada Štrbac[1], Kristina Božinović[1], Vesna Grekulović[1], Aleksandra Mitovski[1], Milica Zdravković[1]

[1]University of Belgrade, Technical Faculty in Bor, V.J. 12, 19210 Bor, SERBIA

[*]*mmarkovic@tfbor.bg.ac.rs*

Abstract

Equilibrium analysis of copper ions biosorption onto walnut shells is presented in this paper. The experimental data were analyzed using three isotherm models, namely, the Langmuir adsorption isotherm model, the Freundlich adsorption isotherm model, and the Temkin adsorption isotherm model. Obtained results indicate that the Langmuir model fits best the experimental data ($R^2 = 0.993$), indicating that the biosorption of copper ions occurs in a monolayer. The small difference between $q_{e,exp}$ and $q_{e,m}$ point to that the walnut shells are almost completely saturated with copper ions.

Keywords: adsorption isotherms, biosorption, walnut shells, copper ions

INTRODUCTION

The growing development of many industrial processes, including mining and metallurgy, has led to the generation of huge amounts of wastewater. Water pollution, i.e. wastewater, is thought to be one of the biggest environmental issues today. This type of pollution occurs as a result of the discharging of many different pollutants into surrounding watercourses without prior treatment [1,2].

Due to the complexity of the process of heavy metal removal from wastewater, a significant number of conventional methods are being applied to water treatment, which include ion exchange, membrane processes, chemical precipitation, solvent extraction, cementation, etc. [3].

Biosorption of heavy metals from aqueous solutions is a new, still in developing process, which has been proven effective on a laboratory scale for treating wastewaters with a low concentration of heavy metals [4].

In the biosorption process, waste biomass is used as an adsorbent. Biomass which has the ability to adsorb metal ions from water solutions is considered as biosorbent. The biosorbent consist of cellulose, hemicellulose, and lignin. These components are made of functional groups, which are capable of binding metal ions into their structure [5].

Adsorption isotherm models give insight into the process mechanism, as well as information about the maximum biosorption capacity. Many empirical models are used to determine the process equilibrium [6].

In this paper, Langmuir, Freundlich and Temkin adsorption isotherm models were used to analyse experimental data.

MATERIALS AND METHODS

Biosorption isotherm data were obtained by bringing into contact 0.5 g of sample (with granulation -1 + 0.4 mm) with 50 mL of the synthetic solution of copper ions (initial concentration 5–200 mg dm^{-3}). The suspension was stirred for 60 minutes, then filtrated, and the filtrate was analysed for the remaining concentration of copper ions.

RESULTS AND DISCUSSION

Adsorption isotherm for copper ions biosorption onto walnut shells

Experimentally obtained adsorption isotherm for copper ions biosorption onto walnut shells is shown in Figure 1a.

Langmuir adsorption isotherm model

This model assumes that the adsorption takes place in a monolayer, at a limited number of definitely localized sites [7].

The Langmuir isotherm model can be expressed as:

$$q_e = \frac{q_m K_L c_e}{1 + K_L c_e} \tag{1}$$

The linear form of the equation (1) is:

$$c_e / q_e = \frac{1}{K_L q_m} + \frac{1}{q_m} c_e \tag{2}$$

where C_e - is the equilibrium concentration of metal ions in the solution (mg dm^{-3}), q_e - is the equilibrium adsorption capacity defined as mass of the adsorbed metal per unit mass of the adsorbent (mg g^{-1}) at equilibrium, q_m - is the maximum adsorption capacity (mg g^{-1}), and K_L - is the Langmuir equilibrium constant (dm^3 g^{-1}).

The obtained experimental isotherm data were fitted using this model, and the results are shown in Figure 1b and in Table 1.

Freundlich adsorption isotherm model

This model is based on the assumption that the surface of the adsorbent is heterogeneous, with adsorption sites of different adsorption energies present [8].

This model is represented by the equation:

$$q_e = K_f c_e^{1/n} \tag{3}$$

In its linear form, equation (3) becomes:

$$\log q_e = \log K_F + \frac{1}{n} \log c_e \tag{4}$$

where C_e - is the equilibrium concentration of metal ions in the solution (mg dm^{-3}); q_e - is the adsorbent capacity (mg g^{-1}) at equilibrium; and K_F - is the Freundlich equilibrium constant ((mg g^{-1}) (dm^3 mg^{-1})$^{1/n}$).

Linear dependence *log*q_e *vs. log*C_e is given in Figure 1c, and the obtained isotherm model parameters are shown in Table 1.

Temkin adsorption isotherm model

This model is most often used for analysing multilayer chemical adsorption processes that are based on strong electrostatic interactions between positive and negative charges [9].

This model can be expressed as:

$$q_e = B\ln\left(K_T c_e\right) \tag{5}$$

The linear form of the equation (5) is:

$$q_e = B\ln K_T + B\ln c_e \tag{6}$$

where: $B = RT/b$ - is the Temkin constant, which refers to the adsorption heat (J mol^{-1}); b - is the variation of adsorption energy (J mol^{-1}); R - is the universal gas constant (J mol^{-1} K^{-1}); T - is the temperature (K); K_T - is the Temkin equilibrium constant (dm^3 g^{-1}); q_e - is the adsorption capacity (mg g^{-1}) at equilibrium; and C_e - is the equilibrium concentration of metal ions in the solution (mg dm^{-3}).

Linear plot $q_e = f(\ln c_e)$ shown in Figure 1d gives the values of the constants B and K_T, shown in Table 1.

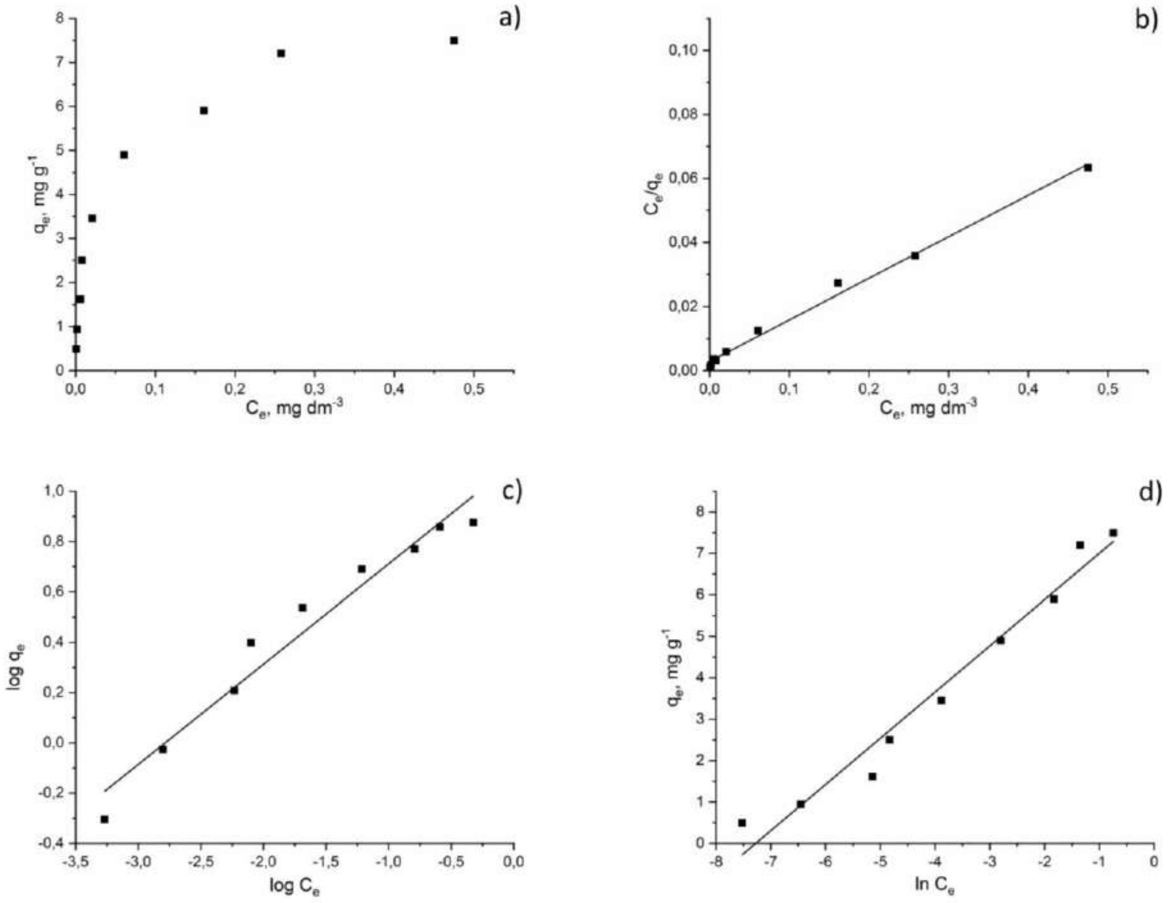


***Figure 1** a) Adsorption isotherm for copper ions biosorption onto walnut shells; b) Langmuir adsorption isotherm model; c) Freundlich adsorption isotherm model; d) Temkin adsorption isotherm model*

Table 1 *Values of isotherm model parameters for the Langmuir, Freundlich and Temkin model*

Langmuir				**Freundlich**			**Temkin**		
K_L (dm^3 mg^{-1})	**q_{exp}** (mg g^{-1})	**q_m** (mg g^{-1})	**R^2**	**K_F**	**1/n**	**R^2**	**B** (J mol^{-1})	**K_T** (dm^3 g^{-1})	**R^2**
45.19	7.50	7.71	0.993	12.87	0.4	0.960	1.11	8.11	0.968

Based on the data shown in Table 1, it can be concluded that the Langmuir model fits best the analysed experimental data (R^2 = 0.993). This leads to the conclusion that the biosorption of copper ions onto walnut shells takes place in a monolayer, at a limited number of definitely localized sites. The negligible difference between q_{exp} and q_m also speaks in favor of the good functionality of this model.

CONCLUSION

In this research, walnut shells were used as a biosorbent for copper ions biosorption from aqueous solutions. The obtained equilibrium data for this process was analysed using Langmuir, Freundlich, and Temkin adsorption isotherm model. The Langmuir model was proven to be the best fit for the analysed equilibrium data (R^2 = 0.993), which led to the conclusion that the biosorption process of copper ions onto walnut shells occurs in a monolayer, at a limited number of localized sites.

ACKNOWLEDGEMENT

The research presented in this paper was done with the financial support of the Ministry of Education, Science and Technological Development of the Republic of Serbia, within the funding of the scientific research work at the University of Belgrade, Technical Faculty in Bor, according to the contract with registration number 451-03-68/2022-14/200131.

REFERENCES

[1] T.V. Ramachandra, N. Ahalya, R.D. Kanamadi, CES Technical Report; 110 7 (4) (2005) 1–34.

[2] S.H. Abbas, Y.M. Younis, M.K. Hussain, *et al*., Rev. Chim; 71 (1) (2020) 1–12.

[3] D. Božić, V. Stanković, M. Gorgievski, *et al*., J. Hazard. Mater; 171 (2009) 237–249.

[4] J. Febrianto, A.N. Kosasih, J. Sunarso, *et al*., J. Hazard. Mater; 162 (2009) 616–645.

[5] N.T. Abdel-Ghani, G. A. El-Chaghaby, IJSTR; 3 (2014) 24–42.

[6] M.J. Mohammed-Ridha, A.S. Ahmed, N.N. Raoof, NJES; 20 (2017) 29–310.

[7] X. Chen, Information; 6 (2015) 14–22.

[8] M. Momčilović, Kinetički i ravnotežni parametri adsorpcionih procesa pri uklanjanju pojedinih štetnih katjonskih sastojaka iz vodenih rastvora aktivnim ugljevima dobijenih hemijsko-termičkom obradom srži ploda divljeg kestena i šišarke crnog bora, Doktorska

disertacija, Univerzitet u Nišu, Prirodno-matematicki fakultet, Departman za hemiju, Niš, (2012).

[9] A. Khan, X. Wang, K. Gul, *et al.*, Egypt. J. Basic Appl. Sci; 5 (2018) 171–182.

DETECTION OF THE TRAFFIC-RELATED POLLUTION BY THE ROADSIDE SOIL AND PLANT MATERIAL

Tanja Kalinović[1*], Jelena Kalinović[1], Snežana Šerbula[1], Jelena Milosavljević[1], Ana Radojević[1]

[1]University of Belgrade, Technical Faculty in Bor, V.J. 12, 19210 Bor, SERBIA

[*]*tkalinovic@tfbor.bg.ac.rs*

Abstract

Biomonitoring abilities of elder (Sambucus nigra) were used in the examination of environmental pollution of the traffic zone in the vicinity of the Bor city (Eastern Serbia). The concentrations of the examined elements in the root zone soil and leaves of elder were determined by the simultaneous dual view inductively coupled plasma atomic emission spectrometer (ICP-AES) after the sample microwave digestion. The obtained results were compared with the biomonitoring data related to the background (not polluted) and urban-industrial (extremely polluted) zones. The results indicated the pollution of the roadside soil with the traffic pollution markers such as Cu, Zn, Pb, As and Cd, which pose the ecological risk due to the surrounding farmland ecosystems. The leaves content of Al, Fe and Zn could not be connected to the traffic, while the traffic emissions contributed to the Cu, Pb and As contents in the elder leaves. The differences (D) between the concentrations of the elements of the washed and unwashed elder leaves indicated the presence of the airborne particulate matter rich in Cu, Pb and As in the examined roadside environment. The pollution emitted from the traffic had far less impact on the quantities of toxic elements in the soil and vegetation samples compared to the pollution from the copper production processes.

Keywords: elder, biomonitoring, traffic pollution markers, environmental pollution

INTRODUCTION

Pollution related to the road traffic usually originates from combustion of fuel and oil, corrosion of metallic parts, tailpipe exhaust, tire wear, lubricants, brake wear and particle resuspension from the road surface (road abrasion). Brake wear emissions have been identified to contain significant amounts of Cu, Fe, Ba, Sb and Mn, while Cd, Pb and Zn are used in tire manufacture. Some metals, typically known as geogenics, such as Ca, K, Mg, Al, Fe and Mn, have been identified to be correlated with traffic markers [1]. Aksu [2] mentioned that the main source of Cu is diesel engines and unleaded gasoline, while Zn is used in lubricating oil. The distance from transport routes and traffic load intensity could influence certain content of the toxic elements in the roadside vegetation and soil [3]. Roadside planting at the particulate matter immission hotspots can substantially and quickly improve the urban air quality and reduce human exposure to it. It was proven that elder had very high capabilities for capture of the airborne ultrafine particles (70.5%) [4].

The aim of this study was to apply biomonitoring abilities of *Sambucus nigra* (elder) [5] in the examination of the roadside environmental pollution in the vicinity of the Bor city.

MATERIALS AND METHODS

Naturally distributed elder (*Sambucu nigra*) and soil from the root zone of the plant were chosen for the purpose of the roadside pollution bimonitoring. The samples of soil and leaves were collected from the background zone without the impact of anthropogenic pollution. The traffic zone was situated along the road of the IB order (Bor-Selište), at the distance which was without the impact of pollution from the mining and metallurgical facilities. The urban-industrial zone was under the pollution emitted from the copper smelter, tailings ponds, city heating plant and the traffic. The root zone soil (10–20 cm depth) of three to five elder plants were sampled after the removal of surface layer of humus, at each sampling site. The samples of leaves were collected at 1.5 to 2 m height above the ground from the outer branches of canopy, in the period from September to mid-October. One half of foliar samples was retained as an unwashed sample (UL), while the other half was thoroughly washed (WL) with running distilled water for about 1 min at room temperature. After air drying at room temperature, the samples were ground to a fine powder and stored at room temperature until analysis. The digestion [6] and chemical analysis of the extracts (simultaneous dual view inductively coupled plasma atomic emission spectrometer, ICP-AES) were determined at the Institute of Mining and Metallurgy Bor (Serbia). The values of Enrichment factor (EF) were calculated by dividing the concentration of a certain element in the sample from the polluted zone by the concentration of the same element in the sample from the background zone. The values of EF>2 indicated environmental pollution [7].

RESULTS AND DISCUSSION

Soil

The concentrations of the studied elements in the soil samples depending on the zones were established in the increasing order as follows: background<traffic<urban-industrial (Table 1). The exception was Al with the maximum content in the soil from the traffic zone.

The enrichment of soil with Cu, Zn, Pb, As and Cd was noticed for the samples from the traffic and urban-industrial zones, with the higher EFs for the samples from the urban-industrial zone. Except the soil from the traffic and industrial zones, the Maximum limit value (MLV) for Cu [8] was exceeded in the soil from the background zone, which was probably the impact of the natural soil composition. The values of MLV for Zn, Pb and Cd were exceeded in the soil from the traffic and urban-industrial zones. The concentration of As in the soil from the urban-industrial zone was also higher than the MLV, while the concentration of As in the soil from the traffic zone was close to the MLV. The noted exceedances indicated that the level of contamination could disturb ecological balance, impose additional examinations of the soil, as well as limitations in soil usage [8], which is of high importance for the landowners engaged in the agricultural production in the studied area. The Remediation values (RV) for Cu, Zn, Pb, As and Cd [8] were not exceeded in the soil from the traffic zone, but only for the given elements in the urban-industrial zone. From the obtained results it could be noted that the pollution of the roadside soil with Cu, Zn, Pb, As and Cd existed and must not be ignored because of the surrounding farmland ecosystems.

Table 1 *Content (mg/kg d.w.) and the values of the Enrichment factor (EF) of the studied elements in the soil samples from the industrial, traffic, and background zones*

	[a]Al	[a]Fe	Cu	Zn	Pb	As	Cd
Urban-industrial	4.59	4.94	9435.06	1836.89	1021.20	1141.29	19.83
Traffic	5.27	4.67	816.58	209.64	94.51	28.67	1.96
Background	3.39	2.44	39.42	84.22	22.70	7.39	<0.3 [b]
EF$_{industrial}$	1.36	2.03	239.37	21.81	44.99	154.50	>66.1 [c]
EF$_{traffic}$	1.56	1.91	20.72	2.49	4.16	3.88	>6.53 [c]
[d]MLV	/ [f]	/ [f]	36	140	85	29	0.8
[e]RV	/ [f]	/ [f]	190	720	530	55	12

[a] The content of element is expressed in %.

[b] The lower limit of determination for Cd.

[c] Values with the sign “>” are obtained by dividing the concentration of a certain element in the soil from a certain zone with the corresponding concentration of the element from the background zone which was below the lower limit of determination.

[d] MLV-maximum limit value according to the Serbian Regulation [8].

[e] RV-remediation value according to the Serbian Regulation [8].

[f] not defined.

Plant material

The lowest Al concentrations were detected in the unwashed and washed elder leaves from the traffic zone, while the highest Al contents were detected in the leaves from the urban-industrial zone (Figure 1a). The calculated D values indicated the highest Al washable content for the leaves from the urban-industrial zone, while the D values for the leaves from the background and traffic zones were similar. According to the presented results, including the EFs (Table 2), it could be said that the Al contents in the leaves from the traffic zone could not be related with the emissions from road traffic.

The Fe concentrations in the washed and unwashed elder leaves from the background and traffic zones did not differ much, while the elder leaves from the urban-industrial zone stood out with the highest Fe contents (Figure 1b). It could be noticed that the D value was lowest for the samples from the background zone, and the highest for the samples from the urban-industrial zone. The Fe contents in the washed elder leaves from the background and traffic zones were not above the Fe excessive content for the leaves of woody plants (500 μg/g) [9], which cannot be said for the contents of the washed leaves from the urban-industrial zone. The enrichment of the elder leaves from the traffic zone was not noticed according to the EFs (Table 2), while the leaves from the urban-industrial zone were enriched with Fe.

The Cu contents in the elder leaves from the background and traffic zones were far below the Cu contents in the leaves from the urban-industrial zone (Figure 1c). The D value for the leaves from the traffic zone existed, but it was much lower than for the leaves from the urban-industrial zone. The critical Cu concentrations for the leaves of woody plants (20 μg/g) [9,10] were not exceeded in the washed leaves from the background and traffic zones. The Cu concentrations in the washed leaves from the urban-industrial zone were about 10 times the critical Cu value.

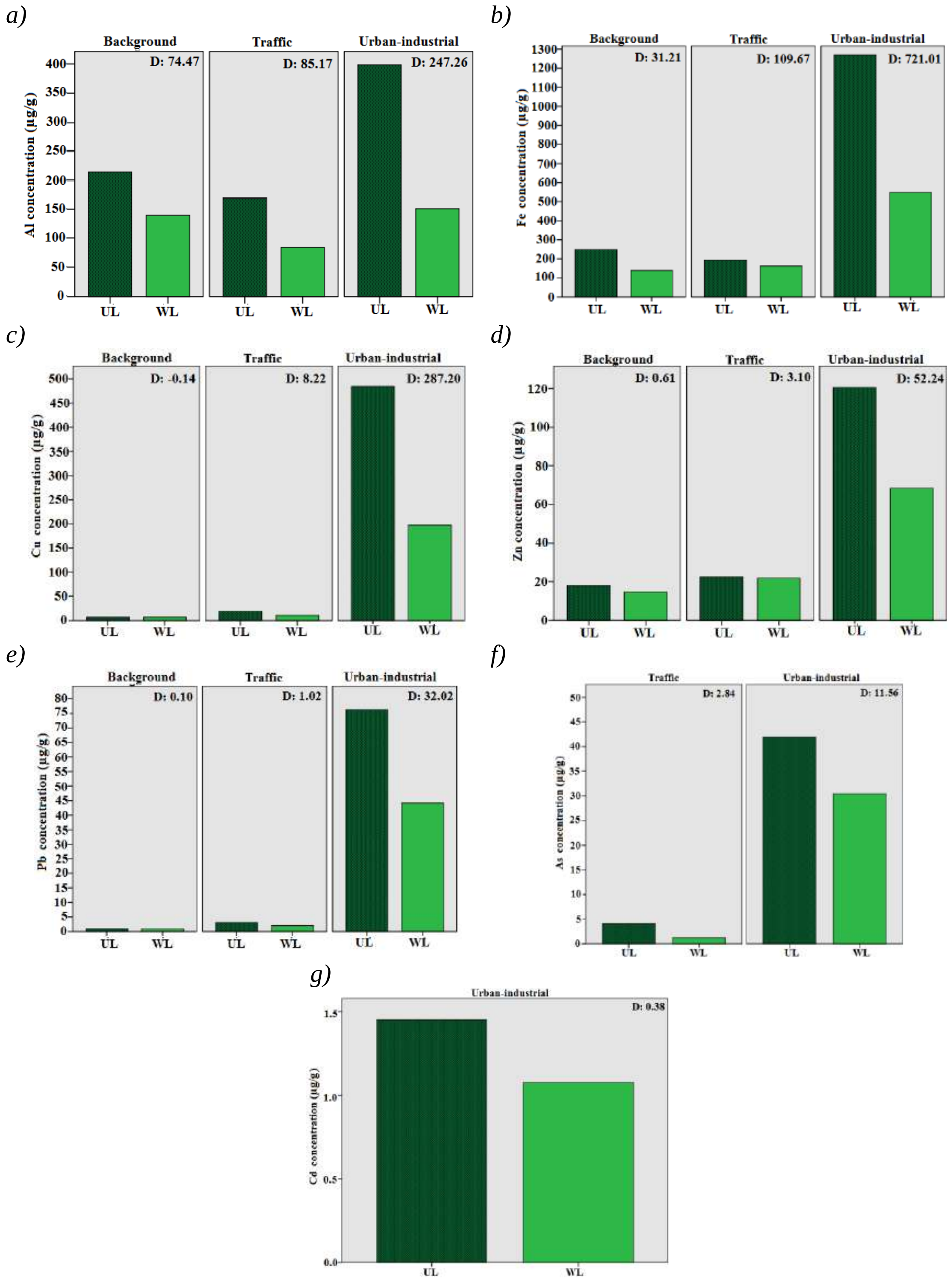


Figure 1 *Concentrations of a) Al, b) Cu, c) Fe, d) Zn, e) Pb, f) As and g) Cd in unwashed (UL) and washed (WL) elder leaves from the background, traffic and urban-industrial zones. The D-difference (µg/g) of a certain element concentration between the unwashed and washed leaves*

The values of EF were >2 for Cu in all the leaf samples, except for Cu in the washed leaves from the traffic zone (Table 2). This indicated that the traffic emissions contributed to some extent on the Cu content of particles deposited on the surfaces of the elder leaves which were sampled in the traffic zone.

Table 2 *The values of Enrichment factor of the analyzed elements in the washed and unwashed elder leaves from the traffic and urban-industrial zones*

	Washed leaves		**Unwashed leaves**	
	traffic	**urban-industrial**	**traffic**	**urban-industrial**
Al	0.60	1.08	0.79	1.86
Fe	0.86	**3.38**	1.28	**6.56**
Cu	1.60	**29.89**	**2.90**	**75.01**
Zn	0.68	**3.14**	0.80	**5.39**
Pb	**2.21**	**46.58**	**2.98**	**72.90**
As	>1.23 [a]	**>30.38** [a]	**>4.07** [a]	**>41.94** [a]
Cd	/ [b]	>1.08 [a]	/ [b]	>1.45 [a]

[a] Values with the sign ">" are obtained by dividing the concentration of a certain element in the leaves from a certain zone with the corresponding lower limit of determination of the element in the leaves from the background zone.

[b] The concentrations of the analyzed elements in the leaves from a certain and background zone were below the lower limit of determination.

The values in bold are >2.

The Zn concentrations, D values and the values of EF for the elder leaves (Figure 1d, Table 2) indicated that emissions from the traffic did not cause chemical disturbance of the roadside environment with this element. The influence of the copper smelter on the Zn content in the leaves was significant, which could be seen from Figure 1d and Table 2. The concentrations of Zn in the washed elder leaves from the background and traffic zones were not above the excessive concentrations (>50–100 μg/g) [9], while the Zn content in the leaves from the urban-industrial zone was in the given range.

The Pb concentrations of the elder leaves, as well as the D values, followed the same increasing order depending on the sampling zone: background<traffic<urban-industrial (Figure 1e). It is significant to emphasize that the EF>2 (Table 2) indicated the enrichment of the leaves from the traffic zone with Pb, which is one of the main indicators of the pollution emitted from the traffic. Nevertheless, the obtained results showed the incomparable influence of the copper production processes on the Pb environmental content of the urban-industrial zone. The excessive Pb concentrations for the leaves of higher plants (30 μg/g) [9] were not exceeded in the washed leaves from the background and traffic zones, which could not be noted for the samples from the urban-industrial zone.

The As concentrations in the leaves from the background zone were below the LOD, and were not presented in the Figure 1f. The As concentrations of the elder washed and unwashed leaves, as well as the D values for the samples from the traffic zone, were far below the As concentrations and the D values for the leaves from the urban-industrial zone. However, the D value for the leaves from the traffic and urban-industrial zones indicated the presence of this carcinogenic element in the atmospheric deposition of the examined environments. These results were supported by the values of EF for As in the unwashed leaves from the traffic zone which were >2. The highest concentration that plants can tolerate in their tissues of 2 μg/g [11] and the toxicity limit value of 20 μg/g [12] were not exceeded in the washed leaves from the background and traffic zones, which cannot be observed for the leaves from the urban-industrial zone.

The Cd concentrations in the leaves from the background and traffic zones were below the LOD, and were not presented in Figure 1 g, so environmental enrichment with Cd in the traffic zone cannot be assessed. The excessive concentrations defined for the leaves of higher plants 1–3 μg/g [9] were observed only in the washed leaves from the urban-industrial zone.

CONCLUSION

The examined root zone roadside soil was polluted with Cu, Zn, Pb, As and Cd, which could lead to the contamination of soil-crop system due to the agricultural activities in the surrounding of the sampling sites. According to the obtained concentrations, the values of EF, and D values for Al, Fe and Zn in the elder leaves it can be concluded that the traffic emissions in the study area did not contribute to the environmental enrichment with these elements. The Cu, Pb and As concentrations in the elder leaves, as well as the washable quantities of these elements, indicated the presence of airborne particulate matter rich in Cu, Pb and As, in the examined roadside environment.

ACKNOWLEDGEMENT

The authors are grateful to the Ministry of Education, Science and Technological development of the Republic of Serbia for financial support, within the funding of the scientific research work at the University of Belgrade, Technical Faculty in Bor, according to the contract with registration number 451-03-68/2022-14/200131. Our thanks go to professor Mara Ž. Manzalović, English language teacher at the Technical Faculty in Bor, University of Belgrade for providing language assistance.

REFERENCES

[1] K. Alexandrino, F. Viteri, Y. Rybarczyk, *et al.*, Ecol. Indic; 117 (2020) 106701.

[2] A. Aksu, J. Environ. Health Sci. Eng; 13 (2015) 79.

[3] S.K. Georgieva, A. Georgieva, Z. Peteva, *et al.*, Environ. Sci. Pollut. Res; 28 (2021) 59277–59283.

[4] H. Wang, B.A Maher, I.A.M. Ahmed, *et al.*, Environ. Sci. Technol; 53 (2019) 6906−6916.

[5] T.S. Kalinovic, S.M. Serbula, A.A. Radojevic, *et al.*, Geoderma; 262 (2016) 266–275.

[6] U.S. EPA (U.S. Environmental Protection Agency), 1996. Acid Digestion of Sediments, Sludges, and Solids (3050B), Washington, DC.

[7] G. Bertolotti, S. Gialanella, Anal. Methods; 6 (2014) 6208–6222.

[8] Official Gazette of Republic of Serbia, Regulation on Limit Values for Polluting, Harmful and Hazardous Substances in the Soil, No 30/2018 (in Serbian).

[9] P. Rademacher, (2003): Atmospheric heavy metals and forest ecosystems, Work Report, No. 2003/12, Federal Research Centre for Forestry and Forest Products (BFH), Institute for World Forestry, Hamburg.

[10] A.M.B. Pählsson, Water Air Soil Pollut; 47 (1989) 287–319.

[11] A. Kabata-Pendias, H. Pendias, Trace Elements in Soils and Plants, 3rd ed., CRC Press, Boca Raton, Florida (USA) (2001), ISBN: 978–0–8493–1575–6.
[12] T. Vamerali, M. Bandiera, G. Mosca, Environ. Chem. Lett; 8 (2010) 1–17.

SYNTHESIS AND CHARACTERISATION OF Ti/SnO$_2$-Sb-TYPE DSA ANODES FOR WASTEWATER TREATMENT

Vladan Nedelkovski[1*], Sonja Stanković[1], Milan Radovanović[1], Milan Antonijević[1]
[1]University of Belgrade, Technical faculty in Bor, V.J. 12, 19210 Bor, SERBIA
**vnedelkovski@tfbor.bg.ac.rs*

Abstract

In this paper, two Ti/SnO$_2$-Sb-type anodes were syntesised via thermal decomposition method, one of which was doped with Mn and Cr in order to achieve increased number of active sites and prolonged service life of said anodes. Six layers of precursor solution were applied on the titanium substrate before the final step of calcination at 550 °C. The characterisation of synthesised anodes comprised of different electrochemical techniques: measurement of oxygen evolution potential (OER), cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) and accelerated lifetime test (ALT). Higher oxygen overpotential, electrocatalytic specific area and service life were achieved with non-doped anode, while possible formation of nonconducting passivating layer and insufficient oxide layer compactness may have caused short service life of doped DSA anode. In comparison with other commercial DSA anodes, syntesised anodes are required to have longer service life for their potential application in industrial processing plants.

Keywords: DSA anodes, electrochemical oxidation, wastewater treatment, termochemical decomposition

INTRODUCTION

In electrochemical oxidation (EO)–a promising alternative for wastewater treatment, the oxidation of toxic, recalcitrant and bio-refractory pollutants can be achieved through direct electron transfer or indirect mediated oxidation in the bulk solution. Ti/SnO$_2$-Sb-type anodes as the most studied non-active anodes, represent the low cost and high overpotential anodes for the oxygen evolution reaction in which $^\bullet$OH radicals are generated [1]. However, amount of $^\bullet$OH radicals responsible for oxidation of toxic compounds is dependant upon the number of active sites on DSA anodes which is further affected by oxide layer composition and structure [2]. Ti/SnO$_2$-Sb-type anodes have proven as very efficient in electrochemical oxidation of highly toxic organic pollutants as p-chlorophenol, acid orange and perfluorooctanic acid [3–5]. Doping SnO$_2$ oxide layer with antimony, enhanced dielectric properties by forming essential oxygen vacancies [6,7]. Possitive effect of Mn doping on DSA service life was reported by Li *et al.* [2] and Massa *et al.* [8], while positive effect of Cr doping on crystallinity and grain size of oxide layer was previosly researched by Shao *et al.* [9].

EXPERIMENTAL

Titanium substrate (3.9 cm×1 cm×0.01 cm) was polished (grits 150 and 1500) in order to remove oxide layer and other surface impurities, washed by distilled water and degreased in ethanol for 10 minutes. Futher, metallic substrate was etched in 10% oxalic acid for 60 minutes at 85°C. Substrate was additionally washed by distilled water and dried at 105°C.

Precursor solutions were prepared by dissolving $SnCl_4 \cdot 5H_2O$ and Sb_2O_3 in 25 ml ethanol with addition of 2 ml conc. HCl. In one of those solutions, $CrCl_3 \cdot 6H_2O$ and $MnCl_2 \cdot 4H_2O$ were additionally added. The composition of precursor solutions is shown in Table 1.

Table 1 *Composition of precursor solutions*

Component	**Mass (g)**	
	Precursor 1	**Precursor 2**
$SnCl_4 \cdot 5H_2O$	5.6413	5.6413
Sb_2O_3	0.2186	0.2186
$CrCl_3 \cdot 6H_2O$	0.2665	/
$MnCl_2 \cdot 4H_2O$	0.2118	/

Prepared precursor solutions were then applied by brush until titanium substrate surface was fully covered. Substrate was dried at 105°C for 5 minutes, and heated in furnace at 550°C for 5 minutes. This proces was repeated 5 times with the final layer being calcined at 550°C for 1 hour. Substrate mass was measured throughout the whole process in order to determine the oxide loading, which is shown in Table 2.

Table 2 *Substrate mass througout preparation and oxide loading of synthesised anodes*

Anode	**Substrate mass (g)**			**Mass DSA (g)**	**Oxide layer mass (g)**	**Oxide loading (mg/cm^2)**
	Initial	**After polishing**	**After etching**			
DSA1	1.4713	1.4520	1.4040	1.4144	0.0104	1.23
DSA2	1.5160	1.4893	1.4140	1.4865	0.0725	7.97

For electrochemical testing of synthesised anodes, potentiostat (IVIUM XRE, IVIUM Technologies) was used, with the appropriate software. The surface redox behaviour of the coatings was characterized in 0.25 M aqueous Na_2SO_4 solution by cyclic voltammetry at 20 mV/s, 50 mV/s and 100 mV/s, with the electrode potential being scanned between 0 and 1 V. The oxygen evolution reaction (OER) was studied via linear voltammetry under potentiostatic control in the same electrolyte between 0.5 and 2.5 V. Applied scan rate was 10 mV/s. EIS measurements were conducted in same solution in the frequency range of 100 kHz–1 Hz. ALT test was conducted in 0.5M H_2SO_4, at constant current density of 500 mA/cm^2, until potential of 10 V was reached. All measurements were conducted at room temperature in naturally aerated solutions.

RESULTS AND DISCUSSION

OER potential values for DSA1 and DSA2, as a direct indicator of electrocatalytic activity of DSA anodes [10], were determined at the intersection point of the tangent and the horizontal line at 0 V potential shown in Figure 1.

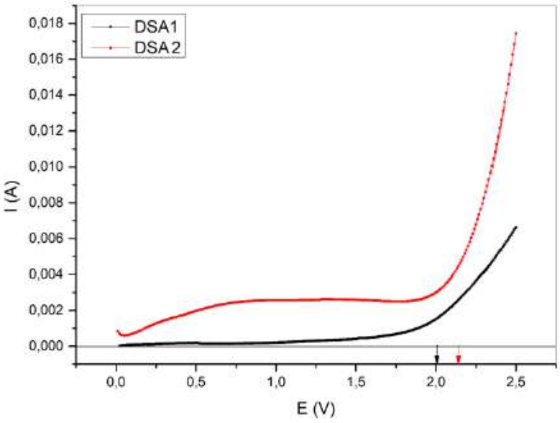


Figure 1 *Linear sweep voltammetry (LSV) of synthesized DSA anodes in 0.25 M* Na_2SO_4

Higher oxygen evolution potential (OEP) values are related to high electrocatalytic activity and better performance of anodes in electrochemical oxidation of recalcitrant organic compounds in water. Lower OEP values indicate shorter service life due to passivation of substrate and degradation of oxide layer; which would lead to higher consumption of electric energy in electrochemical oxidation [11]. OEP for DSA2 was estimated to be 2.14 V, while for DSA1 OEP was 2.01 V, which indicates that non-doped DSA2 anode has better catalytic properties. It is assumed that lower crystallinity, lower number of active sites and speciffic crystal structure could be the cause of lower OEP of DSA1 [12]. However, according to the estimated OEP values are considered to be relatively high and would indicate that synthesised anodes could be used for the processes of electrochemical oxidation [13].

Cyclic voltammetry curves shown in Figure 2, were obtained in potential range from 0 V to 1 V, considered to be optimal for determination of capacitivity in aqueous solutions.

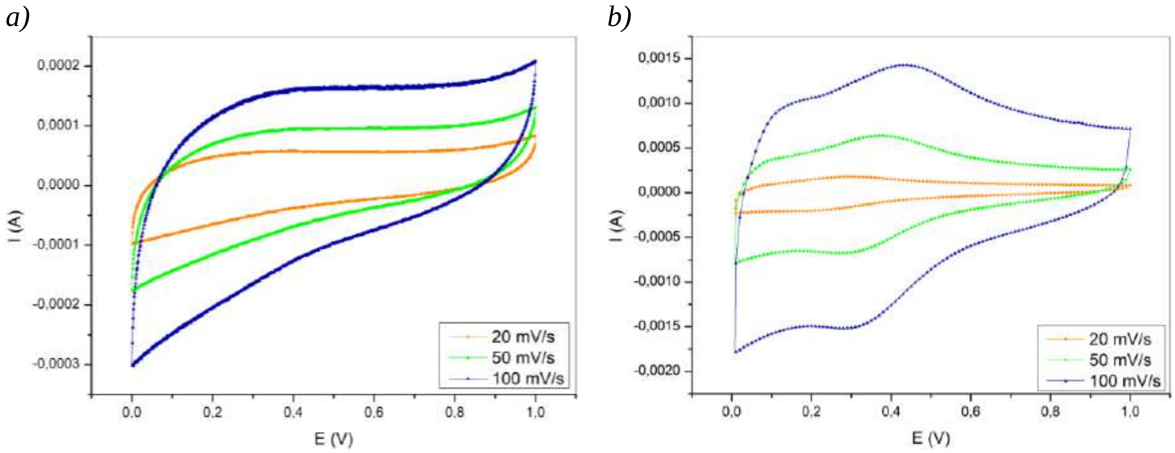


Figure 2 *Cyclic voltammetry curves for a) DSA1 and b) DSA2 anodes at different scan rates*

According to the CV plots shown in Figure 2, the decrease of cathodic current at potentials lower than 0.1 V indicates the reduction of SnO_2 might occur which could further cause degradation of oxide layer [14]. Voltammetric profiles indicate that capacitivity rises with the increase in scan rate, and that higher capacitivity is observed for DSA2 anode [15]. No noticable redox peaks were observed. However, the increase of current at potentials higher than 1.7 V due to intensified oxygen evolution. According to this phenomenon, synthesised anodes are considered non-active anodes [14]. Current peaks noticed at CV curves shown in Figure 2 b), are considered to be due to adsorption (0.4–0.45 V) and desorption (0.35 V) of sulfate ions on the surface of anode [16].

In order for roughness factor (R_f) and voltammetric charge (q*) to be determined and for additional investigation of catalytic activity, specific capacitivity (C_m) of synthesised anodes was calculated using the following equation [15]:

$$C_m = \frac{Q}{2 \cdot \Delta V \cdot m} \text{ (F/g)} \qquad (1)$$

Here Q represents voltametric charge (C)–obtained by integrating the area of voltammetric profiles, ΔV is the potential range in which the curves are positioned and *m* is oxide layer mass. R_f of examined anodes was determined by dividing their calculated capacitivity (given in mF/cm^2) with the capacitivity of rutile type TiO_2 (approximately 60 μF/cm^2). The calculated parameters are summarized in Table 3.

Table 3 *Oxide layer capacitivity, roughness factor and voltammetric charge of synthesised DSA anodes*

Anode	**Oxide loading (g)**	**Scan rate (mV/s)**	**C_m (F/g)**	**C (mF/cm^2)**	**R_f**	**q* (mC/cm^2)**
DSA1	0.01	20	0.1999	0.2368	3.95	0.47
		50	0.1321	0.1565	2.61	0.31
		100	0.1160	0.1374	2.29	0.27
DSA2	0.07	20	0.0700	0.5584	9.31	1.12
		50	0.1065	0.8488	14.15	1.70
		100	0.1332	1.0624	17.71	2.12

Considering the results shown in Table 3, it can be concluded that DSA1 has less active sites on the oxide layer surface, and therfore being less effective than DSA2 anode in terms of electrocatalytic activity [17]. Main cause of larger electrocatalytic active area of DSA2 might be the formation of larger number of smaller-sized crystals [18].

EIS measurements were conducted according to the determined OEP values of syntesised anodes, at which the most dominant process is oxygen evolution. Fitting results were obtained via proposed equivalent circuit model shown in Figure 3.

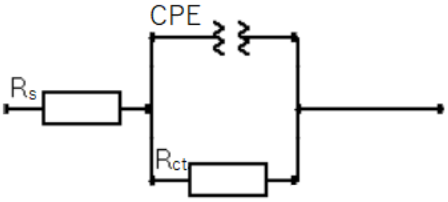


Figure 3 *Equivalent circuit model used for fitting EIS data*

In Figure 3, Randles' circuit model is composed of R_s-resistance of electrolyte solution, R_{ct}-charge transfer resistance during OER, and CPE which is a constant phase element that is usually used instead of a double layer capacitance to account for the non-ideal capacitive response of the interface [19]. Niquist plots for examined anodes are shown in Figure 4.

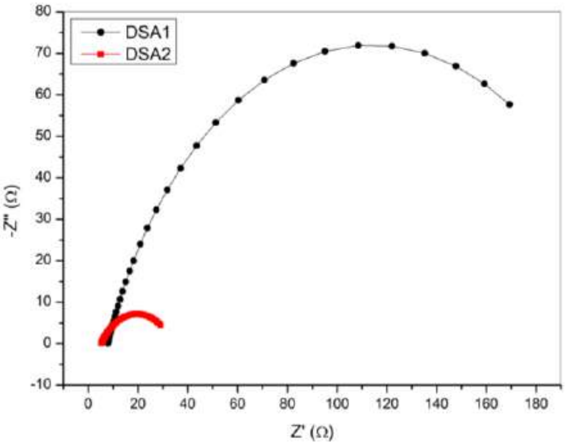


Figure 4 *Niquist plots for DSA1 and DSA2*

Speciffic shape of curves shown in Figure 4, is distinctive for anodes with pronounced roughness, synthesised by thermal decomposition method. The size of half-circle shaped curve is related to the charge transfer resistance, which further shows that better catalytic properties are observed for DSA2 anode [12]. Parameters of equivalent circuit were further determined, and are given in Table 4.

Table 4 *Equivalent circuit parameters*

Anode	**R_s (Ω)**	**R_{ct} (Ω)**	**CPE**	
			Q_{dl}	**n**
DSA1	7.89	$2.12 \cdot 10^2$	$4.79 \cdot 10^{-5}$	0.76
DSA2	5.18	28.8	$5.76 \cdot 10^{-5}$	0.58

It is assumed that higher charge transfer resistance reported for DSA1 anode, might be due to formation of low-conducting TiO_2 during the synthesis procedure or prolonged contact with electrolyte solution [20]. Relatively low n values for DSA1 and DSA2 indicate the existence highly porous and rough oxide layer surface [17]. Finally, ALT test was conducted to estimate real service life. In EO processes, it is desired for anode to have long service life

[20]. ALT test was conducted until potential of 10 V was reached, at which anodes were presumed to be deactivated. ALT test results are shown in Table 5.

***Table 5** ALT test results*

Anode	**Service life (h)**	**Real service life (h) – at 100 mA/cm^2**	**Real service life (h) – at 10 mA/cm^2**
DSA1	0.01	0.23	2.3
DSA2	0.64	16.1	161

Obtained ALT test results indicate that DSA2 anode has significantly longer real service life, while the low service life of DSA1 anode is considered to be the cause of formation of TiO_2 layer and degradation of oxide layer [21].

CONCLUSION

Linear potentiodynamic measurements confirmed that both DSA1 and DSA2 have relatively high OEP, further proving that the synthesised anodes have electrocatalytic properties. These anodes are considered to be a non-active DSA anode type, due to lack of redox peaks on cyclic voltammograms. Better catalytic properties were confirmed for non-doped DSA2 anode in terms of higher values of OEP, capacitivity, voltametric charge and roughness factor. This indicates that intensified hydroxyl radical formation would lead to more effective electrochemical oxidation of organic compounds. Relatively fast deactivation of DSA1 is considered to be due to passivation of substrate and erosion of oxide layer.

ACKNOWLEDGEMENT

The authors would like to acknowledge financial support from Ministry of Education, Science and Technological development of the Republic of Serbia (Agreement No 451-03-68/2022-14/200131).

REFERENCES

[1] G.O.S. Santos, A.R. Dória, V.M. Vasconcelos, *et al.*, Chemosphere; 259 (2020).

[2] D. Li, J. Tang, X. Zhou, *et al.*, Chemosphere; 149 (2016) 49–56.

[3] F. Cao, J. Tan, S. Zhang, *et al.*, J. Chem; (2021) 1–13.

[4] H. Lin, J. Niu, S. Ding, *et al.*, Water Res; 46 (7) (2012) 2281–2289.

[5] Y. Duan, Y. Chen, Q. Wen, *et al.*, J. Electroanal. Chem; 768 (2016) 81–88.

[6] A. Chen, X. Zhu, J. Xi, *et al.*, J. Alloys Compd; 683 (2016) 501–505.

[7] C. Carlesi Jara, G.R. Salazar-Banda, R.S. Arratia, *et al.*, Chem. Eng. J; 171 (2011) 1253–1262.

[8] A. Massa, S. Hernández, A. Lamberti, *et al.*, Appl. Catal. B; 203 (2017) 270–281.

[9] C. Shao, F. Zhang, X. Li, *et al.*, J. Electroanal. Chem; 832 (2019) 436–443.

[10] L. Li, Z. Huang, X. Fan, *et al.*, Electrochim. Acta; 231 (2017) 354–362.

[11] G. Zhao, X. Cui, M. Liu, *et al*., ES&T; 43 (2009) 1480–1486.

[12] L.M. da Silva, G. de Oliveira Santiago Santos, M.M. de Salles Pupo, *et al*., J. Electroanal. Chem; 813 (2018) 127–133.

[13] H. Shekarchizade, M.K. Amini, Int. J. Electrochem; (2011) 1–13.

[14] L. Xu, M. Li, W. Xu, Electrochim. Acta; 166 (2015) 64–72.

[15] S.M. Chen, R. Ramachandran, V. Mani, *et al*., Int. J. Electrochem. Sci; 9 (2014) 4072–4085.

[16] A. Chen, S. Nigro, J. Phys. Chem. B; 107 (2003) 13341–13348.

[17] V.M. Vasconcelos, I.M.D. Gonzaga, A.R. Dória, *et al*., Electrochim. Acta; 364 (2020) 137273

[18] G.O.S. Santos, L. R. A. Silva, Y.G.S. Alves, *et al*., Chem. Eng. J; 355 (2019) 439–447.

[19] W. Choi, J. H. Choi, H. Park, Chem. Eng. J; 409 (2021).

[20] Q. Bi, W. Guan, Y. Gao, *et al.*, Electrochim. Acta; 306 (2019) 667–679.

[21] L. Xu, Y. Wang, W. Zhang, RSC Advances; 9 (67) (2019) 39242–39251.

PROTECTION AND PRESERVATION OF NATURAL RESOURCES

Maja Radić[1*], Mehmed Avdagić[2], Branka Markovic[3], Kenan Ademović[4],
Sumeja Avdagić[5], Sarah Avdagić[6]

[1]Business Academy in Novi Sad, Faculty of Economics and Engineering Management,
Novi Sad, REPUBLIC OF SERBIA

[2]International University in Goražde, Faculty of Social Sciences, Goražde,
BOSNIA AND HERZEGOVINA

[3]Independent University of Banja Luka, Faculty of Ecology, Banja Luka,
BOSNIA AND HERZEGOVINA

[4]Law office Filipović-Ademović and Associates, Sarajevo, BOSNIA AND HERZEGOVINA

[5]Business Academy in Novi Sad, Faculty of Economics and Engineering Management,
Novi Sad, REPUBLIC OF SERBIA

[6]Business Academy in Novi Sad, Faculty of Economics and Engineering Management,
Novi Sad, REPUBLIC OF SERBIA

[*]*maja.radic84@gmail.com*

Abstract

Natural resources are those resources that nature has made available to us. There is no human intervention in the production of these resources. Man has used these resources for centuries to meet many of his needs. Many of these resources are used directly, while others are used indirectly. These resources are used to prepare things that are useful to us in life. From the use of these natural resources to the exploitation of each of them - man has come a long way. We need to conserve natural resources so that our future generations can use them to make their lives enjoyable.

Keywords: environment, resources, nature, protection, conservation

INTRODUCTION

Natural resources are an important resource for every human being and other living beings. That is why it is necessary to preserve nature. The development of natural resources and the environment is a fundamental reference in various development sectors in order to create balance and preserve the environment and to guarantee the lives of people and others.

The use of natural resources should provide opportunities and space for the community to maintain the environment and sustainable development. The ecological problems that arise at this time cannot be separated from human behavior that has consciously or unconsciously changed the earth’s ecosystem to be compromised by balance.

The company's decision to exploit or explore the industry is influenced by environmental conditions. People as part of the life system exaggerate too much in manipulating nature to increase well-being without thinking about the negative impact it has on the survival of life itself. Today, countries facing rapid and rapid industrial growth often cause serious problems that must be controlled immediately. In general, economic development aims to improve the quality of human life. Quality of life can be interpreted as the degree of fulfilment of basic needs. This essential basic need for our lives consists of three parts, namely:

- basic needs for biological survival,
- basic needs for human survival,
- degree of freedom of choice.

PROTECTION AND CONSERVATION OF NATURAL RESOURCES

Natural resources

Natural resources provide fundamental support to life and economic processes. Soil is the foundation of agriculture, which is also a basic building block for all people's lives. Forests help protect water sources, reduce the risk of natural disasters such as landslides and floods, are home to at least 80 percent of remaining terrestrial biodiversity, and are a major source of carbon that mitigates climate change [1].

More than 1.6 billion people depend on forests in some way, and water is necessary for their survival. Nor could the survival of flora and fauna on earth be imagined, that is, life would not be possible. Coastal and marine ecosystems include some of the most diverse and productive habitats on earth. Marine fisheries are an important part of the world's food supply. Ecological processes maintain soil productivity, recycle nutrients, clean air and water, and regulate climate cycles.

At the genetic level, the diversity found in natural life forms supports the breeding programs necessary to protect and improve cultivated plants and domestic animals and thus helps to protect food security. Properly managed natural resources are the foundation for maintaining and improving the quality of life of the world's population and can make an invaluable contribution to sustainable growth.

The degradation of the natural resource base has a significant impact on the economies of developing countries. This directly threatens the quality of life. Deforestation increases vulnerability to natural disasters, as shown by the devastating effects of hurricanes in Central America. Even in the absence of hurricanes, floods and landslides were regular events, causing extensive loss of life and damage to crops and infrastructure. The growing shortage of water and firewood is forcing many - primarily women and children - to travel long distances to gather their daily supplies.

The World Health Organization (WHO) estimates that more than 5 million people die each year from diseases caused by unsafe drinking water and lack of water for sanitation and hygiene [2].

The degradation of the natural resource base also threatens long-term growth. Improving agricultural productivity is an essential part of development and poverty reduction strategies in many countries, but soil and water degradation undermines this goal.

Taking this depletion into account can deduct a few percentage points from gross domestic product (GDP). The impact of this degradation is particularly severe for the poor, who rely heavily on fragile natural resources for life.

In other words, their right to these resources is often weak. Being socially and economically disadvantaged, the poor often reside in peripheral areas, where access to drinking water and adequate sanitation is limited and where higher mortality, morbidity and disease rates are prevalent, or in very vulnerable areas such as floodplains, coastal areas and degraded hills, with reduced capacity to protect against natural shocks and disasters caused by human activity.

Poverty and natural resource management

Natural resource management refers to the use of natural resources such as land, water, air, minerals, forests, fisheries and wild flora and fauna. This discussion begins by identifying key issues and approaches to policies to improve natural resource management and mitigate the impact of natural resource use on poverty. It then considers key issues that arise in the context of some of the most important natural resources: land, forests and water.

The perspective taken by the strategy is that natural resource management should contribute to poverty reduction and that natural resources should be used in a sustainable way to improve human well-being. Sustainable management of natural resources and poverty reduction are generally very compatible. The poor are usually directly dependent on natural resources for their livelihood, and are most vulnerable to the consequences of natural resource degradation [3].

Improving the management of natural resources can thus make a significant contribution to improving the well-being of the poor. Sustainable intensification of agriculture can improve the incomes of poor agricultural households both in the short and long term. It can also help reduce pressures to spread to remaining forest areas, thus avoiding increased damage downstream from floods and sedimentation and conserving biodiversity.

Reducing damage downstream may require limiting the land use opportunities of poor agricultural households in the upper basin. Unless funds are found to compensate these households, such restrictions are likely to be either ineffective or unfair. Improved management of natural resources can result in significant economic gains, and these gains will often directly benefit the poor. But when they don't, the poor should not be asked to pay for them.

New evidence supports a shift in the way we understand natural resource management and the link between poverty and environmental degradation - towards a focus on how micro-level institutions mediate macro-environmental impacts to foster sustainability. This approach begins by analyzing the ways in which people access and use resources as part of their overall life strategy, and how they adapt to the conditions created by macropolitical and political frameworks.

This lens expands the analysis of local resource management options away from natural resource management and agricultural strategies, to look at the multiple, flexible life strategies that people follow and the institutional and cultural context in which they live. It also explicitly assesses local institutions and political economy that determine who in society – men, women, indigenous peoples, farmers or industrialists – have rights to resources and access to resources and capital.

Studies using this approach have documented the importance of social capital at several institutional levels:

- the role of environmental rights, including land and resource ownership,
- values of social and cultural preferences,
- revenue strategies that affect sensitivity to cyclical events or political risks, and
- dynamics of urban-rural remittances of migrants who are still culturally connected to rural areas [4].

These studies offer a wealth of examples of ways in which local populations alleviate poverty caused by environmental degradation or limited access to resources. They also show how local people have reversed patterns of degradation despite less perfect political and legal conditions.

The incentives faced by these decision makers are key to natural resource management. Inefficiencies in the use of natural resources often arise because private and social prices differ and markets are incomplete or distorted. The result is lower overall well-being, especially for the poor. A fundamental distinction needs to be made between the effects of on-site and off-site natural resource problems.

In the case of on-site effects, decision-makers already have strong incentives to address natural resource problems, as they are directly affected. The main need in this case is to remove obstacles to the proper functioning of existing incentives. This often involves the introduction of exclusive rights of use.

Out-of-place effects. On the other hand, in the case of extra-urban effects, decision-makers usually have little or no incentive to tackle natural resource problems, as the consequences do not affect them. Incentives need to be created in such situations. Policy makers should:

- remove distortion-causing policies that undermine the sound management of natural resources,
- complement market signals with taxes or fees that reflect societal opportunity costs or payments that reflect societal benefits, and
- selectively regulate the remaining external effects.

Property rights

Unsustainable and inefficient use of natural resources often occurs because property rights are not complete, exclusive, enforceable and transferable. The issue of property rights is particularly highlighted in the case of open access resources, such as fisheries. In addition, property rights that meet these conditions are often quite distorted. The result is a "smaller pie" than is theoretically possible and a "smaller piece of cake" for the poor.

Although secure property rights do not guarantee greater conservation of resources, they can play an important role in many circumstances. The first task of policy makers should be:

- clarification of property rights where they do not exist, if they are unclear or in dispute,
- the implementation of property rights to support better management of natural resources and thus contribute to poverty reduction, and
- selectively regulate the remaining external effects, using the right incentives.

Inefficiency and inequality in the use of natural resources often occur because many important actors have little real voice in their management. Several areas of work are needed to build social capital and support honest and transparent institutions that are trusted by the local population. Special attention is needed when natural resources are managed by indigenous peoples [5].

The need to preserve and protect natural resources

There is a great need to protect and conserve our natural resources. If we don't protect them now, we won't be able to survive long on this planet. Here are some of the main reasons why we need to protect and conserve these valuable resources:

I. Natural resources are limited

Natural resources are divided into two categories - renewable natural resources and non-renewable natural resources. While many renewable natural resources are available in abundance in nature and are easily regenerated, others need time to make up for it. Examples of natural resources that take time to regenerate include wood, soil and biomass. It is necessary to use such renewable sources carefully because they are limited and we have to wait before they are naturally replenished. Non-renewable resources such as minerals, metals and oil are limited and there is no way to renew them. Therefore, it is extremely important that you use them wisely.

II. Natural resources: essential for human survival

We must protect and preserve natural resources because they are very important for the survival of humans and other living beings. Life on Earth is possible only because of the availability of natural resources. If we continue to exploit natural resources and deplete them at this rate, we will not be able to survive long on this planet.

Not only are we rapidly depleting non-renewable natural resources and facing the risk of depleting them soon, but we are also deteriorating the quality of those available in abundance. Air and water quality has declined due to pollution and are likely to deteriorate further in the coming times. We need to protect and conserve natural resources for our future generations so that they can enjoy a comfortable life just like us.

CONCLUSION

We must all take responsibility for avoiding the waste of our natural resources. We must contribute to the protection and discussion of these precious resources that nature has given us [6].

In order to secure our future and live a comfortable life, we must use our natural resources wisely. There are a number of ways to conserve these resources, such as choosing our vehicles wisely, planting trees, avoiding excessive use of electrical appliances, and avoiding water wastage. If each of us takes responsibility for avoiding the waste of natural resources, and the state takes serious care of the consumption of natural resources, then conservation will be easier.

REFERECES

[1] O.A. Houck, G. Tracy Mehan, Best of the Books: Reflections on Recent Literature in Natural Resources and the Environment, Environmental low institute, Washington (2015), p.40.

[2] M. Carley, P. Spapens, Sharing the World: Sustainable Living and Equity in the 21st Century, Earthscan, London, UK (1998), p.121.

[3] S. Buck, The Global Commons: An Introduction, Island Press, Washington, DC (1998), p.80.

[4] J. Terborgh, Requiem for Nature, DC: Island Press, Washington (1999), p.93.

[5] O.A. Houck, G. Tracy Mehan, Best of the Books: Reflections on Recent Literature in Natural Resources and the Environment, Environmental low institute, Washington (2015), p.64.

[6] *Available on the following link:* https://imp.center/i/conservation-of-natural-resources-essay-9685/ (retrieved 26.03.2022).

Annex 2: FAUNA OF MACROCRUSTACEA (INVERTEBRATA-ARTHROPODA) IN PERMANENT AND EPHEMERAL WATERS OF ZASAVICA WETLAND (SPECIAL NATURE RESERVES)

Mihajlo Stanković[*]
[1]Pokret gorana Sremska Mitrovica, Svetog Save 19, 22000 Sremska Mitrovica, SERBIA
[*]*trogloxen@gmail.com*

Abstract

The Zasavica wetland and peat bog are located on the edge of the Pannonian Plain, formed by the Drina and Sava rivers with the influence of the Drina underground waters. Protected 25 years ago as a Special Nature Reserve of the I category. A total of 21 species of Macrocrustacea were found in the Zasavica wetland and its ephemeral waters. From the subclasses Branchiura the ichthyophage parasitic species Argulus foliaceus is present, and from Malacostraca the cosmopolitan species Asellus aquaticus is present. The amphipod has 5 species, 3 surfaces (Dikerogammarus fluviatilis, Gammarus balcanicus, G. fossarum), one semi-underground (Synurella ambulans) and one underground (Niphargus valachicus - strictly protected in Serbia and has the status of VU). There are 4 species from the Branhipoda class, one from the order Anostraca Chirocephalus brevipalpis, a rare species, and the find on Zasavica is the westernmost of this species and the only one south of the Sava and Danube. Two species of "living fossils" from the Cambrian (500 million years ago) Lepidurus apus were found at the Batar site from the ordo Notostraca as a unique find because it was found in running water and Triops cancriformis was found in a muddy puddle on a forest road. One species of Cyzicus tetrracerus belongs to the ordo Spinicaudata. There are 9 species of ostracods on Zasavica and the species Candona aff. candida is new to the fauna of Serbia. The ostracods found from the genera Ilyocypris and Cyclocpris belong to the fauna of the oldest early Holocene. The species Astacus leptodactylus from the Caspian Sea region is present from the ordo Decapod in two localities (Batar and Trebljevine), introduced into Central Europe in the 19th century and is on the IUCN Red List. Findings of 21 species of Macrocrustacea on Zasavica are new to Serbia.

Keywords: Zasavica wetland, *Macrocrustacea*, Arthropoda

INTRODUCTION

Zasavica Reserve is located on the border of two very important areas of the Balkan Peninsula in terms of crab diversity, which is characterized by extremely rich and specific crab fauna with 783 species, 203 of which are endemic to the Pannonian Plain [1]. The first data on the flora and fauna of Northern Macva (Peripannonian Serbia) and thus the area of today's Special Nature Reserve "Zasavica" are given by Taube [2], Pancic [3] and Dombrovski [4]. A period of over half a century of sporadic research by small groups and individual researchers followed. In 1995, the initiative for the protection of Zasavica was launched and the Decree on Preliminary Protection was passed [5]. At the suggestion of the Institute for Nature Protection of Serbia, the Government proclaimed the Zasavica Special

Nature Reserve [6] in 1997. This paper aims to show the overall diversity of macro crustacean fauna in the Zasavica SRP.

MATERIAL AND METHODS OF WORK

The material for this paper was collected from previously published papers and submitted research reports in the period 1997–2021, with the addition of data that have not yet been published.

RESULTS AND DISCUSSION

During the past eighteen years of research on the fauna of the Zasavica reserve, a total of 21 species of Macrocrustacea have been recorded.

Systematic review of identified species:

Phyllum: Arthropoda
Subclasses: Branchiura
Fam: *Argulidae*
Species: *Argulus foliaceus* (Linnaeus, 1758)
-Subclasses: *Malacostraca*
Ordo: *Isopoda*
Species: *Asellus aquaticus* (Linnaeus, 1758)
Ordo: Amphipoda
Genus: *Dikerogammarus*
Species: *Dikerogammarus fluviatilis* (Mart, 1919)
Genus: Gammarus
Species: 1. *Gammarus balcanicus* (Schaf., 1922)
2. *Gammarus fossarum* (Koch, 1836)
Genus: *Synurella*
Species: 1. *Synurella ambulans* (F. Muller, 1846)
Genus: *Niphargus*
Species: 1. *Niphargus valachicus* (Dobr. & Man., 1933)
Classes: Branhipoda
Ordo: Anostraca
Species: 1.*Chirocephalus brevipalpis* (Orhgidan, 1953)
Ordo: Notostraca
Species: 1. *Lepidurus apus* (Linnaeus, 1758)
2. *Triops cancriformis* (Bose, 1801)
Superordo: Diplostraca
Ordo: Spinicaudata
Species: 1. *Cyzicus tetracerus* (Krynicki, 1830)
Phyllum: Arthropoda
Subphylum: Crustacea
Classes: Ostracoda
Genus: *Candona*
Species: 1. *Candona aff. candida* (O.F. Muller, 1776)
Genus: *Cypria*
Species: 1. *Cypria ophtalmica* (Jurine, 1820)
Genus: *Cyclocypris*
Species: 1. *Cyclocypris laevis* (O.F. Muller, 1776)

2. *Cyclocypris ovum* (Jurine, 1820)
Genus: *Eucypris*
Species: 1. *Eucypris virens* (Jurine, 1820)
Genus: *Bradleystrandesia*
Species: 1. *Bradleystrandesia reticulata* (Zaddach, 1844)
Genus: *Heterocypris*
Species: 1. *Heterocypris incongruens* (Ramdorh, 1808)
Genus: *Cypris*
Species: 1. *Cypris pubera* (O.F. Muller, 1776)
Genus: *Ilyocypris*
Species: *Ilyocypris sp.*
Ordo: Decapoda
Fam: Astacidae
Species: 1. *Astacus leptodactylus* (Eschscholtz, 1823)

The Branchiura subclass in the reserve is represented by Fam: Argulidae and the ichthyophage parasitic species *Argulus foliaceus* (Linnaeus, 1758) [7]. The freshwater isopod *Asellus aquaticus* (Linnaeus, 1758) from the subclass Malacostraca of the order Isopoda is present in the reserve. Freshwater isopods represent ancient organisms originating from the Paleozoic [8]. According to Wilson [9] this is a European cosmopolitan and eurivalent species and is present in the entire reserve area both in the Zasavica riverbed and in the surrounding ephemeral waters. Five species of Amphipods live in the reserve, of which three are surface (*Dikerogammarus fluviatilis* Mart, 1919; *Gammarus balcanicus* Schaf., 1922 and *Gammarus fossarum* Koch, 1836), and one semi-underground (*Synurella ambulans* (F. Muller, 1846) and underground species *Niphargus valachicus* Dobr. & Man., 1933) [10]. Of these amphipods, *Niphargus valachicus* is a strictly protected species in Serbia, and according to Savić [11] the species is on the IUCN Red List with the status of VU B1 + 2 bcde. A total of four species of Branhipods were discovered: the Anostrac species *Chirocephalus brevipalpis* (Orhgidan, 1953), the Notostraca species *Lepidurus apus* (Linnaeus, 1758) and the *Triops cancriformis* (Bosc, 1801) and the Spinicaudata species *Cyzicus tetracerus* (Krynicki, 1830).

Anostraca *Chirocephalus brevipalpis* is a rare species, known from only a few localities in Romania and two areas in Serbia, and the find in Zasavica is the westernmost of this species and the only one south of the Sava and Danube. *Ch. brevipalpis* is an early spring lowland species ordered from late February to mid-May. It inhabits shallow ephemeral waters with or without vegetation and floodplain forests [12]. Within the reserve, it was found in several localities, and the locality where it is regularly found almost every year are depressions on the Valjevac pasture. *Lepidurus apus* is a species with a very limited distribution in Serbia, found in only two localities in central Banat [13]. It inhabits clear waters with sub-frozen vegetation, but also floodplain forests. This is an early spring species and was ordered from February to April [14]. The finding of the species in the tributary Batar is unique because the individuals were found in running water Petrov *et al*. [12]. Generally, *L. apus* is present in the western part of the reserve, where it is found both in the floodplain forests along the tributary Batar and in the ephemeral pond Jovača. Unlike other sites in Serbia where only females were found, here in Zasavica bisexual populations were found in all three habitats [15]. The species *Triops cancriformis* is a "living fossil" that originates from the Upper Cambrian over 500 million years ago [16]. It lives in shallow occasional aquatic habitats and has developed two characteristic features, the ability to reach sexual maturity and produce offspring and to survive in the period without water in the habitat in the form of resistant forms (in the form of dormant fertilized eggs, so-called cysts). For the first time in Yugoslavia, Marinček [17] registered the presence of *Triops cancriformis* (Bosc,1801) near the village of Ečka near Zrenjanin (Banat, Vojvodina), which was later discovered at many other sites, mostly in the Pannonian Plain (e.g. Ritovi donji Potisje, etc.) and now neighboring countries but also in Serbia south of the Danube (e.g. Stara Planina). Only women were present in this collected material [18]. In the vicinity of the village of Melenci, males of this species were found for the first time in Yugoslavia [19]. The finding of this shrimp on Zasavica is new for Serbia and a new species for the reserve.

The species *Cyzicus tetrracerus* is quite common in Srem [13], and inhabits ephemeral waters of various types. Populations of this spring-summer species are few in Jovača.

So far, nine species of ostracods have been discovered in the Reserve, namely: *Candona aff. candida* (O.F. Muller, 1776), *Cypria ophtalmica* (Jurine, 1820), *Cyclocpris laevis* (O.F. Muller, 1776), *Cyclocypris ovum* (Jurine, 1820), *Eucypris virens* (Jurine, 1820), *Bradleystrandesia reticulata* (Zaddach, 1844), *Heterocypris incongruens* (Ramdorh, 1808), *Cypris pubera* (O.F. Muller, 1776) and *Ilyocypris sp.* Although a widespread and common specie on the Eurasian continent, with exceptional tolerance to different habitat conditions, the finding of the species *Candona aff. candida* in Zasavica is the first in Serbia [12] . In Central Europe the species *Candona aff. candida* appears in spring (March-April) and develops rapidly. Hartmann and Hiller [20] consider it a permanent form in waters whose temperature does not exceed 18°C over the summer. Ostracodes in the reserve are mostly found in ephemeral waters on meadows or steamed fields, and have drought-resistant eggs. They have mixed copulation and parthenogenetic reproduction and newborn individuals, the ability to swim immediately. These biological attributes enable them to survive as successfully as possible in these habitats [21]. The most common species in the reserve is *Cypris pubera* [12]. The closest localities to Zasavica where these ostracods were found are in Srem. From the order Decapoda and Fam. Astacidae on Zasavica, the species *Astacus leptodactylus* Eschscholtz was found, 1823 at two localities (Batar GPS coordinate 44°57.694 'N, 19°33.085' E and in the watercourse Zasavica (Trebljevine) near Banovo Polje) [22]. It was introduced to Central Europe in the 19th century from the Caspian Sea region and can grow up to 30 cm in length. *Astacus leptodactilus* favors relatively calm waters (lakes, ponds, wetlands and canals) and is on the IUCN Red List [23]. A complete overview of the species with the localities where they were found is given in Table 1.

Table 1 *Complete overview of the types of sites*

Species	Locality	Biotope
Argulus foliaceus	2a	O
Asellus aquaticus	Present throughout the space reserve	O, +
Dikerogammarus fluviatilis	10	O
Gammarus balcanicus	16	O

Table 1 *continued*

Gammarus fossarum	16	O
Synurella ambulans	3, 4, 10, 11, 12, 13, 14, 15, 16, 17	O, +
Niphargus valachicus	1, 4, 5, 6, 11, 12, 13, 16, 15, 17, 18	O, +
Chirocephalus brevipalpis	1, 2, 4, 5, 6, 8, 9	+
Lepidurus apus	3, 4, 7	O, +
Triops cancriformis	3a	+
Cyzicus tetrracerus	4	+
Candona aff. candida	3	O
Cypria ophtalmica	3	+
Cyclocypris laevis	3, 5	+
Cyclocypris ovum	3	O
Eucypris virens	1	+
Bradleystrandesia reticulata	1	+
Heterocypris incongruens	1, 3	O, +
Cypris pubera	1, 4, 5	+
Ilyocypris sp.	3	O
Astacus leptodactylus	3, 16	O

Locality:
1. Valjevac pasture
2. Valjevac forest
2a. Valjevac water- course
3. Batar
3a. Batar dirt road
4. Jovača
5. Sadžak
6. Prekopac
7. Neškovine
8. Zovik
9. Vrbovac
10. Modran (Bogaz)
11. Šumareva ćup
12. Ljubinkovića ćup
13. Pačija bara
14. Paljevine
15. Simića ćup
16. Trebljevine
17. Preseka
18. Gajića ćup

Symbols:
+ - ephemeral water
O - Zasavica watercourse

As the Zasavica watercourse is connected to the Sava River through the Modran Constitution in Macvanska Mitrovica, it is interesting to compare the presence of the identified species of Macrocrustacea in these two watercourses. According to Petrović [24] the database entitled "Biodiversity of aquatic ecosystems of Serbia, ex situ protection, BASE ex situ" contains data on the findings of macroinvertebrates in aquatic ecosystems in Serbia and in the period from the first bibliographic data 1873 to 2012. According to this author, the isopods *Asellus aquaticus* and amphipodes *Gammarus balcanicus* and *Gammarus fossarum* are present in the Sava River, which are also found in Zasavica, and two species *Argulus foliaceus* and *Astacus leptodactylus* found in Zasavica according to the same database were not found in the Sava River. As part of the Regional Project "The Sava River", which included research on the fauna of aquatic macroinvertebrates of the Sava River from Slovenia (Vrhovo) to Belgrade (confluence with the Danube), in the period 2011 and 2012. The results of this project showed that *Astacus leptodactylus* is also present in the Sava, which was also found in Zasavica [25].

CONCLUSION

A total of 21 species of Macrocrustacea have been recorded in the fauna of the Zasavica reserve. For the ichthyophage parasitic species *Argulus foliaceus*, these are the first published data. The cosmopolitan species *Asellus aquaticus* is also present. A total of five species of amphipods were discovered, of which three are surface species and one is semi-underground and one underground. The amphipod *Niphargus valachicus* is a strictly protected species in Serbia and is on the IUCN Red List with VU status. Of the four species of branhipoda, *Chirocephalus brevipalpis* is a rare species, whose find on Zasavica is the westernmost of this species and the only one south of the Sava and Danube. The finding of the species *Lepidurus apus* in the tributary Batar is unique because the individuals were found in running water, and the finding of the species *Triops cancriformis* on the road near Batar is a new find for Serbia. So far, nine species of ostracods have been discovered in the Reserve, and the finding of the species *Candona aff. candida* in Zasavica is the first in Serbia. The species *Astacus leptodactylus*, which is on the IUCN Red List, was found from the order Decapod in Zasavica. All finds of 21 species of Macrocrustacea in Zasavica are new to Serbia.

REFERENCES

[1] T. Karan, B. Petrov, Ekologija; (2000) 35 (1) 1–44.

[2] W.F. Taube, Historische und geografische Beschreibung des königreiches Slavonien und das Herzogthumes Syrmien, Leipzig (1776).

[3] J. Pančić, Ptice u Srbiji, Državna štamparija, Beograd (1867) (in Serbian).

[4] E. Dombrowski, Osnovi ornitologije sjeverozapadne Srbije, Glasnik Zemaljskog muzeja, Sarajevo (1895).

[5] Official Gazette RS, 51/95 Rešenje o prethodnoj zaštiti prirodnog dobra Zasavica (1995) (in Serbian).

[6] Official Gazette RS, 19/97 Rešenje o zaštiti prirodnog dobra Zasavica (1997) (in Serbian).

[7] G. Harry, L. Born, Fauna Evrope, priručnik za raspoznavanje životinjskih vrsta, Mladinska knjiga, Ljubljana (1981) (in Serbian).

[8] G.D.F. Wilson, Some of the deep-sea fauna is ancient, Crustaceana; 72 (1999) 1019–1030.

[9] G.D.F. Wilson, Hydrobiologia; 595 (2008) 231–240.

[10] S.G. Karaman, Amfipoda (Crustacea, Amphipoda) Specijalnog rezervata prirode Zasavica (Srbija), (247. Prilog poznavanju Amphipoda) Zbornik radova Naučno-stručnog skupa Zasavica 2007 sa međunarodnim učešćem, Sremska Mitrovica (2007).

[11] A. Savić, Proceedings of 9th Symposium on Flora of Southeastern Serbia and Neighbouring Regions, Niš, September 01–03 (2007) 253–260.

[12] B. Petrov, D. Miličić, T. Karan-Žnidaršič, Brachiopodni i ostrakodni rakovi Specijalnog rezervata prirode Zasavica, Zbornik radova Naučno-stručnog skupa Zasavica 2007 sa međunarodnim učešćem, Sremska Mitrovica (2007).

[13] B. Petrov, I. Petrov, The status of Anostraca, Notostraca and Conchostraca in Yugoslavia, Hydrobiologia; 359 (1–3) (1997) 29–35.

[14] B. Petrov, D. Cvetković, Community structure of Brachiopods (Anostraca, Notostraca and Conchostraca) in the Banat province in Yugoslavia, Hydrobiologia (1997).

[15] B. Petrov, (2012) Preliminarni rezultati istraživanja morfoloških i ekoloških karakteristika vrste Lepidurus apus (Linneaeus, 1758) (Crustacea, Branchiopoda, Notostraca) na području Specijalnog rezervata prirode Zasavica, Zbornik naučno-stručnog skupa "Zasavica 2012", Sremska Mitrovica (in Serbian).

[16] D. Miličić, Nalazi rakova kambrijumske starosti (Crustacea, Branchiopoda) na području Pirota i okoline -The cambrian age crustacean findings (Crustacea, Branchiopoda) in the area of Pirot and its surroundings, Pirotski zbornik; 39 (2014) 39–50.

[17] M. Marinček, Some Euphyllopods (Euphyllopoda) of the Pannonian Plain. - Zbornik za prirodne nauke Matice srpske; 20 (1961) 160–163.

[18] M. Marinček, B. Petrov, Bios; 2 (1994) 137–142.

[19] B. Petrov, M. Cvetković, Arch. Biolog. Scienc. Belgrade; 48 (1–2) (1996) 59–62.

[20] G. Hartmann, D. Hiller, Beitrag zur Kenntnis der Ostracoden fauna des Harzes und seinesnördlichen, Vorlandes (unter besonderer Berücksichtigung des Männchens von Candona candona), In: 125 Jahre Naturwissenschaftlicher Verein Goslar (1977) p.99–116.

[21] D.J. Horne, M. Koen, An assessment of the importance of resting eggs for the evolutionary success of non-marine Ostracoda (Crustacea), In: L. Brendonck; L. De Meester, N. Hairston, Evolutionary and ecological aspects of crustacean diapause, 52 Advances in Limnology (1998).

[22] V. Simić, A. Petrović, M. Rajković, *et al.*, Crustaceana; 81 (10) (2008) 1153–1176.

[23] F. Gherardi, C. Souty-Grosset, Astacus leptodactylus IUCN Red List of Threatened Species, Version 3.1. International Union for Conservation of Nature (2010).

[24] A. Petrović, Mogućnost korišćenja baze podataka u strategiji konzervacije biodiverziteta makrobeskičmenjaka kopnenih voda na nacionalnom novou (doktorska disertacija), Univerzitet u Kragujevcu, Prirodno-Matematički fakultet, Kragujevac (2014) (in Serbian).

[25] A. Lucić, M. Paunović, J. Tomović, *et al.*, Aquatic Macroinvertebrates of the Sava River in: R. Milačić, J. Ščančar, M. Paunović, The Sava River, Berlin, Heidelberg: Springer-Verlag, (2015) p. 335–359.

OVERVIEW OF GALLS FAUNA (DIPTERA, HOMOPTER AND HYMENOPTER) – ZASAVICA RESERVE

Mihajlo Stanković[1*]
[1]Pokret gorana Sremska Mitrovica, Svetog Save 19, 22000 Sremska Mitrovica, SERBIA
*trogloxen@gmail.com

Abstract

For the past 25 years of research, a total of 110 species of galls have been recorded, of which 91 species are galls from the order Diptera, 15 species are from the order Hymenoptera and 4 species are from the order Homoptera. The largest number of species was on trees, a total of 51 species and 47 on herbaceous plants. was on the list of 61 species in buds 27. The most common galls recorded in the reserve are: on Rosa sp. - Diplolepis rosae; on Quercus - Cynips hungarica, Cynips quercus-callicis; on Ulmus sp. - Schizoneura ulmi, Schizoneura lonuginosa and Byrsoerypta ulmi.

Keywords: galls fauna, diptera, homopter, hymenopter

INTRODUCTION

Nature creates the most beautiful decorations, and primarily refers to cones or galls or cecidia growths on different parts of the plant caused by pathomorphological changes, mainly hypertrophy and hyperplasia of plant tissue caused by some insects, mites, phytopathogenic fungi and bacteria. The cones are of various shapes and sizes (round or spherical, irregular in shape) and the surface may be bare or overgrown with sparse or denser growths, horns, tufts, hairs, etc., and develop on all parts of the plant [1].

So far, there are more than 13,000 known species of insects that cause cecidiogenesis. These are species from the group of Hemiptera, Diptera and Hymenoptera. To these can be added a small number of Coleoptera and microlepidoptera that induce cones and about 300 species of Thysanoptera, mostly in the tropics, which live in cones but do not induce cone formation [1]. In Serbia, the presence of about 350 species belonging to the best-studied subfamily Cecidomyiinae has been determined [2]. From Hymenoptera these are phytophagous wasps of the pine (Fam. Cynipidae) small insects, black or brown. A large number of species reproduce partheno-genetic and males in some species are not known at all, and in other species there is a change of sexual and asexual generation. Females have an egg-laying nest at the end of the abdomen, which lays eggs in plant tissue, where the larvae then live. By excreting substances, larvae cause deformations and hypertrophies of plant tissue known as bumps or galls. These cones can be of different shapes, sizes and colors, and can grow on all parts of the plant. The shape of the cone is determined by the larva itself, ie. each species creates cones of a specific shape and on the same plant organ, which helps us determine the species. The cones serve the larvae for food and shelter. Inside each cone are numerous chambers with larvae. The peculiarity of the larvae of these wasps is that they do not change clothes but grow constantly, and the adult wasp emerges from the cone by drilling a corridor and an opening. The most common and well-known galica wasp is Rosele wasp (*Diplolepis rosae*), Oak wasp (*Cynips quercusfolii (Diplolepis quercus-folii*); *Andricus quercuscalicus*; Cynips hungarica, ect.

From Diptera galls make the so-called cone flies (lat. Cecidomydae). Biplanes are the most numerous species that induce cones, but taxonomically they are very poorly studied. Most of them belong to the Cecidomyiidae family. These are small flies, 1-3 mm in size, with a delicate body, long and thin legs. The larvae are white, yellow or orange, 2-3 mm long, legless, with a characteristic chitinous scapula (spatula sternalis) on the first thoracic segment, important for species determination. The doll can be a mummy or a barrel. In many species, due to the feeding of larvae, galls or cones are formed on certain plant parts (leaf, flower, fruit, seed). The larvae live inside them, finding quality food and protection from harmful external influences. They induce cones on leaves, stems, flowers, fruits and even roots. Some species of these flies are dangerous pests, primarily in agriculture and horticulture, while some are useful because they live on weed plants, and some are zoophagous [3]. Galls have historically been widely used due to the large amount of tannins in them, where the proportion of tannins reaches up to 70%, and according to the chemical composition, it is an ester of gallic acid, $C_6H_2(OH)_3$ $COOH \cdot H_2O$ and was often used for tanning, as an astringent (agent that tightens the surface of the injured mucosa) and as a textile dye. And until the 1930s, iron-gallon ink was one of the most commonly used writing materials [1].

MATERIALS AND METHODS

The methodology of the work includes an examination of woody, shrubby and herbaceous plants in search of growths on leaves, buds, twigs, fruit, etc. Determination of galls was performed on the basis of morphological, biological and ecological parameters according to the following keys: galls from DIPTERA were determined according to Simova-Tošić [2,4] and Mihajlović [5]; galls from HOMOPTER were determined according to Mihajlović [5]; galls from HYMENOPTER are determined according to Mihajlović [5,6].

RESULTS AND DISCUSSION

This paper presents the overall overview list of the Zasavica gala reserve formed during 25 years of research, (from 1996–2021).

LIST OF GALLS (DIPTERA, HYMENOPTERA and HOMOPTERA) ZASAVICA with the host plant:

1. Diptera-*Acericeris campestris*, on the plant *Acer campestre*, galls on the leaf
2. Diptera-*Acericeris szepligetti*, on the plant *Acer tataricum*, galls on the leaf
3. Hymenoptera-*Andricus (Cynips) caputmeduse*, on the plant *Quercus robur*, galls on the buds
4. Hymenoptera-*Andricus (Cynips) collari*, on the plant *Quercus robur*, galls on the buds
5. Hymenoptera-*Andricus (Cynips) hungaricus*, on the plant *Quercus robur*, galls on the buds

6. Hymenoptera-*Andricus (Cynips) quercuscalicis*, on the plant *Quercus robur*, galls on the fruit-acorn
7. Hymenoptera-*Andricus (Cynips) quercustozae*, on the plant *Quercus robur*, galls on the buds
8. Diptera-*Asphondylia stachydis,* on the plant *Stachys annuua*, galls on flower buds
9. Diptera-*Asphondylia menthae*, on the plant *Mentha aquatica*, galls on flower buds
10. Diptera-*Asphondylia ononidis*, on the plant *Ononis spinosa*, galls on the fruit of the pod and constipation
11. Hymenoptera-*Biorrhiza pallida*, on the plant *Quercus robur*, galls on the buds
12. Diptera-*Boyeriola salicariae*, on the plant *Lythrum salicarium*, galls on leaf and flower buds
13. Homoptera-*Byrsocrypta (Tetraneura) ulmi*, on the plant *Ulmus campestris*, galls on the leaf
14. Diptera-*Contarinia ballotae*, on the plant *Ballota nigra*, galls on leaf buds
15. Diptera-*Contarinia coryli*, on the plant *Corylus avelana*, galls on the flower-fringe
16. Diptera-*Contarinia medicaginis*, on the plant *Medicago sativa*, galls on flower buds
17. Diptera-*Contarinia nasturii*, on the plant *Rorippa amphibia*, galls on flower buds
18. Diptera-*Contarinia petioli*, on the plant *Populus alba*, *P. tremula*, *P. canescens*, galls on leaf stalks
19. Diptera-*Contarinia solani*, on the plant *Solanum dulcamara*, galls on flower buds
20. Diptera-*Contarinia subulifex*, on the plant *Quercus cerris*, galls on the leaf
21. Diptera-*Contarinia tiliarium*, on the plant *Tilia platyphyllos*, galls on a flower stalk, leaf stalks and young twigs
22. Diptera-*Craneiobia corni*, on the plant *Cornus sanguinea*, galls on the leaf
23. Hymenoptera-*Cyinips quercusfolii*, on the plant *Quercus robur*, galls on the leaf
24. Diptera-*Cystiphora sonchi*, on the plant *Sonchus oleraceus*, *S. arvensis*, galls on the leaf
25. Diptera-*Dasineura acrophila*, on the plant *Fraxinus angustifolia*, galls on the leaf
26. Diptera-*Dasineura affinis*, on the plant *Viola odorata*, galls on vegetative tops and leaves
27. Diptera-*Dasineura auritae*, on the plant *Salix cinerea*, galls on the leaf
28. Diptera-*Dasineura capsulae*, on the plant *Euphporbia esula*, galls on terminal buds
29. Diptera-*Dasineura crataegi*, on the plant *Crategus monogyna*, galls on a rosette sheet
30. Diptera-*Dasineura fraxini*, on the plant *Fraxinus ornis*, *Fraxinus angustifolia* galls on central leaf nerves
31. Diptera-*Dasineura gleditchiae*, on the plant *Gleditsia triacacia*, galls on fruit and buds
32. Diptera-*Dasineura glyciphylli*, on the plant *Astragalus cicer*, galls on the leaf
33. Diptera-*Dasineura hyperici*, on the plant *Hypericum perforatum*, galls on leaf buds

34. Diptera-*Dasineura mali*, on the plant *Malus domesticus*, galls on the leaf

35. Diptera-*Dasineura medicaginis*, on the plant *Medicago falcata*, *M.sativa*, galls on leaf buds

36. Diptera-*Dasineura oxycanthae*, on the plant *Crategus monogyna*, galls on flower buds

37. Diptera-*Dasineura plicatrix*, on the plant *Rubus caesius*, galls on young terminal sheets

38. Diptera-*Dasineura potentillae*, on the plant *Potentilla argentea*, galls on flower buds

39. Diptera-*Dasineura pyri*, on the plant *Pyrus communis*, galls on the leaf

40. Diptera-*Dasineura ranunculi*, on the plant *Ranunculus nemorosus*, galls on the leaf

41. Diptera-*Dasineura rosae*, on the plant *Rosa canina* agg., galls on the leaf

42. Diptera-*Dasineura rubella*, on the plant *Acer campestre*, galls on young leaves

43. Diptera-*Dasineura similis*, on the plant *Veronica anagalis-aquatica*, galls on terminal buds

44. Diptera-*Dasineura sisymbria*, on the plant, *Rorippa silvestris*, galls on stems and inflorescences

45. Diptera-*Dasineura spadicea*, on the plant, *Vicia cracca* galls on the leaf

46. Diptera-*Dasineura symphyti*, on the plant, *Symphytum officinale* galls on flower buds

47. Diptera-*Dasineura thomasiana*, on the plant, *Tilia tomentosa*, galls on young apical leaves

48. Diptera-*Dasineura tiliae*, on the plant *Tilia tomentosa*, galls on the leaf

49. Diptera-*Dasineura totrix*, on the plant *Prunus spinosa*, galls on apical leaf buds

50. Diptera-*Dasineura trifolii*, on the plant *Trifolium pratensis*, gale on the leaf

51. Diptera-*Dasineura tubularis*, on the plant *Quercus cerris*, galls on the leaf

52. Diptera-*Dasineura urticae*, on the plant *Urtica dioica*, galls on leaf nerves, stems and flower stalks

53. Diptera-*Dasineura viciae*, on the plant *Vicia sativa*, galls on the leaf

54. Diptera-*Didymonyia tiliacea*, on the plant *Tilia tomentosa*, galls on the leaf

55. Diptera-*Diodaulus linariae*, on the plant *Linaria vulgaris*, galls on the leaf rosette at the tips of the stems

56. Hymenoptera-*Diplolepis rosae*, on the plant *Rosa* sp., galls on the branches

57. Diptera-*Dryomyia circinnans*, on the plant *Quercus cerris*, galls on the leaf

58. Hymenoptera-*Eriophyes populi*, on the plant *Populus alba*, galls on petioles and buds

59. Diptera-*Geocrypta galii*, on the plant *Galium molugo*, galls on stems and flower stalks

60. Diptera-*Hamandiola cavemosa*, on the plant *Populus alba*, *P. canescens*, galls on the leaf

61. Diptera-*Hamandiola globuli*, on the plant *Populus tremula*, galls on the leaf

62. Hymenoptera-*Harmandia petiole*, on the plant *Populus tremulua*, galls on the buds

63. Hymenoptera-*Harmandia tremulae*, on the plant *Populus tremula*, galls na on petioles

64. Diptera-*Helycomia saliciperda*, on the plant *Salix* sp., galls on the branches
65. Diptera-*Iteomyia capreae*, on the plant *Salix caprea*, galls on the leaf
66. Diptera-*Janetia cerris,* on the plant *Quercus cerris,* galls on the leaf
67. Diptera-*Jaapiella chelidonii,* on the plant *Chelidonium majus*, galls on flower buds
68. Diptera-*Jaapiella cucubali*, on the plant *Cucubalus baccifer*, galls on leaf buds
69. Diptera-*Jaapiella floriperda,* on the plant *Silene vulgaris*, galls on flower buds
70. Diptera- *Janetia homocera*, on the plant *Quercus cerris*, galls on the leaf
71. Diptera-*Jaapiella jappiana*, on the plant *Medicago lupulina*, gale on the leaf
72. Diptera-*Jaapiella loticola*, on the plant *Lotus corniculatus*, galls on apical leaf buds
73. Diptera-*Jaapiella medicaginis,* on the plant *Medicago sativa*, galls on the leaf
74. Diptera- *Janetia nervicola*, on the plant *Quercus* sp., galls on leaf nerves
75. Diptera-*Jaapiella veronicae*, on the plant *Veronica chamaedrys*, galls on apical leaf buds
76. Diptera-*Jaapiella volvens*, on the plant *Lathyrus tuberosus*, galls on the leaf
77. Diptera-*Janetiella lemei*, on the plant *Ulmus minor*, galls on leaf nerves
78. Diptera-*Kiefferria pericarpiicola* on the plant *Daucus carota*, galls on the fruit
79. Diptera-*Lasioptera arundinis*, on the plant *Phragmites australis*, galls on lateral shoots
80. Diptera-*Lasioptera carophila*, on the plant *Daucus carota*, galls at the base of the inflorescence
81. Diptera-*Lasioptera populnea*, on the plant *Populus alba*, galls on the leaf
82. Diptera-*Macrolabis lonicerae*, on the plant *Lonicera carpinifolia*, galls on apical leaf buds
83. Diptera-*Macrolabis stellariae*, on the plant *Stellaria holostea*, galls on apical leaf buds
84. Hymenoptera-*Neuroterus quercusbaccarum,* on the plant *Quercus robur*, galls on the leaf
85. Diptera-*Obolodiplosis robiniae*, on the plant *Robinia pseudoacacia*, galls on the leaf
86. Hymenoptera-*Pediaspi aceris*, on the plant *Acer platanoides*, galls on the leaf
87. Hymenoptera-*Pemphigus bursarius*, on the plant *Populus nigra*, galls on the buds
88. Hymenoptera-*Pemphigus piriformis*, on the plant *Populus nigra*, galls on petioles
89. Homoptera-*Pemphigus spirothecae*, on the plant *Populus pyramidalis*, galls on petioles
90. Hymenoptera-*Pemphigus vesicarius*, on the plant *Populus nigra*, galls on the buds
91. Diptera-*Physemococis hartigi*, on the plant *Tilia platyphyllos*, galls on the leaf
92. Diptera-*Physemococis ulmi*, on the plant *Ulmus minor*, *U. pumila*, galls on the leaf
93. Diptera-*Placochela ligustri*, on the plant *Ligustrum vulgare*, galls on flower buds
94. Diptera-*Putoniella pruni*, on the plant *Prunus cerasifera*, *P. spinosa*, galls on leaf nerves
95. Diptera-*Rabdophaga* sp., on the plant *Tanacetum vulgare*, galls on flower stalks

96. Diptera-*Rabdophaga rosaria*, on the plant *Salix alba*, galls on the apical rosette

97. Diptera-*Rabdophaga salicis*, on the plant *Salix* sp., galls on branches and leaf stalks

98. Diptera-*Rhopalomyia tanaceticola*, on the plant *Artemisia vulgaris*, galls on young stems, lateral buds, leaves, flower heads

99. Diptera-*Rabdophaga terminalis*, on the plant *Salix* sp., galls on apical branches

100. Diptera-*Rondaniola bursaria*, on the plant *Glechoma hederaceae*, galls on the leaf

101. Homoptera-*Schizoneura lanuginosa*, on the plant *Ulmus campestris*, galls on the leaf nerve and leaf

102. Homoptera-*Schizoneura ulmii*, on the plant *Ulmus campestris*, galls on the leaf

103. Diptera-*Spurgia esulae*, on the plant *Euphporbia esula*, galls on terminal sheets

104. Diptera-*Spurgia euphporbia*, on the plant *Euphporbia cyperisias*, *E. lucida*, *E. esula*, galls on the tops of the flower stalks

105. Diptera-*Stefaniella brevipalpis*, on the plant *Atriplex tataricunm*, galls on stems, leaf and flower stalks

106. Diptera-*Stefaniella ceconii*, on the plant *Atriplex patulum*, galls on tree and branches

107. Diptera-*Wachtiella persicariae*, on the plant *Polygonum* sp., galls on the leaf

108. Diptera-*Wachtiella stachydis*, on the plant *Stachys palustris*, galls on leaf and flower buds

109. Diptera-*Zeuxidiplosis giardii*, on the plant *Hypericum perforatum*, galls on leaf buds

110. Diptera-*Zygobia carpini*, on the plant *Carpinus betuli*, galls on central or lateral leaf nerves

For the past 25 years of research, a total of 110 species of galls have been recorded, of which 91 species are galls from the order Diptera, 15 species are from the order Hymenoptera and 4 species sui from the order Homoptera. The largest number of species was on trees, a total of 51 species, followed by herbaceous plants with 47 species, while there were 10 species on the bush and two species of galls on creepers. Among woody species, the highest galls was recorded in Quercus 14, followed by Populus 11, Salix 6 and Ulmus 5. In herbaceous species, the highest galls was in Medicago 4 and Euphorbia 3. According to the location where galls occurs on the plant, we distinguish the following groups: Leaf (where: leaf blade, leaf stalk, leaf nerves, leaf rosette), Buds (where: flower and leaf buds, terminal buds), Fruit, Flower (where: flower stalk, all parts of the flower, inflorescence), Branches and twigs and Other (including: vegetative tops, stems of herbaceous plants, shoots, apical rosette. Most galls were on the list of 61 species, followed by 27 buds, 10 flowers, 8 left, 6 on branches, and 4 species on fruit, but we must emphasize that in some species there were cases that galleys were present in several groups like on a leaf and on buds, on one individual. The most common galls recorded in the reserve are: *Diplolepis rosae* on Rosa sp. (*Rosa canina* agg.), on *Quercus robur*, *Cynips hungarica*, *Cynips quercus-callicis*, on *Ulmus campestris*, *Schizoneura ulmi*, Schizoneura lonuginosa on *Ulmus camprstris* and *U. effusa*, *Byrsoerypta ulmi* on *Ulmus campestris*.

CONCLUSION

For the past 25 years of research, a total of 110 species of gala have been recorded, of which 91 species are galls from the order Diptera, 15 species are from the order Hymenoptera and 4 species are from the order Homoptera. The largest number of species was on trees, a total of 51 species and 47 on herbaceous plants were on the list of 61 species in and buds 27. As the most common galls recorded in the reserve are: *Diplolepis rosae* on *Rosa* sp., *Cynips hungarica* on *Quercus robur*, *Cynips quercus-callicis* on *Quercus robur*, *Schizoneura ulmi* on *Ulmus campestris*, *Schizoneura lonuginosa* on *Ulmus camprstris* and *U. effusa*, *Byrsoerypta ulmi* on *Ulmus campestris*.

REFERENCES

[1] P.J. Gullan, P.S. Cranston, The Insects: an outline of entomology, 4th Ed. Wiley-Blackwell, Oxford (2010), p.565, ISBN: 978-1-444-31767-1.

[2] D. Simova-Tošić, Atlas Gala muva galica (Diptera: Cecidomyiidae: Cecidomyiinae), Entomological Society of Serbia, Faculty of Biology, Belgrade (2014), pp.1–170, ISBN: 978-86-81281-07-9.

[3] T. Kereši, A. Konjević, A.Popović, Posebna entomologija 2, Univerzitet u Novom Sadu, Poljoprivredni fakultet Novi Sad, Novi Sad (2019), ISBN: 978-86-7520-464-0.

[4] D. Simova-Tošić, Fauna fitofagnih vrsta muva galica u Srbiji (Diptera: Cecidomyiidae, Cecidomyinae), SANU, Posebna izdanja, knjiga DCXCII, Odeljenje hemijskih i bioloških nauka, knjiga 12, Beograd (2020), ISBN: 978-86-7025-853-2.

[5] Lj. Mihajlović, Šumarska entomologija, Univerzitet u Beogradu, Šumarski fakultet, Beograd (2008).

[6] Anonymous, FAO 1958: Poplar in Forestry and Land use. - Forestry and Forest Products Studies (direc. Forstery Division: Marcel Leloup) No.12., (1958), p.511.

AQUATIC INSECTS DIVERSITY IN THE PART OF NERETVA RIVER DRAINAGE (BOSNIA AND HERZEGOVINA): PRELIMINARY RESULTS

Vanja Marković[1*], Milenka Božanić [1], Oliver Arapović[2], Vukašin Gojšina[1], Anđelina Tatović[1], Katarina Stojanović[1]
[1]University of Belgrade, Faculty of Biology, Studentski Trg 16, 11000 Belgrade, SERBIA
[2]Eu "Majski cvijet" Buna-Zaton, bb, 88000 Mostar, BOSNIA AND HERZEGOVINA
[*]*vanja.markovic@bio.bg.ac.rs*

Abstract

During the research of aquatic macroinvertebrates communities of the Bregava, Trebižat, Buna and Bunica rivers (Neretva basin) conducted in September 2020, a total of 94 aquatic insects taxa were identified. The most diverse were ET taxa, namely Ephemeroptera (20 taxa) and Trichoptera (19 taxa). Considerable diversity was found in Coleoptera (17 taxa) and Diptera (15 taxa). The diversity of insects per rivers was fairly balanced, and ranged from 44 taxa (Trebižat and Buna and Bunica rivers) to 47 taxa (Bregava river). In the Bregava river the most diverse groups were Trichoptera and Diptera (11 taxa each), in Trebižat those were Coleoptera (11) and Trichoptera (10), while in Buna and Bunica rivers the most diverse groups were Ephemeroptera (11 taxa) and Coleoptera (10). Bregava river had the site with the greatest (23 taxa) and with the lowest (4 taxa) diversity. Variable diversity along, and among, the rivers could be linked to heterogenous and diverse habitats present. Considering uncertainty of identification at lower larval stages in many genera, a need for seasonal sampling as well for sampling of adult forms arises. To obtain even more complete knowledge a method of DNA barcoding would be needed, particularly in species with undescribed larval stages.

Keywords: ET taxa, Bregava, Trebižat, Buna and Bunica rivers

INTRODUCTION

Insects are the most diverse group of animals, inhabiting various freshwater and terrestrial environments [1]. Plecoptera, Ephemeroptera, Trichoptera, Odonata, Coleoptera, Diptera, Hemiptera, Megaloptera, Neuroptera and Lepidoptera are the groups having aquatic representatives. Aquatic insects inhabiting different types of aquatic ecosystems often dominate in macroinvertebrate communities [2].

Bregava, Trebižat, Buna and Bunica rivers are among the most large and important tributaries of Neretva river (Neretva river basin, Adriatic drainage). The whole Neretva basin could be recognized as one of biodiversity hotspots in Bosnia and Herzegovina [3]. The knowledge regarding aquatic insects communities of Neretva tributaries is quite scarce, with only a few more comprehensive investigations being conducted so far [4-8]. Our aim is to contribute to the knowledge regarding aquatic insects diversity in this biodiversity hotspot.

MATERIALS AND METHODS

Field research of aquatic insects of the rivers Bregava, Trebižat, Buna, and Bunica was performed in the period 10.09.2020 to 14.09.2020. The samples were taken at 15 localities, five on each river (Figure 1).

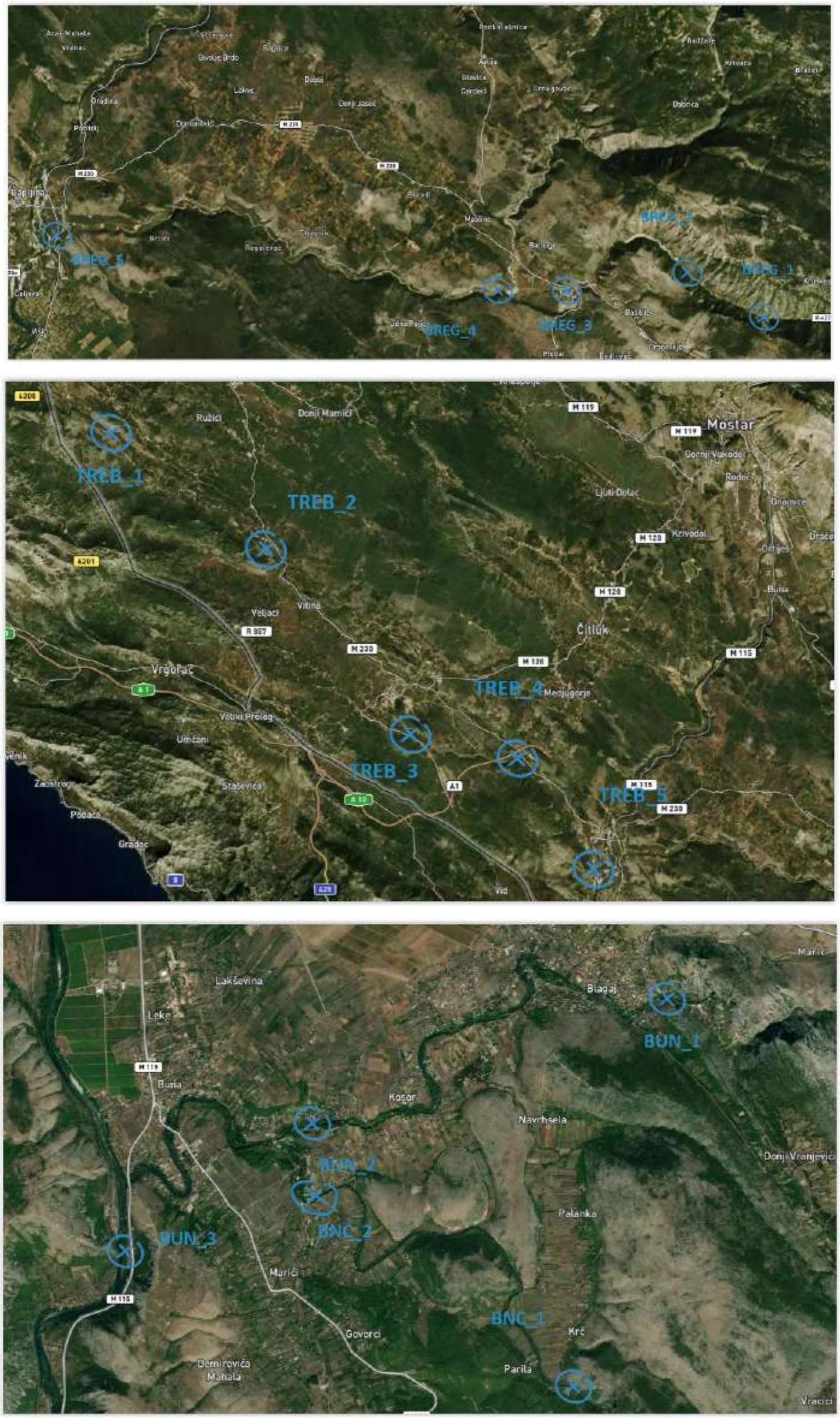


Figure 1 Sampling localities at the rivers Bregava (A), Trebižat (B), Buna, and Bunica (C)

Sampling was performed using FBA standard benthic net (500 µm diameter mesh) according to the multihabitat sampling procedure in line with the EU WFD and the AQEM protocol [9]. The collected material was stored in appropriate plastic packaging and fixed in 70–96% ethanol solution. Further processing and identification of collected material was performed in the laboratory of the Institute of Zoology, Faculty of Biology, University of Belgrade.

RESULTS AND DISCUSSION

During the research of aquatic insects on the rivers Bregava, Trebižat, Buna, and Bunica, a total of 94 taxa from 8 groups were identified. Up to species level 51 taxa were identified, 33 taxa were determined up to genus level, and the rest (10) was left at higher taxonomic categories. The diversity of insects per rivers was fairly balanced, and ranged from 44 taxa (Trebižat, Buna and Bunica rivers) to 47 taxa (Bregava river). Interestingly, locality with the highest diversity (23 taxa), and the locality with the lowest diversity (4 taxa only), both were located on the Bregava river. Overall, the greatest diversity was found within ET taxa, with group Ephemeroptera having 20 identified taxa, while Trichoptera had 19 taxa. Diverse also were groups Coleoptera (17 taxa) and Diptera (15 taxa) (Figure 2).

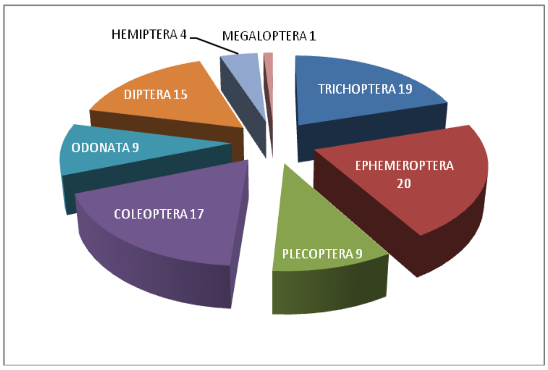


***Figure 2** Overall diversity of main insects groups during the investigation of Bregava, Trebižat, Buna, and Bunica rivers in 2020*

As it can be seen from Figure 3, in the Bregava river the most diverse groups were Trichoptera and Diptera (11 taxa each), followed by Coleoptera (9 taxa). The most diverse groups in Trebižat were Coleoptera (11*)* and Trichoptera (10), while in Buna and Bunica those were Ephemeroptera (11 taxa) and Coleoptera (10).

Fauna of aquatic insects recorded during our investigation was very diverse and taxa rich. It exceeds by great marging diversity found in few comparable investigations in the region. For example, Rađa and Šantić [10] recorded 27 taxa of aquatic insects during many years of research on the river Jadro (Cetina basin, Croatia). We speculate that main reasons for such high diversity could be significant habitats diversity, accompanied by relatively low anthropogenic pressures in general. Pronounced ET taxa diversity we found, could be compared only to ET diversity of clean mountainous watercourses [11,12]. The Bregava river, despite harbouring the greatest diversity overal, also had the site with the highest and with the lowest diversity recorded during our investigation. Situation as such could correspond to the greatest habitats diversity at that particular river. Along the Bregava river were some of well preserved, and some of the most altered (negative anthropogenic impacts) sites among all investigated watercourses.

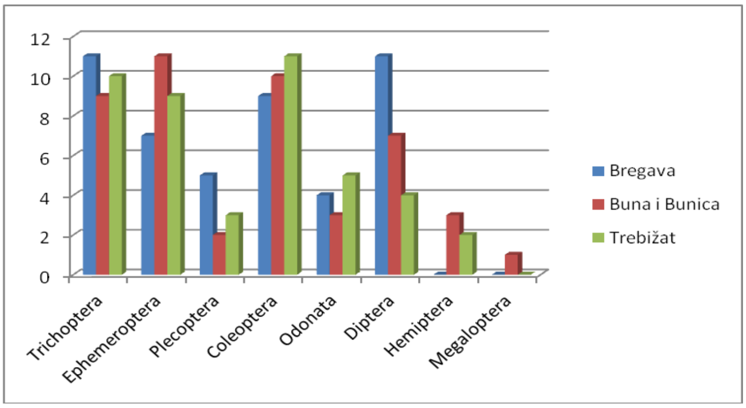


***Figure 3** Diversity of main insects groups per investigated rivers*

Among the studied aquatic insects, order Trichoptera stands out due to its diversity. Considering uncertainty of identification of lower larval stages in many genera of this group, a need for seasonal sampling as well for sampling of adult forms arises. Even more as few rare and endangered endemics should be present in investigated area (*Glossosoma neretvanus*, Marinković 1979, *Hydropsyche smiljae* Marinković 1979, *Allolotricha marinkovicae* Malicky 1977) [5,6,8].

Within the other important component of insects fauna inhabiting studied rivers, Ephemeroptera, similar taxonomic uncertainty apples. In that regard of particular interest could be representatives of genus *Rhithrogena* Eaton, 1881. On the red list of endangered species of Bosnia and Herzegovina it has four species marked as endangered (EN) [13]. Representatives of this genus were recorded in our investigation. To obtain more complete knowledge regarding aquatic insects, a method of DNA barcoding would be helpful, particularly in species with undescribed larval stages, such as *Rhithrogena zernyi* Bauernfeind, 1991 for example.

CONCLUSION

Rich community with 94 aquatic insects taxa was found during our 2020 investigation covering 16 localities at Bregava, Trebižat, Buna and Bunica rivers. Overal diversity per studied river was found to be fairly balanced, ranging from 44 taxa (Trebižat, Buna and Bunica rivers) to 47 taxa (Bregava river). The most diverse component of investigated fauna was ET group (Ephemeroptera and Trichoptera). The Bregava river had the site with the highest (23 taxa) and with the lowest (4 taxa) aquatic insects diversity recorded. Situation as such corresponds to the greatest habitats diversity present at that particular river in comparison with other investigated watercourses. Considering uncertainty of identification of lower larval stages in many genera, a need for seasonal sampling as well for sampling of adult forms arises. To obtain more complete knowledge regarding aquatic insects a method of DNA barcoding would be helpful, particularly in species with undescribed larval stages.

ACKNOWLEDGEMENT

This work is a part of an investigation supported by CEPF-109139 project (Steps Towards the Protection of Neretva Tributaries: Buna, Bunica, Begava and Trebižat, Bosnia and Hercegovina). The authors would like to heartily thank Saša Marić (Faculty of Biology, Belgrade) for valuable help and great companionship during the field work. We are also grateful to Center for Environment (Banja Luka) for providing the opportunity to conduct this research.

REFERENCES

[1] J.V. Ward, Aquatic insect ecology. 1. Biology and habitat, John Wiley & Sons Inc., New York (1992), p.456, ISBN: 978-0-471-55007-5.

[2] I. Živić, Z. Marković, Zoobentos kopnenih voda, Univerzitet u Beogradu–Biološki fakultet, Beograd (2017), p.181, ISBN: 978-86-7078-146-7.

[3] W. Darwall, S. Carrizo, C. Numa, *et al.*, Freshwater Key Biodiversity Areas in the Mediterranean Basin Hotspot: Informing species conservation and development planning in freshwater ecosystems, IUCN: Cambridge, UK and Malaga, Spain (2014), p.86, DOI: 10.2305/IUCN.CH.2014.SSC-OP.52.en.

[4] I. Matoničkin, Z. Pavletić, God. Biol. Inst. Univ. Sarajevo; 1–2 (1960) 41–62.

[5] M. Marinkovic-Gospodnetić, God. Biol. Inst. Univ. Sarajevo; 31 (1978) 115–131.

[6] M. Marinkovic-Gospodnetić, God. Biol. Inst. Univ. Sarajevo; 41 (1988) 41–48.

[7] M. Tanasijević, God. Biol. Inst. Univ. Sarajevo; 37 (1985) 201–210.

[8] S. Stanić-Koštroman, A. Previšić, A. Planinić, *et al.*, Int. Rev. Hydrobiol; 100 (2015) 79–95.

[9] D. Hering, O. Moog, L. Sandin, *et al.*, Hydrobiologia; 516 (2004) 1–20.

[10] B. Rađa, M. Šantić, J. Insect Sci; 14 (54) (2014) 1–10.

[11] I. Živić, Z. Marković, M. Brajković, Arch. Biol. Sci; 53 (3–4) (2001) 109–122.

[12] V. Đikanović, D. Jakovčev-Todorović, V. Nikolić, *et al.*, Arch. Biol. Sci; 60 (1) (2008) 133–144.

[13] Official Gazette of the Federation of Bosnia and Herzegovina, No. 66/13, Red list of wild species and subspecies of plants, animals and fungi (in Bosnian, Croatian and Serbian).

RECYCLED CONCRETE AGGREGATE EFFECT ON SELF-COMPACTING CONCRETE AT LOW TEMPERATURES

Aleksandar Savić[1], Ivana Jelić[2*], Marija Šljivić-Ivanović[2], Slavko Dimović[2]
[1]University of Belgrade, Faculty of Civil Engineering, B.K.A. 73, 11000 Belgrade, SERBIA
[2]University of Belgrade, Vinca Institute of Nuclear Sciences, M.P.A. 12–14, 11351 Belgrade, SERBIA
[*]*ivana.jelic@vin.bg.ac.rs*

Abstract

The paper presents experimental results of the tests conducted on Self-Compacting Concrete (SCC) with recycled concrete aggregate in order to investigate compressive strength at low temperatures. Recycled concrete aggregate was obtained by crushing laboratory concrete cubes. Four mixtures of concrete were made. This approach to concrete proportioning paves a way for a cleaner and more sustainable civil engineering practice.

Keywords: self-compacting concrete, recycled aggregate, sustainable development

INTRODUCTION

One of the greatest challenges, and at the same time the imperative of the modern age, is sustainable development. As constructing is an activity which is harmful to the environment in many ways, there is plenty of room for the principles of sustainable development implementation [1]. Civil engineering generates construction and demolition waste, accounting for almost 75% of waste worldwide [2,3]. The production and utilization of recycled aggregate is a response to several key environmental problems resulting from construction and demolition activity. Namely, concrete is the most used construction material (after water), and for the most part, it is made of aggregates, which leads to the uncontrolled depletion of natural aggregate deposits [1]. Apart from the fact that natural resources are limited, their exploitation also has a great impact on the environment (transformation of the terrain, change of ecosystems, carbon dioxide emissions, etc.). On the other hand, the demolition of buildings due to aging, natural disasters, war destruction, etc., results in huge amounts of construction and demolition waste (CDW). This waste is most often disposed in designated, but often illegal, so-called "wild" landfills, whose areas are constantly increasing.

Self-Compacting Concrete (SCC) is defined as concrete that, without any need for special installation-vibrating means, is installed by itself, under the influence of gravity, passes between reinforcement bars, no matter how densely they are placed, wraps them, and fills the formwork, while achieving high compactness and the required class of concrete [4,5]. This technology originated in Japan in the 1980s, primarily to increase the durability of concrete structures, as well as to protect workers from noise and vibration during concrete installation. The research was led by the Japanese scientist Hajime Okamura from the University of Tokyo [6]. Japanese scientists had significant "potential capital" due to developed technology for the production of chemical additives such as superplasticizers, with high water reduction power. It was only necessary to find a way how much concrete, with a high degree of fluidity, at the same time has a high resistance to segregation of large aggregate and separation of water in the mixture. It was relatively easy to conclude that the share of the smallest particles should be increased, which, with adequate reduction of the share of the largest fraction and limitation of its largest grain, would achieve better cohesiveness of the mixture. Only one more step remained until the final goal, which was done by applying a new type of additive-modifier of viscosity VMA (Viscosity Modifying Admixture) which, without affecting the fluidity of the mixture, further increased the degree of its cohesion [6].

Great progress has been made in the application of SCC concrete with the adoption of European guidelines that have defined both requirements and test methods, recommendations for production, and installation. Subsequently, based on these guidelines, a set of European standards EN 12350 (parts 8 to 12) only for SCC were developed, which was a great recognition of the value of this special type of concrete. The synergy of the chemical and construction materials industries and the development of a new generation of superplasticizers based on polycarboxylic ethers as the main constituent of SCC concrete should be emphasized here, which directly enabled the design of the concrete mix composition of required viscosity and yield strength.

The objective of this investigation was to evaluate SCC concrete made of recycled concrete aggregate at low temperatures in order to promote its wider utilization. In winter conditions, concrete requires special organizational, technical, and technological measures, because the impact of low temperatures on the properties and safety of structures must not be ignored. These measures must be applied if the average air temperature is not expected to be higher than 5°C for more than 3 days. In these circumstances, there is an accelerated cooling of young concrete and slowing down of hydration, which endangers the maturation and reaching the critical strength of concrete. The critical strength of concrete represents the strength of the material at the time of reaching the ambient temperature, i.e. the minimum strength that installed concrete must have at the time of freezing. The critical strength of concrete is a function of the type of cement and the curing conditions, and a strength of 5 MPa can be considered as the relevant value [7].

MATERIALS AND METHODS

Four types of SCC concrete mixtures were made (Table 1). The first type of concrete SCC A represented a standard, basic concrete mixture only with natural aggregate (NA). The standard was made for comparison of characteristics of ordinary SCC with the characteristics of SCC with different proportions of recycled concrete aggregates (RCA).

Concrete mixtures were prepared in a laboratory mixer brand "Beckel" (Germany) with a capacity of 20 L. All components were weighed by mass, including water and additive. Each mixture was prepared in one mixing cycle and their volumes were 6 L each. When preparing concrete with recycled aggregate, a mixing procedure according to TSMA (Two-Stage Mixing Approach) is proposed, as an improvement over NMA (Normal Mixing Approach) [8]. This procedure was applied to all four mixtures, including the standard.

Table 1 *Recipes of the subject mixtures in kg/m^3*

SCC	Cement	Filler	Additive	NA I(0/4)	NA II(4/8)	RCA II(4/8)	NA III(8/16)	RCA III(8/16)
A	380	250	5.7	860	530	0	310	0
B	380	250	5.7	860	265	265	310	0
C	380	250	5.7	860	530	0	155	155
D	380	250	5.7	860	265	265	155	155

[*] In all mixtures was added cca 200 kg/m^3 of water.

The procedure of mixing component materials lasted a total of 6 minutes and consisted of the following stages:

- dry mixing of all fractions of NA and RCA, and limestone filler for 60 s;
- adding 50% water without stopping the mixer and stirring for 30 s;
- adding cement and other 50% of water and mixing for 30 s;
- a superplasticizer is added over the next 30 s;
- stirring is continued for another 3.5 minutes.

All of the mixtures showed very good properties in terms of fluidity, workability, passing ability, and segregation resistance. Mixtures were cast into the molds only with the help of a fangle, trowel, and a small shovel without additional vibration. Prior to installation, the molds were cleaned, marked, and coated with a formwork release agent, to prevent adhesion of concrete and molds.

The shape and dimensions of the samples for compressive strength testing must meet the requirements of the standard SRPS EN 12390-3:2010 [9]. The test was performed on concrete cubes with edges of 10 cm, gradual loading to the breaking of the concrete sample, in the hydraulic press "Amsler" range up to 2500 kN and "Matest" range up to 2000 kN. The load application rate was 0.6 ± 0.4 MPa/s.

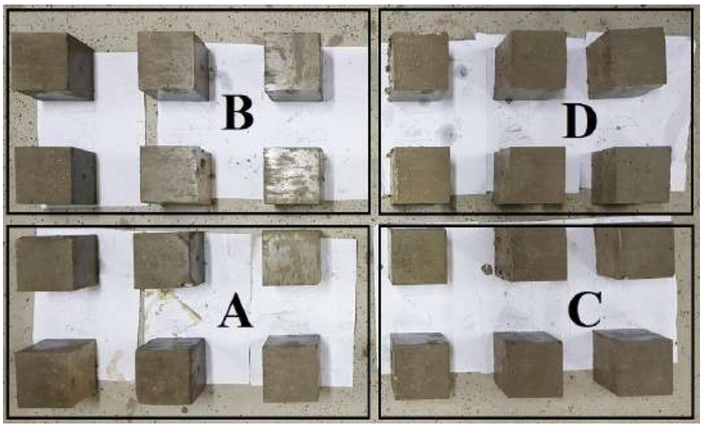


Figure 1 *Concrete samples after removal from the mold*

After production, the concrete molds were placed outside, where they were exposed to external conditions at early ages, at as low temperatures as 5°C to 10°C, and below zero afterward. After 2 hours, the samples were covered with plastic bags, in order to prevent the concrete from drying out quickly. After 24 hours from the moment of casting the concrete mixture in the molds, the mold was carefully detached from the samples (Figure 1), and compressive strength was tested for 8 selected samples (2 from each mixture).

RESULTS AND DISCUSSION

For similar values of the water to powder ratio, the compressive strength does not differ significantly between SCC and Normally Vibrated Concrete (NVC) [10]. However, the choice of aggregates (river, crushed, recycled) has a greater impact on compressive strengths in NVC than in SCC, due to a more homogeneous matrix in SCC and lower content of coarse aggregate, which reduces its impact [11]. Actually, SCC with the same water to cement or water to powder ratio usually has increased compressive strength values, as a result of a better bond between the aggregate and hardened paste due to the absence of vibration. In addition, SCC fills the formwork completely, ensuring reliable "packaging" of the concrete and eliminating segregation [12].

The compressive strength of concrete aged 1, 7, and 28 days was tested. The results are given in Table 2 and Figure 2. For compressive strength at the age of 28 days, the results were converted to a 15 cm edge cube (fp,28, k 15), in order to assess the strength class according to SRPS EN 206-1:2011 [13].

Table 2 *Average values of compressive strength of solid concrete at different ages [MPa]*

SCC	fp,1	fp,7	fp,28	fp,28, k 15	Concrete class according to EN 206
A	8.5	35.8	50.4	47.9	35/45
B	2.2	29.7	53.1	50.4	40/50
C	5.6	33.8	47.7	45.3	35/45
D	4.3	32.8	50.8	48.3	35/45

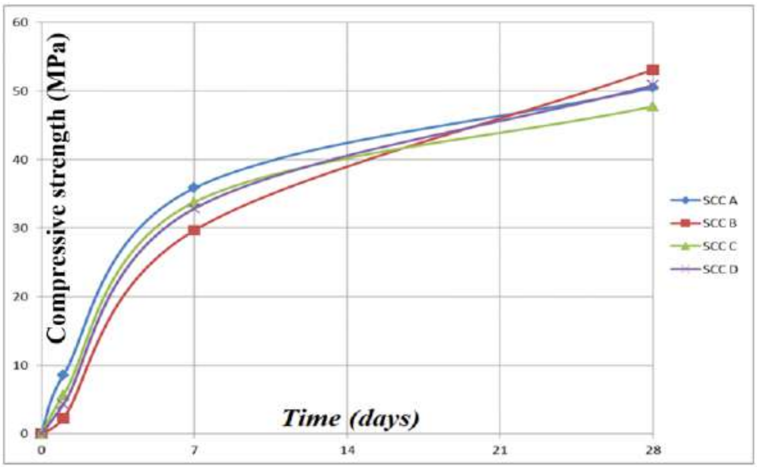


Figure 2 *Compressive strength diagram for all concrete mixtures at different ages*

The diagram shows the fastest increase in compressive strength in the first 7 days, despite low temperatures. Previous investigations of the same mixtures in laboratory temperature conditions have shown 75–80% higher values at the age of 1 day [14,15]. This is also the highest difference induced by the condition because at the older ages the compressive strength values were similar to the previous study [14], which can be attributed also to the significant increase in outdoor air temperatures in that period.

The ultimate strengths are not fully in line with expected values. Three mixtures (including the standard) belong to the concrete strength class C 35/45, while the mixture with recycled SCC B aggregate achieved strength class C 40/50. This is not in line with expectations, as reference mixture A (without recycled aggregate) is expected to have the highest compressive strength [15,16].

CONCLUSION

The results of the investigation of SCC mixtures made with recycled aggregate and cured in ambient conditions are shown in this paper. Fluidity, workability, passing ability, and segregation resistance of all mixtures were in line with the requirements for SCC.

The compressive strength of the investigated mixtures, as a proper quality indicator was monitored over the period of 28 days. It showed that the early age strengths were more influenced by the curing conditions. The concrete mixtures made with recycled aggregate had lower values of compressive strength at 1 day than the reference. The differences in the compressive strengths decreased with the age, which can be attributed both to the age and the higher ambient temperatures at that period.

The values of compressive strength of concrete mixtures with recycled aggregate were in line with the values for mixture with natural aggregate, paving the way for the industrial use of recycled aggregate in SCC in ambient conditions. Nevertheless, all of the principles of design, component investigation, and proportioning, as well as the mixing process have to be applied in order to provide the shown best effects.

ACKNOWLEDGEMENT

The research presented in this paper was done with the financial support of the Ministry of Education, Science and Technological Development of the Republic of Serbia, within the funding of scientific research work at the University of Belgrade, Faculty of Civil Engineering (No. 200092) and the University of Belgrade, Vinca Institute of Nuclear Sciences (Contract No. 451-03-68/2022-14/200017).

REFERENCES

[1] C. Lian, Y. Zhuge, Constr. Build. Mater; 24 (12) (2002) 2664–2671.

[2] V.A. Mymrin, K.P. Alekseev, R.E. Catai, *et al.*, Constr. Build. Mater; 79 (2015) 207–213.

[3] O. Zimbili, W. Salim, M.A. Ndambuki, Int. J. Civil Architect. Struct. Constr. Eng; 8 (2014) 91–95.

[4] C.K. Sarath, P.S. Bendapudi, Int. J. Earth Sci. Eng; 4 (6) (2011) 1017–1023.

[5] M. Vasić, Physical and Mechanical Properties of Green Self-Compacting Concrete Designed by the Method of Maximum Density of Grain Packaging, Faculty of Civil Engineering, University of Belgrade, Belgrade (2019).

[6] H. Okamura, M. Ouchi, J. Adv. Concr. Technol; 1 (1) (2003) 5–15.

[7] H.T. Nam Le, L.H. Poh, S. Wang, *et al*., Cem. Concr. Compos; 82 (2017) 202–216.

[8] V.W.Y. Tam, C.M. Tam, Constr. Build. Mater; 22 (10) (2008) 2068–2077.

[9] SRPS EN 12390-3:2010, Testing hardened concrete – Part 3: Compressive strength of test specimen (2010).

[10] M.C.S. Nepomuceno, L.F.A. Bernardo, Appl. Sci; 9 (Y2019) 1–18.

[11] R. Martínez-García, P. Jagadesh, G. Búrdalo-Salcedo, *et al.*, Materials; 14 (13) (2021) 3480–3492.

[12] P. Dybel, M. Kucharska, Materials; 14 (19) (2021) 5685.

[13] SRPS EN 206-1:2011, Concrete – Part 1: Specification performance, production, and conformity, Withdrawal of Standard: Dec 25, 2017 (2011).

[14] B. Kovačević B., Testing of SCC concrete with partial replacement of natural aggregate with recycled aggregate, Faculty of Civil Engineering, University of Belgrade, Belgrade (2017).

[15] K.C. Panda, P.K. Bal, Procedia Eng; 51 (2013) 159–164.

[16] Z.J. Grdić, G.A. Topličić-Ćurčić, I.M. Despotović, *et al*., Constr. Build. Mater; 24 (7) (2010) 1129–1133.

INVASIVE ALIEN SPECIES IN SERBIA: LEGISLATION, STRATEGY, AND PLANS

Ivana Bjedov[1], Dragica Obratov-Petković[1], Verica Stojanović[2], Marija Nešić[1], Dragana Marisavljević[3]
[1]University of Belgrade, Faculty of Forestry, Kneza Višeslava 1, 11030 Belgrade, SERBIA
[2]Institute for nature conservation of Serbia, Japanska 35, 11070 Novi Beograd, SERBIA
[3]Institute for plant protection and environment, Teodora Drajzera 9, 11000 Belgrade, SERBIA
ivana.bjedov@sfb.bg.ac.rs

Abstract

Considering Europe presents a centre for international trade, migration, and tourism, over many centuries, different alien species have been established in European countries. Many of them are invasive and negatively affect the European habitats, species, human health, and economy. Consequently, the question of legal regulation of the control and suppression of invasive organisms becomes more topical. In 2014, the European Parliament and the Council of the European Union adopted Regulation on the prevention and management of the introduction and spread of invasive alien specie. The Regulation is binding in its entirety and directly applicable in all Member State. However, legislation varies greatly in the non-EU country.Serbia faces many limitations in its efforts to prevent and manage invasive species. This paper aims to review the current state of invasive alien species in Serbia, legislation, strategies and plans and point out to the problems in this fild that make difficult to combat invasive species. Invasive alien species are recognized in national laws on nature conservation, where precise bylaws or action plans on IAS management were not evolved. However, the national legislation on legal regulation in this issue is incomplete.

Keywords: invasive alien species, legal act, national strategy and plan, combat against invasive alien species

INTRODUCTION

Invasive alien species are species of animals, plants, fungi, or microorganisms translocated by humans into environments outside their natural range, in which they establish and spread. According to Richardson *et al*. [1] allochthonous species in new regions become invasive when they escape from the site of initial introduction to establish self-sustaining populations in new locations. Frequently, established allochthonous species spread rapidly into new ecosystems. They interact with native species through competition for resources, spread of disease or by direct competition, parasitism or hybridisation, etc. [2]. Invasive species present one of the most significant factors which cause biodiversity loss. Namely, these species spread easily and quickly in new habitats, suppressing native species, leading to changes in the structure and function of ecosystems. Invasive species affect changes in the richness and diversity of native communities. They cause decreases in richness and diversity of native communities and, in some cases, the extinction of native species. Also, these species can influence genetic diversity. Hybridization between introduced species and native species can lead to the loss of native genetic diversity [3]. Invasive species can negatively impact human health by infecting humans with new diseases, serving as vectors for existing diseases, or causing wounds through bites, stings, allergens, or other toxins [4]. These species have negative economic and social impacts. The economic and social impacts of invasive species include both direct effects of a species on property values, agricultural productivity, public utility operations, native fisheries, tourism, and outdoor recreation, as well as costs associated with invasive species control efforts [5]. According to Haubrock *et al*. [6] costs of biological invasions in Europe between 1960 and 2020 accumulated to a reported total of US$140.20 billion. Approximately 60 % of the total costs were related to damage and loss and 20% of costs were related to management (prevention, control, education).

As Europe presents a centre for international trade, migration, and tourism, over many centuries, different allochthonous species have been established in European countries. Many of them are invasive and negatively affect the European habitats, species, human health, and economy [2,7]. The need for policies and actions to address invasive alien species within the European Union was formally recognised in 2001 and designated as a priority for EU biodiversity policy in 2006 [8]. An important fact is that control of the spread of invasive species is challenging because it requires international cooperation, and this is often difficult to achieve [9]. Given the negative environmental, economic, and social impacts of invasive species globally and locally, this topic has received increasing attention in recent decades. Consequently, the question of legal regulation of the control and suppression of invasive organisms becomes more topical. As Europe has a broad range of ecologically dissimilar regions [10], which reflects the different susceptibility to ecosystem invasion, national strategies on invasive plant species should be urgently developed and adopted.

Having in mind all the above, this paper aims to review the current state of invasive plants in Serbia, legislation, strategies and plans and point out to the problems in this fild that make difficult to combat invasive species.

MATERIALS AND METHODS

The paper is based on the analysis of existing data, both on a global scale level as well as those related to the territory of Serbia. For this analysis, the following were used: scientific papers, publications, and projects; international, regional, and national legal and strategic documents; reports of state bodies and public institutions and results of our field investigation.

All literature data used for the paper is presented in the chapter References.

RESULTS AND DISCUSSION

The importance of control and management of invasive alien species was pointed out through conventions, strategies, plans, and documents that generally concern the protection and conservation of biodiversity, both worldwide and in Europe. Some of the most important are: The Convention on Biological Diversity (CBD), The Convention on the Conservation of European Wildlife and Natural Habitats (Bern Convention), The EU Biodiversity Strategy to 2020, EU Directives (Council Directive on the conservation of wild birds, Council Directive on the conservation of natural habitats and of wild fauna and flora, Directive establishing a framework for Community action in the field of water policy, Directive establishing a framework for community action in the field of marine environmental policy and Directive on the sustainable use of pesticides).

Within the Strategic Plan for Biological Diversity 2011–2020, the CBD has adopted guidance on the prevention, introduction, and mitigation of impacts of alien species that threaten ecosystems, habitats, or species [11]. Goal no. 9 states that by 2020 invasive species and ways of their transmission needs to be identified, a list of priority species has to be formed and measures of control and eradication and prevention of entry and spread need to be implemented [11].

The Bern Convention requires from its members “to strictly control the introduction of nonnative species” (Article 11.2.b) [12]. At the initiative of the Standing Committee of the Bern Convention, European Strategy on Invasive Alien Species was created in 2003 [13]. The common goal of the strategy is reducing threats of introduced species to natural ecosystems and indigenous species, increasing public awareness of invasive species as well as ways to prevent their spread, methods of control, and removal [14].

One of the 6 targets of the EU Biodiversity Strategy to 2020 refers to the control and eradication of invasive species to prevent the loss of European biodiversity and ecosystem services. According to this target, invasive alien species should be identified, priority species controlled or eradicated, and pathways managed by 2020.

EU directives require the restoration of the original environmental conditions of disturbed habitats where species of national and international importance are observed [15].

It is important to emphasize that all these documents suggest that all countries should elaborate on and adopt national strategies and plans of action in the combat against invasive alien species.

In 2014, the European Parliament and the Council of the European Union adopted Regulation on the prevention and management of the introduction and spread of invasive alien species (“Regulation (EU) No 1143/2014 of the European Parliament and of the Council of 22 October 2014 on the prevention and management of the introduction and spread of invasive alien species”). The Regulation is binding in its entirety and directly applicable in all Member States [15]. In order to control invasive alien species, it is necessary to coordinate the joint action of all Member States. They are required to identify their invasive species, draw up priority lists of activities to stop their spread, work on raising awareness, and provide appropriate customs controls. In addition, they must have official custom controls to prevent the intentional introduction of these species. However, legislation varies greatly in the non-EU country.

Serbia faces many limitations in its efforts to prevent and manage invasive species. Invasive organisms have been studied in Serbia for several decades [15–21]. However, there is no integral database on invasive alien species (IAS) at the national level. Also, regardless of the numerous results obtained during these investigations, the national legislation on legal regulation in this issue is incomplete. In Serbia, IAS are recognized in national laws on nature conservation, where precise bylaws or action plans on IAS management were not evolved. So far, Serbia has committed itself to the Law on ratification of the Convention on Biological Diversity [22], and The Convention on the Conservation of European Wildlife flora and fauna and natural habitats - Berne Convention [23] to strictly control the introduction of allochthonous species (Article 11 of the Berne Convention) and to make an effort to monitor and eradicate those alien species that threaten native ecosystems, habitats or autochthonous species. By Law on Nature Protection [24] the introduction of allochthonous species in natural areas is defined and appropriate prohibitions and permits are prescribed. Code on the transboundary movement and trade in protected species [25] regulates the introduction of allochthonous wild species. Other legislative acts regulating the introduction, control, and eradication of alien species are: Law on Game Animal and Hunting, [26], Law on the Protection and Sustainable Use of Fish Stocks [27], Law on Animal Husbandry [28], Law on Products for Plant Protection [29], Low on plant health [30], Ordinance on lists of harmful organisms and lists of plants, plant products and prescribed facilities [31] and Regulation on measures to combat and destruction of the ragweed plant - *Ambrosia artemisifoliia* L. [32].

As a candidate for membership in the European Union, the Republic of Serbia has obligation to harmonize national legislation with European Union regulations. By becoming a member of the EU, the member state begins to apply all the provisions of the Regulation (EU) no. 1143/2014 on the prevention and management of the introduction and spread of invasive alien species. In order to achieve full compliance with EU Regulation no. 1143/201, significant changes and additions are needed within the Law on Nature Protection. On the other hand, the issue of invasive alien species should be regulated by a special law [15]. Adoption of appropriate law is one of the key goals and activities in the combat against invasive alien species. In addition, important activities that are the basis for effective struggle against further invasive species introduction and spread in Serbia are: establishment of competent institutions for coordination of activities, monitoring, and data collection; making a list of invasive alien species; assessment of their invasiveness; establishment of information system for monitoring biological invasions; involvement in international bodies and projects dealing with detection, monitoring, and control of biological invasions; public involvement in the process of controlling invasive species; identification and implementation of measures to prevent the introduction of new invasive alien species and to prevent the spread of already introduced invasive alien species.

A preliminary list of invasive plants, amphibians, reptiles, fish, mammals, and birds of Serbia was established in 2012 by the experts of the Institute for nature conservation of Serbia [19]. This list included general measures of control and reduction of invasive species. According to the Report on invasive species in Serbia [33], there are 318 alien species, of which 173 are plant species. According to the latest literature data, there are 161 invasive alien plants on the territory of the Republic of Serbia [21].

Regarding invasive alien plants, there is currently a weak interaction between researchers, policymakers, and stakeholders dealing with biodiversity. There is no systematic monitoring of the introduction and spread of invasive species. Also, the public awareness of the impact of invasive species on biodiversity, human health, and the economy is very low.

The involvement of national representatives in international organizations dealing with invasive species contributes to finding solutions to combat invasive species. Unfortunately, the Republic of Serbia does not have national representatives from professional institutions (ministry, agency, or institutes) in these organizations. However, Serbian experts from scientific institutes, and faculties are involved in the work of several such organizations (EPPO, ESENIAS, COST) through various projects, programs, etc.

Elaboration of the National Invasive Species Strategy and Action Plan should be a priority as it would enable adequate control and management of invasive alien species. Within the National Strategy and Action Plan strategic goals such as prevention, early detection and rapid response, control and management, restoration, education, risingpublic awareness, and international cooperation should be determined.

CONCLUSION

This study set out to evaluate the current status of invasive plants in Serbia, legislation, strategies, and plans and point out to the problems in this fild that make difficult to combat invasive species. This research has identified that despite many years of research on invasive species, there is no integral database on invasive alien species (IAS) in Serbia. Invasive alien species are recognized in national laws on nature conservation, where precise bylaws or action plans on IAS management were not evolved. However, the national legislation on legal regulation in this issue is incomplete.

Elaboration and adoption of the Law on invasive alien species is the key activity for the effective combat against invasive alien species. Also, taking into account the current situation in the field of invasive species, Serbia is obliged to implement the following activities:

- complete the collection of data on invasive alien species on the territory of Serbia,
- involve the national representatives in the international organizations dealing with the invasive species,
- analyze the pathways of the introduction of IAS, in order to establish methodology for prevention and eradication,
- improve coordination and collaboration among managers, researchers, policymakers, and stakeholders dealing with biodiversity,
- develop and implement prevention programs for identified priority invasive species and areas, based on risk assessments,
- establish early detection and rapid response emergency fund and guidelines to ensure that funds are immediately available to respond to new introductions,
- identify general and specific control measures of invasive alien species,
- educate and raise awareness of public and stakeholders.

All of these activities should be determined within the National Invasive Species Strategy and Action Plan.

ACKNOWLEDGEMENT

The authors are grateful to the Ministry of Education, Science and Technological Development of the Republic of Serbia for the scientific research of the University of Belgrade - Faculty of Forestry in 2022 for financial support (grant number 451-03-9/2022-14/200169).

REFERENCES

[1] D.M. Richardson, P. Pyšek, M. Rejmánek, *et al*., Divers. Distrib; 6 (2) (2000) 93–107.

[2] R.P. Keller, J. Geist, J.M. Jeschke, *et al*., Environ. Sci. Eur; 23 (2011) 1–17.

[3] P. Neil, M. Arim, Encyclopedia of Environmental Health, Elsevier (2011), p.116–123, ISBN: 978-0-444-52272-6

[4] G. Mazza, E. Tricarico, P. Genovesi, *et al*., Ethol. Ecol. Evol; 26 (2–3) (2014) 112–129.

[5] R.D. Zenni, F. Essl, E. García-Berthou, *et al*., The economic costs of biological invasions around the world, *Available on the following link*: https://neobiota.pensoft.net/article/69971/

[6] Ph.J. Haubrock, A.J. Turbelin, R.N. Cuthbert, *et al*., Economic costs of invasive alien species across Europe, *Available on the following link*: https://borea.mnhn.fr/sites/default/files/pdfs/2021%20Haubrock%20et%20al%20-%20NeoBiota%20Europe.pdf

[7] A.J. Turbelin, B.D. Malamud, R.A. Francis, Global. Ecol. Biogeog; 26 (2017) 78–92.

[8] C. Shine, M. Kettunen, P. Brink, *et al*., Technical support to EU strategy on invasive species (IAS) – Recommendations on policy options to control the negative impacts of IAS on biodiversity in Europe and the EU. Final report for the European Commission. Institute for European Environmental Policy (IEEP), Brussels (2009) p. 35.

[9] C. Perrings, S. Burgiel, W.M. Lonsdale, *et al*., Ann. N. Y. Acad. Sci; 1195 (2010) 198–212.

[10] A.K. Sokolova, E.Ie. Tulina, Environmental Policy and Law; 49 (4–5) (2019) 300–305.

[11] CBD/Convention on Biological Diversity/European Union/Biodiversity Targets for 2020, *Available on the following link*: https://www.cbd.int/nbsap/about/targets/eu

[12] Bern Convention action on invasive alien species in Europe, *Available on the following link*: https://rm.coe.int/1680746c12.

[13] P. Genovesi, C. Shine, European strategy on invasive alien species, *Available on the following link*: https://www.cbd.int/doc/external/cop-09/bern-01-en.pdf

[14] N. Vuković, Ekogeografija invazivne flore Hrvatske, Doktorski rad, Prirodoslovno-matematički fakultet, Biološki odsjek, Sveučilište u Zagrebu, (2015), p.104.

[15] V. Stojanović, I. Bjedov, I. Jovanović, *et al*., Odabrane invazivne strane vrste u flori Srbije, Zavod za zaštitu prirode Srbije, Beograd (2021), p. 284, ISBN: 978-86-80877-73-0.

[16] D. Marisavljević, S. Stojanović, D. Pavlović, *et al.*, Acta Herbologica; 16 (2) (2007) 105−125.

[17] S. Radulović, D. Skočajić, I. Bjedov, *et al*., Bulletin of the Faculty of Forestry; 97 (2008) 221–234.

[18] D. Obratov-Petković, I. Bjedov, V. Stojanović, *et al*., Book of Abstracts of IUFRO Conference Forest for cities, forest for people; Perspectives on urban forest governance, 27–28 September 2012, Zagreb, Croatia (2012) 76–77.

[19] P. Lazarević, V. Stojanović, I. Jelić, *et al*., Zaštita prirode; 62 (1) (2012) 5−33.

[20] B. Zlatković, S. Bogosavljević, Weed Research; 60 (1) 85−95.

[21] V. Stojanović, I. Jovanović, Zaštita prirode; 68 (1−2) (2018) 41–59.

[22] Law on ratification of the Convention on Biological Diversity, "Official Gazette of RS - International Agreements" No. 11/2001 (in Serbian).

[23] The Convention on the Conservation of European Wildlife flora and fauna and natural habitats, "Official Gazette of RS - International Agreements" No. 102/2007 (in Serbian).

[24] Law on Nature Protection, "Official Gazette of RS" No. 36/2009, 88/2010, 91/2010, 14/2016, 95/2018 (in Serbian).

[25] Code on the transboundary movement and trade in protected species, "Official Gazette of RS", no. 99/2009, 6/2014 (in Serbian).

[26] Law on Game Animal and Hunting, "Official Gazette of RS", no. 18/2010 (in Serbian).

[27] Law on the Protection and Sustainable Use of Fish Stocks, "Official Gazette of the Republic of Serbia", No 128/2014 and 95/2018 (in Serbian).

[28] Law on Animal Husbandry, "Official Gazette of RS", No. 41/2009, 93/2012 and 14/2016 (in Serbian).

[29] Law on Products for Plant Protection, "Official Gazette of RS", No. 41/2009 and 17/2019 (in Serbian).

[30] Low on plant health, "Official Gazette of RS", No. 41/2009 (in Serbian).

[31] Ordinance on lists of harmful organisms and lists of plants, plant products and prescribed facilities, "Official Gazette RS", No. 7/2010, 22/2012 and 57/2015 (in Serbian).

[32] Regulation on measures to combat and destruction of the ragweed plant - *Ambrosia artemisifoliia* L., "Official Gazette RS", No. 69/2006 (in Serbian).

[33] M. Rat, P. Simonović, P. Glavendekić, *et al*., Overview of the invasive alien species in Serbia. Serbia_country report (2015).

THE EFFECTS OF GEOMECHANICAL RESEARCH "*IN SITU*" ON THE EXPLOITATION CONDITIONS OF THE OPEN PIT BAUXITE MINE "ZAGRAD"

Jelena Majstorovic[1], Milutin Korac[2], Snezana Savkovic[1*]
[1]University of Belgrade, Faculty of Mining and Geology, Đušina 7, 11000 Belgrade, SERBIA
[2]Bauxite mine "Niksic", Novaka Ramova 17, 81400 Nikšić, MONTENEGRO
[*]*savkovicsnezana@yahoo.com*

Abstract

Standard laboratory investigations of ore and accompanying rock usually give authoritative parameters for working benches and final slopes of open pit mines. When the work environment is specific, which is in this case the morraine material whose granulometric composition is varied, from dust to blocks several meters in size, reliable parameters can only be obtained by "in situ" investigations. Paper presents investigations results and results enabled a new stability analysis and much favorable geometry of mine. The thickness of this material goes up to 100 meters. Great savings have been achieved in the excavated tailings, disposal area and transport to the landfill. All the savings also had an impact on the environmental protection effects.

Keywords: laboratory investigations, "*in situ*" investigations, working environmental, morraine material, slope stability

INTRODUCTION

The moraine material is in the red bauxite overlie of the "Zagrad" deposit. Moraine material is formed by the glaciers movement on a rocky base. The glaciers destroy the rocky surface and carry it away. The composition of the material depends on the composition of the rock over which the glacier moved. Sludge, sand, large pieces of rocks and blocks can be found in the material, because it is not grouped by grain size. Moraine material has been little researched. There are few deposits in the world where moraine material is overlied.

MATERIALS AND METHODS

Extensive laboratory investigations were performed, according to the prescribed standards for the Bauxite exploitation "Mining project" needs. The following shear parameters were determined: the angle of internal friction φ = 30° and cohesion c = 5 kN/m^2. Based on this properties, the working benches and working and final slopes were designed (Table 1).

***Table 1** Final slopes geometry based on laboratory investigations [1]*

Working bench		**Final slope**	
h (m)	α (°)	h (m)	α (°)
15	42	100	23

Exploitation, first working benches and partial slopes led to the discovery that there are reserves in safety factor. It was decided to perform subsequent field investigations, which will be adjusted to the moraine material granulometric composition. Figure 1 shows the granulometric composition from some of the elevations at which "*in situ*" investigations were later performed.

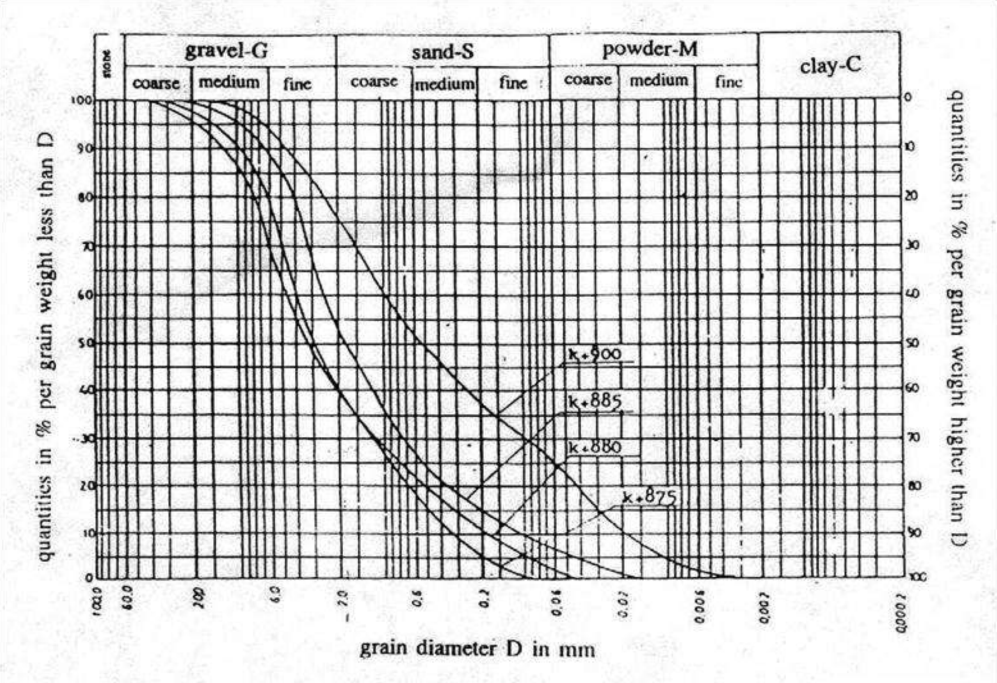


__Figure 1__ Granulometric composition of moraine material [2]

Table 2 shows the values of the degree of non-uniformity degree per Allen Hazenu, for the granulometric composition of one part of the tested samples.

__Table 2__ Non-uniformity degree for disturbed moraine material Open pit mine "Zagrad" [2]

Sample	d_{10} mm	d_{60} mm	Cu	Comment
K+875	$3.3 \cdot 10^{-1}$	4.0	12.12	The soil is of moderately uneven composition
K+880	$1.7 \cdot 10^{-1}$	5.2	30.58	The soil is of uneven composition
K+885	$1.2 \cdot 10^{-1}$	2.5	20.8	The soil is of uneven composition
K+890	$2 \cdot 10^{-2}$	1.0	50.0	The soil is of uneven composition

"*In situ*" investigations for the purpose of excavation slope redesign

Having in mind, the moreine material structure, granulometric composition and binder properties (dusty clay), the investigations performed on larger test bodies, blocks in two ways:

- The shear tests "*in situ*" carried out on the blocks on the predisposed angles α_1, α_2 and α_3,
- The direct shear tests "*in situ*" carried out on the blocks in function σ_1, σ_2 and σ_3.

The shear investigations "in situ" on the blocks on the predisposed angles α_1, α_2 and α_3

The dimensions of the investigations bodies in this case are 5 to 6 diameters of the average grain in the carved test blocks. Test bodies are formed by carving. The cross sectional area of the body was about 60x60 cm. The height is adjusted to the shear angle. Shear was performed on predisposed planes:

- Angle α_1=60° shear area is 7,200 cm^2,
- Angle α_2=45° shear area is 5,100 cm^2,
- Angle α_3=30° shear area is 4,150 cm^2.

Vertical force was applied to the sample by hydraulic cylinder, read on a manometer on a hydraulic press and has tangent and perpendicular component. Vertical force causes the test block shear. A total of 39 blocks with different granulometric composition were examined. The experiments were arranged on benches along the entire depth of mine [3].

The following shear strength parameters were determined:

- Angle of internal friction φ = 30–35° and
- Cohesion c = 100–530 kN/m^2.

The shear tests "in situ" carried out on the blocks in function σ_1, σ_2 and σ_3

Investigations were performed on blocks 40x40x40 cm and 60x60x40 cm, carved in moreine material, with steel molds for normal and horizontal strain. Shearings were performed at the following normal strains:

$\sigma_1 = 75\ kN/m^2$,
$\sigma_2 = 150\ kN/m^2$,
$\sigma_3 = 250\ kN/m^2$.

Horizontal strain increased from 0 to the final shear, the horizontal displacement measured by comparators with accuracy 10^{-2}mm. Four samples of three carved blocks were examined. Data of normal strain, shear strain and horizontal deformation were collected. After breaking the sample, a certain amount of material was taken to determine the humidity. The deformation as a function of the normal strain σ and the normal shear strain σ and τ. The following shear strength parameters were determined:

- Cohesion c = 100–580 kN/m^2 and
- Angle of internal friction = 30–35°.

RESULTS AND DISCUSSION

Slope stability analysis via "*in situ*" established parameters

The following geomechanical parameters were adopted for the analysis of stability of working benches and final slopes:

$\gamma = 23.14\ kN/m^3$,
$c = 200\ kN/m^3$,
$\varphi = 30°$.

Table 3 *Newly designed excavation slope geometry based on "in situ" investigations [4]*

Working bench		**Final slope**	
h (m)	α (°)	h (m)	α (°)
15	75	100	50

In Figure 2, is shown the dependence of the final slope α on the height h for the safety factor $F_s = 1.30$. The diagram clearly shows how much the angle of final slope has increased. The cohesion applied in the calculation was determined "*in situ*" and it is 40 times higher than the one determined in the laboratory.

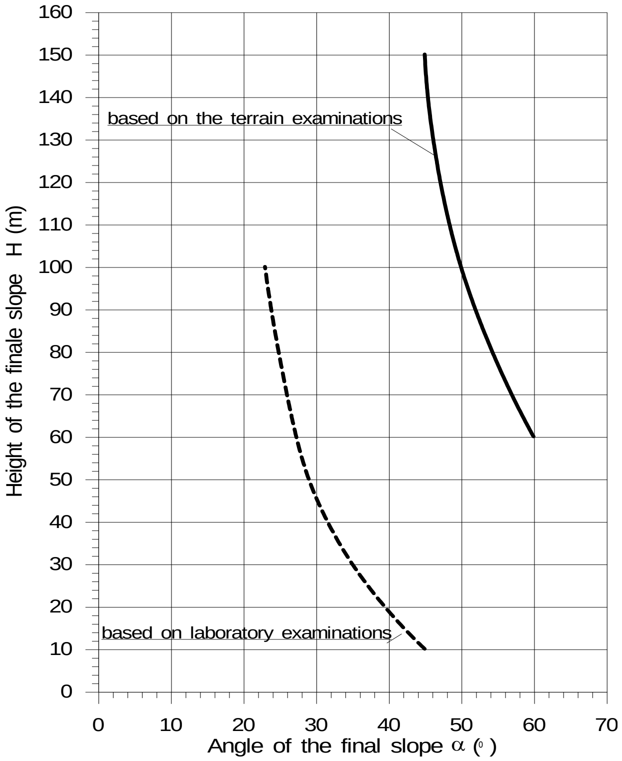


Figure 2 *Diagram of dependence between slope α and height h for safety factor $F_s = 1.30$ [4]*

The newly formed final slopes have repeatedly participated in the reduction of the total bauxite ore exploitation costs. In Figure 3, is very clearly given the effect of total savings, which can be seen in the duration (time) of exploitation and the amount of ore excavated.

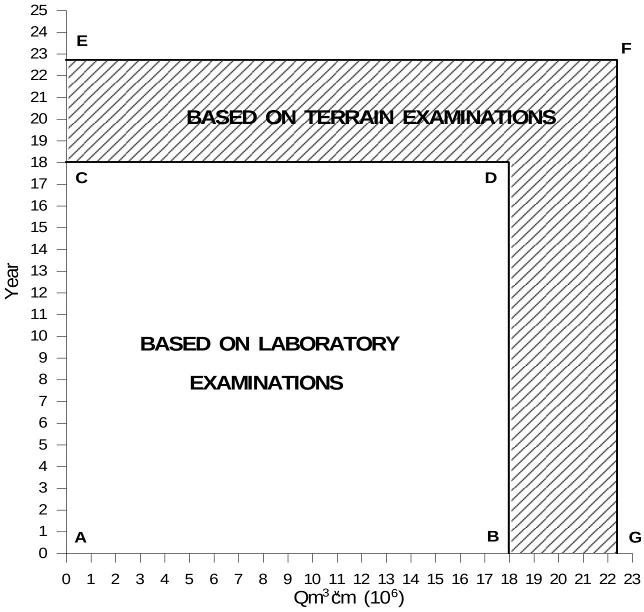


Figure 3 *Graphic view of the time exploitation and the amount of excavated ore for the condition α = 23° and α = 50° (ABCD – time and amount for the final slopes of α = 50° AGEF – time and space for the final slopes of α = 23°)[5]*

CONCLUSION

From the example of the open pit mine "Zagrad" results the conclusion that it is necessary for the geomechanical examination to be carried out permanently from the first investigative works to the end of exploitation. Investigations should be conducted according to current standards and adjusted to the situation on the terrain. Problems often arise at the beginning of exploitation. At first glance investigation may seem extensive and expensive. But in the end they can reduce total costs, ensure safe and cost-effective exploitation. In this case, great savings were in excavation, tailings disposal, transport and a significant increase in the amount of bauxite ore. Confirmation of well-determined angles and slopes is that the exploitation at the "Zagrad" open pit mine was successfully completed.

REFERENCES

[1] Study on geo-mechanical investigations of physical and mechanical rock properties stability analysis of open pit mine and external landfills "Zagrad" near Niksic (Book I/II Geomechanics), Mining Institute, Zemun, 1987.

[2] Geo-mechanical elaborate on implied terrain investigations of moraine material of open pit mine "Zagrad" near Niksic, Faculty of Mining and Geology, Belgrade, 1993.

[3] Results of laboratory and terrain investigations of moraine material and stability analysis, Faculty of Mining and Geology, Belgrade, 1996.

[4] Korac, M.: Research Methodology of Moraine materials as a Function of the System of surface mining, doctoral dissertation, Faculty of Mining and Geology, Belgrade, 2003.

[5] M. Korac, J. Majstorovic, M. Cvetkovic, S. Cvetkovic, 5th Pan–European conference on planning for minerals and transport infrastructure – PEMT'06, Sarajevo, B&H (2006).

ANALYSIS OF HOUSEHOLD'S E-WASTE AWARENESS, AND DISPOSAL BEHAVIOR IN NOVI SAD

Isidora Berežni[1*], Tijana Marinković[1], Veselin Bežanović[1], Miodrag Živančev[1], Bojan Batinić[1]

[1]Department of Environmental Engineering, Faculty of Technical Sciences,
University of Novi Sad, Trg Dositeja Obradovića 6, 21000 Novi Sad, SERBIA
isidoraberezni@uns.ac.rs

Abstract

During the past decades, rapid technological progress resulted in a huge consumption increase of electronic and electrical products. As a result of the expansion of the market and the shorter lifespan of many electronic devices, electronic waste (e-waste) became one of the fastest growing waste streams in the world, with an annual growth rate of 3% to 5%. E-waste is a complex mix of high-value materials, plastics and hazardous components, which makes it both potential source of valuable base metals, such as copper and aluminium, precious and rare earth elements (gold, silver, palladium and platinum), but also potential threat to the environment and human health. This put a focus on how e-waste is handled, especially in developing countries due to improper disposal of this waste stream. This paper evaluates household awareness of e-waste, environmental problems associated with improper disposal, and willingness to engage in managing e-waste. The questionnaire was distributed among 500 households in Novi Sad to gather data on participant's demography, electrical/electronic equipment ownership and usage, and awareness and knowledge about e-waste management. The data were analysed and statistically presented and accordingly suggestions regarding educational interaction and raising public knowledge concerning e-waste were made.

Keywords: e-waste, household's awareness, questionnaire survey, e-waste management system

INTRODUCTION

Waste electrical and electronic equipment (WEEE) represents the fastest growing waste stream in the world, with an annual growth rate of 3% to 5%, triple then other wastes [1,2]. A record of 53.6 million metric tonnes (Mt) of this waste stream was generated and reported in 2019, while projection show that it will grow up to 74.7 Mt by the year of 2030, almost doubling in only 16 years [3].

E-waste is defined as electrical equipment that is no longer useful to the end-user and so discarded as waste. This waste stream is a source of about 1000 different hazardous components with potential threats to human health and environmental quality, thus making its management a challenge [4,5]. The issue is even more serious in developing countries where there is a lack of regulatory measures, infrastructure (collection points, recycling yards and facilities for treatment) and limited awareness in the society [6,7]. Therefore, use, disposal and recycling of e-waste affect many stakeholders in society, including households who play an important role in generation and management of this waste stream. Due to lack of knowledge and information on handling this waste stream, household face greater challenges in the disposal of e-waste than in the case with industrial enterprises and other institutions [8]. Thus, important factor that influence on managing e-waste is the extent to which households are informed and are aware of the problems associated with this waste stream.

Several studies have raised the importance of e-waste knowledge towards the successful management of this waste stream and highlighted the individual recycling attitudes, behavioural dispositions, and waste disposal habits as important factors in defining an efficient e-waste system management [9–11]. For example, study in Romania shows that 40.79% of respondents were willing to take part in e-waste recycling activities promoted on social networks, 56.95% have favourable attitudes toward purchasing easily recyclable electronic devices, while 58.08% wanted to increase their efforts in the e-waste recycling process [12].

Although there are studies on e-waste in Serbia that present current state of the legislative framework, collection system and processing technologies [13–15], to author’s knowledge there are no existing studies on consumers’ or household’s attitudes and awareness regarding this waste stream. Therefore, the aim of this paper is to examine household awareness and participation in managing e-waste in Novi Sad (Serbia). The key questions covered by this study was: (I) What types of electronic devices are used by households in Novi Sad? (II) How much awareness and knowledge exist amongst households regarding e-waste? (III) Is there any willingness amongst households to participate in e-waste management? (IV) What methods are used in disposing away in Novi Sad? This could contribute to raising public awareness on the possibility of sustainable consumption, as well as attitudes toward e-waste collection and recycling. Beside this, it could benefit to different participants in the e-waste management system such as manufacturers, who should minimize e-waste output; consumers, who should follow proper disposal habits; recyclers/informal agents, who need to utilize eco-friendly alternatives; and governmental organizations that implement e-waste policies [4].

MATERIALS AND METHODS

The study area

This survey is conducted amongst the households in Novi Sad. Novi Sad is the largest city of the autonomous province of Vojvodina, north province of Serbia, with a population of 299,294. Thanks to its geostrategic position, Novi Sad after Belgrade represent the centre of economic development in Serbia. The structure of economy is shaped by the existing industries mainly including trade, transport, and processing industry. The disposal of municipal waste in Novi Sad has showed increase of approximately 2% from 2010 (126,628 t) to 2019 (151,332 t), and similarly the proportion of e-waste is expected to rise concomitantly due to economic development and increasing living standards. This create the need for a study to provide ways to manage e-waste and mitigate environmental problems that have been affecting the region.

Data collection and analysis

The aim of this survey was to investigate knowledge and awareness levels related to e-waste and related issues amongst households in Novi Sad. An approach that involves random sampling with intention to bring statistical confidence, as well as data representability, was adopted from Wang *et al*. [16]. In total, 500 questionnaires were administered to household's respondents during survey although only 434 were successfully populated, thus yielding a response rate of 86.8%. The number of participants were sufficient for a city with around 300,000 residents and a significance level of 0.05 according to Adam [17]. The interviews were conducted during the period of November 2020. The questions that made up the questionnaire were grouped into sections related to demographic and socio-economic characteristics of respondents, knowledge and awareness of electronic wastes and environmental problems related to it, and methods of handling and disposing of e-waste, following the example of existing studies [4,6,11]. The data collection was conducted in Serbian to ensure that the respondents did not face any difficulties in understanding the questions, and then were translated into English. Data collected during the interviews were stored in MS Excel for further processing and the results are presented in the next sections by means of tables and different types of statistical illustrations.

RESULTS AND DISCUSSION

Socioeconomic and demographic characteristics of respondents

Table 1 provides a summary of socioeconomic and demographic data of the participants. Of 434 respondents, 230 were man and 204 were woman. In terms of age, largest group represent the one between 31 to 40 years (47%), while category of individuals above 60 years were less represented (1%). When it comes to occupation, most of respondents were employed (55%). In terms of number of family members in a household, 27% of households had 2 people, while the lowest percentage of households had 5 of more people. These factors are important because age and income levels of the respondents, as well as family size, could give an indication of how many electronic goods and devices they would probably buy, and how much e-waste could be expected [4].

Table 1 *Socioeconomic and demographic characteristics of respondents (n=434)*

Variable	**Category**	**Frequency**	**Percentage**
Sex	Men	230	53%
	Women	204	47%
Age	Under 30 years	127	29%
	31–40 years	203	47%
	41–50 years	67	15%
	51–60 years	33	8%
	Above 60 years	4	1%
Occupation	Employed	239	55%
	Unemployed	52	12%
	Student	126	29%
	Retiree	17	4%
Total family income per month (Euros)	0–250	52	12%
	250–500	70	16%

***Table 1** – continued*

	500–800	91	21%
	800–1100	102	24%
	More then 1100	119	27%
Family size	1	82	19%
	2	117	27%
	3	88	20%
	4	113	26%
	5 and more	34	8%

Awareness and knowledge level regarding e-waste

Figure 1 shows different types of electronic devices used in household. The total number of detected devices in the surveyed 434 households amounts to 8,607, of which the largest percentage makes led lamps, kitchen appliances, mobile phones, and TVs. It can be noticed that some households have more than one device of the same category. For example, if we take number of detected mobile phones (1,349) in 434 household, it can be concluded that the average telephone number per household is 3.

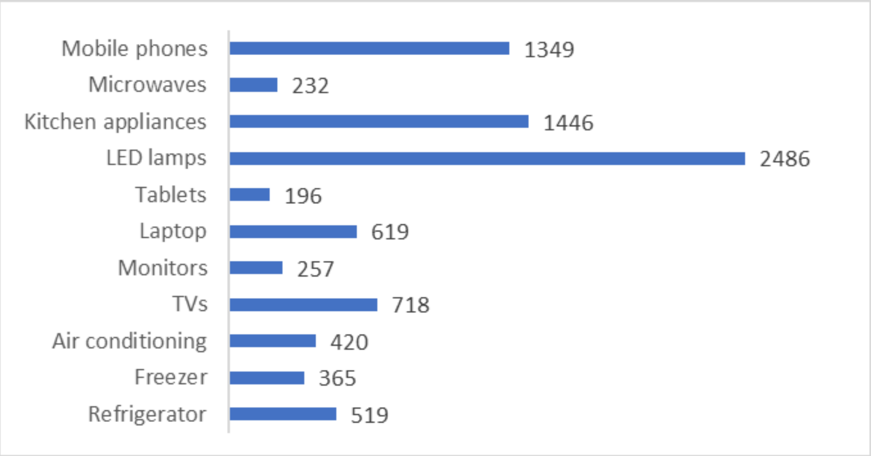


***Figure 1** Electronic devices mentioned by respondents*

The results presented in the Table 2 indicate that half of the respondents were not aware of what e-waste is (51%). Besides, 69% of the study participants don’t know how to dispose their e-waste properly. In addition to the fact that 55% of the respondents are aware that in Novi Sad exist e-waste collectors, 72% still don’t know the difference between formal and informal sector. Although most of the participants (79%) are aware that e-waste contains hazardous substances, answers to other 4 questions showed the need for implementation of educational programs on this topic, as the main basis for e-waste management initiatives. This is also confirmed by the fact that 30% of respondents have never received any information concerning e-waste problem, as shown on Figure 2. Uhunamure *et al*. [18] and Almulhim [11] also confirmed this type of findings.

Table 2 *Statements on e-waste awareness/knowledge among the respondents (n=434)*

Statements	**No**	**Yes**
Are you aware of what e-waste is?	221 (51%)	213 (49%)
Do you know how to dispose e-waste properly?	299 (69%)	135 (31%)
Are you aware of the existence of e-waste collectors/recyclers?	197 (45%)	237 (55%)
Are you aware that e-waste contains hazardous substances?	90 (21%)	344 (79%)
Do you know the difference between formal and informal e-waste sector?	313 (72%)	121 (28%)

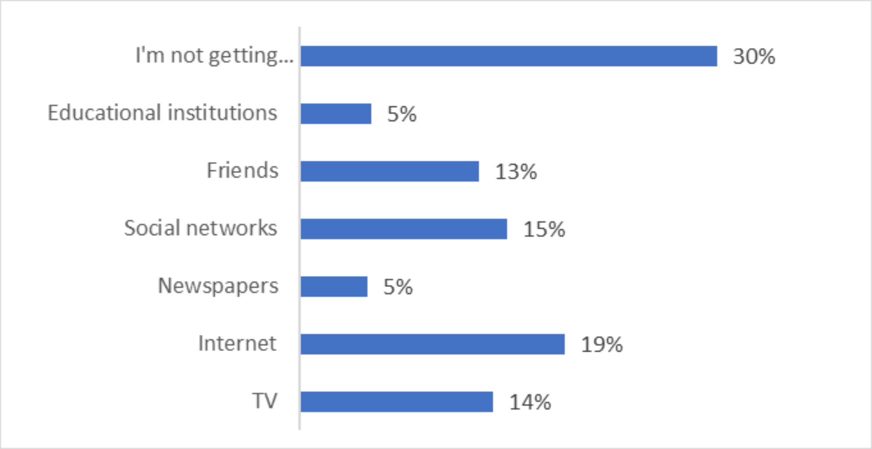


Figure 2 *Sources of learning about e-waste*

Methods of handling and disposing of e-waste

When asked what they do with devices that are no longer functional, as well as with those that are functional but do not used by themselves, respondents were offered a couple of alternatives. As shown on Figure 3, the highest number of participants (46%) said that devices that are no longer functional throws into the container together with municipal solid waste, while just 14% is given to the recyclers. Most of the functional devices (31%) respondents store in the household and keep it as a reserve or give it to a friend (28%).

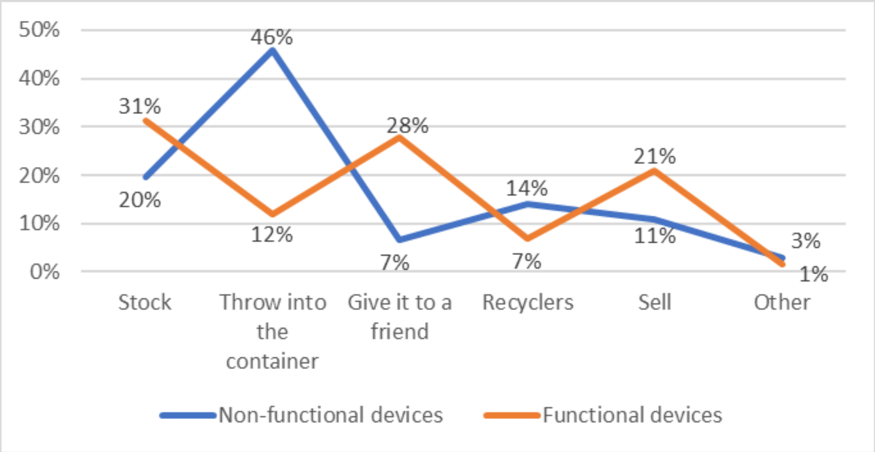


Figure 3 *Handling and disposing of non-functional and functional devices*

Willingness of households to participate in e-waste management system

Results related to households' willingness to participate in e-waste management are given in Table 3. On the question whether they already recycle e-waste, only 9% of the study participants answer with yes. The willingness of the respondents to pay for proper managing of e-waste was 41%. Finally, 68% of participant respond that they would like to be part of educational programs and raise awareness about e-waste problems. Attia *et al*. [19] and Almulhim [11] showed similar results with slightly higher percentage of people willing to participate in e-waste management.

Table 3 *Willingness of participants to engage in e-waste management*

Statements	**No**	**Yes**	**Sometimes**
Do you recycle?	146 (34%)	39 (9%)	249 (57%)
Whether you buy new or used?	New	Used	Both
	258 (59%)	14 (3%)	162 (37%)
Would you recycle e-waste if there is condition for it?	No	Yes	Yes, for monetary compensation
	19 (4%)	323 (74%)	92 (21%)
Would you be willing to compensate someone who will efficiently discard your e-waste?	No	Yes	
	256 (59%)	178 (41%)	
Would you participate in educational programs about e-waste problems?	No	Yes	
	139 (32%)	295 (68%)	

CONCLUSION

This study is conducted to investigate the household awareness on e-waste and willingness to participate in e-waste management in Novi Sad. To reduce the impact on environment and minimize the exposure to harmful components, it is crucial to establish proper waste disposal, reuse, and recycling. Knowledge and awareness on e-waste represent a crucial factor in achieving these goals. On the basis of the finding from this study, the following conclusions and recommendations are made.

Among the respondents there was almost an equal number of men and women, with a slightly higher percentage of men (53%), while the most represented age group one between 31–40 years (47%). Based on the monthly income of the households, where highest percentage of respondents earned more than 1,100 Euros (27%) and between 800–1100 Euros (24%), it can be concluded that there is a greater probability of increasing the capacity to purchase electronic products.

In terms of electronic devices that members of households are more likely to have, results showed that led lamps, mobile phones, kitchen appliances, TVs and laptops are the popular ones and that most respondents own more than one device from these categories in their homes. Furthermore, the level of awareness on what e-waste represent is quite low (49%). Accordingly, the results further showed that 69% of the respondents do not know how to dispose e-waste properly, while 72% do not know the difference between formal and informal sector. Given the fact that 30% of respondents never received any information concerning e-waste these results are to a certain extent expected. Therefore, intervention by the municipalities or other stakeholders of e-waste management needs to be taken to improve awareness level on e-waste among the citizens.

When it comes to non-functional devices, most respondents throw them in containers with municipal solid waste (46%) and in that way it ends up in landfills, which negatively affects the environment and endangers human health. On the other hand, 31% of the study participants store functional devices that no longer use thus creating large stocks of products that will one day end up as waste. Hence, in the future research should be carried out to assess the feasibility of a system such as deposit refund system as part of the legislative initiative.

Most study participants (68%) were willing to participate in educational programs about e-waste. However, for this to have an effect, the involvement of other parties of e-waste management is needed [4,20].

According to Afroz *et al.* [20] questionnaire survey presents the convenient method for identifying people's knowledge and awareness on e-waste. For future research, a larger number of respondents from other regions should be considered to obtain results representative of the country level. These surveys would be valuable resources for future WEEE management planning in Serbia.

REFERENCES

[1] D.S. Khetriwal, P. Kraeuchi, R. Widmer, J. Environ. Manage; 90 (2009) 153–165.

[2] C.P. Baldé, F. Wang, R. Kuehr, *et al.*, The Global E-Waste Monitor – 2014, United Nations University, IAS – SCYCLE, Bonn, Germany (2015), ISBN: 978-92-808-4555-6.

[3] V. Forti, C.P. Baldé, R. Kuehr, *et al.*, The Global E-waste Monitor 2020, Quantities, flows and the circular economy potential, Bonn/Geneva/Rotterdam (2020) 13–15, ISBN: 978-92-808-9115-7.

[4] K.J. Miner, I.T. Rampedi, A.P. Ifegbesan, *et al.*, Sustainability; 12 (3) (2020) 1047.

[5] C. Terada, Nw. J. Int. Hum. Rts; 10 (3) (2012) 153–172.

[6] M.T. Islam, A.B. Abdullah, S.A. Shahir, *et al.*, J. Clean. Prod; 137 (2016) 728–740.

[7] I. Berežni, F.D. Castro, B. Batinić, *et al.*, Waste Manag. Res; 39 (10) (2021) 1302–1316.

[8] W. Wang, Y. Tian, Q. Zhu, *et al.*, J. Clean. Prod; 153 (2017) 299–308.

[9] B. Sivanthanu, Int. J. Appl. Environ. Sci; 11 (2) (2016) 413–423.

[10] R. Akhtar, M.M. Masud, R. Afroz, Malaysian J. Sci; 33 (1) (2014) 32–41.

[11] A.I. Almulhim, Ain Shams Eng. J; 13 (2022) 101729.

[12] E.S. Pandebesie, I. Indrihastuti, S.A. Wilujeng, *et al.*, Environ. Sci. Pollut. Res; 26 (27) (2019) 27930–27939.

[13] B. Batinić, I. Berežni, T. Marinković, *et al.*, 16th International Conference on Environmental Science and Technology, 4 to 7 september 2019, Rhodes, Greece (2019).

[14] B. Batinic, M. Vaccari, V. Savvilotidou, *et al.*, Glob. Nest J; 20 (4) (2018) 706–711.

[15] T. Marinkovic, B. Batinic, N. Stanisavljevic, Wastewaters, municipal waste and hazardous waste, Analysis of WEEE management in the Republic of Serbia (in Serbian), Pirot, Serbia (2017).

[16] Z. Wang, B. Zhang, J. Yin, *et al.*, J. Clean. Prod; 19 (9–10) (2019) 977–984.

[17] A.M. Adam, J. Sci. Res. Rep; 26 (5) (2020) 90–97.

[18] S.E. Uhunamure, N.S. Nethengwe, K. Shale, *et al.*, Recycling; 6 (2) (2021) 39.

[19] Y. Attia, P.K. Soori, F. Ghaith, *et. al.*, Toxics; 9 (10) (2021) 236.

[20] R. Afroz, M.M. Masud, R. Akhtar, *et al.*, J. Clean. Prod; 52 (2013) 185–193.

ECOLOGICAL ETHICS AND ECOLOGICAL EDUCATION

Maja Radić[1*], Mehmed Avdagić[2], Branka Markovic[3], Kenan Ademović[4], Sumeja Avdagić[5], Sarah Avdagić[6]

[1]Business Academy in Novi Sad, Faculty of Economics and Engineering Management,
Novi Sad, REPUBLIC OF SERBIA

[2]International University in Goražde, Faculty of Social Sciences, Goražde,
BOSNIA AND HERZEGOVINA

[3]Independent University of Banja Luka, Faculty of Ecology, Banja Luka,
BOSNIA AND HERZEGOVINA

[4]Law office Filipović-Ademović and Associates, Sarajevo, BOSNIA AND HERZEGOVINA

[5]Business Academy in Novi Sad, Faculty of Economics and Engineering Management,
Novi Sad, REPUBLIC OF SERBIA

[6]Business Academy in Novi Sad, Faculty of Economics and Engineering Management,
Novi Sad, REPUBLIC OF SERBIA

[*]*maja.radic84@gmail.com*

Abstract

It is important to note that much of the international literature on environmental education focuses on the context of formal education. Environmental education is specific and depends on various cultural understandings and interactions with the natural environment. Therefore, it is difficult to define it in such a way as to cover all the activities that take place in its wide range. In order to raise awareness through education in citizens, it is necessary to observe all responsible people in institutions through their business ethics. Certain companies dealing with certain production and companies that give certain services must be aware of their social responsibility. The ultimate goal of environmental education is to understand through education the complexities of the environment and the need for nations to create their own education systems, so that the development of countries is in harmony with the environment.

Keywords: ethics, environment, education, culture, activity, responsibility

INTRODUCTION

Since the mid-1990s, the concept of environmental education has increasingly been replaced by terms and concepts such as "Sustainable Development Education", "Sustainability Education" and in recent time "Climate change" and "education for sustainable societies". This shift indicates a conceptual reconstruction that is encouraged by the complexity of social and political changes that occur all over the world as a result of environmental crises and different perspectives through which they are understood in different contexts.

The background of such changes in terminology can also be linked to numerous recorded hearings among the international community. In 1972, the environmental education was identified as a key point of the agenda UN Human Environment Conference held in Stockholm in Sweden [1].

As a result of the conference and subsequently adopted action plan, UNESCO, UNEP and other interested international bodies have started establishing the International Environmental Program. Consultations around the world were held from 1975–1977 and provided information and data for the conference in Tbilisia in 1977, which initiated the International Environmental Education Program (IEEP).

In recent times, the decade of education for the Sustainable Development of the UN 2005–2014 (Desd) and related initiative "Education on climate change for sustainable education" place greater emphasis on economic, social and cultural components of the environment, confirming the area of environmental education within sustainable development.

ECOLOGICAL ETHICS AND ECOLOGICAL EDUCATION

Environmental Objectives (EE)

Ensuring greater knowledge about nature is a basic goal which is shared by environmental educators around the world. Education on environmental ethics can be made even more efficient understanding of the actions performed at the ecosystem level and at the Group level [2].

In some countries, there is a law which established environmental objectives. For example, in the Law of the Philippines, the 2008 Environment and Education Act, stipulates that the state promotes national awareness of the role of natural resources to economic growth and the importance of preserving the environment and ecological balance for sustainable national development.

This law will be a set of the entire series of environmental concepts and principles, the Laws of Environmental Protection, the Local Environmental Practice, Environmental Degradation and Human Beings, Responsibility of Citizens, Protection Values and distributing natural resources in the environment and the economy in the context of sustainable development.

Here it is important to emphasize that the moral responsibility of such issues of global importance should be done by raising awareness or preaching doomsday scenarios, but go further and empower people to give an active and valuable contribution to solutions.

Methods

Hala suggests that environmental education should be resolved and implemented through formal and informal education sectors. The Tbilisi Agreement encourages teachers to use a wide range of teaching and learning practices that emphasize first-hand experiences and practical activity [3].

Similarly, Riordan and Klein suggest that students and teachers need to work together in finding solutions for environmental problems in real life. By emphasizing problem solving and critical thinking skills, students are encouraged to become active environmental citizens and decision makers [4].

The place and role of the community through its involvement is also considered essential for the success of environmental education. Cooperative connections are considered holistic, integrative and participatory mechanisms that can contribute to community development practices. There is also a strong reason for the involvement of environmental education in the "everyday" curriculum instead of teaching it as a separate subject area.

In many situations, environmental education is integrated into subject areas such as science and technology and / or social sciences. Certain authors suggest that there is still space for the integration of a better understanding that sees that all subject areas contribute to the development of environmental awareness.

Many environmental education efforts are school curricula and although they are needed, they may not be enough to raise environmental awareness among the existing adult population. Patterson and others cite a successful adult education program in Tuticorin, India, where he localized the environmental education was integrated with literacy and computer applications. This example emphasizes that the integration of environmental content can also be used in non-formal education and adult education.

Electronic expansion of information and prints are also vital for environmental education.

Electronic distribution of information is often a cheap and effective way to raise people's environmental awareness, although Phelps and colleagues warn that web-based resources should only be used as an introduction or supplement to community-based learning and experiential learning activities [5].

The press can also play a significant role in environmental education in general. In rural areas and areas in development, the radio was often the main means of non-formal education. In developed regions of Internet, television, cinema and written prints today there are widespread forms of media which have significant potential for raising the level of ecological awareness of the general population. The widespread and critically acclaimed success of 2006's The Inconvenient Truth is credited with raising international awareness of climate change and is an example of the significant role the media and press can play in providing environmental education.

Objectives of ethical environmental education

Ethical education for the environment (EEE) deals with issues of how to live, how to make environmental decisions and how to think about the consequences of our activities. There are many possible goals of teaching environmental ethics. Through the incredibly diverse educational contexts of different countries, with their created cultural and social values, they plan to create curricula and teach environmental ethics. Different educational systems will place different goals and emphasis in studying environmental ethics [6].

Curricula and programs and environmental courses may face several key dilemmas:

- Do natural objects and living beings have moral status?
- Are they a valuable ethical concern?
- Do natural objects have intrinsic value or moral value because there of what they are?
- Or do have only instrumental value?
- What "environmental services" provide a natural ecosystem?

- Should clean air, food, water be considered resources for human use?
- Should human beings be viewed only as a different species, as a part of nature?

Through theoretical and practical education on environmental ethics, a person can have many possible goals, which are relevant to individuals and society as a whole.

Monitoring and evaluation of education on environmental ethics

Evaluation of outcomes and reflection of teaching and learning practices is vital for all professionals in teaching. Monitoring and evaluation are therefore key strategies for assessing the impact of environmental education. Fien and Tilbury suggest that the teacher's ability is to develop skills for critical thinking, self-evaluation and thinking factor that contributes to the success of environmental education initiatives [7].

Curti and Valdez upport this idea and suggest that environmental educators should constantly evaluate their actions to achieve positive results. Researchers in education and policy makers can begin to monitor and evaluate programs to determine their efficiency and to continuously improve. Ethical environmental education can have several types of impact on education participants [8].When evaluating the program, several indicators can be used, for example:

- Input: Are environmental teachers ready to teach the lesson of "environmental ethics"?
- Processes: Did the teachers follow the planned curriculum?

There are many indicators that can be used to analyze change as a result of a particular educational initiative, and countries may devise the frameworks to assess the efficiency of education. Monitoring and evaluation of these changes can help countries learn from experiences and improve their programs.

Before programs can be fully monitored and evaluated, standards and criteria for program evaluation must also be developed. What is important to include in the study of ecological ethics? What are the expected results?

Education can be observed as "intervention", in order to produce a change in behavior such as waste reduction. Or the program can have more inconspicuous goals, such as "encouraging environmental awareness". Some countries may simply want students to be aware of the ethical dimensions of environmental problems, while others may want students to act in an environmentally conscious way.

It is often difficult to arrange how to evaluate study and learning in ethics. Measurement of increasing knowledge and understanding of students - especially changes in attitudes - is a difficult task. There are various instruments used to measure educational outcomes, with differences in reliability and validity.

Data in different countries are not always reliable and comparable, especially with cases such as "environmental ethics", which may not have a common core curriculum. Evaluation of ethics in education is less common compared to the evaluation of the results of literacy tests and mathematics, as common educational indicators. Adoption of value and behavioral changes cannot be covered only by numbers, so a combination of qualitative and quantitative methods can be used.

The research tried to quantify the effect of ethics courses on the moral development of students - in psychological research. Psychological instruments were used by educational and development psychologists to assess the level of "moral maturity" and phases of "moral reasoning" among students. Such instruments are imperfect, and some statistics are more reliable than others. Ethics courses are often valuable using these tools, and environmental courses can surely be evaluated according to this methodology. As an additional point of consideration, the evaluation of ethical programs is sometimes difficult when ethical topics are not assigned to the same grade as preconception.

Assessment can play a role in importance that is attached to ethical concepts, which affects the validity of the measured results. When students are given a small priority of ethical learning, students may not understand their importance. The interpretation of the results of the monitoring and evaluation program will depend on the initial goals.

This raises one of the important questions to be asked, which relates to environmental education and whether the educational program has produced the expected results. In any case, the goal should be to expose students to issues of environmental ethics. The result would be an increased number of students who were involved in discussions on environmental ethics or those who dealt with the topic in class.

- Have the teachers lectured in the manner provided by the curriculum?
- Are the knowledge, attitudes and skills of students changed (as planned)?
- What is the total quality of the program?
- Is the program conducted as provided?

Ethical education is increasingly taught as a formal subject, so the improvement and expansion of education on environmental ethics will need to possess the monitoring and evaluation method.

SOCIAL AND OTHER RESPONSIBILITIES

Man uses, but also pollutes the nature of both individual and corporate action. The contamination of the environment was caused primarily by commercial activities. Increasing industrial production without adhering to the prescribed measures, unfortunately, in many countries is the destruction of flora and fauna, which disturbs the ecological balance. In an irresponsible way by a large number of companies that release certain chemical substances into rivers, in practice it has been shown that all living beings die in those rivers. Society seeks to raise awareness among citizens towards nature protection.

This will undoubtedly affect the reduction in profits and probably the decrease in salaries, but in this way, the sustainability of ecosystem will be ensured. Water pollution is the main problem in the areas of heavy industry. In order to prevent pollution, the societies will jointly establish rules in order to save the planet Earth. However, measurements and analyzes downstream in most river flows show that water remains very polluted with chemicals and untreated wastewater.

Land pollution is often hidden and many experts refuse to admit that there is a bigger problem on this issue. It is in the conditions of increased radiation, use of poisonous substances that are poorly resolved, war, etc., often a bigger problem than water pollution. Only when the plant is dried, the condition of the land is detected, in which the causes of dying of numerous plant species.

CONCLUSION

More research is needed for a better understanding of the EEE, maybe starting by researching some of the following:

- Teaching ethics in environmental science cases, geography or business studies or the presence of ethics in appropriate textbooks.
- Map all school curricula and programs for EEE coverage.

The existing courses and programs can be monitored and evaluated to spread the best practices for further development of broader programs and developing mechanisms for increasing capacity in teaching environmental ethics.

The methods used so far to obtain results have proven to be effective. To obtain results on successful education related to environmental protection, methods were used, among others: questionnaires, formal and informal student interviews, student testing, etc.

REFERENCES

[1] L. Barraza, A.M. Duque-AristiZabal, G. Rebolledo, Environmental Education: From Policy to Practice, Environmental Education Research (2003), p.347.

[2] J. Fien, A. Gough, Studying Society and the Environment: A handbook for teachers, Melbourne, Australia, Macmillan Education Australia (1996), p.200.

[3] M. Hale, Ecology and Environmental Education in the Urban Environment, Melbourne, Australia, Cambridge University Press (1996), p.141.

[4] M. Riordan, E.J. Klein, Environmental Education in Action: How Expeditionary Learning Schools Support Classroom Teachers in Tackling Issues of Sustainability, Teacher Education Quarterly (2010), p.119.

[5] A. Jennings, Community Development Supporting Sustainability Education, New Community Quarterly (2008), p.27.

[6] R. Phelps, Creating Web-based Environmental Education Resources through Community and University Partnerships, Australian Journal of Teacher Education (2008), p.44.

[7] M.M. Baker, M. Grundy, K.D. Junmookda, *et al.*, Enviromental Ethics Education, Christchurch, Bangkok, (2019), p.23, *Available on the following link*: https://www.eubios.info/yahoo_site_admin/assets/docs/EnvironmentEthicsEducationsmall.187122256.pdf (retrieved 13.04.2022).

STONE CRAYFISH *AUSTROPOTAMOBIUS TORRENTIUM* (Schrank, 1803) IN SOUTH-EASTERN SERBIA: CHILDREN KNOWLEDGE SURVEY

Vanja Marković[1*], Katarina Zorić[2], Marija Ilić[2], Simona Đuretanović[3],
Marija Smederevac-Lalić[4]
[1]University of Belgrade, Faculty of Biology, Studentski Trg 16, 11000 Belgrade, SERBIA
[2]University of Belgrade, Institute for Biological Research "Siniša Stanković", National Institute of the Republic of Serbia, Bulevar despota Stefana 142, 11000 Belgrade, SERBIA
[3]University of Kragujevac, Faculty of Science, Department of Biology and Ecology, Radoja Domanovića 12, 34000 Kragujevac, SERBIA
[4]University of Belgrade, Institute for Multidisciplinary Research, Kneza Višeslava 1, 11000 Belgrade, SERBIA
**vanja.markovic@bio.bg.ac.rs*

Abstract

Stone crayfish, an endangered and protected species in Republic of Serbia, inhabits mountain areas of the country. The knowledge and attitude of children from two primary schools (Pirot and Bosilegrad) towards this species was tested. Two surveys with the same questionnaire were conducted. The first one was held at the end of the 6th grade, and the second was conducted a year later. The second survey has shown moderate increase in children's knowledge. To better protect and conserve rare and endangered taxa it is necessary to raise awareness of the public, particularly in the areas where these species are present. Attitudes, values, behaviour, knowledge of citizen and especially young generations form a good basis for the protection and sustainable development planning in local community.

Keywords: endangered species, public awareness, questionnaire

INTRODUCTION

Stone crayfish *Austropotamobius torrentium* (Schrank, 1803) is one of three autochthonous decapod species recorded in Serbia. It inhabits unpolluted mountain streams of the basins of the Danube and Elbe River in Europe [1]. According to IUCN criteria, *A. torrentium* is categorized as "Data Deficient", with decreasing population trends [2]. Eastern and South-Eastern Serbia are areas with moderately abundant populations of this crayfish [3]. Main threats to *A. torrentium* in the region are negative human impacts on the habitats, such as damming/small hydropower plants, pollution, etc. [4]. The importance of public education for more effective conservation and protection measures of European native crayfish has been recognized [5].

Our aim was to examine the basic knowledge of primary school's children regarding stone crayfish, as a rare and endangered invertebrate taxon. Target group was local community in the areas where the species occurs. We have tried to estimate their interest regarding protection and conservation of the nature, reflected through this native crayfish species.

MATERIALS AND METHODS

The study included 104 children, age 12 (the 6th grade of primary school) from two towns in South-eastern Serbia (Pirot and Bosilegrad). The sample comprised of 58.5% (61) girls and 41.5% (43) boys. To assess the knowledge and attitude of children towards crayfish and stone crayfish, specially prepared questionnaire was used (Table 1). The questions used can be divided into "informative" (related to children's awareness toward crayfish, i.e. those that hardly can be rated as right or wrong/correct/incorrect answers) and "proper test" questions (related to children's knowledge that can be rated as right or wrong i.e. correct/incorrect). Prior to distribution of the questionnaires, the children were given instructions and unfamiliar terms were explained to them. All children had good level of knowledge and understanding of Serbian language, which was important because children from Bosilegrad were of Bulgarian nationality). After the questionnaire finished, we organised the lecture dedicated to this topic (crayfish and stone crayfish).

Table 1 *Test questions used in analysis*

Q.1	In which animal group crayfish belong to?
Q.2	Are there any crayfish species in Serbia?
Q.3	Where do crayfish live?
Q.4	Did you hear for stone crayfish before?
Q.5	Where do stone crayfish live?
Q.6	Whether is this crayfish present in your area?
Q.7	Did you ever see stone crayfish in nature?
Q.8	What is main food of stone crayfish?
Q.9	Who preys on stone crayfish?
Q.10	What is the human impact on stone crayfish?
Q.11	Is stone crayfish protected in our country?

Two surveys were conducted, the first one being held at the end of the 6th grade (June, 2017). The same children (and the same questionnaire) were tested again approximately one year later (March/May, 2018).

The data obtained in this study were processed in Excel with main descriptive statistics, displayed through charts.

RESULTS AND DISCUSSION

One third of the respondents (32.7%) have never heard about stone crayfish, while in the second (control) survey this number was reduced to 2.9% (Figure 1a). A small percentage of children was familiar with the presence of this species in their area (14.4%), and 13.4% had never seen the crayfish in nature. In the second (control) survey the number of children who were aware of presence of this rare species raised to 39.4%. The percentage of children who claimed that have seen it in the nature also increased to 20.2% (Figure 1b, 1c).

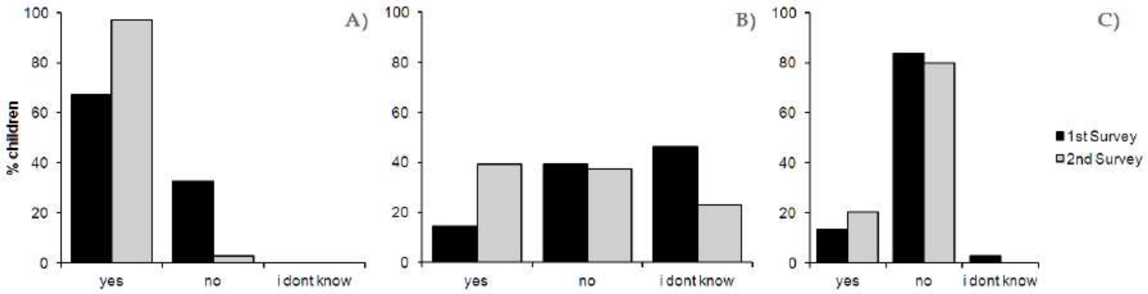


Figure 1 *Distribution of answers to "informative" questions regarding crayfish and stone crayfish: a) Q.4; b) Q.6; c) Q.7*

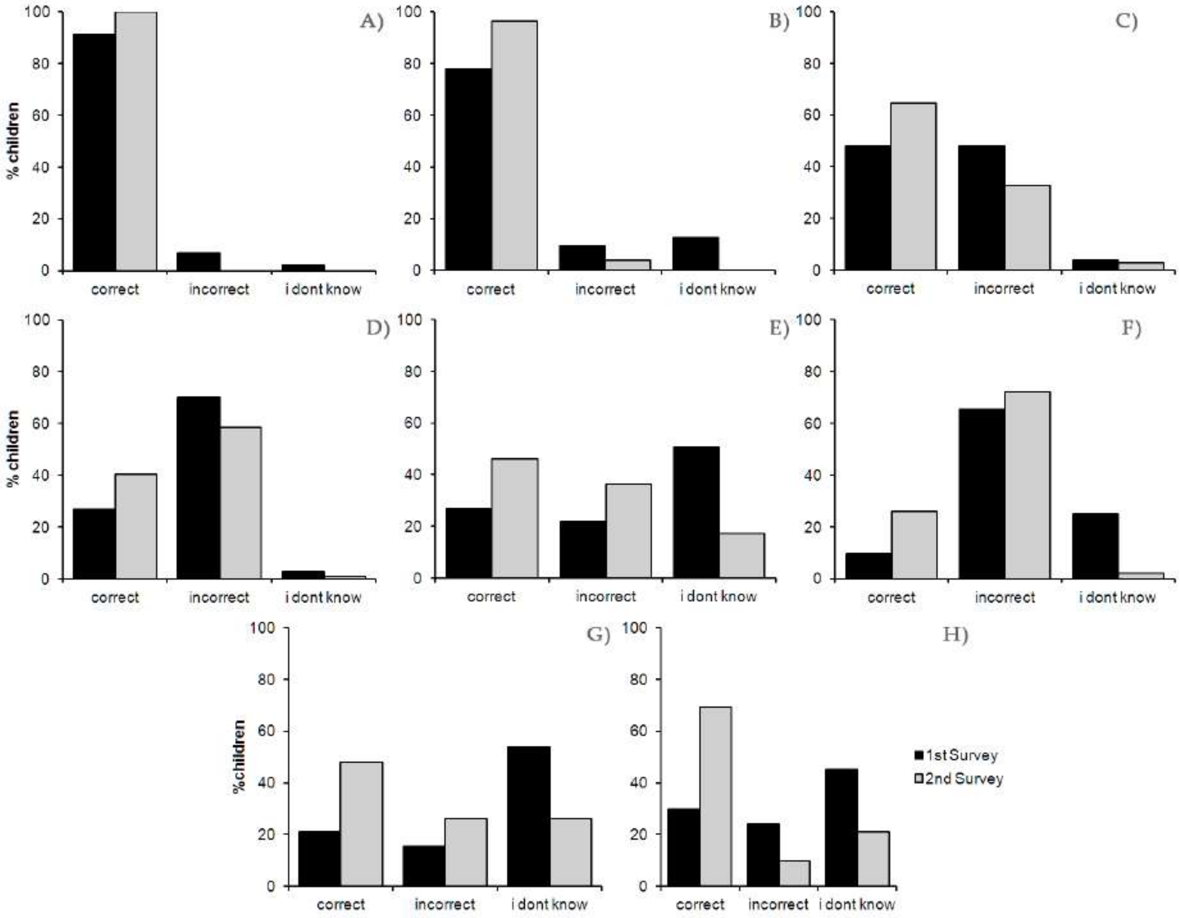


Figure 2 *Distribution of answers to "test" questions regarding crayfish and stone crayfish: a) Q.1; b) Q.2; c) Q.3; d) Q.5; e) Q.8; f) Q.9; g) Q.10; h) Q.11*

Regarding general questions about crayfish, very good to excellent level of knowledge was found with 91.3% of respondents answered correctly to the question in which animal group crayfish belongs to (in the control survey this number raised to 100%). 77.9% were aware of crayfish presence in our country (in the control survey this number raised to 96.1%) (Figure 2a, 2b). Approximately a half of respondents (48.1%) had essential knowledge of crayfish main habitat in the first survey, while in the second survey this number/percentage raised to two thirds (64.4%) (Figure 2c).

In the first survey, 24.3% of children answered correctly to questions regarding stone crayfish ecology (habitat, diet, human impact, protection status), while only 9.6% of children had knowledge of the main predator of stone crayfish in the nature (Figure 2d, 2e, 2f, 2g). In the control survey these numbers raised to nearly a half of children (49.1%) who responded correctly. The particular increase was noticed in regards to knowledge of stone crayfish protection status (from 29.8% to 69.2%, Figure 2h).

Public awareness of crayfish depends on educational and school programmes and on economic and social importance of crayfish [5]. As it has been shown, apart from Scandinavian countries and UK, public knowledge levels about crayfish are fairly low [5]. Lack of adequate information and available documentation has been pointed out as the main cause of such situation in general. The lack of specific educational programmes is particularly noticeable for *Austropotamobius torrentium*, a native species for Danube and Elbe river basins. Particularly low level of knowledge was noted in our neighbouring country Croatia [5]. Recorded low level of public knowledge in Croatia was not linked with low avaiability of informations about crayfish (which was average). Despite in Serbia similar investigations weren't conducted, due to economical, cultural and political connections in the past and present, we could assumme somewhat similar situation here as well. The results of our investigation has shown good level of knowledge regarding crayfish in general, yet fairly low knowledge of stone crayfish (around 20% of children with correct answers). Even in the second survey the knowledge about stone crayfish has only risen up to average level (around 40% of children with correct answers). Obtained results can be explained by school programmes, lack of information about *A. torrentium* and low levels of economic and social importance of crayfish in the region and in our country. It should be underlined that similar investigation regarding public awareness of crayfish and stone crayfish wasn't conducted before in Serbia. To obtain more reliable data, similar research should be conducted in wider region, including different age and social classes. We hope that our pioneering study can be one small step towards preservation of *A. torrentium* and other endangered invertebrates species in our country.

CONCLUSION

Initial children's knowledge regarding stone crayfish was at expected level, having in mind rigid school curriculum, and low level of education and practical activities in the local areas regarding endangered invertebrate species present in our country. Moderate knowledge increase was recorded after the second survey. To better protect and conserve rare and endangered taxa it is necessary to raise awareness of local citizen, especially young generations, particularly in the areas where these species can be found. A similar research, regarding stone crayfish has not been conducted before in Serbia. Hopefully this pioneering study will contribute to wider efforts in preservation of this and other endangered invertebrates species in our country.

ACKNOWLEDGEMENT

This paper was supported by the Rufford Foundation, project Stone crayfish Austropotamobius torrentium (Schrank, 1803) in Serbia: distribution, population density, genetic diversity and conservation. We are very grateful to school teachers and children from elementary schools "Georgi Dimitrov" in Bosilegrad and "Dušan Radović" in Pirot.

REFERENCES

[1] A. Kouba, A. Petrusek, P. Kozák, Knowledge and Management of Aquatic Ecosystems 413 (2014) 05.

[2] L. Füreder, F. Gherardi, C. Souty-Grosset, *Austropotamobius torrentium*, The IUCN Red List of Threatened Species (2010) e.T2431A9439449.

[3] V. Marković, K. Zorić, M. Ilić, *et al*., A contribution to the knowledge on the distribution of native crayfish *Austropotamobius torrentium* (Schrank, 1803) in Serbia, Proceedings of the „EcoIst '17" Conference, 12–15 June 2017, Vrnjačka Banja, Serbia (2017) 96–99.

[4] L. Füreder, L. Edsman, D.M. Holdich, *et al*., Atlas of Crayfish in Europe, Muséum national d'Histoire naturelle, Paris (2006), p.188, ISBN: 9782856535790.

[5] J.D. Reynolds, M. Puky, Roundtable session 4: The importance of public education for the effective conservation of European native crayfish, Bulletin Français de la Pêche et de la Pisciculture, 376–377 (2005) 837–845.

EcoTER'22
29th International Conference Ecological Truth
& Environmental Research
21 - 24 June 2022, Hotel Sunce, Sokobanja, Serbia
www.eco.tfbor.bg.ac.rs

THE IMPACT OF TEXTILE AND CLOTHES PRODUCTION ON THE ENVIRONMENT – PART I: ENVIRONMENTAL ISSUES

Ana Radojević[1*], Jelena Milosavljević[1], Tanja Kalinović[1], Jelena Kalinović[1], Snežana Šerbula[1]

[1]University of Belgrade, Technical Faculty in Bor, V.J. 12, 19210 Bor, SERBIA

[*]*aradojevic@tfbor.bg.ac.rs*

Abstract

The production of clothes has significant impacts on the environment since the textile industry has high demands regarding the use of land, water, energy, chemicals, etc. The major pollution comes from the production phase of textiles. However, various pollutants could be emitted during the specific processes of clothes manufacturing, such as bleaching, dyeing, printing, etc. The lowest impact on the climate change is associated with clothes made from natural fibers compared to the synthetic ones, of which polyester has the lowest impact. Public awareness of the environmental pollution with microplastics is increasing in recent years, while the textile industry is recognized as one of the major sources of microplastics in the oceans.

Keywords: textile, clothes, environmental pollution, microplastics

INTRODUCTION

Textile industry is very important for nowadays society, providing us with clothing, shoes, various household items, furniture, etc. The textile industry is one of the industries that is highly globalised, including millions of manufactures and billions of consumers worldwide [1]. This makes the textile industry the third largest employer in the world, after food and housing. 50% of workers are employed in the clothing production, but only about ¼ of this employment takes place in Europe, illustrating its highly global nature. Most of the textile production takes place in Asia, due to low production costs [2,3]. In the period between 2000 and 2014, the estimation of the global clothing production almost doubled reaching 14 produced items of clothing per every person in 2014. Within the same period, the number of clothing items, purchased by the average consumer, was gradually increasing, reaching 60% more purchased items by 2014 [4]. In Europe, textiles and clothing represent an important manufacturing sector, making Europe, after China, the second largest exporter of textiles and clothing in the world. During 2017, in the European Union (EU) 7.4 kg of textiles per person was produced and nearly 26 kg was consumed [1]. During 2019, the EU textile and clothing sector had a turnover of 162 billion EUR, employing over 1.5 million people across 160,000 companies [2]. Clothing items are high-value products compared to their low weight. For example, during 2020, 9% of EU production related to textiles was equal to 38% of the value of clothes [3]. From the estimated total textile consumption in Europe in 2020, amounting to 15 kg per person, the average consumption of clothing products was 6 kg or approximately 600 EUR spent by Europeans [2].

However, the profit in the textile industry comes with a high environmental impact. The type and magnitude of impacts predominantly depend on the type of fibre from which the textile i.e. clothes are made, followed by the case-specific parameters, including production process, dyeing technique, fabric construction, etc. [4].

Increased attention for the presence of microplastics in the environment is observed in recent years. Microplastics can be released directly into the environment (primary microplastics) or can result from degradation or breakdown of larger plastic items present in the environment (secondary microplastics) with an average size of 0.001–5 mm or even smaller (<0.001 mm). The long-term environmental and health impacts of pollution with microplastics are still poorly understood. However, due to the microplastics size and shape, it is proven that it can be readily ingested by aquatic species, and by entering the food chain, it could lead to chronic human exposure via food products. Textiles are a major source of microplastic pollution of the environment. Since they typically have a fibre shape, microplastics are often called microfibres. The wearing and maintaining (washing, drying and ironing) of clothes made from synthetic fibers is recognised as one of the sources of microplastics in the environment [3,5].

The paper aims to present an overview of the environmental impacts that manufacturing of clothes have made in Europe in recent years.

RESULTS AND DISCUSSION

The impact of textile production on the environment

Environmental impact of the textile production (Figure 1) can be divided in a few main categories: the impact related to the cultivation and production of natural (land and water use, fertilizers and pesticides) and manmade fibres (use of energy and various chemicals); the impact made during manufacturing of textile products (energy and water use and uses of a broad variety of chemicals); transport emissions during distribution and retail; packaging waste and unsold textile products which end up as waste as well. However, four categories in which the textile industry is recognized a major source of environmental pollution are: use of resources, water and land use and greenhouse gas (GHG) emissions [3].

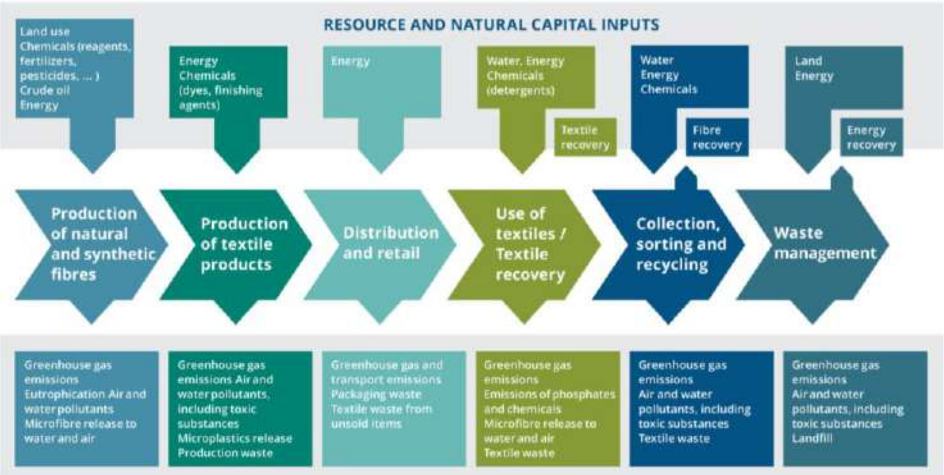


Figure 1 *Environmental impacts across the life-cycle of textiles [3]*

During 2020, of estimated 175 million tonnes of raw materials used in the EU (391 kg per person) roughly 40% was attributed to the clothes production. In terms of primary raw material use, this ranks textile industry as the fifth highest, which is at about the same level as health, furnishings and household goods, recreation and culture sectors [3]. The use of raw materials includes all types of materials needed for producing natural and synthetic fibres (fossil fuels, chemicals, fertilisers, etc.), all building materials, minerals and metals used in the construction of production facilities, as well as transport and retail of the textile products. Only 20% of primary raw materials are produced or extracted in Europe, which implies that 80% of environmental impacts generated by textile consumption in Europe take place outside Europe [2].

Water and land consumption for textiles bought in Europe takes place outside Europe, mostly in China and India where the major production of cotton fibres is done. It is estimated that the production of 1 kg of cotton requires about 10 m^3 of water, which is the most water-consuming phase of textile production. Also, animal-based fibres (e.g. wool), have a significant impact on land use. All this makes textile industry the third most important impact on land use (after food and housing) of which 43% is attributed to the production of clothes [3].

About 80% of the total impact of textile production on the climate change occurs in the production phase, 17% in the use phase, and 3% during the end of life phase. The production of textile products, bought in the EU during 2020, generated 121 million tonnes of CO_2 equivalent (CO_2-eq) or 270 kg of CO_2-eq per person. This makes textiles the sector with the fifth largest impact on climate change (after housing, food, transport and recreation and culture), from which 50% of the GHG emissions are attributed to the production of clothes. About 75% of GHG emissions are released mostly in textile-producing regions, such as Asia. The GHG emissions could appear during fibre (0.5–9.5 kg CO_2-eq/kg fibre), yarn and fabric production, dyeing, finishing steps and confectioning [3].

Clothes made from cotton fibres generally have the lowest climate change impact (Figure 2), while those made of synthetic fibres, such as nylon and acryl, have a much higher climate impact mostly due to their fossil origin, as well as the large energy consumption during production [3]. Since 1975, the global production of textile fibres has almost tripled. Today, 60% of produced textile fibres are synthetic [1]. Since the late 1990s, polyester has surpassed cotton as the most commonly used fibre in textiles [6]. Synthetic textile fibres are produced from non-renewable resources, such as oil and natural gas. GHG emissions are generated mostly during production, consumption and waste handling of synthetic textile fibres. The production itself requires large amounts of energy. On the other hand, the production of synthetic fibres does not use agricultural resources, toxic pesticides or fertilisers, synthetic fibres are cheap and versatile, enabling the production of cheap and high-performance textiles for durable clothing. Polyester is the most commonly used synthetic fibre in the clothes industry. Although it is produced from carbon-intensive processes, requiring approximately 1% of crude oil production at a global level [1,6] compared to the other synthetic fibers, polyester has generally lower impact regarding all seven factors given in the Figure 2. More than 50% of the global synthetic fibre production accounts for polyester production with 55 million tonnes in 2018, while the production of nylon is at the second place with 5 million tonnes in 2018. Production and use of bio-based synthetic fibres is currently negligible [6]. Production of natural fibers besides cotton, which is dominant, includes hemp and linen [2].

Textile manufacturing also involves significant use of heat consumption, particularly during drying and curing operations and wet treatments [7].

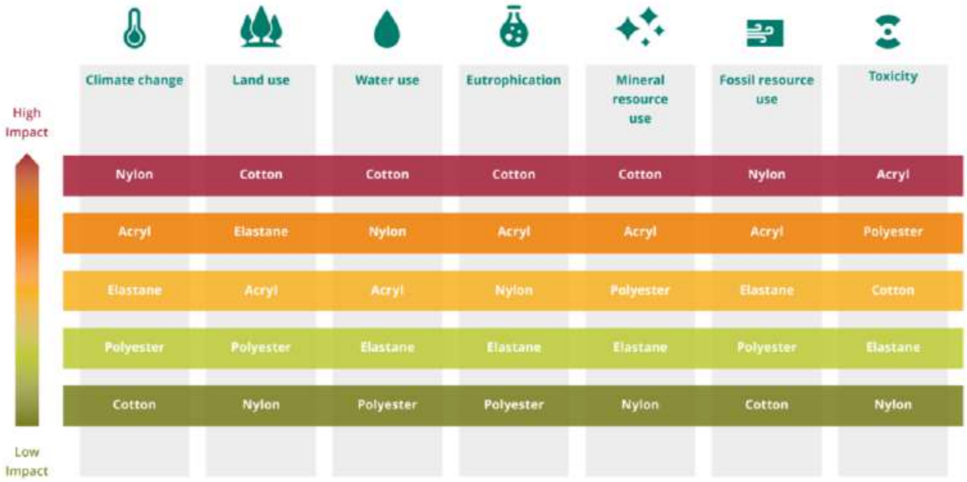


Figure 2 *Comparison of the environmental impacts for the manufacturing of 1 kg of dyed woven fabric to 1 kg of synthetic (nylon, acryl, elastane, polyester) and natural (cotton) fibres [6]*

Types of pollutants emitted during textile production

From approximately 3 500 substances used in the textile industry 750 of them have been classified as hazardous for human health and 440 substances are classified as hazardous for the environment [1]. The hazardous chemicals are often used in other specific processes in order to provide the final product with desired visual and functional properties. Many chemicals used in textiles pose a significant risk to water and human health, including certain phthalates, azo colours and dyes, perfluoroalkyl and polyfluoroalkyl substances, Cr(VI), dimethylfumarate, etc. For example, the production of 1 kg of cotton t-shirts requires about 3 kg of chemicals, such as dyes and finishing agents. Some chemicals which should be avoided include: heavy benzene compounds, dichromates as oxidizing agents, chlorinated and fluoro-chlorinated solvents in open systems, etc. [7].

It is estimated that about 20% of global water pollution is caused by dyeing and finishing textile products, affecting the health of workers and local communities as well [1]. Dyeing can require up to 150 L of water per kilogram of fabric [8]. Wet processing or finishing processes include: desizing, bleaching, mercerizing, dyeing, printing, and other specific treatments. In this phase fabrics are treated with chemicals and liquor baths with several steps of washing, rinsing, and drying. Wastewater effluents consist of suspended solids, mineral oils (antifoaming agents, grease, spinning lubricants, none or low biodegradable surfactants) and other organic compounds: including phenols, colour pigments, halogens, amines from dyeing; halogenated organics, hydrogen peroxide, sodium hypochlorite and sodium chlorite used in bleaching; caustic soda used in mercerizing. Effluents from dyeing process are typically hot and colored and may contain significant concentrations of heavy metals, such as

Cr, Cu, Zn, Pb or Ni. Effluents from natural fibre processing (e.g. cotton) may contain pesticides used in pre-finishing processes, potential microbiological pollutants (bacteria, fungi, and other pathogens), as well as other contaminants (sheep marking dye, tar). Process wastewater originating from the textile manufacturing is typically alkaline and needs to be neutralized [7].

Various air pollutants may be generated during processes of coating, dyeing, printing, fabric preparation, etc. [7]. Textile production includes emissions of formaldehyde, acetic acid, and other volatile compounds (VOCs) such as acetaldehyde, chlorofluorocarbons, dichlorobenzene, ethyl acetate, methylnaphthalene, chlorotoluene, etc. Also, cotton dust is easily combustible and presents a potential explosion hazard [7].

Wastes specific to the textile industry include trials, selvedge, trimmings, cuttings of fabrics, yarns, spent dyes, pigments, printing pastes, and sludge from process wastewater treatment containing mainly fibers and grease [7].

Microplastics

The global consumption of synthetic fibres increased from a few thousand tonnes in 1940 to more than 60 million tonnes in 2018, and it continues to rise. Only during 2017, in European households, roughly 13 million tonnes of textile products were consumed, of which 60% of clothing textiles were made of polyester and nylon [6]. Estimations of the amounts of microplastics released and/or formed in the environment are highly uncertain because of very large number of primary and secondary sources of microplastics and the absence of standardised sampling and measurement methods [5]. They can be dispersed in water, air and soil. The annual estimations are in the range of 16–35% of globally released microplastics to oceans originating from washing plastic based textiles or in the range of 0.2–0.5 million tonnes of emitted microplastics [1,5]. Microplastic is also emitted during textile manufacturing, during clothes wearing and "end of life" disposal, which makes the estimations even more uncertain. For Europe, it is estimated that 13 000 tonnes of textile microfibres (equivalent to 25 grams per person) are yearly released to surface water, accounting for 8% of total primary microplastic emission into water. During wastewater treatment, microplastics are filtered out (Figure 3), but still its significant share eventually ends up in water bodies [5].

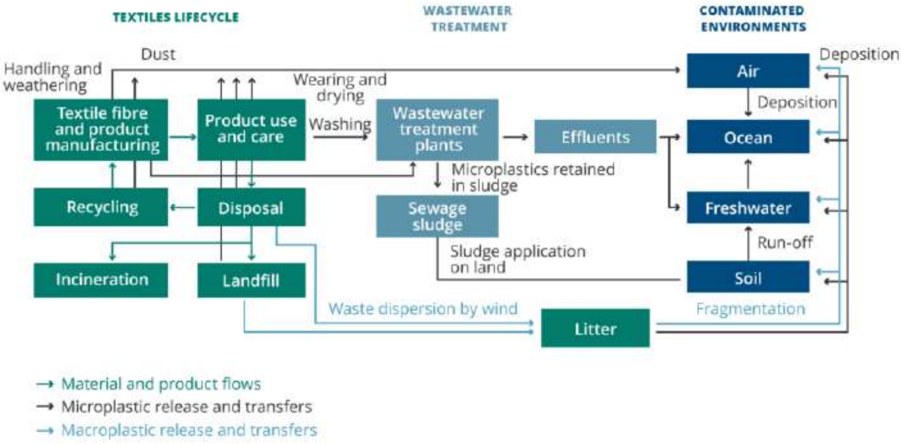


***Figure 3** Release and fates of microplastic fibres from textiles [5]*

CONCLUSION

In the recent years, the rapid development of technologies and material science have led to improvements in the textile industry, enabling faster production of goods, such as clothes. With mass production of clothes, along with the profit, the number and volume of hazardous substances has increased as well. The fibre production, both natural and synthetic, has great impact on the environment, since the process is related to high consumption of energy and water, high usage of land and other resources, as well as emission of wide range of hazardous substances and greenhouse gases. One of the specific-related pollutants from the textile industry is microplastics, which is generated during the production and usage of clothes made from synthetic fibres. The quantity of microplastics in the environment is uncertain, since the standard sampling procedure does not exist yet, but based on the current estimations, microplastic tends to be one of the most hazardous pollutants in the environment.

ACKNOWLEDGEMENT

The authors are grateful to the Ministry of Education, Science and Technological development of the Republic of Serbia for financial support within the funding of the scientific research work at the University of Belgrade, Technical Faculty in Bor, according to the contract with registration number 451-03-68/2022-14/200131. Our thanks go to professor Mara Ž. Manzalović, English language teacher at the Technical Faculty in Bor, University of Belgrade for providing language assistance.

REFERENCES

[1] European Environment Agency (EEA), Briefing No. 10/2019, Textiles in Europe's circular economy (2019), ISBN: 978-92-9480-106-7, ISSN: 2467-3196.

[2] European Environment Agency (EEA), Briefing No. 01/2022, Textiles and the environment: The role of design in Europe's circular economy (2022), ISBN: 978-92-9480-432-7, ISSN: 2467-3196.

[3] T. Duhoux, K. Le Blévennec, S. Manshoven, *et al.*, European Environment Agency (EEA), Report No. 2022/2, Textiles and the Environment – The role of design in Europe's circular economy (2022).

[4] European Environment Agency (EEA), Report No. 15/2021, Progress towards preventing waste in Europe – the case of textile waste prevention (2021), ISBN: 978-92-9480-411-2, ISSN: 1977-8449.

[5] European Environment Agency (EEA), Briefing No. 16/2021, Microplastics from textiles: Towards a circular economy for textiles in Europe (2022), ISBN: 978-92-9480-414-3, ISSN: 2467-3196.

[6] European Environment Agency (EEA), Briefing No. 25/2020, Plastic in textiles: towards a circular economy for synthetic textiles in Europe (2021), ISBN: 978-92-9480-305-4, ISSN: 2467-3196.

[7] Environmental, Health, and Safety Guidelines for Textile Manufacturing (2007), World Bank Group.

[8] N. Šajn, Environmental impact of the textile and clothing industry, European Parliamentary Research Service (EPRS), Briefing, PE 633.143 (2019).

THE IMPACT OF TEXTILE AND CLOTHES PRODUCTION ON THE ENVIRONMENT – PART II: WHAT CAN WE DO?

Ana Radojević[1*], Jelena Milosavljević[1], Tanja Kalinović[1], Jelena Kalinović[1], Snežana Šerbula[1]

[1]University of Belgrade, Technical Faculty in Bor, V.J. 12, 19210 Bor, SERBIA

[*]*aradojevic@tfbor.bg.ac.rs*

Abstract

In recent years, a reduced product lifetime due to a low quality and increased affordability of clothes, led to generation of huge volume of textile waste. Fast fashion trends are based on the unsustainable consumption patterns and encourage disposability of clothes. In order to reduce the environmental and climate change impacts of textile production, circular business model should be implemented for sustainable consumption and usage of raw materials, energy, water and land, as well as for decreasing emission of polluting substances during production phase. One of the main aims of circularity is to reduce volume of waste to a minimum and keep the materials within the production loop as long as possible. Other than textile production improvements, consumption patterns and social habits should undergo changes in order to make clothing production more environmentally sustainable and responsible.

Keywords: textiles, clothes, waste, R strategy, circular economy

INTRODUCTION

Textile industry is one of the industries with the highest environmental impact. During 2017, only in the European Union (EU), the consumption of various textiles was responsible for the emission of 335 million tonnes of CO_2 equivalent and the use of 360 000 km^2 of land, 53 000 million m^3 of water and 676 million tonnes of primary raw materials, including natural fibres, numerous chemicals, fossil fuels for the production of synthetic fibres, transport and processing, etc. [1]. According to some estimation, fashion industry is responsible for 10% of global carbon emissions, which is more than international flights and maritime shipping combined [2]. If the current production/consumption model in the textile industry sustains, it is projected that pollution of the environment would increase by at least 50% by 2030. However, if the number of times a garment is worn is doubled on average, the greenhouse gas (GHG) emissions would be 44% lower [3].

In the resent years, existing trend of lowering quality of clothing led to a decrease of prices, which made both consumers and the textile industry treat garments as "easily disposable products". This global phenomenon is called "fast fashion" which led to acceleration of the clothing consumption and generation of large amounts of waste, since mass-produced clothes are widely accessible and affordable [1,4]. In the period 1996–2018, the clothing prices in the EU dropped by more than 30% [5], resulting in enlargement of the amount of bought clothes per person in the EU by 40% between 1996 and 2012 [3].

Compared to the average clothing brands, which usually release around five collections per year, some fast fashion brands provide more than 20 new clothing collections (Zara for example 24, and H&M between 12 and 16 collections per year). The number of collections increased from two during 2000 to five collections during 2011 [1,3]. Also, a wide range of clothing has become more accessible by online purchases, especially in the past few years during the COVID-19 pandemic [1].

In the EU, consumers annually discard about 5.8 million tonnes of textiles, approximately 11 kg per person, of which about ⅔ of textile are made from synthetic fibres [6]. However, textile waste is not yet in the main focus in most of the countries. Under the 2020 Circular Economy Action Plan – CEAP, the EU is expected to make textile more prominently a part of the next waste prevention programmes, by identifying textile as a "key product value". At the "end of life" various textiles are collected, sorted and reused, recycled or incinerated for energy recovery. Still, a significant amount of textiles end up in the mixed waste, resulting in incineration or landfill [4]. Methane, one of the GHG, is released by the decomposition of textiles in landfills [3]. Textile waste is usually a part of the residential solid waste, categorized as the "other waste". The share of textile waste approximates around 2.5% of a bulk residential waste [7]. In Europe, about ⅓ of textile waste is collected separately, and a large part is exported for reuse or recycling outside Europe. The percentage of the textile waste collection vary significantly in the EU countries, from 4.5% in Latvia to 45% in the Netherlands [6,8], with unclear portion of reusable clothes [3]. In the EU, out of all collected textiles about 60–70% is reused locally or abroad, 10–30% is recycled and 10–20% is incinerated or landfilled. Globally, it is estimated that only 0.06% of all textile waste (typically cotton-rich products) is recycled into fibres for new textile products [6]. The revised Waste Framework Directive 2018/851 obliges separate collection of textile waste in the EU by 2025. It is expected that the amount of textile waste in residential waste will reduce and, at the same time, the amount of waste which is available for reuse or recycling will increase [1].

In the Republic of Serbia, during 2020, the textile was collected with residential waste in the share of 4%, from which 1024 tonnes was reused as secondary material. Also, during the same year, 266 tonnes of textile waste was imported to Serbia [9]. During 2019, the share of textile in residential waste was 3%, while more than 340 tonnes of textile waste was imported [10]. For 2018, the only available data on textile waste in Serbia was the export of 529 tonnes and import of 479 tonnes of textile waste [11].

The aim of the paper is to present the changes in the clothing sector of the textile industry, which needs to be implemented in order to make clothing production more environmentally sustainable and responsible.

RESULTS AND DISCUSSION

Sustainability in the textile industry

In recent years, the well-known "3R strategy – Reduce, Reuse, Recycle" is replaced by the upgraded "R strategy" or "R list", which could be explained through two main guidelines: steps regarding product consumption (Refuse, Rethink, Reduce, etc.) and steps regarding extended life spans and functionality of clothes (Reuse, Repair, Refurbish, Remanufacture, Repurpose, Recover, etc.) [1,4]. The "R list" relies on the long-established waste prevention and management hierarchy (Figure 1) as the optimal option for dealing with waste generation.

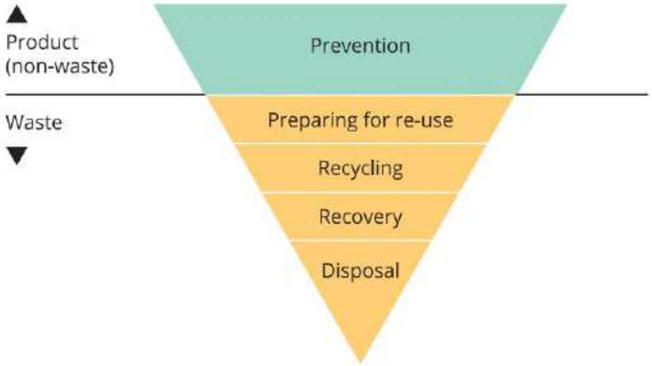


Figure 1 *Waste prevention and management hierarchy [1]*

The selection of materials and design as well as available "end of life" options, reflects the textile industry impact on the environment. The main aim is to enable sustainable production of both synthetic and natural fibres, including recycled and reused materials [5,6].

Among the natural fibres with the highest environmental impact, silk has an especially damaging effect regarding depletion of natural resources and climate change impact, compared to cotton, which is contributing excessively to water scarcity, or wool, contributing to the GHG emissions. Therefore, less frequently used natural fibres, such as hemp, flax, linen and nettle, which require less water, fertilisers and pesticides during production, are tested. The textile industry is also experimenting with bio-based polyester (bio-synthetics), which is at least partly made from renewable resources, such as starches and lipids from corn, sugar cane, beet or plant oils. The main challenge is to find feedstock that is not competitive with food production and that do not require usage of large amounts of water and pesticides. Man-made cellulosics (MMC) is biodegradable and make about 9% of fibres used in clothes in the EU and it is derived from renewable feedstock (wood pulp of trees). The most commonly used MMC is viscose. The main challenge during production is also sustainable sourcing, since the global production of MMC doubled in the period 1990–2017. In the recent years, the textile industry is trying to introduce other sustainable and innovative materials, such as: lyocell (made of cellulose from eucalyptus, which grows quickly and requires no irrigation or pesticides), bemberg (made of cotton linter that cannot be used to spin yarn), and Piñatex (made of pineapple leaves) [3]. It is important to note that not all fibres made from natural resources are biodegradable. For example, bio-based polyester is chemically equivalent to fossil-based polyester and does not biodegrade, and therefore affects the bulk microfiber loads in the environment [12].

During the textile production and finishing steps of clothes manufacture, if avoidance of hazardous chemicals is not possible, it is recommended to minimize the use of hazardous chemicals or replace them with biodegradable, bio-eliminable chemicals that do not generate potentially toxic metabolites [7] or enzymes [3]. The Dutch company DyeCoo is experimenting with novel dyeing processes, such as using CO_2 as the dyeing medium instead of water, while other companies are experimenting with different cuts, computer controlled tools for pattern making in order to minimize cut-offs, garments with no or fewer seams, bonding or gluing instead of sewing, etc. [3].

A circular system of textile production and consumption

One of the future tasks in the textile production is a progress to a circular textile production and consumption system. Along with reductions, the system relies on longer use, more reuse and recycling of garments in order to decrease the impacts of overall clothing consumption. Important measures of circular design of textiles (Figure 2) are aimed to improve the product durability, reparability and recyclability as well to ensure the use of secondary raw materials in the composition of new textile products [8].

Figure 2 *Circular model of textile production and consumption system [8]*

The first step in the circularity is to ensure the longevity and durability of textile products, which allows longer use and reuse of clothes. This includes: 1) technical requirements for colour fastness and fabric resistance, 2) practical requirements making clothes multifunctional and providing repair kits and/or spare parts, 3) eco-design requirements, etc. The second step is optimising resource use to reduce the environmental impact. The main focus is on reducing and optimising water and energy use, air and water pollution by using safe chemicals and biodegradable materials. At the production stage, eco-design principles have been identified to optimise resource use. These include reducing emissions, waste and inputs such as water, chemicals and energy, and producing fibres from renewable and/or recycled sources [8]. According to some reports, the share of sustainable cotton (eco-cotton or bio-cotton) production increased from 6% during the period 2012–2013 to 19% during 2016–2017 [3]. Design requirements with defined minimum content of recycled material could also optimise resource use. The third step includes collection and reuse of textiles. Currently, only about 20% of consumers regularly buy pre-owned clothes. While the previous steps are focused on "slowing down the loop", the last step, regarding recycling and material reuse – "closes the loop". By reducing resource use and prolonging the useful life of textiles, this model enables the loop to be closed by turning waste textiles into raw material for new textiles or other production chains. The recyclability of textiles is rarely considered in the design step because of specific functional needs (stretchiness), visual (prints) or economic reasons (mixing natural fibres with less expensive synthetic fibres) of the new garments. This results in almost ⅓ of all textile waste being unsuitable for fibre-to-fibre recycling [8].

Globally, recycling of clothes faces a number of issues, such as: a lack of technologies for sorting the collected clothing, separating blended fibres, separating fibres from chemicals including colour during recycling, establishing which chemicals were used during the production, etc. In addition, technologies that would enable clothes to be recycled into original fibres are still inadequate. This is the reason why most clothes are recycled mechanically – they are cut up and shredded whereby these fibres are shorter, have lower quality and have lost 75% of their value. The mechanically obtained fibres in this way are rather down-cycled into insulation material, wiping cloths or mattress stuffing than used for the production of new clothes. New technologies enable mechanically recycled cotton to be mixed with polyester or MMC. Technologies for chemical recycling that produce original fibres of a high quality are becoming available for polyester and nylon, but are not yet fully economically viable for cotton and fibre blends [3].

CONCLUSION

In Serbia, the collection of textile waste is at a very low level and clothes end up mixed with the residential waste. Unlike fashion brands H&M and Levi Strauss (which conduct voluntary collection of used clothes and jeans, respectively, regardless of whether they are still usable or not, in return for a small reward), in Serbia recycling of clothes is not widely supported. While technological changes, including the development of sustainable textile fibres, resource-efficient industrial production systems and improved sorting and recycling technologies for high-quality textile recycling are needed in the future, it is clear that consumption patterns and social norms should also undergo fundamental changes and transformations. However, in recent years, some examples of good practice are noticeable, such as garments and shoes made from recycled plastics (especially jackets and sneakers) or cotton products made from cotton-sustainable sources. An important measure for enabling the shift to a sustainable textiles system is the development of eco-design guidelines and requirements to ensure that textile products are fit for circularity. Preventing textile waste has great potential, mainly through reducing consumption, eco-design and reuse – the emphasis should be put on product design to promote durable and long-lasting materials, while support should be given to repair and reuse. Also, raising consumer’s awareness that textiles should be separately collected from residential waste, combined with an adequate collection infrastructure are pathways for incensement of collection rate, and recycling and material reuse. However, all the needed improvements are difficult to introduce because efforts to reduce environmental impacts may result in higher prices for consumers and convincing consumers to buy fewer clothes ("slow fashion") could reduce the overall fashion industry profit.

ACKNOWLEDGEMENT

The authors are grateful to the Ministry of Education, Science and Technological development of the Republic of Serbia for financial support within the funding of the scientific research work at the University of Belgrade, Technical Faculty in Bor, according to the contract with registration number 451-03-68/2022-14/200131. Our thanks go to professor Mara Ž. Manzalović, English language teacher at the Technical Faculty in Bor, University of Belgrade for providing language assistance.

REFERENCES

[1] European Environment Agency (EEA), Report No. 15/2021, Progress towards preventing waste in Europe – the case of textile waste prevention (2021), ISBN: 978-92-9480-411-2, ISSN: 1977-8449.

[2] www.europarl.europa.eu/news/en/headlines/society/20201208STO93327/the-impact-of-textile-production-and-waste-on-the-environment-infographic

[3] N. Šajn, Environmental impact of the textile and clothing industry, European Parliamentary Research Service (EPRS), Briefing, PE 633.143 (2019).

[4] T. Duhoux, K. Le Blévennec, S. Manshoven, *et al.*, European Environment Agency (EEA), Report No. 2022/2, Textiles and the Environment – The role of design in Europe's circular economy (2022).

[5] European Environment Agency (EEA), Briefing No. 10/2019, Textiles in Europe's circular economy (2019), ISBN: 978-92-9480-106-7, ISSN: 2467-3196.

[6] European Environment Agency (EEA), Briefing No. 25/2020, Plastic in textiles: towards a circular economy for synthetic textiles in Europe (2021), ISBN: 978-92-9480-305-4, ISSN: 2467-3196.

[7] D. Hoornweg, P. Bhada-Tata, What a Waste – A Global Review of Solid Waste Management (2012), World Bank, Urban Development & Local Government Unit.

[8] European Environment Agency (EEA), Briefing No. 01/2022, Textiles and the environment: The role of design in Europe's circular economy (2022), ISBN: 978-92-9480-432-7, ISSN: 2467-3196.

[9] Lj. Đorđević, N. Redžić, N. Radovanović, *et al.*, Waste management in the Republic of Serbia in the period 2011–2020, Ministry of Environmental Protection, Serbian Environmental Protection Agency, Belgrade (2021) (*in Serbian*).

[10] Lj. Đorđević, N. Redžić, N. Radovanović, *et al.*, Waste management in the Republic of Serbia in the period 2011–2019, Ministry of Environmental Protection, Serbian Environmental Protection Agency, Belgrade (2020) (*in Serbian*).

[11] Lj. Đorđević, N. Redžić, N. Radovanović, *et al.*, Waste management in the Republic of Serbia in the period 2011–2018, Ministry of Environmental Protection, Serbian Environmental Protection Agency, Belgrade (2019) (*in Serbian*).

[12] European Environment Agency (EEA), Briefing No. 16/2021, Microplastics from textiles: Towards a circular economy for textiles in Europe (2022), ISBN: 978-92-9480-414-3, ISSN: 2467-3196.

EFFECTS OF UN-BIODEGRADABLE AND BIODEGRADABLE PLASTIC SHEETS ON ABIOTIC SOIL PROPERTIES

Giorgia Santini[1*], Valeria Memoli[1], Lucia Santorufo[1,2], Gabriella Di Natale[3], Giulia Maisto[1,2]

[1]Department of Biology, University of Naples Federico II, Via Cinthia, 80126 Naples, ITALY
[2]BAT Center – Center for Studies on Bioinspired Agro-environmental Technology, Naples, ITALY
[3]CeSMA – Centre of Meteorologic and advanced technology services, University of Naples, Federico II, Nicolangelo Protopisani Course, 80146 San Giovanni a Teduccio, Naples, ITALY
[*]*giorgia.santini@unina.it*

Abstract

Microplastic pollution is a global problem. Agricultural soils are the main sink of plastic debris in terrestrial ecosystems. As they are dangerous, recently the biodegradable plastics have been used. Microplastics are also vectors of other pollutants such as metals. Research about the effect of plastics on metal accumulation are still scarce and controversial. Therefore, the aim of the present research was to contribute in filling this gap by comparing changes in element availability in soils covered for six months by biodegradable and un-biodegradable plastic mulches. The research was performed in outdoor mesocosm trial. Un-biodegradable (Unbiod) and biodegradable (Biod) sheets were placed on soils of ten pots. After six months since mesocosm setting up, surface (0–10 cm of depth) soils were collected and analyzed for pH, water content, organic C concentrations, and total C and N concentrations. Besides, the total and available concentrations of Al, Ca, Cu, Fe, K, Mg, Mn, Na, Ni, Pb and Zn were detected. The findings highlighted that un-biodegradable sheets better isolated the soils by the atmosphere, causing C storage. Moreover, although a slightly increase of element availability was observed in sols under biodegradable sheets, six months would seem to be not enough to highlight significant differences.

Keywords: microplastics, mulching film, metals

INTRODUCTION

Microplastic pollution is a global inconvenience [1,2]. There is much talk about plastic-related pollution in the oceans, but much of the plastic waste comes from human activities on land [3–7]. Microplastics can reach soils from a series of sources starting from atmospheric deposition to agricultural mulch residues [6,10]. The plastic mulches widely used in agricultural soils are made in polyethylene (PE) [11] that, because of their durability, can remain in soils for decades [12]. PE mulches, left on soils also after crop harvesting, can be broken into fragments by weathering processes, that include ultraviolet radiation and temperature fluctuations [13], generating microplastics. Numerous researchers have highlighted negative impacts on soil quality due to PE microplastics accumulation in soils [14].

In order to mitigate them, the use of biodegradable mulches has increased in recent years. These mulches can be degraded by biological actions, although their complete degradation can last decades [15]. Moreover, the degradation process still produces a large number of potentially harmful microplastics that accumulate in soils [9,11].

It is well known that microplastics in soils can be vectors of other inorganic and organic pollutants [16]. However, evidences about the effects of biodegradable and un-biodegradable plastic mulches on soil metal and nutrient availabilities are still scarce and controversial.

Therefore, the aim of the present research was to contribute in filling this gap by comparing changes in element availability in soils covered for six months by biodegradable and un-biodegradable plastic mulches.

MATERIALS AND METHODS

Mesocosm setting up

The research was carried out in mesocosms, constituted by 10 pots one meter in diameter, filled for about 40% of the total height (40 cm) with limestone debris of different granulometry (1–4 cm diameter). In November 2020, soil collected in the Natural Reserve of Astroni (Southern Italy) was placed on the limestone debris of each pot (approximately, 50 kg of soil for pot with a thickness of 30 cm).

On January 2021, sheets (40 cm x 40 cm) of un-biodegradable (Unbiod) constituted by little 4 squares (10 cm x 10 cm) were placed on the soil of five pots and sheets of biodegradable (Biod) of the same size were placed on the soil of other five pots. The mesocosms were left outdoors on the terrace of the Department of Biology of the University of Naples Federico II. The used un-biodegradable sheets were made in PE and the biodegradable ones were made in Mater-Bi® (composed of an amylose crystalline phase and an amylopectin complexing phase).

Sampling and analyses

After 6 months since the placement of the sheets, cores of soils (depth: 10 cm; diameter: 10 cm) were collected under a little square of the plastic sheets from each pot.

The sieved (<2 mm) soil samples were characterized for pH, water content (WC), organic C (C_{org}) concentrations, and total C and N concentrations. Soil pH was measured, by an electrometric method, in a soil: distilled water (1:2.5=v:v) suspension; WC was determined gravimetrically by drying fresh soil at 105°C until constant weight; C_{org} was measured by a CNS Analyzer (Thermo Finnigan) on soil samples previously treated with HCl (10%) to exclude carbonates; C and N concentrations were evaluated on oven-dried (105°C) and grounded (Fritsch Analysette Spartan 3 Pulverisette 0) soil samples by a CNS Analyzer (Thermo Finnigan). Details for the above described analyses are reported in previous studies [17].

Total Al, Ca, Cu, Fe, K, Mg, Mn, Na, Ni, Pb and Zn concentrations were measured in oven-dried (75°C) soil samples, ground into a fine powder by an agate mortar (Fritsch

Analysette Spartan 3 Pulverisette 0) and digested by hydrofluoric acid (50%) and nitric acid (65%) at a ratio of 1:2 (v:v) in a micro-wave oven (Milestone-Digestion/Drying Module mls 1200).

The availability of Na, Mg, K and Ca was evaluated by $BaCl_2$ and TEA pH 8.1 [18]. Briefly, to 25 g of oven-dried (75°C) soil samples were added 50 ml of diethylenetriamine pent acetic acid (DTPA), $CaCl_2$ and triethanolamine (TEA) solution at pH 7.3±0.05. The soil suspensions were shaken for 2 h and filtered with Whatman 42 filter. The element concentrations in digests and extracts were measured by Inductively Coupled Plasma Mass Spectrometry (ICP-MS Aurora M90, Bruker). Accuracy of element measurements was checked by concurrent analysis of standard reference material (BCR CRM 142R – Commission of the European Communities, 1994). The effects of both treatments on biological and chemical parameters were assessed through the unpaired t-test. Computations were made with Sigma-Stat 3.0 software and graphical displays with Sigma-Plot 9.0 software (Jandel Scientific, USA).

RESULTS AND DISCUSSION

The averages of the main soil abiotic properties are shown in Table 1. Among them only C and N concentrations showed significant differences between treatments (Table 1). In fact, C and N concentrations in soils covered by un-biodegradable sheets (C: 4.49% d.w. and N: 0.39% d.w.) were statistically ($P<0.01$) higher than in soils covered by the biodegradable ones (C: 3.71% d.w. and N: 0.34% d.w.). Thus, could be due to the nature of the un-biodegradable sheet that prevents carbon exchange with the atmosphere, causing C storage [19,20].

Table 1 *Mean values (±s.e.; n=5) of abiotic properties in soils covered by un-biodegradable (Unbiod) and biodegradable (Biod) sheets, after six months of mesocosms setting up. The asterisks show statistically significant differences in soil properties between treatments (unpaired t-test)*

	Biod	**Unbiod**
pH	8.12±0.02	8.13±0.01
WC (% d.w.)	36.6±0.88	37.2±0.73
C (% d.w.)	3.71**±0.06	4.49±0.17
N (% d.w.)	0.34**±0.005	0.39±0.012
C_{org} (% d.w.)	2.52±0.0008	2.61±0.002
C/N	10.9±0.24	11.5±0.26

WC: water content,
C: Carbon concentrations,
N: Nitrogen concentrations,
C_{org}: organic carbon concentrations,
**$P<0.01$.

The total element concentrations, on average, were slightly higher under biodegradable than un-biodegradable sheets (Table 2) with the exception of Al and Fe elements that were, approximately, 1.5-fold higher under biodegradable sheets with statistically ($P<0.01$) significant differences.

The availability of the investigated elements did not show significant differences in soils covered by different sheets (Figures 1, 2). Only Fe, with values, approximately, 1.5-fold higher in soils covered by biodegradable sheets was statistically (P<0.01) higher than in soil covered by un-biodegradable sheets (Figure 2).

Table 2 *Mean values (±s.e.; n=5) of total element concentrations in soils covered by un-biodegradable (Unbiod) and biodegradable (Biod) sheets, after six months of mesocosms setting up*

	Biod	**Unbiod**
Al (*mg g^{-1} d.w*)	70.7*±1.62	57.6±3.64
Ca (*mg g^{-1} d.w*)	54.8±3.34	30.9±2.05
Cu (*µg g^{-1} d.w*)	98.25±6.08	105±12.8
Fe (*mg g^{-1} d.w*)	31.5**±0.92	26.1±1.3
K (*mg g^{-1} d.w*)	33.7±0.60	33.0±0.86
Mg (*mg g^{-1} d.w*)	10.1±0.38	7.48±0.68
Mn (*µg g^{-1} d.w*)	26.6±1.38	18.4±1.96
Na (*mg g^{-1} d.w*)	16.4±0.32	15.6±0.44
Ni (*µg g^{-1} d.w*)	0.11±0.06	0.11±0.05
Pb (*µg g^{-1} d.w*)	13.1±2.53	9.11±1.12
Zn (*µg g^{-1} d.w*)	101.5±4.21	95.4±3.75

**P<0.01-The asterisks show statistically significant differences in soil properties between treatments (unpaired t-test).

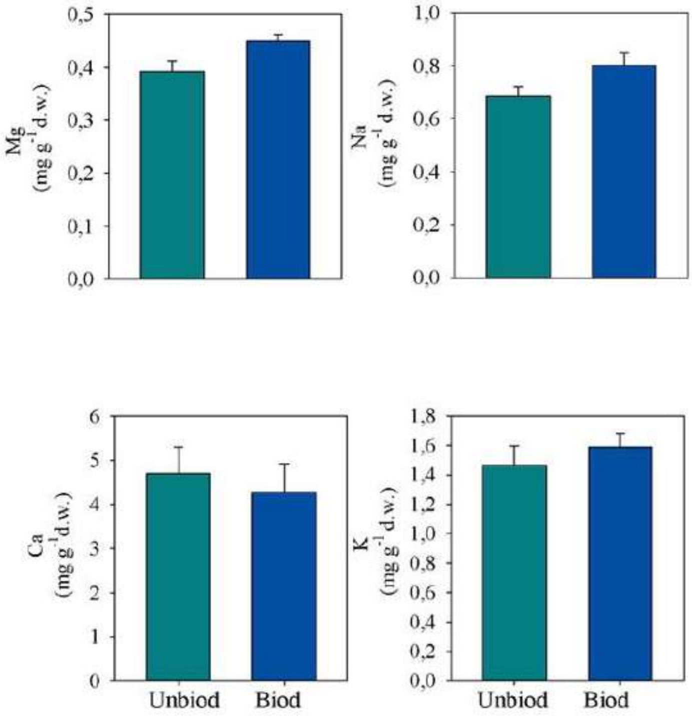


Figure 1 *Mean values (±s.e.; n=5) of available Mg, Na, Ca and K in soils covered by un-biodegradable (Unbiod) and biodegradable (Biod) sheets, after six months of mesocosms setting up*

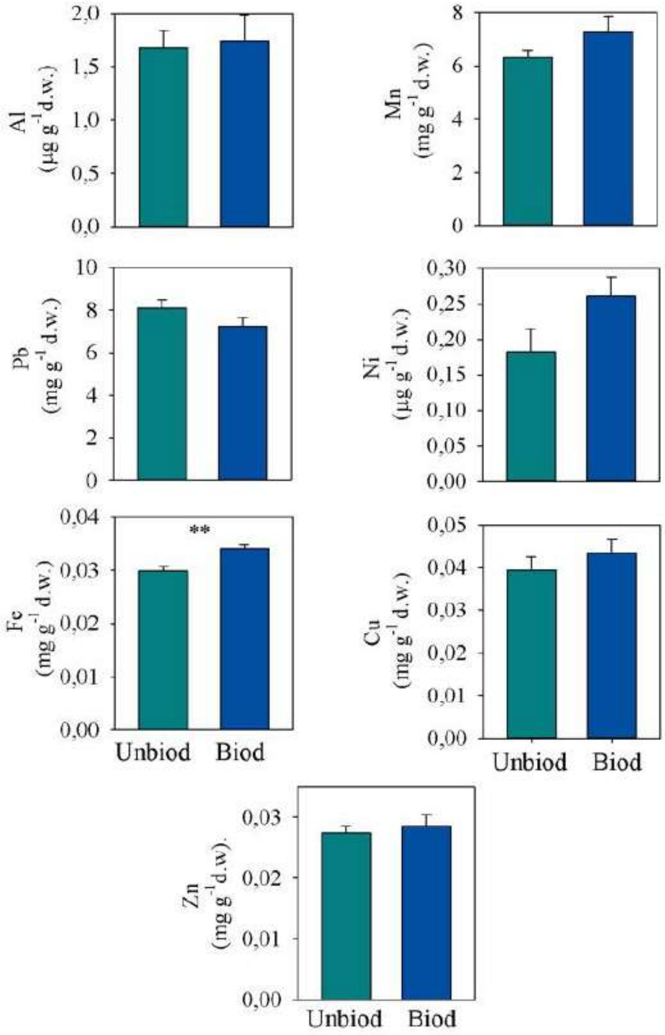


***Figure 2** Mean values (±s.e.; n=5) of available Al, Mn, Pb, Ni, Fe, Cu and Zn in soils covered by un-biodegradable (Unbiod) and biodegradable (Biod) sheets, after six months of mesocosms setting up. The asterisks show statistically significant differences in soil properties between treatments (unpaired t-test; **P<0.01)*

CONCLUSION

In conclusion, the findings highlighted that un-biodegradable sheets better isolated the soils by the atmosphere limiting the carbon exchange and causing C storage.

Moreover, six months were not enough to highlight significant differences in element availability in soils covered by the two investigated plastic sheets. However, it would seem that under biodegradable sheets the element availability was slightly higher, as suggested by Fe behaviour.

ACKNOWLEDGEMENT

The research was funded by the Biology Department of University Federico II of Naples.

REFERENCES

[1] G.A. de Lucia, I. Caliani, S. Marra, *et al*., Mar. Environ. Res; 10 (2014) 10–16.

[2] A. Isobe, K. Kubo, Y. Tamura, *et al*., Mar. Pollut. Bull; 89 (2014) 324–330.

[3] A.A. Horton, C. Svendsen, R.J. Williams, *et al*., Mar. Pollut. Bull; 114 (2017) 218–226.

[4] A.A. Horton, A. Walton, D.J. Spurgeon, *et al*., Sci. Total Environ; 586 (2017) 127–141.

[5] O.S. Alimi, J. Farner Budarz, L.M. Hernandez, *et al*., Environ. Sci. Technol; 52 (2018) 1704–1724.

[6] X. Yu, J. Peng, J. Wang, *et al.*, Environ. Sci. Technol; 214 (2016) 722–730.

[7] J. Yu, P. Wang, F. Ni, *et al.*, Mar. Pollut. Bull; 145 (2019) 153–160.

[8] R.R. Hurley, L. Nizzetto, Environ. Sci Health; 1 (2018) 6–11.

[9] R. Dris, J. Gasperi, M. Saad, *et al*., Mar. Pollut. Bull; 104 (2016) 1–2.

[10] K. Bester, C.S. McArdell, C. Wahlberg, *et al*., Env. Poll; (2010) 3–26.

[11] L. Ramos, G. Berenstein, E.A. Hughes, *et al*., Sci. Total Environ; 523 (2015) 74–81.

[12] H. Qian, M. Zhang, G. Liu, *et al*., Water Air Soil Pollut; 229 (8) (2018) 261.

[13] A.L. Andrady, H. Hamid, A. Torikai, Photochem. Photobiol. Sci; 10 (2011) 292–300.

[14] C. Fajardo, C. Martin, G. Costa, *et al*., Chemosphere; 288 (2022).

[15] H.Y. Sintim, A.I. Bary, D.G. Hayes, *et al*., Sci. Total Environ; 727 (2020)

[16] S. Kasirajan, M. Ngouajio, Agron. Sustain. Dev; 32 (2012) 501–529.

[17] V. Memoli, E. Eymar, C. García-Delgado, *et al*., Sci. Total Environ; 636 (2018) 1099–1108.

[18] W.N. Lindsay, W.A. Norwell, Agron. Abstr; (1969) 69–87.

[19] F.M. Li, Q.H. Song, J.H. Hao, *et al*., Soil Biol. Biochem; 36 (2004) 1893–1902.

[20] L.M. Zhou, S.L. Jin, C.A. Liu, *et al*., Field Crops Res; 126 (2012) 181–188.

RADIONUCLIDE CONTENT IN SAMPLES OF BERRIES

Milica Rajačić[1]*, Dragana Todorović[1], Jelena Krneta Nikolić[1],
Ivana Vukanac[1], Nataša Sarap[1], Marija Janković[1]
[1]University of Belgrade, Vinča Institute of Nuclear Sciences, National Institute of the Republic of Serbia, Radiation and Environment Protection Department,
Mike Petrovića Alasa 12−14, 11351 Belgrade, SERBIA
**milica100@vinca.rs*

Abstract

After the Chernobyl accident, the presence of artificial radionuclides in foodstuff, especially in berries (blueberries, cranberries etc.), was heightened. Legislative, presented in Rulebook on Radioactivity Control of Goods During the Import, Export and Transit (Official Gazette RS, 86/19 and 90/19), establishes the mandatory gamma spectrometry measurement of berries, while the limits of radionuclide content in these products is defined in the Rulebook on Limits of radionuclide content in drinking water, foodstuff, feedstuff, medicines, items of general use, building materials and other goods placed on the market (Official Gazette RS, 36/18). At the Radiation and Environment Protection Department of the Vinča Institute of Nuclear Sciences, measurements of the radionuclide activity in foodstuff are readily performed. In this paper, the results of the investigation of berries in the period of 2014 to 2021 are presented along with the amount of this produce that can be ingested by the various age groups without exceeding the annual effective dose limit of 0.1 mSv.

Keywords: radioactivity, gamma spectrometry, berries

INTRODUCTION

One of the most significant pathways of atmosphere contamination are nuclear tests, which were dominant in the period of 1945–2009 as well as the nuclear accidents, especially the one on the nuclear reactor in Chernobyl. Due to relatively long half–life of about 30 years, radionuclides ^{137}Cs and ^{90}Sr released in that period are still detectable in the environment. These radionuclides belong to a group of so called biologically significant radionuclides because they migrate and are easily incorporated in the food chain, thus representing the potential danger to all living beings.

Berries, the group of fruit such as blueberries, cranberries, currants and other, is also called forest fruit because it often grows in forests of different origin (for instance, blueberries grow mostly in the zone of deciduous, especially beech forests). It is known that this kind of fruit accumulates radionuclides, and in this way can cause the contamination of people through the food chain: air−earth−plant−animal–man [1].

Values of the ^{137}Cs activity reported in the literature vary significantly. In blueberries, during 2014 values of this radionuclide measured in Checz Republic were 16−87 Bq/kg [2]. That same year, in Switzerland, the range of measured values was 30−40 Bq/kg [3], while in Italy, during 2021, measured values reached as high as 234 Bq/kg [4].

During 1986, after the Chernobyl accident, on the teritory of former Yugoslavia, measured value of ^{137}Cs in blueberries was 240 Bq/kg (location of Kupinečki Kraljevac) [5], while during 1987, in the city of Zadar, the measured value was 58 Bq/kg [6].

Today in the Republic of Serbia, there are two Rulebooks which refer to the radioactivity control of berries. The first Rulebook [7], defines the method of the control at the border crossing, while the allowed values of the radionuclide activity are stated in the Rulebook [8]. Radiation and Environment Protection Department of the Vinča Institute of Nuclear Sciences has been measuring radioactivity in the environmental samples such as air, precipitation, water, soil, food etc, for years.

In this paper, radioactivity measurement results of berries in the period of 2014 to 2021 are presented, along with the amount of this produce that can be ingested by the various age groups without exceeding the annual effective dose limit of 0.1 mSv.

MATERIALS AND METHODS

Measurement of the fruit samples was conducted in accordance with international recommendations [9]. Preparation of the samples of berries consisted of weighing and placing the sample into the appropriate measurement geometry (Marinelli beakers). The samples were measured in native state.

The analysis was performed by gamma spectrometry, using three High Purity Germanium (HPGe) detectors, with the relative efficiency of 18 %, 20 % and 50 % respectively, produced by CANBERRA company. The resolution of the detectors is 1.8 keV on the energy of 1332 keV.

The calibration of the detection system was performed using a certified radioactive standard in Marinelli beaker, filled with the silica resin matrix produced by Czech Metrology Institute, Praha, certificate number 9031−OL−420/12, total activity 71.48 kBq on the day of August 31, 2012 (containing ^{241}Am, ^{109}Cd, ^{139}Ce, ^{57}Co, ^{60}Co, ^{137}Cs, ^{113}Sn, ^{85}Sr,^{88}Y and ^{203}Hg) and Czech Metrology Institute, Praha, certificate number 1035−SE−40845−17 total activity 80.64 kBq on the day of December 22, 2017 (containing ^{241}Am, ^{109}Cd, ^{139}Ce, ^{57}Co, ^{60}Co, ^{137}Cs, ^{113}Sn, ^{85}Sr,^{88}Y, ^{51}Cr and ^{210}Pb).

Measurement results are given with the measurement uncertainty expressed as the expanded measurement uncertainty with a coverage factor k=2, which corresponds to a 95 % level of confidence for the normal distribution.

RESULTS AND DISCUSSION

A total of 1038 samples of berries were analyzed in the period from 2014 to 2021. Specification of the samples along with measurement results and estimated annual effective dose are presented in the Table 1.

In 1.2 % of the total number of analyzed samples of berries, a certain activity of the artificial radionuclide ^{137}Cs has been detected, as was expected due to its half life of 30 years corresponding to the time that has passed since the Chernobyl accident of 1986. In the samples of certain species (currants, strawberries, raspberries and goji berries) the detected activities of ^{137}Cs did not exceed the minimal detectable activity (MDA). Minimal measured values for all species is equal to the MDA. It can be seen, based on the values presented in the Table 1, that the maximal value was measured in blueberries and was (330 ± 20) Bq/kg. The maximal average value was also obtained for blueberries and was equal to 70.8 Bq/kg. Due to the wide range of the results, spanning from 2.1 Bq/kg to 330 Bq/kg, standard deviation of the detected activity was close to 82 Bq/kg. For other species of berries, average value of ^{137}Cs activity does not vary significantly and is within the range from 11.7 Bq/kg for blackberries to 18 Bq/kg for chokeberry. Measured activities of ^{137}Cs are similar to those found in the literature [2−4].

Table 1 *Activity of* ^{137}*Cs in berries samples (A) and effective annual dose* (H_E)

Type of berry	**Number of samples**	**Number of samples with A > MDA**	**A_{max} [Bq/kg]**	**A_{min} [Bq/kg]**	**A_{avr} ± St. Dev [Bq/kg]**	**H_E [mSv]**
Blueberry	836	174	330 ± 20	<10	70.8 ± 81.7	0.007−0.220
Cranberry	76	8	50 ± 5	< 8	13 ± 16	0.005−0.033
Blackberry	32	8	33 ± 6	< 5	11.7 ± 9.8	0.003−0.022
Currants	27	0	/	< 4	/	/
Red mix	27	5	22 ± 3	< 6	11.8 ± 8.9	0.004−0.015
Strawberry	14	0	/	< 4	/	/
Raspberry	14	0	/	< 3	/	/
Chokeberry	11	2	24 ± 4	< 6	18.0 ± 8.5	0.004−0.016
Goji berries	1	0	/	< 2	/	/

According to the legislative enforced in the Republic of Serbia [8], allowed value of the ^{137}Cs content in berries (150 Bq/kg) is exceeded in 1.2 % of tested samples. Measured activities in these samples ranged from 150 to 330 Bq/kg and were all detected in the samples of blueberries.

The limits of activity of detected radionuclides is obtained in such a way that ensures that the annual effective dose by ingestion for the public does not exceed 0.1 mSv. The annual effective dose (H_E) is determined according to the following equation:

$$H_E = M \cdot A \cdot F \tag{1}$$

where M represents the average annual consumption of the investigated produce in kg, A – value of the ^{137}Cs activity in the investigated produce in Bq/kg, and F is a dose conversion factor for the given radionuclide (Sv/Bq). The values of dose conversion factors depend on the age group for which the annual effective dose is calculated and can be found in the Annex of the Rulebook on Limits of Radioactive Contamination of People, Working and Living Environment and Ways of Performing Decontamination [10].

Since there are no data regarding the annual consumption of berries in the Republic of Serbia, based on the allowed activity of ^{137}Cs in berries [8] and dose conversion factor for different age groups [10], the quantity of berries consumed, which would not lead to the exceeding the 0.1 mSv annual effective dose, are calculated. Thus calculated maximal allowed consumption for different age groups are presented in the Table 2.

Using this information, the intervals of the annual effective dose received by each age group by consuming the investigated samples in the amounts defined in the Table 2, are presented in the last column of the Table 1.

Table 2 *The quantity of annual consumption of berries with respect to the population age group*

Age of the population	**< 1**	**1−2**	**2−7**	**7−12**	**12−17**	**> 17**
Dose conversion factor for ^{137}Cs, F (10^{-8} Sv/Bq)	2.1	1.2	0.96	1	1.3	1.3
Annual intake [kg]	31.7	55.6	69.4	66.7	51.3	51.3
Daily intake [g]	87.0	152.2	190.3	182.6	140.5	140.5

It can be seen from the Table 2, that the estimated intake of berries for the population over 17 years of age is 51 kg (about 140 g/day), while for babies up to 1 year of age it is close to 32 kg (about 87 g/day). It is also assumed that the largest amount of berries is consumed by the children aged 2–7 years, about 70 kg per year.

Table 3 presents the activity concentration of ^{137}Cs for different age groups, with respect to the estimated annual consumption, that would lead to the exceeding of the 0.1 mSv annual effective dose limit.

Table 3 *Activity concentration of ^{137}Cs in berries samples which leads to the exceeding of the annual effective dose limit of 0.1 mSv, with respect to the different amounts of annual consumption and population age group*

Annual intake [kg]	**36**	**18**
Age of the population	A(^{137}Cs) [Bq/kg]	
< 1	132	265
1−2	231	463
2−7	289	579
7−12	278	556
12−17	214	427
> 17	214	427

From this estimation it can be concluded that with a smaller intake of 36 kg (about 100 g/day) or 18 kg (about 50 g/day) persons of 12 years of age and above can safely consume even berries that have ^{137}Cs activity of 210 Bq/kg and 420 Bq/kg, respectively.

Using the same amounts, the population of 2−7 years of age can safely consume berries that have 290 Bq/kg and 580 Bq/kg of ^{137}Cs, respectively.

Taking into account that the maximal detected activity of ^{137}Cs was 330 Bq/kg, all investigated samples may be considered safe for consumption for the population above 1 year of age in the amount that does not exceed 18 kg per year. Only 2 of all 1038 investigated samples (blueberries) were not safe for consumption for age groups below 2 and above 12 years of age, in the amounts larger than 36 kg per year. The sample with the maximum detected ^{137}Cs activity, could be safely consumed by the population of 2–7 years of age, in the amounts no larger than 31 kg per year, while for all other age groups, the safe amount would be up to 14 kg per year.

CONCLUSION

In the Radiation and Environment Protection Department of the Vinča Institute of Nuclear Sciences, 1038 samples of berries, of which 80 % were blueberries, were analyzed in the period from 2014 to 2021. All measured activities of ^{137}Cs are similar to those found in the literature [2−4].

Activities of ^{137}Cs that exceed the values allowed by the Rulebook [8] were in the range of 150−330 Bq/kg and were detected only in the samples of blueberries (total of 12 samples). Minimum and maximum average ^{137}Cs activity were 11.7 Bq/kg for blackberries and 70.8 Bq/kg in blueberries, respectively. Due to wide range of detected activities (2.1–330 Bq/kg), standard deviation of ^{137}Cs activity in blueberries was close to 82 Bq/kg. In all other species of berries, except blueberries, the measured activity was below or equal 18 Bq/kg.

It is estimated that by consuming majority of tested samples in the quantities provided for certain age groups of the population, the received effective dose would not contribute to the increase of the total received annual dose by more than 0.1 mSv. Thus, depending on the age and living habits (consumption of certain species of berries), it is safe to consume even those berries in which the ^{137}Cs activity exceeds the limit of 150 Bq/kg.

Taking into account that, at the moment of investigation, the information about the geographical origin of samples was not available, it is not possible to establish a connection between the origin of the sample and the measured ^{137}Cs activity.

ACKNOWLEDGEMENT

This research was financially supported by the Ministry of Education, Science and Technological development of the Republic of Serbia (Project no: 451−03−68/2022−14/200017).

REFERENCES

[1] R.L. Kathren. Radionuclides in the Environment: Sources, Distribution and Surveillance, Harwood Academic Press, New York (1984), p. 397.

[2] A. Cervinkova, M. Poschl, Radiocaesium in forest blueberries in selected location of Jeseníky protected landscape area, *Available on the following link*: https://mnet.mendelu.cz/mendelnet2014/articles/52_cervinkova_1062.pdf

[3] M. Zehringer. Radionuclides in wild grown berries, Annual Report of the State Laboratory Basel−City, Basel (2014), 41–45.

[4] C. Cantaluppi, D. Zannoni, M. Calabrese, J. Food Sci. Nutr. The; 7 (1) (2021) 018−024.

[5] Radioaktivnost životne sredine u Jugoslaviji, Podaci za 1986. godinu, Socijalistička Federativna Republika Jugoslavija, Savezni sekretarijat za rad, zdravstvo, boračka pitanja i socijalnu politiku, Beograd (1989).

[6] Radioaktivnost životne sredine u Jugoslaviji, Podaci za 1987. i 1988. godinu, Socijalistička Federativna Republika Jugoslavija, Savezni sekretarijat za rad, zdravstvo, boračka pitanja i socijalnu politiku, Beograd (1990).

[7] Rulebook on Radioactivity Control of Goods During the Import, Export and Transit, Official Gazette of the Republic of Serbia, No. 86/19 and 90/19, Belgrade (2019).

[8] Rulebook on Limits of Radionuclide Content in Drinking Water, Foodstuff, Feedstuff, Medicines, Items of General Use, Building Materials and Other Goods Placed on the Market, Official Gazette of the Republic of Serbia, No. 36/18, Belgrade (2018).

[9] International Atomic Energy Agency. Measurement of Radionuclides in Food and the Environment, A Guide book, Technical Reports Series No. 295, IAEA, Vienna (1989).

[10] Rulebook on Limits of Radioactive Contamination of People, Working and Living Environment and Ways of Performing Decontamination, Official Gazette of the Republic of Serbia, No. 38/11, Belgrade (2011).

MICROPLASTIC OCCURRENCE IN URBAN AND SUBURBAN SOILS OF BOR, EASTERN SERBIA

Ivana Mikavica[1*], Dragana Ranđelović[1], Jovica Stojanović[1], Jelena Mutić[2]

[1]Institute for Technology of Nuclear and other Minerals Raw materials,
Boulevard Franchet d`Esperey 86, Belgrade, SERBIA

[2]University of Belgrade, Faculty of Chemistry, Studentski trg 12–16, P.O. Box 51,
11158 Belgrade, SERBIA

**i.mikavica@itnms.ac.rs*

Abstract

Microplastics (MPs) are a newly acknowledged, pervasive pollutants found even in distant Earth areas and represent a matter of global concern. This study inspects, for the first time, microplastic content in terrestrial environments in the city of Bor, known as one of the most polluted industrial cities in Serbia. Soils from the park in the II kilometer and the periphery of the Bor (Brezonik settlement) were collected and analyzed. Plastic particle extraction from the soil matrix was performed using the flotation method based on density separation. MP content differed significantly between the two sites. Urban soil contained around 3800 items kg^{-1}*, while suburban held 600 particles per kilogram. The outstandingly high difference likely originates from the distinction in the anthropogenic activity levels of the two localities. There was no notable difference in appearance. All extracted items were white to transparent fragments. The morphological shape of plastic particles indicated defragmentation as a governing origin source. Future investigations should be concentrated on the MPs' correlation with other contaminants, namely heavy metals, and the eventual recognition of MP`s role as the metal pollution vector in the investigated area.*

Keywords: enviroment, soil, microplastic, isolation

INTRODUCTION

Plastic waste has been internationally recognized as one of the massive environmental pollutants for decades already. However, the discovery of microscale plastic fragments, ubiquitous in almost all ecosystem components originating from plastic degradation, has recently made this contaminant an important ecological focal point for researchers. Plastic particles smaller than 5 mm, measuring the longest dimension, represent microplastics (MPs) [1]. MPs origins are categorized into primary (microbeads) and secondary sources. Microbeads are plastics originally produced micro-sized. Secondary-sourced plastics undergo various degradation processes - chemical (corrosion, high temperatures exposure, photooxidation), mechanical (wave action, abrasion, erosion), and biodegradation (microbial activity), leading to fragmentation into MPs [2]. Due to the persistence and durability of MPs, after ending up in the environment, it remains there indefinitely. Even remote areas, such as Mount Everest, Antarctica, and the Arctic, were found to contain microplastic debris [3,4]. According to the degradation level, plastics are involved in all ecosystem compartments – atmosphere, aquatic and terrestrial systems, and even in biota, just as various chemical elements. Additional hazard occurs with MPs associated with other toxic chemicals. Owing to sorption capacity for heavy metals, hydrophobic organic contaminants (HOC), and biological pollutants MPs act as a vector for multiple contaminants [5]. The majority of them are bioaccumulative and harmful to humans and the environment.

Microplastic pollution has substantially increased and become omnipresent in marine environments, making up about 80–85% of marine litter [6]. The existence and abundance of MPs in ocean waters are mainly a consequence of land activities, closely associated with transportation pathways in which rivers play a principal role. MPs in freshwater bodies impair water quality, and hence require high-level monitoring, as well. The entering of MPs into the food web was demonstrated by ingested particles detected in a wide range of organisms. Once it enters the food chain, it can cause tissue and organ dysfunction and disrupt metabolic processes, causing injuries or even death [7,8].

Additionally, microplastics are extensively detected in terrestrial environments, as soils are considered sinks for MPs. Occurrence in soils originates from various sources, such as tire wear, municipal solid waste, wastewater treatment plants, soil amendments (biosolids and composts), plastic mulching films, materials used in greenhouses, etc. [9]. Transport of MPs through soil systems may lead to uptake by terrestrial species causing severe biochemical consequences and groundwater contamination. Published literature on particle detections in soils has significantly expanded in the past decade. Several methods of MPs isolation from soil samples have been developed so far, of which flotation based on density separation is currently regarded as the most reliable [10]. However, many modifications of this method are currently in use, trying to optimize extraction conditions for various complex soil matrices. Thus, a modified density separation method was used in our research.

The aims of this study were: 1) determining the presence of microplastic particles in urban and suburban soils from Bor, 2) quantification of particles and determination of their differences between the soil types, and 3) identification of potential sources of MPs in both sampling locations.

MATERIALS AND METHODS

Study area and sample collection

The study area was located in the city of Bor, in eastern Serbia. The first sampling point was in Brezonik, the suburban area of the Bor city, while the location of the urban soil sampling was a city park in the II kilometer. Soils were collected using stainless steel shovels. About 1 kg of the composite formed from five subsamples, was taken from each site. After sampling at the first site, the shovel was cleaned and washed. To avoid contamination, all afterward manipulations and storage were performed without potential contact with plastic materials.

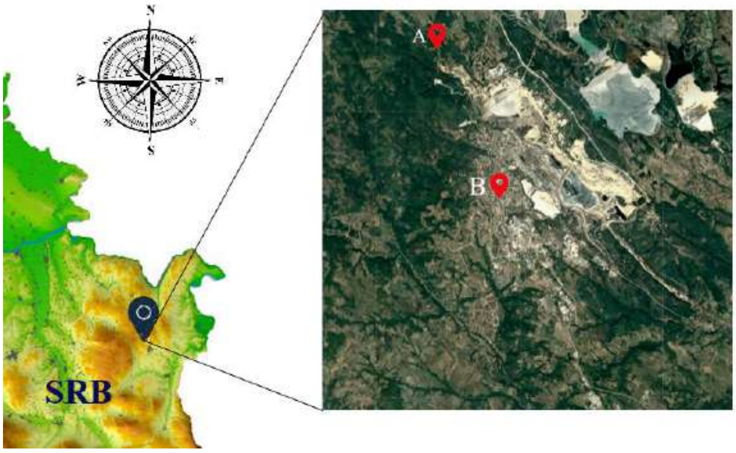


Figure 1 *Map of eastern Serbia and Bor with marked sampling points*

MPs extraction and observation

Soil samples were air-dried for two weeks and sieved through a 2 mm sieve. Soils were additionally dried in the heating oven at 60˚C to a constant weight, and then 5 g was measured for the analysis. Microplastic particles were extracted by the flotation method based on Zhou *et al*. (2019) [11]. Soils were covered with 60 ml of saturated NaCl solution with a density of 1.2 g cm^{-1} and left overnight. Around 30 ml of supernatant, was taken from the top with a glass dropper. The suspension containing MP and OM particles was filtered through stainless steel filter with a porosity of 20 µm. The filter was left in a 30% H_2O_2 solution in an ultrasonic bath for 10 min and rinsed thoroughly afterward. The suspension stood at 60˚C for 24h in order to digest the OM and filtered it through a steel filter. Observation and MPs counting was done using a polarizing microscope (Carl Zeiss Jena Pol-U).

RESULTS AND DISCUSSION

The average abundances of MPs in 5 g of soils from Amfi park and Brezonik were 19 and 3 MPs, respectively, i.e., 3800 items kg^{-1} and 600 items kg^{-1}, respectively.

Table 1 *Abundance and size distribution of MPs detected in soils*

Sample	**Location**	**Sublocation**	**MPs kg^{-1}**	**MPs per 5 g of soil**	**Diameter (µm)**				
					< 50	**≈ 50**	**50–100**	**≈ 100**	**> 100**
BOA	Bor	Citypark on II kilometer	3800	19	400	800	1000	800	800
BOB	Bor	Brezonik	600	3	-	400	200	-	-

"–" - no observed particles

MPs found in BOA were generally uniform regarding particle size distribution. Only 10% accounted for particles smaller than 50 µm, while the majority of them were between 50 and 100 µm in diameter. Knowing that the filter mesh size was 20 µm, the small-scale plastic pieces were in a size range of 20–50 microns. The proportion of 20% of MP debris was close to 50 µm, or 100 µm, and above 100 µm (Figure 2). Considering medium (50–100 µm) and larger (≥ 100 µm) particle size distribution is consistent with the results of previous studies, demonstrating MPs quantity increment with decreasing the particles size [12]. On the other hand, small plastic debris (≤ 50 µm) was less abundant than the medium-sized. Furthermore, the number of MPs around 50 microns was twice higher compared to the smaller ones. Some authors found dominance of MPs higher than 100 µm among detected particles [13,14]. Filters used during the extraction were not the limiting factor as the pore size was 2 µm and 7 µm, respectively.

Table 2 *MPs abundance, dominant size, shape and colors in investigated urban soils*

Location	**MPs abundance ($n\ kg^{-1}$)**	**Dominant size (%)**	**Dominant shape (%)**	**Dominant color (%)**	**Ref.**
Baoding City, China	Not characterised	< 15 µm (49%)	Not characterised	Not characterised	[12]
Ahvaz metropolis, Iran	100–3135	100–250 µm (33%)	Fibers (70%)	White/transparent (52%)	[13]
City of Amsterdam, The Netherlands	4825 on average	190–400 µm (47%)	Not characterised	Not characterised	[14]
Beijing, China	22001.67 on average	< 500 µm (88.06%)	Not characterised	White/transparent	[15]
Shihezi City, China	287–3227	20–500 µm (64.8%)	Fibers (69.9%)	Black (36.7%)	[16]

The shape and color of the particles were consistent. All MPs were white to transparent colored. The only morphotype occurring was a fragment.

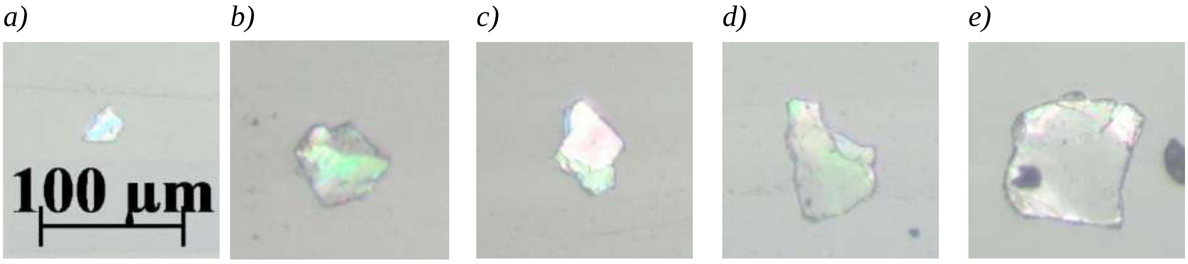


Figure 2 *MPs found in BOA a) < 50 µm; b) ≈ 50 µm; c) 50–100 µm; d) ≈ 100 µm; e) < 100 µm*

MPs detected in BOB were dominantly smaller-sized, i.e., around 50 µm in diameter or slightly larger (Figure 3). Particles were white and transparent fragments, without significant differences in their appearance from the ones found in BOA.

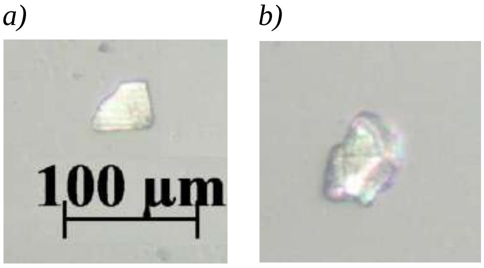


Figure 3 *MPs found in BOB a) ≈ 50 µm; b) 50–100 µm*

Although MPs abundance could be underestimated due to lower NaCl density than usually used $ZnCl_2$, it was generally accordant with the number of particles detected in recent studies in city areas in different countries, such as Ahvaz metropolis, Iran, Shihezi City, China, or Amsterdam, The Netherlands (Table 2), so as MPs color [15]. Contrary to these findings, revealing fibers as the most representative morphotype [16], MPs extraction from soils in Bor demonstrated that fragments are the only particle shape present. Detected MPs were possibly derived from the macroplastic disintegration. A closure of parking places, crowded sidewalks, resting places, and following anthropogenic activity likely affect outstandingly increased MPs abundance in BOA. Hence, MPs mostly originate from the weathered macroplastic pieces of frequently used products with plastic wrapping. The second sampling site is outside the urban city area, consequently considered less polluted with microplastic, due to the less frequent anthropogenic activity. MPs could also be transferred via long-distance migration, rainfalls, and aerial transport.

CONCLUSION

For the first time, microplastic presence was inspected in the soils of the city of Bor, known for its pollution with heavy metals due to high-level mining activities. Two sampling sites, urban and suburban, were selected for the examination. MPs detected in both locations were white to transparent fragments. A significant difference in the number of MPs between the two sites was noticed. Soil from the city park on II kilometer contained 6-fold more plastic particles than soils from Brezonik, which is likely affected by the excess overload of the consumed plastics, deemed to be one of the prevailing anthropogenic sources of MPs accumulation in urban environments. The future investigations will be focused on establishing if MPs act as vectors for other pollutants, i.e., finding the potential relation between heavy metals content and MPs' presence in the soils.

ACKNOWLEDGEMENT

This study was supported by the Ministry of Education, Science and Technological Development of the Republic of Serbia (Grant No.451-03-68/2022-14/200023, Grant No.451-03-68/2022-14/200168).

REFERENCES

[1] R.C. Thompson, Science; 304 (5672) (2004) 838–838.

[2] E.H. Lwanga, N. Beriot, F. Corradini, *et al.*, Chem. Biol. Technol; 9 (2022) 20.

[3] I.E. Napper, B.F.R. Davies, H. Clifford, *et al*., One Earth; 3 (5) (2020) 621–630.

[4] A. Cincinelli, C. Scopetani, D. Chelazzi, *et al*., Chemosphere; 175 (2017) 391–400.

[5] G. Caruso, Mar. Pollut. Bull; 146 (2019) 921–924.

[6] H.S. Auta, C.U. Emenike, S.H. Fauziah, Environ. Int; 102 (2017) 165–176.

[7] S.N. Kanade, A.B. Ade, Mitigation of the Plastic Pollution in the Marine Environment to Conserve the Marine Biota: An Overview. In: M. Shahnawaz, M.K. Sangale, Z. Daochen, *et al*., (eds.) Impact of Plastic Waste on the Marine Biota. Springer, Singapore (2022) 175–182.

[8] U.R. Gurjar, K.A.M. Xavier, S.P. Shukla, *et al*., Chemosphere; 288 (2022) 132484.

[9] P.D. Dissanayake, S. Kim, B. Sarkar, *et al*., Environ. Res; 209 (2022) 112734.

[10] M. Liu, S. Lu, Y. Chen, *et al*., Analytical Methods for Microplastics in Environments: Current Advances and Challenges. In: D. He, Y. Luo (eds.) Microplastics in Terrestrial Environments. The Handbook of Environmental Chemistry, Springer (2020) 3–24, ISSN:1616-864X.

[11] Y. Zhou, X. Liu, J. Wang, Sci. Total Environ; 694 (2019) 133798.

[12] C. Du, H. Liang, Z. Li, J. Gong, Int. J. Environ. Res. Public Health; 17 (3) (2020) 845.

[13] M.J. Nematollahi, B.K. Keshavarzi, F. Mohit, *et al*., Sci. Total Environ; 819 (2022) 152051.

[14] Q.M. Cohen, M. Glaese, K. Meng, *et al*., Environments; 9 (2022) 5.

[15] M. Zhang, L. Liu, D. Xu, *et al*., Environ. Pollut; 304 (2022) 119121.

[16] X. Liu, S. He, Y. Tong, *et al*., Environ. Sci. Pollut. Res; (2022) DOI: 10.1007/s11356-022-20083-7.

BIOSORPTION OF METAL IONS FROM SYNTHETIC SOLUTIONS USING DIFFERENT PARTS OF PLANT MATERIAL – A REVIEW

Maja Nujkić[1*], Vladimir Stiklić[2], Žaklina Tasić[1], Snežana Milić[1], Dragana Medić[1], Aleksandra Papludis[1], Ivan Đorđević[3]

[1]University of Belgrade, Technical Faculty in Bor, V.J. 12, 19210 Bor, SERBIA

[2]Serbia Zijin Copper doo, Đorđa Vajferta 29, 19210 Bor, SERBIA

[3]Elixir Prahovo, Braće Jugovića 2, 19330 Prahovo, SERBIA

[*]*mnujkic@tfbor.bg.ac.rs*

Abstract

In recent years, increasing water pollution with heavy metals from anthropogenic sources has been observed. Heavy metals can be extremely toxic to living organisms and for that reason it is necessary to find an adequate method of water purification. Biosorption has proven to be a very favorable method for removing heavy metals from polluted water with a number of advantages over conventional methods. This paper presents an overview of scientific research on the application of eight different biosorbents for the removal of the most common heavy metals from water. The aim of this paper is to determine the basic characteristics of biosorbents (metal removal efficiency, capacity) and the influence of various factors (amount of biosorbent, particle size, pH value, contact time, temperature, initial concentration of metals in solution) on biosorption.

Keywords: Biosorption, biosorbents, heavy metals

INTRODUCTION

Water is the most important resource that enables the presence of life on earth and access to clean water is important for people and the entire ecosystem. Heavy metal ions are among the pollutants that are released in large quantities into the environment and therefore cause great concern [1]. Trace elements such as heavy metals can occur in both surface and groundwater's as a result of the impact of several anthropogenic activities (*e.g.* agriculture, energy producing, industry, manufacturing, mining, etc.) [2]. Mining and industrial processing for the purpose of extracting mineral raw materials and their later application in industry and agriculture have led to an increase in the concentration of heavy metals in biochemical cycles [3]. Use of biological materials, i.e. biosorbents, have been important in recent years [4]. The biosorption method reduces operating costs by 36%, investment costs by 20% and total costs by 28% compared to standard methods. As a result, interest in the application of this cheap method is growing [5].

BIOSORPTION OF HEAVY METALS FROM WATER USING DIFFERENT BIOSORBENTS

Agricultural waste can be used as a biosorbent with very little processing. It has been observed that HCl-treated tomato waste can remove 92.08% of Cu(II) ions from a 50 ppm solution. These results were achieved under optimal conditions: biosorbent mass (0.2 g), solution volume of Cu(II) ions (50 mL) and pH=8. Langmuir adsorption isotherm was found to best fit the adsorption data, and reaction kinetic was best described by pseudo-second order. By increasing the mass of the biosorbent, there was a slight increase in the removal efficiency of Cu(II) ions and a decrease in the adsorption capacity of the biosorbent (q_e), as shown in Figure 1 [6].

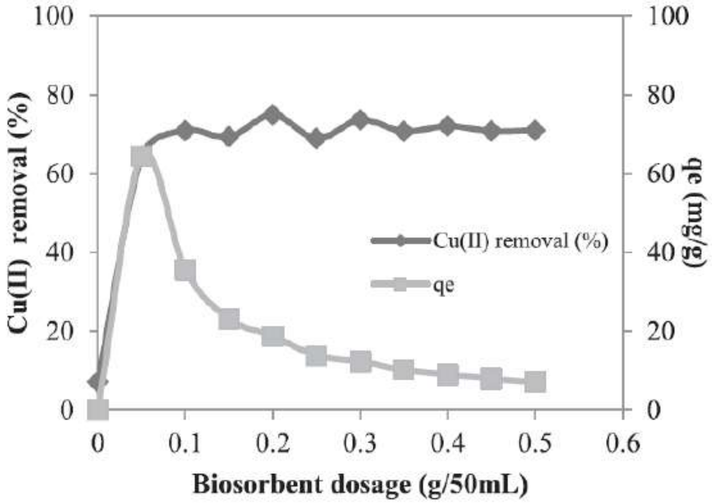


Figure 1 *Effect of tomato waste biosorbent dosage on Cu(II) ions biosorption (pH=8, Cu(II) ions concentration: 100 mg* L^{-1}*, temperature: 293 K, contact time: 1h) [6]*

It has been found that brown algae (*Sargassum sp.)* can be successfully used to remove nickel and copper ions from both synthetic water solutions and electroplating effluents. Maximum biosorption capacity for water solution was 1.404 mmol L^{-1} for Ni(II) ions and 1.656 mmol L^{-1} for Cu(II) ions. After regeneration of the biosorbent, it retained 75% of the initial biosorption capacity. During biosorption from the effluent, a reduction in capacity of 29.69% for Ni(II) and 26.24% for Cu(II) ions was observed in comparison with synthetic solution. Nonetheless, the high biosorption efficiency of brown algae makes it a very effective biosorbent for removing heavy metals from water [7].

In the study of removal of Cu(II) ions from water using algae *Codium vermilara*, it was found that it is possible to remove 85.5% of Cu(II) ions, under optimal conditions (biosorbent mass: 0.75 g, initial copper concentration: 48.75 mg L^{-1}, pH=5.28, contact time: 70.51 min). Scanning electron micrograph (SEM) analysis (Figure 2) confirmed the presence of pores on the algal biosorbent, which contributes to higher biosorption efficiency. Morphological changes on the surface of the biosorbent were also observed, after the binding of Cu(II) ions [8].

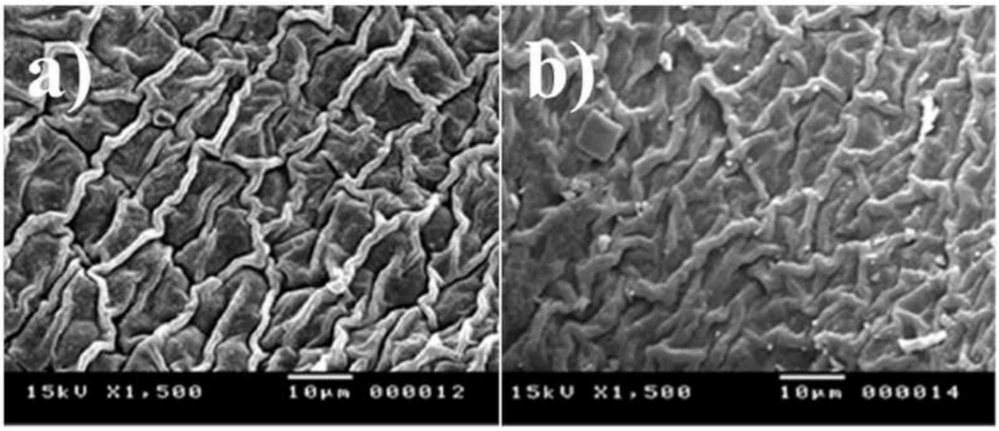


***Figure 2** Scanning electron micrograph of C. vermilara biosorbent a) before and b) after biosorption of Cu(II) ions [8]*

Alium Cepa seeds were found to have a good biosorption properties when removing heavy metal ions like Cu(II), Cr(VI), Zn(II), Pb(II) and Cd(II) from water effluents. In order to better understand binding mechanisms of *Alium Cepa* seeds, authors conducted Fourier-transform infrared spectroscopy and scanning electron micrograph analysis, which confirmed pourousness of biosorbent surface and presence of OH^- i $COOH^-$ functional groups. Optimal experiment conditions were found to be: biosorbent mass (0.4 g), initial metal concentration (50 mg L^{-1}) and pH=7. Optimal biosorption time for Cu(II), Cd(II) and Pb(II) were 90 min, and for Zn(II) and Cr(VI) 120 min. By fitting the experimental data in Freundlich and Langmuir isotherms (Table 1), Langmuir model had bigger regression coefficient and fitted the best [4].

***Table 1** Regression coefficients (R^2) of Langmuir and Freundlich isotherms for ions Cr(IV), Cd(II), Zn(II), Cu(II) and Pb(II) [4]*

	Cr(IV)	**Cd(II)**	**Zn(II)**	**Cu(II)**	**Pb(II)**
R^2 (Langmuir)	0.99	0.97	0.95	0.97	0.90
R^2 (Freundlich)	0.98	0.79	0.86	0.88	0.87

Tea is second most popular drink after water and its large consumption creates a lot of tea waste material. The experiment conducted by Shah *et al.* [9] aimed to determine the effectiveness of using tea leaves (*Camellia sinensis*) treated with formaldehyde as a biosorbent to remove Ni(II) ions from water. It has been found that formaldehyde can increase biosorption capacity and can prevent leaching of organic matter from biosorbents, thus preventing further pollution of water. At optimal biosorption conditions (biosorbent mass: 0.13 g, biosorption time: 90 min, pH=7) it was observed 100% of Ni(II) ions removal efficiency. By shaking samples, biosorption of Ni(II) ions was increased by 10%. No interfering effect from other ions was observed when conducting biosorption of Ni(II) ions from mixture of other ions (Na(I), K(I), Mg(II) and Ca(II)), thus making a *Camellia sinensis* tea waste an effective biosorbent for removing of Ni(II) ions from water [9].

The biosorbent obtained by carbonization of medicinal plants was tested for its removal efficiency of Zn(II), Pb(II) and Cd(II) ions from synthetic wastewater by the author Jan *et al.* [10]. Physical and chemical activation of carbonized biosorbent were conducted to increase biosorption efficiency, and it was found that physical activation using water vapor is more advantageous than chemical activation from the economic and environmental point of view. Optimum biosorbent carbonization conditions were observed at 650°C carbonization temperature, 60 min carbonization time. Maximum biosorption efficiency was 90%, reached at optimal bisorption conditions (biosorbent mass: 5 g L^{-1} for Zn(II) and Pb(II), 4 g L^{-1} for Cd(II), temperature: 25°C, contact time: 90 min, pH=5). Different efficiency of biosorption was observed depending on the type of water and the number of heavy metals. Lower biosorption removal efficiency was observed in multi element water in comparison with single element water, while the lowest biosorption efficiency of heavy metals was achieved in lechate, as shown in Figure 3 [10].

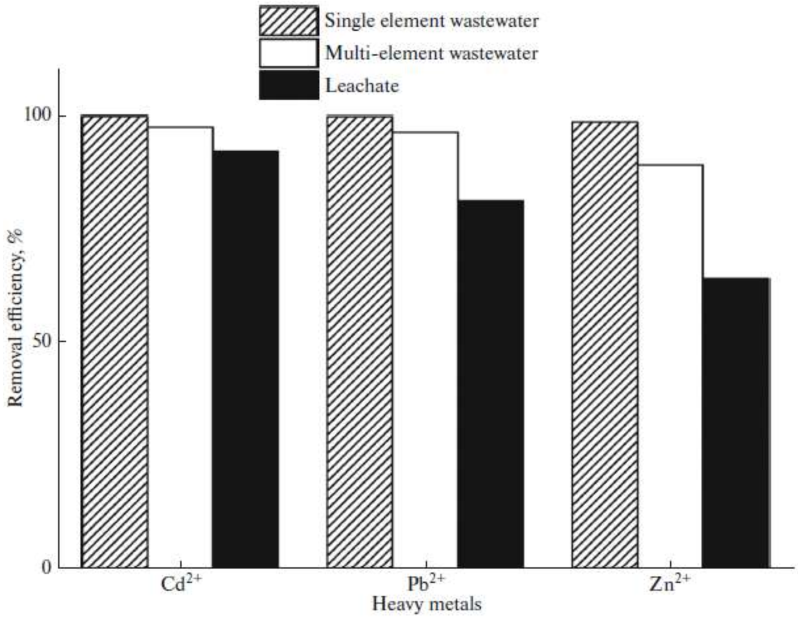


***Figure 3** Biosorption removal rate of Cd(II), Pb(II) and Zn(II) ions depending on wastewater type and number of metals [10]*

Ion exchange can significantly aid the biosorption process in removing Pb(II) and Cd(II) ions from water, as shown in research of Jokar *et al.* [11]. Chicory modified by $CaCl_2$ compound has a high biosorption capacity, reaching 123.5 mg g^{-1} for Pb(II) ions and 64.5 mg g^{-1} for Cd(II) ions. Thermal modification of chicory biosorbent must be performed at the lower and strictly controlled temperatures, because degradation and surface damage have been observed at temperatures above 25°C, which significantly reduces the biosorption capacity. The best ions removal rate was achieved with particle size of the biosorbent of 500 µm. Langmuir model best described the biosorption process. Metal recovery from biosorbent was atempted by using water, $CaCl_2$, HNO_3 and NaCl. In all cases, except using water, metal ions recovery was successful. This research has shown that chicory waste can effectively be used for removing Pb(II) and Cd(II) ions from water [11].

Use of Chinese sugar cane straw as a bisorbent for removing roxarson ($C_6H_6AsNO_6$), As(III) and As(V) ions from aqueous solution have been analyzed by Zang *et al*. [12]. Modification of biosorbent have been performed by $FeCl_3$ and with SEM analysis it was observed that mostly flat biosorbent surface became porous and wrinkled. The best results were obtained by using 1 g of biosorbent, at pH=5, bisorption temperature of 25°C. The experiment data best fitted the Langmuir, and the biosorption reaction took place according to the pseudo-second order kinetic model of the process. Maximum biosorption capacities per gram of biosorbent were: 12.4 mg g^{-1} for roxarson, 5.3 mg g^{-1} for As(III) and 23.0 mg g^{-1} for As(V). It was concluded that Chinese sugar cane straw is a cheap and effective biosorbent that can effectively be used for removal of roxarson, As(III) and As(V) ions from water [12].

CONCLUSION

Based on previous researches, it can be concluded that depending on the type of plant material, the optimal conditions of biosorption varies a lot. The initial characteristics of plants (porousness, the presence of functional groups) are significant and determine the later behavior of the biosorbent during biosorption. Also, chemical modifications of biosorbents can increase available adsorption sites by increasing surface area, pores and number of metal binding functional groups. Most of the papers are based on synthetically prepared heavy metal solutions with only one metal ion. Using plant materials, as low-cost biosorbent, has proven to be very effective for removing heavy metals from water. Future research should continue to identify additional low-cost materials that are effective at removing heavy metals.

ACKNOWLEDGMENT

The research presented in this paper was financial supported by the Ministry of Education, Science and Technological Development of the Republic of Serbia, within the funding of the scientific research work at the University of Belgrade, Technical Faculty in Bor, according to the contract with registration number 451-03-68/2022-14/200131.

REFERENCES

[1] C. Zamora-Ledezma, D. Negrete-Bolagay, F. Figueroa, *et al.*, Environ. Technol. Innov; 22 (2021) 101504.

[2] C.S. Santana, D.M.M. Olivares, V.H.C. Silva, *et al.*, J. Environ. Manage; 273 (2020) 111148.

[3] Q. Zhou, N. Yang, Y. Li, *et al.*, Glob. Ecol. Conserv; 22 (2020) 00925.

[4] Z. Sheikh, M. Amin, N. Khan, *et al.*, Chemosphere; 279 (2021) 130545.

[5] E. Oguz, Environ. Prog. Sustain. Energy; 40 (2021) 13659.

[6] A.S. Yargıç, R.Z.Y. Şahin, N. Őzbay, *et al.*, J. Clean. Prod; 88 (2015) 152–159.

[7] C.E.R. Barquilha, E.S. Cossich, C.R.G. Tavares, *et al.*, J. Water Process. Eng; 32 (2019) 100904.

[8] M.A. Fawzy, Adv. Powder. Technol; 31 (2020) 3724–3735.

[9] J. Shah, M.R. Jan, A. ul Haq, *et al.*, J. Saudi Chem. Soc; 19 (2015) 301–310.

[10] C.Z. Yan, M.G. Kim, H.U. Hwang, *et al.*, Theor. Found. Chem. Eng; 54 (5) (2020) 973–982.

[11] M. Jokar, N. Mirghaffaria, M. Soleimania, *et al.*, J. Water Process. Eng; 28 (2019) 88–99.

[12] S. Zang, Y. Zuo, J. Wang, *et al.*, Acta Geochim; 40 (2021) 409–418.

ANALYSIS OF CHANGES OF MECHANICALLY ACTIVATED SODIUM CARBONATE SAMPLE

Nataša Đorđević[1*], Slavica Mihajlović[1]

[1]Institute for Technology of Nuclear and Other Mineral Raw Materials, Franchet d'Esperey Blvd. 86, Belgrade, SERBIA

**n.djordjevic@itnms.ac.rs*

Abstract

For mechanical activation of sodium carbonate, a vibro mill at a frequency of 3000 oscillations per minute was used for 28 minutes. After activation, samples were placed for 31 days in the air at room conditions. In aim to monitor the kinetics of the transformation process of sodium carbonate to bicarbonate, Fourier-transform infrared (FTIR) spectroscopy analysis was used. As a function of relaxation time characteristic groups were observed: CO_3^{2-}, HCO_3^- and OH^-. The obtained results provided kinetics parameters for the transformation of carbonate into bicarbonate as a result of chemisorption of moisture and carbon dioxide from the atmosphere.

Keywords: sodium carbonate, mechanical activation, mechanochemical transformation

INTRODUCTION

In the world, the activation of materials is widely used as a procedure for bringing energy to the system so that it begins to react in a controlled manner. This allows the system to skip over the "energy barrier" on the reaction path [1,2]. The method of mechanical activation, which, in various technical and technological ways, brings mechanical energy to solid materials thus changing and regulating many physico-chemical characteristics related to increasing the system's reactivity, is becoming more and more topical [3,4]. With the development of this procedure, many research fields related to obtaining new materials and monitoring the kinetics of the solid phase reactions have been opened and significant savings compared to classical methods of material activation achieved [5].

MATERIALS AND METHODS

The sodium carbonate used in this study was anhydrous and in p.a. quality. According to the MERCK index 11.8541, the chemical composition of sodium carbonate is: 99.5% Na_2CO_3, 0.002% Cl^-, 0.005% SiO_2, 0.0005% Pb, 0.0005% Fe, 0.01% Al, 0.0005% Mg, 0.01% K, 0.005% SO_4^{2-}, 0.005% Ca, and 0.5% loss on drying at 180°C; specific mass 2500 kg/m^3; decomposition temperature 851°C. Na_2CO_3 has a monoclinic crystal lattice (a=8.907, b=5.239, c=6.043); the bond energy values are: Na–O (364 kJ/mol), C–O (1076.4 kJ/mol), C=O (532.2 kJ/mol).

Sodium carbonate was mechanically activated in the high-energy mill KHD Humboldt Wedag AG. Samples in the amount of 50 g each were activated for 28 minutes (activation time) at a frequency of 3000 oscillations per minute thus obtaining four series for further investigation. Relaxation time was 31 days.

The effects of mechanical activation were monitored by FTIR spectroscopy analysis. FTIR spectroscopy is a very important non-destructive method, given the high sensitivity and precision of frequencies, excellent resolution, quick recording, and possibility to repeat recording as well as different ways to interpret the obtained data. Changes were observed on the characteristic groups: CO_3^{2-}, HCO_3^- and OH^-. FFT infrared spectra of the samples were recorded on a spectrometer Bomem-Hartman & Braun Michelson MB-100, in the wave numbers range of 4000–300 cm^{-1} and at a resolution of 2 cm^{-1}. Samples were prepared in the form of a suspension using "Nujol". Changes in the peaks' areas, as well as the widths at the half-heights, were observed for the given characteristic groups: CO_3^{2-}, HCO_3^{2-} and OH^-. The results are presented as a function of relaxation time for all four series, i.e. for different activation periods.

RESULTS AND DISCUSSION

FTIR spectrogram of the initial, non-activated sodium carbonate sample is presented in Figure 1.

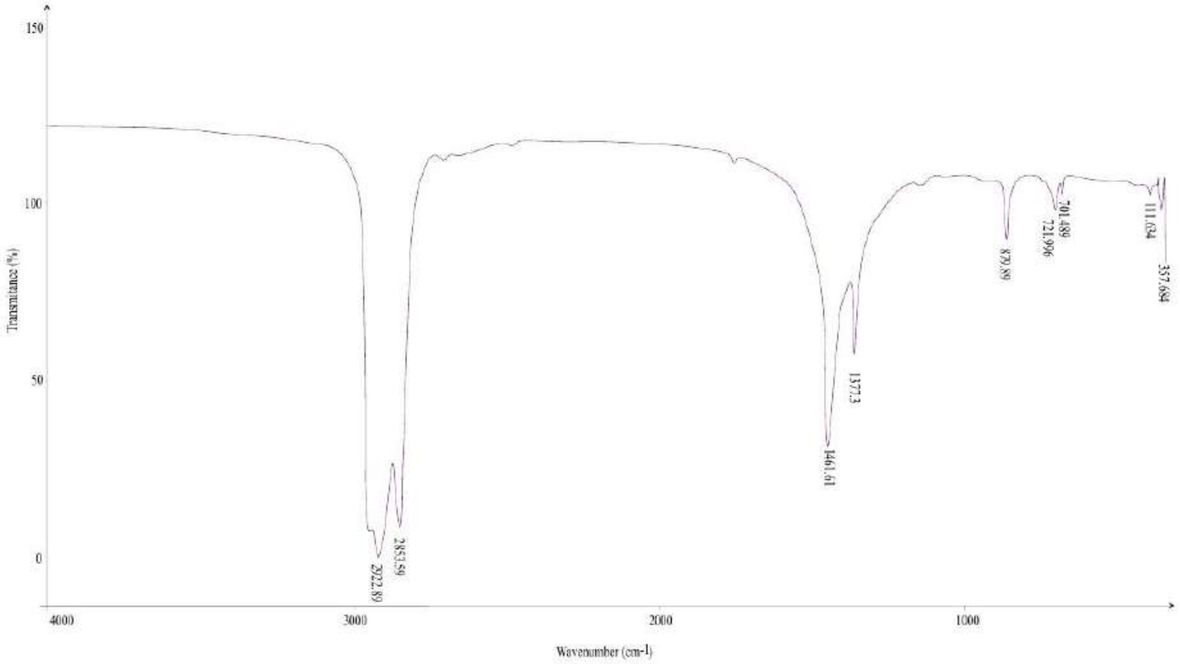


Figure 1 *FTIR spectrogram of non-activated* Na_2CO_3

Table 1 shows the wavelengths of the characteristic peaks monitored by FTIR spectroscopy in this study.

Table 1 *Wavelengths of characteristic groups of sodium carbonate, sodium bicarbonate and intermediate compound*

Na_2CO_3	$NaHCO_3$	CO_3^{2-}	HCO_3^-	OH^-	$CO_2 + H_2O$
1775 cm^{-1}	1800 cm^{-1}	1461.61 cm^{-1}	1800–1980 cm^{-1}	350–3600 cm^{-1}	2300–2400 cm^{-1}
1420 cm^{-1}	1000 cm^{-1}	1090 cm^{-1}	1000 cm^{-1}	1645 cm^{-1}	
878 cm^{-1}		874 cm^{-1}		590–720 cm^{-1}	
702 cm^{-1}		725 cm^{-1}			

Figure 2 shows comparative FTIR spectrograms of all four series of sodium carbonate samples for different relaxation periods at room conditions.

The change in the characteristic peaks as a function of relaxation time is clearly noticeable in the diagrams in Figure 1. The initial curves (0 days of relaxation) for all four activation times, at a wavelength of 3500–3600 cm^{-1}, do not have clearly defined peaks, and with the increasing relaxation time. The appearance of the OH group in the activated sodium carbonate sample, as well as changes in the peak area of the OH group, can be explained by the fact that the Na_2CO_3 sample, due to the energy obtained by mechanical activation and disturbed crystal structure had increased adsorption and chemisorption affinity to moisture from the atmosphere during relaxation. The valence OH groups bind to the crystal lattice of activated Na_2CO_3, and the diagrams show that the peak characterizing the OH group increases with the increasing relaxation time. A similar change is observed at a wavelength of 1645 cm^{-1}, and the database revealed that these changes are also related to the OH group.

At a wavelength of 1420 cm^{-1}, which characterizes Na_2CO_3, that is CO_3^{2-} ion, a tendency of peak decrease with the increasing relaxation time can be seen. Similar changes are observed at a wavelength of 873 cm^{-1}. This is a consequence of the conversion of carbonate to bicarbonate ion due to the absorption of moisture and carbon dioxide from the air. Parallelly with this change, a peak characteristic for the bicarbonate ion at a wavelength of 1800 cm^{-1} appeared. This peak is more pronounced with the increasing relaxation time.

At wavelengths from 2300 to 2400 cm^{-1}, a peak that principally disappears gradually with the progress of relaxation time can be observed. These wavelengths are typical for adsorbed moisture and carbon dioxide. During relaxation, chemisorption of moisture and carbon dioxide occurs and the conversion of carbonate to bicarbonate, which explains the decrease and disappearance of this peak on the observed curves.

At wavelengths from 700 to 800 cm^{-1}, with emphasis on 725 cm^{-1}, a peak, while both the intensity and the surface area are decreasing with the increasing relaxation time, can be observed. The analysis determined that it is a carbonate ion, whose amount decreases as a function of the relaxation time due to the process of chemisorption of moisture and carbon dioxide from the air. Parallelly with this result, the peak characteristic for the HCO_3^- group increases, which is a consequence of the transformation of carbonate into bicarbonate.

In the discussion that follows, based on the obtained FTIR spectrograms of activated sodium carbonate, areas of peaks characteristic for ion groups CO_3^{2-}, HCO_3^-, and OH^-, as well as peaks widths at half-height during relaxation time were estimated and graphically presented.

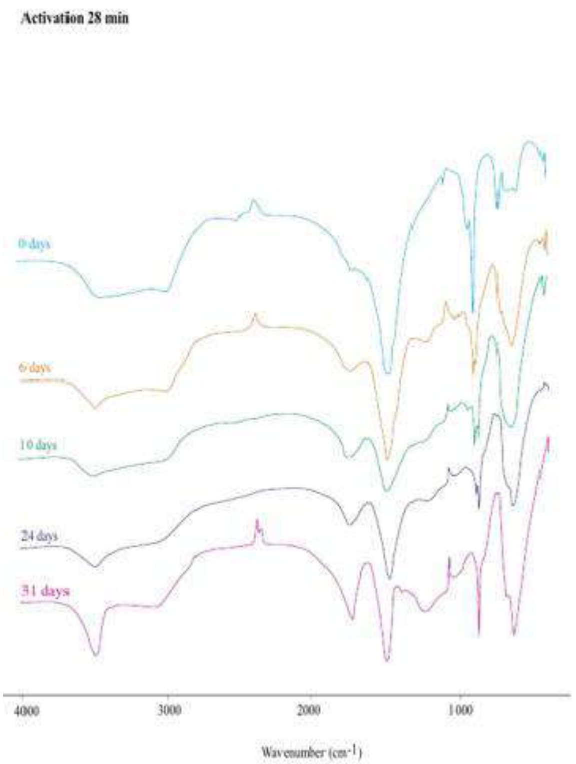


Figure 2 *FTIR spectrograms of* Na_2CO_3 *samples activated for 28 min during relaxation time (0, 1, 6, 10, 24, and 31 days) at room conditions*

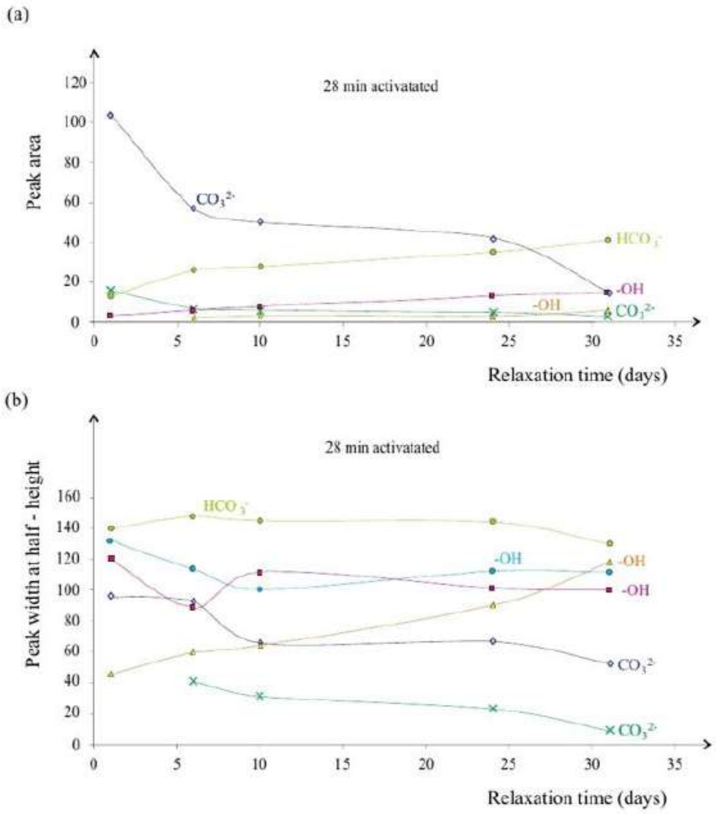


Figure 3 *a) Areas of peaks characteristic for ion groups; b) Widths at peak half-height, for* Na_2CO_3 *sample activated for 28 min as a function of relaxation time*

The peak area characteristic for the CO_3^{2-} ion (Figure 3a) decreases with the relaxation time progress, whereby this drop is sharp during ten days, especially on the first day of the sample aging. The phenomenon can be explained by a significantly enhanced energy of just activated sodium carbonate due to the energy delivered to the system by mechanical activation as well as by the weakened bonds in the crystal. This caused the sudden adsorption of moisture and carbon dioxide from the air as well as the formation of a bicarbonate ion, which is reflected in the increased width of the peak characteristic for the HCO_3^- ion. A similar trend of corresponding width changes at the half-heights of the characteristic peaks can be seen in the diagram shown in Figure 3b. The reduced width value at the half-height of the peak characteristic for the CO_3^{2-} ion is considerable. The most significant changes for all ions occur in the first 10 days of relaxation time.

CONCLUSION

The results of this study showed a gradient of changes in the analyzed samples during relaxation depending on the activation time. The changes in terms of reducing the number of carbonate ions in all four series of samples in favor of the formation of HCO_3^{2-} ions during the relaxation period are clearly noticeable. The key moment in the transformation process is the weakening of the Na–O chemical bond, where during the relaxation time the Na^+ ion was replaced by the H^+ ion, thus forming the OH group. The formation of sodium bicarbonate began by bonding the valence OH group to the activated crystal lattice of sodium carbonate. This transformation was taking place after the 25th day of the relaxation period owing to the existence of a sufficient amount of the OH group which directed the reaction towards the bicarbonate formation.

ACKNOWLEDGEMENT

This work was financially supported by the Ministry of Education, Science and Technological Development of the Republic of Serbia (Grant Nos. 451-03-68/2022-14/200023).

REFERENCES

[1] N. Obradovic, V. Blagojevic, S. Filipovic, *et al.*, J. Therm. Anal. Calorim; 138 (5) (2019) 2989–2998.

[2] N. Obradović, W.G. Fahrenholtz, S. Filipović, *et al.*, Ceram. Int; 45 (9) (2019) 12015–12021.

[3] B. Praveenkumar, H.H. Kumar, D.K. Kharat, *et al.*, Mater. Chem. Phys; 112 (1) (2008) 31–34.

[4] A. Kumar, V.V. Bhanu Prasad, K.C. James Raju, J. Alloys Compd; 599 (2014) 53–59.

[5] N. Obradovic, S. Filipovic, N. Djordjevic, *et al.*, Ceram. Int; 42 (12) (2016) 13909–13918.

ELECTRIC ARC FURNACE DUST – HAZARDOUS INDUSTRIAL WASTE WHOSE TREATMENT IS UNAVOIDABLE

Vanja Trifunović[1*], Snežana Milić[2], Ljiljana Avramović[1], Radojka Jonović[1], Stefan Đorđievski[1]

[1]Mining and Metallurgy Institute Bor, Zeleni bulevar 35, 19210 Bor, SERBIA

[2]University of Belgrade, Technical Faculty in Bor, V.J. 12, 19210 Bor, SERBIA

**vanja.trifunovic@irmbor.co.rs*

Abstract

Electric arc furnace dust (EAF dust), which is formed as a by-product of the steel production process from secondary raw materials, contains significant amounts of Zn, Fe, Pb, Cd, Ca, K, Cr, Mn, Si, Mg, Na, Ni, Cu, F, Cl, etc. Due to the content of heavy metals in the EAF dust, which in its inadequate disposal and the impact of atmospheric conditions can lead to a negative impact on the environment, it is characterized in the world as hazardous industrial solid waste. For environmental protection, it is necessary to do a treatment of the EAF dust so that it can be safely disposed of in a landfill without negative effects on the environment and human health. In addition to environmental benefits, the EAF dust treatments can also have economic benefits.

Keywords: EAF dust, hazardous waste, environmental protection

INTRODUCTION

World production of crude steel takes place in two ways: processing of primary raw materials, primarily iron oxide ore, melting in the Basic Oxygen Furnace (BOF) and processing of iron-based secondary raw materials by melting in an Electric Arc Furnace (EAF) [1–4].

Using secondary raw materials, i.e. scrap iron, as a raw material for steel production, and electricity as an energy source, steel production in electric arc furnaces has become more prominent than any other steel production process in the world [5–11]. The main sources of secondary raw materials for steel production are construction material waste, old cars, appliances and household waste, which means that waste can contain a large number of metals, plastics and rubber, glass, paint, oil, and even salt [2,5–8,12]. Figure 1 shows an example of scrap iron used as a batch for an electric arc furnace [13].

During the melting process of scrap iron in the electric arc furnace at a temperature of 1600ºC, a by-product of the process-dust from the electric arc furnace is forming. Emission of the electric arc furnace dust (EAF dust) is proportional to the steel production so that with the increasing steel production there is an increase in the amount of the EAF dust: for each ton of produced crude steel about 10–20 kg of the electric arc furnace dust is also produced. About 5–7 million tonnes of dust are generated annually in the world, of which 0.5–0.9 million tonnes of dust come from steel plants in Europe [2,4–6,8,10,11,14,15].

Figure 1 *Scrap iron used as a batch in the steel production process from secondary raw materials [13]*

Formation of the EAF dust occurs since volatile elements, such as Zn, Pb and Cd in the batch of the furnace mostly evaporate in the early stages of the operation, and eventually, all of them go into the gas phase. Other elements, such as Fe, Cr, Ni and Mn, are generated from gaseous products during the refining period, mainly due to oxygen injection. Volatile components are rapidly converted into the corresponding oxides in contact with air after the combustion and cooling of the exhaust gases [1,2,5,7]. Oxides in the slag mixed with metal vapors and generated dust are extracted from the furnace by hot gas flow, to a gas purification system where gases are cooled down, and finally, the EAF dust is formed which can be collected in a gravity collector, electrostatic dust collector, or filter bags [1,5,14].

EAF DUST CHARACTERIZATION

Electric arc furnace dust occurs in the form of very fine reddish-brown or dark brown particles, which can spread in the air [5,7]. Due to the difference in the procedures for obtaining steel in an electric arc furnace and the methods of collecting the EAF dust, the physical characteristics of EAF dust will vary within the appropriate range. For example, depending on the way the EAF dust is collected, the size of its particles will vary. When the EAF dust is collected with a gravity collector, 85% of dust particles are <10 μm, by collecting in filter bags, 90% of particles are <50 μm, and in an electrostatic collector, more than 90% of dust particles are <100 μm in size [5].

To a large extent, the composition of the EAF dust depends on the operating conditions of the electric arc furnace, the characteristics of the scrap iron batch, the working period, the specifications of the produced steel, and is also specific to each plant [1,2,6,8,14]. The composition of EAF dust can be variable and can change from day to day in the same steel plant [1]. EAF dust is the final result of a series of physical and chemical phenomena through which substances that create EAF dust pass and they define its physical aspect, chemical and mineral composition. Basically, EAF dust should consist of iron oxides, however, due to the presence of different types of scrap iron, which contains several different elements, its composition becomes complex [1,11]. It can be seen from Table 1 that the chemical composition of EAF dust from different sources can vary significantly.

Table 1 *Comparative chemical composition of the EAF dust from different sources*

Elements (%)													Ref.
Zn	**Fe**	**Pb**	**Ca**	**Cd**	**Na**	**K**	**Cl^-**	**Mn**	**Si**	**Cr**	**Cu**	**Al**	
22.73	14.40	4.22	13.32	0.09	1.25	1.61	4.75	1.00	1.45	-	-	-	[3]
29.10	24.00	3.64	3.16	-	-	1.76	1.56	4.11	1.57	-	0.25	0.52	[12]
17.80	4.20	2.34	0.80	-	-	-	1.60	0.62	8.14	-	-	0.73	[17]
33.00	26.50	2.17	0.90	-	-	-	-	2.30	-	0.20	0.20	-	[19]
24.24	34.38	1.76	2.27	-	-	-	4.72	-	-	-	-	-	[14]
7.79	37.29	1.16	5.33	-	2.78	3.11	2.63	1.18	2.21	0.15	-	-	[18]

As for the mineral composition, because the EAF dust is formed in oxidative conditions, most metals are present in the form of oxides. Zinc occurs in the form of ZnO and $ZnFe_2O_4$, while iron mainly occurs in the oxide form as Fe_3O_4 and Fe_2O_3 [1,2,6,8,11]. Calcium is present in the form of CaO, $CaCO_3$, calcium silicate, and calcium aluminosilicate. Lead, copper, chromium, and nickel can occur in the form of oxides, chlorides, sulfides, or sulfates. In recent years, there has been an increase in chlorine levels in the EAF dust due to an increase in impurities containing chlorine in scrap iron (most commonly rubber, paints, polymers, etc.), and it occurs in the form of alkali metal chlorides [1,2].

EFFECT OF EAF DUST ON THE ENVIRONMENT

The presence of metals such as Pb, Zn and Cd in the EAF dust can pose a threat to the environment and human health due to the mobility of these toxic elements, and for this reason, EAF dust is considered hazardous industrial solid waste in many countries [1,4–6,8]. According to the Environmental Protection Agency (EPA) in the United States it is characterized as hazardous solid industrial waste K061 [4], according to the Brazilian standard ABNT 10004: 2004, EAF dust is listed as hazardous waste from a specific source K061 [5,20], in the catalog of the European Union Waste [21] it is included in the list of hazardous substances with the code 10 02 13, and according to the European catalog of waste [22] it is classified as a hazardous waste of category 10 02 07 [6]. It is also considered an air pollutant because the gas purification system captures only 70% of the EAF dust, while the rest goes into the atmosphere. Therefore, EAF dust is a solid hazardous waste that has the potential for long-term environmental pollution [23].

The pollution potential of this type of waste lies in the possibility of self-leaching elements such as Zn, Cu, Cr, Ni, Pb, Cd, F, and Cl. Factors that play a significant role in increasing the solubility of heavy metals from the EAF dust in the environment are pH, redox potential, and temperature. Controlling these factors, the risk of environmental contamination with heavy metals from the EAF dust can be reduced [23]. Disposal of this hazardous waste has become a serious problem in recent years since increasing steel production increases the amount of hazardous waste that needs to be adequately treated, in prescribed landfills, to prevent its negative impact on the environment and human health. It is understood that when disposing of the EAF dust in hazardous waste landfills, the EAF dust must be protected from rain to prevent the formation of leachate that could contaminate the land and watercourses in the surrounding area [4,24]. Figure 2 shows the “mountain” of disposed EAF dust generated from steel production in Egypt [14]. As can be seen from the figure, this method of disposal is not adequate since hazardous waste is completely exposed to external atmospheric influences and it is very easy to contaminate the environment with heavy metals from the dust [4,15,24].

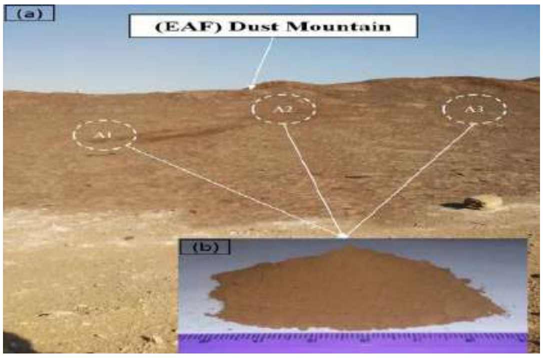


Figure 2 *a) "Mountain" of the EAF dust generated from steel production in Egypt; b) a representative sample of the EAF dust [25]*

EAF DUST TREATMENT TO ENVIRONMENTAL PROTECTION

For environmental protection and the protection of human health, it is necessary to do a treatment of this type of hazardous waste. Certain treatments of the EAF dust, in addition to reducing the amount of hazardous waste and/or its transformation into non-hazardous waste to protect the environment, would also make savings on the cost of its disposal. Also, in addition to environmental benefits, economic benefits could be achieved by extracting zinc for commercial quality products and using iron concentrates suitable as raw materials in steel or pig iron production [1,6,14].

Although very rich in iron, EAF dust cannot be recycled directly into the steel production process, because it contains large amounts of Zn (from 2–40% [3,8,12,14,17–19]), which negatively affects the electric arc furnace and thus endangers the economy of the furnace. Although chrome and lead are not problematic for the steel production process itself, they are toxic to humans and their content is regulated by the European Commission. Consequently, metal separation has become a desirable option, as the EAF dust is a quality secondary raw material for zinc production – EAF dust contains approximately 7% of world zinc production that would otherwise be thrown in landfills. With the constant increase in demand for zinc and with limited possibilities of its substitution in materials and the depletion of reserves from its primary sources, the need for secondary sources of zinc is growing. Therefore, the EAF dust treatment process must be able to remove Zn from the dust, while the remaining valuable metals are compatible with iron and steel so that the iron-containing material can be recovered and recycled in the steel production process, or to obtain a solid residue that can be safely disposed of as non-hazardous waste [8]. Efficient extraction of zinc from secondary sources has several advantages such as: saving intact resources and fossil resources used to supply energy in primary mining processes, increased resource efficiency, reduced landfill disposal and loss of zinc or any metal returned to landfill, waste remediation, as well as reduction of environmental impact [23].

Given the potential environmental and economic benefits from the EAF dust, it is important to develop appropriate processes for its treatment. The chemical composition of the EAF dust, as well as its available amount, provides opportunities and conditions for deciding on the best sustainable method for its treatment. For the recycling of the EAF dust for zinc separation to be economically viable, the dust must contain Zn concentrations higher than 15% [20]. In general, there are two basic processes in the EAF dust treatment: the pyrometallurgical process and the hydrometallurgical process. Both processes have their advantages and disadvantages. Pyrometallurgical processes require high temperatures, expensive equipment, and large capacity plants, which leads to high energy consumption. For the treatment of the EAF dust by pyrometallurgical processes, the minimum zinc content in the dust must be >15% to ensure the economy of the process. By applying this process, a product ZnO of low commercial value is obtained, which requires additional hydrometallurgical treatment. Also, in this process other solid residues are formed and need additional treatment before disposal [2,5]. On the other hand, the hydrometallurgical process can be economical with a zinc content in dust lower than 15%. These processes have significantly lower capital and operating costs compared to pyrometallurgical ones, can be installed in situ, and commercial quality products can be obtained. However, large amounts of wastewaters are generated that require further treatment to be safely discharged to recipients. Solid residues of these processes may or may not be subsequently treated before disposal. Extraction of zinc from the EAF dust by the hydrometallurgical process is very complicated and consists of several related processes, such as leaching, purification of pregnant leaching solution, and separation of metals/compounds [3,5,6,8,14].

Other methods of recycling the EAF dust were also investigated, not to separate valuable metals and obtain non-hazardous waste, but for direct disposal of the dust by incorporating dust containing zinc in a concentration of less than 15% in existing products. Products in which EAF dust can be incorporated are blue shales [15] for use in the cement industry, bricks [4], kaolin clay used for 3D printing in the construction industry [10], ceramic tiles, etc. In addition to saving on the costs of disposing of the EAF dust, its incorporation into existing products leads to improved physical characteristics of these products [4,10,15].

CONCLUSION

Dust from the electric arc furnace generated in the steel production process from secondary raw materials contains significant amounts of Zn, Fe, and Pb, as well as variable amounts of Cd, Ca, Cr, Mn, Si, Mg, Na, F, Cl, etc. Due to the content of heavy metals in the EAF dust, which can contaminate the surrounding lands and watercourses due to its inadequate disposal, and the influence of atmospheric conditions, it is characterized in the world as hazardous industrial solid waste.

EAF dust treatment processes for the recovery of valuable metals can be pyrometallurgical and hydrometallurgical processes, depending on dust chemical composition and the amount available for processing. All processes have their advantages and disadvantages.

For environmental protection, it is necessary to do the treatment of the EAF dust so that it can be safely disposed of in a landfill without negative effects on the environment and human health. In addition to environmental benefits, the EAF dust treatment can also have economic benefits.

The impact of incorporated EAF dust on the environment has not been sufficiently investigated.

ACKNOWLEDGMENTS

The authors are grateful to the Ministry of Education, Science and Technological development of the Republic of Serbia for financial support (Grant No. 451-03-68/2022-14/200052 and Grant No. 451-03-68/2022-14/200131).

REFERENCES

[1] P. Keglevich de Buzina, N. Heckb, A. Vilela, J. Mater. Res. Technol; 6 (2) (2017) 194–202.

[2] C. Pickles, Miner. Eng; 22 (2009) 977–985.

[3] V. Montenegro, S. Agatzini-Leonardou, P. Oustadakis, *et al.*, Waste Biomass Valori; 7 (6) (2016) 1531–1548.

[4] E. Dominguez, R. Ullmann, Appl. Clay Sci; 6 (1996) 237–249.

[5] J. Wang, Y. Zhang, K. Cui, *et al.*, J. Cleaner Prod; 298 (2021) 126788.

[6] F. Kukurugya, T. Vindt, T. Havlík, Hydromet; 154 (2015) 20–32.

[7] V. Silva, J. Silva, *et al.*, J. Mater. Res. Technol; 8 (6) (2019) 5504–5514.

[8] P. Hazaveh, S. Karimia, *et al.*, Ecotoxicol. Environ. Saf; 202 (2020) 110893.

[9] O. Ruiz, C. Clemente, M. Alonso, *et al.*, J. Hazard. Mater; 141 (2007) 33–36.

[10] E. Ordoñez, S. Neves Monteiro, H. Colorado, Mater. Des; 217 (2022) 110617.

[11] V. Trifunović, Lj. Avramović, R. Jonović, *et al.*, Proceedings of the 52nd International October Conference on Mining and Metallurgy, November 29th–30th, Bor, Serbia (2021) 209–212.

[12] C. Lanzerstorfer, J. Cleaner Prod; 174 (2018) 1–6.

[13] M. Siame, J. Kaoma, N. Hlabangana, *et al.*, S. Afr. J. Chem. Eng; 27 (2019) 35–42.

[14] R. Fujimoto, K. Maruyama, T. Miki, *et al.*, Hydromet; 159 (2016) 120–125.

[15] S. Cholake, R. Farzana, T. Numata, *et al.*, J. Cleaner Prod; 171 (2018) 1128–1139.

[16] P. Oustadakis, P. Tsakiridis, A. Katsiapi, *et al.*, J. Hazard. Mater; 179 (2010) 1–7.

[17] P. Dvořák, H.N. Vu, J. Pol. Min. Eng. Soc; (2017) 195–199.

[18] H. Wang, J. Gao, W. Liu, *et al.*, Hydrom; 166 (2016) 1–8.

[19] T. Havlík, B. Vidor e Souza, *et al.*, J. Hazard. Mater; B135 (2006) 311–318.

[20] J. Araújo, V. Schalch, J. Mater. Res. Technol; 3 (3) (2014) 274–279.

[21] Review of the European List of Waste
https://ec.europa.eu/environment/pdf/waste/low_review_oekopol.pdf

[22] European Catalog of Waste, Available on the following link:

https://www.scribd.com/doc/26038172/Evropski-katalog-otpada

[23] M. Al-harahsheh, J. Al-Nuairat1, A. Al-Otoom, *et al.*, J. Environ. Chem. Eng; 7 (2019) 102856.

[24] E. Ledesma, A. Lunar, J. Ayuso, *et al.*, Constr. Build. Mater; 183 (2018) 365–375.

[25] R.M. Khattab, M.M. El-Sayed Seleman, M.F. Zawrah, Ceram. Int; 43 (2017) 12939–12947.

OPTIMIZATION OF ZINC DIMETHYLDITHIOCARBAMATE SYNTHESIS PROCESS (ZIRAM)

Goran Milentijević[1], Tijana Marinković[1], Milica Rančić[2], Milena Milošević[3], Ivan Đuričković[4], Aleksandar D. Marinković[4], Milutin M. Milosavljević[1*]

[1]Faculty of Technical Science, University of Priština, Knjaza Miloša 7, 38220 Kosovska Mitrovica, SERBIA

[2]Faculty of Forestry, University of Belgrade, Kneza Višeslava 1, 11030 Beograd, SERBIA

[3]University of Belgrade, Institute of Chemistry, Technology and Metallurgy, National Institute of the Republic of Serbia, Njegoševa 12, 11000 Belgrade, SERBIA

[4]University of Belgrade, Faculty of Technology and Metallurgy, Karnegijeva 4, 11000 Belgrade, SERBIA

[*]*milutin.milosavljevic@pr.ac.rs*

Abstract

This work presents an optimized laboratory procedure for the synthesis of zinc dimethyldithiocarbamate (Ziram) by the reaction of the sodium salt of dimethyl dithiocarbamic acid and zinc sulfate. The reaction of synthesis of the sodium salt of dimethyl-dithiocarbamic acid takes place starting from dimethylamine, carbon disulfide and sodium hydroxide solution. To the prepared acidified aqueous solution of zinc sulphate, a solution of the sodium salt of dimethyl dithiocarbamic acid was added, whereby zinc dimethyldithiocarbamate is formed in the form of a suspension. The suspension is filtered, the filter cake is washed with water to remove the sulfate ion and dried. The structure of the obtained Ziram was confirmed by IR, ^{1}H and ^{13}C NMR and MS instrumental methods, and the purity was determined by the classical analytical method. The obtained product zinc dimethyldithiocarbamate was ground, formulated and used in pomiculture as fungicide under the trade name Ziram.

Keywords: ditiocarbamates, zinc dialkyl, ziram, fungicide

INTRODUCTION

Dithiocarbamates have been attracting the attention of researchers for many years. In the seventies of the last century, these compounds were mostly interesting due to their use as fungicides, vulcanization accelerators in the rubber industry and as additives to lubricating oils. [1,2]. Dithiocarbamates (alkaline or metal salts of dithiocarbamic acid) represent a very broad class of compounds that find application in various fields of chemical technology. In the last years of the last century, and at the beginning of this, dithiocarbamates and their complexes with appropriate amines and metals, attract special attention of researchers due to the possibility of application in the pharmaceutical industry [3–6]. Also, thiocarbamates are derivatives of thiocarbamic acid, namely thiol and thion esters [7]. These compounds have a pronounced biological activity [8] with a very wide spectrum of action and are used as fungicides, bactericides, herbicide, germicides, pesticides, pesticides, insecticides, etc. [9–11].

Zinc dialkyldithiocarbamates represent additives for liquid lubricants, antioxidants (oxidation inhibitors), and oil additives for the transmission car mechanism [12]. Zinc dialkyldithiocarbamates combine antioxidant properties with an ability to inhibit corrosion and to function as antiwear and as extreme pressure agents for motor oils and automatic transmission fluids [13]. Dithiocarbamates are salts of dithiocarbamic acid with different amines and a divalent cation which determines the area of their application. Zinc dimethyldithiocarbamates represent zinc salts of dimethyl dithiocarbamic acid and can be presented by the following formula:

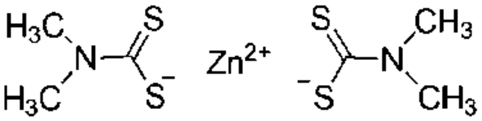


Figure 1 *Structure of zinc bis(dimethyldithiocarbamate), Ziram*

This manuscript presents an optimized laboratory procedure for the synthesis of zinc dimethyldithiocarbamate by the reaction of the sodium salt of dimethyldithiocarbamic acid and zinc sulfate.

EXPERIMENTAL

Procedure for the synthesis of Ziram under laboratory conditions

In the three-neck round-bottom flask (4 dm^3) that was equipped with magnetic stirrer, condenser, thermometer, water bath and addition funnel, 730 cm^3 (5.74 mol, 40%) of dimethylamine and 855 cm^3 of water was added with stirring. Afterwards, 370 cm^3 (6.01 mol, 98%) of carbon disulfide was added from addition funnel during one hour with maintaining a temperature from 28 to 35^{o}C. Then, 549.5 cm^3 (5.74 mol, 30%) of sodium hydroxide solution (231.67 g, 99% NaOH in 532.87 cm^3 of H_2O, ρ=1.334 gcm^{-3}) was added to the reaction mixture through addition funnel with maintaining a temperature in the range 28 to 35^{o}C during an hour. At the end, yellow solution of sodium dimethyldithiocarbamate was obtained (2340 cm^3, ρ=1.130 gcm^{-3}, sodium dimethyldithiocarbamate content: 29.4%, pH=9.5, yield: 98.03%). In reaction between zinc sulphate heptahydrate and sodium dimethyldithiocarbamate (Nadim), zinc dimethyldithiocarbamate (Ziram) was obtained in the following way: in the laboratory beaker (15 dm^3), 797.13 g of zinc sulphate heptahydrate (2.72 mol, 98%) and 8.41 dm^3 of water was added. Zinc sulphate heptahydrate was dissolved in water and reaction mixture was stirred and heated to reach a solution temperature in the range 40 to 45^{o}C. Then, 2340 cm^3 of Nadim (5.44 mol, 29.4 %) was added to obtained aqua suspension of Ziram (pH = 6.5). White precipitate of Ziram was filtered, washed with water (to a negative reaction to sulphates) and dried on 85–90^{o}C during ten hours. At the end, dried product of Ziram was obtained (821.97 g, purity: 98.7%, moisture content: 0.19%, yield: 97.73%).

Purity analysis

An amount of 0.5–0.6 g of the sample (Ziram) was measured in dry flask (250 ml). An aqueous solution of lead acetate (20–25 ml) was poured into the first adsorber and aqueous solution of potassium hydroxide (20–25 ml) into a second adsorber. The reaction flask was equipped with the condenser. Sulfuric acid was added to the reaction flask through the funnel of condenser, the apparatus was connected to vacuum so that the three bubbles per second pass through the adsorber. After an hour and half of boiling, the content of second adsorber was poured into erlenmeyer flask (500 ml) and washed using distilled water. In obtained solution one to two drops of phenolphthalein was added, neutralized with acetic acid and titrated using iodine solution. At the end, starch was added and titration was continued. The endpoint of the titration is identified as the first permanent trace of a dark blue-black colour. Calculation:

$$\%\text{Ziram}=\frac{\text{V}\cdot\text{F}\cdot\text{E}\cdot 100}{\text{G}} \tag{1}$$

where: V(ml) = volume of standard solution of iodine (0.05M); F = factor of standard iodine solution; E = equivalent of Ziram, and G = sample mass (g).

Analysis of moisture content

The infrared dryer (type Mettler Toledo LJ16) is used to determine water or moisture content by a gravimetric method. Simply load moist sample, close drying cover and press start key. The material is weighed and dried on the balance, which gives a constant readout of moisture content as a % moisture, % solids, or weight. The final result can be determined after a set drying time or by automatic mode (constant weight). Read weight on balance or use RS232C interface for connections to PC or LC-P45 printer (Z31,196-0) to record results.

pH measurement

pH meter (type Jenco Electronics LTD Microcomputer pH-Vision 6071N) is used for pH measurement.

Structural instrumental analysis

^{1}H and ^{13}C NMR spectra were obtained using Bruker Avance III 500 spectrometer at room temperature in deuterated chloroform ($CDCl_3$) with TMS as the internal standard. IR spectra were recorded using Nicolet™ iS™10 spectrometer (Thermo Scientific) in the attenuated total reflectance (ATR) mode.EI (electron impact) mass spectra were recorded on a Thermo Finnigan Polaris Q ion trap mass spectrometer, which includes a Trace GC 2000 (ThermoFinnigan, Austin, TX, USA), integrated GC-MS/MS system. The DIP (direct insertion probe) mode was used to carry the samples to the column. Ionization conditions: ion source temperatures 200^{o}C, maximum electron excitation energy 70 eV, current strength 150 μA. Elemental analysis was performed on a VARIO EL III Elemental analyzer, and the obtained analysis results are in good agreement with the calculated values (± 0.3%).

RESULTS AND DISCUSSION

This manuscript presents the laboratory procedure for the synthesis of zinc dimethyldithiocarbamate (Ziram). The procedure consists of two phases of synthesis. The first phase is the synthesis of the sodium salt of dimethyldithiocarbamic acid (Nadim) and takes place starting from dimethylamine, carbon disulfide and sodium hydroxide solution. To the prepared acidified aqueous solution of zinc sulphate, a solution of the sodium salt of dimethyldithiocarbamic acid is added, whereby zinc dimethyldithiocarbamate is formed in the form of a suspension. After filtration, drying and homogenization, the obtained product was analyzed in order to confirm the structure, purity and physical properties. The results of chemical analyzes of the five comparative syntheses are shown in Table 1.

***Table 1** Results of analysis of synthesized Ziram in laboratory conditions*

Exp.	**Yeld** (%)	**Purity** (%)	**Moisture** (%)	**pH**
1	97.73	98.60	0.20	6.06
2	97.60	99.45	0.20	6.28
3	96.90	98.90	0.10	5.96
4	97.59	99.20	0.21	5.98
5	97.85	99.20	0.09	6.12

Based on the results of the analysis presented in Table 1, it can be seen that a significant yield and product quality was achieved according to the described synthesis procedure. In experiment 5, the highest yield of 97.85%, high active substance content of 99.20% and low moisture content of 0.09% was achieved. In this experiment, the longest time to add Nadim is 2 hours in tempered zinc sulfate solution. The results of the instrumental methods clearly confirm the structure of Ziram, and an example of the IR analysis of Experiment 5 is presented in Figure 2.

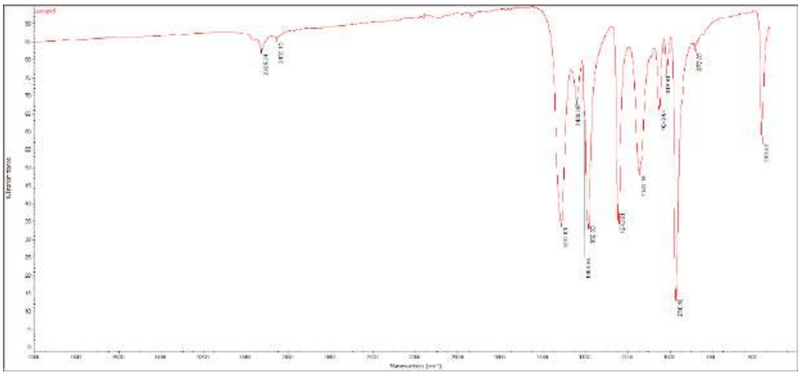


***Figure 2** IR image of Ziram obtained in Experiment 5 (Table 1)*

The synthesis reaction takes place in two phases, where the first phase is the reaction of dimethylamine amine, carbon disulfide and sodium hydroxide to form the amine salt of dimethyldithiocarbamic acid. Thus, one half of the present amount of dimethylamine reacts with carbon disulfide to form dimethyldithiocarbamic acid in aqueous solution. However, as in an alkaline environment, amino acid can not exist but it transforms into the amine salt. Thus, there was practically only a reaction between amine and disulfide. So, one half of the amine reacted with the acid, and the other half produced the acid with the disulfide. In this way, one half of the carbon disulfide remains unreacted, which begins to react successively by adding sodium hydroxide. Namely, sodium hydroxide gives with the amine salt of dimethyldithiocarbamic acid to the sodium salt, while the released amine now reacts in portions with carbon disulfide present in the reaction mixture. This can be represented by the reaction scheme in Figure 3.

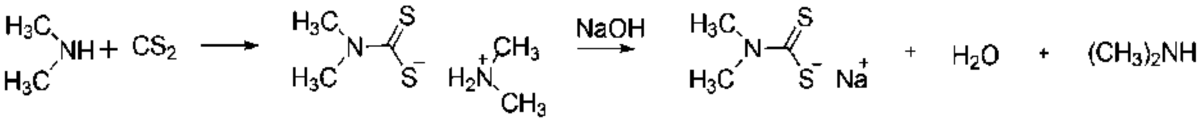


Figure 3 *Reaction scheme of Nadima synthesis*

The second phase of the reaction is the synthesis of Ziram from synthesized Nadim and an acidified solution of zinc sulfate heptahydrate with sulfuric acid to pH 3 that is shown by the following reaction scheme in Figure 4.

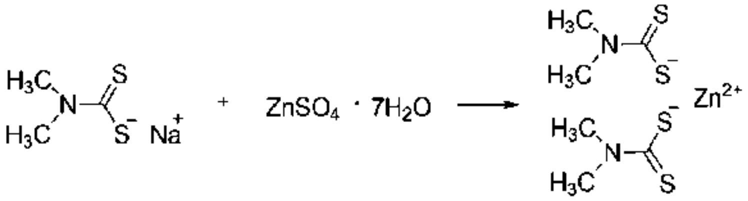


Figure 4 *Ziram synthesis reaction in the form of an aqueous suspension*

Ziram synthesis process at industrial conditions

Based on the reproductive results obtained in the laboratory conditions of the synthesis, a trial production of Ziram in industrial conditions was performed in the plant of C.I. "Župa" in Kruševac.

In the reactor (4 m^3) equipped with magnetic stirrer, condenser, thermometer, pH-meter and jacket for cooling, 645.10 kg of dimethylamine (40%) and 855 dm^3 of water was added. 466.90 kg of carbon disulfide (98%) was added from addition dozer with maintaining a temperature from 28 to 35°C. In reaction mixture, 733.08 kg of sodium hydroxide solution (30%) was added from dozer with maintaining a temperature (30 to 35°C) during 1.5 hour. At the end, yellow solution of sodium dimethyldithiocarbamate was obtained (2340 dm^3, ρ=1.130 gcm^{-3}, purity: 29.4%, pH = 9.5, yield: 94.8%). In the reaction between zinc sulphate heptahydrate and sodium dimethyldithiocarbamate (Nadim), zinc dimethyldithiocarbamate (Ziram) was obtained: in the reactor (15 m^3) that was equipped with cross type of stirrer, heater, pH-meter and thermometer, 797.13 kg of zinc sulphate heptahydrate and 8410 dm^3 of water was added. Zinc sulphate heptahydrate was dissolved in water and reaction mixture was heated to reach a solution temperature of 40 to 45°C. Afterwards, Nadim (2340 dm^3, ρ=1.130 gcm^{-3}) was added into obtained aqua suspension of Ziram (pH=6–6.5). A continuous-type filter (Oliver filter) was used for filtration obtained suspension of Ziram. Filter cake dried on 85–90°C, ground, formulated and packed. At the end, dried product of

Ziram was obtained (821.97 kg, purity: 98.7%, moisture content: 0.19%, yield: 97.73%). The technological scheme of the production process of zinc dimethyldithiocarbamate (Ziram) at industrial level is shown in Figure 5.

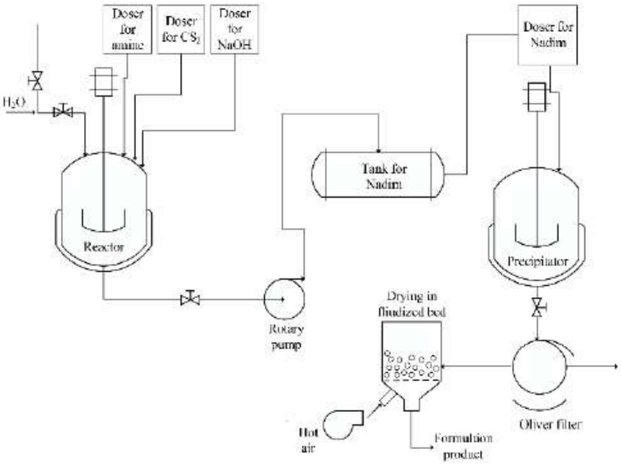


Figure 5 *Technological scheme of zinc dimethyldithiocarbamate production (Ziram)*

CONCLUSION

This manuscript presents an optimized laboratory procedure for the synthesis of zinc dimethyldithiocarbamate (Ziram) by the reaction of the sodium salt of dimethyldithiocarbamic acid and zinc sulfate. A significant yield and a high degree of product purity were achieved. The reaction of synthesis of the sodium salt of dimethyldithiocarbamic acid takes place starting from dimethylamine, carbon disulfide and sodium hydroxide solution. A solution of the sodium salt of dimethyldithiocarbamic acid is added to the prepared acidified aqueous zinc sulphate solution to give zinc dimethyldithiocarbamate (Ziram) in suspension form. The resulting zinc dimethyldithiocarbamate product is filtered off, dried, ground and formulated to obtain a commercial package. For the formulation of a commercial product, fillers, wetting agents and dispersants are added to pure Ziram, which enables application for plant protection.

ACKNOWLEDGEMENT

This work was supported by the Ministry of Education, Science and Technological Development of the Republic of Serbia (Contract Nos. 451-03-68/2022-14/200135; 451-03-68/2022-14/200026; 451-03-9/2022-14/200169).

REFERENCES

[1] M.M. Milosavljević, A.D. Marinković, J.M. Marković, *et al.*, Chem. Ind. Chem. Eng. Quarterly (CI&CEQ); 18 (2012) 73–81.

[2] A. Marinković, M.M. Milosavljević, D. Milenković, *et al.*, Chem. Ind. Chem. Eng. Q; 14 (2008) 251–255.

[3] S. Rathore, G. Varshney, S.C. Mojumdar, *et al*., J. Therm. Anal. Calorim; 90 (2007) 681–686.

[4] V.K. Tiwari, A. Singh, H.A. Hussain, *et al*., Monatsh. Chem; 138 (2007) 653–658.

[5] H.S. Rathore, K. Ishratullah, C. Varshney, *et al*., J. Therm. Anal. Calorim; 94 (2008) 75–81.

[6] A. Trevisan, C. Marzano, P. Cristofori, *et al*., Arch. Toxicol; 76 (2002) 262–268.

[7] W. Walter, K.D. Bode, Angew. Chem; 79 (1967) 281–293.

[8] A.B. Glazsrin, A.N. Denisov, V.P. Talzi, *et al*., Moskva; (1988) 1–32.

[9] V.P. Savin, V.P. Tolzi, N.O. Bek, Org. Hbv; 20 (1984) 1842.

[10] M.M. Milosavljević, S. Ražić, Vaprosy himii i himicheskoi tehnologii; 3 (2005) 50–54.

[11] P.G. Ruminski, US patent 5457134 (1995).

[12] M. Kakizaki, S. Kondo, M. Ishijima, *et al*., WO 2008007671 (2008).

[13] V.K. Verma, R. Singh, V. Srivastava, *et al*., Lubric. Sci; 16 (2004) 195–203.

STABILITY OF SOYBEAN PEROXIDASE IMMOBILIZED ONTO HYDROGEL MICRO-BEADS FROM TYRAMINE-PECTIN

Miloš Prokopijević[1*], **Dragica Spasojević**[1], **Olivera Prodanović**[1], **Nevena Pantić**[1], **Dragana Bartolić**[1], **Ksenija Radotić**[1], **Radivoje Prodanović**[2]

[1]University of Belgrade, Institute for Multidisciplinary Research, Kneza Višeslava 1,
11030 Belgrade, SERBIA

[2]University of Belgrade, Faculty of Chemistry, Studentski trg 12–16,
11158 Belgrade, SERBIA

[*]*milos.prokopijevic@imsi.rs*

Abstract

The application of enzymes for phenol removal from polluted waters is an effective and environmentally favorable method and an ongoing worldwide research topic. Oxidoreductive enzymes, like Soybean peroxidase (SBP), catalyze oxidation and polymerization of phenolic compounds in the presence of H_2O_2. The industrial application, however, requires enzyme immobilization on various carriers to overcome the disadvantages of using the soluble form. Chemically modified pectin has been chosen as a carrier for entrapment of SBP inside a three-dimensional polymeric network. Immobilization of SBP was performed in an emulsion polymerization reaction producing enzymes entrapped in covalently crosslinked tyramine-pectin in the shape of micro-beads. The specific activity of immobilized SBP was determined using pyrogallol as a substrate. In this study, the stability of the immobilized SBP onto modified pectin in three different molar ratios was tested to determine the carrier with the best performance. Immobilized peroxidase has potential for application as a biocatalyst for phenol removal from wastewater.

Keywords: immobilization, soybean peroxidase, pectin, tyramine, hydrogel

INTRODUCTION

Soybean peroxidase (SBP, E.C. 1.11.1.7) is a glycoprotein that belongs to the class III plant peroxidase family and catalyzes oxidation and polymerization of aromatic substrates using H_2O_2 as electron acceptor [1,2]. With a growing number of applications, from phenol removal from wastewater, and organic syntheses to analytical tests, SBP is an excellent candidate for wider usage due to its availability and relatively easy extraction and purification [3]. Removal of toxic aromatic pollutants from wastewaters by enzymatic method using oxidoreductive enzymes is highly specific, efficient, and causes less environmental impact compared to traditional methods [4].

The application of soluble enzymes as biocatalysts in industrial processes is limited due to some disadvantages, such as their short storage life, lack of operational stability, expensive and time-consuming recovery, and practically no reusability [5,6]. Immobilization of enzymes on solid supports can improve their catalytic efficiency, performance in organic solvents, stability and resistance to environmental changes in pH and temperature [6]. Focus on the discovery of novel immobilization systems for wastewater treatment is a major research challenge.

Hydrogels are an insoluble, hydrophilic, polymeric network that has the ability to absorb and retain large amounts of water. Due to their properties, there is a growing interest in the application of hydrogels as carriers for enzyme encapsulation [7]. Pectin is a natural heteropolysaccharide and a major structural component of plant cell walls capable of producing hydrogels by ionotropic gelation in the presence of Ca^{2+} ions or chemical crosslinking and is frequently used due to its gelling properties and nontoxicity [8,9]. Tyramine-pectin has been synthesized by chemical modification of pectin as described by Prokopijević *et al.* [10] and used as a carrier for SBP immobilization. Entrapment is an immobilization technique defined as physical restriction where enzymes are confined inside a polymeric network that permits substrates and products to pass through [11].

The aim of this research was to test the storage stability of SBP immobilized inside tyramine-pectin micro-beads after 24 hours of storage. Three carriers with different degrees of modification were chemically crosslinked in an emulsion polymerization reaction and tested for SBP immobilization.

MATERIALS AND METHODS

Materials

Pectin, glucose oxidase (160 U/mg), tyramine hydrochloride, triton X-100 (t-octylphenoxypolyethoxyethanol), pyrogallol, span 80 (sorbitan monooleate), and mineral oil were purchased from Sigma-Aldrich (St. Louis, MO, USA). TRIS was purchased from SERVA Electrophoresis GmbH (Heidelberg, Germany). Sodium cyanoborohydride was obtained from Fluka Chemie GmbH (Buchs, Switzerland) and glucose from Zorka Pharma (Šabac, Serbia). Soybean peroxidase was isolated from soybean hulls by coprecipitation with acetone and ammonium sulfate described in previously published research [12].

Polymer modification

Tyramine-pectin was synthesized according to the previously published procedure by Prokopijević *et al.* [10]. Pectin was oxidized using sodium metaperiodate in three molar ratios (2.5 mol%, 10 mol%, and 20 mol%), and in a reductive amination reaction tyramine was bound to newly formed vicinal hydroxyl groups in the presence of sodium cyanoborohydride.

SBP immobilization

Solution of 20 % (w/v) tyramine-pectin in 0.1 M Tris HCl buffer pH 7 was prepared, and 300 μl of that solution was mixed with 0.1 U of glucose oxidase, 0.8 U of SBP, and 10 mM glucose. The obtained mixture was instantly poured into 0.6 ml of light mineral oil with 3 % (v/v) Span 80 while gently stirring on a magnetic stirrer. After 15 min. tyramine-pectin micro-beads were formed and 1 ml of 0.5 % (v/v) Triton X-100 in 5 % (w/v) $CaCl_2$ was added to stop the reaction. Micro-beads with encapsulated enzyme were rinsed 3 times with 1 ml of 5 % (w/v) $CaCl_2$ solution containing 0.5 % (v/v) Triton X-100 and afterward 3 times with 5 % $CaCl_2$ and stored in the same solution at 4 °C. Activity of unbound soluble SBP, measured in the collected $CaCl_2$ solution after rinsing of the micro-beads, was used to calculate bound activity.

Enzyme activity

The specific activity of SBP encapsulated inside obtained micro-beads was tested with 13 mM pyrogallol in 0.1 M Tris HCl buffer pH 7. Typical enzyme assays were carried out in a 3 ml reaction mixture by adding 150 µl of 60 % hydrogel suspension into a buffered substrate with 0.1 U glucose oxidase and 0.1 M glucose. The reaction mixture was stirred and aliquots were collected after 5, 10, and 15 minutes. Absorbance was measured at 420 nm on a UV-VIS spectrophotometer (Shimadzu Corporation UV-2501PC, Japan).

RESULTS AND DISCUSSION

The specific activity of SBP immediately after immobilization onto three tyramine-pectin carriers with different degrees of periodate oxidation and after 24 h of storage was compared. Obtained results are presented in Figure 1.

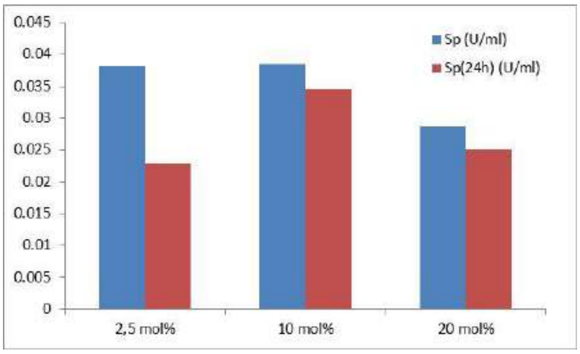


Figure 1 *Specific activity (U/ml) of SBP immobilized onto tyramine-pectin micro-beads (blue) and residual activity after 24 h of storage (red)*

Although the highest specific activity (0.038 U/ml) was obtained when 2.5 mol% and 10 mol% tyramine-pectin were used as carriers, their respective retained activity after 24 hours of storage distinctly differs: 59.95 % and 89.64 % (Table 1). Tyramine-pectin with higher degrees of modification (10 mol% and 20 mol%) possesses higher residual activity while the highest bound activity was achieved with 20 mol% modification.

Table 1 *Specific activity (U/ml), bound activity (%) and residual activity (%) of SBP immobilized onto tyramine-pectin micro-beads after 24 h of storage*

	2.5 mol%	10 mol%	20 mol%
Specific activity (U/ml)	0.038	0.038	0.029
Bound activity (%)	78.60	75.83	85.90
Residual activity after 24 h (%)	59.95	89.64	87.05

Better storage stability and higher activity after the observed period may be due to the reduced leakage of the enzyme from the carriers with a higher degree of pectin modification. Tyramine-pectin with 10 mol% periodate oxidation expressed the highest specific activity

(0.038 U/ml) and storage stability (89.64 %), therefore it is a suitable candidate for further application.

CONCLUSION

This research confirmed that SBP was successfully immobilized on all 3 tyramine coupled natural polymers with different degrees of modification. The bound activity was above 75 % for all of the used carriers. Tyramine-pectin with the molar ratio of 10 mol% periodate oxidation expressed the highest specific activity and residual activity after 24 h of storage. Immobilized SBP has the potential for application in the removal of toxic aromatic compounds from polluted waters.

ACKNOWLEDGEMENT

This research was funded by grant no. 451-03-68/2022-14/200053 provided from the Ministry of Education, Science and Technological Development of the Republic of Serbia.

REFERENCES

[1] J.K.A. Kamal, D.V. Behere, J. Inorg. Biochem; 94 (3) (2003) 236–242.

[2] M. Prokopijević, O. Prodanović, D. Spasojević, *et al.*, Bioprocess. Biosyst. Eng; 37 (5) (2014) 799–804.

[3] M. Monier, D.M. Ayad, Y. Wei, *et al.*, Int. J. Biol. Macromol; 46 (3) (2010) 324–330.

[4] A. Bódalo, J.L. Gómez, E. Gómez, *et al.*, Desalination; 195 (1–3) (2006) 51–59.

[5] I. Alemzadeh, S. Nejati, J. Hazard. Mater; 166 (2009) 1082–1086.

[6] R. Ahmad, M. Sardar, Biochem. Anal. Biochem; 4 (2) (2015) 1–8.

[7] E. Caló, V.V. Khutoryanskiy, Eur. Polym J; 65 (2015) 252–267.

[8] P. Srivastava, R. Malviya, Indian J. Nat. Prod. Resour; 2 (1) (2011) 10–18.

[9] V. Urias-Orona, A. Rascón-Chu, J. Lizardi-Mendoza, *et al.*, Int. J. Mol. Sci; 11 (10) (2010) 3686–3695.

[10] M. Prokopijevic, O. Prodanovic, D. Spasojevic, *et al.*, Appl. Microbiol. Biotechnol; 101 (2017) 2281–2290.

[11] N.R. Mohamad, N.H.C. Marzuki, N.A. Buang, *et al.*, Biotechnol. Biotechnol. Equip; 29 (2) (2015) 205–220.

[12] J. Liu, H. Liu, Y. Zhang, *et al.* Appl. Microbiol. Biotechnol; 74 (1) (2007) 249–255.

COVALENT IMMOBILIZATION OF HORSERADISH PEROXIDASE ON NOVEL MACROPOROUS POLY(GMA-CO-EGDMA) FOR PHENOL REMOVAL

Nevena Pantić[1,2], Milica Spasojević[3], Miloš Prokopijević[1*], Dragica Spasojević[1], Ana Marija Balaž[4], Radivoje Prodanović[5], Olivera Prodanović[1]

[1]University of Belgrade, Institute for Multidisciplinary Research, Kneza Viseslava 1, 11030 Belgrade, SERBIA

[2]Cener for Green Technologies, Institute for Multidisciplinary Research, Kneza Viseslava 1, 11030 Belgrade, SERBIA

[3]University of Belgrade, Innovative Centre of the Faculty of Chemistry, Studentski trg 12–16, 11000 Belgrade, SERBIA

[4]University of Belgrade, Institute of Chemistry, Technology and Metallurgy, Njegoševa 12, 11000 Belgrade, SERBIA

[5]University of Belgrade, Faculty of Chemistry, Studentski trg 12–16, 11000 Belgrade, SERBIA

[*]*milos.prokopijevic@imsi.rs*

Abstract

For the purpose of immobilization, one of the most commonly used enzymes is horseradish peroxidase (HRP). Different carriers can be used as supports for the immobilization of HRP: alginate, pectin, magnetic-beads, macroporous copolymers, silicas etc. Covalent binding of an enzyme to the carrier leads to the formation of strong linkage, thus preventing the enzyme leakage. Macroporous copolymers with different porous characteristics were used for the immobilization of horseradish peroxidase by employing periodate and glutaraldehyde method. Five and 25 mg of HRP were immobilized per gram of the copolymer. Increasing the amount of added enzyme leads to the increase of specific activity of immobilized enzyme. Copolymer with the pore diameter of 297 nm showed the most promising results in terms of specific activity. Immobilized enzymes can be used for the removal of phenolic compounds from waste effluents.

Keywords: macroporous copolymer, periodate immobilization, horseradish peroxidase, dispersion polymerization, phenol removal

INTRODUCTION

Horseradish peroxidase (HRP, E.C.1.11.1.7) is one of the most frequently used plant peroxidases. Inactivation of the enzyme by its own substrate during long-term use is a major issue, which directly affects enzyme activity and its operational stability [1]. Immobilization of HRP on different carriers enables the repeated use of enzyme and enhances its properties [2,3]. Various support materials can be used as immobilizing agents (natural polymers such as alginate, pectin, chitosan, magnetic-beads [1,2,4–6], silica [7] and polyacrylamide gels [8]).

The immobilization of horseradish peroxidase can be acquired by using different methods: covalent binding, entrapment, adsorption and cross-linking. Covalent binding provides strong linkage between the enzyme and carrier, thus preventing the enzyme leakage from the support [9]. Macroporous copolymers have been widely used as carriers in covalent immobilization reactions [3]. A wide application of these supports relies on the presence of epoxide groups that can be easily transformed into more reactive groups such as amino, keto, carboxyl or hydroxyl.

Porosity of macroporous carriers is considered as one of the most important parameters that directly affects the activity and stability of immobilized enzymes [10]. This property can be controlled during the suspension copolymerization reaction by a careful choice of cross-linking agent as well as the type and amount of inert components [11,12].

Peroxidase immobilized onto macroporous carriers can be widely used in different areas, such as development of biosensors [13,14], decolorization of textile dyes [15], removal of phenolic compounds from wastewaters etc. [1,2]. The removal of phenols with immobilized HRP from waste effluents is of major interest due to high toxicity of phenol like compounds even at low concentrations and its great abundance in watercourses worldwide.

MATERIALS AND METHODS

Materials

Glycidyl methacrylate (GMA), ethylene glycol dimethacrylate (EGDMA), 1-dodecanol, cyclohexanol, horseradish peroxidase (150–250 U/mg), pyrogallol used as a substrate for peroxidase oxidation reaction, glutaraldehyde (25% solution in water) and sodium periodate were purchased from Sigma Aldrich (St. Louise, Mo, USA). Ethylenediamine was obtained from Merck (Kenilworth, New Jersey, USA). Hydrogen peroxide was purchased from AppliChem GmbH (Darmstadt, Germany).

Copolymer Preparation and Amination

A continuous phase consisting of 2.78 wt% PVP (Mw = 24 000 g/mol) in ethanol was heated to 70 °C. A monomer phase (5.0 g of both the monomer GMA and cross-linking agent EGDMA (GMA/EGDMA = 60/40)), initiator (0.05 g of AIBN) and inert phase (2.25 g of 1-dodecanol and 2.25 g of cyclohexanol) was added to the continuous phase and stirred for 6 h. The obtained copolymer was washed 5 times with ethanol and dried at room temperature. After the amination of epoxide groups with ethylenediamine, the polymer particles were washed first with ethanol and subsequently with water until the pH value of the filtrate was 6. The samples were dried in the oven at 50 °C.

Copolymer Characterization

The pore size distributions of the synthetized copolymers poly(GMA-co-EGDMA) were determined by a mercury porosimetry (Carlo Erba 2000, software Milestone 200). Scanning electron microscope (Tescan FE-SEM Mira 3 XMU) was employed to characterize the morphology of poly(GMA-co-EGDMA).

Horseradish Peroxidase Immobilization by Glutaraldehyde Method

Aminated copolymers were first deaerated for 10 min in sodium phosphate buffer pH 8 (0.1 mol/L) and rinsed twice with the same buffer. Prepared copolymers were incubated for 2h in a glutaraldehyde solution. Subsequently, the copolymers were incubated with different amounts of horseradish peroxidase (5 and 25 mg/g). After the incubation, copolymers were rinsed twice with sodium phosphate buffer pH 7 (0.1 mol/L), resuspended in the same buffer and stored at 4 °C until further use.

Horseradish Peroxidase Immobilization by Periodate Method

Sodium periodate solution (50 mmol/L) in sodium acetate buffer pH 5 was used for the oxidation of horseradish peroxidase. Oxidized HRP was dialyzed overnight against sodium acetate buffer pH 5. The aminated copolymers were first deaerated in sodium phosphate buffer pH 7 (0.1 mol/L), rinsed with the same buffer and subsequently, incubated with different amounts of oxidized HRP (5 and 25 mg/g) for 48 h. Copolymers with immobilized enzyme were rinsed with sodium phosphate buffer pH 7 (0.1 mol/L) and stored in the same buffer at 4 °C until further use.

Enzyme Activity Studies

In order to determine peroxidase activity, pyrogallol and hydrogen peroxide (H_2O_2) were used as substrates. In the most common assay, 10 µL of the enzyme dilution from the washings and 10 µL of H_2O_2 (9.7 mmol/L) were introduced into 1 mL of the pyrogallol solution (13 mmol/L) in sodium phosphate buffer pH 7. Absorbance was measured for 3 min at 420 nm using UV–VIS spectrophotometer (Shimadzu Corporation UV-2501PC, Japan). To measure the activity of the immobilized enzyme, 9.0 mg of the copolymer with immobilized HRP and 30 µL of H_2O_2 were introduced into 3 mL of pyrogallol. Every 60 s aliquots were taken out from the mixture, filtrated and the absorbance at 420 nm was measured. One unit of enzyme activity was defined as the amount of enzyme that produces 1mg of purpurogallin in 20 s at 20 °C.

RESULTS AND DISCUSSION

Dispersion polymerization was used for the synthesis of macroporous poly(GMA-co-EGDMA) copolymers. The spherical nature of particles with diameter of around 1.5 µm is presented in Figure 1.

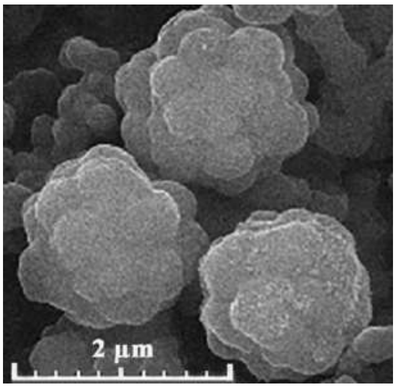


Figure 1 *SEM image of poly(GMA-co-EGDMA) copolymer*

Various studies have shown that the porosity of particles obtained by suspension copolymerization method is greatly affected by the amount of added cross-linking agent and polarity of used solvent [11,12]. An increase in the water content leads to decrease in the average pore diameter (Table 1).

***Table 1** Porous properties of copolymer samples*

Sample ID	ZP2	ZP5	ZP12
GMA:EGDMA (wt:wt%)	60:40	60:40	60:40
Ethanol:water (mL:mL)	30:15	20:25	15:30
Average pore diameter (nm)	460	297	235

The immobilization of horseradish peroxidase was performed via two different methods: glutaraldehyde and periodate method. Periodate method involves covalent binding to a copolymer surface through carbohydrate moiety located on the enzyme molecule. The other method used for this study (glutaraldehyde method) implies binding of an enzyme to a glutaraldehyde-activated carrier via amino groups presented on the surface of the protein (Figure 2).

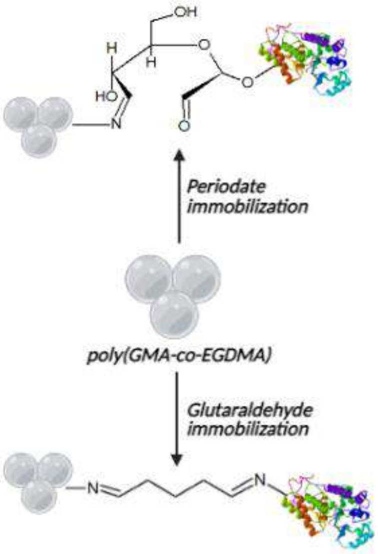


***Figure 2** Covalent immobilization of horseradish peroxidase onto poly(GMA-co-EGDMA) copolymer*

Different amounts of HRP were added per gram of the copolymer (5 and 25 mg/g) and specific activity of the immobilized enzyme was calculated. Results presented in Figure 3a show that specific activity increases with the increase in the amount of added enzyme per gram of the copolymer, regardless of the method used. Copolymer labelled as ZP5 with the pore diameter of 297 nm showed the most promising results. Immobilization of the enzyme by periodate method provides higher specific activities than immobilization by the glutaraldehyde method, under the same conditions (the same copolymer and the same amount of immobilized peroxidase) (Figure 3b). This is probably a consequence of preserved structure of enzyme active site which resulted from the oxidation of carbohydrate moiety.

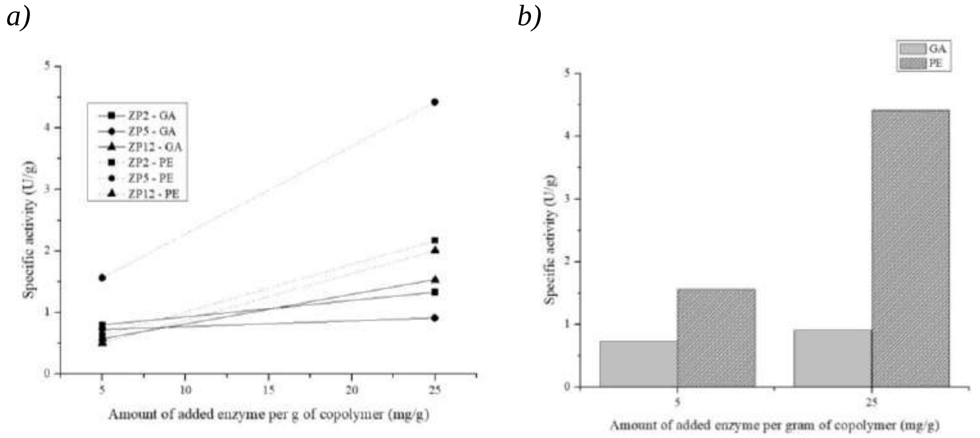


Figure 3 *a) Effect of the amount of added enzyme on the specific activity of immobilized HRP; b) Differences in specific activities of enzymes immobilized by periodate and glutaraldehyde method*

CONCLUSION

Macroporous copolymers were successfully synthesized by the dispersion polymerization. Periodate and glutaraldehyde methods were used for the immobilization of horseradish peroxidase. Obtained results showed that the increase in the amount of added enzyme per gram of the copolymer leads to the increase in the specific activity of immobilized enzyme. When two methods for HRP immobilization were compared, more promising results were obtained by the periodate method. Horseradish peroxidase immobilized onto macroporous copolymers can be used for the removal of phenolic compounds.

ACKNOWLEDGEMENT

This work was supported by the Ministry of Education, Science and Technological Development of the Republic of Serbia (Grant No. 451-03-68/2022-14/200053, University of Belgrade, Institute for Multidisciplinary Research).

REFERENCES

[1] I. Alemzadeh, S. Nejati, J. Hazard. Mater; 166 (2009) 1082–1086.

[2] G. Bayramoglu, M.Y. Arica, J. Hazard. Mater; 156 (2008) 148–155.

[3] L. Pramparo, F. Stüber, J. Font, *et al.*, J. Hazard. Mater; 177 (2010) 990–1000.

[4] M. Monier, D.M. Ayad, Y. Wei, *et al.*, Int. J. Biol. Macromol; 46 (2010) 324–330.

[5] L. V. Bindhu, E.T. Abraham, J. Appl. Polym. Sci; 88 (2003) 1456–1464.

[6] M. Prokopijevic, O. Prodanovic, D. Spasojevic, *et al.*, Bioprocess Biosyst. Eng; 37 (2014) 799–804.

[7] R. Voss, M.A. Brook, J. Thompson, *et al.*, J. Mater. Chem; 17 (2007) 4854–4863.

[8] Z. Temoçin, M. İnal, M. Gökgöz, *et al.*, Polym. Bull; 75 (2018) 1843–1865.

[9] G. Fernández-Lorente, M. Terreni, C. Mateo, *et al.*, Enzyme Microb. Technol; 28 (2001) 389–396.

[10] R.M. Prodanović, N.B. Milosavić, S.M. Jovanović, *et al.*, J. Serb. Chem. Soc; 71 (2006)

339–347.

[11] S.M. Jovanovic, A. Nastasovic, N.N. Jovanovic, *et al.*, Mater. Sci. Forum; 214 (1996) 155–162.

[12] D. Horak, F. Svec, M. Ilavsky, *et al.*, Die Angew. Makromol. Chemie; 95 (1981) 117–127.

[13] M.A. Alonso-Lomillo, O. Domínguez-Renedo, L. del T. Román, *et al.*, Anal. Chim. Acta J; 688 (2011) 49–53.

[14] D. Yu, B. Blankert, J. Kauffmann, Biosens. Bioelectron; 22 (2007) 2707–2711.

[15] F. Gholami-Borujeni, A.H. Mahvi, S. Naseri, *et al.*, Res. J. Chem. Environ; 15 (2011) 217–222.

PREPARATION OF CROSSLINKED TYRAMINE-ALGINATE HYDROGEL USING EDC/NHS WITH SELF-IMMOBILIZED HRP

Dragica Spasojević[1], Miloš Prokopijević[1*], Olivera Prodanović[1], Nevena Pantić[1], Mira Stanković[1], Ksenija Radotić[1], Radivoje Prodanović[2]

[1]University of Belgrade, Institute for Multidisciplinary Research, Kneza Višeslava 1,
11000 Belgrade, SERBIA

[2]University of Belgrade, Faculty of Chemistry, Studentski trg 12–16,
11000 Belgrade, SERBIA

[*]*milos.prokopijevic@imsi.rs*

Abstract

Alginate is a natural polymer present in the cell wall of brown algae. Due to its many advantages, it has been used extensively in the food industry, pharmacy, and biomedicine. To enhance properties, such as stability and biodegradability, alginate is often chemically crosslinked. In this study, alginate was crosslinked using N-hydroxysuccinimide, 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride and tyramine hydrochloride. Horseradish peroxidase was self-immobilized within hydrogel microbeads during the polymerization reaction. The glucose oxidase/glucose system generates H_2O_2 *internally, which can prevent the detrimental effect of excess peroxide. A small amount of leaking enzyme shows potential for longer storage and reuse.*

Keywords: alginate, horseradish peroxidase, chemical modification, immobilization

INTRODUCTION

Alginic acid is a natural biopolymer derived from brown algae. It is widely used as an immobilization matrix for cells, enzymes and drugs. The main advantages of alginate compared to other biopolymers are the low cost of extraction and the great potential for modification [1]. Covalent and enzymatic crosslinking is usually a method of choice to modify the mechanical properties of alginate and obtain hydrogel with high mechanical stability [2]. Hydrogels are polymeric networks with the ability to absorb large amounts of water while maintaining a 3-dimensional structure [3,4]. Horseradish peroxidase (HRP) is one of the most studied peroxidases, isolated from plants and a common model system for enzyme immobilization [5]. Immobilization of HRP onto insoluble carriers enables researchers to increase its performance, preserve its catalytic activities through several cycles, prolong its storage time, etc. [6]. HRP immobilizates can be used in wastewater remediation (removal of phenolic compounds and azo dyes), syntheses of organic compounds, as biosensors, etc. [7,8].

The aim of this study was to chemically modify alginate in a way that it can easily form hydrogel with self-immobilized HRP.

MATERIALS AND METHODS

Chemical modification of alginate

1% (w/v) alginate solution in water was prepared by dissolution of 0.25 g of sodium alginate in 25 mL distilled water. Another solution in water was made by dissolving 2.25 g tyramine hydrochloride, 0.14 g NHS (N-hydroxysuccinimide), and 0.13 g EDC (1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride) in 25 mL of distilled water. Solutions were mixed and placed under constant stirring for 24 hours. After that time, the reaction mixture was dialyzed against distilled water. When dialysis was over, the solution was frozen and vacuum dried and obtained powder was stored at room temperature.

Formation of hydrogel microbeads and HRP immobilization

Dry powder of tyramine-coupled alginate was dissolved in 50 mM Tris buffer pH 7.0 at a final concentration of 2% in 0.3 mL mixture volume. 0.5 U of HRP and 3 U of glucose oxidase (GOx) were added. The polymerization reaction started with the addition of glucose solution in a final concentration of 133 mM and the mixture was rapidly poured into 0.6 mL Light Mineral Oil with 3% Span 80 detergent. The mixture was left for 15 min on a magnetic stirrer and after that time the reaction was stopped by the addition of 1 mL of 0.5% Triton X-100 in water with 0.5 mM H_2O_2. Stirring was continued for 5 minutes, and HRP-immobilized microbeads were collected and washed 4-5 times to remove any unbound enzyme as well as detergents. Supernatants were kept for the determination of unbound activity. Microbeads were stored in Tris buffer with 5mM $CaCl_2$ and left in the fridge for 24 hours.

Enzyme activity assay

HRP activity was measured in hydrogel microbeads for a specific activity and in supernatants after washing beads for unbound activity. Pyrogallol and H_2O_2 were used as substrates and absorbance was measured at 420 nm. The activity of immobilized HRP was determined with 100 µL of microbeads suspension (10%) in 3 mL of 13 mM pyrogallol solution after the addition of 30 µL of 0.97 M H_2O_2. The reaction was monitored for 15 min under constant stirring and aliquots were taken every 5 minutes. Specific activity was calculated per volume of hydrogel (U/mL). The leaching of the enzyme from tyramine-coupled alginate was measured after 24 hours. 1 unit (U) of HRP activity was defined as the amount of enzyme that produces 1 mg of purpurogallin in 20 s at 20 °C.

RESULTS AND DISCUSSION

Tyramine moieties were introduced within alginate chains, which have been confirmed with increased UV absorbance (from 260 to 280 nm) (Table 1).

Table 1 *Absorbance (at 260 nm and 280 nm) of 0.1% (w/v) polysaccharide in water*

Wavelength (nm)	260	280
Alginate	0.125	0.112
Tyramine-alginate	1.443	1.700

Modified alginate formed hydrogel microbeads in a peroxidase – induced emulsion polymerization reaction, with HRP encapsulated. Slow and continuous release of hydrogen peroxide (with glucose as a substrate for glucose oxidase) could prevent HRP substrate inactivation. The results of HRP immobilization are shown in Table 2. Obtained specific activity (Sp) of microbeads was 0.17 U/mL of suspension. Enzyme leaching after 24 hours was 0.004 U, which shows potential of the immobilizate for storage and repeated uses.

Table 2 *Immobilization parameters (specific activity, unbound activity and enzyme leaching) for HRP in tyramine-alginate microbeads*

Parameters	Sp (U/mL)	Unbound activity (U)	Leaching (U)
Immobilized HRP microbeads	0.171	0.067	0.004

CONCLUSION

This study presented modified tyramine-alginate hydrogel with EDC/NHS as the crosslinking agent. HRP was successfully self-immobilized within hydrogel microbeads. GOx with added glucose serves as an internal generator of H_2O_2, a substrate for immobilized peroxidase. The immobilized system can be stored in the fridge and reused. Further experiments are planned focused on optimization of the immobilization technique and testing the immobilized enzyme. With the introduction of tyramine onto the polymeric chains of alginate, novel charged groups within the hydrogel polymer could increase the binding of enzymes and other biomolecules, while also contributing to water solubility and changing the mechanical properties of the hydrogel. That is a favorable effect for different applications, such as drug delivery or tissue engineering.

ACKNOWLEDGEMENT

The authors are grateful to the Ministry of Education, Science and Technological development of the Republic of Serbia for financial support (451-03-68/2022-14/200053).

REFERENCES

[1] L. Pereira, Alginates - Recent Uses of This Natural Polymer, IntechOpen, London (2020), p.150, ISBN: 978-1-78985-642-2.

[2] D. Nataraj, N. Reddy, J. Chem. Res; 4 (1) (2020) 1–17.

[3] J. Kopecek, Biomaterials; 28 (34) (2007) 5185–5192.

[4] Q. Chai, Y. Jiao, X. Yu, Gels; 3 (1) (2017) 1–15.

[5] D. Spasojević, M. Prokopijević, O. Prodanović, *et al.*, Hem. Ind; 68 (1) (2014) 117–122.

[6] Q. Chang, H. Tang, Molecules; 19 (10) (2014) 15768–15782.

[7] W.M. Alshawafi, M. Aldhahri, Y.Q. Almulaiky, *et al*., Artif. Cells Nanomed. Biotechnol; 46 (3) (2018) 973–981.

[8] S.M.U. de Souza, E. Forgiarini, A.A.U. de Souza., J. Hazard. Mater; 147 (3) (2007) 1073–1078.

THE ROLE OF HYDROXYL AND SULFATE RADICALS IN THE UV ACTIVATED PERSULFATE DEGRADATION OF TEXTILE DYE RO16

Jelena Mitrović[1*], **Miljana Radović Vučić**[1], **Nena Velinov**[1], **Slobodan Najdanović**[1], **Miloš Kostić**[1], **Milica Petrović**[1], **Aleksandar Bojić**[1]

[1]University of Niš, Faculty of Sciences and Mathematics, Višegradska 33, 18000 Niš, SERBIA

[*]*jelena.mitrovic1@pmf.edu.rs*

Abstract

Activation of persulfate ($S_2O_8^{2-}$) with UV light forms sulfate radicals ($SO_4^{\bullet-}$) that during the radical interconversion produce hydroxyl radicals ($HO^{\bullet}$) under alkaline conditions. Both radicals ($SO_4^{\bullet-}$ and $HO^{\bullet}$) can be present either individually or simultaneously in the persulfate oxidation system. The main hypothesis of this research is that these radicals contribute to various degree in degradation of textile dye C. I. Reactive Orange 16 (RO 16) at different pH values in the UV/$S_2O_8^{2-}$ system. In this paper, we use selective quenching agents, methanol (MeOH) and tert-butyl alcohol (TBA), to identify $SO_4^{\bullet-}$/$HO^{\bullet}$ radicals and their role in degradation of textile dye RO 16. Results revealed that the contribution rate of $HO^{\bullet}$ radicals were higher in alkaline than that obtained in acidic conditions, while $SO_4^{\bullet-}$ radicals were dominant radicals at lower initial pH values. The results also indicated that the use of selective quenching method with MeOH and TBA is suitable for differentiating of $SO_4^{\bullet-}$ and $HO^{\bullet}$ radicals' reactivity toward the textile dye RO 16 in persulfate oxidation system. This study provided some practical basis for the formation of radicals in UV activated persulfate process, which can be applied for the degradation of various organic pollutants.

Keywords: Advanced oxidation processes, pH value, radicals, decolorization

INTRODUCTION

Reactive dyes are widely used for dyeing cotton and cellulose fibers in the textile industries. In general, the fiber materials are bound by the dyes' reactive groups, with the formation of covalent bonds. However, as reactive dyes are highly water soluble, they can also react with water to be transformed into their hydrolyzed form [1]. The main problem associated with the use of reactive dyes is their low affinity for fabrics and resulting in relatively high dye concentrations in textile wastewaters [2]. It is estimated that approximately 50% of an unbound reactive dye remains in the wastewater after the dyeing process [3]. The main problem associated with dyes are their degradation by-products, which can include a large variety of substituents in aromatic structures (e.g., amines) with a high potential to develop different types of cancer [4]. The treatment of textile effluents is complex owing to the presence of compounds of low biodegradability and/or non-biodegradability [5]. Thus, powerful oxidation methods are then needed to destroy these pollutants from wastewaters to avoid their dangerous effects on living beings.

Various physical, chemical, and biological methods have been used for the removal of textile dyes from wastewater. Advanced oxidation technologies (AOPs) are considered as a promising alternative to the conventional wastewater treatment technologies for textile dye degradation since they can eliminate non-biodegradable organic components and avoid the need to dispose of residual sludge [6]. Advanced oxidation processes rely on the formation of highly reactive hydroxyl ($^{\bullet}OH$, HR-AOPs) and sulfate ($SO_4^{\bullet-}$, SR-AOPs) radicals as intermediates which degrade even the most bio-recalcitrant molecules into biodegradable products. Based on energy applied to generate $^{\bullet}OH$ and $SO_4^{\bullet-}$ radicals, the AOPs can be classified as photochemical and non-photochemical processes. Due to its relatively high-water solubility and stability, as well as moderate cost, persulfate ($S_2O_8^{2-}$, PS) is becoming the commonly used precursor of $SO_4^{\bullet-}$ radicals. Sulfate radicals can be produced from the activation of PS by heat, transition metals, ultraviolet light, bases, and sonolysis [7]. In comparison with $^{\bullet}OH$ radicals, $SO_4^{\bullet-}$ radicals show higher reduction potential ($SO_4^{\bullet-}/SO_4^{2-}$, E = 2,5 3,1V) at pH 7 [8]. In the acidic pH range, both $^{\bullet}OH$ and $SO_4^{\bullet-}$ radicals show similar reduction potential [9]. Two sulfate radicals ($SO_4^{\bullet-}$) are formed when peroxydisulfate is activated by UV irradiation (reaction (1)).

$$S_2O_8^{2-} + h\upsilon \rightarrow 2SO_4^{\bullet-} \qquad (1)$$

It has been demonstrated that the conversion of $SO_4^{\bullet-}$ to $^{\bullet}OH$ is a pH dependent process, and becomes pronounced at alkaline pH values (i.e. pH > 8.5) (reactions (2) and (3)) [10].

$$\text{All pHs: } SO_4^{\bullet-} + H_2O \rightarrow SO_4^{2-} + {}^{\bullet}OH + H^+ \qquad (2)$$

$$\text{Alkaline pH: } SO_4^{\bullet-} + OH^- \rightarrow SO_4^{2-} + {}^{\bullet}OH \qquad (3)$$

Recently, identification of sulfate and hydroxyl radical yield in persulfate oxidation processes using chemical probe method, have been intensively investigated. The chemical probe method was developed based on the use of an excess of probe compounds and ensuring that all radicals were scavenged by probe compound. Generally, rate constant of $> 10^9$ $M^{-1}s^{-1}$ between probe compound and radicals should be achieved for their effective scavenging. Different compounds can be used in chemical probe method, such as anisole, benzoic acid, benzene, methanol, and phenol for scavenging of both radicals, and nitrobenzene and *tert*-butyl alcohol for effective quenching of hydroxyl radicals [10].

In this work, persulfate was activated with UV irradiation (254 nm) and used as a source of $^{\bullet}OH$ and $SO_4^{\bullet-}$ radicals. Textile azo dye Reactive Orange 16 was selected as target pollutant to explore the contribution rate of $^{\bullet}OH$ and $SO_4^{\bullet-}$ radicals at various pH values with two quenching agents (MeOH and TBA).

MATERIALS AND METHODS

Chemicals

Textile dye Reactive Blue 16 (dye content about 50 %) was purchased from Sigma-Aldrich (St. Louis, MO, USA) and used without further purification. Regent grade $K_2S_2O_8$ was provided by VWR (USA). Methanol (MeOH) and *tert*-butyl alcohol (TBA) were ACS reagent grade and supplied from Merck (Germany). All solutions were prepared with high water purity obtained from Smart2Pure system with a conductivity of 0.055 µSm^{-1} (Thermo Scientific, USA).

Degradation experiment

Degradation experiments were conducted in a batch photoreactor equipped with ten low pressure mercury lamps, emitting at 253.7 nm which were fixed in parallel at the top of the photoreactor. The distance between the solution surface and UV lamps was kept constant at 220 mm. On the surface of the solution, the light intensity was measured by a UV radiometer Solarmeter model 8.0 UVC (Solartech, USA). The scheme of photoreactor used for irradiation experiments is given elsewhere [11].

All experiments were carried out with 100 mL of working solution, with initial persulfate concentration of 1 mmol dm^{-3}, RO 16 dye concentration of 50 mg dm^{-3}, and at three initial pH values (3.0, 7.0 and 10.0) in glass Petri dishes. The effect of radical scavengers was investigated by spiking working solution with the calculated volume of MeOH and TBA solution to obtain their concentration of 100 mmol dm^{-3}. At predetermined intervals (2, 4, 6, 8, 10, 15, 20, 30 and 40 min) samples were collected and residual RO 16 concentrations were measured. All the tests were performed in triplicate and the average of the three values are presented.

Pseudo first order kinetic model, which can be described by equation (4), was used to follow the kinetic of RO 16 dye decolorization.

$$\ln\frac{c_t}{c_0} = -k_{app}t \tag{4}$$

where c_0 is the initial RO 16 dye concentration, c_t is RO 16 dye concentration at time t, k_{app} is the apparent rate constant, t is the irradiation time. In the case of RO 16 dye degradation, a straight line with $R^2 > 0.98$ was observed for all experiments, when $\ln c_t/\ln c_0$ was plotted against the time, which confirmed the proposed model.

Analytical methods

The residual RO 16 concentration was determined using UV-Vis spectrophotometry (UV 1800, Shimadzu, Japan). The pH of the RO 16 dye solution was adjusted by pH meter (Orion Star A214, Thermo Scientific, USA).

RESULTS AND DISCUSSION

Methanol and *tert*-butyl alcohol can be used as radical scavengers to distinguish the contribution of $SO_4^{\bullet-}$ and $^{\bullet}OH$ radicals during oxidative persulfate process. As illustrated in equations (5)–(6), the second-order reaction rate constants of MeOH with $SO_4^{\bullet-}$ and $^{\bullet}OH$ radicals are 1.1–3.2 x 10^7 $M^{-1}s^{-1}$ and 5.8–9.7 x 10^9 $M^{-1}s^{-1}$, respectively [12]. It is generally accepted that MeOH can be used as scavenger for both $SO_4^{\bullet-}$ and $^{\bullet}OH$ radicals. On the other side, the rate constants for reaction between *tert*-butyl alcohol and $^{\bullet}OH$ is significantly higher than that between *tert*-butyl alcohol and $SO_4^{\bullet-}$ radicals [10]. Thus, *tert*-butyl alcohol can be used as effective quencher for $^{\bullet}OH$ radicals (equations (7)–(8)).

$$^{\bullet}OH + MeOH \rightarrow \text{products},\ k = (1.1\text{–}3.2) \times 10^7\ M^{-1}s^{-1} \tag{5}$$

$$SO_4^{\bullet-} + MeOH \rightarrow \text{products},\ k = (5.8\text{–}9.7) \times 10^9\ M^{-1}s^{-1} \tag{6}$$

$$^{\bullet}OH + TBA \rightarrow \text{products},\ k = (3.8\text{–}7.6) \times 10^8\ M^{-1}s^{-1} \tag{7}$$

$$SO_4^{\bullet-} + TBA \rightarrow \text{products},\ k = (4\text{–}9.1) \times 10^5\ M^{-1}s^{-1} \tag{8}$$

As depicted in Figure 1a, the RO16 decolorization was inhibited in presence of MeOH at concentration of 100 mM at all studied pH values. The degradation rate constant od RO 16 dye reduced from 1.71 x10^{-2} min^{-1} to 0.62 x10^{-2} min^{-1} in acidic conditions, from 1.54 to 0.45 x10^{-2} min^{-1} at neutral conditions, and from 1.39 x10^{-2} min^{-1} to 0.12 x10^{-2} min^{-1} at basic conditions when the concentration of MeOH increased from 0 up to 100 mM.

Presence of *tert*-butyl alcohol also had negative impact on decolorization rate of textile dye RO 16 (Figure 1b). The degradation rate constant od RO 16 dye decreased from 1.71 x10^{-2} min^{-1} to 1.5 x10^{-2} min^{-1} in acidic conditions, from 1.54 to 1.2 x10^{-2} min^{-1} at neutral conditions, and from 1.39 x10^{-2} min^{-1} to 0.15 x10^{-2} min^{-1} at basic conditions when the concentration of *tert*-butyl alcohol increased from 0 up to 100 mM.

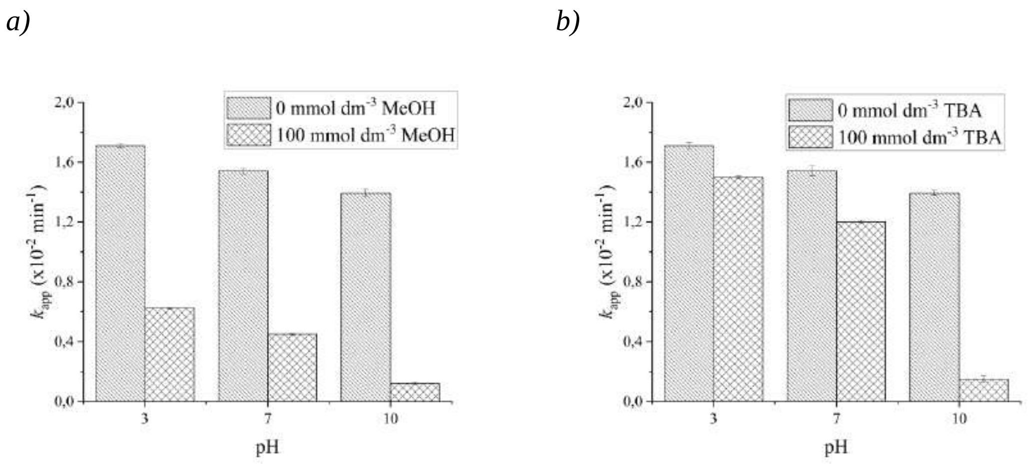


Figure 1 *Pseudo-first order constants of RO 16 dye decolorization in UV/$S_2O_8^{2-}$ process in presence of radical scavengers under various pH (3.0, 7.0 and 10.0) a) image left in presence of MeOH; b) image right in presence of TBA. c_0(RO 16) = 50 mgdm^3, c_0($S_2O_8^{2-}$) = 1 mmol dm^3, UV light intensity = 1950 µW cm^{-2}, temperature = 25 ± 0.5 ºC*

The relative contribution of $SO_4^{\bullet -}$ and $^{\bullet}OH$ radicals under various pH values can be calculated in sulfate-radicals based AOPs according to following equations (9) and (10) [13].

$$r_{\bullet OH} = \frac{k_{\bullet OH}}{k_{RO\,16}} = \frac{k_{RO\,16} - k_{RO\,16+TBA}}{k_{RO\,16}} \tag{9}$$

$$r_{SO_4^{-\bullet}} = \frac{k_{SO_4^{-\bullet}}}{k_{RO\,16}} = \frac{k_{TBA} - k_{RO\,16+MeOH}}{k_{RO\,16}} \tag{10}$$

where $r_{\bullet OH}$ (%) and $r_{SO_4^{\bullet -}}$ (%) are the contribution rates of $^{\bullet}OH$ and $SO_4^{\bullet -}$ to RO 16 degradation in UV/$S_2O_8^{2-}$ process, respectively. k_{RO16} (min^{-1}) is the degradation rate constant of RO 16 dye without scavenger in persulfate oxidation system, and $k_{RO16+TBA}$ (min^{-1}) and $k_{RO16+MeOH}$ (min^{-1}) are the degradation rate constants of RO 16 with TBA and MeOH in UV/$S_2O_8^{2-}$ process, respectively. Calculated contribution rates of $^{\bullet}OH$ radicals in degradation of textile dye RO 16 were 12%, 22% and 89% at pH values 3.0, 7.0 and 10.0, respectively, while contribution rates of $SO_4^{\bullet -}$ were 51%, 48% and 2% at acidic, neutral, and basic conditions. It is evident that both radicals took part in decolorization of textile dye RO 16 but their contribution depends on initial pH value of solution. The differences between contribution of $^{\bullet}OH$ and $SO_4^{\bullet-}$ radicals can be attributed to the interconversion of sulfate radicals at various pH values.

CONCLUSION

The use of a chemical probe method with MeOH and TBA is suitable way to assess the formation of $^{\bullet}OH$ and $SO_4^{\bullet-}$ radicals in UV activated persulfate. Results revealed that both radicals participated in decolorization of textile dye RO 16, since that decolorization rate decreased in presence of added scavenging agents. According to contribution rates of $^{\bullet}OH$ and $SO_4^{\bullet-}$ radicals, it can be concluded that $SO_4^{\bullet-}$ radicals were dominant at acidic, while $^{\bullet}OH$ radicals were dominant at alkaline conditions.

ACKNOWLEDGEMENT

The authors are grateful to the Ministry of Education, Science and Technological development of the Republic of Serbia for financial support (Agreement No 451-03-68/2022-14/200124).

REFERENCES

[1] J.M. Fanchiang, D.H. Tseng, Environ. Technol; 30 (2) (2009) 161–172.

[2] M. Siddique, R. Farooq, Z. Mehmood Khan, *et al.*, Ultrason. Sonochem; 18 (2011) 190–196.

[3] Z. He, S. Song, H. Zhou, *et al.*, Ultrason. Sonochem; 14 (2007) 298–304.

[4] J.R. Torres-Luna, R. Ocampo-Perez, M. Sanchez-Polo, *et al.*, Chem. Eng. J; 223 (2013) 155–163.

[5] R.M.R. Santana, L.C.V. Charamba, G.E.N. Nascimento, *et al.*, Water Air Soil Pollut; 230 (2019) 136.

[6] G. Boczkaj, A. Fernandes, Chem. Eng. J; 320 (2017) 608–633

[7] L.W. Matzek, K.E. Carter, Chemosphere; 151 (2016) 178–188.

[8] J. Sharma, I.M. Mishra, V. Kumar, J. Environ. Manage;156 (2015) 266–275.

[9] G.D. Fang, D.D. Dionysiou, Y. Wang, *et al.*, J. Hazard. Mater; 227–228 (2012) 394–401.

[10] C. Liang, H.-W. Su, Ind. Eng. Chem. Res; 48 (2009) 5558–5562.

[11] J. Mitrović, M. Radović, D. Bojić, *et al.*, J. Serb. Chem. Soc; 77 (4) (2012) 465–481.

[12] C. Ye, X. Ma, J. Deng, *et al.*, Chemosphere; 288 (2022) 132337.

[13] X. Liu, Y. Liu, S. Lu, *et al.*, Chem. Eng. J; 385 (2020) 123987.

ELECTROSYNTHESIZED CERIUM OXIDE CATALYST FOR ATMOSPHERIC PRESSURE PULSATING CORONA PLASMA DEGRADATION OF RB 5

Milica Petrović [1*], Tijana Jovanović [1], Saša Rančev[2], Miljana Radović Vučić[1], Jelena Mitrović[1], Slobodan Najdanović[1], Aleksandar Bojić[1]

[1]University of Niš, Faculty of Science and Mathematics, Department of Chemistry,
33 Višegradska str., 18000 Niš, SERBIA

[2]University of Niš, Faculty of Science and Mathematics, Department of Physics,
33 Višegradska str., 18000 Niš, SERBIA

[*]*milicabor84@gmail.com*

Abstract

Cerium oxide catalyst was synthesized by potentiostatic electrodeposition. It was characterized by SEM, EDX and XRD, and used for the degradation of Reactive Black 5 dye by atmospheric pressure pulsating corona plasma. The submicrocrystalline catalyst was composed of pure face-centred cubic CeO_2 *in the form of polyhedrons of different shapes and sizes, varying mainly between about 60 and 165 nm. The catalyst enhanced plasma dye degradation by promoting decomposition of plasma produced* H_2O_2 *into ·OH radical which degraded the dye. The degradation rate was enhanced about 2.5 times in the presence of catalyst. The reaction kinetics followed the pseudo – first order kinetics.*

Keywords: CeO_2, plasma, dye, catalysis, degradation

INTRODUCTION

Cerium oxide (CeO_2) have been investigated and applied as a catalyst in various photocatalytic degradations of harmful organic compounds which can potentially cause the environmental problem if present in wastewaters. CeO_2 catalytic potential is related to its crystal structure and the ability to easily lose lattice oxygen, which creates defects that further act as catalytic sites [1].

Several plasma techniques have been applied for degradation of various organic compounds, particularly dyes. It is based on exposure of the dye solution to plasma discharge, which generates reactive species from the gas or liquid, such as hydroxyl radical, OH, a powerful oxidant that degrades the dye. Recently, some metal oxides and ceramics were investigated as the potential plasma degradation catalysts [2–4].

In this work, CeO_2 was prepared by potentiostatic electrodeposition and used as the catalyst for atmospheric pressure pulsating corona plasma degradation of Reactive Blac 5 (RB 5) textile dye. CeO_2 was chosen because of many possibilities to adjust and control its properties due to its electronic structure. The role of the catalyst in the process and degradation kinetic were examined.

MATERIALS AND METHODS

Materials and methods

$Ce(NO_3)_3 \cdot 6H_2O$, RB 19, ethanol, HNO_3 and NaOH (Sigma Aldrich) were of reagent grade and used without further purification. All solutions were prepared with deionized water (18 MΩ).

Preparation and characterization of the catalyst

Electrodeposition was done in 0.25M $Ce(NO_3)_3 \cdot 6H_2O$ water-ethanol (1:1) solution using an Amel 510 DC potentiostat (Materials Mates, Italy), controlled by VoltaScope software, at 25 ± 0.5°C in one compartment three electrode cell using Ti sheet as a working electrode, a Pt as auxillary electrode and calomel reference electrode, at constant potential of of 1.40 V during 60 minutes. After deposition, the material was peeled of the electrode surface, rinsed with deionized water and dried in air at 100°C for 120 minutes.

For SEM analysis, samples were attached to aluminium stubs with Leit-c conductive carbon cement. Secondary electron images were collected with a Hitachi High Technologies SU8030 (Tokyo, Japan) field emission gun SEM operated at an accelerating voltage of 2 kV. Samples were imaged uncoated. EDX data was collected on the same instrument at 20 kV with a Thermo Scientific System 7 Ultradry EDX detector (Massachusetts, USA). Five random areas were analyzed on each sample. For XRD analysis, samples were packed into Si low background holders and data collected on a Bruker D8 Advance X-ray Diffractometer (Bruker-AXS, Germany) in theta-theta geometry in reflection mode. Data was collected between 10-80° 2θ using DIFFRAC plus XRD Commander version 2.6.1 software (Bruker-AXS), qualitative assessment with the aid of EVA version 5 (Bruker-AXS) and the PDF-2 2020 database (ICDD).

Dye degradation experiments

Plasma degradation experiments were done using the self-made open plasma reactor, based on atmospheric pressure non-thermal positive pulsating corona electrical discharge. Power supply contained DC pulse generator and high voltage output stage (the highest output voltage was 50 kV with respect to the ground level; maximal power output was 110 W). The multipoint anode was made of stainless steel needles. The reactor cell with the treated solutions (cathode) was of cylindrical shape with the electric contact at the bottom and it was directly exposed to the plasma discharge. The discharge current density was set to of 9.15 $\mu A\ cm^{-2}$ by changing the distance between multipoint anode and a liquid surface. Dye concentration was measured using UV-VIS spectrophotometer Shimadzu UV-1650 PC at 585 nm. Hydrogen peroxide was determined by iodometric method [5].

RESULTS AND DISCUSSION

Characterization of the catalyst

XRD pattern of CeO_2 (Figure 1a) consisted of sharp, narrow peaks which indicated a high crystallinity. The peaks positioned at 2θ of 28.52°, 33.02°, 47.24°, 56.07°, 58.87°, 69.11° and 76.26°, corresponding to (111), (222), (220), (311), (222), (400) and (331) planes respectively showed the presence of pure face-centred cubic (fluorite) structure of CeO_2 (PDF 67-0121).

The lattice parameter a, crystallite size, and cell volume were 5.4438 Å, 49.85, and 161.32 Å^3, respectively ($\alpha = \beta = \gamma = 90°$). No other crystalline phase was detected.

CeO_2-E (Figure 2a) consisted of polyhedrons of irregular shape and different size of 90 nm average (the size of polyhedrons varies between less than 60 nm and little more than 160 nm), with many seemed to be mutually sintered.

EDX analysis showed that the surface of CeO_2 catalyst contained Ce and O atoms with the Ce:O atomic ratio (%) of 29.64:70.36, which was close enough to theoretical value for stoichiometric CeO_2 (33.33:66.67). Higher content of oxygen might be due to adsorption of ambient water.

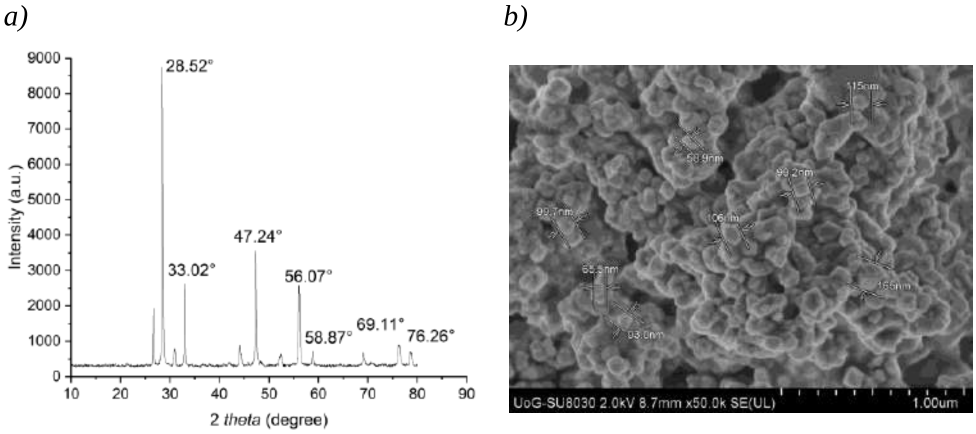


***Figure 1** a) XRD pattern and b) SEM micrograph of CeO_2 catalyst*

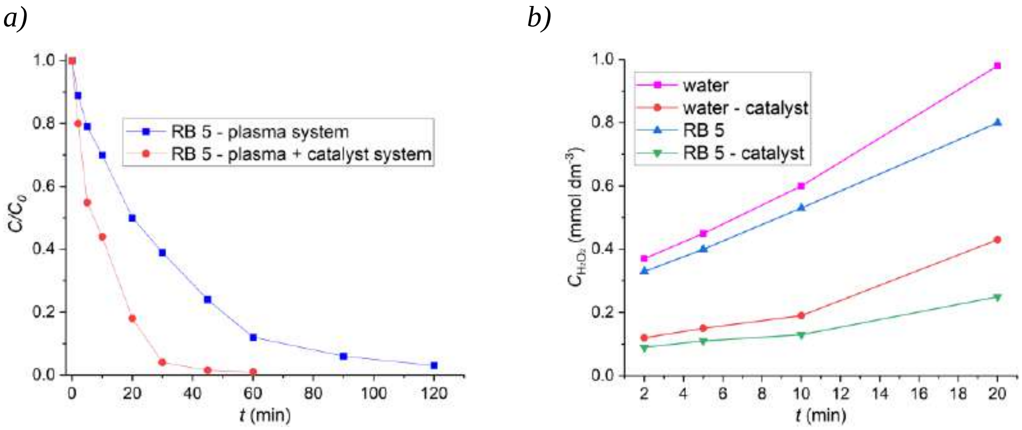


***Figure 2** a) Plasma degradation of RB 5 with and without a catalyst, b) Content of H_2O_2 in deionized water and RB 5 water solution during the plasma treatment with and without a catalyst*

Dye degradation

CeO_2 enhanced plasma degradation of a dye, which proceeded about 2.5 times faster in the presence of the catalyst (Figure 2a).

Plasma formation and decomposition of H_2O_2 and role of the catalyst

H_2O_2 was detected in plasma treated solutions, both with and without the catalyst. It was also detected in deionized water treated with plasma the same way (Figure 2b). H_2O_2 was formed in the reactions caused by the strikes of high energy species, such as positive ions and radicals, as well as the fast electrons, generated in the gas discharge zone and accelerated by the high voltage during the plasma treatment. The reactions which took place when those reactive species stroke the liquid surface can be represented by the equations 1 and 2 [2,3]:

$$H_2O + e^- \rightarrow \cdot H + \cdot OH + e^- \tag{1}$$

$$\cdot OH + \cdot OH \rightarrow H_2O_2 \tag{2}$$

The concentration of H_2O_2 increased both in the system with and without the catalyst. It was lower in dye solutions than in deionized water in both cases, which indicates that it was consumed during the dye degradation. H_2O_2 cannot degrade RB 5. The addition of DMSO, an ·OH scavenger, caused the drop of the reaction rate by almost 90% both with and without the catalyst, therefore, it was assumed that ·OH was the major dye degrading reagent and that it was formed by decomposition of plasma generated H_2O_2 during the treatment (equation 3).

$$H_2O_2 \rightarrow 2\cdot OH \tag{3}$$

The increase of H_2O_2 concentration was lower in the system with the catalyst (Figure 2b) but, at the same time, the dye degradation rate was higher. This indicates that the catalyst consumed H_2O_2 molecules, producing more ·OH radicals for the dye degradation. During the plasma treatment, ion wind provided a constant motion of the catalyst particles and their good distribution in the bulk and at the surface of a liquid. Catalyst particles at the surface could be excited by the strikes of active species, generated in plasma discharge gap (gas between anode and liquid surface – cathode) and accelerated toward liquid by the electric field [6]. Such strikes could induce the electron (e^-) - hole (h^+) pair formation, i.e., the excitation of the catalyst [7,8]. The streamers with the energies of 1-10 eV propagated through the air in the discharge zone, reached the liquid surface and bulk, stroke the catalyst, and caused its excitation as well [9]. Once formed, the electrons and holes reacted with the present H_2O_2, decomposing it to ·OH radicals, which further attacked the dye:

$$e^- + H_2O_2 \rightarrow \cdot OH + OH^- \tag{4}$$

$$h^+ + H_2O \rightarrow \cdot OH + H^+ \tag{5}$$

$$\cdot OH + \text{dye} \rightarrow \text{degradation products} \tag{6}$$

Degradation kinetics

Linear decrease of ln (C/C0) in the function of time, indicates that plasma catalytic degradation followed the pseudo-first order kinetics, which is described by the equation:

$$\ln(C/C_0) = -kt \qquad (7)$$

where C_0, C, and k are the initial dye concentration, dye concentration after reaction time t, and the reaction rate constant (min^{-1}), respectively (Figure 3).

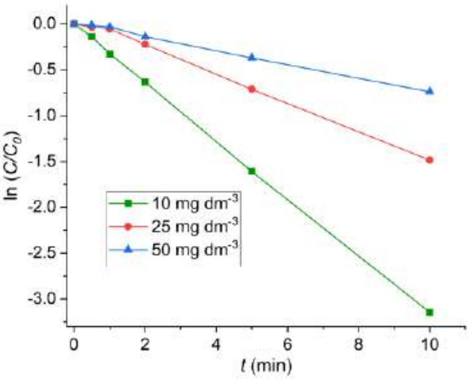


***Figure 3** Pseudo-first order kinetics for catalytic plasma degradation of RB 5*

Reaction rate constants decreased with the increase of the initial dye concentration, being 0.3157, 0.1530 and 0.0760 min^{-1} for the C_0 of 10, 25 and 50 mg dm^{-3}, respectively, with the R^2 values of 0.998, 0.997 and 0.996 for the same C_0 values, respectively. The pseudo-first order kinetics is in accordance with the literature data concerning plasma catalytic degradation of dyes [4], which further confirms that the degradation proceeded via ·OH radicals.

CONCLUSION

Electrosynthesized CeO_2 submicrocrystalline catalyst enhanced the plasma degradation of RB 5 dye by more than 2.5 times. Degradation proceeded mostly via oxidation of a dye by the ·OH radicals, generated by plasma decomposition of the plasma generated H_2O_2. The catalyst enhanced the degradation process by enhancing the decomposition of H_2O_2, and therefore, the formation of ·OH radicals on its active sites. Degradation reactions followed the first order kinetic model.

ACKNOWLEDGEMENT

The authors would like to acknowledge financial support from the Ministry of Education, Science and Technological Development of the Republic of Serbia (Agreement No 451-03-68/2022-14/200124).

REFERENCES

[1] M. Kurian, J. Environ. Chem. Eng; 8 (2020) 104439.

[2] M.R. Ghezzar, F. Abdelmalek, M. Belhadj, *et al*., J. Haz. Mat; 164 (2009) 1266–1274.

[3] H. Hentit, M.R. Ghezzar, M. Womes, *et al*., J. Mol. Catal. A: Chem; 39 (2014) 37–44.

[4] K.N. Pandiyaraj, D. Vasu, M.C. Ramkumar, *et al*., Sep. Purif. Technol; 258 (2021) 118037.

[5] S. Ziembowicz, M. Kida, P. Koszelnik, Proceedings of the 2nd International Electronic Conference on Water Sciences, 16–30 November, 2, 2017, 188–198.

[6] A. Bogaerts, X. Tu, R.C.Whitehead, *et al*., J. Phys. D: Appl. Phys; 53 (2020) 443001.

[7] A. Rousseau, O. Guaitella, L. Gatilova, *et al*., Appl. Phys. Lett; 87 (2005) 221501–3.

[8] A. Abroyan, M.A. Eremeev, N.N. Petrov, Sov. Phys. Usp; 10 (1967) 332–367.

[9] P.J. Bruggeman, M.J. Kushner, B.R. Locke, *et al*., Plasma Sources Sci. Technol; 25 (2016) 053002–59.

PHOTOCATALYTIC DEGRADATION OF RANITIDINE BY BISMUTH OXO CITRATE

Slobodan Najdanović[1*], Milica Petrović[1], Miloš Kostić[1], Nena Velinov[1], Jelena Mitrović[1], Danijela Bojić[1], Aleksandar Bojić[1]

[1]University of Niš, Faculty of Sciences and Mathematics, Department of Chemistry,
Višegradska 33, 18000 Niš, SERBIA

[*]*najda89@gmail.com*

Abstract

Bismuth oxo citrate (BioxoCit) was synthesized by precipitation method following by the thermal treatment at 200 ºC. It was characterized by SEM-EDX, XRD, FTIR and nitrogen adsorption/desorption methods. Morphologically, it is composed of polyhedrons of different sizes and shapes with a smooth surface. The specific surface area of BioxoCit was 8.92 m^2 g^{-1}*. The obtained BioxoCit was applied as photocatalyst for the degradation of ranitidine. The results showed that 88.01% of ranitidine concentration of 50 mg* dm^{-3} *was degraded during the 30 min of photocatalytic treatment.*

Keywords: material synthesis, precipitation, characterization, pharmaceuticals, water treatment

INTRODUCTION

A vast collection of pharmaceuticals has been found in the drinking water supplies and wastewaters. As some of these compounds remain intact from conventional treatment plants, they pose a serious environmental problem [1].

Ranitidine is histamine H_2 receptor antagonist, and which is prescribed for the treatment of peptic ulcer and gastroesophageal reflux. Because ranitidine cannot be fully absorbed and metabolized, approximately 70% of the drug dose is excreted in the urine as unchanged drug [2].

Advanced oxidation processes (AOPs) were extensively considered as promising technologies for the degradation of organic contaminant [3]. Among AOPs, heterogeneous photocatalysis is based on the ability of certain semiconductor materials (photocatalysts) to generate hydroxyl and other reactive radicals under the radiation. The photocatalytic process can achieve complete mineralization of pollutants to carbon dioxide, water and inorganic salts [4].

The aim of this study was the synthesis and characterization of photocatalysts based on bismuth oxo citrate and its application for ranitidine degradation.

MATERIALS AND METHODS

Synthesis of photocatalyst

The synthesis of photocatalysts was performed by precipitation from a solution of bismuth nitrate, which was obtained by dissolving 4.0 g of bismuth nitrate in 20.0 cm^3 of nitric acid concentration of 2.0 mol dm^{-3}. Then, 6.0 cm^3 of ethylene glycol, 1.6 g of citric acid and 60.0 cm^3 of deionized water were added to the bismuth nitrate solution. After that, NaOH solution (4.0 mol dm^{-3}) was added dropwise, the pH was adjusted to 3.5 and the solution was stirred for 180 min. The pH of the solution was maintained at 3.5 during all 180 min of stirring. Adjusting the pH to 3.5 causes formation of a precipitate. The obtained precipitate was washed several times with warm deionized water, separated by centrifugation, and dried in a laboratory dryer for 6 h at 80 ºC. After that, thermal treatment was performed in the air atmosphere at 200 ºC for 60 min with a heating rate of 15 ºC min^{-1}. After the thermal treatment, the materials were cooled to room temperature and ground to a powder, after which they were ready for use in photocatalytic processes.

Photocatalytic treatment procedure for RB19 dye degradation

The photocatalytic activity of the obtained material was determined by decolorization of aqueous solutions of textile dye RB19. Photochemical experiments were performed in a photoreactor with a radiation intensity of 1950 μW cm^{-2} with a maximum emission at 253.7 nm. Photocatalytic treatment was performed by transferring 50.0 cm^3 of the working solution to a Petri dish, which was placed on a magnetic stirrer in a UV photoreactor. An appropriate dose of photocatalyst was added to the solution and photocatalytic treatment was started. 4.0 cm^3 of solution was taken after 0, 1.0, 2.0, 4.0, 6.0, 10.0, 15.0 and 30.0 min of treatment. All samples were filtered through a regenerated cellulose membrane filter with a pore size of 0.45 μm (Agilent Technologies, Germany) to remove any photocatalyst particles that may interfere with the measurement of absorbance on a UV-Vis spectrophotometer. The concentration of RB19 in the samples was determined using a UV-Vis spectrophotometer UV-1800 (Shimadzu, Japan), by measuring the absorbance of the solution at 313 nm. The photocatalytic activity of the material was determined based on the decolorization efficiency (*DE*, %) of RB19, which was calculated according to the equation:

$$DE = \frac{c_0 - c_\mathrm{t}}{c_0} \cdot 100\%$$

where: c_0 is initial concentration of dye in solution (mg dm^{-3}), and c_t is concentration of dye (mg dm^{-3}) at a certain time t (min).

Characterization of the photocatalyst

Morphology and chemical composition of the material surface were determined by SEM-EDX analysis on a scanning electron microscope with electron beam with cold-cathode emission field SU8030 (Hitachi, Japan) and a system for semi-quantitative EDX analysis Noran NSS 7 (Thermo-scientific, USA) with ultra-dry X-ray detector.

N_2 adsorption/desorption measurements were performed on a Gemini 5 Surface Area Analyzer (Micromeritics, USA). Prior to measurement, the samples were degassed in a stream of nitrogen at a pressure of about 0.1 Pa and a temperature of 40 ºC for 20 h. The specific surface area of the material was determined by the BET model [5], while the BJH model was used to determine the diameter, surface area and volume of the pores [6].

The crystal structure of the material was determined by X-ray diffraction on an Ultima IV powder diffractometer (Rigaku, Japan). For X-ray diffraction analysis, filtered Cu Kα (λ = 1.5406 nm) radiation generated at a current of 40 mA and a voltage of 40 kV was used. The experiments were performed in the scan range $2\theta = 5–90°$, with a scan speed of 5° min^{-1} and a step of 0.02° θ. Prior to measurement, angular correction was performed using a high-quality crystalline Si standard.

FTIR analysis was used for qualitative analysis of functional groups and structural characterization of materials. The BOMEM MB-100 FTIR spectroscope (Hartmann & Braun, Canada) was used to record the FTIR spectrum. FTIR spectra were recorded by transmission technique in the spectral range 4000–400 cm^{-1}, at a resolution of 2 cm^{-1}, with 16 scans to eliminate noise.

Elemental (CHNS/O) analysis of the material determined the chemical composition of the material, i.e., the percentage of carbon, hydrogen, nitrogen, sulfur, and oxygen in the dry sample. Sample analysis was performed using a 2400 Series II CHNS/O Elemental Analyzer (Perkin-Elmer, USA) using acetanilide as a standard.

RESULTS AND DISCUSSION

SEM analysis

Surface morphology is a very important characteristic of photocatalysts because the process of photocatalysis mostly takes place at the contact of the liquid-solid phases [7]. SEM micrographs of the BioxoCit photocatalyst obtained by the precipitation method are shown in Figure 1.

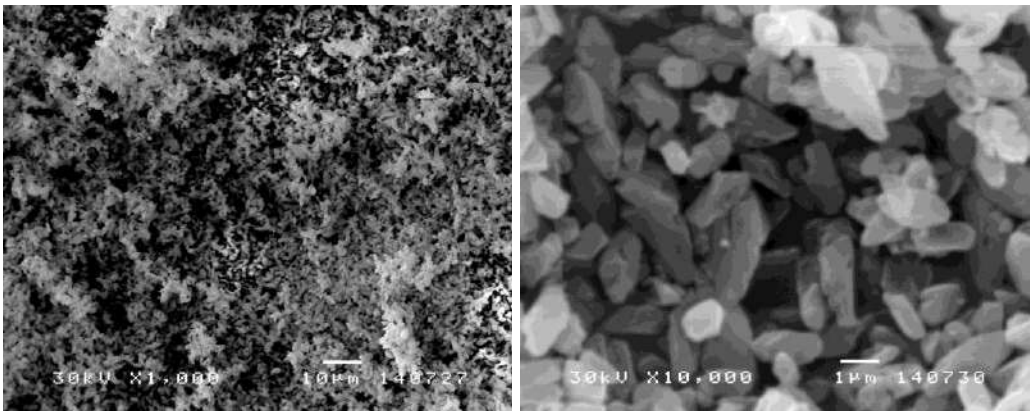


***Figure 1** SEM micrographs of the BioxoCit surface at magnifications: a) x1000 b) x10000*

Based on SEM analysis, it can be concluded that the material consists of polyhedral particles of different irregular shape and size. Their length varies between 0.5 µm and 3.0 µm, and the thickness between 0.3 µm and 1.0 µm. The resulting polyhedrons have a seemingly smooth surface. Some polyhedrons appear to be partially sintered, probably due to thermal treatment at 200 ºC. Overall, the morphology of the obtained material gives a visual impression of high crystallinity.

N_2 adsorption/desorption method

The N_2 adsorption/desorption isotherm of BioxoCit, shown in Figure 2, belongs to type IV according to the IUPAC classification. A hysteresis loop occurring in the relative pressure range of 0.76 to 1.0 indicates that the resulting material is mesoporous. The specific surface area of the photocatalyst determined by the BET model is 8.92 $m^2\ g^{-1}$. The results obtained by the BJH model show that the photocatalyst contains a mesopores, the presence of which has a significant impact on improving the photocatalytic performance of the material. The pore surface area obtained by the BJH model is 8.17 $m^2\ g^{-1}$, the pore volume is 0.032 $cm^3\ g^{-1}$, with the average pore diameter of 16.0 nm.

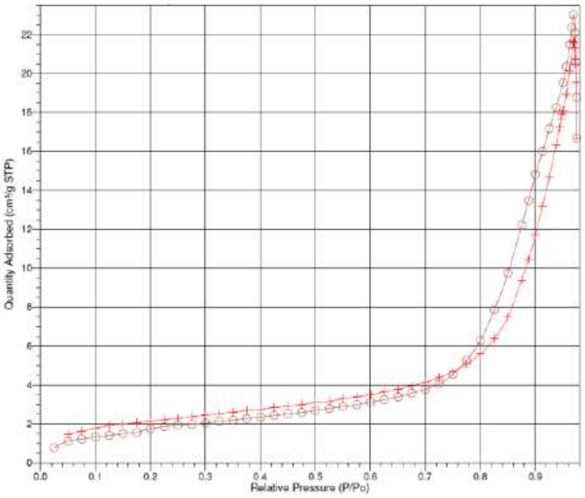


Figure 2 *N_2 adsorption/desorption isotherm of BioxoCit*

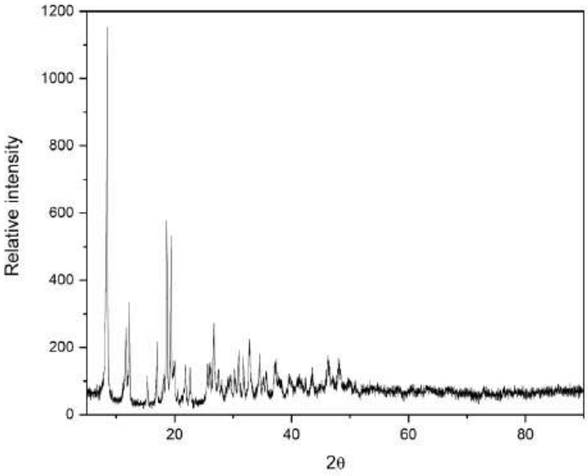


Figure 3 *XRD pattern of the BioxoCit*

XRD analysis

The results of the XRD analysis, shown in Figure 3, indicate that the synthesized photocatalyst is bismuth-oxo-citrate, most likely in the form of $BiOC_6H_7O_7 \cdot H_2O$. This is indicated by diffraction maxima with *d* values equal to 10.26, 5.63, 4.64, 3.92, 3.37 and 2.11 Å, which coincide with the already published results for this compound [8]. The peaks are sharp, indicating that the resulting BioxoCit is completely crystallized. The amorphous phase was not detected by XRD analysis. The crystallite size, determined by the Scherer method based on the peak width at the half-height of the maximum, is 50.2 nm.

FTIR analysis

Since XRD analysis determined that the photocatalyst was chemically bismuth oxo citrate, FTIR analysis was necessary to confirm the presence of functional groups characteristic of this compound.

The bands in the FTIR spectrum of BioxoCit (Figure 4) at 1642 and 1536 cm^{-1} correspond to asymmetric valence vibrations of carboxyl groups ν_{as} (–COO–), and the band at 1426 cm^{-1}

corresponds to symmetric valence vibrations of carboxyl groups ν_s (–COO–). These bands prove the presence of citrate, in the form of bismuth-oxo-citrate salt [8].

Other characteristic absorption bands are bands in the range of 800–300 cm^{-1} that can be attributed to valence vibrations of Bi–O bonds, and bands of medium intensity at 630, 561, 507 and 403 cm^{-1} that are attributed to valence vibrations of the Bi–O bond [9].

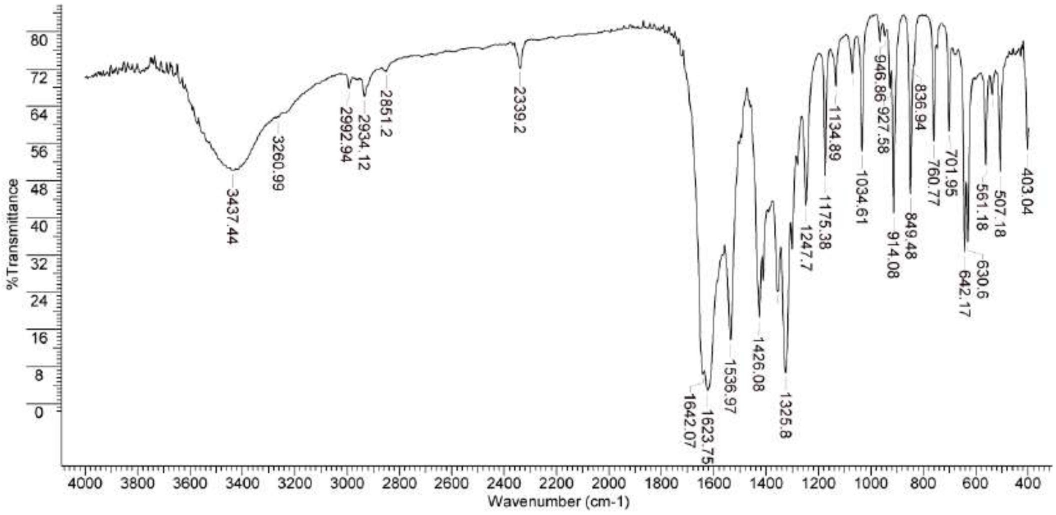


Figure 4 *FTIR spectrum of the BioxoCit*

EDX and CHNS/O analysis

Semi-quantitative EDX analysis showed that the weight percentage of elements Bi, O and C are 50.30%, 35.51% and 14.19%, respectively. CHNS/O analysis showed that weight percent of C and H are 16.03% and 1.93%, respectively. This is a good agreement between the obtained results and the theoretical values of the weight percentages of elements in $BiOC_6H_7O_7 \cdot H_2O$, which is another confirmation of the structure of the obtained photocatalyst.

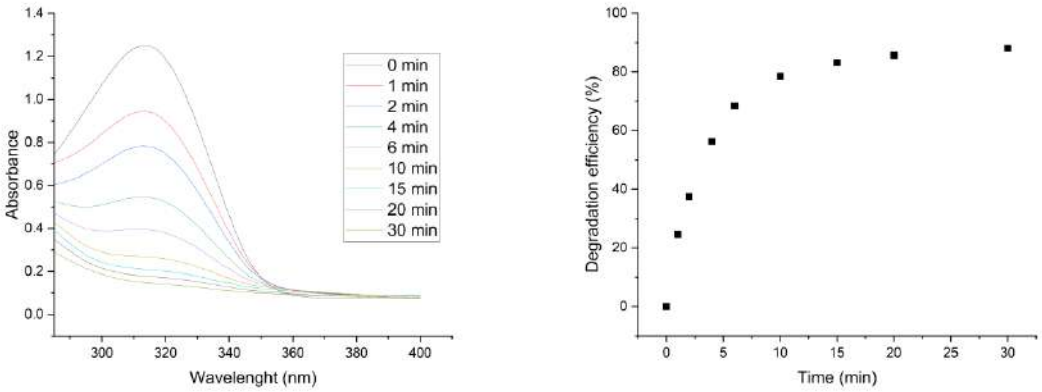


Figure 5 *UV-Vis spectrum of ranitidine and degradation efficiency during the photocatalytic treatment:* $c_{ranitidine}$ *50 mg dm*$^{-3}$*, BioxoCit dose 500 mg dm*$^{-3}$*, native pH, temperature 20.0 ± 0.5 ºC, UV light intensity 1950 µW cm*$^{-2}$

The photocatalytic activity of BioxoCit

The photocatalytic activity of the obtained BioxoCit was investigated in the process of photocatalytic degradation of ranitidine. Figure 5 show the results of ranitidine degradation during the photocatalytic process.

The results show that the absorption peak of ranitidine in the UV region decreases rapidly during photocatalytic treatment. During 30.0 minutes of treatment, the efficiency of ranitidine degradation was 88.01%, which is a very good result considering the high concentration of ranitidine in the initial solution. Such high concentrations of ranitidine were taken to show the photocatalytic performance of BioxoCit, although they do not occur in real conditions.

CONCLUSION

In summary, during this study, the BioxoCit synthesis process via precipitation method was successfully developed. The chemical, morphological and textural properties of the BioxoCit were determined by material characterization. The obtained material showed exceptionally good photocatalytic performance during the treatment of ranitidine degradation. In a relatively short time (30.0 min), this photocatalyst successfully degraded the high concentration of ranitidine (44.05 mg dm^{-3}). Overall, given the simple way of synthesis, low cost and environmentally friendly starting materials, high efficiency, BioxoCit could be a promising material for the degradation of ranitidine from aqueous solutions.

ACKNOWLEDGEMENT

The authors would like to acknowledge financial support from the Ministry of Education, Science and Technological Development of the Republic of Serbia (Agreement No 451-03-68/2022-14/200124).

REFERENCES

[1] P.H. Chang, J. Guo, J. Li, *et al.*, Colloids Surfaces A Physicochem. Eng. Asp; 639 (2022) 128395.

[2] Y. Ma, B. Ji, X. Lv, *et al.*, Chem. Eng. J; 435 (2022) 135126.

[3] Y. Ma, H. Wang, X. Lv, *et al.*, Chem. Eng. J; 443 (2022) 136495.

[4] F. Ghanbari, M. Moradi, Electrooxidation Processes for Dye Degradation and Colored Wastewater Treatment, Advanced Nanomaterials for Wastewater Remediation, Eds. Boca Raton: CRC Press, (2016) 61–108.

[5] S. Brunauer, P.H. Emmett, E. Teller, J. Am. Chem. Soc; 60 (2) (1938) 309–319.

[6] E.P. Barrett, L.G. Joyner, P.P. Halenda, J. Am. Chem. Soc; 73 (1) (1951) 373–380.

[7] W. Xiaohong, Q. Wei, L. Li, *et al.*, Catal. Commun; 10 (5) (2009) 600–604.

[8] E.S. Naydenko, Y.M. Yukhin, L.I. Afonina, Chem. Sustain. Dev; 20 (2012) 189–196.

[9] V. Fruth, M. Popa, D. Berger, *et al.*, J. Eur. Ceram. Soc; 24 (2004) 1295–1299.

CAFFEINE AS A GREEN CORROSION INHIBITOR FOR COPPER IN SYNTHETIC BLOOD PLASMA SOLUTION

Ana Simonović[1*], Žaklina Tasić[1], Milan Radovanović[1], Marija Petrović Mihajlović[1], Milan Antonijević[1]

[1]University of Belgrade, Technical Faculty in Bor, V.J. 12, 19210 Bor, SERBIA

[*]*asimonovic@tfbor.bg.ac.rs*

Abstract

Caffeine as a green inhibitor for copper in synthetic blood plasma solution was investigated. Potentiodynamic measurements and open circuit potential measurements were used to study caffeine as a corrosion inhibitor of copper. Gathered results point out that caffeine has a good inhibitory characteristic. Adsorption of caffeine on the copper surface, which is important in the inhibition mechanism, follows Langmuir adsorption mechanism.

Keywords: caffeine, blood plasma solution, copper, corrosion inhibition

INTRODUCTION

Copper is relatively noble metal that does not corrode readily unless some oxidizing agent or oxygen is present. That is the reason for its wide use in the manufacturing of electronics, thermal exchangers, and electrical conductors [1]. To protect metals and alloys surfaces from corrosion caused by aggressive ions suitable inhibitor can be applied.

In order to protect the metal surface in aggressive media, various organic substances are used which block reactive sites on copper surface [2]. Literature data showed that most effective inhibitors of corrosion are the organic molecules consisting of a π-system and/or containing atoms such as nitrogen, oxygen or sulphur in their molecule structures [3–5]. The inhibition mechanism can take place through two processes either by forming a protective tin film via inhibitor adsorption or by forming a precipitate on the surface of the electrode [6].

This paper deals with corrosion inhibitory effect of different concentrations of caffeine on copper electrode in blood plasma solution.

MATERIALS AND METHODS

The solutions used were made from chemicals p.a. cleanliness. Synthetic blood plasma solution (BM-3) was used as the base during the study, while caffeine played the role of inhibitor (1,3,7-trimethylxanthine) of the following concentrations $1.0 \cdot 10^{-2}$ M, $5.0 \cdot 10^{-3}$ M, $1.0 \cdot 10^{-3}$ M and $5.0 \cdot 10^{-4}$ M.

By diluting the caffeine solution with a concentration of $1.0 \cdot 10^{-2}$ M by adding the BM-3 stock solution, a series of lower concentration inhibitor solutions was obtained. The composition of the artificial blood plasma solution (BM-3) is shown in Table 1.

Table 1 *Compounds that are part of the BM-3 solution, shown in grams*

Compound	Mass (g)
NaCl	4.7865
KCl	0.3975
$MgCl_2 \cdot 6H_2O$	0.1655
$CaCl_2 \cdot 2H_2O$	0.2646
$NaHCO_3$	3.7005
$NaH_2PO_4 \cdot H_2O$	0.1250

Electrochemical measurements were performed in a three-electrode system. All electrochemical tests were conducted on potentiostat (IVIUMSTAT XRe, IVIUM Technologies) with the appropriate software. Electrochemical methods applied for investigation were: open circuit potential (OCP), linear potentiodynamic polarization (LV) and cyclic potentiodynamic voltammetry (CV). All measurements were performed at room temperature.

The open circuit potential was determined in 30 minutes, after which measurement of linear voltammetry was continued from the value of the open circuit potential to -0.300 V_{SCE} while in the cathodic direction and up to 0.300 V in the anodic direction. The rate of potential change in LV was 1 mV/s. In cyclic voltammetry, the polarization curves were recorded in the potential interval of -1.000 V_{SCE} to 1.000 V_{SCE}. These measurements were performed at a scan rate 10 mV/s. The potential is expressed in relation to the saturated calomel electrode.

RESULTS AND DISCUSSION

Open circuit potential

Open circuit potential (OCP) was determined prior to the potentiodynamic polarization of copper electrode. From Figure 1 it is obvious that the addition of caffeine leads to the potential shift towards more positive values of potential and this is attributed to the improved corrosion resistance because of adsorption and formation of protective layer on the copper electrode surface [7].

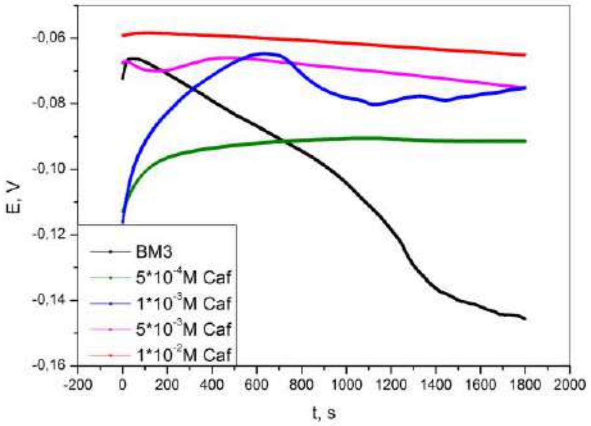


Figure 1 *The open circuit potential of copper electrode in BM-3 solution without and with the addition of different concentrations of caffeine*

Since the shifted values of the open circuit potential are shifted less than 85 mV, it can be concluded that caffeine as copper corrosion inhibitor can be considered as mixed-type inhibitor [8].

The cyclic voltammetry measurements

In order to test the behaviour of copper in solution of the artificial blood plasma with and without the presence of caffeine, voltammograms were recorded and presented in Figure 2. Results indicated that the presence of different concentrations of the used inhibitor has the effect of reducing the current density that is particularly pronounced at higher concentrations, which can be explained by the formation of protective film on the copper surface [2]. Figure 2 also showed that in the positive sweep, pitting corrosion occurs. Literature data indicate that pitting corrosion occurs when there is a sudden increase in current density and when the reverse current density is greater in the reverse sweep than in the positive sweep in the anodic region [9].

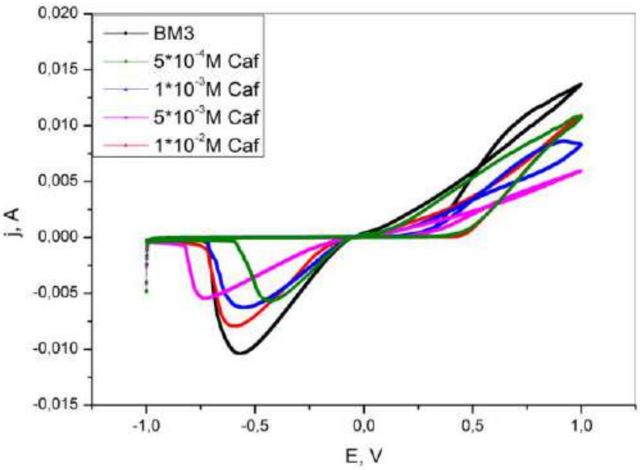


Figure 2 *Cyclic voltammetry curves recorded for copper in artificial blood plasma without and with the addition of caffeine*

Linear potentiodynamic polarization

Figure 3 presents the potentiodynamic polarization curves obtained after the determination of OCP. Potentiodynamic polarization curves for copper were recorded in blank BM-3 solution and in presence of caffeine as corrosion inhibitor.

Applied caffeine as a corrosion inhibitor leads to decrease of the current density value suggesting that caffeine is adsorbed on the copper surface and hinders anodic and cathodic reactions. All electrochemical corrosion parameters were calculated by potentiodynamic polarization curves, which are shown in Figure 3.

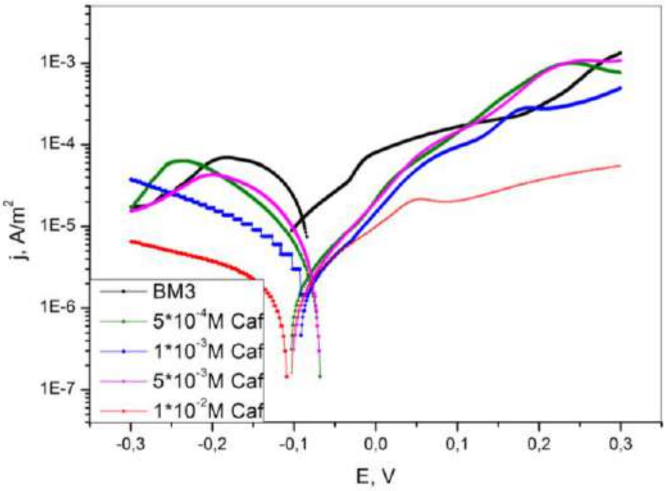


Figure 3 *Potentiodynamic polarization curves of copper in BM-3 solution without and with the addition of different concentrations of caffeine*

Inhibition efficiency was calculated from the linear voltammograms according to the following equation:

$IE = ((j_{corr} - j_{inh})/j_{corr})\cdot 100\ [\%]$ (1)

where j_{corr} and j_{inh} are corrosion current densities for basic BM-3 solution and with the addition of caffeine.

Table 2 *Electrochemical parameters and inhibition efficiency of copper corrosion in BM-3 solution without and with the addition of different concentrations of caffeine*

Solution	**E_{corr} (V)**	**$j_{corr}\cdot 10^6$ (A)**	**IE (%)**
BM-3	-0.0898	23,30	/
Caffeine $5\cdot 10^{-4}$	-0.0775	3.991	82.87
Caffeine $1\cdot 10^{-3}$	-0.0816	3.701	84.12
Caffeine $5\cdot 10^{-3}$	-0.0807	3.578	84.64
Caffeine $1\cdot 10^{-2}$	-0.0848	2.429	96.64

The adsorption mechanism-the adsorption isotherm

The adsorption mechanism is investigated by application of Langmuir adsorption isotherm. The adsorption of the inhibitor on the copper electrode surface could be observed as the adsorption of caffeine at the copper solution interface and substitution process between the organic compound from the aqueous medium and the water molecules associated with the metal surface:

$Inh_{(sol)} + xH_2O_{ads} \rightarrow Inh_{ads} + xH_2O$ (2)

where "x" is the number of water molecules replaced by the adsorption of one caffeine molecule [10].

Gibbs free energy of adsorption was calculated according to the equation:

$-\Delta G = [\ln K_{ads} - \ln(1/55.55)]RT$ (3)

where R stands for the universal gas constant (J/Kmol) and T is the thermodynamic temperature (295 K).

The value of calculated Gibbs free energy of caffeine adsorption on copper electrode surface was -31.80 kJ/mol, which indicates strong adsorption of caffeine on copper surface.

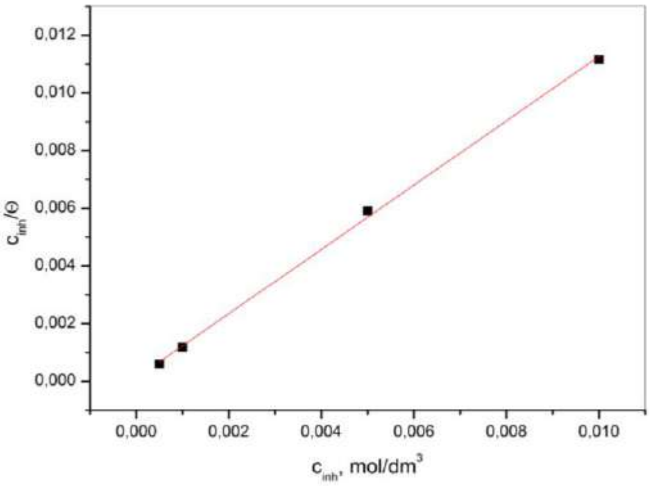


Figure 4 *Langmuir adsorption isotherm of caffeine on the copper surface*

CONCLUSION

According to the results caffeine can be applied as copper corrosion inhibitor taking into account value of inhibition efficiency when highest concentration of caffeine was applied. The potentiodynamic polarization measurements lead to conclusion that this organic molecule act as a mixed type of inhibitor. The adsorption of caffeine had been found to be obeying Langmuir adsorption isotherm. The negative value of Gibbs free energy points to fast and spontaneous adsorption. This research reveals that caffeine is environmentally friendly and effective inhibitor.

ACKNOWLEDGEMENT

The research presented in this paper was done with the financial support of the Ministry of Education, Science and Technological Development of the Republic of Serbia, within the funding of the scientific research work at the University of Belgrade, Technical Faculty in Bor, according to the contract with registration number 451-03-68/2022-14/200131.

REFERENCES

[1] A. Ali Mahmoud, M. Ouf Abdulfattah, A. El-Hossiany, *et al.*, Biointerface Res. Appl. Chem; 12 (4) (2022) 5116–5130.

[2] A.T. Simonović, Ž.Z. Tasić, M.B. Radovanović, M.B. Petrović Mihajlović, M.M. Antonijević, ACS Omega; 5 (22) (2020) 12832–12841.

[3] A.K. Maayta, N.A.F. Al-Rawashdeh, Corros. Sci; 46 (2004) 1129–1140.

[4] M. Petrović, A. Simonović, M. Radovanović, *et al.*, Chem. Pap; 66 (2012**)** 664–676.

[5] A.M. Ridhwan, A.A. Rahim, A.M. Shah, Int. J. Electrochem. Sci; 7 (2012) 8091-8104.

[6] M. Scendo, Corros. Sci; 49 (2007) 3953–3968.

[7] E.-S.M. Sherif, R.M. Erasmus, J.D. Comins, Electrochim. Acta; 55 (2010) 3657–3663.

[8] E.S. Ferreira, C. Giacomelli, F.C. Giacomelli, A. Spinelli, Mater. Chem. Phys; 83 (2004) 129–134.

[9] H. Bi, G.T. Burstein, B.B. Rodrigez, *et al*., Corros. Sci; 102 (2016) 510–516.

[10] P. Thanapackiam, S.K.M. Rameshkumar, S.S. Subramanian, Anti-Corros. Method M; 64 (2017**)** 92–102.

RECYCLING GOLD FROM WASTE PRINTED CIRCUIT BOARDS

Dragana Medić[1*], Snežana Milić[1], Slađana Alagić[1], Maja Nujkić[1], Aleksandra Papludis[1], Stefan Đorđievski[2], Silvana Dimitrijević[2]

[1]University of Belgrade, Technical Faculty in Bor, V.J. 12, 19210 Bor, SERBIA

[2] Mining and Metallurgy Institute Bor, Zeleni Bulevar 35, 19210 Bor, SERBIA

[*]*dmedic@tfbor.bg.ac.rs*

Abstract

The rapid growth of the world's population and the permanent need of modern consumer society for more energy-efficient products, have led to the accumulation of electronic waste. In order to protect the environment and preserve the concept of sustainability, intensive work has been done in recent years on the development of recycling technologies. Among the numerous components of discarded electronic devices, printed circuit boards stand out for their high content of precious metals. This paper provides an overview of previous research in the field of hydrometallurgical process, such as gold recovery from waste printed circuit boards. Therefore, solutions containing cyanides, thiosulfates, thiourea, halides, and aqua regia are used for gold leaching from waste printed circuit boards. However, due to the high toxicity and possible side effects on the environment and human health, research has focused on the use of non-cyanide solutions in recent years.

Keywords: waste printed circuit boards, recycling, leaching, gold, non-cyanide solutions

INTRODUCTION

The development of the electronics industry has led to increased demand for precious metals. Since the annual need for gold exceeds the capacity of mining, the lack of gold is compensated by recycling [1]. Cyanide solutions are most often used in primary production (mining) for leaching gold ores. From the obtained leach solutions, gold is recovered by the method of adsorption on activated carbon, followed by stripping steps, before gold metal is deposited by electrowinning or cementation [2]. Primary gold production using cyanide solutions leads to increased emissions of hydrogen cyanide, as well as the production of huge amounts of tailings, given the low concentrations of gold in minerals [3]. The production of gold from secondary sources is accompanied with huge energy savings, which is a consequence of the chemical composition of electronic waste. On average, waste printed circuit boards (PCBs) contain 40% metal, 30% plastic and 30% ceramic [4]. Ventura *et al*. [5] in their study state that 1 t of waste PCBs can contain 250 g of gold, which is a significantly higher share of metal compared to gold ore, where average gold concentrations range from 1–10 g/t ore. The following methods are used in the process of gold recovery from waste PCBs: hydrometallurgy, bio-hydrometallurgy, pyrometallurgy and physical-mechanical methods. Compared to other methods, hydrometallurgy is characterized by a high degree of process efficiency, reduced emissions and easier control of the production process. Hydrometallurgical treatment of waste PCBs can be divided into two phases, leaching and metal extraction. In the process of leaching, the PCBs dissolve and the solid metal is converted to dissolved form. From the obtained leach solutions, metals are converted from dissolved to solid form using the following methods: adsorption, ion exchange, electrodeposition and solvent extraction [6].

This paper gives an overview of hydrometallurgical procedures for obtaining gold from waste PCBs. The emphasis is placed on the leaching process because it is the most demanding step in the hydrometallurgical process of gold recovery from electronic waste.

GOLD LEACHING FROM WASTE PCBs

The process of gold recovery from waste PCBs begins with pre-treatment. Pre-treatment of electronic waste involves mechanical and physical operations that can be divided into three phases: disassembly, shredding and separation of materials. The goal of pre-treatment of waste PCBs is the preparation of metallic granules and the concentration of targeted metals, which facilitates the leaching process. The leaching process is followed by purification of metals from leaching solution and recovery of metals as final products. A schematic representation of the hydrometallurgical process of gold valorization from waste PCBs is given in Figure 1.

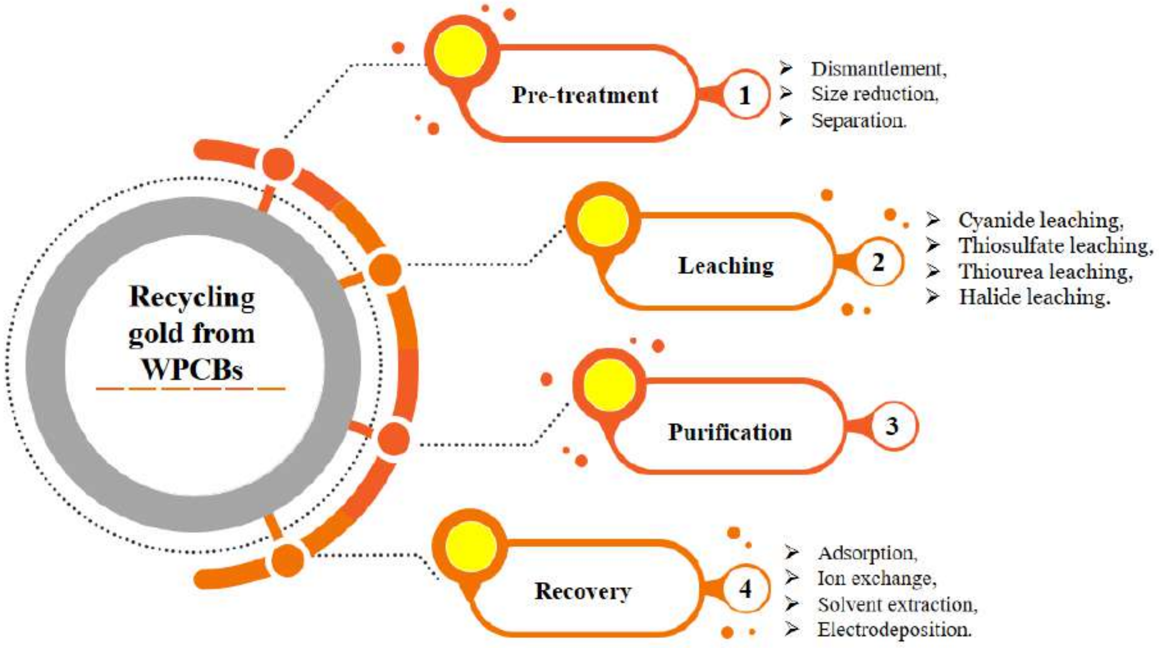


Figure 1 *Process flow of recovery of gold from WPCBs*

Cyanide leaching

Valorization of gold from primary production using cyanide solution is a process that has been used for more than 100 years. In recent years, intensive work has been done on the development of other non-cyanide methods, due to the high toxicity of the applied procedure. However, the high efficiency of this procedure, as well as its simple implementation, is the reason why cyanide leaching is also used in the process of gold recovery from electronic waste [7].

Gold cyanidation is an electrochemical process that can be divided into two half-reactions. In the anodic reaction (reaction 1) there is an alkaline dissolution of gold and the formation of a cyanide complex ($Au(CN)^-{}_2$). At the same time, the cathodic reaction takes place, i.e. the reduction of oxygen after reaction 2. The cumulative reaction of dissolving gold using cyanide is represented by reaction 3 [8]:

Cathode reaction: $4Au + 8CN^- \rightarrow 4Au(CN)^-{}_2 + 4e^-$ (1)

Anode reaction: $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$ (2)

Sum: $4Au + 8CN^- + O_2 + H_2O \rightarrow 4Au(CN)^-{}_2 + 4OH^-$ (3)

The chemical reaction of gold leaching using cyanide can be represented by the following reactions [8]:

$2Au + 4CN^- + O_2 + H_2O \rightarrow 2Au(CN)^-{}_2 + H_2O_2 + 2OH^-$ (4)

$2Au + 4CN^- + H_2O_2 \rightarrow 2Au(CN)^-{}_2 + 2OH^-$ (5)

Sum: $4Au + 8CN^- + O_2 + H_2O \rightarrow 4Au(CN)^-{}_2 + 4OH^-$ (6)

The solubility of gold in cyanide solutions depends on the oxygen concentration, temperature, mixing rate, pH value, surface area of gold ore/concentrate /waste, as well as the presence of other anions or cations. Among the mentioned parameters, the pH value of the alkaline solution is the most important factor in the leaching process of waste PCBs. If the pH value of the cyanide solution is lower than 9, toxic hydrogen cyanide is released, the substance that can seriously damage human health. In order to reduce the amount of cyanide solution used in the process of gold leaching from PCBs, a two-stage leaching was introduced. In the first phase, base metals are leached, while in the second phase of the process, precious metals are leached. Another way to reduce the amount of reagent is to use a new alkaline agent, which in combination with cyanides will form metal complexes [9].

Li *et al.* [10] state in their paper that glycine can complex gold according to reaction 7:

$2Au + 1/2O_2 + 4Gly^- + H_2O \rightarrow 2Au(Gly)_2^- + 2OH^-$ (7)

Adding copper ions to the glycine-peroxide solution can further accelerate the dissolution of gold. This indicates that $Cu(Gly)_2$ may act as an additional oxidant in the glycine-cyanide system during leaching of waste PCBs [10].

The introduction of new compounds in the cyanide process can reduce, but not completely eliminate the toxic effects of cyanide. For this reason, in recent years, preference has been given to non-cyanide solutions, among which the most common are thiosulfate and thiourea solutions.

Thiosulfate leaching

Thiosulfates ($S_2O_3^{2-}$) are widely used in photography and in the pharmaceutical industry, and are often used as a suitable alternative to cyanide solution in the gold leaching process [11]. Thiosulfate leaching is based on the formation of a stable anionic complex according to the following reaction [12]:

$2Au + 0.5O_2 + 4S_2O_3^{-2} + H_2O \rightarrow 2Au(S_2O_3)_2^{-3} + 2OH^-$ (8)

Although the thiosulfate complex is quite stable, an alkaline environment is necessary to maintain its stability [12]. It is known that the presence of ammonia and copper ions facilitates the conversion of gold into thiosulfate solution by forming gold(I) thiosulfate complex (reaction 9). This process was followed by reduction of copper(II) ions by thiosulfate (reaction 10). It is important to note that reaction 10 not only reduces the concentration of copper ions, but also the consumption of thiosulfate ions [13].

$$Au + Cu(NH_3)_4^{2+} + 5S_2O_3^{2-} \rightarrow Au(S_2O_3)_2^{3-} + Cu(S_2O_3)_3^{5-} + 4NH_3 \quad (9)$$

$$2Cu(NH_3)_4^{2+} + 8S_2O_3^{2-} \rightarrow 2Cu(S_2O_3)_3^{5-} + S_4O_6^{2-} + 8NH_3 \quad (10)$$

The main disadvantage of thiosulfate leaching is the high consumption of reagents with extremely unfavourable process kinetics. In the presence of ammonia, the use of oxygen as an oxidant can accelerate the kinetics of the process, but the high consumption of reagents makes the process uneconomical [12].

Thiourea leaching

Thiourea leaching is a hydrometallurgical process, where thiourea is used as a leaching agent. Since thiourea is unstable in alkaline environment, leaching reactions should take place in an acidic medium. If ferrous ions are used as an oxidant, the total gold leaching reaction in an acidic medium can be shown as follows [14]:

$$Au + 2CS(NH_2)_2 + Fe^{3+} \rightarrow Au[CS(NH_2)_2]^+ + Fe^{2+} \quad (11)$$

However, thiourea is easily oxidized in an acidic environment by ferrous ions, forming formamidine disulfide (reaction 12).

$$2CS(NH_2)_2 + 2Fe^{3+} \rightarrow (SCN_2H_3)_2 + Fe^{2+} + 2H^+ \quad (12)$$

Since formamidine disulfide is not stable in acidic media, it decomposes to form sulfur and cyanamide:

$$(SCN_2H_3)_2 \leftrightarrow CS(NH_2)_2 + NH_2CN + S \quad (13)$$

One part of the thiourea is also lost by the formation of a stable ferric sulphate complex:

$$Fe^{3+} + SO_4^{2-} + CS(NH_2)_2 \rightarrow [FeSO_4^{2-} \cdot CS(NH_2)_2]^+ \quad (14)$$

Leaching kinetics as well as low toxicity make thiourea solution more efficient in the process of leaching gold from waste PCBs compared to alkaline thiosulfate leaching [15]. However, the main disadvantage of these procedures is reflected in the high consumption of reagents, its instability and the need for additional mechanical treatment.

Halide leaching

Halide leaching involves the use of halides (fluorine, chlorine, bromine, iodine and astatine) in the process of leaching gold. Gold can form both Au^+ and Au^{3+} complexes with chloride, bromide and iodide according to the following reactions [7]:

$$2Au + L_2 + 2L^- \rightarrow 2ML_2^- \quad (15)$$

$$2Au + 3L_2 + 2L^- \rightarrow 2ML_4^- \quad (16)$$

Where L are halide elements, L_2 is the oxidizing agent, and L^- are the complexing agents.

The traditional medium for dissolving gold is an aqueous medium, i.e. a mixture of hydrochloric and nitric acid in a ratio of 3: 1. The mechanism of dissolving gold in aqua regia takes place according to the following reactions [12]:

$$2HNO_3 + 6HCl \rightarrow 2NO + 4H_2O + 3Cl_2 \qquad (17)$$

$$2Au + 11HCl + 3HNO_3 \rightarrow 2HAuCl_4 + 3NOCl + 6H_2O \qquad (18)$$

Chlorination rates are favoured by low pH, high chlorine and chloride concentrations, high temperatures and high surface areas. However, the process of chloride leaching requires special equipment due to the corrosive nature of the agent used and constant monitoring due to the release of toxic chlorine [11].

Table 1 shows the optimal conditions for leaching gold from waste PCBs using different leaching agents. Based on the presented data, it can be concluded that all leaching agents provide high efficiency of the gold valorization process. However, the economic aspect of the hydrometallurgical process, the generation of significant amounts of wastewater, the toxicity and corrosive properties of the leaching agents make it difficult to apply these processes at the industrial level.

Table 1 *The studies of leaching Au from used PCBs*

Raw material	Reaction conditions	Recovery rate of Au, %	References
PCBs from computer	4 × stoichiometric amount of glycine, 250 ppm **cyanide**; pH = 11; leaching time 96 h; room temperature.	**90.1**	[10]
PCBs of waste mobile phones	24 g/L **thiourea**, 0.6% Fe^{3+}; pH = 1; leaching time 2h; room temperature.	**90.0**	[14]
PCBs of waste mobile phones	0.5 M **thiourea** in 0.05 M H_2SO_4, 0.01 M Fe^{3+}; leaching time 2 h, temperature 45 °C.	**90.0**	[16]
PCBs of cell phones	0.7 M sodium **thiosulfate**; ammonia added dropwise until the solution reached a pH = 10.5; leaching time 6 h; room temperature.	**81.0**	[17]
PCBs of waste mobile phones	Ammonium **thiosulfate** (20 mM copper, 0.12 M thiosulfate, 0.2 M ammonia); pH = 10-10.5; leaching time 10 h; room temperature.	**90.0**	[18]
PCBs of waste mobile phones	**iodine–iodide system** (I_2 40 mM, KI 200 mM); pH 9, leaching time 2 h; room temperature.	**98.5**	[19]
PCBs	**iodine–iodide system** (I_2 2 g/L, KI 12 g/L); leaching time 12 h; temperature 40°C.	**99.0**	[20]
PCBs	**Aqua regia** (HNO_3/HCl-1/3); leaching time 10 h; room temperature.	**97.0**	[21]

CONCLUSION

Hydrometallurgical processes are traditional methods of obtaining gold from primary and secondary sources. The high efficiency of these processes justifies their application. However, a large part of the analysed studies is focused on the selective leaching of individual metals, without the development of an integrated hydrometallurgical process of valorization of all valuable metals from electronic waste. Also, the conducted numerous researches do not provide a detailed techno-economic analysis of the process, in order to justify their application at the industrial level. A review of the available literature indicates that the gold valorization from waste PCBs is a current topic, and there is plenty of room for further research.

ACKNOWLEDGEMENT

The research presented in this paper was done with the financial support of the Ministry of Education, Science and Technological Development of the Republic of Serbia, within the funding of the scientific research work at the University of Belgrade, Technical Faculty in Bor, according to the contract number 451-03-68/2022-14/200131, and within the funding of the scientific research work at the Mining and Metallurgy Institute Bor, according to the contract number 451-03-68/2022-14/ 200052.

REFERENCES

[1] B. Fritz, C. Aichele, M. Schmidt, Int. J. Life Cycle; 25 (2020) 1930–1941.

[2] S. McCarthy, A.L.W. Jie, D. C. Braddock, *et al*., Molecules; 26 (2021) 5217.

[3] M. O. Fashola, V.M. Ngole-Jeme, O.O. Babalola, Int. J. Environ. Res. Public Health; 13 (2016) 1047.

[4] P.M.S. Sousa, L.M. Martelo, A.T. Marques, *et al*., Chem. Eng. J; 434 (2022) 134604.

[5] E. Ventura, A. Futuro, S.C. Pinho, *et al*., J. Environ. Manage; 223 (2018) 297–305.

[6] W. Zhou , H. Liang , H. Xu, J. Hazard. Mater; 411 (2021) 125011.

[7] H. Li, J. Eksteen, E. Oraby, Resour. Conserv. Recycl; 139 (2018) 122–139.

[8] A. Akcil, C. Erust, C.S. Gahan, *et al*., Waste Manage; 45 (2015) 258–271.

[9] J. Hao, Y. Wang, Y. Wu, *et al*., Resour. Conserv. Recycl; 157 (2020) 104787.

[10] H. Li, E. Oraby, J. Eksteen, Waste Manage; 125 (2021) 87–97.

[11] J. Cui, L. Zhang, J. Hazard. Mater; 158 (2008) 228–256.

[12] S. Syed, Hydrometallurgy; 115–116 (2012) 30–51.

[13] V. H. Ha, J-c. Lee, T. H. Huynh, Hydrometallurgy; 149 (2014) 118–126.

[14] L. Jing-ying, X. Xiu-li, L. Wen-quan, Waste Manage; 32 (2012) 1209–1212.

[15] F. Gu, P.A. Summers, P. Hall, J. Clean. Prod; 237 (2019) 117657.

[16] M. Gurung, B. B. Adhikari, H. Kawakita, *et al*., Hydrometallurgy; 133 (2013) 84–93.

[17] S. Gamez, K. Garces, E. de la Torre, *et al*., Hydrometallurgy; 186 (2019) 1–11

[18] V.H. Ha, J-c. Lee, J. Jeong, *et al*., Hydrometallurgy; 178 (2010) 1115–1119.

[19] F.R. Xiu, Y. Qi, F.S. Zhang, Waste Manage; 41 (2015) 134–141.

[20] B. Altansukh, K. Haga, H. Huang, *et al*., Mater. Trans; 60 (2019)287–96.

[21] Y.J. Park, D.J. Fray, J. Hazard. Mater; 164 (2009) 1152–1158.

CHARACTERIZATION OF CARBON AND LOW-ALLOY STEEL AFTER DIFFERENT HEAT TREATMENTS

Uroš Stamenković[1*], Svetlana Ivanov[1], Ivana Marković[1]
[1]University of Belgrade, Technical Faculty in Bor, V.J. 12, 19210 Bor, SERBIA
ustamenkovic@tfbor.bg.ac.rs

Abstract

The aim of this paper was the characterization of carbon and low-alloy steel after different heat treatments. Two steels were investigated, medium carbon C45 steel and low-alloy chrome-vanadium 51CrV4 steel. Two steels were also compared based on their chemical composition. Heat treatment of both steels included: normalizing at 880°C for 1 hour and cooled in air after which the samples were separated and investigated, second assortment of samples were again heated at 850°C for 1 hour and then quenched in water. Investigation was conducted after every step in heat treatment process. After every step, hardness was measured, tensile strength was calculated from hardness values, and thermal properties were also investigated. Metallographic studies were performed on every sample and analyzed. Results show increase in hardness and tensile strength values in quenched samples in comparison to the normalized samples. Also, thermal properties had lower values after quenching which is in accordance with the literature data. Metallographic investigation shows the typical ferrite-pearlite microstructure after normalizing and martensitic microstructure after quenching.

Keywords: C45 steel, 51CrV4 steel, heat treatment, hardness, thermal properties

INTRODUCTION

Steels, as one of the most used materials, can be very versatile based on the microstructure obtained by different heat treatments. One of the most important characteristics of steel is that it can be recycled continuously without any major changes in its properties. Carbon steels, besides tool steels, stainless steels and cast irons are one of the most used materials in the world. Medium-carbon steels are used for different applications where good combination of ductility and strength are required i.e. for various heavy-duty machinery, tractors and mining equipment [1,2]. Chrome-vanadium steels are often used for making different parts which can withstand high stresses. 51CrV4 steel is one of them, and it is used for making springs, small tools and auxiliary parts due to its elasticity, high tolerance for dynamic loads and sufficient wear resistance [3,4]. Both of these steels are very susceptible to heat treatment. Most common heat treatments of steel include: normalizing heat treatment in order to obtain fine pearlite, and quenching for obtaining martensite [1,5]. In order to improve performance and applicability of steels quenching must be done [6]. To achieve this, steels are heated to γ area in order to austenitize them after heating steels are rapidly cooled (quenched) in different mediums depending on the type of steel and other applications [7]. The aim of this paper is to expand the knowledge related to medium carbon steels and low-alloyed chrome-vanadium steels and how mechanical, thermal and microstructural properties change with different heat treatments. Also, since the carbon content in the investigated steels is almost equal, our secondary goal was to investigate the influence of alloying elements (chromium and vanadium) on investigated properties of steel after different heat treatments.

MATERIALS AND METHODS

Experimental investigation was performed on two different types of steels, medium-carbon (C45) and chrome-vanadium steel (51CrV4). Both steels were received in the form of hot rolled bars with the diameter of 20 mm. The Table 1 represents the chemical composition of the investigated steels.

***Table 1** Chemical compositions of investigated steels (mass. %)*

C45 medium-carbon steel					***51CrV4 low-alloyed steel***					
Fe	**C**	**Mn**	**S**	**P**	**C**	**Mn**	**Si**	**Cr**	**V**	**Fe**
98.51–98.98	0.42–0.5	0.6–0.9	≤0.05	≤0.04	0.51	0.9	≤0.4	1.05	0.18	Rem.

Firstly, all the samples were normalized at 880°C for 1 hour in an electric resistance furnace Vims elektrik LPŽ-7,5 S in order to remove as fabricated structure and then cooled in air. Normalized samples were heated up again at 850°C for 1 hour and quenched in water. After each heat treatment sample were separated and investigated. The heat treatment process can be seen on Figure 1.

***Figure 1** Heat treatment of steel samples in an electric resistance furnace*

Hardness was measured on the VEB Leipzig Vickers hardness tester using a 20 kg load and a 15 s dwelling time. Tensile strength was calculated using the hardness value and a conversion chart which gives tensile strength values based on the measured hardness values according to ISO 18265:2013 standard [8,9]. Xenon flash method was applied to determine the thermal diffusivity of the investigated samples after different heat treatments by irradiating the disc shaped specimens with a diameter of 12.7 mm with the xenon lamp in nitrogen atmosphere. The thermal conductivity as a function of temperature was calculated according to the equation:

$$\lambda(T) = \rho(T) \times c_p(T) \times \alpha(T) \quad (1)$$

where, λ – thermal conductivity; (W/mK), ρ – density; (kg/m^3), c_p – specific heat capacity; (J/kgK), α – thermal diffusivity; (cm^2/s), T – temperature; (°C).

For investigation of the microstructure optical microscopy was used. Preparation of the samples included wet grinding on a series of SiC papers, polishing with alumina suspension with two different granulation of Al_2O_3: particle sizes of 0.3 μm and 0.05 μm. 4% Nital solution was used for etching of the samples by immersion to reveal the microstructure. The microstructures were examined on the optical microscope Carl Zeiss Jena "Epytip 2"

RESULTS AND DISCUSSION

The properties of investigated samples after normalizing

After normalizing, as fabricated structure has been removed, thus structure has been normalized. Table 2 shows the results after normalization heat treatment of the investigated steel samples.

Table 2 *Different properties of the investigated steels after normalizing*

Type of steel	Hardness (HV_{20})	Calculated tensile strength (MPa)	Thermal diffusivity (cm^2/s)	Thermal conductivity (W/mK)
C45	232	748	0.1697	60.9
51CrV4	300	965	0.124	43.3

Table 2 shows typical values for these types of steel after normalizing. Hardness values are low due to normalization of the structure and slow cooling which provided formation of the fine ferrite-pearlite microstructure. By comparing two steels, the influence of chromium and vanadium can be clearly seen. Values of hardness and tensile strength are higher for the low-alloyed steel due to formation of fine chromium and vanadium carbides which have extremely high values of hardness. Consequently, values of thermal properties are lower than those measured for C45 steel. This is due to the fact that any presence of alloying elements causes the scattering of electrons which are primary carriers of heat in this case [10,11].

Figures 2a and 2b show the microstructure of the C45 and 51CrV4 steel after normalizing, respectively.

From the presented Figure it can be seen typical ferrite-pearlite microstructure. According to Duka *et al.* [12] C45 steel has around 66% pearlite and 34% ferrite. Microstructures given in Figures 2a-b are somewhat similar, which is to be expected due to similar carbon content. Chromium and vanadium carbides have influence on mechanical properties but have not so much influence on the microstructure.

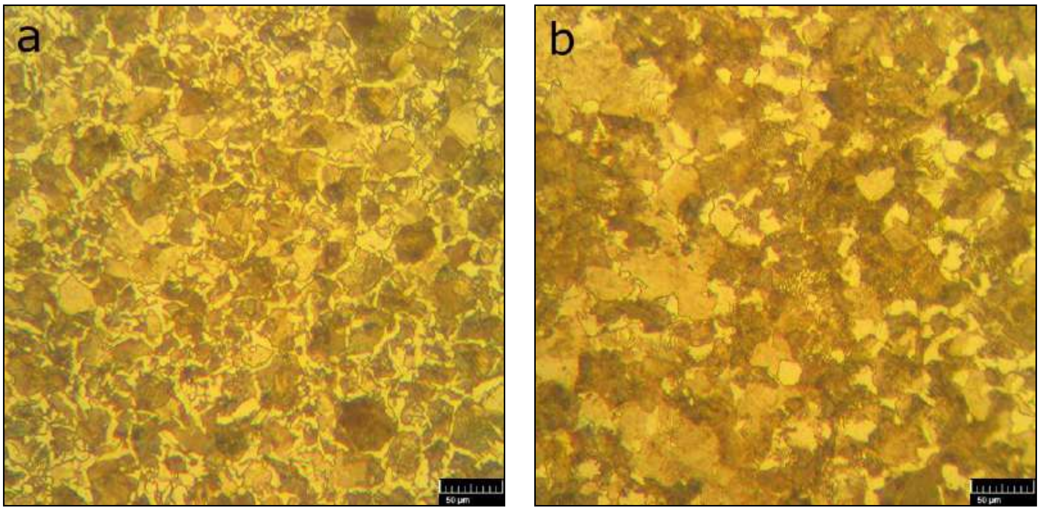


Figure 2 *Microstructure of the investigated steels after the normalization heat treatment a) C45; b) 51CrV4 magnification is x500*

The properties of investigated samples after quenching

Following the normalizing heat treatment, samples were again heated to temperature in austenite region and quenched to room temperature. Table 3 shows the results after quenching of the investigated steel samples.

Table 3 *Different properties of the investigated steels after quenching in water*

Type of steel	Hardness (HV_{20})	Calculated tensile strength (MPa)	Thermal diffusivity (cm^2/s)	Thermal conductivity (W/mK)
C45	550	1810	0.1367	45.5
51CrV4	661	2220	0.09	32.9

Comparison of the results given in Table 2 and Table 3 shows that hardness values are twice as high as the values obtained for samples after normalizing. Tensile strength, due to direct proportionality, shows roughly the same trend. Somewhat similar results were obtained by other authors [13–15]. For both steels, thermal diffusivity and thermal conductivity had lower values after quenching, as seen in Table 2 and 3.

The reason for obtaining higher values for investigated mechanical properties, as well as for the decrease in values for the thermal properties lies in the formation of martensite during quenching. Quenching of steel creates a supersaturated solid solution in the structure, carbon atoms are being retained in the newly formed crystal lattice, as well as atoms of other alloying elements. During the formation of martensite, dislocation and twin density increases. In addition, the number of sliding systems decreases in the newly formed tetragonal lattice, which leads to intense hardening due to dislocation hindering [4,16,17]. All of these processes caused by quenching lead to a weaker flow of electrons due to their scattering in the lattice, which causes an increase in electrical resistance in hardened steels [4]. Besides that, any presence of alloying elements in the lattice causes the scattering of electrons, and with that values of electrical and thermal properties decline [10,11]. Also, as well as after the normalizing, the influence of chemical composition is evident after quenching. 51CrV4 steel has higher values of hardness and tensile strength in comparison to the C45 steel. In addition, values of thermal properties are lower than those measured for C45 steel after the same heat treatment.

Figures 3a and 3b show the microstructure of the C45 and 51CrV4 steel after quenching, respectively. From presented figure it can be concluded that martensitic structure has been obtained in both of investigated steels. There is not as much difference in the microstructures. In the case of the 51CrV4 steel, the microstructure appears somewhat denser and finer. The cause of that can be found in the fact that alloyed steel are much easier to quench, i.e. martensite can be easier to obtain. Higher values of hardness obtained for the 51CrV4 steel in comparison to the C45 steel can be ascribed to that and to the formation of the chrome and vanadium carbides, which are likely to be present after applied heat treatments.

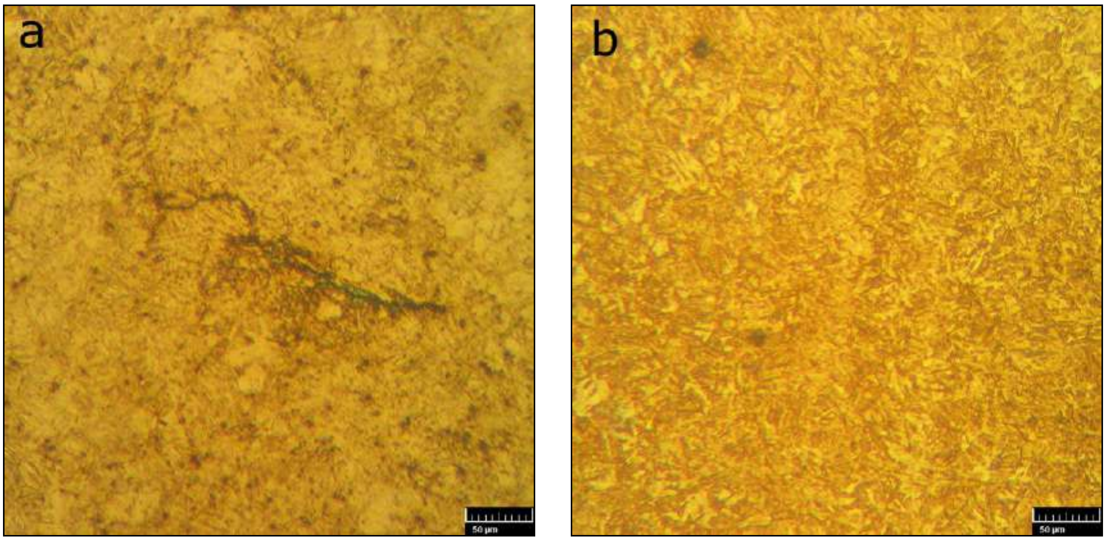


Figure 3 Microstructure of the investigated steels after quenching
a) C45; b) 51CrV4 magnification is x500

CONCLUSION

The conclusion in this paper can be summarized as:

1. After normalizing at 880°C for 1 hour and cooling in air
    - Steel had the lowest values of hardness and tensile strength in relation to other investigated states, as well as the highest values of thermal properties;
    - Optical microscopy showed a relatively small-grained ferrite-perlite microstructure.
2. After heating at 850 °C for 1 hour and quenching in water:
    - The highest hardness values of all investigated states were obtained. The relative increase in hardness values in relation to the normalized sample is 137% for C45 steel and 120% for 51CrV4 steel. The relative increase in tensile strength for the

C45 steel is 142%, while for the sample of 51CrV4 steel this value is 130%, compared to the normalized sample;

- The values of thermal diffusivity and thermal conductivity decreased in relation to the values obtained for the normalized samples. The relative decrease in the value of thermal diffusivity is 19% for C45 steel, and 30% for the 51CrV4 steel. The value of thermal conductivity for the C45 steel sample decreased by 25%, while for the 51CrV4 steel sample it decreased by 24% compared to the normalized sample;
- The strengthening of steel as well as the decrease in thermal properties lies in the formation of martensite during hardening.

ACKNOWLEDGEMENT

The research presented in this paper was done with the financial support of the Ministry of Education, Science and Technological Development of the Republic of Serbia, within the funding of the scientific research work at the University of Belgrade, Technical Faculty in Bor, according to the contract with registration number 451-03-68/2022-14/200131.

REFERENCES

[1] D.R. Askeland, P.P. Fulay, Essentials of Materials Science and Engineering Second Edition, SI, Cengage Learning, Stamford (2010), p.493.

[2] N. Nishimura, K. Murase, T. Ito, *et al.*, Open Eng; 2 (2012) 650–655.

[3] Tech Team, The Difference Between Chrome Vanadium and Chrome Molybdenum, *Available on the following link*: https://capritools.com/the-difference-between-chrome-vanadium-and-chrome-molybdenum

[4] S. Ivanov, Termička obrada metala, Univerzitet u Beogradu, Tehnički fakultet u Boru, Bor (2018).

[5] W.F. Smith, H. Javad, Foundations of Materials Science and Engineering McGraw-Hill Series in Materials Science 4th edition, McGraw-Hill, Boston (2006).

[6] L.H. Pizetta Zordão, V.A. Oliveira, G.E. Totten, Int. J. Heat Mass Transf; 140 (2019) 807–818.

[7] G. Krauss, Principles of Heat Treatment of Steel, American Society for Metals, EUA, Ohio (1980).

[8] Hardness to tensile strength conversion table, *Available on the following link:* https://www.bbshalmstad.se/en/infocenter/hardness-conversion-table

[9] Standard ISO 18265:2013 Metallic materials – Conversion of hardness values, *Available on the following link*: https://www.iso.org/standard/53810.html

[10] R.P. Reed, A.F. Clark, Materials at low temperatures, American Society for Metals, Metals Park, Ohio (1983).

[11] H. Wenzl, J.M. Welter, Int. J. Mater. Res; 65 (1974) 205–214.

[12] E. Duka, H. Oettel, T. Dilo, Proceedings of the 2nd International Advances in Applied Physics and Materials Science Congress, 26–29 April, Antalya, Turkey (2012) 47–51.

[13] C. Civi, M. Yurddaskal, E. Atik, *et al.*, Mater. Test; 60 (2018) 614–618.

[14] D. Hauserova, J. Dlouhy, J. Kotous, Arch. Metall. Mater; 62 (2017) 1473–1477.

[15] B. Senčić, V. Leskovšek, Mater. Tehnol; 45 (2011) 67–73.

[16] Y. Lakhtin, Engineering, physical metallurgy and heat-treatment, English translation from the Russian by Nicolas Weinstein, Second printing, Mir Publishers, Moscow (1983).

[17] H. Šuman, Metalografija (prevod sa nemačkog jezika 9. izdanja), Univerzitet u Beogradu, Tehnološko-metalurški fakultet, Beograd (1989).

THE FOREST FIRES IN BULGARIA: THE TRENDS AND THE INFLUENCE OF TELECONNECTIONS

Violeta Babić[1*], Milan Milenković[2], Zoran Govedar[3], Snežana Stajić[4], Branko Kanjevac[1]
[1]University of Belgrade, Faculty of Forestry, Kneza Višeslava 1, 11030 Beograd, SERBIA
[2]Geographical Institute "Jovan Cvijić" Serbian Academy of Sciences and Arts,
Djure Jakšića 9, 11000 Belgrade, SERBIA
[3]University of Banja Luka, Faculty of Forestry, Bulevar vojvode Stepe Stepanovića 75a,
78000 Banja Luka, REPUBLIC OF SRPSKA, BOSNIA AND HERZEGOVINA
[4]Institute of Forestry, Kneza Višeslava 3, 11030 Beograd, SERBIA
violeta.babic@sfb.bg.ac.rs

Abstract

In the period 1991-2020, 15,895 forest fires were recorded in Bulgaria (about 530 per year on average), while the total burned area was 263,012 ha (8,767 ha per year on average). In both cases, insignificant downward trends were observed. Pearson's correlation coefficient (r) was used to investigate the connection between forest fires in Bulgaria and climate indices. Statistically significant connections were found in the North Atlantic Oscillation (NAO), the Arctic Oscillation (AO) and the East Asia/West Russia (EA/WR). The highest degree of correlation was obtained in studies with the NAO index determined on the basis of sea surface air pressure data from the stations Reykjavik (Iceland), Gibraltar and Ponta Delgada (Azores). Statistically significant values of the correlation coefficient ($p \leq 0.05$) were determined for July, for the burned area ($r=-0.378$), and for the number of fires, as well as for the average size of the fire ($r=-0.377$). A statistically significant connection was also found for November of the previous year and the average size of the fire (0.380). The obtained connections are too weak for these results to be applied in the forecast of forest fires in Bulgaria.

Keywords: forest fires, Bulgaria, NAO, burned area

INTRODUCTION

Bulgaria is facing a serious problem of forest fires, although it is not one of the European countries particularly affected by this problem (Portugal, Spain, France, Italy and Greece [1]).

The total area of Bulgaria is 110,993.6 km^2, while the land area is 108,560 km^2. According to the results of the 2011 census, the population was 7,364,570 [2], but it has been in constant significant decline in recent years.

Compared to most other European countries, biodiversity is particularly pronounced in Bulgaria. Forests are mostly in the western, southern, southwest, as well as in the central parts. Forest cover is about 35%, with deciduous trees accounting for over two thirds, and the rest are conifers. The most common deciduous species are oaks and beech, while the most common coniferous species are spruce, fir and pines. Forests are mostly in mountainous areas, with oaks mostly up to about 1000 m and beech mostly up to 1500 m (western parts of

Bulgaria). The coniferous belt goes up to about 2100 m, with the upper limit of the forest being at about 2300 m [3].

During the previous decade, the greatest damage from forest fires was recorded in 2012, when the total burned area was 12,730 ha. In 2020, 499 forest fires were recorded with burned area of 5258 ha. According to official data for 2020, 67% of forest fires were caused by human negligence, 3% were arson, 3% were caused by natural forces, while in 27% of the cases the cause was not identified [1].

However, some authors believe that fires occur under the influence of solar activity, i.e. the action of solar wind particles. According to this theory, high-energy particles of the solar wind, under certain conditions penetrate the Earth's magnetosphere and reach its surface causing fires [4–6].

There are numerous studies on the impact of climate on fires, but only a small part of researchers also deals with the impact of teleconnections on fires. Teleconnections are climatic anomalies that are interconnected and affect climatic conditions at long distances (thousands of kilometres). The link between forest fires and teleconnections has been established for the United States [7–10]. As far as Europe is concerned, a link has been established between the AMO and the forest fires in France [11] and Portugal [12], as well as the NAO and fires in Finland [13].

The objectives of this paper are to determine the connection of certain teleconnections with forest fires in Bulgaria (period 1991–2020), as well as to determine the trends of basic indicators of forest fires on the annual level.

MATERIALS AND METHODS

The data on forest fires in Bulgaria in the period 1991–2020 were downloaded from the European Commission report [1] and they cover:

- the annual number of forest fires;
- the annual burned area;
- the average burned area per fire.

For these datasets linear trends were determined. In addition, statistical significance of linear trend was determined for (n-2) and on the basis of the coefficient of determination (R^2). For the testing of the significance *t* test was used equation (1):

$$t = R\left[\frac{(n-2)}{(1-R^2)}\right]^{-1} \qquad (1)$$

where n – the length of the series.

For the calculation of correlation Pearson correlation coefficient (r) on the basis of linear trend was used. Statistical significance was tested on $p \leq 0.05$ and $p \leq 0.01$. The data for the period September to December were not included in the research, since the main fire season in Bulgaria is in July and August.

Monthly and seasonal values of climate indices were used in the research. The data from the previous year were also used. Climate indices used are shown in the table 1.

In the case of NAO, three different databases were used in the research, signed as NAO1, NAO2 and NAO3 (Table 1).

Table 1 *Climate indices and sources*

Climate index	Source
North Atlantic Oscillation (NAO): NAO1, NAO2, NAO3	https://psl.noaa.gov/data/correlation/nao.data https://www.cpc.ncep.noaa.gov/products/precip/CWlink/pna/norm.nao.monthly.b5001.current.ascii.table https://crudata.uea.ac.uk/cru/data/nao/nao_3dp.dat
Arctic Oscillation (AO)	https://psl.noaa.gov/data/correlation/ao.data
Atlantic Multidecadal Oscillation (AMO)	https://psl.noaa.gov/data/correlation/amon.us.data
Atlantic Meridional Mode (AMM)	https://psl.noaa.gov/data/timeseries/monthly/AMM/ammsst.data
Eastern Asia/Western Russia (EA/WR)	https://psl.noaa.gov/data/correlation/ea.data
Tropical Northern Atlantic (TNA)	https://psl.noaa.gov/data/correlation/tna.data
Western Hemisphere warm pool (WHWP)	https://psl.noaa.gov/data/correlation/whwp.data

RESULTS AND DISCUSSION

In the period 1991–2020, 15,895 fires were recorded in Bulgaria, or about 530 a year. The downward trend of the annual number of forest fires is not statistically significant (Figure 1).

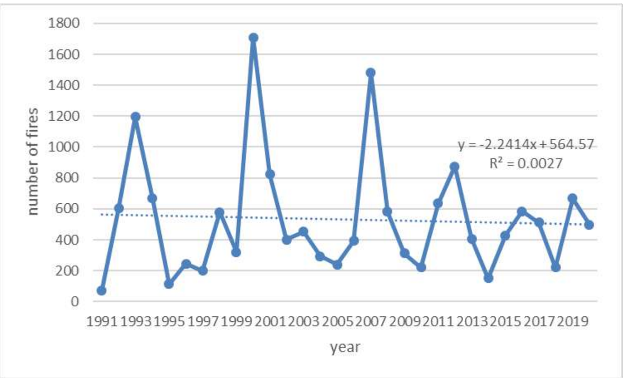


Figure 1 *The annual number of forest fires in Bulgaria (1991–2020) with the trendline [1]*

The maximum number of fires was recorded in 2000 (1710), and the minimum in the initial year of the series - 1991 (73).

The total burned area in Bulgaria in the research period is 263,012 ha (average 8767 ha per year). The downward trend is not statistically significant (Figure 2). The largest burned area was recorded in 2000 (57,406 ha), and the smallest in 1991 (511 ha).

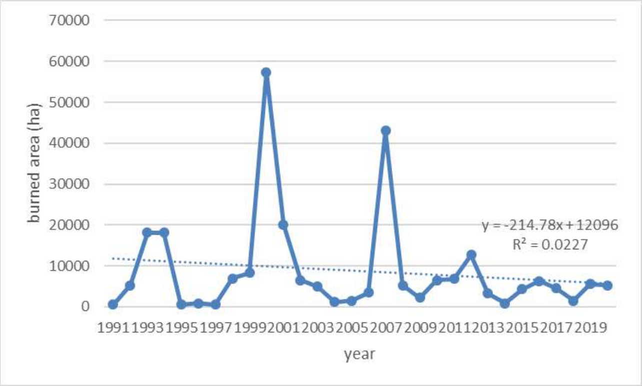


Figure 2 *The annual burned area in Bulgaria (1991–2020) with the trendline [1]*

The average burned area per fire in the research period is about 16.5 ha. The trend is also descending and not statistically significant (Figure 3). The highest value was recorded in 2000 (about 33.6 ha), and the lowest in 1997 (about 3 ha).

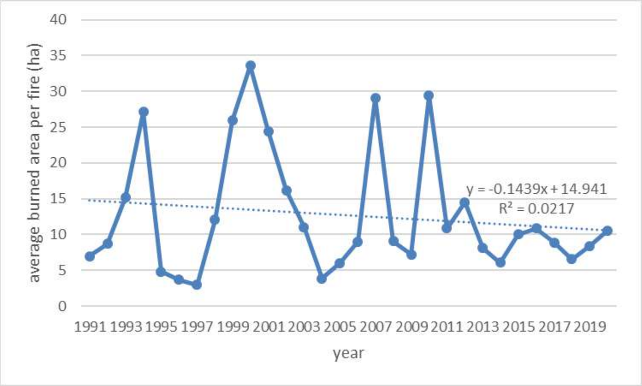


Figure 3 *The average burned area per fire in Bulgaria (1991–2020) with the trendline [1]*

Downward trends for all three indicators have been identified also for the last decade (2011–2020). Similar trends were observed in neighbouring Serbia, with the average burned area per fire with a very weak downward trend (almost no trend).

In the research of the connection between forest fires in Bulgaria and climate indices, some statistically significant connections were found only at NAO, AO and EA/WR. No statistically significant correlations were found for other researched climate indices (AMO, AMM, TNA and WHWP).

At AO, the connection ($p \leq 0.05$) was determined only for January and the number of fires (0.420), and at EA/WR for February and the number of fires (0.412). At NAO1, a statistically significant connection ($p \leq 0.05$) was determined for July of the previous year and the average burned area per fire (-0.387), while at NAO2 there were no statistically significant correlation coefficients. However, at NAO3, significant connections ($p \leq 0.05$) for July and all three investigated parameters of forest fires were determined (-0.378 for the burned area and -0.377 for the number of fires and the average size of fire). A statistically significant connection was found also for November of the previous year and the average size of fire (0.380).

NAO is important factor which affects the temperature in the Balkans. It is characterized by both positive and negative phases. Strong negative phases of NAO are often associated with higher temperatures and lower precipitation across southern Europe. NAO index is calculated on the basis of the difference in the sea surface air pressure between Iceland (low) and the Azores (high) [14]. However, calculations for NAO3 were done on the basis of the stations Reykjavik (Iceland), Gibraltar and Ponta Delgada (Azores). The data on the sea surface air pressure (stations Reykjavik and Gibraltar) were also used in the research. For Reykjavik, statistically significant connections were established for July - the number of fires (0.524, $p \leq 0.01$) and the burned area (0.408, $p \leq 0.05$), and at the seasonal level for summer - the number of fires (0.408, $p \leq 0.05$) and burned area (0.370, $p \leq 0.05$). As for the values of the previous year, the most significant connection was determined for November and the number of fires (0.426, $p \leq 0.05$). With Gibraltar data, statistically significant connections ($p \leq 0.05$) were determined for the number of fires - February (0.391), March (0.364), and winter (0.427).

Therefore, the established links are weak. Given the connection between the Mediterranean Oscillation Index (MOI) and forest fires in neighbouring Romania [15], future research should focus on climate indices for the Mediterranean.

CONCLUSION

In the period 1991-2020, insignificant downward trends of all researched annual indicators of forest fires (number, burned area and average size of fire) were recorded in Bulgaria. Similar trends have been identified for the last decade (2011-2020).

Quite weak connections between these indicators and the researched climate indices were also found. In NAO, AO and EA/WR there is some correlation, while in the cases of AMO, AMM, TNA and WHWP no statistically significant connections were observed.

In the case of NAO, the strongest connections were found in studies in which the NAO index was determined based on data from Reykjavik (Iceland), Gibraltar and Ponta Delgada (Azores) stations. Thus, antiphase connections ($p \leq 0.05$) for July and all three indicators of forest fires were determined (-0.378 for the burned area and -0.377 for the number of fires and the average size of fires). For November of the previous year and the average size of the fire, the sign of the connection is opposite (0.380).

REFERENCES

[1] Y. San-Miguel-Ayanz, T. Durrant, R. Boca, *et al.*, Forest Fires in Europe, Middle East and North Africa 2020, *Available on the following link*: https://publications.jrc.ec.europa.eu/repository/handle/JRC126766

[2] Republic of Bulgaria, National Statistical Institute, 2011 Population Census in the Republic of Bulgaria (final data), *Available on the following link*: https://www.nsi.bg/census2011/PDOCS2/Census2011final_en.pdf

[3] R. Penin, Physical Geography of Bulgaria, Bulvest 2000, Sofia (2007), p.280, ISBN: 978-954-18-0546-6.

[4] M. Radovanović, Y. Vyklyuk, A. Jovanović, *et al.*, J. Geogr. Inst. Cvijic; 63 (3) (2013) 23–32.

[5] M.M. Radovanović, Y. Vyklyuk, M. Milenković, *et al.*, Therm. Sci; 19 (5) (2015) 1649–1661.

[6] M. Radovanović, J.F. Pereira Gomes, A.A. Yamashkin, *et al.*, J. Geogr. Inst. Cvijic; 67 (2) (2017) (213–218)

[7] M. Milenković, V. Ducić, V. Babić, The Pacific Decadal Oscillation and forest fires in the USA in the period 1983-2015, Forestry (Šumarstvo) 2016 (1–2) (2016) 91–100.

[8] T. Schoennagel, T.T. Veblen, W.H. Romme, *et al.*, Ecol. Appl; 15 (6) (2005) 2000–2014.

[9] J.S. Sibold, T.T. Veblen, J. Biogeogr; 33 (5) (2006) 833–842.

[10] M. Harrison, Southeast. Geogr; 53 (4) (2013) 381–402.

[11] M. Milenković, V. Ducić, D. Burić, *et al.*, J. Geogr. Inst. Cvijic; 66 (1) (2016) 35–44.

[12] M. Milenković, A. Yamashkin, V. Ducić, *et al.*, J. Geogr. Inst. Cvijic; 67 (1) (2017) 27–35.

[13] M. Milenković, V. Ducić, J. Mihajlović, *et al.*, J. Geogr. Inst. Cvijic; 69 (1) (2019) 75–82.

[14] National Weather Service, Climate Prediction Center, North Atlantic Oscillation, *Available on the following link:* https://www.cpc.ncep.noaa.gov/data/teledoc/nao.shtml

[15] M. Milenković, V. Ducić, V. Babić, Forum Geogr; XV (2) (2016) 126–132.

EcoTER'22
29th International Conference Ecological Truth
& Environmental Research
21 - 24 June 2022, Hotel Sunce, Sokobanja, Serbia
www.eco.tfbor.bg.ac.rs

THE IMPORTANCE OF FIRE PROTECTION ON SHIPS

Martina Petković[1*], Marijola Božović[2], Anita Klikovac[3], Dragan Knežević[4]
[1,2]Kosovo and Metohija academy of applied studies, Department Zvečan, SERBIA
[3]Department of Emergency Situations in Smederevo, Sector for Emergency Situations, Ministry of the Interior, SERBIA
[4]LOGOS Center, Mostar, BOSNIA AND HERZEGOVINA
[*]*martinaeco@yahoo.com*

Abstract

Vessels, whether sea or river type, belong to a special category of facilities due to the danger of fire. Ship fire protection is based on the design and construction of maritime transport. For that purpose, fire-resistant materials are used, piping systems are installed, surfaces are treated with fire extinguishers and insulation between fire sectors is provided. But in the presence of all planned measures, ships are still fire-hazardous facilities, so additional measures are needed to protect them from fire. The paper gives an overview of the choice of preventive fire protection measures on ships in order to preserve material goods and life, as well as environmental protection.

Keywords: ships, fire protection, prevention

INTRODUCTION

A ship is defined as a vessel capable of navigating all types of water, transporting cargo or passengers or performing some other, special tasks (fishing, towing, scientific research, acrobatics, etc.). Maritime transport of passengers is the subject of increased attention and therefore strict requirements of international and national regulations apply to it. Passenger ships, as a special category of ships, must meet strict technical requirements regarding the safety of navigation, which as a rule implies a higher degree of safety compared to other types of ships [1]. As a maritime transport of global proportions, the International Maritime Organization is developing in accordance with international standards. Some of the most important international agreements are: the International Convention for the Prevention of Pollution from Ships MARPOL [2], the International Convention for the Protection of All Countries of Human Life at Sea (SOLAS) [3], and the International Convention on Standards of Training, Certification and Certification and the Conduct of Seafarers (STCV) [4].

Each of these regulations has its own specifics, but the main goal is to preserve safe and healthy conditions for long-term operation of vessels, vessel users and the preservation of the living and working environment.

Water fires are dangerous because:

- ways and possibilities of evacuation are limited;
- there are large amounts of fuel or volatile gases at storage sites;
- firefighting work must be carried out taking into account the preservation of hull

stability.

However, the main causes of the fire are related to the negligent behavior of the crew: operation of faulty electrical equipment; smoking in places not equipped for that; disorder in the area, including evacuation routes; careless handling of flammable liquids [5].

Fires can also be caused by the wrong actions of the captain or shipowner:

- reloading of warehouses with flammable cargo;
- improper storage of various types of materials;
- improper operation of fire extinguishing systems on ships.

ANALYSIS OF ELEMENTS THAT CAN LEAD TO FIRE ON SHIP

Experience in ship operation, firefighting and accident analysis shows that all sources of ignition can be divided into 3 main groups [6]:

- thermal manifestation of chemical reactions;
- thermal manifestation of electricity;
- thermal manifestation of mechanical energy.

Thermal manifestation of chemical reactions. Open fire is manifested by smoking, the use of torches and blowers; flame emission from steam boiler furnaces, combustion chambers for gas turbines, gas channels of heat engines; during gas welding, gas cutting. The flame temperature of matches and cigarettes reaches 700–800°C, and gasoline lighters 1200–1300°C. Hot combustion products have a very high temperature (600–1100°C) and in the presence of cracks, combustion and other leaks in boiler furnaces, gas openings of diesel engines, turbines, combustion products coming out of them are a powerful source of ignition. Sparks are solid incandescent particles of incompletely burned carbon of various solids and fuels. Sparks can only ignite items prepared for combustion [7].

Electricity as a source of ignition is manifested in the following way:

- short circuit of current parts of electrical equipment (electric arc temperature is in the range of 1500–4000°C);
- sparking and heating of electrical parts due to poor contact or vibration;
- overload of electrical equipment, long-term use of electrical equipment intended for short-term work, excess power above the allowable value;
- static electricity (accumulates when dielectrics rub against each other).

In ship conditions, static electricity accumulates when liquid is poured into tanks (reservoirs) by a falling jet, moving along metal and plastic pipelines and rubber hoses [8].

Thermal manifestation of mechanical energy expressed in the following way:

- sparks from the impact of solid bodies, when working with various tools, are a piece of metal heated to a gloss of 0.1–0.5 mm. Their temperature reaches 1200–1600°C. Sparks usually create hot spots of smoldering and then combustion;
- warming of the body from friction when moving with each other (reason - poor lubrication);

- heating flammable gases and air during compression.

Regarding fire, the following terms and processes are known: flash, ignition, self-ignition, spontaneous combustion, explosion [9]. The temperatures at which these processes take place characterize the flammability of flammable objects. Based on these concepts, we can approach the adequate analysis of data in order to create preventive and organizational technical measures for protection against fire and explosion on vessels.

CLASSIFICATION OF FIRE ON SHIPS

Fires on ship are classified according to the following criteria [10]:

- according to the fire location;
- by type of flammable materials;
- according to the amount and strength of the necessary materials for fixing.

Distinguish between external and internal fires. In the case of external fires, the source of the fire is outside the hull (on the deck, superstructure, pier, water area). Internal fires are fires in the rooms and compartments of vessels. Such fires can be open and hidden. During the inspection of the area, hot spots of open fire are easily detected. Hidden fires are detected only by secondary signs (smoke, heating of buildings, the smell of burning). According to the size of the combustion zone (by volume) ship fires are divided into: - Fire fire; small fire; big fire. The classification of fires allows to make the right decision in the fight for the survival of the ship, as well as to attract the appropriate forces and means for extinguishing the fire [11].

Depending on the type of combustible material in the Russian Federation, it is divided into 5 main classes (Appendix No. 3 "Rules of fire protection in the Russian Federation" 1993).

- Class A fires - these are fires associated with the combustion of ordinary solid carbon substances, mainly of organic origin, whose combustion is accompanied by smoldering (wood, paper, fabrics, rubber, ropes, etc.);
- Class B fires are fires of flammable liquids or molten solids (petroleum products, paraffins, paints, solvents, cooking oils, waxes, etc.);
- Class C fires - these are gas fires (methane, propane, butane, acetylene, etc.);
- Class D fires are fires of metals and their alloys (sodium, potassium, lithium, magnesium, titanium, aluminum, iron and steel powder);
- Class E fires - fires related to the combustion of electrical equipment and live electrical installations (generators, electrical panels, electric motors, switchgear, cables).

For successful firefighting, it is necessary to use the most suitable extinguishing agent, the choice of which should be resolved almost immediately. His correct choice will reduce damage to the vessel and danger to the entire crew. This task is greatly facilitated by the introduction of fire classification and their division into four types, ie classes, which are denoted by the Latin letters A, B, C, D. Each class includes fires associated with the ignition of materials that have the same properties during combustion and require the use of the same or fire extinguishers. Therefore, knowledge of these classes, as well as the flammability characteristics of the materials available on board, is absolutely necessary for successful firefighting. The classification of fires has several standards, for example: ISO 3941 (International Organization for Standardization) and NFPA10 (National Association for Fire Protection). Here's the last one:

- Class A fires are fires associated with the combustion of solid (ash) flammable materials that can be extinguished with water and aqueous solutions. These materials include: wood and wood-based materials, fabrics, paper, rubber and some plastics.
- Class B fires are fires caused by the combustion of flammable or combustible liquids, flammable gases, fats and other similar objects. Extinguishing these fires is done by stopping the supply of oxygen to the fire or preventing the release of flammable vapors.
- Class C fires are fires that occur when electrical equipment, conductors or live electrical appliances catch fire. Non-conductive fire extinguishers are used to extinguish such fires.
- Class D fires are fires associated with the ignition of flammable metals: sodium, potassium, magnesium, titanium or aluminum, etc. Heat-absorbing fire extinguishers are used to extinguish such fires, e.g. some powders that do not react with flammable metals.

The main purpose of developing such a classification is to assist crews in choosing the appropriate extinguishing agent. However, it is not enough to know that water is the best class A fire extinguisher because it provides cooling, or that powder is good for extinguishing flames when igniting liquids, it is necessary to know how to properly apply extinguishing agent with accurate fire.

FIRE PROTECTION ON SHIPS

Types of firefighting equipment used on ships

The complex construction of ships and the availability of space for various purposes require a reasonable approach to equipping facilities with protective equipment. Different fire extinguishing systems are used on the ship, taking into account the characteristics of the space and the purpose of the ships themselves. The most common method of extinguishing is with water. Methods for extinguishing fires with water are set during the construction of ships. Ring and line pipelines are used. Several pumps with protective silencers are used to extinguish the fire [12].

On ships with a high risk of fire (tankers, gas ships) it is used on a ship that provides a quick reaction and the maximum amount of extinguishing agent. In areas where passengers and crew sleep, it is desirable to ensure the possibility of evacuation of people and property. Where the use of water does not have the desired effect or even poses a danger, such as motors and pumps, foam fire extinguishers are used. Water at high temperatures turns into hot steam and becomes dangerous to people, nothing less than fire. Vessels carrying explosive and flammable objects, such as gases, are equipped with powdered agents that stop the fire and prevent it from spreading further. The main extinguishing systems have the principle of a stationary system. Along with them, portable, mobile systems (fire extinguishers) are used, which serve to suppress small local fires. The combination of different systems and methods of extinguishing is considered the most efficient [13].

Due to the great danger of fire on all sea and river vessels, ship fire alarms were set. Preference is given to automatic systems, because they do not need constant human control, ie. they do not deter the ship's crew from performing their immediate duties. Automatic systems are complemented by manually activated detectors located in public places. In most cases, automatic fire alarm systems on river fleet ships supplement the audible warning to warn passengers and crew members of danger. The fire alarm on board is presented in the following types:

- electrical appliances;
- pneumatic circuits that do not depend on the presence of mains voltage;
- smoke detectors;
- temperature sensors that respond to maximum readings;
- automatic and manual types of signaling;
- combined systems that include several types of sensors at the same time in order to increase the functionality and reduce accidental activation of the ship's fire alarm system and unreasonable activation of firefighting equipment.

Stationary fire extinguishing systems are the main means of protecting maritime traffic. The basic structures are placed in the shipyard while the ship is on land. After that, shipowners supplement existing systems, upgrade or replace obsolete models [6]. Locations of stationary fire extinguishing systems on board are the most dangerous areas and spaces:

- engine room with diesel engines;
- marine generators or other premises in which there are sources of electricity and branches of the electricity network;
- compartments with electric motors and pumps;
- ventilation networks.

Also, it is planned to install APS on the ship in the places of the crew, i.e.:

- in living quarters;
- in the kitchen;
- in the hallways.

Gas and dust devices are installed in cargo warehouses or compartments, which are very efficient, but dangerous for people in the impact zone.

Selection of fire protection systems

The safety of watercraft-vessels largely depends on how well-chosen the fire-fighting systems on board are. When choosing, consider the following facts [13]:

- the purpose of water transport and the degree of fire hazard of the transported goods;
- dimensions of the building as a whole and individual rooms, as well as design characteristics of individual parts of the building;
- the number of fire-hazardous equipment and its layout in the premises;

- the presence, scope and manner of storage of goods and indicators of its fire hazard.

When evaluating fire extinguishers, attention is paid to the following indicators:

- possibility of use in various types of fires (A, B, C and so on);
- the surface covered with extinguishing agents, taking into account the height of the compartment;
- reaction speed and operating time of the fire protection system;
- automatic operation and the possibility of switching on in manual mode;
- danger to people and damage that may occur to property endangered by fire;
- possibility of installation in cramped conditions or in non-standard water transport.

CONCLUSION

It is necessary to apply active and passive protection in order to achieve safe conditions for the longest possible operation of vessels, preservation of material goods, environment and preservation of users' lives. The key to success in the modern maritime industry lies in the end product that will meet all the criteria in terms of safety, comfort and economy. Systems and devices must meet the strictest maritime safety regulations to ensure end-user confidence. As the construction of passenger ships has become more widespread in recent years, new trends are emerging that keep pace with the times. The paper gives a general overview of fire protection on ships, with all the specifics, pointing to the fact that the correct choice of fire protection is crucial for long-term operation of vessels and user safety, as well as environmental protection.

REFERENCES

[1] A. Lompar, Nauka o brodu, Univerzitet Crne Gore, Kotor (2002).

[2] *Available on the following link:* http://www.azo.hr/MARPOL

[3] Jugoslovenski registar brodova, Međunarodna konvencija o žaštiti ljudskog života na moru (konvencije SOLAS 1974, SOLAS protokola 1978, amandmana 1981. i 1983. na SOLAS) , Split (1987).

[4] M. Radulović, Međunarodno javno pomorsko pravo, Kotor (2005).

[5] *Available on the following link:*
http://documents.tips/documents/solas-1974-konvencija.html

[6] Z. Nikolić, G. Počuča, Brodske električne mašine i uređaji, Institut tehničkih nauka, Beograd (2003).

[7] S. Šilović, Čamac brod brodogradnja, Zagreb (1989).

[8] F. Marinka, Stabilnost broda, Tiskara Znanje d.d., Zagreb (1999).

[9] *Available on the following link:*
https://en.wikipedia.org/wiki/Global_Maritime_Distress_and_Safety_System

[10] *Available on the following link:*

http://documents.tips/documents/solas-1974-konvencija.html

[11] *Available on the following link:*

https://en.wikipedia.org/wiki/Global_Maritime_Distress_and_Safety_System

[12] *Available on the following link:*

http://www.imo.org/en/About/Conventions/ListOfConventions/Pages/International-Convention-for-the-Safety-of-Life-at-Sea-(SOLAS)

[13] *Available on the following link:*

http://biblioteka.sf.bg.ac.rs/index.php?p=show_detail&id=3347

EcoTER'22
29th International Conference Ecological Truth
& Environmental Research
21 - 24 June 2022, Hotel Sunce, Sokobanja, Serbia
www.eco.tfbor.bg.ac.rs

PESTICIDES – IMPACT ON HUMAN HEALTH AND THE ENVIRONMENT

Darko Stojićević[1*], Zlata Živković[1], Markola Saulić[1], Tatjana Sekulić[1], Vladanka Stupar[1]

[1]Academy of Applied Technical Studies Belgrade, College of Applied Engineering Sciences, Nemanjina 2, 12000 Požarevac, SERBIA

[*]*darko.stojicevic@vts-pozarevac.edu.rs*

Abstract

The world's population is growing rapidly, so primary goal of modern agriculture is to meet the food need of the population. With the increase in the number of inhabitants, it is necessary to increase agricultural production and productivity, and therefore the use of chemical inputs such as pesticides has increased. Today, pesticides are used in most areas of plant production to provide raw materials without damage from harmful agents, provide high profits to farmers, prices and quality of products that are affordable and appealing to consumers. The use of pesticides brings with it some merits effects on humans and the environment, but risks associated with their use far outweighs these merits. The aim of this paper is to examine the impact of pesticides primarily on human health and the environment, given their growing global use in modern agriculture.

Keywords: pesticides, agriculture, environment, human health

DEFINITION OF PESTICIDES

Pesticide means any substance or mixture of substances of naturally, chemical or biological origin that is intentionally released into the environment in order to prevent, deter, control and/or kill and destroy populations of insects, weeds, rodents, fungi or other harmful organisms. Pesticides work by attracting and then destroying or mitigating the pests [1,2]. Pesticides are used to control various pests and disease carriers, such as mosquitoes, ticks, rats and mice. Also, are used in agriculture to control weeds, insect infestation and diseases. In addition, they are used for to kill and/or slowing the growth of algae (Algaecides), to control germs and microbes such as bacteria and viruses (Disinfectants), to control fungal problems like molds, mildew, and rust (Fungicides), to control insects (Insecticides), to disrupt the growth and reproduction of insects (Insect Growth Regulators), to kills rodents like mice, rats, and gophers (Rodenticides), to make wood resistant to insects, fungus and other pests (Wood Preservatives) (United States Environmental Protection Agency - EPA) [3]. Based on toxicity of pesticides, WHO (World Health Organisation) classified them into four classes: extremely dangerous, highly dangerous, moderately dangerous and slightly dangerous [4]. Definition of pesticides has changed over time and countries but the essence of pesticides remains basically the same i.e., it is a (mixed) substance that is poisonous and efficient to target organisms and is safe to non-target organisms and environments [5]. Pesticides can be natural compounds or they can be synthetically produced. Pesticide formulations contain active ingredients along with inert substances, contaminants and occasionally impurities. When released into the environment, pesticides are broken down into substances known as metabolites that are in some situations more toxic to the active ingredients. Pesticides enable the effective destruction of harmful agents, but unfortunately, the risks associated with their use have outweighed their beneficial effects. In addition, non-selective pesticides kill non-target plants and animals along with the target [2].

HISTORY OF PESTICIDE PRODUCTION AND APPLICATION

The oldest known substance that has a pesticidal effect as a fungicide is sulfur. In his records from the 9th century BC, Homer mentions "yellow powder" as a pest repellent [6]. Sumerians, Greeks, and Romans killed pests using various compounds such as sulphur, mercury, arsenic, copper or plant extracts [1]. In the period around 900 AD, in China, arsenic has been used as an insecticide in gardens. Until of the 15th century, arsenic, mercury and lead were used to prevent the spread of pests and a mixture of arsenic and honey became popular for control ants [7]. Significant use of sulfur as a fungicide to protect grapevines from powdery mildew was noted in the drug polyviny of the 19th century in France, after the causative agent of this disease, *Erysiphe necator*, was introduced in 1845 in North America, and significantly reduced wine production in ten years in this country [6]. The first inorganic fungicides appeared in the second half of the 19th century. Compared to other pesticides, herbicides are more recent formulations. In 19th century their use was in the form of sodium nitrate, ammonium sulfate, iron sulfate [8]. After the Second World War, DDT, aldrin, dieldrin, endrin and 2,4-D were use like the more effective, easy to use, inexpensive, and thus enormously popular [1,5]. Today, production without of herbicides is inconceivable. Farmers use herbicides from correction in the control of weeds that have survived despite the applied agro-technical and physical measures, and in most cases this measure is considered the solution with the best and fastest effect [9]. As a consequence of the favoring of certain crops, more problematic weed species and pests appear more intensively, and short-term crop rotations, i.e. continuous cultivation of crops in monoculture lead to the risk of soil erosion and reduction of biological diversity [10]. Today, is predict that nearly 3 billion kg of pesticides are used every year, with a budget of 40 billion USD [11].

MECHANISMS OF ACTION OF PESTICIDES

Different pesticides have different mechanisms of action on the cultivated plant and harmful agents. Most fungicides have a direct effect (action on the parasite itself), while on other hand some have indirect effect on the host plant by stimulating plant to make substances (phytoncides) that adversely affect to the parasite. Fungicides most commonly act on SH enzymes, denaturation of proteins, cell membrane destruction, inhibition of sterol biosynthesis, action on cell division, and cellular respiration. Commercial herbicides exhibit many different mechanisms of action, such as biosynthesis of amino acids, inhibit photosynthesis, lipid synthesis, inhibiting mitosis, biosyntesis of nucleic acids and proteinsand cell membranes [12]. Sometimes, inadequate application of herbicides can do more damage than weeds, so it must be used very carefully. Most of today's insecticides have an effect on sodium and calcium channels, as regulators of insect growth, acetylcholinesterase inhibitors, acetylcholine mimics, octopamine mimics, anticoagulant rodenticides [13]. Agricultural pesticides most often are applied as liquids sprayed on the crop and/or the soil. Sometimes pesticides are incorporated or injected into the soil or applied as granules or as a seed treatment. Pesticides are of different chemical composition, toxicological properties and persistence. After a certain period, the pesticide decomposes due to the action of plant metabolism and environmental factors on non-toxic components. But, sometimes the degradation intermediates are often more persistent than the starting compound, and remain in the soil or water (groundwater) for a long time.

RISK OF PESTICIDE USE

Humans have been farming for 10,000 years. Today, pesticides touch every aspect of our lives, from residues on our produce to increased chronic disease to biodiversity loss (Pesticides Action Networks - PAN) [14]. Pesticides are considered as one of the main factors involved in environmental contamination of today's world [15]. The number of registered pesticides and their use worldwide is increasing dramatically with the increase of human population and crop production. Environmental pollution is a global phenomenon. The worldwide use of pesticides in agriculture results in residues of pesticides being commonly found in many environments. Pesticides are designed to destroy harmful agents, but their mode of action is not always species-specific, so they often kill or harm non-target organisms, including humans. In addition, the application of pesticides is often not very precise. The WHO estimates that there are 3 million cases of pesticide poisoning each year and up to 220,000 deaths, primarily in developing countries. Pesticides results in production of reactive oxygen species, which results of reduction in the levels of antioxidants in the human body and their defense against oxidative damage in the cellular system. When pesticides disturb the oxidative balance, they pave way for variosu diseases [4].

The risks of using pesticides are considered to outweigh their beneficial effects. Globally 4.6 million tons of chemical pesticides are annually sprayed into the environment [5]. Pesticides affect animal and plant biodiversity, aquatic as well as terrestrial food webs and ecosystems and have drastic effects on non-target species. One of the main disadvantages of pesticides is their high volatility (over 80% will evaporate after application) and thus act on non-target organisms. Uncontrolled use of pesticides has resulted in reduction of several terrestrial and aquatic animal and plant species. Additionally, air, water and soil bodies have also being contaminated with these chemicals. Water soluble pesticides get dissolve in water and enter ground water and surface water causing harm to untargeted species, while fat soluble pesticides enter the bodies of animals. They get absorbed in the fatty tissues of animals hence resulting in persistence of pesticide in food chains for extended periods of time [2]. Pesticide can cause pesticide resistance in some pests, reduction of biodiversity and nitrogen fixation, destruction of marine and birds’ life and/or genetically defects in their next generations [16]. Pesticides can adversely affect the proliferation of beneficial soil microorganisms and their associated biotransformation as well as the inactivation of microorganisms that fix nitrogen and dissolve phosphorus [17]. Insecticide spray drift can kill birds in the vicinity of crops [18] and poses a great danger to waterfowl [19].

Under constant chemical pressure, some pests became genetically resistant to pesticides. Then, pesticides have a great effect on pollinators. Inadequate use of agricultural pesticides for pest control was evinced as one of the foremost causes of these pollinator declines [20]. A large number of pesticides have been excluded from use for these reasons (organochlorine insecticides, methyl bromide), mostly due to the potential risk to human health, environmental pollution and effects on non-target organisms [21].

MERITS OF PESTICIDES USE

In view of the limited croplands in the world and the growing population, it is necessary to take all measures to increase plant production in order to ensure food safety. If the use of pesticides were banned, food production would fall sharply and food prices would jump dramatically [5]. About 9,000 species of insects and mites, 50,000 species of plant pathogens and 8,000 species of weeds damage crops worldwide. Pesticide is indispensable in agricultural production, without their application the loss of fruits, vegetables and cereals from pests would be significantly increased. Agricultural productivity is the key to providing food at an affordable price and plant protection products help increase productivity and usable crop yields. Pesticides reduce crop losses both before and after harvest and increase crop yields Pesticides reduce crop losses both before and after harvest and increase crop yields [16]. Up to 40 percent of the world's potential crop production is already lost annually due to weeds, pests and diseases [16]. They also destroy the persistent indoor household pests such as cockroaches which contribute asthma and allergies (EPA). Pesticides contribute to the health of the population by destroying insects that cause many diseases (Malaria, Dengue fever, Lyme disease, and West Nile virus loom large) or fungiborne carcinogens, like aflatoxins, which is proceeding to hepatic and other cancers. The most significant example is malaria control, which was responsible for an average of 5,000 deaths per day [22]. EPA registers several pesticide products, including repellents, that may be used to control the vectors that spread these diseases Avian flu (bird flu) is an infection that occurs naturally and mainly in birds, although can also occur in humans, but the risk is generally low. The EPA is working to register and make available antimicrobial pesticides that can be used to kill and to prevent the spread of avian flu viruses, which would be used in the poultry industry to disinfect all facilities. Pesticides protect forests and other wildlife habitats from invasive plant species and non-native insects and other pests [2].

CONCLUSION

Pesticide use in agriculture can cause undesirable effects on humans and the natural environment. Every potential pesticide compound is today being thoroughly tested chemically, biologically and toxicologically before its use in plant protection is approved. One of the biggest problems that accompanies the application of pesticides is the great pollution of water, both surface and groundwater, which is especially unfavorable if we know how important groundwater is for life on Earth. Great attention is paid to the development of methods that would help purify water contaminated with pesticide residues in order to reduce their further harmful effects on humans, plants, animals and the environment. Benefits of use pesticides include increased crop and livestock yields, improved food safety, human health, quality of life and longevity, and reduced drudgery, energy use and environmental degradation. From all the above, it can be concluded that there is a need for the development of alternative protection systems in the future and that they must be implemented as a supplement or replacement to the conventional application of pesticides. The development of new agrochemicals with novel modes of action, improved safety profiles, and adapted to the changing requirement of the food and feed production chain are more than ever the challenge. It is necessary to produce a healthy agricultural product with minimal or permanent impact on the environment and the health of people and other beings on Earth.

REFERENCES

[1] C.A. Damalas, Sci. Res. Essays; 4 (10) (2009) 945–949.

[2] I. Mahmood, S.R. Imadi, K. Shazadi, *et al.*, Effects of pesticides on environment in: Plant, soil and microbes, K. Hakeem, M. Akhtar, S. Abdullah (Eds.), Springer, Cham. (2016) 253–269.

[3] United States Environmental Protection Agency – EPA, *Available on the following link*: https://www.epa.gov/safepestcontrol/why-we-use-pesticides.

[4] R. Kaur, G.K. Mavi, S. Raghav, *et al.*, Int. J. Curr. Microbiol. Appl. Sci; 8 (3) (2019) 1889–1897.

[5] W. Zhang, F. Jiang, J. Ou, Global pesticide consumption and pollution: with China as a focus, Proceedings of the International Academy of Ecology and Environmental Sciences, 1 (2) (2011) 125.

[6] M. Stević, Fungicidi. Univerzitet u Beogradu, Poljoprivredni fakultet (2020).

[7] K.S. Delaplane, Pesticide Usage in the United States: History, Benefits, Risks, and Trends. Cooperative Extension Service, The University of Georgia, College of Agricultural and Environmental Sciences (1996). *Available on the following link*: https://people.forestry.oregonstate.edu/steve-strauss/sites/people.forestry.oregonstate.edu.steve-strauss/files/PestUse1996.pdf

[8] V. Janjić, Mehanizam delovanja pesticida. Društvo za zaštitu bilja Srbije, Akademija nauka i umjetnosti Republike Srpske, Institut za pesticide i zaštitu životne sredine, Zemun – Beograd (2009).

[9] M.D. Owen, I.A. Zelaya, Pest Manag. Sci; 61 (2005) 301–311.

[10] I. Molnar, J. Crop Prod; (2003) 622–647.

[11] A. Sharma, A. Shukla, K. Attri, *et al.*, Ecotoxicol. Environ. Safety; 201 (2020) 110812.

[12] S.O. Duke, Environ. Health Perspect; 87 (1990) 263–271.

[13] S. Đorđević, Primena mikroorganizama u organskoj proizvodnji In Organska poljoprivreda, B. Lazić, J. Babović (Eds.), Institut za ratarstvo i povrtlarstvo, Novi Sad (2008) 534–539.

[14] Pesticides Action Networks – PAN, *Available on the following link*: www.panna.org/pesticide-problem/pesticides-big-picture

[15] S. Mostafalou, M. Abdollahi, Toxicol. Appl. Pharmacol; 268 (2) (2013) 157–177.

[16] S.S.S.Saravi, M. Shokrzadeh, Role of Pesticides in Human Life in the Modern Age: A Review In: Pesticides in the modern world – Risks and benefits, M. Stoytcheva (Ed.), (2011) 3–12, ISBN: 978-953-307-458-0.

[17] S. Hussain, T. Siddique, M. Saleem, *et al*., Adv. Agron; 102 (2009) 159–200.

[18] P. Mineau, Environ. Toxicol. Chem; 21 (7) (2002) 1497–1506.

[19] F. Sánchez-Bayo, J. Environ. Anal. Toxicol. S:4; (2012) S4–002.

[20] A.C. de Oliveira, C.N. Junqueira, S.C. Augusto, J. Agric. Res; 58 (1) (2019) 2–8.

[21] M. Grahovac, D. Inđić, S. Lazić, *et al.*, Pestic. fitomed. (Beograd); 24 (4) (2009) 245–258.

[22] G. Ross, Lancet 366 (9499) (2005) 1771–1772.

ORGANIC AGRICULTURE: POTENTIAL OF THE FUTURE

Zlata Živković[1], Markola Saulić[1], Darko Stojićević[1], Milica Jevtić Đorović[1], Vladanka Stupar[1*]

[1]Academy of Applied Technical Studies Belgrade, College of Applied Engineering Sciences,
Nemanjina 2, 12000 Požarevac, SERBIA

[*]*vladanka.stupar@vts-pozarevac.edu.rs*

Abstract

Agriculture is an important factor in environmental damage, agricultural systems are degrading land, water, biodiversity and climate globally. Intensive agriculture using large amounts of inputs in the form of fertilizers and pesticides has led to long-term pollution of land, water resources, air and has had a strong impact on biodiversity. On the other hand, the world's population is constantly growing, currently numbering close to 8 billion people. Of that number, it is estimated that about a billion people in the world are chronically hungry. In order to meet the future needs of the population for food raw materials, food production must increase significantly and at the same time, the impact of agriculture on the environment and natural resources must be drastically reduced. Organic agriculture is seen as one of the solutions to this problem and has therefore developed rapidly around the world in recent years. The concept of organic agriculture is considered more eco-friendly compared to conventional agriculture and results in less nutrient leaching and greater carbon storage, less erosion and lower pesticide levels in water systems. Organic agriculture is an integrated food production system that is environmentally and socially acceptable and economically viable.

Keywords: conventional agriculture, organic agriculture, eco-friendly, food

CONVENTIONAL AGRICULTURE

Agriculture is the basis for the lives of over 2.5 billion people worldwide and provides food for all 7.9 billion people on the planet [1]. Agricultural activities have significantly changed the land surface of our planet. About 40% of the global ice-free area is already under agricultural production. These areas include land that is most suitable for agriculture, while most of the rest is covered by deserts, mountains, tundra, cities and other lands that are not suitable for agriculture. Agriculture is partly or fully responsible for environmental problems such as tropical deforestation and biodiversity loss, fragmentation and habitat loss, emissions of important greenhouse gases, loss of soil quality by erosion and salinization, reduction of water resources, regional climate change, declining air quality and rising infectious diseases. On the other hand, the expansion and intensification of agriculture has provided a key service to humanity by meeting the food needs of a rapidly growing population [2]. Conventional agriculture is one of the main causes of environmental degradation due to excessive consumption of irrigation and fertilizers [3], mechanization, high-yielding newly created varieties and breeds, high energy consumption. All these factors together have led to high yields on the one hand, but also to the loss of mixed farms, which are the basis of sustainable development [4]. Conventional farming focuses on producing large quantities of one crop in one location, a practice called monoculture [4,5]. This has led to a reduction in plant and animal diversity, a reduction in humus levels, excessive acidification (acidification) and salinization (salinization) of the soil. This has led to the disruption of ecosystems, and agriculture itself as a branch of industry has become a “victim of itself” in the areas of the most intensive use of chemicals [4]. The term “conventional agriculture” refers to standard, dominant approaches to agriculture practiced by farmers and growers around the world and does not impose any management restrictions other than those prescribed by law [6].

WHAT IS ORGANIC AGRICULTURE?

Organic agriculture (OA) is a comprehensive system of agricultural production that combines the best environmental standards, conservation of natural resources and biodiversity and production methods in accordance with the preferences of certain consumers, the use of natural substances and processes in food production [7]. OA can also be seen as a holistic production management system that promotes and enhances the health of agroecosystems, including biodiversity, biological cycles and biological activity of land [8]. Another definition of organic production could be described as an approach to agriculture that aims to create integrated, environmentally sustainable agricultural systems. productions that rely as much as possible on self-regulating agroecosystems and renewable resources obtained from the farm by biological and environmentally friendly processes and where dependence on external inputs (chemical) is reduced as much as possible. OA is a way of protecting the environment because it is based on the limited use of mineral fertilizers, which reduces the use of fossil fuels and greenhouse gas emissions (carbon dioxide, nitrogen dioxide and methane). Organic farming also contributes to improving soil quality by supporting microorganisms, worms, fungi and bacteria and allows for minimal pollution of the environment at the farm level [5]. The term “organic agriculture” encompasses the complete organic and biodynamic supply chain from input data to final goods produced, as well as cultural and social aspects of movement, not just aspects of agricultural production. The term “conventional agriculture” refers to standard, dominant to agriculture practiced by farmers and growers around the world and does not impose any management restrictions other than those prescribed by law [6]. OA uses only natural chemicals to control pests and diseases, so for these reasons the best control technologies are not always available to organic farmers and yields can be 30–40 percent lower than other agricultural methods [9].

DEVELOPMENT AND CURRENT STATE OF ORGANIC AGRICULTURE

The origins of or OA are intertwined with the birth of today's conventional agriculture. Many organic farming practices were the only option for farmers before the advent of chemically synthesized fertilizers, mechanization, and fossil fuels that enabled industrial agriculture to function. In such conditions, farmers had no choice but to work within biological and ecological systems. For example, the only source of fertilizer to replace nutrients from sown fields was human and animal manure and legumes. It can be said that OA is the original and main agriculture, and conventional is the one that deviates from the practices that agriculture has followed since its beginning [6]. The idea of ‘modern’ OA emerged in the early twentieth century in German-speaking and English-speaking countries [10]. The term ‘organic’ was first used in relation to farming by Northbourne (1940) in the book Look to the Land [6]. The originator of the idea and forerunner of today's organic production is Rudolf Steiner, an Austrian philosopher and social reformer. He was the first to introduce a biodynamic system of production, establishing a farm with a closed system of circulating organic matter. Today's principles of OA were founded in 1972, with the establishment of the International Federation of Organic Agriculture Movements (IFAOM) [11]. Beyond the industrialised countries of western Europe and North America, a large growth in OA was occurring during the 1980s in parts of Oceania, Central and South America, Asia and Africa. Many of these regions had existing indigenous farming systems that could be readily adapted to OA [6]. Today, Europe has the highest average percentage of areas of 6.2%. Serbia has only 0.44% of the area under this method of production [11]. The global area under certified OA has increased significantly, from 15 million ha in 2000 to 51 million ha in 2015. Although a fast-growing sector, it is estimated that about 1% of agricultural land worldwide is managed by OA practices during the decade of 2010 [10,12,13]. On the other hand, consumer demand for organic food, especially in Europe and the United States, is growing [13] and is projected to continue to increase globally [5,9,14].

ORGANIC AGRICULTURE'S PRINCIPLES

The basic standards of OA are based on appropriate means to minimize environmental pollution and nutrient losses at the farm level [15]. Organic production may not use food, feed, processing aids, plant protection products, soil improvers, reproductive material, microorganisms or animals that are GMOs or products obtained from or using GMOs. Ionizing radiation cannot be used in the processing of organic food or raw materials used in the production of organic food [15,16]. Today, more than 100 countries publicly support organic standards [17]. which are typically based on the standards developed by the IFOAM [18]. Most organic standard is similar, they may differ in certain details depending on the agro-ecological and specific conditions of each country. Organic standards cover different areas of agriculture and involve activities that are prohibited or restricted and other activities that are required or recommended. In organic systems of plant production recommendations are crop rotations with legumes, recycling of nutrients and the use of organic fertilizers. It emphasizes managing pests naturally, diversifying crops, and improving the soil with compost additions and animal and green manures. Use of synthetic fertilizers and chemical pesticides is prohibited. Compliance with organic standards is verified on an annual basis through farm inspections undertaken by accredited certification agents [16,17,19]. Methods of organic plant production include selection of plant species and varieties, crop rotation, soil cultivation system, means and method of fertilization, soil fertility maintenance system, method of controlling plant diseases, pests and weeds, method of collecting wild species from natural habitats, in accordance with the law regulates organic production. Agrotechnical measures applied in organic plant production should prevent or minimize environmental pollution. In organic plant production, hydroponic production cannot be performed. Protection against pests, diseases and weeds is primarily carried out by natural enemies, selection of plant species and varieties, appropriate crop rotation, land cultivation, thermal processes, use of allelopathic relationships and establishment of protective plant belts, as well as other agrotechnical measures. The total amount of fertilizers used in organic production, namely manure, dry manure and dehydrated poultry manure and composted animal excrement, including poultry manure, composted manure and liquid animal excrement, may not exceed 170 kg per year, due to possible contamination of soil and water with nitrates. The use of mineral nitrogen fertilizers is not allowed in organic plant production [16].

ADVANTAGES OF ORGANIC AGRICULTURE

Some studies on OA indicate better performance in terms of species richness and abundance, soil fertility, nitrogen uptake by crops, water infiltration rates and retention capacity, as well as energy use and efficiency compared to the same parameters in conventional agriculture [20]. Inorganic N fertilizer, which is used for plant nutrition in conventional tanks, is the most mobile form of nitrogen: in conventional tanks, about 20% of the applied nitrogen is lost by leaching. In organic systems, inorganic N and P fertilizers are prohibited, and the intake of nutrients is done through organic matter, where most of the N is in an organic form that is chemically more stable. Nitrogen is the main nutrient used by plants for nutrition, but in overdoses it can cause major problems. Such a case happened in the 1970s and 80s, when it was noticed that the quality of water in rivers and lakes began to deteriorate. The reason was the increased growth of algae, which led to the depletion of oxygen, with a negative impact on the life of plants and animals. The cause of algae growth was the supply of nutrients - nitrogen and phosphorus - from agriculture and wastewater [5]. In terms of the chemicals it uses, organic farming differs from conventional farming in that it does not lead to the release of chemical pesticides into the environment, or the leaching of fertilizers. Organic pesticides include azadiractin, paraffin oil, spinosad (insecticides), copper and sulfur (fungicides), iron phosphate $FePO_4 \cdot 2H_2O$ (limacides), tea tree oil, *Bacillus subtilis* strain Z3, BS10 and C13, *Pythroviod oligandrum* SC1, *Bauveria bassiana* strain ATCC 74040 (biopesticides) etc. [21]. Pest control in organic farming involves combining many techniques, such as: using predators to control pests, rotating crops each year to interrupt pest reproduction cycles; use of row covers for crop protection during the period of pest migration. Organic farming also provides an acceptable level of pest damage [5]. Land managed by organic farming can have a much higher water retention capacity than land managed in a conventional way which is especially in drought conditions and soil loss by erosion can also be significantly reduced. Surface and groundwater quality due to non-use of conventional synthetic pesticides is also better in organic compared to conventional agriculture [15]. Although all the necessary nutrients can be provided through organic fertilizers, nutrient management is more difficult in organic production systems resulting in differences in yields in organic and conventional agriculture [12]. Regarding the impact on the environment, it has been noticed that organic farming systems are more environmentally friendly than conventional farming systems because they have higher levels of carbon in the soil, better soil quality and less soil erosion compared to conventional systems [22,23], greater plant diversity, greater fauna diversity (insects, soil fauna and microbes, birds) and often more habitat and landscape diversity [24]. There is widespread belief that organic farming is more environmentally friendly and more sustainable than conventional systems.

CONCLUSION

In order to produce a sufficient amount of food for a growing world population while minimizing the negative impact on the environment, it is necessary for conventional agriculture to innovate, become more efficient and with improved agronomic practices. On the other hand, increasing importance is given to OA, which can play a role in solving the problems of land degradation, climate change, poverty alleviation, hunger, health and biodiversity management, and also has a positive impact on safe food production. Although the yields achieved by organic plant breeding are lower than in conventional agriculture, the demand for organic food is growing, and thus the area under organic farming, so in the future more and more agricultural land will be cultivated by organic methods, but it is necessary to find new production technologies adapted to different agro-ecological conditions of each climate. The challenge will be to increase food production, so it will be necessary to innovate the types of technologies used.

REFERENCES

[1] Food and Agriculture Organization of the United Nations – FAO 2021. Tracking progress on food and agriculture-related SDG indicators 2021: A report on the indicators under FAO custodianship, Food and Agriculture Organization of the United Nations, Rome, *Available on the following link*: https://doi.org/10.4060/cb6872en

[2] N. Ramankutty, A.T. Evan, C. Monfreda, *et al.*, Global Biogeochem. Cy; 22 (1) (2008) p.19.

[3] J.A. Foley, N. Ramankutty, K.A. Brauman, *et al*., Nature; 478 (7369) (2011) 337–342.

[4] N. Lešnjak, G. Ilić, B. Đorđević, Organska poljoprivreda – priručnik iz voćarstva, Udruženje Toppas Kuršumlija, Institut za istraživanja u poljoprivredi Srbija, 5 (2005) ISBN: 86-7384-030-9.

[5] O. Elmaz, H. Cerit, M. Özçelik, *et al.*, Fresenius Environ. Bull; 13 (11) (2004) 1072–1078.

[6] P. Kristiansen, C. Merfield, Overview of organic agriculture. Organic agriculture: A global perspective, CSIRO PUBLISHING (2006). *Available on the following link*: https://orgprints.org/id/eprint/14043/1/14043.pdf

[7] N. Mirecki, T. Wehinger, P. Repič *et al*., Priručnik za organsku proizvodnju – za osoblje savetodavne službe, Biotehnički fakultet, Podgorica (2011), ISBN: 978-9940-606-00-8.

[8] Food and agriculture organization of the United Nations FAO, Organic Agriculture, Food and Agriculture Organization of the United Nations, Rome (1999). *Available on the following link*: www.fao.org/unfao/bodies/COAG/COAG15/X0075E.htm.

[9] F.M. Santucci, Market issues in organic meat and dairy markets, (2002).

[10] E.M Meemken, M. Qaim, Annu. Rev. Resour. Econ; 10 (2018) 39–63.

[11] M. Tabaković, M. Simić, V. Dragičević, *et al*., Selekcija i semenarstvo; 23 (2) (2017) 45–53.

[12] U. Niggli, Sustainability of organic food production: challenges and innovations. Proceedings of the Nutrition Society, 74 (1) (2015) 83–88.

[13] H. Willer, J. Lernoud, The World of Organic Agriculture 2015: Summary In: H. Willer, J. Lernoud (Eds.), The World of Organic Agriculture, Statistics and Emerging Trends 2015. FiBL-IFOAM Report, Frick, Switzerland, Bonn, Germany (2015) 24–30.

[14] K. Lorenz, R. Lal, Adv. Agron; 139 (2016) 99–152.

[15] T. Gomiero, D. Pimentel, M.G. Paoletti, Crit. Rev. Plant Sci; 30 (1–2) (2011) 95–124.

[16] *Official Gazette of the Republic of Serbia* No. 5, No. 30/10 and No. 17/19 (2021) (in Serbian).

[17] V. Seufert, N. Ramankutty, T. Mayerhofer, Food Policy; 68 (2017) 10–20.

[18] International Federation of Organic Agriculture Movements – IFOAM, *Available on the following link*: www.ifoam.bio/

[19] J.P. Reganold, J.M. Wachter, Nature Plants; 2 (2) (2016) 1–8.

[20] L.C. Ponisio, L.K. M'Gonigle, K. Mace, *et al.*, Diversification practices reduce organic to conventional yield gap. Proceedings of the Royal Society B: Biological Sciences, 282 (2015) 20141396.

[21] Ministarstvo poljoprivrede, šumarstva i vodoprivrede, Uprava za zaštitu bilja, Republika Srbija, *Available on the following link*:

https://uzb.minpolj.gov.rs/wpcontent/uploads/2021/12/Lista_sredstva_za_zastitu_bilja_za_organsku_proizvodnju_na_03dec2021.pdf

[22] A. Gattinger, A. Muller, M. Haeni, *et al.*, Enhanced top soil carbon stocks under organic farming. Proceedings of the National Academy of Sciences, 109 (44) (2012) 18226–18231.

[23] D.H. Lynch, N. Halberg, G.D. Bhatta, Environmental impact of organic agriculture in temperate regions. CAB Review, 7 (10) (2012) p.17.

[24] D.W. Crowder, T.D. Northfield, M. R. Strand, Nature; 466 (7302) (2010) 109–112.

CHANGES IN NITRATE AND NITRITE CONTENT IN FOR LETTUCE, CHARD AND SPINACH AFTER FREEZING

Tatjana Anđelković[1*], Kristina Kitanović[2], Ivana Kostić Kokić[1], Bojan Zlatković[2], Danica Bogdanović[1]

[1]University of Niš, Faculty of Science and Mathematics, Department of Chemistry,
Višegradska 33, 18000 Niš, SERBIA

[2]University of Niš, Faculty of Science and Mathematics, Department of Biology and Ecology,
Višegradska 33, 18000 Niš, SERBIA

[*]*tatjana.andjelkovic@outlook.com*

Abstract

The leafy vegetables are the major source of nitrate and nitrite entry in the human body. The present study was conducted to investigate influence of freezing on nitrite and nitrate content in three commonly used leafy vegetables, lettuce, spinach and chard. Extraction procedure was performed by deionized water, and determination of nitrite and nitrate ions was performed using ion chromatography. The highest level of nitrite content before freezing showed samples of spinach, while the highest content of nitrate content was obtained for samples of lettuce. Results obtained by analysing samples after freezing showed that the highest content of nitrite ion was determined in samples of chard, while the lowest content was obtained by analysing samples of lettuce. Also, all investigated samples showed higher content of nitrate ion and lower content of nitrite ion after freezing comparing to results before freezing.

Keywords: nitrate, nitrite, vegetables, ion chromatography

INTRODUCTION

Nitrogen has a crucial role in life on the earth. Through nitrogen cycle, nitrogen is connected to food product properties. By different pathways that include plants, microorganisms, and agricultural activities, gas formations of nitrogen become incorporated into terrestrial nitrogenous compounds. Intermediate compounds of these transformations are nitrites and nitrates [1].

Vegetables play an important role in human nutrition and present source of minerals, vitamins, and biologically active compounds. They content a lot of different anions such as chloride, nitrate, sulphate, and nitrites. Nitrates are present naturally in most vegetables and human nitrate intake is manly from vegetables [2]. Also, human can intake nitrates from water and additives that are used as preservatives in meat and meat products. Some investigations showed that about 70-90% of total nitrate content in a normal diet is direct result of vegetable intake and it is attributed to vegetables especially green leafy vegetables including spinach, red beetroot, lettuce, etc. The nitrate levels in vegetables are very variable and may reach level up to 10 g/kg if they are grown in extreme conditions [3–5].

Nitrate reaction products and metabolites, including nitrite, nitric oxide, and N-nitroso compounds, have potentially adverse effects and health implications. These products and metabolites are related to the gastric diseases, bladder cancers and methemoglobinemia syndrome. Due to increased usage of nitrogen fertilizers and additives that contain nitrite, human exposure to nitrogen-containing compounds such as nitrites and nitrates are increasing and it is becoming an important public health issue [6–8].

Various methods are reported to determine nitrites and nitrates in water, food and other matrices. Different analytical techniques, such as potentiometry, spectrophotometry, ion chromatography, as well as high liquid chromatography have been used [9].

In this work, nitrite and nitrate level from samples of spinach, lettuce, and chard before and after freezing are reported. The analyses were carried out by ion chromatography.

MATERIALS AND METHODS

Sample preparation

Fresh and frozen plant material

Fresh vegetables including spinach, chard and lettuce were purchased from local open supermarket. Each vegetable was rinsed with water to remove any soil or wind-borne particles. From the fresh vegetables, subsamples were taken for determination of native nitrite and nitrate content in vegetables. Subsamples taken for determination of nitrite and nitrate content after freezing were putted into snap-lock plastic bags. All subsamples for freezing were labelled and stored in freezer for 3 months.

Sample preparation

A 10 g portion of each vegetable was homogenized by mixer (Bosh, Germany). From each homogenised sample, three subsamples of 1.0 g were weighed out by analytical balance with precision ± 0.00001 g (Kern, Germany) and 40 mL of ultrapure water was added to each subsample. Prepared samples were placed at 70°C for 20 min and after cooling mixtures were filtered through the Whatman No. 41. Then, obtained filtrates were filtered through 0.2 µm cellulose filter prior to chromatographic analysis. A dilution with ultrapure water was necessary due to high concentrations of ions. The supernatant was diluted to one twenty-fifth to match the dilution for analysis on ion chromatograph.

Instrumentation

The three replications were analysed for nitrate concentrations as follows. Volume of 5 mL of each filtrate sample was placed into the Dionex AS 50 model autosampler vials. Each of samples was loaded automatically into the ion chromatograph. Separation was achieved using Dionex IonPac AS22 column (4 × 250 mm) with the guard column Dionex IonPac AG22 (4 × 50 mm). The ion chromatograph used mix of 4.5 mM sodium carbonate and 1.4 mM sodium bicarbonate as an eluent at a flow rate of 1.2 mL/min. The concentration of nitrate and nitrite anions in samples was detected by the Dionex AERS 500, Carbonate, 4 mm, conductivity detector. Dionex Seven Anion Standard (Product No. 056933) was used for preparing standard solutions. The nitrate and nitrite concentration values were calculated automatically based on previous made processing method using Chromeleon 7 software.

RESULTS AND DISCUSSION

All vegetable samples were diluted to one twenty-fifth prior to analysis on ion chromatograph. All sample solutions analysed on IC successfully met the criterion of availability. Concentration of diluted solutions were between 0.25 and 10 mg/L and after conversion to nitrate content to vegetables, it was ranged from 13 to 1550 µg/kg.

Calibration curves obtained for nitrite and nitrate ion showed good correlation coefficients, 0.99989 and 0.99899, respectively. Figure 1 presents the calibration curves that were used for quantification of nitrite and nitrate ion. Figure 2, 3 and 4 present the chromatograms obtained after analysing samples of spinach, lettuce and chard, before and after freezing.

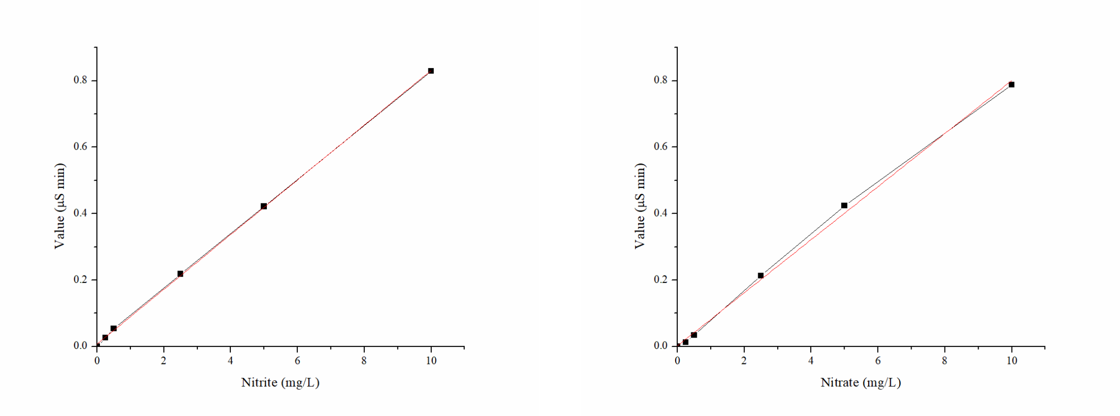

a) *b)*

Figure 1 *Standard curves for a) nitrite; b) nitrate*

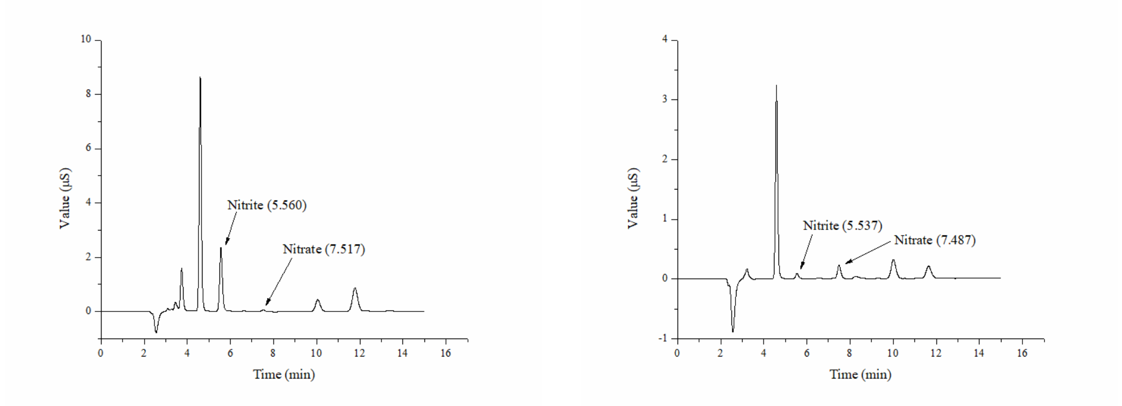

a) *b)*

Figure 2 *Chromatogram of spinach sample a) before freezing; b) after freezing*

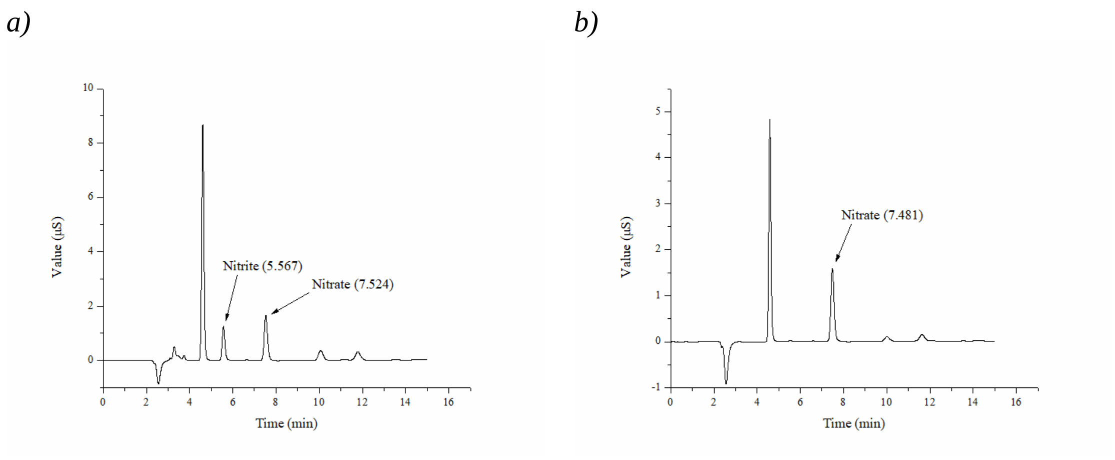


Figure 3 *Chromatogram of lettuce sample a) before freezing; b) after freezing*

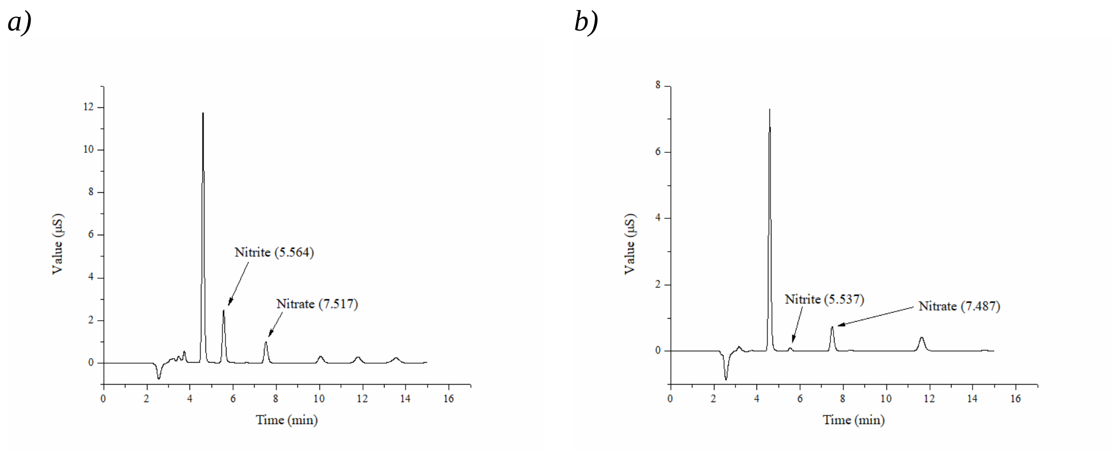


Figure 4 *Chromatogram of chard sample a) before freezing; b) after freezing*

Results of nitrite and nitrate quantification are presented in Table 1.

Table 1 *Nitrite and nitrate content in lettuce, spinach and chard determined before and after freezing*

Vegetable	**Anion**	**Concentration of ion (µg/kg)**	
		Before freezing	**After freezing**
Lettuce	NO_2^-	533.62	/
	NO_3^-	874.64	1543.21
Spinach	NO_2^-	1074.44	16.31
	NO_3^-	13.93	182.28
Chard	NO_2^-	1024.77	90.87
	NO_3^-	478.02	677.61

The highest level of nitrite content before freezing showed samples of spinach (1074.44 µg/kg), while the lowest content was determined in samples of lettuce, almost double lower (533.62 µg/kg). Samples of chard showed the slightly lower content than samples of spinach (1024.77 µg/kg). The highest value of nitrate content before freezing showed samples of lettuce, 874.64 μg/kg, while nitrate content in samples of chard was 478.02 μg/kg. Samples of spinach showed the lowest content of nitrate ion before freezing (13.93 μg/kg). By comparing the results of nitrite and nitrate content in samples before freezing, only samples of lettuce showed higher level of nitrate then nitrite content.

Results obtained using samples of vegetables after 3 months of freezing, showed that only samples of spinach and chard, contain nitrite ions at concentrations 16.31 and 90.87 μg/kg, respectively. In chromatograms obtained by analysing of lettuce samples, peaks which correspond to the nitrite ion were not detected. The highest level of nitrate content was obtained for the samples of lettuce, 1543.21 μg/kg, while the lowest value for content of nitrate ions was obtained for samples of spinach, 182.28 μg/kg. The nitrate content that was obtained for samples of chard was 677.61 μg/kg. By comparing the results of nitrite and nitrate content in samples after freezing, all samples showed higher content of nitrate then nitrite ion.

Bearing in mind that process of conversion nitrite to nitrate ion can occur in freezing conditions, this is probably reason of lower content of nitrite ion in samples before freezing, and the higher content of nitrate ion after freezing.

CONCLUSION

The nitrite and nitrate content in three commonly consumed fresh leafy vegetables in Serbia was determined. The effect of freezing on nitrite and nitrate content with regards to the leafy vegetables has also been established. Reported values indicate that all investigated samples before freezing showed the values of nitrite and nitrate content similar to results that has been found previously in the literature. Also, all investigated samples showed higher content of nitrate ion and lower content of nitrite ion after freezing comparing to results before freezing.

ACKNOWLEDGEMENT

This study was supported by the Ministry of Education, Science and Technological Development, Republic of Serbia (Contract Number 451-03-68/2022-14/200124).

REFERENCES

[1] M. Iammarino, A. Di Taranto, M. Cristino, Food Chem; 140 (2013) 763–771.

[2] S. Prasad, A.A. Chetty, Food Chem; 106 (2008) 772–780.

[3] A.C. Chang, T.Y. Yang, G.L. Riskowski, Food Chem; 138 (2013) 382–388.

[4] A.C. Chang, T.Y. Yang, G.L. Riskowski, Food Chem; 136 (2013) 995–960.

[5] Z. Bahadoran, P. Mirmiran, S. Jeddi *et al.*, J. Food Compos. Anal; 51 (2016) 93–105.

[6] H.B. Novaes, D.S. Vaitsman, P.B. Dutra, Quim. Nova; 32 (6) (2009) 1647–1650.

[7] M.C. Kyriacou, G.A. Soteriou, G. Solla *et al.*, Food Chem; 285 (2019) 468–477.

[8] J. Hsu, J. Arcot, N. Alice Lee, Food Chem; 115 (2009) 334–339.

[9] T-H. Zu, S-P. Hsieh, C-M. Su *et al.*, Int. J. Anal. Chem; (2018), Article ID 6285867, page 6, https://doi.org/10.1155/2018/6285867.

CAN LASER MODIFICATION OF COATED ELECTRODES IMPROVE THE HYDROGEN EVOLUTION REACTION IN ALKALINE ELECTROLYSERS?

Ivana Perović[1], Snežana Brković[1,*], Nikola Zdolšek[1], Gvozden Tasić[1], Mina Seović[1], Stefan Mitrović[1], Jovan Ciganović[1]

[1]University of Belgrade, Vinča Institute of Nuclear Sciences, National Institute of
the Republic of Serbia, Mike Alasa 12–14, 11351 Vinča, SERBIA

[*] *snezana.miulovic@vin.bg.ac.rs*

Abstract

Special attention in this work is devoted to the influence of laser radiation on the possibility of improving the activity of electrodes for the hydrogen evolution reaction. Using TEA CO_2 *lasers, Co and Mo based electrode coatings were modified and their morphology, composition and electrocatalytic activity were examined. It was found that the laser modification of Co-Mo coating did not significantly affect the cathodic activity. Therefore, it was concluded that this type of modification under test conditions does not significantly improve the energy efficiency of the alkaline electrolysis process.*

Keywords: hydrogen, alkaline electrolysis, laser radiation, EIS

INTRODUCTION

Alkaline electrolysis in industrial applications nowadays, is a relatively expensive and low efficiency method for hydrogen production. Through the development and application of new electro-catalytic materials and the introduction of new methods regarding the additional light sources during an electrolytic process, it is possible to overcome these deficiencies and make alkaline electrolysis one of the leading hydrogen production technologies. In wide variety of light sources applicable in this terms, laser radiation stands out due to its uniqueness in terms of the characteristics of the radiation itself: monochromaticity, spatial orientation, intensity and coherence [1]. Various physico-chemical processes characterize the interaction of laser radiation with matter in solid, liquid or gaseous state. The consequences of this interaction depend on the conditions in which the processes take place and on the properties of the material itself that is affected by the laser radiation. By varying the conditions and parameters of the laser, it is possible to achieve the desired modification of the matter by changing the chemical surface of the material, its morphology and crystal structure [2]. In this paper, the effects of the interaction of a pulsed nanosecond carbon dioxide laser with a Co-Mo deposit on a nickel electrode were investigated in order to explore the possibility of applying laser electrode modification for use in alkaline electrolyzers for hydrogen evolution reaction (HER).

MATERIALS AND METHODS

Electrochemical deposition of Co-Mo coatings

For the purpose of examining the influence of laser modified cathode coatings on the process of alkaline electrolysis, in this paper we tested coatings based on Co and Mo, electrochemically deposited on nickel plates with a purity of 99.9% using a citrate - precipitation bath.

The precipitation of Co and Mo was done in a two-electrode electrochemical cell with Ni plate, active surface area 0.7 cm^2 as cathode and platinum mesh, significantly larger active surface area, as anode. The electrodeposition bath consisted of a solution of cobalt and molybdenum salts ($CoSO_4 \cdot 6H_2O$ and $Na_2MoO_4 \cdot 2H_2O$) in deionized water, with the addition of three sodium citrate dihydrate as a complexing agent. The pH of the bath was 6.6 and was not adjusted during precipitation. For the composition of the applied bathroom, the optimal ratio of factors was taken, which gave the best characteristics in terms of uniformity and durability of coatings, based on previous research by Pellicer *et al.* [3,4]. The composition of the bathroom is given in Table 1.

Table 1 *Composition of citrate bath for electrochemical precipitation Co and Mo*

$c(CoSO_4 \cdot 6H_2O)$/ mol dm^{-3}	$c(Na_2MoO_4 \cdot 2H_2O)$/ mol dm^{-3}	$c(Na_3C_6H_5O_7 \cdot 2H_2O)$/ mol dm^{-3}	pH
0.1	0.012	0.2	6.6

The deposition process was performed at a current density of -5, -10 and -25 mA cm^{-2} for 5, 2.5 and 1 h, respectively, with the aim that all depositions were done with the same charge flow through the cell. Two electrodes were deposited under the same conditions (current density and time), i.e. a total of six electrodes for the purposes of the experiment. The deposition current was maintained constant using the Interface 1000E potentiostat/galvanostat (Gamry Instruments Inc.). All depositions were done without additional electrolyte mixing, at room temperature.

One electrode from each set of deposition (same current density and time) was tested in a solution of KOH concentration of 6 mol dm^{-3} in a three-electrode electrochemical cell, by recording polarization curves (Tafel analysis) and EIS spectrum, while the other two were laser modified. In Tafel and EIS tests, the obtained Co-Mo electrodes were used as working electrodes, Pt mesh was used as a counter electrode, and Hg/HgO electrode was used as a reference electrode. Before each experiment, the electrolyte was purged with hydrogen for 30 min. Measurements were performed at room temperature, 298K. To investigate the effect of laser modification of Co-Mo coatings on the kinetics of the hydrogen reaction on all tested electrodes, the first step was HER at constant current density of $j = -300$ mA cm^{-2} for 1200 s, then the electrodes were kept at constant value of the potential at which the current density for hydrogen evolution was less than -300 mA cm^{-2} for 800 s, and only then the polarization curves were recorded, with a potential change rate of 1 mV s^{-1} starting from the applied potential in step 2 to a value of approximately -1.10 V (step 3). Polarization curves were recorded with correction for voltage drop through the electrolyte ("current interrupt" technique) [5]. Impedance spectra were recorded in the frequency range from 0.1 Hz to 100 kHz, at overpotential from -20 mV to 200 mV. The amplitude of the alternating signal was 10 mV. The electrolyte in the electrochemical cell was at room temperature, 298K.

TEA CO_2 laser modification of electrodes

The remaining three electrodes with deposited Co-Mo coating (described above) were irradiated using TEA CO_2 laser at different operating parameters. They were then tested in a three-electrode electrochemical cell in the same way and under the same conditions as the unmodified coatings. To obtain laser-induced plasma for coating modification, a TEA CO_2 laser was used, which was developed and constructed in the Laboratory of Physical Chemistry at Vinča Institute. This compact, ultraviolet pre-ionized gas system is a radiation source that emits light with a wavelength of 10.6 µm in the form of short pulses, high power output and high pulse energy. The laser consists of a laser chamber connected to a gas and energy-electric system. A gas mixture of $CO_2/N_2/He$ composition (1:1:4.6) is constantly maintained in this chamber. The output energy of the applied laser pulse was 150 mJ, the width at half the maximum height of the initial "peak" is about 100 ns, while the duration of the pulse (peak + tail) is much longer, over 2 µs. About 35% of the total radiated energy of the laser pulse is concentrated in the initial peak of the laser pulse. The divergence of the laser beam was approximately 10 mrad, and the frequency of pulse repetition was 1.3 Hz. During the experiment, a ZnSe lens was used to focus the beam, and the focus was at a distance of 13 cm. The electrodes were irradiated in different atmospheres and at different distances from the maximum focus, and the display of varied parameters is given in Table 2. The experiments were performed at room temperature.

Table 2 *Display of varied parameters in laser irradiation of electrodes*

Electrode	5 mA cm^{-2}	10 mA cm^{-2}	25 mA cm^{-2}
Atmosphere	Air	Helium	Air
Distance from focus	7.5 cm	9 cm	9 cm

RESULTS AND DISCUSSION

Influence of laser modification of Co-Mo coatings on the rate and mechanism of hydrogen evolution reaction

The electrochemical activity of Co-Mo coatings, obtained by deposition at different current densities, was investigated by the method of Tafel analysis before and after laser modification of TEA CO_2 laser. The obtained polarization curves are shown in Figure 1 [6].

Polarization curves and experimentally obtained kinetic parameters (Table 3) show that the values of the Tafel slope range from -31 to -40 mV dec^{-1} [6]. This indicates that the decisive stage for the hydrogen evolution reaction in all tested systems is the Heyrovsky stage. It is observed that the slopes of the polarization curves for non-laser modified coatings differ very little from the slopes obtained for electrodes that have undergone laser modification. From this it can be concluded that the changes that occurred on the surface of the electrode coating due to the interaction of laser radiation did not significantly affect the change in the reaction mechanism of hydrogen evolution.

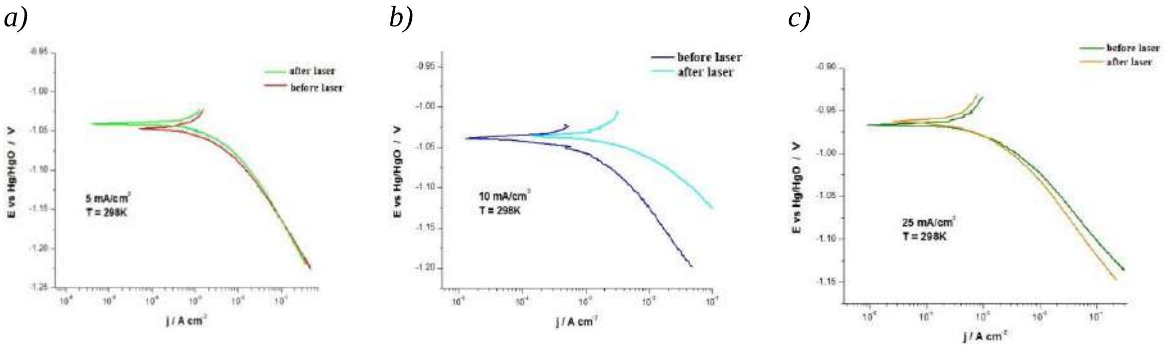


Figure 1 *Polarization curves for the hydrogen evolution reaction on Ni electrodes with Co-Mo coatings deposited at densities of 5 mA cm^{-2} a); 10 mA cm^{-2} b) and 25 mA cm^{-2} c); without and after laser modification [6]*

Table 3 *Kinetic parameters of Co-Mo coating, for HER at T=298K*

Electrods	- b/mV dec^{-1}	j_o /A cm^{-2}
CoMo 5 mA no laser	33.44	$744.6 \cdot 10^{-6}$
CoMo 5 mA with laser	31.84	$649.1 \cdot 10^{-6}$
CoMo 10 mA no laser	38.73	$340.6 \cdot 10^{-6}$
CoMo 10 mA with laser	38.93	$303.1 \cdot 10^{-6}$
CoMo 25 mA no laser	33.77	$407.1 \cdot 10^{-6}$
CoMo 25 mA with laser	39.82	$370.6 \cdot 10^{-6}$

From the presented kinetic parameters, it can be seen that the exchange current density (j_0) has lower values for coatings that have been exposed to laser radiation. This leads to the conclusion that the resulting changes in the electrode coatings do not favour their catalytic activity.

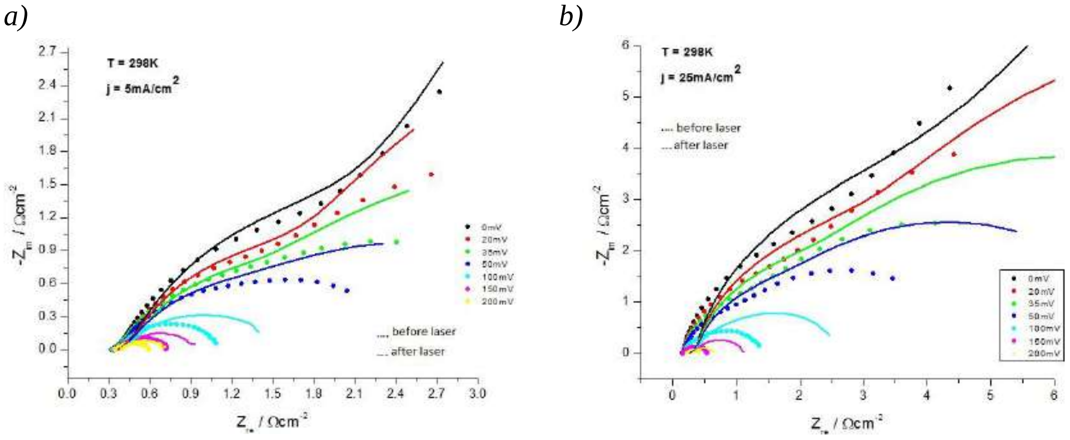


Figure 2 *EIS diagrams for HER on Co-Mo coatings deposited on 5 a) and 25 mA cm^{-2} b), without and after laser modification, obtained at different overpotential [6]*

Insight into the mechanism of electrochemical reaction is provided by recording the electrochemical impedance spectra shown in Figure 2. The obtained data were fitted according to the model of Armstrong equivalent circuit in which the capacity of the double electric layer was replaced by a constant phase element and shown in Table 4 [6].

Table 4 *Parameters obtained by fitting experimental EIS spectra recorded at different overpotential values, for the tested Co-Mo coatings at 298K*

j = 5 mA cm^{-2} BEFORE LASER MODIFICATION

T/K	- η/mV	R_e/Ω cm^{-2}	R_{ct}/Ω cm^{-2}	C_{dl}/F cm^{-2}	C_p/F cm^{-2}	R_p/Ω cm^{-2}	σ
298	20	0.351	3.800	0.2393	0.952	2.40	11966
	35	0.328	0.026	0.0028	0.261	3.30	142
	50	0.339	0.032	0.0033	0.209	2.20	168
	100	0.337	0.062	0.0073	0.119	0.73	366
	150	0.343	0.051	0.0054	0.254	0.09	274
	200	0.354	0.039	0.0053	0.079	0.21	265

j = 5 mA cm^{-2} AFTER LASER MODIFICATION

T/K	- η/mV	R_e/Ω cm^{-2}	R_{ct}/Ω cm^{-2}	C_{dl}/F cm^{-2}	C_p/F cm^{-2}	R_p/Ω cm^{-2}	σ
298	20	0.376	4.520	0.2813	0.589	9.08	14069
	35	0.374	4.370	0.4510	0.017	1.24	22551
	50	0.375	2.602	0.3052	0.016	1.16	15262
	100	0.374	0.120	0.0103	0.072	1.07	515
	150	0.373	0.103	0.0059	0.051	0.48	295
	200	0.372	0.095	0.0036	0.020	0.28	180

j = 25 mA cm^{-2} BEFORE LASER MODIFICATION

T/K	- η/mV	R_e/Ω cm^{-2}	R_{ct}/Ω cm^{-2}	C_{dl}/mF cm^{-2}	C_p/mF cm^{-2}	R_p/Ω cm^{-2}	σ
298	20	0.158	4.284	0.0854	0.278	6.77	4271
	35	0.159	3.386	0.0917	0.312	3.44	4585
	50	0.160	2.699	0.0991	0.366	1.77	4955
	100	0.159	0.044	0.0143	0.049	1.25	715
	150	0.160	0.026	0.0120	0.072	0.36	604
	200	0.175	0.060	0.0057	0.106	0.30	287

j = 25 mA cm^{-2} AFTER LASER MODIFICATION

T/K	- η/mV	R_e/Ω cm^{-2}	R_{ct}/Ω cm^{-2}	C_{dl}/mF cm^{-2}	C_p/mF cm^{-2}	R_p/Ω cm^{-2}	σ
298	20	0.303	8.691	0.0791	0.229	9.47	3959
	35	0.304	7.146	0.0836	0.277	4.05	4180
	50	0.300	5.620	0.0918	0.373	3.37	4592
	100	0.296	0.045	0.0025	0.092	2.38	126
	150	0.297	0.046	0.0029	0.067	0.79	145
	200	0.300	0.045	0.0022	0.048	0.30	110

Comparing the obtained parameters for the tested Co-Mo coatings deposited at 5 and 25 mA cm^{-2}, it is noticeable that with increasing overpotential, the resistance to charge transfer, R_{ct}, and the resistance to mass transfer, R_p, decrease, as expected. However, it is noticeable that in the case of laser-modified coatings R_{ct} and R_p are slightly higher, compared to their values in the case of unmodified coatings. This observation is in accordance with the data obtained from Tafel's analysis, where it was concluded that laser modification does not favor an increase in the catalytic activity of the cathode coating. The values of the roughness factor also correspond to the previous observations, in terms of slight changes caused by laser modification. From all the above, it can be concluded that laser modification of TEA CO_2 laser, at least in the case of tested coatings under given experimental conditions, does not have a favorable effect on improving the energy efficiency of electrolytic hydrogen evolution in alkaline media.

CONCLUSION

The results of the study of the influence of laser-modified Co-Mo cathodic coatings on the mechanism and kinetics of the hydrogen evolution reaction in the process of alkaline electrolysis showed that laser modification of coatings did not lead to significant changes in catalytic activity. There was no change in the decisive degree of the hydrogen evolution reaction. Resistance to mass and charge transfer in the case of laser-modified coatings is slightly higher compared to unmodified coatings, and the roughness factor has remained almost unchanged. Inspecting the electrocatalytic activity of the tested coatings, it can be concluded that laser modification of TEA CO_2 laser, at least in the case of tested coatings under given experimental conditions, does not favourably improve the energy efficiency of electrolytic hydrogen production in alkaline environment.

ACKNOWLEDGEMENT

The authors are grateful to the Ministry of Education, Science and Technological development of the Republic of Serbia for financial support (grant number 451-03-68/2022-14/200017).

REFERENCES

[1] D.U. Chang, in SAE Tech. Pap., Springer, (1985) p.558.

[2] M.S. Brown, C.B. Arnold, Chapter 4 Fundamentals of Laser-Material Interaction and Application to Multiscale Surface Modification, K. Sugioka, *et al.*, (eds.), in Laser Precision Microfabrication (2010) 91–120.

[3] E. Pellicer, E. Gómez, E. Vallés, Surf. Coatings Technol; 201 (2006) 2351–2357.

[4] E. Gómez, E. Pellicer, E. Vallés, Surf. Coatings Technol; 197 (2005) 238–246.

[5] G. Tasić, Primena novih katodnih materijala za izdvajanje vodonika dobijenih elektrohemijskim taloženjem Ni i Co sa Mo i W i ispitivanje uticaja mikrotalasnog polja na njihova fizičkohemijska svojstva, Univerzitet u Beogradu (2013) (in Serbian).

[6] I.M. Perovic, Uticaj primene jonskih aktivatora na bazi d-metala Zn, Co, Cu, Ni, Mo i laserskog zračenja na energetsku efikasnost procesa dobijanja vodonika alkalnom elektrolizom, Univerzitet u Beogradu (2018) (in Serbian).

NEW GENERATION OF ELECTROCHEMICAL SUPERCAPACITORS

Nikola Zdolšek[1], Snežana Brković[1*], Ivana Perović[1], Milica Ćurčić[1], Slavko Dimović[2], Milica Vujković[3]

[1]University of Belgrade, VINČA Institute of Nuclear Sciences - National Institute of the Republic of Serbia, Department of Physical Chemistry, Mike Petrovića Alasa 12–14, 11000 Belgrade, SERBIA

[2]University of Belgrade, VINČA Institute of Nuclear Sciences - National Institute of the Republic of Serbia, Department of Radiation and Environmental Protection, Mike Petrovića Alasa 12–14, 11000, Belgrade, SERBIA

[3]University of Belgrade, Faculty of Physical Chemisrty, Studentski trg 12–16, Belgrade, SERBIA

[*]*snezana.miulovic@vin.bg.ac.rs*

Abstract

In this paper we synthesised new hybrid porous carbon/MWCNT material using ionic liquid. Characterization of surface chemistry showed that hybrid porous carbon/MWCNT material, beside oxygen functionalities, has nitrogen as well as sulphur surface functional groups. This hybrid material was further tested as electrode material for multivalent ions electrochemical supercapacitors. The results showed that multivalent ions (i.e. Al^{3+} *ions) are responsible for increase operating voltage and specific capacitance value compare to the commercial and most used* H_2SO_4 *electrolyte.*

Keywords: electrochemical supercapacitors, multivalent-ion electrolytes, carbon materials, ionic liquid

INTRODUCTION

Electrochemical supercapacitors attracted great attention as energy storage devices in the last decade. Supercapacitors have remarkable performances such as fast charge-discharge rates, stable cyclic capability and high power density. However, low energy density limits application of electrochemical supercapacitors in modern energy devices.

Mentioned drawback of supecapacitors can be solved using two different approaches: develop of new high capacitance electrode materials and develop of new electrolytes with large operation potential voltage.

Using first approach, different new nanomaterials have been developed. The most popular and most cheap are porous carbon materials [1]. Porous carbon materials showed high capacitance values, some of them even around 1000 F g^{-1}. The charge storage properties of carbon materials cold be improved by doping with different heteroatoms such as N, S, O, P, F, etc. Introducing heteroatom or combination of heteroatoms in carbon structure increase conductivity, wettability, charge transfer, etc. [1,2]. Furthermore, beside porous carbon materials other forms of carbon are also suitable for application in electrochemical supercapacitors. For example, multi-walled carbon nanotubes (MWCNTs) could be potential electrode materials [3].

The second approach using formulation of new electrolytes with larger operating voltage compare to standard and most used electrolytes in supercapacitors (strong acids and bases). These new electrolytes are usually organic electrolytes [4]. Organic electrolytes are expensive, flammable and toxic. For that reasons, in order to eliminate in the first line expensive electrolytes, different new and non-ogranic aqueous electrolytes have been formulated with large operating potential windows.

In this paper we used two mentioned approaches to improve performances of electrochemical supercapacitors. We develop hybrid materials porous carbon/MWCNT doped with heteroatoms using ionic liquid as porous carbon precursor. Furthermore, obtained hybrid material was tested in multivalent-ions electrolytes containing Al^{3+} and Ca^{2+} and compare with standard H_2SO_4.

MATERIALS AND METHODS

Synthesis of hybrid material

Preparation of hybrid material porous carbon/MWCNT was done in two steps. In first step, MWCNT was dispersed in ionic liquid 1-Butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide. Mixture of MWCNT and ionic liquid was sonicated for 8h at room temperature (E=8064 kJ). After ultrasound treatment, stable and dark dispersion was formed.

In the second step, dispersion was carbonized at 800 °C in nitrogen atmosphere with a heating rate 10 °C min^{-1}. After reaching 800 °C material was kept at this temperature for 1h, and then cool down to room temperature in nitrogen atmosphere. The material was denoted as carbon/MWCNT.

Characterization of material

Material was characterized using Fourier transformed infrared spectroscopy (FTIR). FTIR spectroscopy was performed using Nicolet iS5 FTIR spectrometer (Thermo Fisher Scientific). FTIR spectra were measured in the range of 4000 – 400 cm^{-1} using KBr pellet technique.

Electrochemical measurements

The working electrode was prepared by mixing carbon material and 5% Nafion (Sigma Aldrich) as a binder in the ratio 95:5. The obtained mixture was suspended in ethanol and sonicated in an ultrasonic bath for 1 h. Part of homogenized mixture was transferred onto a glassy carbon electrode (GCE) and dried in oven at 80 °C for 2 h. All electrochemical measurements, including cyclic voltammetry (CV) were performed using Gamry 1000E potenciostat/galvanostat. Three electrodes electrochemical cell was used, with platinum as counter electrode, saturated calomel electrode (SCE) as reference electrode and modified GCE as working electrode. All measurements were done at room temperature. As supporting electrolytes were used 1M H_2SO, 1M $Al(NO_3)_3$ and 1M $Ca(NO_3)_2$. Specific capacitance (F g^{-1}) of electrode was calculated using cathodic or anodic charges integrated from CV voltammograms, Equation (1):

$$C = \frac{\int I \cdot V \cdot dV}{m \cdot v \cdot \Delta V} \tag{1}$$

where I is the measured current, V is the potential, m is the mass of electroactive material layer onto the GCE, v is the applied scan rate and ΔV is the used potential window.

RESULTS AND DISCUSSION

Material synthesis and characterization

For the first time, hybrid materials consist of porous carbon and MWCNT was prepared using ionic liquid approach. 1-Butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide has different functional groups with N, S and F atoms and it could be served not only as porous carbon precursor, but also as heteroatoms precursor. With this method hybrid material porous carbon/MWCNT can be easily prepared.

FTIR spectroscopy was used to investigate surface chemistry of obtained material. As can be seen form Figure 1 broad band at around 3450 cm^{-1} could be attributed to OH stretching vibration. The peaks at 2919 cm^{-1} and 2850 cm^{-1} correspond to the asymmetric and symmetric stretch vibrations of C-H groups [5]. Other peaks located below 2000 cm^{-1} indicate presence of oxygen, nitrogen and sulphur surface functional groups. Peak at 1630 cm^{-1} could be assigned as C=X (where X=O, C or N) [6]. Presence of C-O functional group was determined by peak at 1120 cm^{-1}. Presence of N and S atoms in carbon structure was further confirmed by peaks located at 800 cm^{-1} (C-N) and 700-600 cm^{-1} (C-S). According to the FTIR analysis it can be concluded that using 1-Butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ionic liquid as porous carbon precursor hybrid material N, S-doped carbon/MWCNT can be prepared.

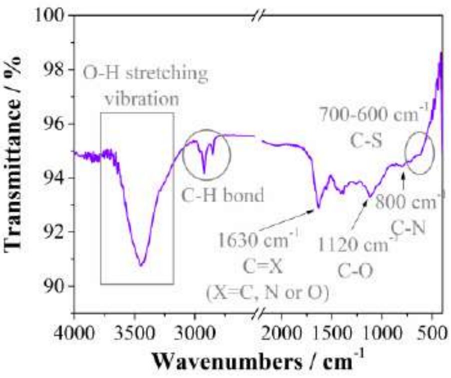


Figure 1 *FTIR spectrum of hybrid N,S-doped carbon/MWCNT material*

This heteroatoms-doped hybrid carbon material represents suitable electrode material for electrochemical supercapacitors. From that reasons, this materials was tested not only in conventional 1M H_2SO_4 electrolyte, but also in multivalent-ions electrolytes 1M $Al(NO_3)_3$ and 1M $Ca(NO_3)_2$. Figure 2 showed cyclic voltammetry (CV) of investigated material in three mentioned electrolytes. As can be seen, the potential windows for multivalent ions electrolyte are lager when compared to acidic electrolyte. For both multivalent ions electrolytes potential window is 1.2 V, while for H_2SO_4 electrolyte potential window is shorter (0.9 V). Calculated specific capacitance (at 5 mV s^{-1}) form CV curves was higher for 1M $Al(NO_3)_3$ (240 F g^{-1}), followed by 1M H_2SO_4 (208 F g^{-1}) and $Ca(NO_3)_2$ (109 F g^{-1}).

Enhanced charge storage behaviour of carbon/MWCNT hybrid material in Al^{3+} ion containing electrolyte is reflected in larger operating potential windows and high capacitance value compare to potential window and specific capacitance obtained for 1M H_2SO_4 electrolyte.

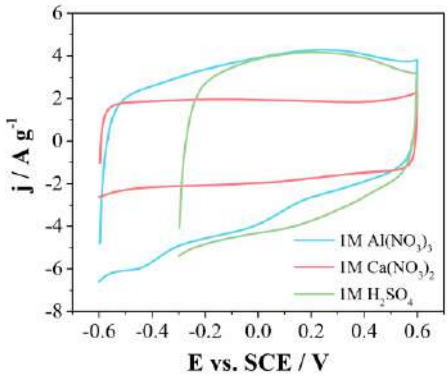


Figure 2 *CVs of carbon/MWCNT in three investigated electrolytes at 20 mV s^{-1}*

Important question arises here: are Al^{3+} ions responsible for larger operating voltage compare to H_2SO_4, or the dominant role has nitrate anions? For that reason we investigated and compared pure 1M HNO_3 electrolyte, as well mixture of 1M HNO_3 and 1M $Al(NO_3)_3$. As can be seen from Figure 3, hydrogen evolution in 1M HNO_3 starts at around -0.1 V vs. SCE, while for 1M $Al(NO_3)_3$ starts after -0.6 V vs. SCE. This implies that H^+ and Al^{3+} ions are responsible for operating potential window. Namely, the decrease of protons concentration in the electrolyte mixture leads to an increase in its pH, which inhibits the water decomposition reaction thus extending the workable potential window.

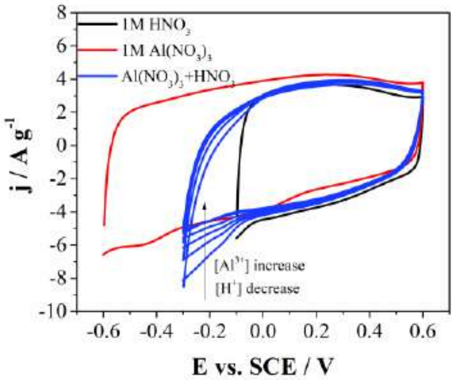


Figure 3 *CVs of carbon/MWCNT in 1M $Al(NO_3)_3$, 1M HNO_3 and mixture of $Al(NO_3)_3$ and HNO_3 in different ratios*

CONCLUSION

Ionic liquid was used to synthesize hybrid material based on porous carbon and MWCNT. Using 1-Butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, hybrid material was dual doped with nitrogen and sulphur. This method, based on application of ionic liquid in carbon material synthesis offers possibility of easy preparation heteroatom dual doped hybrid material. Charge storage behaviour of porous carbon/MWCNT was tested in multivalent ions electrolytes (1M $Al(NO_3)_3$ and 1M $Ca(NO_3)_2$) and compared with 1M H_2SO_4 electrolyte. Calculated specific capacitance was higher for 1M $Al(NO_3)_3$ (240 F g^{-1}), followed by 1M H_2SO_4 (208 F g^{-1}) and $Ca(NO_3)_2$ (109 F g^{-1}). Besides, operating potential window was larger for multivalent ions electrolytes (1.2 V), compare to H_2SO_4 (0.9 V). This new strategy based on application of new hybrid carbon material and multivalent ions electrolytes opens up new possibilities for improving performances of electrochemical supercapacitors.

ACKNOWLEDGEMENT

This research was supported by the Science Fund of the Republic of Serbia, PROMIS, #6062667, HISUPERBAT.

REFERENCES

[1] Z. Li, K. Xu, Y. Pan, Nanotechnol. Rev; 8 (2019) 35–49.

[2] P.E. Lokhande, U.S. Chavan, A. Pandey, Electrochem. Energy Rev*;* 31 (3) (2019) 155–186.

[3] S. H. Aboutalebi, A. T. Chidembo, M. Salari, *et al.*, Energy Environ. Sci; 4 (2011) 1855–1865.

[4] F. Béguin, V. Presser, A. Balducci, *et al*., Adv. Mater; 26 (2014) 2219–2251.

[5] M. Varga, T. Izak, V. Vretenar, *et al.*, Carbon N. Y; 111 (2017) 54–61.

[6] S. Biniak, G. Trykowski, M. Walczyk, *et al.*, J. Appl. Spectrosc; 83 (2016) 580–585.

THE HYDROGEN PRODUCTION ON Ni ELECTRODE CO-DEPOSITED WITH Co+V_2O_5: THE ELECTROCALYTIC SYNERGETIC EFFECT

Nebojša Potkonjak[1*], Đuro Čokeša[1], Mirjana Marković[1]
[1]University of Belgrade, VINČA Institute of Nuclear Sciences, National Institute of the Republic of Serbia, Mike Petrovica Alasa 12–14, 11000 Belgrade, SERBIA
[*]*npotkonjak@vin.bg.ac.rs*

Abstract

The hydrogen evolution reaction (HER) was studied on Ni support electrode electrodeposited with Co and/or V_2O_5 *species at 298 K in 1 M KOH. In order to examine the electrocatalytic activity of the Ni,* V_2O_5*/Ni, Co/Ni and Co+*V_2O_5*/Ni electrodes for HER, the quasi-potentiostatic polarization, potentiostatic and galvanostatic techniques were applied. Electrocatalytic activity of these electrodes was compared through exchange current density, resulting values of overpotential measured at fixed current density and resulting current density at fixed overpotential. Presented results showed that increased of electrocatalyticc activity of* V_2O_5*/Ni and Co/Ni electrodes if compared with Ni, can be ascribed to the increase of electrochemical surface by electrodeposition. On the other hand Co+*V_2O_5*/Ni electrode revile the highest electrocatalytic activity which has pointed to the existence of a synergetic electrocatalytic effect.*

Keywords: hydrogen evolution reaction, cobalt species, vanadium pentoxide, co-deposition electrocatalysis

INTRODUCTION

Considering a worldwide need for renewable energy sources, much attention has been given to the hydrogen economy. Currently the hydrogen production from alkaline water electrolysis is facing the problem concerning high energy consumption [1]. Therefore, new cathodic materials used for hydrogen production based on the concept of electrocatalytic synergism are particularly of a great importance [2]. The strict definition of electrocatalysis is: the effect of an electrode material on the electrode reaction rate. However, this effect can be real (intrinsic) [3] or only apparent [4]. Among various proposed electrocatalysis systems, oxide electrodes have been shown to possess interesting electrocatalytic activity for the hydrogen evolution reaction (HER) [3–5]. Hydrogen evolution reaction (HER) is one of the most investigated electrochemical reactions for which a modern theory of electrocatalysis has been developed. The reason is that the reaction proceeds through a limited number of steps with the only one type of intermediate.

MATERIALS AND METHODS

All experiments were carried out in a thermostated three-electrode electrolytic cell at 293 K, with a nickel rectangular plate (99.99% purity, surface area 5.0 cm^2) which served as the support and working (comparative) electrode. A counter electrode was a large-area platinum mesh. A Hg/HgO/1M KOH electrode was utilized as a reference electrode. The electrolyte solution was 1 M KOH.

The co-electrodeposition of V_2O_5 and/or Co species was conducted in 1 M KOH solution by adding 100 mg l^{-1} of each element which were in the form of V_2O_5 (Fisher certified Reagent) and $[Co(en)_3]Cl_3$ (was synthesized from components of p.a. purity). The Ni electrode (5 cm^2) served as the support electrode. The freshly prepared Ni support electrode was immersed in a bath and electrodeposition was carried out at the constant current density of -50 mA cm^{-2}.

Quasi-potentiostatic polarization, potentiostatic and galvanostatic techniques were performed using Solartron 1286 electrochemical interface. Quasi-potentiostatic polarization curves were recorded at the scan rate of 1 mV s^{-1}. Potentiostatic and galvanostatic measurements were carried out at the applied overvoltage of -250 mV and current density of -300 mA cm^{-2} respectively.

The analysis of the electrode surface was done by the X-ray fluorescence (XRF) spectrometer (ARL Optim'X 108) with a wavelength dispersive analysis system was used to analyse the $Co/V_2O_5/Ni$ electrode surface. The excitation was done by the Rh X-ray tube operated at 50 kV and 1 mA. The 2θ angle of the spectrometer was scanned with steps of 0.1°, and the counting time was 1 s in each step.

RESULTS AND DISCUSSION

The XRF spectra has reveal the composition of the cathode prepared from co-deposition of Co and V_2O_5 onto Ni support (Figure 1). As expected the presence of Co and V spectral lines confirmed the existence of Co and V species deposited on Ni.

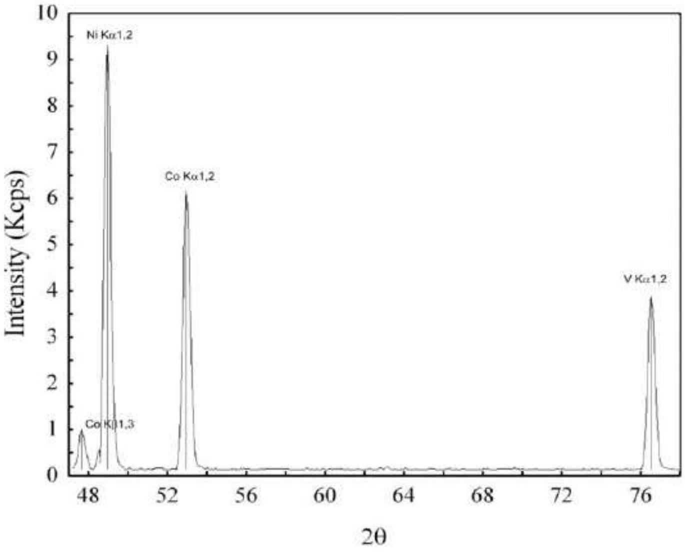


Figure 1 *The XRF spectra of the Co+V_2O_5/Ni electrode after co-deposition in 1 M KOH*

The Tafel slopes, for the HER for all investigated electrodes ranged from 116.1 V dec^{-1} to 104.3 V dec^{-1}, indicating that the charge-transfer (Volmer) reaction is the rate-determining step (RDS) for the HER. According to the general model for the HER mechanism, if the Volmer reaction, is the rate-determining, the resulting Tafel curve should yield a slope of 118 mV dec^{-1} at 20 °C. Concerning the exchange current density values, increase of j_o, especially for Co+V_2O_5/Ni electrode imply to the existence of electrocatalytic synergetic effect of co-deposited species. This is even more odious when the effective exchange current density, the exchange current density divided by roughness factor (σ), Table 1.

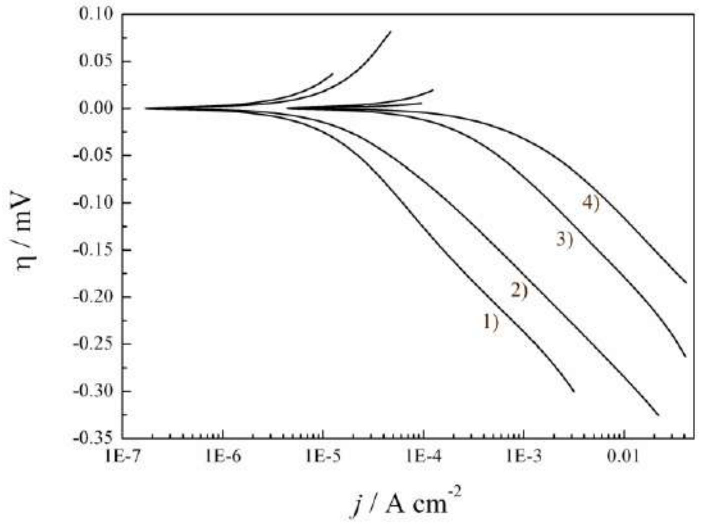


Figure 2 *Quasi-potentiostatic polarization curves for the investigated cathodes: 1) Ni, 2) V_2O_5/Ni, 3) Co/Ni and 4) V_2O_5+Co/Ni at 298 K*

Hence, in order to compare the electrocatalytic activity of investigated electrode at the conditions relevant for the operation of a commercial electrolizers, we fixed current density at -300 mA cm^{-2} (i.e. fixed hydrogen production rate) and obtained the resulting overpotentials which are required to reach the given current density value. Overpotential values for each investigated electrode are given in the Table 1 and presented in Figure 3. Results have confirm conclusions from the Tafel analysis, namely Co+V_2O_5/Ni electrode required the lowest energy input (overpotential), -251 mV and Ni electrode required the largest energy input (overpotential), -530 mV.

Table 1 *The HER kinetic parameters ($j_{o,}$ b) obtained form of quasi-potentiostatic polarization curves with roughness factor (σ). Resulting current density (j_{-250}) obtained at fixed overpotential (η) -250 mV and η needed for a fixed hydrogen production of -300 mA cm^{-2}*

Electrode	**-b (mV dec^{-1})**	**-j_0 (A cm^{-2})**	**-η_{300} (mV) at 300 mA cm^{-2}**	**-j_{250} (mA cm^{-2}) at -250 mV**	**σ**	**j_0 /σ (A cm^{-2})**
Ni	116.1	$7.5 \cdot 10^{-6}$	530	1.8	3.5	$2.1 \cdot 10^{-6}$
V_2O_5/Ni	108.2	$7.1 \cdot 10^{-5}$	429	12.1	3.7	$1.9 \cdot 10^{-5}$
Co/Ni	107.4	$1.8 \cdot 10^{-4}$	423	13.4	29.8	$6.0 \cdot 10^{-6}$
Ci+V_2O_5/Ni	104.3	$6.4 \cdot 10^{-4}$	251	39.5	4.4	$1.5 \cdot 10^{-4}$

An effective way of comparing the electrocatalytic activity of different HER electrocatalysts is to fix the overpotential (η) of the investigated electrode by potenciostatic measurement. By doing this, energy input is controlled and the resulting current densities can be compared, i.e. the amount of hydrogen that would be produced by each catalyst through the Faraday law. The results for overpotential of -250 mV (which is in the range expected for a hydrogen generator operation) are presented in Table 1 and Figure 3. Similarly to previous observations electrodeposited species increases current density if compared with Ni electrode. The Co+V_2O_5/Ni electrode yield the best electrocatalytic activity, this electrode has showed by applying it in water alkaline electrolysis the amount of hydrogen that could be produce will be 22 times larger than if Ni electrode.

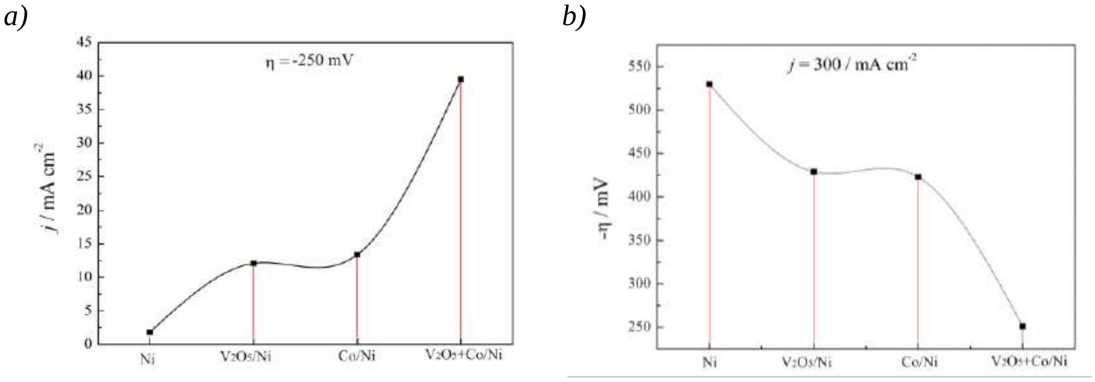


Figure 3 *The electrocatalytic activity of the investigated cathodes for HER in terms of steady-state values of: a) current density at a fixed overpotential; b) overpotential at a fixed current density*

CONCLUSION

In the light of optimization of hydrogen production V and/or Co species were electrodeposited onto Ni electrode. On the bases of obtained diagnostic parameters for electrocatalytic activity of electrode for hydrogen evolution reaction it was possible to compare electroactivity of Ni, V_2O_5/Ni, Co/Ni and V_2O_5+Co/Ni electrodes. If comparing with Ni electrode, observed increase of the exchange current density, the resulting overpotential measured at fixed current density and the resulting current density at fixed overpotential for V_2O_5/Ni and Co/Ni electrodes was found. Furthermore, V_2O_5+Co/Ni electrode has showed the highest exchange current density, the lowest overotential and the largest current density. The enhanced electrocatalytic activity of V_2O_5/Ni and Co/Ni has been discussed in the light of increased electrode surface and of V_2O_5+Co/Ni in the light of the synergetic electrocatalytic effect. The investigated electrode has shoved the increase of electrocatalytic activity for HER in the following order: V_2O_5+Co/Ni > V_2O_5/Ni ≈ Co/Ni > Ni.

ACKNOWLEDGEMENT

This work was supported by the Ministry of Education, Science and Technological Development of the Republic of Serbia (Grant No. 451-03-68/2022-14/200017).

REFERENCES

[1] A.M. Oliveira, R.R. Beswick, Y.Yan, Curr. Opin. Chem. Eng; 33 (2021) 100701.

[2] P.C. Okonkwoa, E.M. Barhoumi, I.B. Mansir, *et al*., Vacum; 198 (2022) 101878.

[3] G. Lu, P. Evans, G. Zangari, J. Electrochem. Soc: 150 (2003) A551.

[4] X. Lei, K. Yu, H. Li, *et al*., Electrochim. Acta; 269 (2018) 262–273.

[5] R. Rashkov, M. Arnaudova, G. Avedeev, *et al*., Int. J. Hydrog. Energy; 34 (2009) 2095–2100.

EFFECTS OF CLIMATE CHARACTERISTICS ON THE DIAMETER INCREMENT OF CEDAR IN THE CITY OF BELGRADE (SERBIA)

Tatjana Ratknić[1], Gordana Šekularac[2*], Mihailo Ratknić[3],
Zoran Poduška[1], Miroljub Aksić[4]

[1]Institute of Forestry, Kneza Višeslava 3, 11000 Belgrade, SERBIA

[2]University of Kragujevac, Faculty of Agronomy,
Cara Dušana 34, 32000 Čačak, SERBIA

[3]Faculty of Applied Ecology - Futura, Požeška 83a, 11000 Belgrade, SERBIA

[4]University of Priština, Kosovska Mitrovica, Faculty of Agriculture,
Kopaonička nn, 38219 Lešak, SERBIA

[*]*gordasek@kg.ac.rs*

Abstract

The paper presents the results of research dealing with the influence of climatic factors on the size of earlywood and latewood and the total diameter increment of cedar (Cedrus atlantica (Endl.) Man. ex Carr.). Samples taken from 30 trees at a height of 1.3 m were used in the analysis. The values were correlated with the mean monthly air temperature and precipitation sums (from April to September). In addition, the tree age expressed in years was included as an important factor. The analysed parameters explained 53.9% of the current diameter increment, 30.7% of the latewood and 51.6% of the earlywood share.

Keywords: cedar, earlywood, latewood, diameter increment, climatic factors

INTRODUCTION

Climate change has intensified the issue of introducing non-native tree species as part of an adaptive forest management strategy [1]. Changing climate has become a tough challenge for forests and forestry [2]. Although the extent of climate change is difficult to predict at the regional level [3], it is beyond any doubt that the forests of southern Europe, especially in the Balkans, will be strongly affected by climate change with unforeseeable consequences [4]. One of the solutions is to establish mixed stands of tree species that are more adaptable to warm climatic conditions characterised by a reduced amount of soil moisture during the growing season [5]. Based on climate models and changes in forest ecosystems [4], most autochthonous tree species are assumed not to be able to adapt to future climatic conditions. Therefore, allochthonous species should be introduced into the urban forests of Belgrade. As these species are more adapted to future climatic conditions than autochthonous species, they are expected to increase the number of species in this area. A species commonly recommended for the Belgrade area is the Atlas cedar.

The Atlas cedar originates from the Atlas Mountains of Morocco (Middle Atlas, High Atlas), the Rif and the Tell Atlas in Algeria. A lot of authors consider it a separate species –

Cedrus atlantica [6,7], while some believe it is a subspecies of Lebanese cedar *Cedrus libani* subsp. *atlantica* [8]. In natural habitats, it builds forests at altitudes from 1370 to 2200 meters in pure stands or in mixed with *Abies numidica*, *Juniperus oxicedrus*, *Quercus ilex* var. *ballota* and *Acer opalus*. The most extensive diebacks have been recorded in the area of Belezma National Park, where large areas are occupied by *Fraxinus xanthoxyloïdes*. In some parts, Atlas cedar has been completely replaced by *Quercus ilex*.

Cedar was introduced to Serbia at the beginning of the 19th century, but some authors believe that it was an integral part of European forests during the Last Glacial Period [9]. Cedar is a species that is resistant to industrial and urban pollution [10].

MATERIALS AND METHODS

The research was performed in an artificially raised Atlas cedar stand in Šuplja Stena near Belgrade (Serbia). The investigated stand was established in 1961 in the site of (*Quercetum farnetto-cerris aculeatetosum*). It is located at an altitude of 276 meters with a slope of 50º and a western aspect. It grows in eutric cambisol, 60 cm deep, overlying serpentine bedrock. The stand has a complete canopy closure and is well preserved.

We used statistical modeling to determine the relationship between stand characteristics and growth elements, on the one hand, and site factors, on the other. The ability of the model to adapt to the character it describes was the criterion used to select the most appropriate model. For this purpose, we used an improved forward “STEPWISE" regression.

Principal Component Analysis (PCA) was applied to determine the variability of data between and within the analysed climate characteristics in order to select the best variables for discrimination. The results of these analyses are presented numerically and graphically.

RESULTS AND DISCUSSION

General data on the artificially established cedar stand are shown in Table 1. As can be seen, the total number of trees is 458 per ha. The maximum number of trees (or 50.2%) is in the diameter degree of 37.5 cm. The mean stand height amounts to 24.6 m, and the mean diameter is 39.7 cm. It has a tree distribution line typical of even-aged stands. The volume distribution line is also typical of even-aged stands. The total basal area is 56.4 m^2 ha^{-1} and the total wood volume is 341.9 m^2 ha^{-1}. The distribution of tree volume by diameter class results from the distribution of the number of trees. The maximum is in the diameter class of 37.5 cm.

The dependence of the current diameter increment and the width of earlywood and latewood on climatic characteristics (monthly precipitation sums and mean monthly air temperature in the growing season – from April to September) was examined (Table 2). The independent variables were:

- precipitation sums in April (AP_P), May (MA_P), June (JU_P), July (JL_P), August (AU_P) and September (SE_P) and
- mean air temperature in April (AP_T), May (MA_T), June (JU_T), July (JL_T), August (AU_T) and September (SE_T).

Table 1 *General data on the artificially-established cedar stand*

Diameter class (cm)	N		H_{mean}	G		V (m^3)	
	1 ha	%	(m)	(m^2 ha^{-1})	%	1 ha	%
27.5	35	7.6	19.9	2.2	3.7	10.1	3.0
32.5	53	11.6	22.2	4.3	7.7	23.8	7.0
37.5	230	50.2	24.0	25.1	44.7	148.8	43.5
42.5	53	11.6	25.4	7.4	13.2	46.6	13.6
47.5	53	11.6	26.0	9.3	16.5	59.6	17.4
52.5	17	3.7	26.6	3.7	6.5	23.9	7.0
57.5	17	3.7	27.0	4.3	7.8	29.1	8.5
∑	458	100.0		56.4	100.0	341.9	100.0

Table 2 *The influence of age and analysed climatic factors on current diameter increment (Zi), share of latewood (Ka) and share of earlywood (Ra)*

Independent variable	Dependent variable					
	Zi		Ka		Ra	
	Parameters	Error	Parameters	Error	Parameters	Error
CONSTANT	3.51507	5.49560	0.40177	1.06784	4.60545	5.06950
Year	-0.05312	0.02647	-0.00260	0.00215	-0.04263	0.02442
AP_P	-0.00936	0.00732	0.00126	0.00135	-0.00684	0.00675
MA_P	0.00597	0.00456	0.00133	0.00130	0.00487	0.00421
JU_P	-0.00318	0.00440	-0.00152	0.00123	-0.00445	0.00406
JL_P	-0.00613	0.00449	0.00176	0.00177	-0.00517	0.00414
AU_P	0.00747	0.00625	0.00284	0.00181	0.00517	0.00577
SE_P	0.00257	0.00615	-0.00214	0.03691	-0.00063	0.00567
AP_T	-0.07113	0.14174	0.05849	0.04727	-0.10590	0.13075
MA_T	0.24427	0.15941	0.02157	0.04902	0.19210	0.14705
JU_T	-0.26011	0.17639	-0.00320	0.05031	-0.31356	0.16271
JL_T	0.19227	0.18462	-0.09588	0.04509	0.18134	0.17031
AU_T	-0.16232	0.15925	0.03514	0.03989	-0.08750	0.14690
SE_T	0.08442	0.13470	0.40177	1.06784	0.05476	0.12426
R		0.7344		0.5539		0.7181
R^2		53.9372		30.6822		51.564
Standard error		1.12969		0.33522		1.0421
F-test		2.88		1.22		2.62

According to this regression method, the total volume increment decreases with increasing age and increases with increasing precipitation in August. The August precipitation sums have the greatest influence on the size of the latewood. The size of the earlywood decreases with age (Table 3).

Five components were isolated in the principal component analysis (PCA). The results of this analysis are shown in Table 4. According to the eigenvalues and percentage values obtained, the first five components (coordinates) are sufficient to explain 74.762% of the total variability of data. The value of each variable (climatic factor) contributes to the overall variability of data (according to the first, second and third axes), as shown in Table 4. The scatter plot shows the geometric distance between the studied climate parameters and the variability between them. According to the first breakpoint, two components were further analysed in PCA.

Table 3 *Influence of age and analysed climate factors on current diameter increment (Zi), share of latewood (Ka) and share of earlywood (Ra) (Stepwise regression)*

Independent variable	**Dependent variable**					
	Zi		**Ka**		**Ra**	
	Parameters	**Error**	**Parameters**	**Error**	**Parameters**	**Error**
CONSTANT	2.95369	0.52792	0.33436	0.08749	2.99967	0.40623
Year	-0.05300	0.01272			-0.05133	0.01188
AV_P	0.01037	0.00447	0.00289	0.00128		
R		0.6118		0.3210		0.5457
R^2		37.4134		10.3059		29.7796
Standard error		1.1359		0.3302		1.0701
F-test		12.85		5.060		18.66

There is a significant positive correlation between the temperature (June and September) and the diameter increment due to the influence of the first and second components. The effect of the first component brought about the positive correlation between the tree diameter increment and the temperature in May, April, July and August, while the correlation between the mentioned months and the tree growth was negative under the influence of the second component.

Table 4 *Eigenvalues and percentage values with the share of each coordinate in describing the total variability of data*

Component number	**Eigenvalue**	**Variance percentage**	**Cummulative percentage**
1	4.0862	31.432	31.432
2	1.6509	12.699	44.131
3	1.5234	11.719	55.850
4	1.3817	10.629	66.479
5	1.0768	8.283	**74.762**
6	0.8240	6.339	81.100
7	0.7573	5.825	86.925
8	0.5349	4.115	91.040
9	0.3544	2.726	93.767
10	0.3213	2.471	96.238
11	0.2101	1.616	97.854
12	0.1560	1.200	99.054
13	0.1230	0.946	100.000

A negative correlation was found between precipitation (April, June, August and September) and the diameter increment under the influence of the first and second components.

The effect of the second component determined the positive correlation between the precipitation (May and July) and the diameter increment, and a negative correlation was found between the measured precipitation and the tree growth due to the influence of the first component.

Under the influence of the first and second components, a positive correlation was found between the age and the tree growth. Based on the sharpness of the vector angle for the age of cedar trees, a positive highly significant influence of the first component on the diameter increment was stated.

CONCLUSION

The exploitation of introduced species arouses significant interest because it provides information about their climate adaptability. Some species, especially tree species, could adapt to more diverse climatic conditions than they are known to be able to in their natural range of distribution.

The size of the diameter increment of Atlas cedar is most influenced by precipitation variability, while temperatures proved to be secondary climate variables. The increase in precipitation in the period from August to September is crucial for the growth of Atlas cedar [11].

For forest management purposes, new growth models that are sensitive to climate characteristics and their changes in forest ecosystems need to be developed.

ACKNOWLEDGEMENT

The authors are grateful to the Ministry of Education, Science and Technological Development of the Republic of Serbia for financial support (451-03-68/2022-14/200027; 451-03-68/2022-14/200088; 200189).

REFERENCES

[1] R. Ennos, J. Cottrell, J. Hall, *et al*., Forest Ecol. Manag; 432 (2019) 718–728.

[2] M. Lindner, M. Maroschek, S. Netherer, *et al*., Forest Ecol. Manag; 259 (4) (2010) 698–709.

[3] G.E. Hemery, Int. Forest Rev; 10 (4) (2008) 591–607.

[4] T. Ratknić. Application of adaptive measures in the adaptation of forest ecosystems to climate change in the City of Belgrade, Final Report (2021).

[5] M. Milad, H. Schaich, W. Konold, Biodivers. Conserv; 22 (5) (2013) 1181–1202.

[6] C.Y. Qiao, JH. Ran, Y. Li, *et al*., Ann. Bot; 100 (3) (2007) 573–580.

[7] A. Farjon, A Handbook of the World's Conifers (Vol 1), Brill, Leiden, Boston (2010).

[8] E.F. Debazak, Handbook on Conifers, Association of Engineers and Technicians of Forestry and Wood Processing Industry of SR Serbia (1967).

[9] J. Messinger, A. Güney, R. Zimmermann, *et al*., Eur. J. Forest Res; 134 (2015) 1005–1017.

[10] V. Vratuša, N. Anastasijević, Proceedings of the 8th Symposium on Flora of Southeastern Serbia and Neighbouring Region, June 20-24, Niš, Serbia and Montenegro (2005) 175 –179.

[11] J.C. Linares, P.A. Tíscar, J.J. Camarero, *et al*., Tree growth decline on relict Western-Mediterranean mountain forests: Causes and impacts, In: Forest Decline: Causes and Impacts, © 2011 Nova Science Publishers, Inc., (2011), p.20, ISBN: 978-1-61470-002-9.

RECYCLED POLY(ETHYLENE TEREPHTHALATE) BASED- PLASTICIZER FOR PVC REGRANULATES PRODUCTION

Natalija Čutović[1*], Marija Vuksanović[2], Milena Milošević[3], Mladen Bugarčić[4], Jovana Bošnjaković[5], Jelena Gržetić[6], Aleksandar Marinković[1]

[1]University of Belgrade, Faculty of Technology and Metallurgy, Karnegijeva 4,
11000 Belgrade, SERBIA

[2]University of Belgrade, Vinča Institute of Nuclear Sciences – Institute of National
Importance, Mike Petrovića Alasa 12–14, 11351 Vinča, Belgrade, SERBIA

[3]University of Belgrade, Institute of Chemistry, Technology and Metallurgy,
National Institute of the Republic of Serbia, Njegoševa 12, 11000 Belgrade, SERBIA

[4]Insitute for Technology of Nuclear and Other Mineral Raw Materials,
Bulevar Franš d' Eperea street 86, 11000 Belgrade, SERBIA

[5]R&D Institute Lola L.T.D., Kneza Višeslava 70a, 11030 Belgrade, SERBIA

[6]Military Technical Institute, Ratka Resanovića 1, 11030 Belgrade, SERBIA

[*]*natalijacutovic@gmail.com*

Abstract

Due to the increasing use and widespread of plastics, poly (ethylene terephthalate) (PET) and poly (vinyl chloride) (PVC) are becoming one of the major threats to the environment. The aim of this paper is obtaining plasticizers from recycled PET, and hot/cold mixing thereof with PVC to produce new materials. Plasticizer was obtained from PET using ethylene glycol (EG) in the presence of catalyst FASCAT 4100, followed by treatment with maleic anhydride and finally 2-ethylhexanol (2-EtHex). The obtained glycolysate and plasticizer, individually or mixtures thereof, were used for the production of polygranulates based on waste PVC in order to obtain an expanded mass of homogenized PVC with glycolysate/plasticizer. The abovementioned procedures and test results for the regranulates and products indicate that the proposed technology offers a solution to the problem of waste PET and PVC through transesterification in order to obtain plasticizer based on PET and EG, called 2-EtHex/MA/PG/PET/EG/MA/2-EtHex used in the processing of PVC waste and in regranulate. The obtained regranulates are further processed by injection molding or extrusion into commercial products such as slippers, footwear, boots, garden hoses, mats, floor mats, etc.

Keywords: PET, PVC, recycling, plasticizers, environment protection

INTRODUCTION

Paying attention to sustainable development is becoming an obligation for socially responsible manufacturers. Recycling as a concept is not enough on its own, so new trends bringing great attention to the circular economy, by increasing the content of recycled material in their final products are being introduced [1]. This puts more pressure on product choice among consumers; the quality and characteristics of the products that are produced must show social responsibility, but also responsibility for the preservation of the environment and resources. Facing these challenges requires improving the quality of recycled granules, speeding up production by expanding the choice of collected industrial waste material. Nowadays, plastic has become a widely used material, due to its low weight and good mechanical properties [2]. PVC and PET are among the most common types of this material [3], because of their possibility of use for food and beverage packaging, as well as in electrical appliances. Due to the diverse application of plastic, it is one of the major polluters of the environment, which is why it is necessary to approach the process of its recycling. Recycling itself involves the processing of waste materials, in order to obtain new, usable materials with appropriate characteristics. Protection of natural resources, as well as lower eco-footprint, represent some of the most important aspects of recycling.

The method applied for recycling of PET was mechanical, in which plastic waste is cut, crushed into granules, flakes or pellets of appropriate quality for production, and then melted to form objects by extrusion [4]. The plastic waste recycled in this way was used to make shoe soles. The degree of injection and extrusion of PVC waste was varied with three different formulations, and the optimal composition of PVC mixtures (extrusion/injection; 70/30) provided good mechanical and physical properties of the sole. By reviewing the literature, in the patent [5], relates to the production of soles for shoes from a composition composed of polyvinyl chloride and organic cellulose. It is necessary to achieve a better quality/price ratio of the produced regranulates and at the same time expand the production capacities. All this will be the result of primary efforts to increase the amount of recycled plastic and reduce the negative impact it has on the environment (when disposed of in landfills without any processing).

The aim of the paper is to achieve a better relationship between the quality and price of produced regranulates and to expand production capacities at the same time. This should be the result of primary efforts to increase the amount of recycled plastic and reduce the negative impact it has on the environment (when disposed of in landfills without any processing).

MATERIALS AND METHODS

Materials

For this study, the following materials were used for the recycling of waste PET: propylene glycol (PG) – Merck, ethylene glycol (EG) – Centrohem. FASCAT 4100 (pmc organometallix) was used as a catalyst for the depolymerization reaction. Ethanol (Sigma-Aldrich), was used to dissolve hydroquinone (Sigma-Aldrich). All chemicals were used without preparation for further purification. Maleic anhydride (MA) - Sigma-Aldrich, was used for esterification of glycolysates based on PET. Other than this, tetrabutyl titanate (Fluka) was also used as a catalyst, and toluene (Sigma-Aldrich) was used in order to remove azeotropic water. Finally, 2–ethyl hexanol (RKS Composites) was used for the synthesis of plasticizers.

Material characterization

Fourier transform infrared (FT–IR) spectroscopy

FT-IR is used for qualitative analysis of functional groups, as well as for structural analysis of various compounds of organic and inorganic origin. FT-IR spectroscopy is applied in the infrared region of electromagnetic radiation with a wave number 4000 - 400 cm^{-1}. The ThermoScientific Nicolet iS10 instrument was used to record the IR spectrum.

Nuclear magnetic resonance

Spectra were recorded at room temperature in deuterated chloroform ($CDCl_3$) or deuterated dimethyl sulfoxide (DMSO-d_6) in 5 mm cuvettes. Chemical shifts are expressed in ppm (d) values relative to TMS (tetramethylsilane) in ^{1}H NMR spectra and solvent residual signal in ^{13}C NMR spectra. NMR spectra were recorded on a Bruker Avance III 500/125 MHz instrument, at 500 MHz when recording ^{1}H NMR and 125 MHz when recording ^{13}C NMR spectra.

Synthesis of 2-EtHex/MA/PG/PET/EG/MA/2-EtHex

The 2-ethyl hexanol terminated plasticizer, based on propylene glycol (PG), was synthesized as follows: 68 g of propylene glycol (0.867 mol) was gradually added to the previously measured PET (167 g, 0.867 mol) in a 1000 ml reactor. The reaction is performed with a gradual increase in temperature to 205-210 °C for 4 hours from the moment all PET is dissolved with addition of 1.5 g FASCAT 4100 as the reaction catalyst. The mixture was gradually cooled to 90 °C, and nitrogen (gas) was introduced due to the inert condition. After that, prepared ethanolic solution of hydroquinone (70 mg of hydroquinone in 0.20 ml of ethanol, 0.02 wt. % was carefully added, followed by 170 g of maleic anhydride (MA, 1.733 mol). The reaction is carried out for 30 minutes at 90 °C and then the temperature is gradually increased to 150 °C.

When the temperature (150 °C) was reached, 2-ethyl hexanol 225.4 g (1.734 mol) was added. A catalyst, tetrabutyl titanate, 1.89 g (0.3% TBT) was added dropwise to support the esterification reaction. Esterification was continued for 1 hour, after which Dean-Stark was adjusted, and toluene was added to remove azeotropic water and the temperature was raised to 210 °C. When 28 ml of water (expected 32.3 ml) was removed from the reaction mixture, the nitrogen inlet was removed and the reactor was vacuumed and distilled until the temperature dropped to 90-100 °C (distillate ceases to separate). The product is poured into a container and used in the processing of waste PVC.

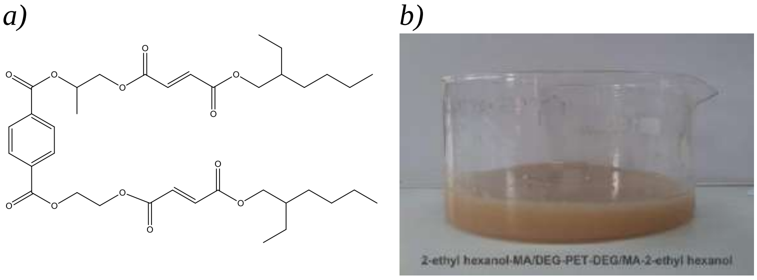


Figure 1 *a) Assumed structure of the obtained plasticizer; b) 2-EtHex/MA/PG/PET/EG/MA/2-EtHex sample*

Production of PVC regranulate based on 2-EtHex/MA/RG/PET/EG/MA/2-EtHex plasticizers obtained from waste PET

Waste PVC is obtained in the form of strips, in bales, which are transported to the mill, where it is prepared for grinding. The waste is grounded through a sieve Ø from 1 mm to 20 mm. The ground waste is mechanically (manually) dosed into a hot mixer. When mixing, the temperature starts at 30 °C. During mixing, 2-EtHex/MA/PG/PET/EG/MA/2-EtHex is added. 10, 50, 100, 150, 200, 250 and 300 g of the plasticizer, depending on the desired hardness, is added per 1000 g of waste PVC. When the temperature reaches 35 °C, the synthesized plasticizer is added to the hot mixer at such a rate that all of the plasticizer is added in up to 5 minutes, mixing with the waste PVC. When the temperature reaches 135 °C, i.e. when the pointer on the ammeter of the upper mixer calms down, this batch is discharged into the cold (lower) mixer. Since the mass from the upper mixer is hot and doughy, after adding to the cold mixer, the mass is converted into a flour form by cooling and bringing to a temperature of 45 °C. It is then drained from the lower mixer and in such a form can be used as a raw material for making the final product - by injection molding. There is no waste during this process, and such a semi-finished product does not have the characteristics of a hazardous product and is ready for further use and production of final products, or can be processed by injection molding to obtain regranulate. The characteristics of the product obtained after formation by extrusion (Figure 2) were tested, and it was determined that the optimal properties of the product are obtained at a mass ratio of PVC/2-EtHex/MA/PG/PET/EG/MA/2-EtHex of 50, ie. 200 g 2-EtHex/MA/PG/PET/EG/MA/2-EtHex per 1000 g PVC, and the material properties obtained in this ratio are shown in Table 1.

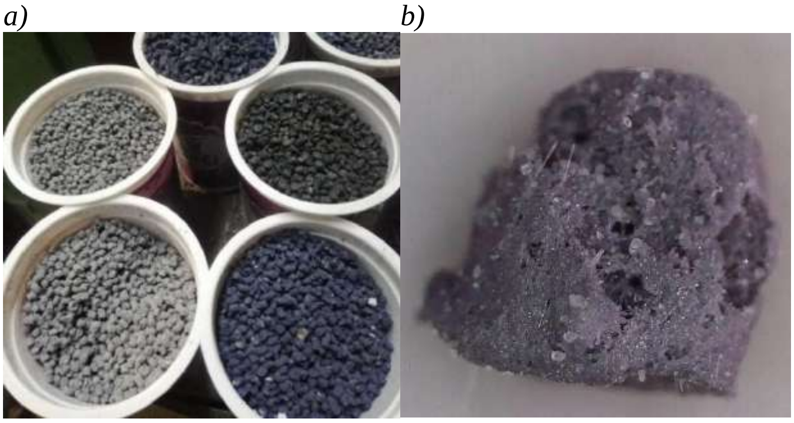


Figure 2 *Structure of regranulate obtained*

RESULTS AND DISCUSSION

FT–IR analysis

On the recorded spectrum, the tensile vibration of the hydroxyl group was observed as a broad band at 3430 cm^{-1}, while the aromatic and vinyl C-H tensile vibration was visible as a shoulder at 3056 cm^{-1}. Asymmetric and symmetric tensile vibrations of the methyl, CH_3 and methylene, CH_2 group, were observed in the range 2977–2873 cm^{-1}, while corresponding bending vibrations occurred at 1454 and 1379 cm^{-1}. The elongation vibration of the ester carbonyl group was assigned a band at 1715 cm^{-1}. The main absorption bands between 1300 and 1100 cm^{-1} are caused by asymmetric and symmetric C-O extensible vibrations found in ester and ether groups.

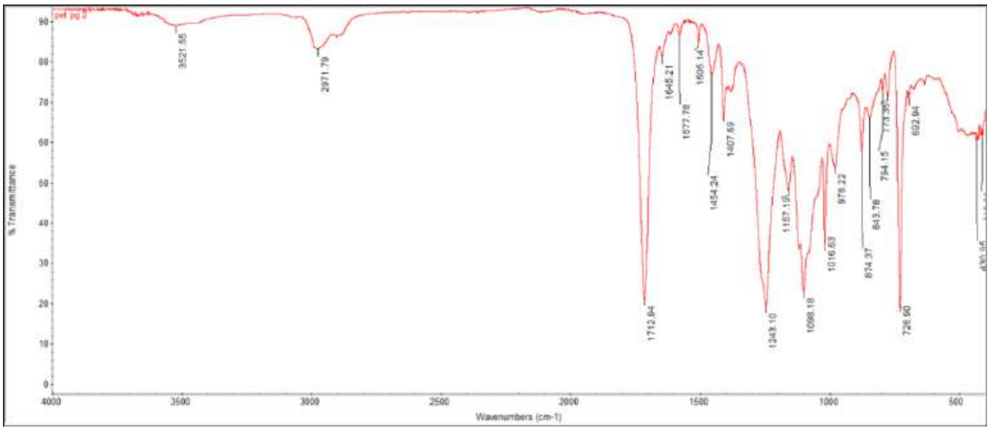


Figure 3 *FTIR spectrum of synthesized* ***2-EtHex/MA/PG/PET/EG/MA/2-EtHex*** *plasticizer*

^{1}H and ^{13}C NMR results

Results of ^{1}H and ^{13}C NMR analysis of **2-EtHex/MA/PG/PET/EG/MA/2-EtHex** plasticizer are:

^{1}H NMR ($CDCl_3$): 0.91–1.33 (m, 9H, 3xCH_3), 3.62–3.69 (m, 4H, 2xCH_2-OH), 4.38–4.71 (m, 2H, -O-(CH_3)CH-CH_2-O-), 4.75–4.77 (m, 2H, 2x-O-(CH_3)CH-CH_2-OH), 4.95 (s, 2H, 2x-CH_2-OH), 5.33–5.38 (m, 2H, 2x-O-(CH_3)CH-CH_2-O-), 6.50–7.06 (m, 4H, 2x-CH=CH), 7.88–8.15 (s, 4H, HPh);

^{13}C NMR ($CDCl_3$):17.51 (3xCH_3), 65.22–72.59 (7xCH_2 and 3xCH), 129.75–133.55 (4xCPh and 2xCH=CH), 165.22–167.81 (6xCOO).

Chemical, physical, electrical and mechanical properties

From the given table it can be seen that regranulates based on synthesized plasticizer have very good characteristics, due to their low ability to adsorb water, as well as resistance to weathering and chemicals.

Table 1 *Characteristics of the product obtained from PVC regranulate in the ratio of 1000g PVC/200g 2-EtHex/MA/RG/PET/EG/MA/2-EtHex*

Chemical properties	
Concentrated acids	Good
Dilute acids	Good
Alcohol	Good
Bases	Good
Aromatic hydrocarbons	
Fats and oils	Good
Halogens	Good
Ketones	Good

Table 1 *continued*

Electrical properties	
Dielectric constant at 1 MHz ASTM D150	4.3
Dielectric strength (125 v mil^{-1}) ASTM D149	370
Dissipation factor at 1kHz ASTM D150	0.05
Volume resistance AST D257 (Ohm cm) at 22.8 ºC 50% RH	5.5×10^{13}
Mechanical properties	
Elongation ASTM D638 (%)	67
Tensile strength ASTM D638	50 MPa
Bending resistance ASTM D790	52.3 MPa
Compressive strength ASTM D695	50.8 MPa
Young's modulus ASTM D638	2.8 GPa
Modulus of elasticity ASTM D790	1.9 GPa
Rockwell hardness R ASTM D785	106
Toughness (J m^{-1})	26
Tearing module (GPa)	2.6
Breaking voltage (MPa)	84
Physical properties	
Density (g cm^{-3}) ASTM D792	1.34
Flammability	Self-extinguishing
Oxygen limiting index (%)	22
Refractive index	1.532
Resistance to UV radiation	Good
Water adsorption (%)	<0.6
Water adsorption - within 24 h (%) ASTM D570	0.74
Coefficient of thermal expansion ($\times10^{-6}$ K^{-1})	46
Lower operating temperature (°C)	-40 to -60
Specific heat (J K^{-1} kg^{-1})	1258
Thermal permeability (W m^{-1} K^{-1})	0.26 at 23 °C

CONCLUSION

This paper aimed to examine the characteristics of plastic materials acquired by mixing PVC with plasticizers obtained by physicomechanical treatment of PET waste. The composition of the gained materials was examined using FTIR spectroscopy and NMR spectroscopy. Based on the presented results, it is possible to conclude that the materials obtained by adding these plasticizers into PVC (extrusion/injection; 70/30) show good mechanical and chemical properties. In addition, due to the acceptable content of acids and bases, as well as good physicochemical and mechanical characteristics, regranulates obtained by mixing the synthesized plasticizer in PVC, will avoid numerous negative effects on the environment. Regranulates with the best characteristics were obtained by mixing 200 g of plasticizer with 1000 g of PVC.

ACKNOWLEDGEMENT

This work was supported by the Ministry of Education, Science and Technological Development of the Republic of Serbia (Contract Nos. 451-03-68/2022-14/200066; 451-03-68/2022-14/200023; 451-03-68/2022-14/200135; 451-03-68/2022-14/200026; 451-03-68/2022-14/200017; 451-03-68/2022-14/200325).

REFERENCES

[1] K. Winans, A. Kendall, H. Deng, Renew. Sustain. Energy Rev; 68 (2017) 825–833.

[2] H. Ritchie, M. Roser, Plastic pollution, Our World Data (2018).

[3] A. Sangroniz, J.B. Zhu, X. Tang, *et al.*, Nat. Commun; 10 (2019) 1–7.

[4] J.H. Clark, J.A. Alonso, J.A. Villalba, *et al*., RSC; (1999).

[5] A. Cohen, Polyvinyl chloride shoe sole composition (1982), *Available on the following link:* https://patents.google.com/patent/US4405730A/en

EcoTER'22
29th International Conference Ecological Truth
& Environmental Research
21 - 24 June 2022, Hotel Sunce, Sokobanja, Serbia
www.eco.tfbor.bg.ac.rs

SYNTHESIS OF NEW Ag DOPED CHALCOGENIDE GLASS FOR APPLICATION IN ENERGY CONVERSION AND MEMORY STORAGE

Robert Vigi[1*], Goran Štrbac[1], Dragana Štrbac[2], Mladenka Novaković[2]
[1]University of Novi Sad, Faculty of Sciences, Department of physics,
Trg Dositeja Obradovića 4, 21000 Novi Sad, SERBIA
[2]University of Novi Sad, Faculty of Technical Sciences, Department of Environmental Engineering, Trg Dositeja Obradovića 6, 21000 Novi Sad, SERBIA
robert1995@uns.ac.rs

Abstract

In the frame of the testing of chalcogenide glasses as potentially new materials that could be used for photovoltaic cells in solar panels and for phase-changing memories, the synthesis of glasses of the $Ag_x(As_{40}Se_{30}Te_{30})_{100-x}$ *system was performed. The synthesis procedure consisted of cascade heating and quenching in the air. The complexity of synthesis is determined by the character of the starting elementary components and structural units that are expected as elements of the structural network of complex glass. This process yielded quality glass. The amorphous character was confirmed by XRD and polarization microscopy. Density measurements were also performed and the linear dependence of density on the percentage of silver in the glass composition was determined.*

Keywords: Amorphous materials, Chalcogenides, Solar cell, Phase-changing memories

INTRODUCTION

There is a direct correlation between standard of living and economic progress on the one hand, and electricity consumption in society on the other. Electricity can be obtained from a variety of sources, from the combustion of raw materials to complex nuclear reactor systems. However, due to global concerns about climate change today, electricity and energy production, in general, must be shifted to renewable sources such as solar energy. The use of fossil fuels as a primary source of energy, in addition to limited quantities, includes not only serious pollution due to emissions of harmful greenhouse gases but also very high water consumption, at a time when a shortage of this resource is becoming a key issue for many countries. Special attention today is focused on increasing efficiency in the production of electricity from renewable sources, including the optimization of photovoltaic cells [1,2] which use solar energy, but also on the most efficient conversion and utilization of electricity. Also, large amounts of energy in modern society are used to store information, and any savings in this field is a major advance in terms of reducing electricity needs. One of the steps in that direction is the development of new types of memories [3,4]. Progress in both fields has significant aftermath on the energy map of the whole society.

When it comes to photovoltaic cells, the most important requirements imposed on commercially successful solar cell technology are efficiency, long-term stability, minimal resource use, and the lowest possible costs. In recent years, the energy consumption of computer systems has increased dramatically and much of this energy is spent on storing huge amounts of data. In this regard, among other things, researchers have proposed the use of new types of permanent memories, such as phase-changing memories (PCM) [4,5] which have a short read time, that refers to how long it takes to receive data request and to find and access real data from storage media.

The perspective materials for use in solar cells, but also in PCM memory are amorphous materials [6]. Semiconducting material absorbs the incoming photons and converts them into electron-hole pairs. In an ideal case, all the photons with energy higher than the band gap energy contribute to the photogeneration. The optical band gap in amorphous semiconductors is characterized by the localized states between valence and conduction bands. Band gap structure depends on the technological process of obtaining and elemental composition.

There are two major groups of inorganic amorphous semiconductors – the elements from IV group of PSE and III-V amorphous semiconductors (Ge, Si, C, SiC, InSb, GaAs, GaSb); the second group includes the chalcogenide semiconductors, those which contain Se, S or Te [6]. Phase changing memories (PCM) exploits the large resistance contrast between the amorphous and crystalline states in so-called phase change materials [7]. Renewed interest in PCM technology was triggered by the discovery of fast (<100 nanoseconds) crystallizing materials such as $Ge_2Sb_2Te_5$ (GST) or Ag and In doped Sb_2Te (AIST) [8,9]. Based on these considerations, the synthesis of glasses with a composition of $Ag_x(As_{40}Se_{30}Te_{30})_{100-x}$ was performed, with the aim to obtain amorphous material applicable in photovoltaic cells and as PCM.

MATERIALS AND METHODS

As already pointed out in the introductory part, it is to be expected that the glasses of $Ag_x(As_{40}Se_{30}Te_{30})_{100-x}$ system will exhibit efficient energy conversion.

The amorphous matrix consists of the three-component system $As_{40}Se_{30}Te_{30}$. The area of glass formation in the As-Se-Te system is shown in Figure 1 [10] and it can be seen that compact glass can be obtained in a wide range of different proportions of elementary components. The glass-forming region in the examined three-component system was determined previously by Frezer [11] and Borisova [12]. The maximum temperature of the synthesis was 950 °C, at which the sample was maintained for 5 hours and then quenched in the air [12].

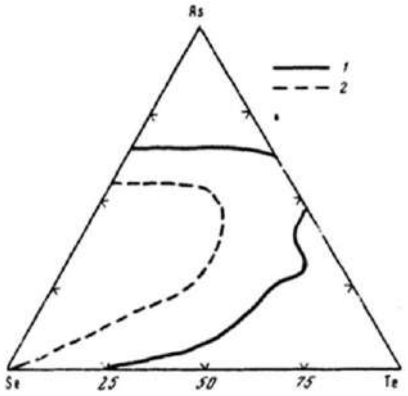


Figure 1 *Amorphous forming region in a ternary system As-Se-Te [10]*

The composition of the selected matrix in which silver is introduced is deep within the amorphous region, which should ensure the production of glass under non-extreme synthesis conditions, especially when it comes to cooling rates. Also, it is expected that silver can be introduced into such a matrix while preserving the amorphous state of matter. All this indicates a real chance that quality glass can be synthesized in the four-component Ag-As-Se-Te system by careful selection of the technological process.

For the synthesis of glasses with the desired composition, the classical method of cascade heating and rapid cooling in the air was chosen. This cascade method of heating to the maximum synthesis temperature consists of successive heating performed at optimal speeds in each of the temperature intervals determined by the properties of the elementary components in the melt and maintained at a certain temperature which allows the reaction between the individual components to occur at minimum temperatures, as well as to avoid a rapid increase in the vapor pressure in the ampoule itself. At these critical temperatures, the melt is maintained for twelve hours. Heating speeds in different stages are different and they are a characteristic of each individual system, and the choice of these speeds is a complex problem that requires special analysis. An important, if not a key part of the synthesis is the rapid cooling of the melt (quenching). This means that the ampoule with the sample from the maximum synthesis temperature is pulled out into the air in order to preserve the glass structure that corresponds to the structure of the melt at the maximum synthesis temperature. A sufficiently high cooling rate prevents the constituent components from rearranging themselves in accordance with the spatial distribution of the dominant chemical bonds and thus forming a crystalline, ordered state.

Figure 2 *Elementary components loaded into cleaned quartz tubes*

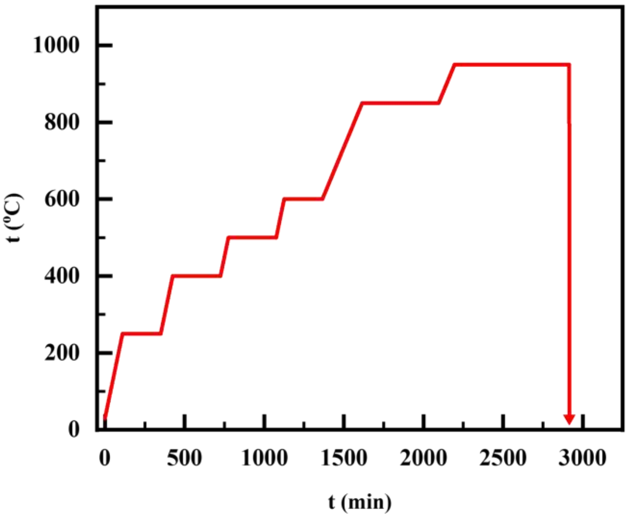


Figure 3 *Temperature program of synthesis of amorphous* $Ag_x(As_{40}Se_{30}Te_{30})_{100-x}$

All glasses were produced using high purity elementary components (at least 99.99 %). The weighted elements in a total of 12 g were loaded into cleaned quartz tubes (Figure 2) and then sealed under a vacuum using an acetylene/oxygen torch. Masses were measured by analytical balance METTLER B-6 with an accuracy of $\pm 5 \cdot 10^{-8}$ kg. The temperature program of melting is given in Figure 3. After synthesizing, in advance prepared temperature program, ampoule was removed from the furnace and quenched at room temperature in Al_2O_3 powder to minimize quench-related stress.

As previously said, the temperature regime of synthesis depends on the melting and boiling points of starting components and characteristics of expected structural units in the glass. Table 1 shows relevant temperatures of elemental components and compounds that possibly can be formed in the glass structure.

Table 1 *Melting and boiling point of elemental components and structural units expected in the glass system of glass*

Element	Melting point [°C]	Boiling point [°C]	Compound	Melting point [°C]
Ag	961	2162	Ag_2Te	955
As	816	615 (sublimation)	AsSe	573
Se	221	685	As_2Se_3	377
Te	449	988	Ag_2Se	880
			$AgAsSe_2$	410
			Ag_3AsSe_3	400

X-ray diffraction (XRD) was carried out using RigakuMiniFlex 600 instrument, with CuK_α radiation of 0.154178 nm wavelength.

Another technique for determination of amorphous structure is polarization microscopy. All synthesized samples were analyzed under an Axioskop 40 (Carl Zeiss) polarization microscope.

The density of all examined samples was determined using hydrostatic scales. Masses were measured by analytical balance METTLER B-6 with an accuracy of $\pm 5 \cdot 10^{-8}$ kg. Measurements were conducted in air and distilled water, including corrections for air pressure.

RESULTS AND DISCUSSION

Quality glasses were obtained by the selected technological process of synthesis.The first indicators of quality and amorphous structure are immediately noticeable metallic luster and the appearance of shell fractures. Shell fractures are the result of residual stresses in the material itself during rapid cooling. Figure 4 shows the appearance of as synthesized $As_{40}Se_{30}Te_{30}$ sample as an example.

All synthesized glasses were checked if there was unwanted crystallization using X-ray diffraction (XRD) measurements. The diffractograms of the synthesized samples, shown in Figure 5, do not contain any sharp diffraction peaks above the background of the device and thus indicate a high degree of their amorphous structure. Two broad diffraction bands are clearly observed at about $2\theta = 30^0$ and 50^0 degree. They arise from the short-range (mostly nearest neighbor) covalently networking structures.

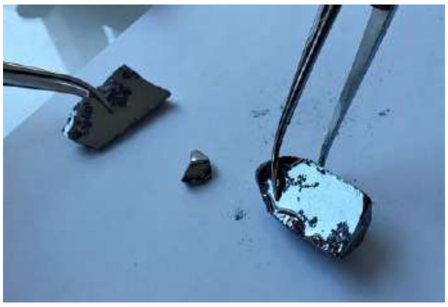


Figure 4 *Example of newly synthesized* $As_{40}Se_{30}Te_{30}$

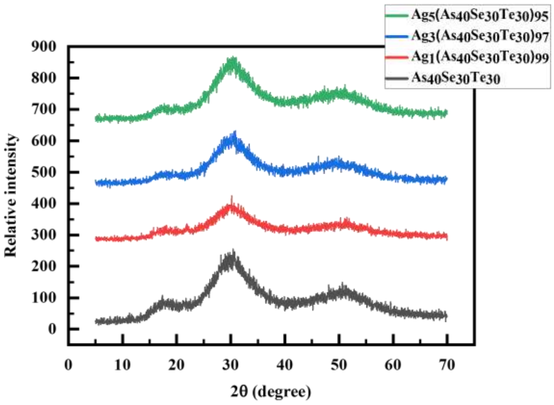


Figure 5 *XRD patterns of synthesized $Ag_x(As_{40}Se_{30}Te_{30})_{100-x}$ system*

All synthesized samples were analyzed under polarization microscope. The appearance of the samples in reflection mode is shown in the Figures 6 a-d. These observations confirmed the absence of any crystalline, optically active centers.

Absence of any crystallization centers or optical anisotropy characteristic for crystalline structure scan is noticed in all pictures in Figure 6. All previous observations lead to the conclusion that synthesized structures are amorphous.

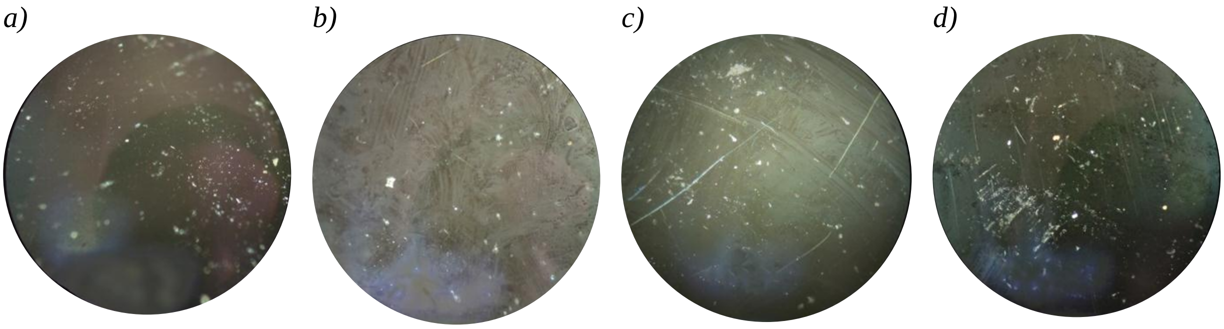

a) *b)* *c)* *d)*

Figure 6 *Polarization microscope images of synthesized chalcogenides a-d with 0%, 1%, 3%, 5% at of Ag respectively from left to right*

In Figure 7 is shown graphical dependence of density in the function of the atomic content of Ag in glass systems, which displays linear dependence which is a direct consequence of an increase in the content of Ag that has a higher density.

The monotonous functional dependence of the density on the Ag percent content, is a common dependence for amorphous chalcogenide systems. The linear functional dependence is determined by the equation:

$$y=5.055(7)+0.0542(24)x \qquad (1)$$

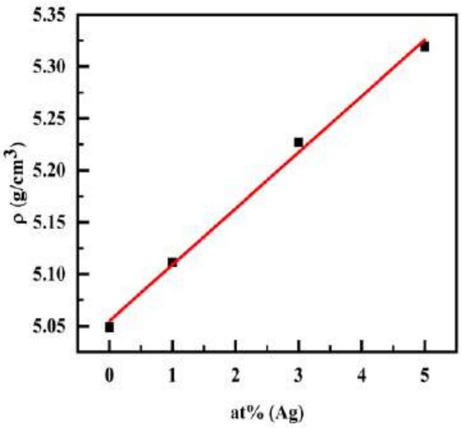


Figure 7 *Correlation between density and cocontent of Ag in $Ag_x(As_{40}Se_{30}Te_{30})_{100-x}$ system*

ACKNOWLEDGEMENT

The authors are grateful to the Provincial Secretariat for Higher Education and Scientific Research for financial support (Project: Novel chalcogenide materials for efficient transformation and use of energy, 142-451-2678/2021-01/2) and on financial support of the Ministry of Education, Science and Technological Development of the Republic of Serbia (Grant No. 451-03-68/2022-14/200125).

The authors also are grateful to Prof. Dr Rakić Srđan for XRD measurements.

REFERENCES

[1] A. Blakers, N.S. Zin, K.R. Mclntosh, *et al*., Energy Procedia; 33 (2013) 1–10.

[2] J.A. Luceño-Sánchez, A.M. Díez-Pascual, R.P. Capilla, Int. J. Mol. Sci; 20 (4) (2019) 976.

[3] A. Allan, Proceedings of International technical roadmap for semiconductors, 14–16 July, San Francisco, USA (2008).

[4] G.W. Burr, B.N. Kurdi, J.C. Scott, *et al*., IBM J. Res. Dev; 52 (4/5) (2008) 449–464.

[5] G.W. Burr, M.J. Breitwisch, M. Franceschini, *et al*., J. Vac. Sci. Technol. B; 28 (2) (2010) 223–264.

[6] K. Gmucova, J. Mullerova, Amorphous materials, Nova Science Publisher, UK (2013), p.1, ISBN: 978-1-62417-678-4.

[7] S. Raoux, G.W. Burr, M.J. Breitwisch, *et al*., IBM J. Res. Dev; 52 (4/5) (2008) 465–480.

[8] N. Yamada, E. Ohno, K. Nishiuchi, *et al*., J. Appl. Phys; 69 (5) (1991) 2849–2856.

[9] J. Tominaga, T. Kikukawa, M. Takahashi, *et al*., Appl. Phys; 82 (7) (1997) 3214–3218.

[10] G.Z. Vinogradova, Glass formation and phase equilibrium in chlacogenide systems (russ.), Nauka Publ. House, Moscow (1984), p.60, IBN: 27601.

[11] W.A. Fraser: United States Patent Office Pat 2883291 (USA) Arsenic-Ttritelluride glasses - Publ. 21.4.1959., *Available on the following link:* https://patentimages.storage.googleapis.com›pdfs

[12] Z.U. Borisova, V.R. Panuds, A.A. Obrazcov, The region of glass formation in the Aresic-Selenium-tellur system, Official Gazette of Leningrade State University Physics and chemistry, No. 22121–125 (1970).

SUSTAINABLE UTILIZATION OF CATHODE-RAY TUBE WASTE GLASS IN CEMENTITIOUS MATERIALS – A REVIEW

Tatjana Miljojčić[1], Ivana Jelić[1], Marija Šljivić-Ivanović[1], Slavko Dimović[1], Uzahir Ramadani[1]

[1]University of Belgrade, Vinca Institute of Nuclear Sciences, M.P.A. 12–14, 11351 Belgrade, SERBIA

**tatjana.miljojcic@vinca.rs*

Abstract

The advances in the electronic industry have led to a generation of an extensive amount of electrical waste (E-waste) before the end of its proper life span. Excessive usage and production of cathode-ray tubes (CRT), which is the fundamental part of old monitors and screens, has become an immense problem worldwide regarding the environmental issues, since the last few decades thin-film transistors (TFT) and liquid crystal display (LCD) replaced CRTs almost entirely. Consequently, it is of crucial importance to expand and deploy new, renewable methods to manage CRT glass waste. There is an appreciable prospective to use CRT waste glass for new products manufacture, or as an admixture to existing ones, hence the requirement for reusing this kind of waste is favorable. Many investigations have confirmed the positive effect of using grounded CRT waste glass as a fine aggregate. However, this waste is classified as hazardous due to the high lead content. Mixing CRT glass with mortar constructively decreases the amount of cement consumption. Features of this paper relate to a review of recent developments regarding the reuse of CRTs in cementitious materials. Emphasis was placed on their physico-mechanical properties to evaluate the possibility of CRT usage in mortar mixtures.

Keywords: e-waste, recycled aggregate, sustainable development

INTRODUCTION

Concrete is the second most used material worldwide, right after water [1]. Its production implies the utilization of immense amounts of natural aggregates, cement, and water. As a consequence, the pressure on the environment is noticeably growing. In addition to the higher energy efficiency demands, that the sustainable leap brings, there is also the need for overall environmental preservation, and the development of a so-called "circular economy", which implies the efficient use of raw materials [2]. Due to high aggregates consumption, which surpasses 40 billion tons annually [3], questions arise regarding the possible solutions for the replacement of natural raw materials. The extraction of these materials has noticeable and irreversible aftermath on the water supply, ecosystem, soil, wildlife, and the biosphere.

Aggregates that are exploited are categorized as fine or coarse [4]. The most used fine aggregate in mortar mixtures is river sand. One of the issues is the extraction levels of this aggregate that are far beyond the replenishment levels. Consequently, the investigators are searching for alternative solutions in substitute materials to conclude the crisis of sand depletion. It is highly possible to reduce the supply of virgin materials in construction applications through the reuse of recycled aggregates [5]. A supported and more environmentally friendly solution could be the use of substitutes for aggregates such as industrial by-products and waste materials.

Waste glass represents appreciative material that could be efficiently used as an aggregate replacement. Glass is not bio-degradable, it has many different compositions, forms, and appearances, and has versatile applications [6]. Numerous utilization of glass materials are reflected in disproportionate amounts of this kind of wastes annually that later requires a long time to break down naturally. However, glass waste has immense potential for recycling and reuses [7]. Its hardness and low permeability can complement the performance of the latter concrete [5]. There is a great potential for cathode-ray tubes (CRTs) utilization in mortar mixtures since they are made of 85% glass, which is also linked with appropriate waste management and immobilization of hazardous waste disposal [8]. Also, this approach corresponds to better environmental practice: recycling this waste diminishes energy consumption and reduces CO_2 emissions. However, two main concerns arise during the usage of CRT waste glass as a fine aggregate: the leaching of heavy metals and alkali-silica reaction (ASR) representing the disruptive reaction within concrete [9]. The high lead content is stored in the glass, funnel, and panel section, thus this landfilling non-eco-friendly aspect triggered the call for a solution since the presence of lead in CRT glass means that common disposal methods are not the option. Most of the experimental research that integrated CRT glass in mortar mixtures used it as a total or partial substitute for river sand, due to its ability to reduce energy consumption and cost, and generally has a positive environmental impact. Also, CRT glass is high in silica, and it behaves like a pozzolanic material in mortar mixtures [9]. Hence, it could be used as a supplementary cementitious material (SCM) [10].

This paper includes an evaluation of the recent developments regarding the recycling and reuse of CRT glass, as well as the implementation of this waste in mortar mixtures with prominence on their physico-mechanical properties. The following tests were overviewed: consistency, density, water absorption, strengths at static loads, ASR, and lead leaching.

RECYCLING OF CRTs

Technological leaps brought many advantages regarding commodity, usefulness, and luxury in the electronic industry, but on the other hand, e-waste became the fastest-growing problem worldwide that will not cease to slow down any time in the future [8]. Disposal of the immense bulk of old computer monitors and TV screens in landfill sites causes considerable environmental concerns. Convenient recycling of CRT glass has to be accomplished to withdraw possible environmental problems. There are two correct ways to recycle CRT waste glass: closed-loop and open-loop recycling. The first type of recycling method is obsolete since it refers to the recycling of old CRT screens in order to obtain new screens. Since new and improved technologies replaced the need for such screens, this is rarely practiced. The second type of recycling is more exacting, but the technological process is more appropriate since it refers to the employment of CRT waste in order to get new products. Products obtained by this process have greater environmental value and are more cost-efficient [11].

CRT monitor/screen consists of three main parts: funnel glass, front panel glass, and the electron gun. The main constituent of CRTs is silica, but different compounds can be found: barium, strontium, and lead compounds mostly. Recycling of CRTs begins with the separation of the plastic casing, external, and metallic parts. The funnel and panel glass thereafter are separated by laser cutting. Lead content in panel and funnel is different, hence the procedure after separation and recycling for those two differ. Panel glass recycling involves the removal of fluorescent powder, followed by mechanical crushing used to break the glass into smaller particles. After this process, panel glass has a low lead content and it is safe to use it as a fine glass aggregate. Funnel glass has a higher amount of lead, and it has to be immersed in a bath of 5% of HNO_3 solution, for at least 3 h, to extract lead from the surface [12]. After that, it can be mechanically crushed and is ready for usage. It is of great interest to properly recycle CRT glass and thus maximize environmental safety [12].

OVERVIEW OF TEST METHODS AND RESULTS

Consistency

The mortar consistency refers to its property to keep all ingredients together without segregation. Many studies predict better consistency due to the use of CRT glass as a recycled aggregate, mainly in consequence to its low permeability and soft surfaces. In addition, harsh texture and sharp edges may reduce the flow. Methods of CRT glass grounding and its further treatment have a great impact on a slump. Hue and Sun [13] replaced fine aggregate (river sand) with 100% treated and non-treated CRT glass in the production of mortar. CRT glass in mortar mixes was responsible for a detectable increase in slump flow in contrast to a mortar with river sand. It was also reported that utilization of non-treated CRT glass produced higher slump flow than treated CRT glass. In other research, Ling and Poon [14] used different replacement levels of river sand with CRT glass in mortar: 0, 25, 50, 75, and 100%. Due to smooth and imperishable surface of CRT glass, the flow spread diameter expanded. The authors also stated that the consistency of the mortar mixture reduces with the decrease of CRT glass amount.

Density

Many investigations showed that the presence of CRT glass in mortar leads to an increase in density compared to river sand based mortar [15]. In general, higher density is preferred in some applications, such as use for underwater constructions. In the experiment that Zhao and Poon conducted, the river sand was replaced with non-treated and treated CRT glass at replacement levels of 0, 25, 50, and 75% [16]. It was noticed that the substitution of river sand with non-treated CRT glass increases wet density higher than the usage of treated CRT glass.

Water absorption

The replacement of river sand with 100% treated CRT glass significantly decreases water absorption [17]. This outcome was predictable because CRT glass has a lower absorption than the river sand. A decrease in permeability was also observed with an increase in the amount of CRT glass content. Investigators concluded that the smaller particle size of grounded CRT glass led to a further decrease in water absorption [17].

Strengths at static loads

Integration of grounded CRT as a fine aggregate, instead of river sand, leads to higher compressive and flexural strength [13]. After a curing period of 28 days, the compressive strength of CRT mortar was 41% higher than the mortar with river sand, due to the enhancement of particle packing. The higher amount of CRT glass integrated into the mortar, the higher the strength. Similar results were obtained in other studies [18] which showed that non-treated CRT glass improved compressive strength after the curing period. Other investigations [19] notice a decrease in compressive and flexural strength by an increase of CRT glass replacement levels in mortar in the early period of curing. This was probably the result of a feeble bond with the cement paste and lower adhesion, because of the smooth surface of CRTs. However, in the later stages of curing, due to pozzolanic activity, there was less decrease in strength.

ASR

Researchers reported that utilization of CRT waste glass promotes expansion due to ASR [20]. It was noticed that even after 14 days CRT mortar mixtures continued to expand. However, combination with fly ash as SCM led to a decrease in further expansion. It was reported that the presence of fly ash in concrete alleviated the expansion due to pozzolanic activity, i.e. mitigation in alkali content. Zhao *et al*. [21] found similar results, stating that the use of treated CRT glass affected the ASR response within the allowable limit, due to integrated fly ash. Wang *et al*. [20] validated these results, announcing that ASR reaction could be reduced by surface treatment of CRT glass, hence pozzolanic materials are not needed in this case. The conclusion was that ASR could be partially prevented with the use of pozzolanic materials such as metakaolin or fly ash, which leads to denser microstructure, or by CRT glass surface treatment.

Lead leaching

Management of CRT has raised some concerns regarding the lead content which is present in the wasted glass. Removal of the lead could be conducted with acid treatment, which could be expensive and ineffective. Many investigations showed that lead could be adequately immobilized in a mortar matrix since it has been proven that the alkalinity of cement mortar reduces lead leaching. Kim *et al*. [22] reported that lead leaching was almost 0% in the case of a combination of different types of biopolymers. These results were similar to other studies. Romero *et al*. [17] stated that if biopolymer was added into the mixture of mortar with 20% of CRT glass as an aggregate, lead leaching was within the allowable limit. Likewise, there are other methods of lead encapsulation, e.g. the utilization of graphene oxide nanoparticles. Researchers came to the conclusion that usage of 50% of treated CRT glass lead leaching decreases below the limit, while a mixture with 50% of non-treated glass surpasses the acceptable limit. Therefore, it was recommended the utilization of a maximum of 25% non-treated CRT glass to prevent lead leaching above limits. Due to pozzolanic properties, utilization of an additional quantity of fly ash is also advisable [20]. Hence, a number of methods can be done in order to prevent lead leaching: CRT glass amount limitation, fly ash addition, CRT treatment, encapsulation in an alkaline environment, and other techniques.

CONCLUSION

In the light of recent discoveries, utilization of all kinds of industrial by-products and waste has brought a new perspective and insights. Environmental concerns have been raised regarding natural resource depletion. Concrete production implies the utilization of immense amounts of natural aggregates and energy, affecting the overall environment through climate change, pollution, and waste generation.

This review considers the possibility of CRT waste glass utilization in mortar mixtures as a fine aggregate. It has been proven that as a river sand replacement, CRT glass improves some concrete properties. For instance, consistency is enhanced due to the low water absorption and smooth surface. Substitution of river sand by CRTs leads to higher compressive and flexural strength. Also, the risk of ASR can be reduced by using SCMs (metakaolin, fly ash, etc.). Numerous techniques reassure that lead leaching could be successfully controlled by acid treatment, immobilization by mortar mixtures, graphene oxide and biopolymers, limitation in the volume of CRT glass, and SCM addition. The results of reviewed investigations showed that the properties of mortar mixtures containing CRT glass as an aggregate are highly encouraging. However, more investigations are needed to explore all potential benefits.

ACKNOWLEDGMENT

The research presented in this paper was done with the financial support of the Ministry of Education, Science and Technological Development of the Republic of Serbia, within the funding of scientific research work at the University of Belgrade, Vinca Institute of Nuclear Sciences (Contract No. 451-03-68/2022-14/200017).

REFERENCES

[1] J. Khatib, O. Baalbaki, A. Elkordi, Waste and Supplementary Cementitious Materials in Concrete., Elsevier, Beirut (2018), p.493.

[2] J. Bawab, J. Khatib, S. Kenai, *et al*. Buildings; 179 (2021).

[3] P. Peduzzi, Environ. Dev; 11 (2014) 208–218.

[4] L. Gallagher, Sand and Sustainability: Finding New Solutions for Environmental Governance of Global Sand Resources. United Nations Environment Programme, Geneva (2019), p.1, ISBN: 978-92-807-3751-6 .

[5] S.K. Kirthika, S.K. Singh, A. Chourasia, J. Clean.Prod; 268 (2020).

[6] K. Zheng, Eco-Efficient Concrete, Woodhead Publishing Ltd., Cambridge (2013), ISBN: 9780857094247.

[7] R.K. Dhir, J. De Brito, G.S. Ghataora, *et al*. Use of glass cullet as a sand component, Sustainable Construction Materials, Elsevier, Amsterdam (2018), p.167, ISBN: 9780081009840.

[8] N. Singh, J. Li, X. Zeng, WASTE Manag; 57 (2016) 187–197.

[9] A. Popovici, O. Corbu, G.E. Popita, *et al*. Mater. Plast; 52 (2015) 588–592.

[10] B. Hilton, K. Bawden, K. Winnebeck, *et al*. Resour. Conserv. Recycl; 151 (2019) 104451.

[11] N. Singh, J. Li, X. Zeng, J. Clean. Prod; 133 (2016) 188–200.

[12] X. Shi, G. Li, Q. Xu, *et al*. Mater. Rev; 11 (2011) 1–29.

[13] Z. Hui, W. Sun, Constr. Build. Mater; 25 (2011) 4059–4064.

[14] T.C. Ling, C.S. Poon, J. Hazard. Mater; 192 (2011) 451–456.

[15] D. Romero, J. James, R. Mora, *et al*. Waste Manag; 33 (2013) 1659–1666.

[16] H. Zhao, C.S. Poon, Constr. Build. Mater; 148 (2017) 900–909.

[17] T.C. Ling, C.S. Poon, Green Mater; 2 (2014) 43–51.

[18] L.A.P. Oliveira, J.C. Gomes, DBMC; (2008) 11–14.

[19] S.B. Park, B.C. Lee, Cem. Concr. Res; 34 (2004) 1145–1152.

[20] J. Wang, S. Guo, Q. Dai, *et al*. J. Clean. Prod; 226 (2019) 85–95.

[21] H. Zhao, C.S. Poon, T.C. Ling, J. Clean. Prod; 51 (2013) 184–190.

[22] D.Kim, I.G. Petrisor, T.F. Yen, J. Air Waste Manage. Assoc; 55 (2005) 961–969.

ECOTURISM AS A FORM OF GREEN ECONOMY

Dejan Riznić[1], Aleksandra Fedajev[1], Adrijana Jevtić[1*]
[1]University of Belgrade, Technical Faculty in Bor, V.J. 12, 19210 Bor, SERBIA
[*]*ajevtic@tfbor.bg.ac.rs*

Abstract

Intensive technological development has led to significant changes in the structure of tourist supply and demand. So today the concept of sustainable tourism development dominates, which means the development of tourism that meets the needs of current tourists, tourist destinations and all participants in tourism, while preserving and increasing the potential for future tourism resources, without compromising the ability of future generations to meet their own needs. The critical question of sustainable tourism is how to turn sustainable development into practice in all tourism activities- from mass to nature tourism and special forms of tourism. We identify ecotourism as a chance to improve tourism in many destinations. Ecotourism is one component of sustainable tourism that can play a significant role in preserving a particular destination's natural and anthropogenic values. As a new form of touristic offer, ecotourism is an environmentally responsible tourist trip that shows specific areas to stay and enjoy nature. Today, in the world of eco-tourism, it is increasingly becoming a global phenomenon that includes not only movements related to staying in certain tourist facilities but also various adventure trips.

Keywords: sustainable development, ecotourism, green economy, ecology, ecological economy

INTRODUCTION

Tourism is one of the leading economic branches, and more and more people need it in the technological age, to rest with some time spent at a tourist destination. It is interesting that today, tourism is one of the major forms of production. According to the UNWTO (World Tourism Organization), transactions in the tourism market amount to approximately $5 billion every day and move 20 percent of the world's population (over 1,400 million people), which makes at least one tourist trip a year.

The growth in the number of people traveling each year is exponential, as are the consequences. We have noticed that most tourists avoid destinations with disturbed environments. Forms of spending free time are increasingly taking place in a natural environment where rich cultural, historical, ethnographic, and Eco content is always welcome. Given the unexpectedly rapid development of tourism, which posed a serious risk to the environment and the well-being of the population, tourism has gradually developed into an important factor in sustainable development. This has caused many destinations, in order to adapt to new trends, to allow tourists to enjoy and gain knowledge about the natural, historical and cultural characteristics of a unique environment while preserving the integrity of the place and encouraging economic development and local community well-being.

Ecotourism, or at least the idea of ecotourism on paper, was born as a concept contrary to the conventional tourism model and seeks balance, in the same way, that sustainable tourism applies to the urban environment [1]. Ecotourism has been just one way to travel. The partial collapse of the tourism sector marked the year of the Covid-19 virus pandemic, which we left behind. Despite all that, social networks are flooded with photos of those who are exploring, mountain peaks, villages and hamlets, hills, and forests of Serbia for the first time. During the pandemic year, nature was our enemy, and yet it seemed miraculously close, taking us back, at least for a moment, to some old, different times. Eco-tourism, as a form of green economy and a topic in scientific and professional papers, is insufficiently processed, and it can be said that it is neglected.

ECOTOURISM

Meaning of Ecotourism

Ecotourism is a specific form of travel to relatively unpolluted areas of nature to admire and enjoy the landscapes, wild plants, and animals, but also in all the accompanying cultural facilities of a particular location. TIES (International Society for Ecotourism) defines ecotourism as: "Responsible travel in nature, which protects the environment and supports the well-being of the local population" [2].

The basic principles of eco-tourism are: minimizing the negative effects on nature and local communities; influencing the long-term participation of the local population in decision-making; providing economic and other benefits to local communities; contributing to the protection and management of protected and other natural resources [3]. And the most common misconceptions about eco-tourism are reflected in the following factors: an underdeveloped area is an ideal area for the development of eco-tourism; an opinion that the environmental awareness of the local population and tourists is at a high level; equating eco-tourism with rural tourism.

Ecotourism strives to achieve the results of sustainable development in all its forms. However, it is important to note that all tourism activities-whether related to mass tourism or specific forms of tourism-should aim at sustainability. From this, it is concluded that the planning and development of tourism infrastructure, its further functioning, as well as its marketing, should focus on environmental protection, social, cultural, and economic criteria of sustainability [4].

Experiencing the natural environment actually means respecting and preserving the area in which we are, whether it is a village, mountain, river, or forest. The most important concepts of this new type of tourism are respected and preserved.

Ecotourism in Republic of Serbia

Serbia has huge potential for ecotourism development. Beautiful, peaceful rivers, rich forests, and mountains give tourists the opportunity to enjoy. Let us mention only the region of Lake Vlasina, the slopes of Zlatibor, Divčibare and Kopaonik. Many travel agencies also offer these types of arrangements: trips to preserve nature. Tourist adventures in Serbia provides an incomparable experience of a pure, untouched nature. We know that travel has the power to protect nature; it brings benefits to the community and contributes to the preservation of cultural heritage. These three principles should become not only our goal, but also our responsibility.

Ecotourism is in direct functional connection with the environment. It should preserve the soil and ecosystem in every way. This refers to the protection and restoration of environmentally sensitive land, natural resources, agricultural land, watersheds and water resources, cultural and historical spaces, increasing the quality and availability of open space and recreational opportunities.

Natural resources should be used wisely: to build facilities and infrastructure for tourists, but with the preservation of natural resources, reduction of waste, and reduction of pollution through efficient use of land, energy, water, and materials. As far as transport is concerned, there is room for improvement-clearing paths for cyclists and pedestrians, cleaning river canals and shores, and using land transit. Development projects in the field of transport and housing are very important here. The trend of sustainable development is widespread and increasing in development.

The promotion of clean energy means increasing energy efficiency through the renewable energy system and the energy distribution system. Strive to reduce greenhouse gas emissions and consumption of artificial fuels. Protection of autochthonous culture and traditions: preservation of culture and traditions of the autochthonous population of the region, conservation and preservation of archeological sites and historical sites. Besides the above positive effects of ecotourism on the environment and the local community, there are several negative parameters that must be considered for a protected area of untouched nature. This type of sustainable tourism includes any type of tourism that contributes to protecting the environment, social and economic integrity, and the promotion of natural values. It is crucial that tourism activities, as well as capacity building and infrastructure activities, do not harm nature (watercourses, coastal areas, wildlife).

Unfortunately, there is an obvious lack of adequate infrastructure in Serbia, which would support the development of sustainable tourism. There is also a lack of efficient planning of waste management in tourist places, in order to minimize the negative impact of tourist activities on the environment. We should place special emphasis on the development of "environmentally friendly technologies" such as Eco toilets, which are currently insufficiently present in Serbia.

The fact, which we cannot deny, is that Serbia is an extremely beautiful country, which has a preserved environment. At every step, we can see a trace that nature has made with its processes and left behind. We legally protected these national parks, but rivers, lakes, parks, waterfalls, natural landscapes, etc. Sometimes we are not aware of the beauty we possess. We will list only some of them: nature reserves Uvac, Zasavica, Carska bara. There are also many mountains, lakes and rivers that create magnificent waterfalls, one of the biggest attractions for tourists [5].

The future of ecotourism in Republic of Serbia and its impact on the green economy

In order to better understand the concept of ecotourism, Fennell (2001) studied 85 definitions of ecotourism (mostly from a 20-variable perspective), using a content analysis method. Based on this study, he concluded that the variables that are most often mentioned in the definitions include: 1. areas where ecotourism occurs, e.g. natural areas; 2. protection; 3. culture; 4. benefits for the local community, and 5. education [6].

Ecotourism, as a specific market niche and part of a broader concept of sustainable tourism, is a responsible journey to relatively preserve natural areas that preserve the environment and cultural values, stimulating the increase in the standards of the local population [7].

Eco-tourist destinations with their population are set as certain catalysts in the restoration of ecotourists, tourists who come from a modern society in which the evaluation of the natural environment is different [8]. In order for a destination to receive the epithet of an eco-tourist destination, it is necessary to meet certain criteria. The criteria adopted by international ecotourism agencies that should meet "real" ecotourism are: preservation of bio and cultural diversity through the achievement of minimal impact on the natural resources of protected areas; generating sustainable and legal income for the benefit of local communities; involvement of local communities, ecotourists, tour operators and state institutions in planning and development processes; improving environmental and cultural knowledge through respect for local traditions and culture; generation of revenues intended for the preservation of protected areas; training of the shareholders on their role in the process of nature protection and conservation [9].

One advantage of ecotourism is the impact on the environment, which is less than with conventional tourism, although this is no effect, as many promoters say because it is impossible. It fosters respect for local traditions and cultures and economic benefits to the local population (through income from activities). This marks a difference from conventional tourism, which mainly benefits large restaurant chains, hotels, and travel agencies, usually multinational.

One of the major disadvantages of ecotourism is that, although environmental pollution is less than with mass tourism, it is still an enormous mass of the population that moves (and generates waste). It also generates that many buildings are used to accommodate tourists, and this is impossible to limit, especially when it is tourists who offer profits to the local population. The social difference between those who visit and have the money for it, and those who have to serve, clean and entertain these guests is as insignificant as with conventional tourism and does nothing to change the situation, except offering a layer of green to unevenness.

The risks of ecotourism are equal to the risks of conventional tourism. Overcrowding is very difficult to control, especially when a place becomes "modern". It also creates a problem for the land and water of the place, whether people go by car or other means of transport, such as boats and buses. Extensions used to accommodate tourists, as well as land for planting food, are taken directly from the surrounding natural areas. The waste generated by tourists and tourism, as well as energy consumption (water, electricity) is still huge and directly affects the environment. Wild animals are affected by the reduction of their habitat, noise, people walking, and others, which significantly changes their well-being.

A large number of tourists in recent years have left their mark on tourist destinations, and many places have felt the negative impact of mass tourism. After a long period of isolation and work from home, there was a significant increase in visits to national parks. Queues for painting in front of waterfalls and lookouts and outdoor activities have replaced the trend of visiting big cities, museums, and concerts. Eco-tourism, which has seen a slight increase in recent years, is now a new opportunity that can save tourism in the post-covid era. What used to be only the potential but also the hope of many environmental organizations is now a reality. Since the onset of the coronavirus crisis, the tourism industry has come under significant global pressure-research shows that environmentally conscious vacations in nature, rural and less populated areas are what attract tourists in these circumstances.

When it comes to Serbia, tourist organizations throughout the country have noticed an increase in interest in the numerous natural beauties that Serbia can provide. As an indisputable proof of that, the increased number of tourist visits supports this.

CONCLUSION

Although economists are extremely satisfied with the financial effects of tourism, over 70% of the world's population ignores one extremely important fact, and that is that this lucrative activity has many negative aspects, including endangering the environment. The International Union for Environmental Protection at the United Nations (IUCN) warns that an additional source of danger is the negligence of tourists who often use significantly more resources than they need for a pleasant vacation, causing serious damage to both locals and the planet Earth.

We live in a world where many areas are destroyed and environmentally polluted. Food, water, air, and land are contaminated, the climate has changed, and all this affects tourism. In order for this not to happen, we need to engage in eco-innovation and its realization. The first thing is to gain awareness and knowledge about protecting the natural environment, as well as about the economic and cultural aspects of a certain area and place. Thus, the tourist will become a socially responsible person who enthusiastically participates in environmental issues. While the nature-oriented tourism is essentially a simple journey to areas with beautiful nature, ecotourism benefits the local population in environmental, cultural, and economic terms-the green economy.

Tourism development is best if it is planned and based on modern requirements of sustainable development (green economy) that put in the forefront such landscaping for tourism so that it is without violating basic environmental laws, regardless of whether it is legally protected facilities parks, nature reserves, etc.), or nature. Abuses of natural resources in order to expand tourist travel and increase tourist traffic have led to environmental problems and threats to natural heritage, but also to raising awareness of the need to establish and constantly apply the concept of sustainable tourism development.

Sustainable tourism should enable the optimal use of environmental resources that are a key element of tourism development, in order to enable the heritage preservation and sustainable business. In order to realize the idea of sustainability and eco-tourism, it is necessary to establish an innovation system for eco-innovation, because they are of fundamental importance for the preservation of the environment, mostly the most beautiful places on the planet. As an important segment of sustainable tourism, ecotourism is a responsible journey into relatively preserved natural areas that preserves the environment and cultural values and the values of ecotourism destinations. Through the improvement of the tourist offer, ecotourism can have multiple positive effects on increasing the standards of the local population and the overall sustainable economic development of the local (ecotourism) community.

It can be concluded that Serbia has significant potential for the development of eco-tourism and that an increasing number of people are interested in investing in this branch of tourism, but also that concrete projects are needed, as well as cooperation with European Union countries brings eco-tourism.

REFERENCES

[1] A. Mathieson, G. Wall, Tourism: change, impacts, and opportunities, Pearson Prentice Hall, London (2006), ISBN: 0-130-99400-6.

[2] A. Dukić, D. Riznić, N. Filipović, International scientific conference on the fourth industrial revolution-the importance for green economy progress and environmental protection, 16–18 September, Belgrade, Serbia (2020) 120–122.

[3] A. Drumm, A. Moore, Ecotourism Development, A Manual for Conservation Planners and Managers, The Nature Conservancy, Arlington, Virginia, USA (2005), ISBN: 1-886765-14-6.

[4] B. Bramwell, Sustainable Tourism Management-Principles and Practice, Tilburg University Press (1996).

[5] S. Štetić, Posebni oblici turizma, Beograd (2007).

[6] M. Honey, Ecotourism and Sustainable Development: Who Owns Paradise? Island Press, Washington D. C. (1999), ISBN: 1559635827.

[7] J. Milivojević, K. Kanjevac Milovanović, D. Rajković, *et al.*, FQ2011 Festival kvaliteta, Zbornik radova: 38. Nacionalna konferencija o kvalitetu i 6. Nacionalna konferencija o kvalitetu života, Kragujevac (2011).

[8] S. Vujović, J. Spajić, D. Vukosavljević, Ekonomika poljoprivrede, 58 4 (529–804) (2011), Beograd, YU ISSN: 0352–3462.

[9] D. Bulatović, Ekoturizam u zaštićenim područjima Republike Crne Gore-doktorska disertacija, Ekonomski fakultet, Subotica (2011).

DIET OF TWO CYPRINID SPECIES, WHITE BREAM (*BLICCA BJOERKNA*) AND COMMON ROACH (*RUTILUS RUTILUS*) IN THE DANUBE RIVER, BELGRADE

Vesna Điković[1*], Jelena Vranković[1], Katarina Jovičić[1]

[1]University of Belgrade, Institute for biological research "Siniša Stanković", National
Institute of Republic of Serbia, Department of Hydroecology and Water Protection,
Bulevar despota Stefana 142, 11060 Belgrade, SERBIA

[*]*djiki@ibiss.bg.ac.rs*

Abstract

Food and feeding habits of white bream (Blicca bjoerkna) and common roach (Rutilus rutilus) specimens sampled from the Belgrade section of the Danube River in April 2021 were investigated. Stomach contents of 20 individuals of both cyprinid fish species were analyzed and no individual had an empty stomach. There was a small difference in the stomach contents of these two analyzed fish. The food items in stomach showed a wide spectrum, ranging from crustacean, molluscs to aquatic insects. Therefore, analyzed fish species displayed an omnivorous feeding. Based on the obtained data, the indices of frequency, abundance and significance for each of the identified prey categories were calculated. Trichoptera (aquatic insects) and Gammaridae (Crustacea) were found to be the most common and abundant prey utilized by all analyzed species. The attained results, since these are relatively small samples collected during one monthly outing (April), can be considered preliminary and require further research.

Keywords: Cyprinid fish, feeding, stomach content, urban river locality, biotic indices

INTRODUCTION

Fish have different habits and food needs, depending on age, physiological condition of fish, time of day or season. The food and diet knowledge is very important for fish biology [1]. Fish dietary ecology and feeding habits can be useful in searching the distribution of a fish population for successful management of fishery [1]. Few factors can influence fish diet composition and make variation in intestine content among analyzed individuals, like the fish size and its feeding habits.

European cyprinids are characterized by a variety of diets and feeding modes and have specialized representatives as zooplanktivores, herbivores, piscivores and benthivores [2]. Although none of the cyprinids are strictly monophagous, many may feed on only one type of food organism, depending on its availability [2].

White bream (*Blicca bjoerkna*) and common roach (*Rutilus rutilus*) are omnivorous cyprinid freshwater fish species found in Europe and Asia, autochthonous in Serbian freshwater ecosystems. They feed on plankton, benthic invertebrates and plant material [3].

The white bream does not have any commercial value because of its unpleasant taste [4] and great number of intermuscular bones [5]. However, it is an important food supply for predator species inhabiting aquatic habitats.

Data regarding the biology, including feeding of cyprinids in Serbia/Serbian Danube are scarce. Krpo-Ćetković *et al.* [6] published a paper concerning the biology of *Aspius aspius* (Linnaeus, 1758), while Đikanović [7] analyzed intestinal parasites and feeding biology of the 14 fish of the Belgrade region. Also, Egerić *et al.* [8] have published notes of feeding preference of 4 cyprinid fish species in the Danube River, downstream from Belgrade city.

This study was conducted on the Danube River locality Visnjica, which is exposed to the discharge of the largest wastewater collector in the city of Belgrade.

The main aim of this study was to investigate diet spectrum of white bream and common roach by analyzing the stomach contents and present (available) food resources at Visnjica locality, Serbia, and to compare our results with findings of the previous studies. The samples represents a part of the study related to the use of biomarkers in order to determine the impact of wastewater discharge at the Visnjica locality.

MATERIALS AND METHODS

A total number of 20 specimens of white bream and common roach (ten individuals of each species) were collected by professional fishermen in April 2021 at the locality Visnjica, situated on the right bank of the Danube River (1162 river kilometre).

***Figure 1** Location map of the Visnjica locality, Serbia*

Specimens were measured for their total body length (Lt, cm) and total body weight (M, g). For dietary analyses a complete digestive tract was examined. Dietary analyses were performed using a binocular microscope (Zeiss Stemi 508) for the determination (mainly order level was observed) and counting of ingested organisms. It has shown that intestine content analysis was difficult as regards identifying and counting prey, given that tissues were masticated or digested.

Sampling of benthic fauna was also performed at the same locality. The samples of aquatic macroinvertebrates were collected by a benthic hand net (mesh size 500 μm) in shallow water (at depths up to 1.5 m) and by an Ekman dredge (225 cm^2) in deeper water (up to 10 m), according to the EN 27828 Standard. Part of the sampled material was examined on site and the rest was preserved in 70% ethanol and processed at the laboratory. The collected individuals were identified using the appropriate identification keys.

Data analyses included calculation of the percentage of occurrence (F), percentage share (Cn - numerical abundance) and significance index (PV - prominence value) as follows: $\%F=(N_i/N_t)x100$; where N_i is the number of fish with food item i, N_t is the total number of fish in the sample with stomach content; %A=($\Sigma S_i/\Sigma S_t$)x100 where S_i is the number of food item i, and S_t the total number of food items in the entire sample [9] and PV=Cn$\sqrt{F}$; then PV(%)=(PV/ΣPV)x100 [10,11]. **The Ivlev's index** was applied to assess the preferences of cyprinid fishes to available prey in the local habitat. The following equation was used: E=(ri–pi)/(ri+pi), where *'E'* is the measure of selectivity for various prey items in the fish rations; *'ri'* is the relative abundance of prey category *'i'* in the digestive tract (as a proportion or percentage of all digestive tract contents); and *'pi'* is the relative abundance of this prey in the environment. The values of this index range from −1 to +1, with negative values indicating rejection or inaccessibility of the prey, zero values – random feeding, and positive values – active selection.

RESULTS AND DISCUSSION

Cyprinid fish white bream (*Blicca bjoerkna*) and common roach (*Rutilus rutilus*) from the Belgrade section of the Danube River were collected and examined. The total length (TL) range was 22.0–28.0 cm, while the body weight (W) range was 190.0–390.0 g (Table 1). All sampled fish specimens had intestines filled with food items. The examination of the stomach contents revealed that white bream at the studied localities fed mainly on aquatic insect of Trichoptera larvae (68.97%), followed by crustaceans belonging to the family Gammaridae, and one individual of Mollusca. In addition, representatives of the Bivalvia, Gastropoda and Gammaridae have dominated in the stomach contents of common roach specimens, with a share of about 30% of each category. The Trichoptera (5.81%), Mollusca (17.44%) and one juvenile crab were also identified in the common roach diet (Table 2). In total, 144 food items have been determined and counted in the fish stomach contents. For white bream 58 food items have been counted, and for common roach 86, respectively.

Table 1 *The total length (TL) and body weight (W) of the examined two cyprinid fish species in the investigated locality. The parameters are presented with a mean value, standard deviation (±SD), and a range of the values (in parentheses)*

Fish species	Total body length (cm)	Total body weight, with stomach content (g)	Stomach content (g)
Blicca bjoerkna	26.0 ± 2.14 (22.0–28.0)	285.71 ± 73.68 (190.0–390.0)	7.71 ± 2.43 (4–10)
Rutilus rutilus	26.07 ± 1.79 (24.0–29.0)	272.86 ± 70.41 (200.0–400.0)	6.57 ± 2.07 (3–9)

Analyses of the stomach content of two cyprinid fish species applying selected biotic indices is performed. The percentage number/share (Cn), frequency of occurrence (F) and significance index/prominence value (PV, PV %) of identified food items are given in the Table 2.

Table 2 *Analysis of identified stomach prey items of white bream and common roach sampled in investigated locality, applied biotic indices*

Species/Taxonomic group	Percentage frequency	Percentage share	Significance index	
			PV	PV (%)
		Blicca bjoerkna		
Trichoptera	71.43	68.97	4926.11	85.11
Gamaride	28.57	29.31	837.44	14.47
Mollusca	14.29	1.72	24.63	0.43
		Rutilus rutilus		
Trichoptera	14.29	5.81	83.06	2.33
Bivalvia	42.86	29.41	1260.50	35.33
Gastropoda	28.57	24.42	697.67	19.56
Gammaridae	57.14	22.35	1277.31	35.80
Mollusca	14.29	17.44	249.17	6.98
crab juvenile	14.29	1.16	16.61	

According to present results, representatives of Trichoptera were dominant in the stomach contents of examined white bream specimens, while diet of common roach consisted mostly of Bivalvia (*Dreissena* spp.) and Gammaridae.

The qualitative and quantitative composition of the diet of two cyprinid fish species and bottom macroinvertebrate fauna at the sampling locality were compared and the results are presented in the Tables 3 and 4. Ivlev's index of prey selectivity indicated the different preference for food items of collected fish. The results showed that *Blicca bjoerkna* exhibited strong dietary preferences for Gammaridae, while *Rutilus rutilus* had preferences for Bivalvia and Gammaridae (Table 3). Oligochaeta were dominant taxa group in bottom fauna in the environment, followed by representatives from family Chironomidae (Diptera) (Table 4).

According to the studies performed from 2007 to 2009, the most frequent food categories in the intestine contents of white bream and common roach in the Belgrade sector of the Danube river, were organisms of macrozoobenthos from the group Annelida and Oligochaeta. The second frequent group were Crustacea [7]. Egerić *et al.* [8] in their study noticed that Blicca bjoerkna showed a higher preference for gammarids (26%), followed by molluscs (17%).

Table 3 *Food items of examined fish based on relative abundance (%) of the identified taxonomic groups and the Ivlev's index of prey selectivity (E)*

Fish species/prey category	Relative abundance in stomach contents	Ivlev's index (E)
	Blicca bjoerkna	
Trichoptera	68.97	
Mollusca	1.72	
Gammaridae	29.31	0.98
	Rutilus rutilus	
Trichoptera	5.81	
Bivalvia	29.07	0.91
Gastropoda	24.42	0.75
Mollusca	17.44	
Gammaridae	22.09	0.98
crab juven.	1.16	

Table 4 *Relative abundance of identified taxa in the bottom fauna*

Taxa	Relative abundance in bottom fauna
NEMATODA	1.3
HIRUDINEA	0.3
OLIGOCHAETA	71
GASTROPODA	3.5
BIVALVIA	1.42
AMPHIPODA-Gammaridae	0.2
DIPTERA - Chironomidae	22
ODONATA	0.3

According to the data from FISHBase [12], feeding habits of common roach [13] consist mostly of zoobenthos, representatives of Mollusca (*Dreissena* spp.) and Gammaridae. In the paper of Hellawell [14] the diet of *R. rutilus* was predominantly plant-based, and the most important animal component were aquatic insect larvae. Also, the same study found that diet habits varied with age: with molluscs being important to older roach, while younger roach consumed large amounts of substrate material.

CONCLUSION

The attained results, considering that this is relatively small sample collected during one monthly outing (April), can be considered as preliminary and further research is required.

ACKNOWLEDGEMENT

This research was supported by the Ministry of Education, Science and Technological Development of the Republic of Serbia (No. of contracts: 451-03-68/2022-14/ 200007).

REFERENCES

[1] V.L.M. Ramana, R.C. Manjulatha, Eur. J. Acad. Res; 2 (8) (2014) 11065–11075.

[2] E.H.R.R. Lammens, W. Hoogenboezem, Diets and feeding behaviour, In: Cyprinid Fishes, Springer, Netherlands (1991), p.353–376, ISBN: 978-94-011-3092-9.

[3] M. Kottelat, J. Freyhoff, Handbook of European freshwater fishes, Kottelat, Cornol, Switzerland and Berlin, Germany, (2007), pp.646, ISBN 978-2-8399-0298-4.

[4] S. Yılmaz, O. Yazıcıoğlu, R. Yazıcı, *et al*., J. Limnol. Freshw. Fisheries Res; 1 (1) (2015) 9–18.

[5] H.C. Okgerman, M. Elp, S. Atasağun, Turk. J. Biol; 36 (1) (2012) 125–134.

[6] J. Krpo-Ćetković, A. Hegediš, M. Lenhardt, J. Appl. Ichthyol; 26 (4) (2010) 513–521.

[7] V. Đikanović, Fauna endohelminta riba Dunava beogradskog regiona, sa osvrtom na prelazne domaćine iz grupe makrozoobentosa, PhD thesis, Faculty of Biology, University of Belgrade, Serbia (2011), p.182 (in Serbian).

[8] M. Egerić, D. Škraba, M. Ilić, *et al*., Wat. Res. Manag; 5 (3) (2015) 35–40.

[9] P.A. Amundsen, H.M. Gabler, F.J. Staldvik, J. Fish Biol; 48 (1996) 607–614.

[10] P. Hickley, R. North, S.M. Muchiri, *et al*., J. Fish Biol; 44 (1994) 607–619.

[11] M. Lorenzoni, M.Corboli, A.J.M. Dorr, *et al*., Bull. FR. Peche Piscic; 365/366 (2002) 537–547.

[12] *Available on the following link:* https://www.fishbase.se

[13] L.N. Belova, J. Ichthyol; 26 (3) (1986) 50–56.

[14] J. M. Hellawell, J. Fish Biol; 4 (4) (1972) 469–486.

EVNIRONMENTAL PERFORMANCE CLASSIFICATION OF BALKAN COUNTRIES BASED ON TOPSIS-SORT METHODOLOGY

Aleksandra Radić[1*], Danijela Voza[1], Đorđe Nikolić[1], Milovan Vuković[1]
[1]University of Belgrade, Technical Faculty in Bor, V.J. 12, 19210 Bor, SERBIA
[*]*aradic@tfbor.bg.ac.rs*

Abstract

This paper analyzes the values of the Environmental Performance Index (EPI) in 2020 for the Balkan countries. The aim of the research is to use the TOPSIS-Sort methodology, based on a sample of ten countries, in order to classify them into those with acceptable (Class 1) and those with less acceptable (Class 2) EPI values in the field of environmental policy. A sorting procedure has been realized in relation to the reference value determined in accordance with the data of countries. In addition, a sensitivity analysis was performed by changing the benchmark used to classify countries. The results of the conducted analyzes show that under strict criteria for the formation of Class 1, no country can be classified in the class of belonging. Only during the conducted sensitivity analysis and less strict formation of Class 1 do the countries join the belonging class. Greece and Slovenia are the first to be classified in Class 1.

Keywords: EPI, TOPSIS, environmental performance, sensitivity analysis, Balkan countries

INTRODUCTION

Environmental protection is an imperative of the modern age. In this regard, there is a need to develop and improve the environmental index in order to facilitate environmental decision-making [1]. Modern methods of monitoring performance in the field of environmental protection strive to obtain qualitative and quantitative data, which will direct decision-makers to the weaknesses of the monitoring and environmental protection system. One such metric is the Environmental Performance Index (EPI).

The EPI aims to quantify the key outcomes of the implemented environmental policy [2]. This index has been used since 2006, when it was developed by the World Economic Forum, Yale University and Columbia University [3]. The most recent data on the values of EPI are from 2020. The report on the EPI index for 2020 provides a summary of the state of sustainability around the world based on measured data, using 32 indicators classified into 11 categories [4].

A review of the literature indicates that the researchers' efforts to date have focused on processing the EPI index using multicriteria decision-making methods (MCDM). In 2012 Ismail and Abdullah proposed the Analytical Hierarchy Process (AHP) methodology for ranking the environmental performance of Southeast Asian countries. Subjecting to this methodology the EPI values of certain countries, the authors came to the conclusion that different weights of criteria, obtained by applying the Satie scale, led to a different ranking of countries according to the value of this index [5].

In 2017 Abdullah ranked Southeast Asia countries using the fuzzy Technique for Order of Preference by Similarity to Ideal Solution (TOPSIS), considering eleven countries (as alternatives) and ten environmental policy areas (as criteria), determining the weights of the criteria using the entropy method [6]. A similar study was conducted by Mohaghar *et al.* in 2019, when they used the TOPSIS method to rank OECD Countries according to the value of the EPI index from the 2016 report, according to nine environmental policy areas. The weights of the criteria were also determined using the entropy method [7].

On the other hand, Digkoglou and Papathanasiou used the Preference Ranking Organization Method for Enriched Evaluation (PROMETHEE) to rank 28 European Union countries based on two criteria (Environmental Health and Ecosystem Vitality) for the period 2006–2018, using the same weight of criteria [8].

The weights of the criteria used to determine the final EPI rank of countries have also been analyzed and it has been noted that additional attention should be paid to the process of determining the importance of indicators [9]. On the other hand, the author Pinar analysed the weights of the criteria (indicators) used to generate the EPI score and gave his critical view of how important the criterion should be, based on the analysis of stochastic dominance [10]. This points to the need for a more consistent determination of the importance of the criteria used to rank countries based on EPI index values.

Having in mind the above, it can be concluded that MCDM methods are applicable in the ranking of countries based on the value of environmental policy areas used by the EPI methodology. The aim of this research is to examine the possibility of applying another of this group of methods - TOPSIS-Sort methodology, for the purpose of classifying the Balkan countries according to their environmental performance.

MATERIALS AND METHODS

TOPSIS-Sort methodology

The following section gives a brief explanation of the proposed TOPSIS-Sort model. The sorting problem involves the assignment of a set of alternatives $A=\{a_1, a_2, \dots, a_m\}$ into K predefined ordered classes $C_1, C_2, \dots, C_K$ [11] by taking in the consideration conflict criteria $F=\{g_1,\dots,g_n\}$. For that purpose it can be used several MCDM methods including TOPSIS-Sort methodology. Algorithm details the TOPSIS-Sort procedure, adopted by Sabokbar *et al.* [12] in 2016. There are several steps according to this algorithm:

Step 1: Determine the Decision Matrix $X = [x_{i,j}]m\times n$

Step 2: Establish a Profile limit (*Pl*)

Step 3: Establish a new Decision Matrix $M=[Mi,j](m+1)\times n$ formed by the set of alternatives and aditional Profile limit.

Step 4: Normalize Decision Matrix M, by trasnforming it in to a form of matrix $R = [r_{i,j}](m+ 1)\times n$ by the equation:

$$r_{ij} = \frac{M_{ij}}{\max\limits_{1\le i\le (m+1)} M_{ij}} \tag{1}$$

where: $i=1, \ldots, (m+1); j=1, \ldots, n$

Step 5. Calculate the weighted nnomalized decision matrix $V = [v_{ij}]m\times n$:.

$$v_{ij} = w_j \cdot r_{ij}; i=1,2..., m+1; j=1,2,..., n \tag{2}$$

Where w_j represents weight of corresponding criterion Fj, and:

$$\sum_{j=1}^{n} w_j = 1; j=1,2,..., n \tag{3}$$

Step 6.: Determine the ideal (v^*) and anti-ideal (v^-) solutions.

$$v^* = [v_1^*, v_2^*, ..., v_n^*]; v_j^* \begin{cases} \max\limits_{1\le i\le m+1} v_j; g_j \in F^+; j=1,2,..., n \\ \min\limits_{1\le i\le m+1} v_j; g_j \in F^-; j=1,2,..., n \end{cases} \tag{4}$$

$$v^- = [v_1^-, v_2^-, ..., v_n^-]; v_j^- \begin{cases} \min\limits_{1\le i\le m+1} v_j; g_j \in F^+; j=1,2,..., n \\ \max\limits_{1\le i\le m+1} v_j; g_j \in F^-; j=1,2,..., n \end{cases} \tag{5}$$

Step 7.: Calculate the Euclidian distances of each alternative as well Profile limit (Pl) for the ideal and antiideal solutions.

$$d_{ai}^* = \sqrt{\sum_{j=1}^{n} (v_{ij} - v_j^*)^2}; i=1,2,..., m+1 \tag{6}$$

$$d_{ai}^- = \sqrt{\sum_{j=1}^{n} (v_{ij} - v_j^-)^2}; i=1,2,..., m+1 \tag{7}$$

Step 8.: Calculate the closeness coefficient Cl(a_i) of each alternative to the ideal solution based on the distances obtained in the previous Step 7.

$$Cl(a_i) = \frac{d_{ai}^-}{d_{ai}^* + d_{ai}^-}; i=1,2,..., m \tag{8}$$

Step 9: Calculate the closeness coefficient Cl(Pl) of the Profile limit (Pl) to the ideal solution based on the distances obtained in the Step 7.

Step 10: Classify the alternatives a_i (i=1,2,...,m) into the Class 1 or Class 2 by performing comparisons between closeness coefficients Cl(a_i) and Cl(Pl), according to the following rules:

$$\begin{aligned} & a_i \in Class\_1 \quad iff \quad Cl(a_i) \ge Cl(Pl) \\ & or \\ & a_i \in Class\_2 \quad iff \quad Cl(a_i) < Cl(Pl) \\ & i=1,2,...,m \end{aligned} \tag{9}$$

Research data

According to the 2020 report [4], the calculation of the EPI index is based on eleven indicators. However, in the case of the Balkan countries, there is a lack of certain data. In order to avoid the risk of making insufficiently reliable conclusions, the authors excluded two criteria from the further analysis (Waste Management and Fisheries), in which are significant number of missing values. The final data set consisted of the values of nine categories of environmental performance (Air Quality, Sanitation and Drinking Water, Heavy Metals, Biodiversity, Ecosystem Services, Climate Change, Pollution Emissions, Agriculture and Water Resources) for ten countries (Albania, Bosnia and Herzegovina, Bulgaria, Croatia, Greece, Montenegro, Northern Macedonia, Romania, Serbia and Slovenia) located on the Balkan Peninsula. In the next step, all the considered criteria were given equal weight. Table 1 shows the initial decision matrix, which includes the EPI index values for the Balkan countries evaluated in 2020.

Table 1 *The EPI index values for Balkan countries in 2020*

	Air Quality	***Sanitation and Drinking Water***	***Heavy Metals***	***Biodiversity***	***Ecosystem Services***	***Climate Change***	***Pollution Emissions***	***Agriculture***	***Water Resources***
Albania	41.2	54	46.1	68.2	43.2	56.8	100	37.6	2.7
B&H	31.6	61.4	42.9	32.9	53.4	57.5	78.1	25.1	1.1
Bulgaria	33	68.3	45.8	77.7	41.4	69.5	100	63.6	13.9
Croatia	50.8	70.2	75.1	82.6	40.3	70	90.8	65.4	51.7
Greece	67.5	98.2	69.4	72.6	43.9	66.5	78.9	52.6	81.7
Montenegro	33.9	65.6	65.2	36.6	44.3	65.5	85.2	19.2	8.4
N. Macedonia	26.5	61.1	46.7	62.1	42.3	75.2	100	40.9	0.9
Romania	43.6	55.9	51.4	85	40.9	84.6	100	65.7	30.4
Serbia	33.6	65.5	51.1	57.54	45.8	68.1	89	69.9	1.7
Slovenia	60.9	74.7	88.1	86.4	37.1	75.2	90	47	89.1
Pl (Profile Limit)	51.1	80.52	70.02	65	46.88	73.48	91.24	49.62	53.82
wj	**0.11**	**0.11**	**0.11**	**0.11**	**0.11**	**0.11**	**0.11**	**0.11**	**0.11**

Data for the virtual alternative Pl (*Profile Limit*) were obtained according to formula 10, and in Table 1 the values for *c* = 40% are shown. The value of the Profile limit alternative was subjected to sensitivity analysis by changing the coefficient *c* (%).

$$Pl_j = \begin{cases} \max\limits_j X_{ij} - (\max\limits_j X_{ij} - \min\limits_j X_{ij}) \cdot c[\%];\ g_j \in F^+; i = 1,2,..., m; j = 1,2,..., n \\ \min\limits_j X_{ij} + (\max\limits_j X_{ij} - \min\limits_j X_{ij}) \cdot c[\%];\ g_j \in F^-; i = 1,2,..., m; j = 1,2,..., n \end{cases} \tag{10}$$

RESULTS AND DISCUSSION

The results obtained by processing the data using the TOPSIS-Sort method and conducting sensitivity analysis are shown in Table 2. For each individual case of change in the value of the coefficient *c* (%) the country belongs to Class 1 (C1 - countries with favourable EPI indexes) or Class 2 (C2 - countries with non-favourable EPI indexes).

Table 2 *TOPSIS-Sort results with sensitivity analysis*

Countries	*c=10%*		*c=20%*		*c=30%*		*c=40%*		*c=50%*		*c=60%*		*c=70%*		*c=80%*		*c=90%*	
	C_1	C_2	C_1	C_2	C_1	C_2	C_1	C_2	C_1	C_2	C_1	C_2	C_1	C_2	C_1	C_2	C_1	C_2
Albania		✓		✓		✓		✓		✓		✓		✓	✓		✓	
B&H		✓		✓		✓		✓		✓		✓		✓		✓	✓	
Bulgaria		✓		✓		✓		✓		✓		✓	✓		✓		✓	
Croatia		✓		✓		✓	✓		✓		✓		✓		✓		✓	
Greece		✓		✓	✓		✓		✓		✓		✓		✓		✓	
Montenegro		✓		✓		✓		✓		✓		✓		✓		✓	✓	
N. Macedonia		✓		✓		✓		✓		✓		✓		✓	✓		✓	
Romania		✓		✓		✓		✓		✓	✓		✓		✓		✓	
Serbia		✓		✓		✓		✓		✓		✓	✓		✓		✓	
Slovenia		✓		✓	✓		✓		✓		✓		✓		✓		✓	

The results of the research showed that, in the case of strict definition of Class 1 (c = 10% and c = 20%), no country has been characterized by a sufficiently high level of environmental performance that would classify them in the Class 1. Only when the value of c = 30% is adopted, Class 1 is formed, to which Greece and Slovenia belong. This leads to the conclusion that these two countries have the most satisfactory values of environmental performance indicators compared to other countries analysed.

With the lowering of the criteria for the formation of Class 1, an increasing number of countries are joining it. Thus, in the cases of c = 40% and c = 50% in Class 1, Croatia has been additionally classified. Considering the results, it can also be seen that at c = 70% a significantly larger number of countries are assigned to Class 1 countries. However, this case is extreme, and cannot be taken as a reliable criterion.

CONCLUSION

This paper analyses the data on the Environmental Performance Index (EPI) according to the latest available Report on EPI values for 2020. The TOPSIS-Sort method was used in order to classify the Balkan countries in the class of favourable and the class of non-favourable in relation to their EPI index values. Consequently, the applicability of this method on the considered data set has been proven.

It has been determined that countries with a strict definition of Class 1 cannot be classified as favourable related to the EPI index, i.e. those with better environmental performance. According to the conducted sensitivity analysis within this study, the countries that were firstly classified into Class 1 are Greece and Slovenia, and those that were lastly classified in Class 1 are B&H and Montenegro. This shows that Greece and Slovenia are the Balkan countries that have the best environmental performance in the observed sample of 10 countries, while B&H and Montenegro are countries with a very low level of environmental performance.

With the exception of Slovenia and Greece, which are ranked 18th and 25th in the EPI methodology's ranking of 180 nations in 2020, the remaining analysed countries cannot boast of environmental protection or high environmental performance. On this basis, it can be concluded that the majority of Balkan Peninsula countries need to engage much more effort in order to improve environmental conditions.

ACKNOWLEDGMENT

The research presented in this paper was done with the financial support of the Ministry of Education. Science and Technological Development of the Republic of Serbia, within the funding of the scientific research work at the University of Belgrade, Technical Faculty in Bor according to the contract with registration number 451-03-68/2022-14/200131.

REFERENCES

[1] J. Munksgaarda, L.B. Christoffersend, H. Keidingb, *et al.*, Ecol. Econ; 64 (2007) 119–130.

[2] A. Otoui, G. Grădinaru, Ecol. Indic; 93 (2018) 1209–1221.

[3] I.G. Breabăn, A. Bănică, A. Sandu, Reporting for sustainability; (2013) 275–281.

[4] Z.A. Wendling, J.W. Emerson, A. de Sherbinin, *et al.*, (2020) Environmental Performance Index, New Haven, CT: Yale Center for Environmental Law & Policy, *Available on the following link:* https://epi.yale.edu/

[5] W.K.W. Ismail, L. Abdullah, Environ. Skep. Crit; 1 (3) (2012) 39–47.

[6] L. Abdullah, WSEAS Trans. Environ. Dev; 13 (2017) 349–359, *Available on the following link:* https://www.wseas.org

[7] A. Mohaghar, M. Azani, R. Ghasemi, International Conference on Law, Management, Business, Economics and CSR, Dubai (2018).

[8] P. Digkoglou, J. Papathanasiou, Int. J. Sustain. Agric. Manag. Inform; 4 (2018) 290–305.

[9] M.J. Bellenger, A.T. Herlihy, Ecol. Econ; 69 (2010) 1043–1050.

[10] M. Pinar, J. Environ. Manage; 310 (2022) 1–15.

[11] H.F. Sabokbar, A. Hosseini, A. Banaitis, *et al.*, Business Administration and Management; 19 (2) (2016) 87–103.

[12] D. De Lima Silva, F. Teixeira, A. Filho, Comput. Ind. Eng; 141 (2020) 1–15.

CITIZEN PARTICIPATION OFFERS LESSONS TO CLIMATE CHANGE MANAGEMENT

Marijana Pantić[1*], Tamara Maričić[1], Saša Milijić[1]

[1]Institute of Architecture and Urban & Spatial Planning of Serbia, Bulevar kralja Aleksandra 73/II, 11000 Belgrade, SERBIA

[*]*marijana.d.pantic@gmail.com*

Abstract

The paper presents some lessons learned from the view and experience of the local population on climate change impacts. A survey among the rural population in Serbia measured their awareness, impact of climate change, and actions applied against it. The results indicated that respondents recognize the role of human activities in climate change; TV and the internet are primary information sources; the distinction between adaptation and mitigation is unclear; whereas droughts, floods, and hail are the most frequent manifestations of climate change in rural Serbia. In conclusion, further awareness of climate change details should be channeled through TV and the internet as the most popular sources of information, especially regarding the unclear difference between adaptation and mitigation. Future financial measures should address repairmen of the damages caused by the most common issues.

Keywords: climate change, spatial planning, survey, participative approach, Serbia

INTRODUCTION

It was the end of the 19th century when Svante Arrhenius, a Swedish researcher, brought up the idea that the use of fossil fuels adds CO_2 to the atmosphere thus altering some parameters of climate conditions [1]. In the 1950s researchers started to test the hypothesis with technically improved methods [2] when monitoring showed a constant rising in CO_2 concentration and temperature [3].

In 1988, the World Meteorological Organization established the Intergovernmental Panel on Climate Change (IPCC) for following climate change trends and scientific research. Since then, it is vigorously involved in the preparation of climate change assessment reports to keep up a transparent insight for the governments worldwide. Following IPCC efforts, the United Nations proclaimed "urgent action to combat climate change and its impacts" as one of the sustainable development goals in 2015 [3]. To show awareness of climate change issues and put solutions into practice, 175 parties adopted the Paris Agreement at the Conference of Parties (COP21) in Paris in 2015 [3].

According to the latest IPCC report [4], Serbia records, similarly to other European countries, a decrease in the number of cold days and nights and an increase in the number of warm days and nights. The most extreme increase in hot weather events is expected in central and south-eastern Europe, where Serbia is located. This is associated with the increased expectance of drought [5], which will probably increase the mortality and morbidity of populations [4]. The Second Report of the Republic of Serbia towards the UN Framework Convention on Climate Change – Climate Change Chapter Summary [6] states that the future will most likely bring an increase in precipitation until 2040, followed by a decrease. The estimations and general agreement address these changes as very likely the consequences of human activity that doubles the occurrence probability [4].

In the past decades, the involvement of the local population and other stakeholders has become a requirement [7]. A wide range of authors confirms the necessity of the participatory approach and collaboration with stokeholds to holistically address climate change challenges [8,9]. Acquaintance with local observations and traditional knowledge secures more efficient measures [8].

The climate change impact in urban areas is larger as a greater number of people is exposed, where the damage on public infra- and suprastructure or private property can be repaired. In contrast, the majority of the rural population is disadvantaged both by damaged infrastructure, buildings, and also crops that are the main source of the rural economy [10]. Their crops rely on the availability of rainwater, whereas droughts, floods, and fires harm crop productivity [5,11], causing soil salinization in drier areas [10], fluctuation of livestock [5], and ultimately the overall rural economy. This makes rural communities particularly vulnerable [4,10,11]. Additionally, the rural population is usually exposed to a higher level of poverty, remoteness, and information accessibility, and is frequently left out of the decision-making process [4].

MATERIALS AND METHODS

The main research question is: what can be learned from the citizens' perspective on climate change. Assuming that insight into citizens' views on and experiences with climate change indicate massages that can be integrated into climate change management, an individual perspective (usually easily omitted) was analyzed. The data was collected in a survey filled out by 37 persons as representatives of their households in rural areas. A criterion for respondents was to inhabit rural areas or hold an actively used agricultural plot. The respondents came from villages in Aranđelovac, Arilje, Brđani, Brus, Čačak, Gornji Milanovac, Kraljevo, Krupanj, Lajkovac, Loznica, Ljubovija, Nova Varoš, Obrenovac, Prijepolje, Raška, Smederevo, Smederevska Palanka, Sopot, Topola, Užice, and Valjevo local administrative units.

The survey was conducted between 14th August and 12th September 2018. Means of questionnaire dissemination and collection of answers were the internet and telephone. The questionnaire included thirteen questions divided into four sections. The first section offered questions on personal attitudes and experiences regarding climate change understanding, occurrence, and consequences (five questions). The second section was about climate change measures (three questions), third was focused on sources of information and knowledge on climate change (two questions). Finally, the fourth section was oriented toward future actions (three questions). All were multiple-choice questions, except for questions about measures, which were open-ended questions.

RESULTS AND DISCUSSION

Some authors criticize the focus on CO_2 reduction and advocate other GHG (e.g. water vapor) as more significant for climate change mitigation [12]. However, the sample analyzed here has shown a strong inclination towards the mainstream attitude and complies with a vast of scientific sources (e.g. [13,14]) and efforts of the IPCC.

More than half of respondents (54%) believe that the human factor has an impact on climate change to a certain extent. The second-largest group (40%) is more convinced by accepting the impact without a doubt. Only 3% stated that they do not know and another 3% does not agree to a certain extent, while no respondent disagreed.

The majority of the citizens think that the human factor has a stronger impact than natural events or that the human factor equally causes climate change as natural variability (Figure 1). In contrast, no respondent expressed that natural processes are the only factor for climate change. The greatest share of citizens reported drought and flood as a result of extreme weather conditions and the most common problem related to climate change. Landslides appear to be rather location-specific and dependent on the type of soil and geomorphology of the terrain. Interestingly, only a few respondents noted premature snow melting as a noticeable issue.

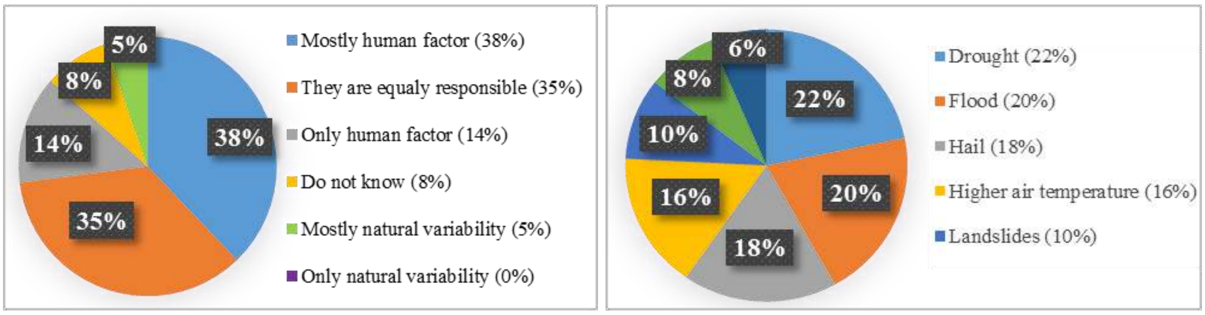


Figure 1 *Responsibility factors and the most common climate change impacts*

Similarly, the citizens selected floods and then drought and hail as the main problems in the climate change domain. More than a half fewer citizens are stressed by higher air temperature, landslides, and weather extremes, thus leaving premature snow melting as the least significant impact on their households. Some of the IPCC reports also stress the particular issue of water [15], which is the issue on which respondents of the survey comply. For the majority of respondents, the least influential impact comes from the premature melting of snow. This concern is in contrast to the efforts of Alpine countries to socio-economically adapt to climate change – looking for a solution to prevent avalanches or prolong the skiing season [16]. The reason behind this might be the fact that the majority of households in rural Serbia still prevailingly depend on agriculture instead of tourism. Therefore, they do not notice premature snow melting as a particular threat to their economy or health.

When estimating material damage to households caused by climate change in the last five years, a significant majority of the respondents indicated that the consequences are noticeable (Figure 2). The share of respondents decreases with the decrease of impact.

The respondents were asked how they inform themselves about climate change mitigation and adaptation measures. The most significant sources turned out to be TV (78%), internet (70%), and daily newspapers (41%). About 1/3 of respondents get informed from communicating with their neighbors and friends (32%). Respondents who inform themselves from only one source are informed on the Internet (16%). Besides, a bit more than a fifth of the citizens (22%) rely on more than three sources to get informed about climate change. Radio (16%), locally organized seminars (11%), and the formal education system (11%) were not reported as significant sources of information. As expected, professional/scientific conferences have shown to be the least relevant (3%). Citizens indicated that professional organizations (43%) are considered the most relevant in their informativeness on climate change. Certain relevance was given to scientific organizations (22%) and local self-government (19%). An insignificant role was given to the state government activities (8%) and international non-governmental organizations (NGOs) (5%), whereas the least relevant are national and local NGOs (3%).

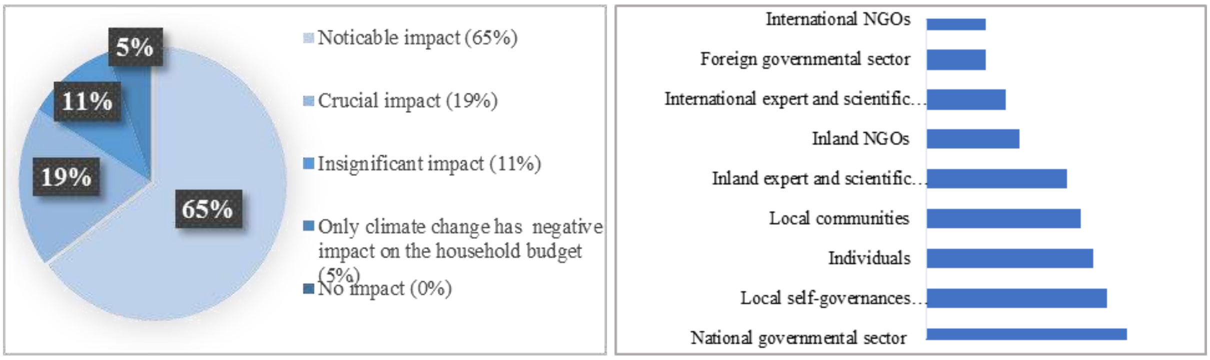


Figure 2 *Climate change impact on the household budget and the leading stakeholders in combating climate change*

In the eyes of the respondents, the national governmental sector (81%), local self-governance (73%), and individual actions and behavior (68%) are the top leaders in the future combat climate change (Figure 2). In contrast, foreign bodies (international NGOs and foreign governmental sector) are seen as the least relevant. Regarding agility to engage themselves in the activities for climate change prevention, about half of the respondents (51%) stated that they are ready to get engaged but not as initiators. About one-fourth expressed a strong possibility for engagement (24%) and 14% are even ready to initiate an action. No citizen declined potential participation, although 5% stated that they most probably would not find themselves engaged.

The citizens were asked about adaptation and mitigation measures in two separate questions, but it was obvious from their answers that they did not make a clear distinction. Therefore, their answers were analyzed without insisting on the difference. The lowest share of respondents (3%) listed measures such as reparation of buildings after a flood, use of nets against the sun, rising awareness of environmental protection and active engagement (e.g. reduction of GHG), plans for the case of flooding/draught, and crops and harvest insurance for registered agricultural holdings. On the one hand, 8% of respondents stated that there is no measure of climate change protection and adaptation in their municipality/city, while another 8% listed some sort of phyto-measures (e.g. specific crop distribution, the specific timing of sowing, and cropping). Between 10% and 20% of citizens listed afforestation, forest-cutting control, and landslide recovery. The most significant number of responses addressed water regulation measures on agricultural land (22%), and some sort of river bed regulation (41%).

Out of all listed measures, the anti-hail system and regulation of river bed is the most common answer when it comes to the adaptation and mitigation measures that the citizens are aware of as implemented measures in their community. Among water regulation measures on agricultural land, respondents listed drainage (25%), channels (25%), and irrigation (75%). Those who addressed anti-hail measures mainly referred to state anti-hail stations (80%), while the smallest portion addressed private systems such as anti-hail netting of orchards or vegetable plantations (21%). A quarter of correspondents also underlined that anti-hail stations exist, but they do not function properly or they are not in operation due to the lack of staff or equipment.

CONCLUSION

The most common aspect of climate change impact in rural Serbia are floods, droughts, and hail. Some of the difficulties that will remain in the future are financial support in the implementation of climate change measures and regulations that might be costly, both for governments (due to a large number of users) and citizens (that already encounter financial shortages caused by climate change). However, climate change impacts can be mitigated by the improvement of the existing spatial, sectoral (e.g. flood or heatwave risk management plans), and urban planning practices (local authorities may define climate-resilience standards for existing and future buildings, promote green and blue spaces in the local development plan and investments in technical equipment and strategic, construction, organizational, financial, and legislative adaptation and mitigation measures against hail, floods, fire, etc.

As the government is the main responsible for future activities related to climate change, TV and the Internet (recognized as the main sources of information about climate change) should be used as the main communication channels in this regard. This can also improve the weak distinction of citizens regarding climate change adaptation and mitigation measures. Support that citizens expect from local or state governments also involves financial compensation or reimbursement. Therefore, some changes in economic incentives and support should be introduced and specifically aimed at climate change consequences and unloading the financial burden of the households.

All respondents have encountered at least one of the consequences that can be related to climate change, whereas none of them has declared to be free of material damage that can be related to climate change. This indicates that the consequences of climate change are broadly present and noticeable, so efficient measures from the state and local levels are required.

ACKNOWLEDGEMENT

This research was supported by the Ministry of Education, Science and Technological Development of the Republic of Serbia (Grant No. 451-03-68/2022-14/200006).

REFERENCES

[1] E. Crawford, Arrhenius: From Ionic Theory to the Greenhouse Effect, Watson Publishing – Science History, Canton, MA. (1996), p.320, ISBN: 978-0881351668.

[2] J.R. Fleming, The Callendar Effect, The Life and Work of Guy Stewart Callendar (1898–1964), the Scientist Who Established the Carbon Dioxide Theory of Climate Change, American Meteorological Society, Boston, MA (2007), p.176, ISBN: 978-1878220769.

[3] United Nations, Sustainable Development Goals – Goal 13: take urgent action to combat climate change and its impacts, *Available on the following link*: www.un.org/sustainabledevelopment/climate-change/

[4] Intergovernmental Panel on Climate Change, Climate Change 2022: Impacts, Adaptation and Vulnerability – Summary for Policymakers, *Available on the following link*: www.ipcc.ch/report/ar6/wg2/downloads/report/IPCC_AR6_WGII_FinalDraft_FullReport.pdf

[5] Intergovernmental Panel on Climate Change, Global Warming of 1.5°C, *Available on the following link*: www.ipcc.ch/site/assets/uploads/sites/2/2019/06/SR15_Full_Report_High_Res.pdf

[6] UNDP, Rezime poglavlja promene klime, pogođenost i adaptacija Drugog izveštaja R. Srbije prema Okvirnoj konvenciji UN o promeni klime, *Available on the following link*: www.klimatskepromene.rs/wp-content/uploads/2017/04/SNC_VA_rezime.pdf

[7] S.M. Wheeler, Planning for Sustainability: Creating Livable, Equitable and Ecological Communities, Routledge, Milton Park, Oxon (2004), p.424, ISBN: 9780415809894.

[8] R. Swart, A.G.J. Sedee, F. de Pater, *et al.*, J. Environ. Policy Plan; 16 (1) (2014) 55–74.

[9] H. Shalaby, S. Aboelnaga, Proceedings of the 1st International Conference on Towards a Better Quality of Life, 24–26 November, El Gouna, Egypt (2017) 1–13.

[10] L.M. Hunter, Climate Change, Rural Vulnerabilities, and Migration, *Available on the following link*: www.prb.org/climatechangeinruralareas/

[11] European Landowners' Organization (ELO) (2015), Climate Change and the Rural Economy – Managing Land in the Face of Climate Change, *Available on the following link*: www.europeanlandowners.org/multimedia/publications/2015

[12] O. Halidullin, Am. J. Biomed. Sci; 1 (3) (2019) 122–123.

[13] A.P.K. Tai, M. Val Martin, C.L. Heald, Nat. Clim. Change; 4 (2014) 817–821.

[14] G.T. Pecl, M.B. Araújo, J.D. Bell, *et al.*, Science; 355 (2017) 6332.

[15] B.C. Bates, Z.W. Kundzewicz, S. Wu, *et al.*, Climate Change and Water. Technical Paper of the Intergovernmental Panel on Climate Change, IPCC Secretariat, Geneva (2008), p.210, ISBN: 978-92-9169-123-4.

[16] S. Agrawala, Climate Change in the European Alps – Adapting Winter Tourism and Natural Hazards Management, OECD, Berlin (2007), p.131, ISBN: 9789264031692.

INVESTIGATION OF ZrO_2 AND ZrO_2/TiO_2 ELECTRODES BY CYCLIC VOLTAMMETRY

Tanja Brdarić[1], Danka Aćimović[1], Branislava Savić[1*], Nadica Abazović[3],
Mirjana Čomor[3], Marija Ječmenica Dučić[1], Danijela Maksin[2]

[1]University of Belgrade, VINČA Institute of Nuclear Sciences – National Institute of the Republic of Serbia, Department of Physical Chemistry, Mike Petrovića Alasa 12–14,
11000 Belgrade, SERBIA

[2]University of Belgrade, VINČA Institute of Nuclear Sciences – National Institute of the Republic of Serbia, Department of Chemical Dynamics & Permanent Education,
Mike Petrovića Alasa 12–14, 11000 Belgrade, SERBIA

[3]University of Belgrade, VINČA Institute of Nuclear Sciences – National Institute of the Republic of Serbia, Department of Radiation Chemistry and Physics,
Mike Petrovića Alasa 12–14, 11000 Belgrade, SERBIA

[*]*branislava@vin.bg.ac.rs*

Abstract

The subject of this study were electrochemical characteristics of transition metal oxide electrodes, consisting specifically of ZrO_2 *and* TiO_2*, which have different crystallographic structure and lattice parameters. Metal oxides are a significant class of materials which have found vast applications in electrocatalysis. Composites of diverse semiconductors typically display much enhanced electronic conductivity and decreased charge transfer resistance. The goal of this study was to hopefully prepare and investigate electrodes with improved properties, through combination of heterostructures of chemically and structurally dissimilar and wide-bandgap semiconductors. Electroactive surface area was determined by employing cyclic voltammetry peak current method.*

Keywords: electroactive surface area, zirconium oxide, titanium oxide, Randles-Sevcik equation

INTRODUCTION

Transition metal oxides are an important class of materials displaying multifunctionality and uniqueness. They have received a great deal of attention during the last decade, for the purpose of applications in microelectronic and optoelectronic devices [1] such as dye senzitized solar cells [2,3] in electrocatalysis [4,5] electrochemical cells [1] etc. owing to their stability in all pHs, ease of synthesis, and environmental friendliness.

It is also important to select metal/metal oxide couple with necessary chemical stability and sensitivity in the pH ranges of interest under extreme conditions [6]. Catalytic activity of transition metal oxides is usually compromised by their low in-plane conductivity and high charge transfer resistance, primarily affected by large bandgap. However, new electronic states at the interface of two chemically and structurally dissimilar metal oxide heterostructures can be created, which enable the charge movement across the metal oxide/electrolyte interface and can bring down the work function of the composite material [7]. The contrast in oxygen coordination of Zr and Ti cations in the composite metal oxide heterostructure, can bring about the existence of new acid active sites.

The aspect of in-plane conductivity of the catalyst was shown to be a major factor in electrocatalysis. It can be uplifted upon creating oxygen vacancies on the framework in metal oxides. Oxygen vacancies leave behind the excess of electrons, which occupy the empty 3d orbitals of the transition metal oxide, just below the conduction band. In addition, the interphase between two dissimilar metal oxide phases is expected to contain newly formed electronic states, which can alter the charge transfer kinetics in the composite [7].

When ZrO_2 is incorporated into TiO_2 matrix, huge changes were imparted in its electronic states. The new surface states formed near the valence band edge. The negative charge sites (Brönsted sites) generated after ZrO_2 incorporation in TiO_2 matrix were found to attract the protons to keep the electroneutrality of the structure intact [6].

It was reported in the literature that dye senzitized solar cells, fabricated by ZrO_2/TiO_2 mixed oxide electrode, which are gaining popularity, considerably enhanced solar energy conversion efficiency in comparison with a cell that was manufactured only by pure component of TiO_2, to which more than likely contributed the fact that mixed oxide powder has a larger BET surface area than pure TiO_2 [2]. Many other properties of the nanostructure mixed metal oxides were reported better than TiO_2 [3].

The aim of this paper was to investigate the effect of TiO_2 introduced to the oxide layer of ZrO_2/TiO_2 electrodes on electrochemical behaviour as well as the electroactive surface area of these electrodes.

MATERIALS AND METHODS

Cyclic voltammetry measurements of electroactive surface area were conducted in the following fashion. A three-electrode electrochemical cell was utilized for measuring the electroactive surface area of the porous specimens. Ag/AgCl reference electrode and a Pt foil as counter electrode were used, while the ZrO_2 or ZrO_2/TiO_2 (75:25) [8] specimens served as the working electrode. The electrolyte was 5 mM $K_4Fe(CN)_6$ in 0.1 M KOH solution (all chemicals from Sigma Aldrich without further purification). The oxidation reaction of ferrocyanide on the working electrode surface is:

$$[Fe(CN)_6]^{4-} \xrightarrow{oxidation} [Fe(CN)_6]^{3-} \tag{1}$$

This reaction is governed by the diffusion of ferrocyanide ions and has a good reversibility. One of the reliable indicators that cyclovoltammogram provides that indicate that the observed process is reversible is that the peak current is proportional to the square root of the scan rate i. e. reversible processes show a $v^{1/2}$-dependence of their current peaks according to the Randles-Sevcik equation. Therefore, the peak current is proportional to the electroactive surface area of the working electrode [9]:

$$I_p = (2.69 \cdot 10^5) n^{3/2} A D_0^{1/2} v^{1/2} c \tag{2}$$

where I_p (A) is the peak current, n is the number of electrons transferred in the redox reaction (n =1 here), A (cm^2) is the electroactive surface area, D (cm^2/s) is the diffusion coefficient for

$K_3[Fe(CN)_6]$ is $7.6 \cdot 10^{-6}$ cm^2 s^{-1}) [10], c (mol/cm^3) is the concentration of the reaction species in the electrolyte ($[Fe(CN)_6]_4$ here) and v (V/s) is the scan rate.

The electroactive surface area measured by the CV peak current method is expected to reflect the Nernst diffusion layer thickness [11].

The diffusion layer thickness can be adjusted by varying the scan rate: at slow scan rates, the diffusion layer is thick, while at faster scan rates the diffusion layer is thinner. Since the electrochemical process reflects the competition between the electrode reaction and the diffusion, faster scan rates will favor electrochemical irreversibility [12].

RESULTS AND DISCUSSION

The I_p vs $v^{1/2}$ curves are linear as reflected in the values of the coefficients of determination. The Randles' slopes would be nonlinear if the redox reactions were either quasi-reversible or irreversible [12].

As can be seen in Figure 1, there are no remarkle differences between the cyclic voltammograms asquired for ZrO_2 and ZrO_2/TiO_2 samples.

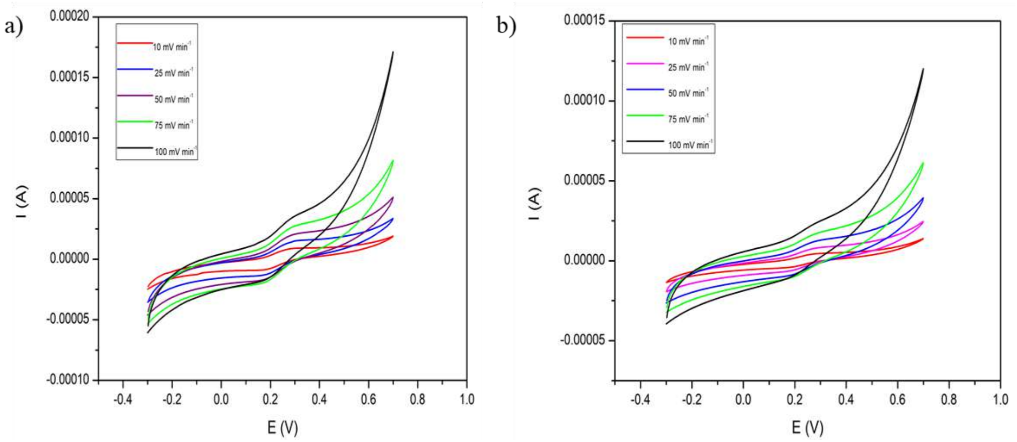


Figure 1 *Cyclic voltammograms at a) ZrO_2 and b) ZrO_2/TiO_2 working electrodes at various scan rates (10-100 mV min^{-1})*

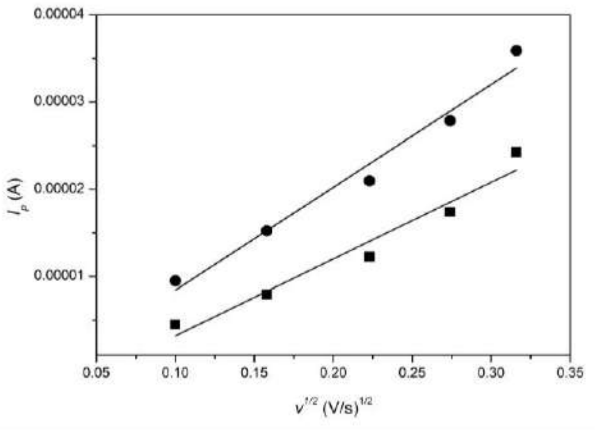


Figure 2 *Randles-Sevick fit for ZrO_2 (black circles) and ZrO_2/TiO_2 (black squares) working electrodes*

Randles-Sevick fit for ZrO_2 (black circles) and ZrO_2/TiO_2 (black squares) working electrodes and data calculated from Randles-Sevcik plots are presented in Figure 2 and Table 1. The results show a decrease in the calculated surface area, with the introduction of TiO_2.

Table 1 *Reduction of the calculated surface area, with the introduction of* TiO_2

Working electrode	**Randles slope (A/(V/s)$^{1/2}$)**	**Surface area (cm^2)**	**R^2**
ZrO_2	0.0001178	0.0318	0.96859
ZrO_2+TiO_2	0.00008803	0.0238	0.94264

CONCLUSION

It can be seen from the obtained results that the working electrode synthesized from ZrO_2/TiO_2 nanopowder mixture had a smaller electroactive surface area than the ZrO_2 working electrode, contrary to what was expected based on the available literature. At this point in time, the synthesis process should be reevaluated in order to achieve the desired outcome.

ACKNOWLEDGEMENT

This work was supported by the Ministry of Education, Science and Technological Development of Republic of Serbia; grant number 451-03-68/2022-14/200017.

REFERENCES

[1] R. Zhang, X. Zhang, S. Hu, Sens. Actuators, B; 149 (2010) 143–154.

[2] A. Kitiyanan, S. Yoshikawa, Mater. Lett; 59 (29) (2005) 4038–4040.

[3] A. Kitiyanan, S. Ngamsinlapasathian, S. Pavasupree, *et al.*, J. Solid State Chem; 178 (4) (2005) 1044–1048.

[4] K.P. Singh, C.-H. Shin, H.-Y. Lee, *et al.*, ACS Appl. Nano Mater; 3 (4) (2020) 3634–3645.

[5] M. Mazloum-Ardakania, H. Beitollahi, M.K. Amini, *et al.*, Sens. Actuators B; 151 (2010) 243–249.

[6] X.T. Zhang, R.H. Zhang, S.M. Hu, *et al.*, High Technol. Lett; 10 (2004) 360–363.

[7] K.P. Singh, C.-H. Shin, H.-Y. Lee, *et al.*, ACS Appl. Nano Mater; 3 (4) (2020) 3634–3645.

[8] M. Carević, N. Abazović, T. Savić *et al.*, J. Am. Ceram. Soc; 101 (4) (2018) 1420–1431.

[9] C. Brett, A.M. Oliveira Brett, Electrochemistry: Principles, Methods and Applications, Oxford University Press, Oxford (1993) p. 464, ISBN–10: 0198553889.

[10] R.E. Smith, T.J. Davies, N.de B. Baynes, *et al.*, J. Electroanal. Chem; 747 (2015) 29–38.

[11] P. Zhu, Y. Zhao, RSC Adv; 7 (2017) 26392–26400.

[12] N. Aristov, A. Habekost, World J. Chem. Educ; 3 (5) (2015) 115–119.

TESTING THE ELECTROCHEMICAL BEHAVIOR OF BPA ON GC, WO_3 AND MWCNT ELECTRODES

Branislava Savić[1*], Danka Aćimović[1], Tanja Brdarić[1], Miloš Ognjanović[2], Dragana Vasić Anićijević[1], Marija Ječmenica Dučić[1], Marija Simić[1]

[1]University of Belgrade, VINČA Institute of Nuclear Sciences – National Institute of the Republic of Serbia, Department of Physical Chemistry, Mike Petrovića Alasa 12–14, 11000 Belgrade, SERBIA

[2]University of Belgrade, VINČA Institute of Nuclear Sciences – National Institute of the Republic of Serbia, Department of Theoretical Physics and Condensed Matter Physics, Mike Petrovića Alasa 12–14, 11000 Belgrade, SERBIA

**branislava@vin.bg.ac.rs*

Abstract

Bisphenol A (BPA) is an organic compound used in large scale at the plastics industry and as a precursor in the synthesis of polycarbonates and epoxy resins, which lead to frequent detections of BPA in surface waters. Therefore, it is necessary to develop and improve methods for BPA detection and monitoring. The electrochemical behavior of Bisphenol A at WO_3 and carbon-based electrodes, like glassy carbon (GC) and multi-walled carbon nanotubes (MWCNT), were compared using cyclic voltammetry (CV). Therefore, WO_3 nanoparticles were obtained by hydrothermal method and characterization was done using XRDP. The results showed that the responses of the WO_3 electrode were 30 times larger compared to another examined electrode. This implies that WO_3 electrode can be useful for the detection BPA in nature media.

Keywords: BPA, GC, WO_3, MWCNT, electrochemical

INTRODUCTION

Bisphenol A or 2,2′-bis (4-hydroxyphenyl) propane is a well-known chemical that causes endocrine disruption and shows hormone-like properties [1].

It is one of the most commonly used chemicals for the synthesizing of polycarbonate and epoxy resins which have being used for food storage, packaging and drinking cans [2]. Japan, the U.S. Environmental Protection Agency (USEPA), the European Union and the World Wildlife Fund (IMF), placed BPA on the list of priority pollutants [3]. Many researchers have been exploring the efficiency of electrochemical oxidation of BPA on anode materials such Ti/BDD, Ti/Sb–SnO_2, Ti/RuO_2, Ti/SnO_2, Ti/PbO_2 and Ti/Pt [4].

Glassy carbon has widespread application due to their cheap, simple and diverse surface modification. GC is impermeable to gas, electrically conductive and chemically inert material. In analytical laboratory glass carbon is the most commonly used electrode based on carbon. Although GC electrodes have favorable electrochemical characteristics, GC surface modifications have been the subject of research due to the many potential improvements of electrodes caused by different electrochemical requirements [5].

Over the past decades, tungsten (VI) oxide (WO_3), has been used in solar energy conversion, photocatalysts, storage cells, solar water splitting cells, gas sensors, electrochromic and photochromic devices, secondary batteries, and others [2–10]. WO_3 is an important n-type semiconductor whose crystal structure is dependent on temperature [11] and cheap material with high stability in aqueous solutions in acidic conditions and it is not susceptible to photo corrosive processes [12]. WO_3 has received much attention because of its ability to absorb in the area of visible light.

Carbon nanotubes (CNTs) are hollow nanometer size tubes of graphitic carbon. The open structure of carbon nanotubes (CNTs) offers a large surface area, faster kinetics and higher adsorption capacity due to the easy and unobstructed access of pollutants to reactive sites and have a huge potential to replace activated carbon [13]. CNTs mainly can be divided into two types: single-walled carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes [14]. The multi-walled nanotubes can be described as a number of concentric SWCNTs having different diameters. Multi-walled carbon nanotubes are very durable; they have good capacities of conducting both thermal and electrical energy, and therefore it can be found in a wide number of applications.

To date no single study simultaneously studied and compared electrochemical properties of WO_3 and carbon-based electrodes. Also, previous studies have not investigated their application for detecting bisphenol A. In this work are compared the electrochemical behavior WO_3 and GC and MWCNT toward BPA. For this purpose, WO_3 nanoparticles were synthesized by hydrothermal method and characterized using XRDP. The electrochemical response characteristic for bisphenol A on different modified electrodes was investigated by cyclic voltammetry.

MATERIALS AND METHODS

Materials

The following chemicals were used for synthesis of nanosized WO_3: tungsten (VI) oxide nanopowder (<100 nm particle size) (Sigma Aldrich) and hydrogen peroxide (ZORKA Pharma). The experiments were performed with carbon nanotubes, multi-walled with particle size 7–15 nm x 3–6 nm x 0.5–200 µm (Sigma-Aldrich) and dimethylformamide (Sigma-Aldrich). For monitoring of electrochemical behavior of different electrodes bisphenol A (Sigma-Aldrich) in phosphate buffer (Merck) was chosen.

Synthesis nanomaterials

Synthesis of nanosized WO_3

WO_3 was synthesized using the procedure proposed by Zhongcheng *et al.* [15], with a small modification. WO_3 are produced by hydrothermal treatment of commercial WO_3 using H_2O_2. A common technique implies dissolving of 0.3 g commercial WO_3 powders into 11 mL of 30% H_2O_2 solution. Then, mixture was stirred at 30°C for 30 min using a magnetic stirrer. Afterwards, the obtained mixture was transferred into a stainless-steel autoclave and heated to 225°C for 12 h. Finally, the precipitate was filtrated, washed with deionized water and dried at 100°C overnight.

Electrode modification

Electrode modification was done following procedure proposed by Stanković *et al.* [16]. GC electrodes was polished by water, ethanol, acetone and dried for about 30 minutes. WO_3 was dispersed in dimethylformamide by sonication for 2 h and dripped on a clean GC electrode. The modified electrodes were dried out using infrared lamps for about twenty minutes. Using the above-described procedures, the glass carbon electrode was modified with commercial MWCNT.

Characterization methods

The crystal structure of the WO_3 were analyzed with X-ray powder diffraction (XRPD). The analysis was performed using a Smart Lab® X-ray diffractometer (Rigaku, Japan) with Cu Kα radiation ($\lambda = 0.1542$ nm). The data were collected in the 2θ range from 10° to 90° in steps of 0.02° and with an exposition of 2 s per step with a divergent slit of 0.5 mm, operated at 40 kV and 30 mA.

RESULTS AND DISCUSSION

XRPD

The crystalline nature of WO_3 was confirmed by XRPD studies. As can be seen in the Figure 1 the WO_3 show Bragg's diffractions at 2θ values 14.09°, 23.19°, 24.16°, 27.16°, 28.12°, 33.63° and 36.73° corresponding to the (100), (001), (110), (101), (200), (111) and (201) crystallographic planes of *P6/mmm* space group of hexagonal crystal system [17].

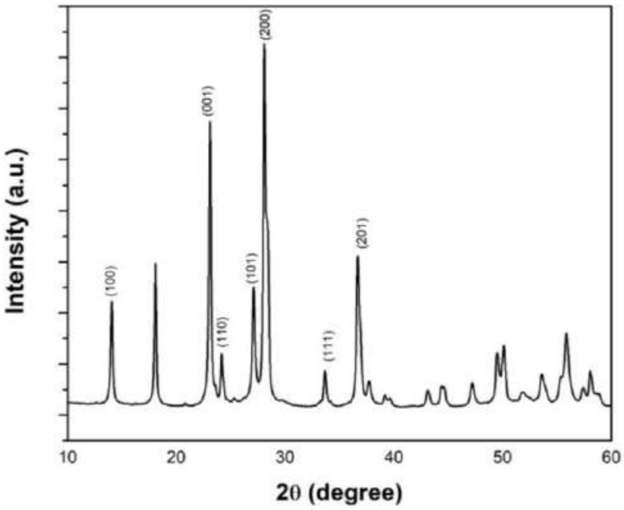


Figure 1 *XRPD pattern of* WO_3

The average crystal size of the WO_3 was determined using the XRPD patterns from peak at (2θ) at 28.12° via the well-known Debye-Scherrer equation (1):

$$D = k\lambda/\beta\cos\theta \tag{1}$$

where β is the width at half maximum intensity of the peak, θ Braggs diffraction angle, λ is the wavelength of X-ray source used in XRPD (Cu Kα radiation, 0.1542 nm) and k constant (0.89) and was found to be 27.4 nm.

Electrochemical behavior

To observe the electrochemical behavior of GC, GC/WO_3 and GC/MWCNT in presence of BPA, the cyclic voltammograms (CVs) of different electrodes were obtained in 0.1 M phosphate-buffered saline (PBS) containing 50.0 µmol L^{-1} of BPA (pH 6.0). Figure 2 includes CV of GC, GC/WO_3 and GC/MWCNT electrodes. Bare GC showed a very low irreversible oxidation peak at +0.71 V, suggesting a poor electrochemical behavior of BPA. At other electrodes, an enhanced oxidation peak and a negatively shifted potential (20 mV) were found. The significant improvement was observed in the current response and shape cyclic voltammograms. By contrast, peak current of GC/MWCNT and GC-WO_3 electrodes was exhibited as highly enhanced oxidation peak, indicating the favorable electrocatalytic oxidation. The strongest current response to BPA appeared at GC-WO_3 electrode. Its peak current ($I_{p,a}$) was about 3 and even 30 times bigger than GC/MWCNT and bare GC electrodes, respectively. The substantial increase of $I_{p,a}$ proved that the WO_3-GC electrode displayed a very good behavior to BPA and can be useful for highly sensitive detection of BPA. Also, the cyclic voltammograms of the GC/WO_3 electrode presented in Figure 2 have the rectangular shape typical for pseudo-capacitive behavior which is also characteristic of WO_3 base electrode [18].

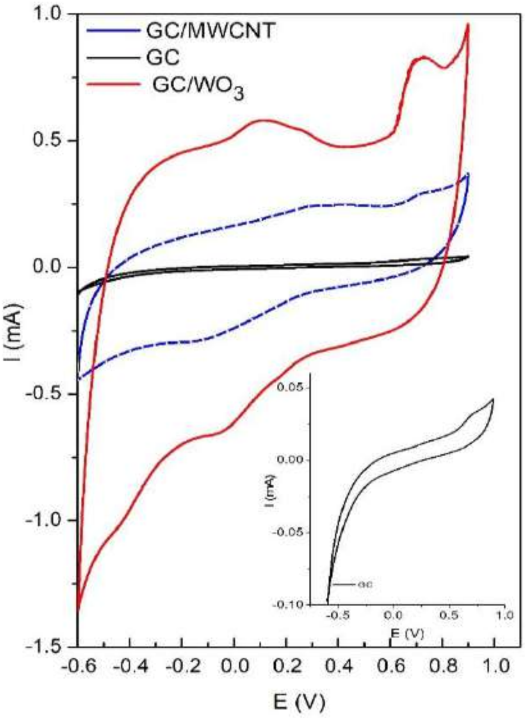


Figure 2 *Cyclic voltammograms of GC, GC/WO_3 and GC/MWCNT electrodes in 0.1 M PBS with 50.0 µmol L^{-1} of BPA at pH 6.0*

CONCLUSION

A previously synthesized nanoparticle of WO_3 proved to be the most efficient electrode for BPA compared to carbon-based electrodes. Therefore, these results provide a starting point for further investigations in the field of application of WO_3 nanocomposite anodes for the detection of BPA and various similar organic pollutants.

ACKNOWLEDGEMENT

This work was supported by the Ministry of Education, Science and Technological Development of Republic of Serbia; grant number 451-03-68/2022-14/200017.

REFERENCES

[1] N. Benachour, A. Aris, Toxicol. Appl. Pharmacol; 241 (3) (2009) 322–328.

[2] C. Liao, K. Kannan, Environ. Sci. Technol; 45 (21) (2011) 9372–9379.

[3] C. Zhu, C. Hu, J. Lu, Russ. J. Electrochem; 51 (4) (2015) 353–361.

[4] Y. Cui, X. Li, G. Chenc, Water Res; 43 (2009) 968–976.

[5] P. Hadiyan, A. Rouhollahi, M. Adibi, *et al.*, Int. J. Nanosci. Nanotechnol; 11 (1) (2015) 53–57.

[6] R. Huang, Y. Shen, L. Zhao, *et al.*, Adv. Powder Technol; 23 (2) (2012) 211–214.

[7] C.O. Avellaneda, L.O.S. Bulhões, Solid State Ion; 165 (1–4) (2003) 117–121.

[8] G.R. Bamwenda, H. Arakawa, Appl. Catal. A: Gen; 210 (1–2) (2001) 181–191.

[9] M. Sadakane, K. Sasaki, H. Kunioku *et al.*, Chem. Comm; (48) (2008) 6552–6554.

[10] S.S. Thind, M. Tian, A. Chen, Electrochem. Commun; 43 (2014) 13–17.

[11] M.G. Peleyeju, E.L. Viljoen, J. Water Process Eng; 40 (2021).

[12] D.B. Hernandez-Uresti, D. Sánchez-Martínez, A. Martínez-De La Cruz, *et al.*, Ceram. Int; 40 (2014) 4767–4775.

[13] H. Wang, H. Ma, W. Zheng *et al.*, ACS Appl. Mater. Interfaces; 6 (12) (2014) 9426–9434.

[14] S.N. Ahmad, S. Hakeem, R.A. Alvi, *et al.*, J. Phys. Conf. Ser; 439 (2013) 1–8.

[15] Z. Li, Y. Zhou, Qing Y. *et al.*, Mater. Lett; 236 (1) (2019) 197–200.

[16] D. Stanković, M. Ognjanović, A. Espinosa, *et al.*, Electrocatalysis; 10 (2019) 663–671.

[17] B. Gerand, G. Nowogrocki, J. Guenot, *et al.*, J. Solid State Chem; 29 (3) (1979) 429–434.

[18] V. Kumbhara, J. Leea , Y. Choia, *et al.*, Thin Solid Films; 709 (2020).

DISASTER RISK MANAGEMENT FRAMEWORK

Marijola Božović[1], Martina Petković[1], Sanja Marković[1], Bojan Stojčetović[1*]
[1]Kosovo and Metohija Academy of Professional Studies, Zvečan department, Nušićeva 6, 38227 Zvečan, SERBIA
[*]*bojan.stojcetovic@akademijakm.edu.rs*

Abstract

Disasters are as old as humanity itself. They have followed humanity during its development with undiminished intensity, proving that no society and community is immune to them. People's lives, material goods and the environment were constantly exposed to various types of dangers. Disaster risk reduction is directly conditioned by appropriate risk management so that risk management as a discipline includes preparation for disasters before they occur, disaster response and support to society for disaster recovery. Risk exposure can be measured in terms of the probability, frequency and severity of the hazard, so an important aspect of risk management is risk assessment.

Keywords: disasters, risk management, risk reduction, emergency situations

INTRODUCTION

During the 21st century, with the rapid development of the global economy and urbanization, society has been greatly affected by natural disasters (e.g. floods, droughts, earthquakes, etc.). According to the report on the frequency of natural disasters in the United Nations EM-DAT (Emergency Events Database, 2015), the losses and effects caused by these disasters are increasing. United Nations data (EM-DAT, 2015) reveal strong evidence that many regions of the world are exposed to different types of hazards [1].

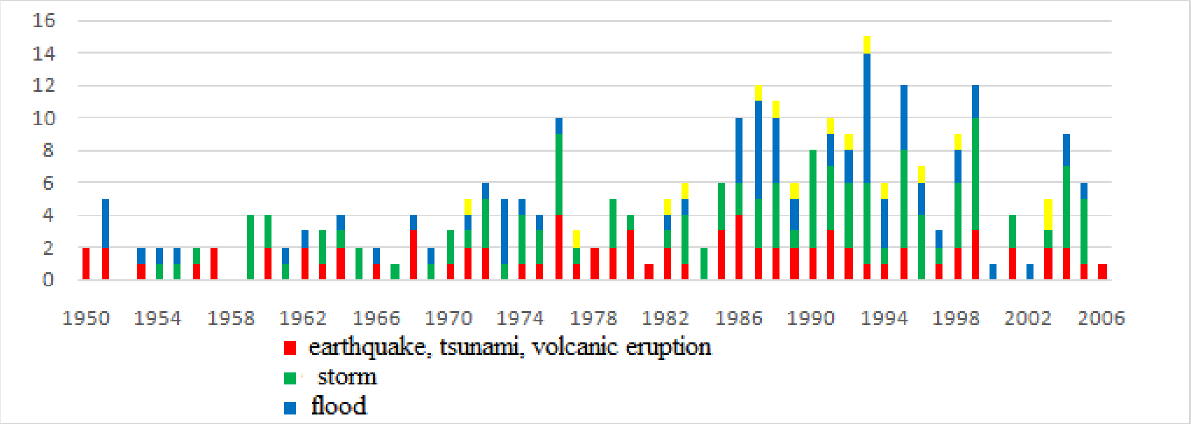


Figure 1 *Total number of natural disasters since 1950 [1]*

The emergence of new sources and types of threats increases their destructive power and the consequences that will affect the entire society and communities. For that very reason, no state is able to deal with all these threats and dangers on its own. In addition to local and national action, international cooperation and assistance are necessary for the readiness of a society to face potential dangers, as well as for an efficient response to disaster risks. Due to all the above, intensive cooperation is being developed in the UN system and regional organizations, as well as at the bilateral level. This cooperation has resulted in the adoption of a significant number of conventions and bilateral agreements as well as numerous resolutions, guidelines and other instruments [2].

A REVIEW ON DISASTER RISK MANAGEMENT AND EMERGENCY SITUATIONS

The frequency of natural disasters and its consequences have become a global problem which is why the UN General Assembly is the period from 1990–1999 proclaimed the International Decade for Natural Disaster Reduction (IDNDR) [2]. In addition to the main goal, reduction of loss of life, destruction of property, numerous activities and conferences were launched within IDNDR, and at the end of the period, the UN Office for Disaster Risk Reduction was established. One of the activities and tasks was the organization of world conferences on disaster reduction. The First World Conference on Natural Disasters was held in Yokohama, Japan in 1994 and adopted the Yokohama Strategy for a Safer World [3]. The UN General Assembly officially adopted the International Strategy for Disaster Reduction on December 20, 2013 [4]. The International Strategy for Disaster Reduction has introduced a number of innovations in this area, and the most important was to shift the focus from disaster response to disaster reduction. The Strategy is a huge step towards promoting a "culture of prevention", so this aspect of the Strategy is of particular importance, as disasters are inevitable and it is not possible to eliminate all risks [5].

Disasters continued to occur with all their might, so in 2005 the Second World Conference on Disaster Reduction was held in Kobe, resulting in the Hyogo Framework for Action, HFA 2005–2015) which is the most important international legal document for the implementation of disaster risk reduction, and which calls for improved preparedness and ability to act at all levels [6].The decision of the UN General Assembly convened the Second World Conference on Disaster Risk Reduction, which adopted the Hyogo Framework for Action 2005–2015: Developing Disaster Resistance of Nations and Communities [7].

Despite the results achieved, the Hyogo framework has certain gaps that needed to be filled, and these facts resulted in the adoption of the Sendai Disaster Risk Reduction Framework adopted at the Third World Conference on Disaster Risk Reduction, held in 2015 in Sendai, Miyag, Japan. Like the Hyogo Framework, the Sendi Framework in its central part contains priorities for action and within them key activities to be undertaken in the period 2015–2030 [8].

Following European and global trends in the field of emergency management, the Law on Disaster Risk Reduction and Emergency Management was adopted in Serbia in 2018 [9]. The main goal of this Law was to legally regulate the system of disaster risk reduction and emergency management as part of a unified national security system in the Republic of Serbia, by creating legal conditions for establishing a unified and integrated system [9]. The most important obligations that the Law brings concern the preparation of documents, namely: Disaster Risk Assessments, Disaster Risk Reduction Plan and Protection and Rescue Plan [10].

According to the Law on Disaster Risk Reduction and Emergency Management, risk management includes a set of measures and activities implemented in order to implement disaster risk reduction policy as well as administrative, operational and organizational skills and capacities for their implementation [9].

DISASTER RISK REDUCTION FRAMEWORK

The risks of natural disasters are reflected in the potential loss of human lives, material goods and threats to the environment. In order to reduce the risk of natural disasters, it is necessary to take actions in accordance with appropriate risk management. When we look at risk from the aspect of disaster risk management, it is necessary, based on the review of available literature, to state the definition of risk as defined by the UN-ISDR, i.e. as the probability of harmful consequences or expected losses (death, injury, property, livelihood, disrupted economic activities or environmental damage) resulting from interactions between (natural or man-made) hazards and vulnerable conditions [11].

Disaster risk management is focused on prevention, as indicated by the definition of Disaster Risk Reduction (DRR), as well as the definitions of Disaster Risk Management (DRM). Disaster risk reduction refers to the conceptual framework of elements considered with the possibility of minimizing vulnerability and risk of disasters in society as a whole, avoiding (preventing) or limiting (mitigating and preparedness) the harmful effects of hazards, in the broad context of sustainable development [12]. Disaster risk management seeks to avoid, reduce or redirect adverse impacts through hazards through prevention, mitigation and preparedness activities and measures [12].

The ISDR Disaster Risk Reduction Framework describes the general context and primary activities of disaster risk management and the elements considered necessary for overall disaster risk. The framework for disaster risk reduction consists of the following fields of action, as described in ISDR's 2004 publication "Living with Risk", i.e. contains the following main components, Figure 2 [13]:

- Awareness raising for change in behavior;
- Knowledge development: information, education and research;
- Political commitment and institutional development or governance;
- Early warning, monitoring and forecasting of risk management applications and instruments;
- Disaster preparedness, contingency planning and emergency management.

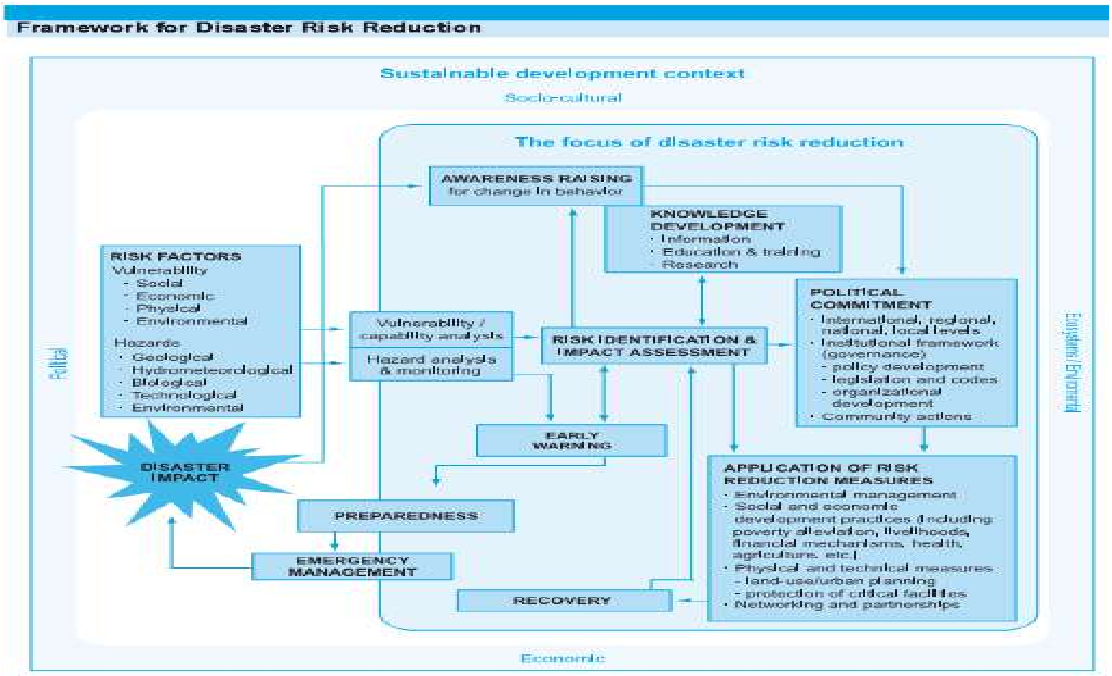


Figure 2 Framework for Disaster Risk Reduction [13]

Figure 3 shows the traditional disaster risk management process where the process is presented as a cycle, in which different phases will follow each other until the next catastrophic event occurs. This includes several phases: prevention, preparedness, assistance (response), recovery and reconstruction [13]. The presented cyclical way of disaster risk management has been discussed in scientific circles and the general opinion is that the ideal way of presenting disaster risk management is in the form of a circle that gets bigger every time due to improvements in the process. At some point, the manifestation of danger will not turn into catastrophic events and there will be no need to monitor the reaction. It will take more time before a major dangerous event continues to become a disaster, which is ultimately the goal, and that is to break the cycle. Due to adequately applied measures during all phases before the disaster, a dangerous event no longer turns into a catastrophic event. Of course, there will always be dangerous events, it is impossible to avoid them in some cases (such as earthquakes or floods), but the losses and damage from them would decrease more and more with each subsequent step taken, i.e. phase [13]:

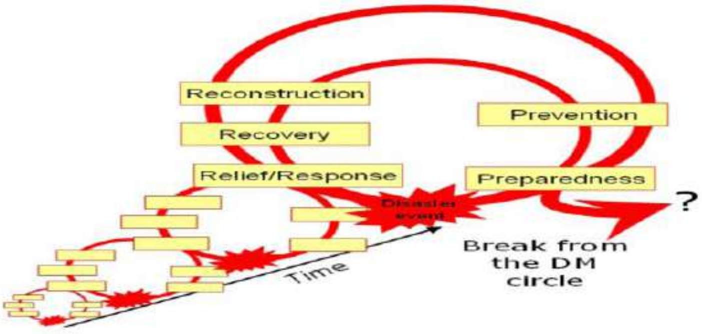


Figure 3 Overview of the disaster management cycle [13]

Based on the adopted Terminology for Disaster Risk Reduction from 2009, which seeks to jointly adopt, use and interpret terms in the field of disaster risk reduction, prevention means completely avoiding the negative effects of hazards and disasters. Prevention (i.e. disaster prevention) expresses the concept and intention of completely avoiding potential negative impacts by action taken in advance. It is often unrealistic to expect losses to be completely avoided, and mitigation measures need to be taken [12].

Preparedness is the knowledge and capacity developed by governments, response and recovery organizations, communities, and individuals to effectively anticipate, respond to, and recover from the impact of likely, imminent, or current hazards or conditions. Developing preparedness takes place in the context of disaster risk management and aims to build the capacity needed to effectively manage all types of emergencies and move from responding to sustainable recovery (reconstruction). Preparedness is based on disaster risk analysis and good links with early warning systems, and includes activities such as emergency response planning, procurement of equipment and stockpiling, development of coordination, evacuation and public information plans, and related training and practical exercises [12].

Response is the provision of emergency services and assistance to the public during or immediately after the disaster in order to save lives, reduce the impact on health, public safety and meet the basic daily needs of vulnerable people. There is no clear line between the response phase and the subsequent recovery phase [12].

Recovery or reconstruction involves undertaking reconstruction tasks, such as rehabilitation and reconstruction begin immediately after an emergency, and should be based on existing strategies and policies that help clarify institutional responsibilities for reconstruction activities and enable public participation [12].

CONCLUSION

Starting from the necessity of every responsible society to continuously work on improving the level of its resistance to threats and dangers from catastrophes, as well as the fact that threats of this kind are more and more present on the global level in the last decade, and that can be expected their increase in the future it is necessary continuous improvement of the system of disaster risk reduction and emergency management as part of the unified national security system in the Republic of Serbia. The priority action in disaster risk management is to assess the risks that exist in a particular area and plan measures for timely response in situations before, during and after natural disasters.

The Disaster Risk Reduction Framework describes the general context and primary activities of disaster risk management and the elements considered necessary for comprehensive disaster risk with the potential to minimize vulnerability and disaster risk across society, avoid (prevent) or limitation (mitigation and readiness) harmful effects of hazards, in the broad context of sustainable development.

REFERENCES

[1] EM-DAT (2015) The International Disaster Database, *Available on the following link*: http://www.emdat.be/classification

[2] M. Božović, Development of a database for risk management at work of fire and rescue units in the conditions of multi-risk, doctoral dissertation, Faculty of Occupational Safety in Nis, University of Nis (2021), *Available on the following link*: https://www.znrfak.ni.ac.rs/serbian/013-OGLASENI-DOKUMENTI/DOKTORSKE%20DISERTACIJE/Marijola%20Bozovic/DIS_UNI_Marijola_M_Bozovic_2021_javni%20uvid.pdf

[3] A report on the Yokohama Strategy and Action Plan for a Safer World (A/CONF.206/L.1), *Available on the following link*: https://www.google.com/search?q=Jokahoma+strategija+ya+sigurniji+svet+1994&oq=Jokahoma+strategija++ya+sigurniji+svet+1994&aqs=chrome..69i57.34137j0j8&sourceid=chrome&ie=UTF-8

[4] A. Jazić, MP; 1 (2015) 64–78.

[5] M. Božović, E. Mihajlović, S. Živković, Facta Universitatis, Series: Working and Living Environmental Protection, 16 (3) (2019) 161–169.

[6] M. Božović, S. Živković, Facta Universitatis, Series: Working and living environmental protection, 14 (1) (2017) 75–85.

[7] Hyogo Framework for Actions 2005–2015: Building the Resilience of Nations and Communities to Disasters/Extract from the final report of the World Conference on Disaster Reduction (A/CONF.206/6) 2007, United Nations-Geneva, *Available on the following link*: https://www.unisdr.org/2005/wcdr/intergover/official-doc/L-docs/Hyogo-framework-for-action-english.pdf

[8] Sendai the Disaster Risk Reduction Framework 2015–2030. *Available on the following link*: https://www.google.com/search?q=sendai+okvir+za+smanjenje+rizika+od+katastrofa&oq=sendai+&aqs=chrome.1.69i57j69i59j0l4.5219j0j8&sourceid=chrome&ie=UTF-8

[9] Law on Disaster Risk Reduction and Emergency Management ("Official Gazette of RS", No. 18/2019) (in Serbian).

[10] Instruction on the Methodology of Development and Content of Disaster Risk Assessment and Protection and Rescue Plan, ("Official Gazette of RS", No. 80/2019).

[11] UNISDR: UNInternational Strategy for Disaster Reduction Sec, 15 January 2009, *Available on the following link*: http://www.unisdr.org/eng/library/lib-terminology-eng.htm

[12] UNISDR Terminology 2009, Disaster Risk Reduction, *Available on the following link*: https://www.seesac.org/f/tmp/files/failovi/409.pdf

[13] C. J. Van Westen, D. Alkema, M. C. J. Damen, N. Kerle, N. C. Kingma, Multi-hazard risk assessment, Distance education course, Guidebook, ITC School on Disaster Geo-information Management, United Nations University (2011).

Author Index

Authors are responsible

for the content of their papers.

Platinum Donor of the Conference

ZiJin

塞尔维亚紫金铜业有限公司

SERBIA ZIJIN COPPER DOO

tfbor.bg.ac.rs
eco.tfbor.bg.ac.rs

EcoTER'22

ISBN 978-86-6305-123-2