



*International Symposium on Functional Biomass-derived
Carbon Materials*

9th–11th March 2021 | ONLINE

Book of Abstracts

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Welcome to *GreenCarbon2020*!

The primary aim of *GreenCarbon2020* is to increase dissemination of the research activities conducted within the GreenCarbon European Training Network (project H2020-MSCA-ITN-721991). For this purpose, the fourteen early-stage researchers involved in the GreenCarbon project will present the most important findings from their PhD projects.

GreenCarbon 2020 is also open for the global research community as well as policy makers and representatives from the industrial sector. The event also includes the participation of renowned keynote speakers. The topics covered during the symposium include, but are not limited to:

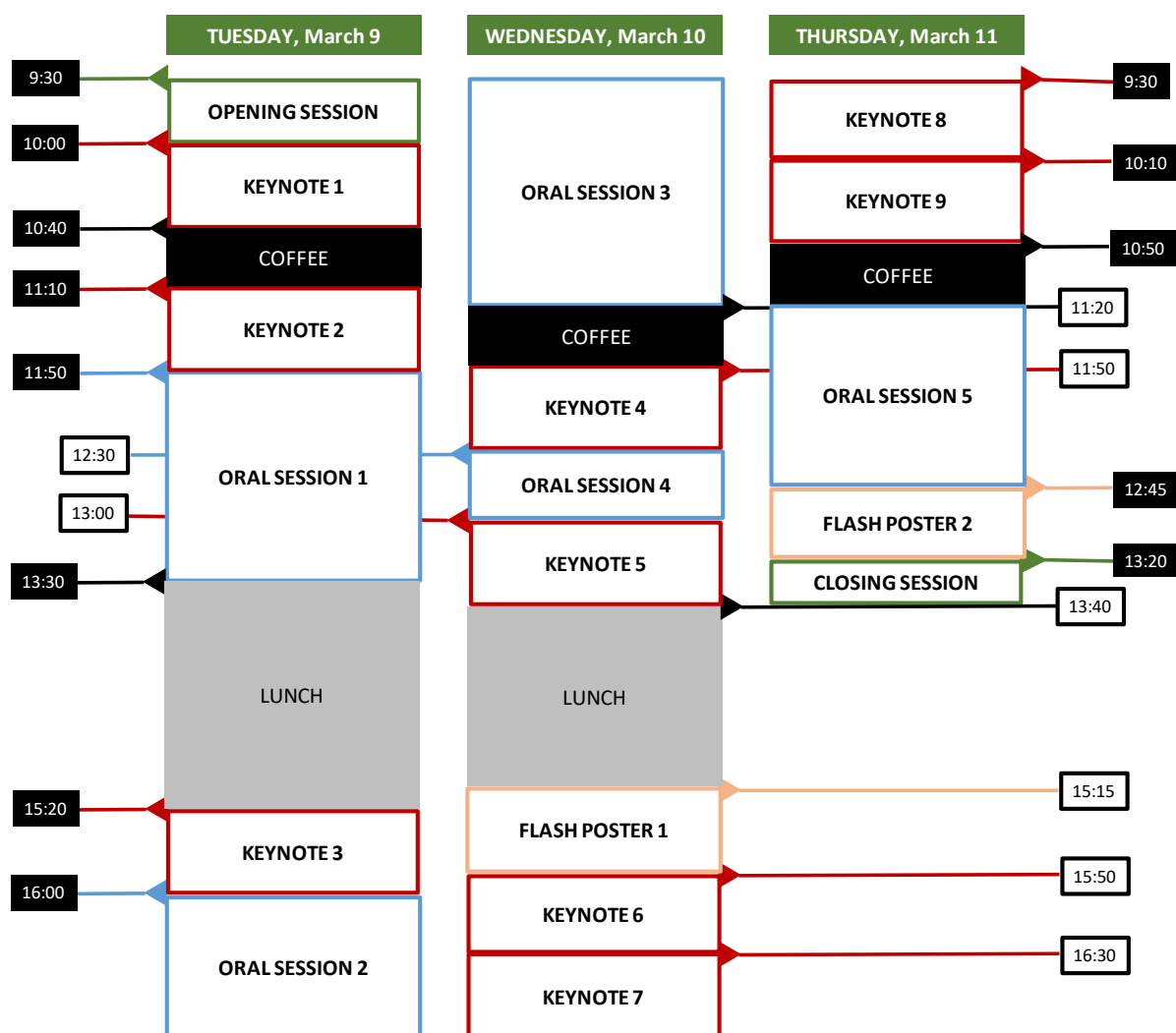
- Production and characterization of biomass-derived carbons through thermochemical processes.
- Synthesis of biomass-derived porous carbons (and composites) and their application in adsorption, catalysis and electrochemical energy storage.
- Biomass-derived carbons for soil conditioning (biochar) and related environmental benefits.
- Other emerging applications of biomass-derived carbons (e.g., in direct carbon fuel cells, as reductants in metallurgical industry, in cementitious composites, etc.).

Selected abstracts have been invited to submit a journal paper to a special issue in the MDPI's *Sustainability* journal (ISSN 2071-1050).

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Joan J. Manyà – Chairman *GreenCarbon2020*

Programme at a glance



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Detailed Programme

Tuesday, March 9, 2021

09:30 – 10:00	Opening session
10:00 – 10:40	<u>Keynote presentation 1</u> Pyrolysis fundamentals and pyrochar characterization Frederik Ronsse, Ghent University, Belgium
10:40 – 11:10	Coffee Break
11:10 – 11:50	<u>Keynote presentation 2</u> HTC fundamentals and hydrochar characterization Andrea Kruse, University of Hohenheim, Germany
11:50 – 13:30	<u>Oral session 1</u> Production of biomass-derived carbons (BCs) through pressurized slow pyrolysis under N₂ and CO₂ atmosphere Gianluca Greco, University of Zaragoza, Spain Methodology for the design of a rotary kiln for the pyrolysis of biomass Jorge López-Ordovás, Aston University, UK Prediction accuracy in modelling beech wood pyrolysis at different temperatures using a comprehensive, CFD-based single particle pyrolysis model Przemysław Maziarka, Ghent University, Belgium Valorization of the poultry litter through wet torrefaction and different activation treatments Pablo J. Arauzo, University of Hohenheim, Germany Influence of reaction conditions on hydrothermal conversion of sugars Pierpaolo Modugno, Queen Mary University of London, UK
13:30 – 15:20	Lunch time
15:20 – 16:00	<u>Keynote presentation 3</u> Advanced carbon materials from tannins Vanessa Fierro, Institute Jean Lamour (CNRS), France
16:00 – 17:10	<u>Oral session 2</u> Comparison of different methods to determine ash and volatile matter content of biochars Markus Lang, RWTH Aachen University, Germany Kinetics characterization of barley straw pyrolysis using the Distributed Activation Energy Model (DAEM) Javier Pallarés, University of Zaragoza, Spain Impact of particle size and ash chemical composition on pyrolysis and CO₂ gasification of barley straw for activated carbon applications Antonia Gil, University of Zaragoza, Spain Hydrothermal carbonization of glucose in the presence of iron ions Vahid Saadattalab, Stockholm University, Sweden

Wednesday, March 10, 2021

09:30 – 11:20

Oral session 3

Biomass based carbon materials for gas storage and separation

Sabina Alexandra Nicolae, Queen Mary University of London, UK

Macroscopic rods of self-assembled monodispersed colloidal hydrochar and related templated SiC and Cu₇Si₂

Xia Wang, Stockholm University, Sweden

Influence of slow pyrolysis conditions on the adsorption of organic dyes from water

Filipe Rego, Aston University, UK

Production of biomass-derived activated carbons for bio-oil and biogas upgrading

Christian Di Stasi, University of Zaragoza, Spain

Heterogeneous transformation of CO₂ to methanol—Structural study of the support

Anthony E. Szego, Stockholm University, Sweden

Sequential biochar systems

Christian Würzer, The University of Edinburgh, UK

11:20 – 11:50

Coffee break

11:50 – 12:30

Keynote presentation 4

Biomass-derived carbons for heterogeneous catalysis

Elsa Weiss-Hortala, IMT Mines Albi, France

12:30 – 13:00

Oral session 4

Aqueous phase hydrogenolysis of glycerol over Ni/AC catalysts

Raquel Raso, University of Zaragoza, Spain

Adsorption of propylene glycol on activated carbon: kinetics experiments

Jorge Fortea, University of Zaragoza, Spain

13:00 – 13:40

Keynote presentation 5

Biomass-derived carbons for adsorption in gas phase

Niklas Hedin, Stockholm University, Sweden

13:40 – 15:15

Lunch time

15:15 – 15:50

Flash poster presentations 1

Hydrothermal carbon as metal-free catalyst and electrocatalyst

Enrique García-Bordejé, Instituto de Carboquímica (ICB-CSIC), Spain

Synthesis of porous carbon materials from nanocellulose

Lucas Güemes, Instituto de Carboquímica (ICB-CSIC), Spain

Turkish hazelnut shells as precursor of sustainable CO₂ adsorbent

Ayşe Sever Akdag, Hacettepe University, Turkey

Carbon-nanoparticles hybrids as electrodes in electrochemical energy storage systems

Sergio Aina, University of Zaragoza, Spain

Wednesday, March 10, 2021 (continued)

Studying carbons derived from urban pruning waste as additives in Li-ion battery anodes

Iván Esteve-Adell, Instituto Tecnológico de la Energía (ITE), Spain

Biomass-based activated nitrogen doped carbons for energy applications

Ance Plavniece, Latvian State Institute of Wood Chemistry, Latvia

15:50 – 16:30

Keynote presentation 6

Biomass-derived carbons for Na-ion batteries

Maria Magdalena Titirici, Imperial College London, UK

16:30 – 17:10

Keynote presentation 7

Biomass-derived carbons for redox flow batteries

Ana Jorge-Sobrido, Queen Mary University of London, UK

Thursday, March 11, 2021

- 09:30 – 10:10 **Keynote presentation 8**
Sequential uses of biochar
Ondrej Masek, The University of Edinburgh, UK
- 10:10 – 10:50 **Keynote presentation 9**
Biochar for soil restoration
Gabriel Gascó, Universidad Politécnica de Madrid, Spain
- 10:50 – 11:20 Coffee break
- 11:20 – 12:45 **Oral session 5**

Biochar from greenhouse waste: Production, characterization and evaluation for its potential use in the horticultural growing media
Dilani Rathnayake, Ghent University, Belgium

Role of biochar in the implementation of a phytomanagement strategy on soils presenting polymetallic pollution
Manhattan Lebrun, University of Orléans, France

Biochar from agro residues in adsorption tests for water treatment
Lydia Fryda, UniLaSalle-Ecole des Métiers de l'Environnement, France

Examining samarium sorption in biochars and carbon-rich materials for water remediation: batch vs. continuous-flow methods
Joan Serra, University of Barcelona, Spain

Comparative analysis of biochars to be used in greenhouse gas abatement and first trends of their application to pig manure
Josephine Getz, Technological University Dublin, Ireland
- 12:45 – 13:20 **Flash poster presentations 2**

HTC as promising route for enhancing thermal insulation in bioarchitecture
Silvia Román, Universidad de Extremadura, Spain

The effect of biomass-derived carbon materials on the recovery of metals from mining tailings by hydrometallurgical processes
Gabriel Gascó, Universidad Politécnica de Madrid, Spain

Copper and zinc leaching from complex sulphide ore: The effect of biomass-derived activated carbon as catalyst
Ana Méndez, Universidad Politécnica de Madrid, Spain

The use of magnetic biochars as catalysts in the lixiviation of metals from mining tailings
María L. Álvarez, Universidad Politécnica de Madrid, Spain
- 13:20 – 13:40 Closing session

ABSTRACTS

Production of biomass-derived carbons (BCs) through pressurized slow pyrolysis under N₂ and CO₂ atmosphere

Gianluca Greco^{1,*}, Christian Di Stasi¹, María Videgain², Belén González¹, Joan J. Manyà¹

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Keywords: *Pressurized pyrolysis; Biochar; Energy and exergy analysis; CO₂ activation; Soil amendment.*

Abstract

Biochar is widely considered as a renewable, promising solution to mitigate critical issues such as the global warming, the environmental pollution and the growing food demand [1]. It is a form of charred organic matter produced through the pyrolysis of biomass, deriving from several sources, such as forestry or agricultural residues, municipal solid waste and sewage sludge. Biochar can be used in a wide range of applications [2], including —but not limited to— soil amendment, energy production, adsorption and catalysis. In this sense, depending on its final use, biochar must present specific properties, which will depend on the pyrolysis process conditions applied to produce it. Nevertheless, given the high number of variables affecting the pyrolysis process (e.g., pressure, peak temperature, type of carrier, gas residence time) and the wide range of available biomass sources, several types of biochar with different properties should be expected. Hence, one of the main challenges nowadays is to optimize the process conditions of pyrolysis for a given biomass feedstock, in order to obtain biochar with the best properties for each application. Therefore, the main task of this study is to evaluate the effects of absolute pressure (0.2–0.9 MPa), peak temperature (400–550 °C), gas residence time (100–200 s) and gas atmosphere (pure N₂ or a binary mixture of CO₂ and N₂, 60:40 v/v) on the pyrolysis behavior of wheat straw pellets and wood waste biomass in a bench-scale fixed-bed reactor. Not only the effect of these parameters individually but also the possible effects derived from the interactions between them have been considered. For this purpose, 2-level factorial designs of experiments have been adopted to objectively analyze the effect of these parameters on the response variables (e.g., yield of products, fixed-carbon yield, atomic H:C and O:C ratios, and BET surface area). Furthermore, energy and exergy assessments of the slow pyrolysis system were included as response variables in the factorial designs in order to investigate the influence of the operating parameters on the thermodynamic performance. In addition to the parametric assessment described above, the present study aims at analyzing the real-time mass loss of the biomass along the pyrolysis process. This valuable information, together with the simultaneous analysis of the gas composition and the temperature profiles, represents a novel approach to assess the role played by the studied factors in the pyrolysis behavior. More details about the reactor configuration adopted are given elsewhere [3]. Two different lines of research were then conducted using the biochars produced in the framework of the above-mentioned set of experiments. More in detail, the wheat straw-derived chars were physically activated with CO₂ at 800 °C for further applications in CO₂ adsorption from binary CH₄/CO₂ mixtures, with the goal of evaluating how the slow pyrolysis process conditions can affect the textural properties of the resulting physically activated carbons. The second line of investigation is focused on finding a correlation between the slow pyrolysis operating conditions selected and the potential phytotoxicity of the produced wood waste-derived biochars on the seed germination of watercress and barley. In this sense, the goal of this preliminary study is to optimize the pyrolysis operating conditions in order to obtain the best biochar characteristics with the aim at employing it as soil amendment.

Acknowledgement: This project has received funding from the European Union's Horizon 2020 research and innovation program under the Marie Skłodowska-Curie grant agreement No 721991.

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Methodology for the design of a rotary kiln for the pyrolysis of biomass

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Keywords: *pyrolysis, rotary kiln, modelling, kinetic model, heat transfer*

Abstract

Rotary kilns have a broad range of applications, yet the methodology for the process design of a rotary kiln for the slow pyrolysis of biomass is not well defined. The objective of this work was to create a model to enable the design of a rotary kiln providing the following information for several defined feedstocks: reactor length, diameter, temperature and conversion profile, gas flow within the reactor and the heat requirement. The user selects their configuration by choosing the following variables: the type of feedstock (selected from a group of three chosen for the GreenCarbon project), the moisture content, particle size, biomass capacity and the reaction temperature or preferred product.

The calculations are based around in-built mass and energy balances, combined with reaction kinetics, conversion of the biomass and the formation of the pyrolysis gases. To study the conversion of the feedstock along the length of the reactor and to facilitate the modelling, the reactor is divided into theoretical slices. The criteria for the design is to obtain a final conversion value within the range 94.5-95.5 wt.% on a dry basis. The model is composed of three sub-models:

- **Bed of solids:** Rotary kilns are rotating shells at a specific kiln angle which drive the biomass forward. An important parameter to ensure thorough mixing and a more homogeneous product at the end is the final filling degree. The reactor length is calculated from the initial and final filling degree, the radius and the kiln angle together with some properties from the feedstock such as the repose angle. The residence time of the biomass is calculated from all previously collected data. The bed of solids sub-model calculates all the previously mentioned parameters.
- **Heat transfer:** Within the rotary kiln, the three heat transfer methods (conduction, convection and radiation) take place between all components (bed of solids, gases inside the reactor, and the heat source outside the kiln). Since the reactor is divided into theoretical slices, the heat transferred in each slice depends on the average temperature, and consequently on the initial and final temperature. The final temperatures are re-calculated for each slice until they converge to calculate the temperature profile within the reactor.
- **Kinetic:** The production of char has been performed for many years, but the kinetics behind the process remains relatively unknown. The char, condensable and non-condensable fraction of gases from pyrolysis varies with the composition and process parameters. This variability makes the study more difficult, and therefore, the models are simplified. From experiments on a TGA at different heating rates, the number of reaction steps for each feedstock is determined, and for each reaction step, the reaction order of the feedstock, pre-exponential factor and activation energy are determined to simulate the behaviour of the feedstock under pyrolysis conditions. The average temperature of the bed of solids, previous conversion value and the residence time determine the final conversion value for each of the slices.

This work presents the model, and final results of the study carried out by the ESR 3 for the GreenCarbon Project.

Acknowledgement: This project has received funding from the European Union's Horizon 2020 research and innovation program under the Marie Skłodowska-Curie grant agreement No 721991.

Prediction accuracy in modelling beech wood pyrolysis at different temperatures using a comprehensive, CFD-based single particle pyrolysis model

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Keywords: wood, biochar, pyrolysis, single particle, CFD modeling

Abstract

CFD modelling is a novel approach to overcome problems in predicting the pyrolysis outcome in a reliable and repeatable way. It allows through real-time, model-based investigation the assessment of parameters that are impossible to be analysed experimentally. The aim of this study was to establish a comprehensive 2D single particle model of beech wood pyrolysis, which would be a reliable tool for process optimization with respect to the properties of the resulting liquid and solid pyrolysis products (biochar). The model comprised the primary biomass degradation according to the RAC kinetic scheme (48 compounds). Modelled wood cylinders were in a dry state and had a size of Ø8 mm x 10mm, with 660 kg/m³ bulk density and 1430 kg/m³ true density. The model was validated with experimental data of pyrolysis of dry beech wood cylinders, conducted in a single-particle reactor at 5 different temperatures (300, 400, 500, 700, 900 °C). The validation dataset consisted of the evolution of particle's center and surface temperatures, mass loss, and composition of 14 evolved volatiles (CO₂, CO, H₂O, CH₄, C₂H₄, formaldehyde, acetic acid and furfural, among others). Prediction of the particle's temperature and mass loss evolution were deemed accurate. For all products, up to 500 °C, the predictions differed from the experimental data by a few %. For the temperature range between 700 °C and 900 °C, the model however, strongly over-predicted the yield in bio-oil at the expense of pyrolysis gases. The implemented primary kinetic scheme showed satisfactory results in the investigated temperature range. However, the model did not reflect very well the pyrolysis products evolution at higher temperatures (thermal tar cracking and gasification range), so implementation of accurate secondary kinetic schemes are deemed necessary.

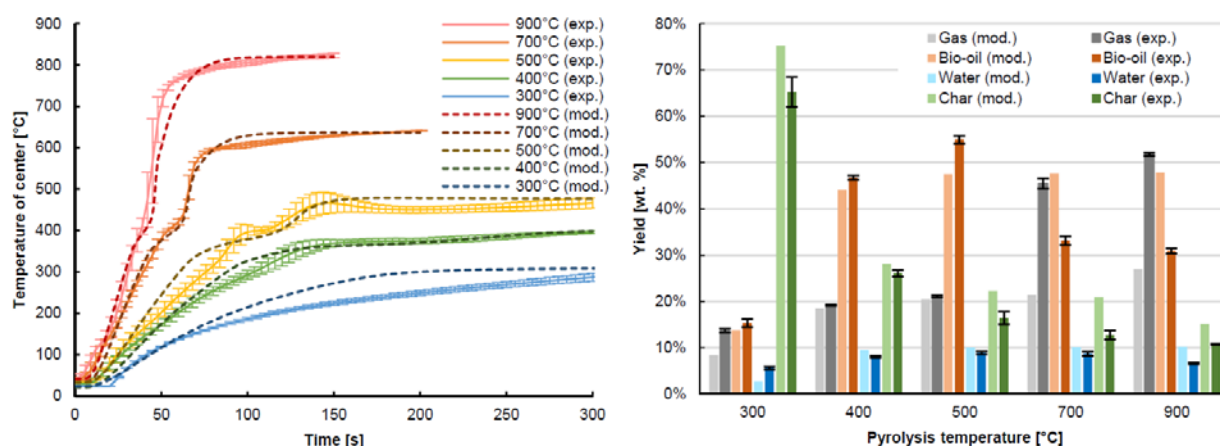


Fig. 1. Comparison of the temperature of the particle's center between averaged experimental values and modelled values for different temperatures of pyrolysis (left), yields of pyrolysis gases, bio-oil, pyrogenic water and pyrochar between averaged experimental values and modelled values for different temperatures of pyrolysis (right).

Acknowledgement: This project has received funding from the European Union's Horizon 2020 research and innovation program under the Marie Skłodowska-Curie grant agreement No 721991.

Valorization of the poultry litter through wet torrefaction and different activation treatments

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Keywords: *Poultry litter, wet torrefaction, activated carbon, physical activation, chemical activation, water treatment.*

Abstract

The increment of the global population is strongly related with increase of the demand on energy and food, as well as amount of wastes that is released to environment. Animal farming, among other sectors of human activity generate a significant amount of residues. Poultry farming requires the release and treatment of a huge amount of residues called poultry litter (PL). Such material is composed out of poultry faeces, urine, feathers, straw and its current utilization ways is no environmental friendly nor efficient. Annual growth of the poultry meat production leads to increase of the environmental problem due to the big amount produced per year, so the issue of effective management of the poultry waste is a relevant problem to tackle.

The present work is aimed on the assessment of valorization possibilities of the PL via activated carbon (ACs) and soil and soil amendment. Due to the sanitation reasons the initial PL was terrified in a fluidized bed reactor with steam at 300 °C leading to wet terrified poultry litter (WTPL) and such material was used for further investigation. In this study the WTPL was activated in 3 different procedures: thermal (only temperature effect), physical (temperature and oxidizing agent effect) and chemical treatment (temperature and chemical reagent effect) at two different temperatures (600 °C and 800 °C) during 30 min. Bulk properties of ACs were analyzed with elemental analyzer, ICP-OS and measurement of pH of their solution. The structural properties of ACs were analyzed with FT-IR, SEM and sorption properties via sorption of N₂ and CO₂ and methylene blue (MB). ACs produced by chemical activation showed highest specific surface area (SSA) and lowest ash concentration among other samples. Chemically activated ACs had the mesoporous SSA (991 and 1117 m²/g) which led to highest MB absorption. It reveals the possibility of their use waste water treatment as absorbent. ACs from thermal and physical adsorption showed high concentration of phosphorus and nitrogen compounds (values wt. %) and pH reducing effect important for soils, which indicates possibility of their use as soil amendment or fertilizer.

Acknowledgement: This project has received funding from the European Union's Horizon 2020 research and innovation program under the Marie Skłodowska-Curie grant agreement No 721991.

Influence of reaction conditions on hydrothermal conversion of sugars

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Keywords: *hydrothermal carbonization, sugars, hmf, kinetics*

Abstract

Hydrothermal carbonization (HTC) is regarded as a highly effective method to convert cellulosic waste into a source of valuable chemicals and carbon materials. The intricate series of transformations that take place during HTC lead to the depolymerization of cellulose and formation of various dehydration and polymerization products that we divide in three classes: gaseous products (mainly water and CO₂), water-soluble organic compounds (small molecules or large polymers) and the insoluble hydrothermal carbon (HC). Some of the water-soluble chemicals have been recognized as platform chemicals for a transition to a greener, fossil based chemistry¹. Hydrothermal carbon is just starting to display its huge versatility in the field of energy storage².

5-hydroxymethyl furfural (HMF) and levulinic acid (LevA), among the several soluble organic compounds, deserve great attention as they are the most valuable and versatile chemicals found in hydrothermal medium. HMF in particular, derived from the dehydration of hexoses, is known to be the building block for the formation and growth of HC. LevA is the product of a reaction of ring opening of the HMF cycle. Therefore we see that the reaction paths which lead to the formation of these two kinds of products are intertwined; so, depending on which one is the product of interest, the other is regarded as a byproduct and vice versa. The huge potential of this process relies on the ability of selectively driving the reaction towards one of these two products to maximize the yield.

Although the general conditions required for the conversion from cellulose to dehydration products are known, reaction parameters such as pH, catalyst, temperature and reaction time still need to be optimized, in order to achieve the best yield of the desired product and the scalability of the process.

In this work, we have extensively explored the influence of reaction condition (substrate, residence time, temperature, initial pH and catalyst) on the yield of solid and dissolved products and on the morphology of HT. In the first part of this study, we have used fructose, glucose and xylose to evaluate the different reactivity of the main natural hexoses and pentoses keeping track of three parameters. Varying the reaction time from 2 to 12 hours; keeping the reaction time and working pH constant and varying the homogenous acid catalyst; keeping the rt constant and varying the gas feed and the starting pressure in the reactor. This first series of experiments has shown that fructose is much more active towards dehydration compared to glucose, with xylose having an intermediate reactivity. HMF acts as an unstable intermediate of dehydration of glucose and fructose and harsher conditions promote its degradation to levulinic acid and HT. Furfural is the analogue of HMF when it comes to xylose reactivity and its tendency to polymerize to form HT is lower.

The second part of the study has involved the characterization of the hydrothermal carbon obtained in the first series of experiments. SEM, FTIR and ss ¹³C NMR showed a common chemical structure, with minor obvious differences in the case of xylose derived HT. The HT evolves to a more condensed structure as reaction time increases, converging to a chemical structure that resembles the HT obtained at low initial pH. By looking at the HT spheres formation via in situ SAXS analysis, we were able to observe a kinetic that confirms the observation made on the liquid face analysis (fructose>xylose>glucose). Finally, the MALDI-ToF-MS analysis of HT carbon spheres showed the partial solubility of this material and the presence of oligomers that are common in glucose and fructose derived carbon. These oligomers double or triple their size as the reaction time increase.

Acknowledgement: This project has received funding from the European Union's Horizon 2020 research and innovation program under the Marie Skłodowska-Curie grant agreement No 721991.

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Comparison of different methods to determine ash and volatile matter content of biochars

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Keywords: *biochar, pyrolysis, characterization, ash content, volatile matter*

Abstract

Proximate analysis can be used as a fast determination method for the material composition of biochar (moisture, ash, volatile matter and carbon content). As with other analytical methods, there is not yet a standard for biochar published. In contrast to elemental analysis, for example, there is less known about the comparability of different standards for proximate analysis of biochars. Most times the standards for solid biofuels or fossil coal are used for analysis. Even the European Biochar Certificate (EBC) recommend these standards for biochar analysis [1]. In some investigations ([2], [3]) the authors modified the determination methods without comparing the results with the usual standard procedures. Only Aller et al. have investigated the effects of these modification on the resulting ash and volatile matter content [4]. They found out that the lowest temperature to determine the volatile matter content for biochar should be 800 °C². Above this temperature, the mass loss rate is significantly lower than at temperatures below 800 °C. Nevertheless, even at higher temperatures a small difference in the mass loss rate is still visible, for example by comparing the determination method at 900 and 950 °C for the volatile matter according to the European and American standard, respectively [3], [4].

The aim of the presented work is to compare the determination methods for proximate analysis, especially ash and volatile matter content, with different devices under similar conditions. In a first step, all relevant standards are compared. As there are no standards for biochars yet published, analysis of all feedstocks will be done with the standards for solid biofuels and for fossil coal. The following feedstocks are used to cover a wide range of different substances from fossil coal to the biomass structural components as well as different biomasses and their associated biochars: lignite, cellulose and lignin, raw material and biochar of spruce wood and rapeseed straw. On the one hand the ash and volatile matter content of these feedstocks were determined by muffle furnace as it is required by standard. On the other hand, the different constituents were measured by using a thermogravimetric analyzer (TGA). To better compare the results of both devices the parameters of muffle furnace experiments are also used for the analysis with TGA. In addition to the equipment comparison, investigations were also carried out with regard to other sample quantities and modified analysis procedures, such as longer residence times. The results shall help to standardize the proximate analysis of biochars and to improve the comparability of different analysis.

References

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Kinetics characterization of barley straw pyrolysis using the Distributed Activation Energy Model (DAEM)

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Keywords: Biomass, Activated bio-carbon, Pyrolysis, DAEM

Abstract

Apart from the traditional uses of activated carbon (AC) in many industrial sectors, mainly related to the treatment and purification of water and polluting gases, there is a growing interest in new applications of this adsorbent in the energy field. Examples of these applications are its use as adsorbent for the reduction and capture of CO₂, VOC's and heavy metals emissions, as solid fuel in direct carbon fuel cells (DCFC), as adsorbent material in adsorption cooling systems using solar thermal energy, and as electrodes build-in material for supercapacitors improving batteries performance to store energy. Furthermore, in the search for renewable alternatives to traditional non-renewable precursors for the production of activated carbon, recent investigations have revealed promising results in the used of biomass by-products and residues (activated bio-carbon) obtaining adsorption properties comparable to those of commercial activated carbons [1,2].

It is therefore a new field of study with high potential and future perspectives. However, for its development, it is necessary to continue investigating in the search for new precursor materials, in the pretreatments and process conditions to optimize AC properties and selectivity for a specific end use, and in the modelling of the mechanisms involved in the conversion process.

In this study, kinetics characterization of barley straw pyrolysis using the Distributed Activation Energy Model (DAEM) was investigated. DAEM model assumes that the thermal decomposition occurs as a result of a number of independent parallel first order reactions with different activation energies representing the rupture of different chemical bonds. The number of reactions is so large that activation energy can be described by a continuous distribution function. Then, the evolution in total volatiles is modelled as follows:

$$V/V^* = 1 - \int_0^\infty \exp\left(-k_0 \int_0^t e^{(-E/RT)} dt\right) f(E) dE$$

DAEM has been widely used for modelling pyrolysis of biomass [3], improving the results obtained from more simplify approaches such as the Single First Order Reaction model (SFOR) or the Two Competitive Reaction Model (2CRM).

In order to estimate the normalized distribution curve of the activation energy $f(E)$ and the pre-exponential factor $k_0(E)$, the integral method proposed by Miura et al. (1998) was applied [4]. This method allows to estimate $f(E)$ and $k_0(E)$ without a priori assumptions (typically Gaussian distribution for $f(E)$ and constant k_0). To this purpose, thermogravimetric analysis at five different heating rates (5, 10, 15, 20 and 30 °C/min) from 30 °C to 900 °C in nitrogen atmosphere were conducted. Then, Arrhenius graphs at different V/V^* were plotted to determine E and k_0 . Finally, the V/V^* vs E relationship was differentiated to obtain $f(E)$.

Results show a good correlation ($R^2 > 0.9$) in the conversion range 0.1 to 0.85, with activation energies distributed from 186 to 280 kJ/mol. The poor fit of the k_0 vs E in the small and large E regions corresponding to small and large V/V^* values may be associated with the accuracy of the experimental data [4,5]. Finally, the calculated DAEM curves were obtained and compared with TGA experimental data, showing a good agreement.

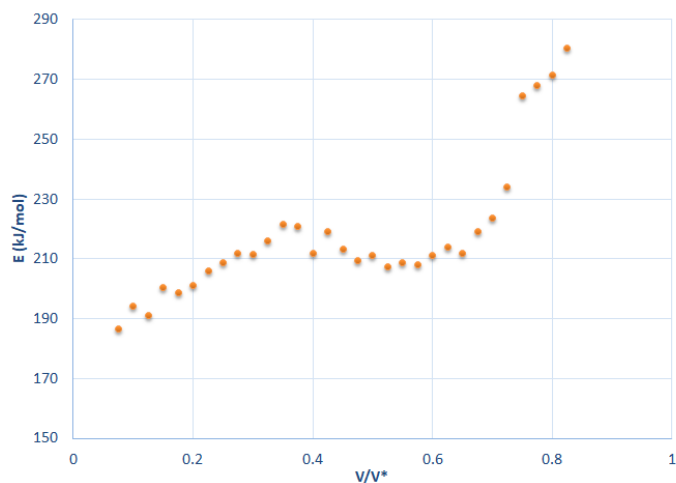


Fig. 1. Activation energy vs conversion rate calculated from the Arrhenius plot.

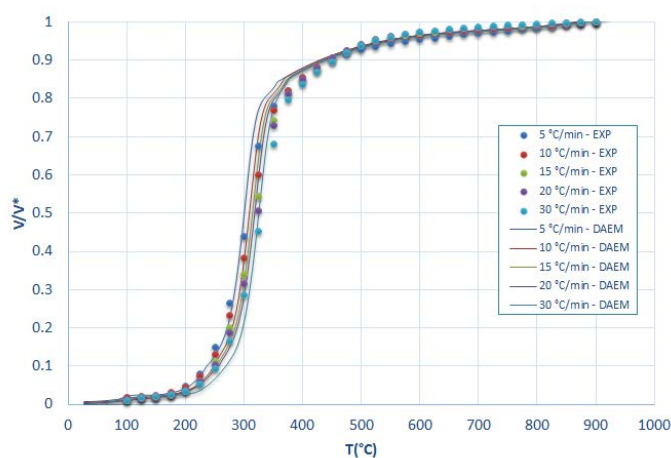


Fig. 2. Experimental and calculated (DAEM) conversion curves at different heating rates.

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Impact of particle size and ash chemical composition on pyrolysis and CO₂ gasification of barley straw for activated carbon applications

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Keywords: activated bio-carbon, barley straw, pyrolysis, physical activation,

Abstract

Biomass-derived activated carbon has attracted a growing interest in recent years due to its excellent characteristics as a precursor, availability and low cost. Despite their advantages, the inherent physical and chemical heterogeneity of biomass residues may affect the surface morphology and pore development during the activation process, affecting its final quality [1]. In this work, we test samples of different particle sizes to evaluate how the heterogeneity of the chemical and physical properties of the precursor material can affect the pyrolysis and activation behaviour. We use barley straw, a very widespread biomass residue, as feedstock. The raw material, previously grounded and sieved to 0.5 mm size is classified into five different size ranges, according to 0.5-0.355 mm (R1); 0.355-0.25 mm (R2); 0.25-0.15 mm (R3); 0.15-0.10 mm (R4) and < 0.15 mm (R5) mesh sizes. Proximate, ultimate and ICP-OES analysis are conducted to each particle size interval. The pyrolysis behaviour is investigated using non-isothermal thermogravimetric analysis from ambient conditions to 900°C at five heating rates (5-10-15-20-30 K/min) in an inert atmosphere (N₂). The thermal evolution of the biomass chars during physical activation is also evaluated by TGA at different atmospheres. The biomass samples are first pyrolysed with N₂ up to 500°C at 10 °C/min. After one hour of holding time with N₂ at 500°C, samples are activated up to 900 °C with 100% CO₂ (% vol.) and 11% CO₂- 89% N₂ (% vol.) as oxidising agents under dynamic conditions, at heating rates of 5-10-15 °C/min.

As particle size decreases, the fixed carbon and volatile matter contents of the samples monotonically decrease. The opposite is found for the ash content, being 8.8% and 3.9% (in d.b.) for the finest (R5) and coarsest ranges (R1), respectively. Results of ICP-OES analyses to the raw samples (fig.1) agree with proximate results, showing an increased mineral content from R1 to R5, including minor elements (Al, Fe and S). The finest fraction is enriched in K>Si>Ca>Mg (>0.2%wt) and P>Na>Al>Fe>S (<0.2%wt). Potassium and calcium are nutrients needed for plants growth, but often increased by the use of fertilizers. Although silicon contributes to stalk rigidity, it might probably be originated from inorganic impurities during harvesting, transporting and storage processes, also noticed by an increased presence of Al and Fe in the finest sizes.

Pyrolysis evolution shows that the thermal decomposition occurs in three stages, related to hemicellulose, cellulose and lignin, in accordance with other experiences with barley straw [2, 3]. The maximum temperature at which cellulose decomposition takes place decreases at lower particle sizes and lower heating rates. In addition, slight differences in the shape of the DTG curves are detected, especially for R5, which could be attributed to the small size and high alkali content of R5. Small particles, due to their larger surface areas have higher mass and heat transfer rates, which leads to faster kinetic rates. Also, the presence of alkali metals (i.e. potassium) has been reported as acting as reaction catalysts which could promote the faster release of volatile matter [2].

Finally, results of the gasification tests confirm the influence of the heating ratio, particle size and oxidation atmosphere on the gasification kinetics of the char samples after pyrolysis. The increase of the heating rate delays the time (and temperature) for achieving the same char conversion, which might also be related to heat and mass transfer effects, caused by the large energy requirement needed for char gasification. The trends of the curves for particle ranges R1 to R3 agree with similar works [4-6]. However, the reaction rate-conversion profiles found in the present research (fig. 2) show a different evolution as a function of particle size, especially for the smaller fractions R4 and R5. Below 750°C, higher reactivity is found for the finest fraction R5; beyond that point, the reaction rate decreases at higher temperatures. Besides the differences in char structure after pyrolysis, the high alkali content of the finest fraction might promote the catalytic effect of minerals on gasification reactivity at lower temperatures, but hinder the reaction by blocking the pores at higher temperatures by forming low melting-point potassium aluminium silicates [7-9]. Apart from the detailed kinetic results from the pyrolysis and activation stages, the results from the current work may help to design operation

strategies to enhance activated carbon quality and prevent ash sintering problems. Detailed kinetic results are discussed in the paper.

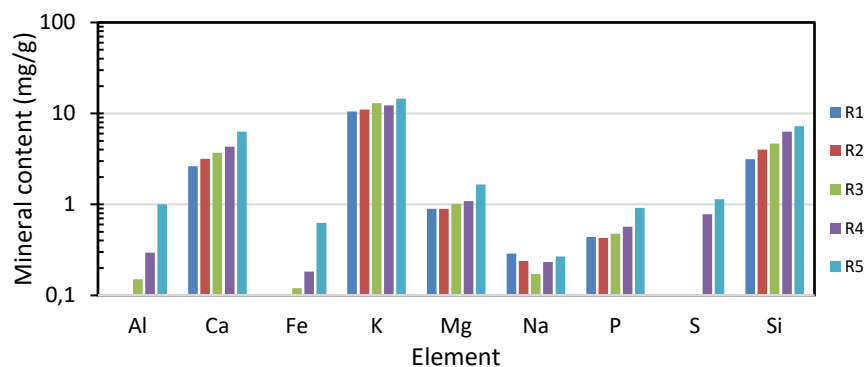


Fig. 1. Mineral content in raw biomass samples (mg/g, d.b.) by ICP-OES.

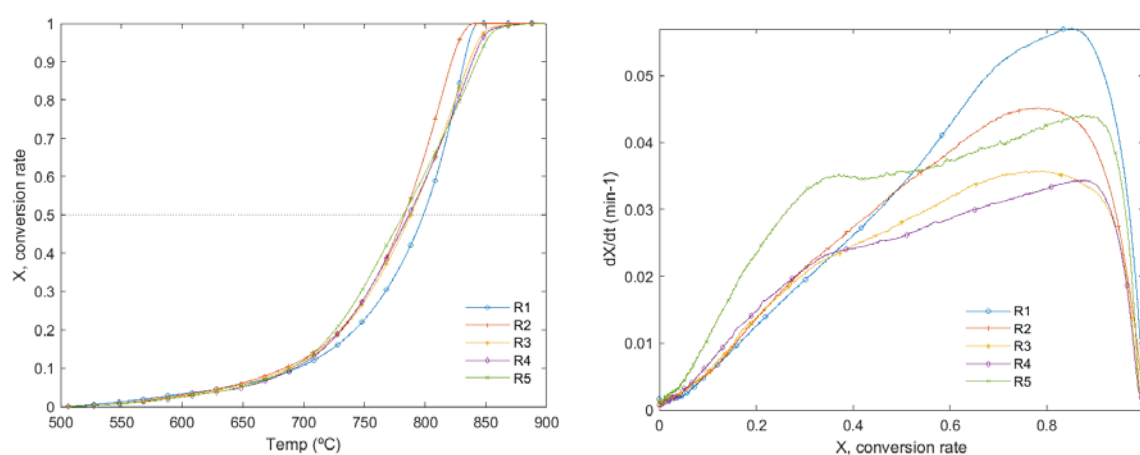


Fig. 2. Conversion vs temperature (left). Reaction rate vs conversion rate during the gasification stage (right) (100% CO₂, at 5 K/min heating rate).

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Hydrothermal carbonization of glucose in the presence of iron ions

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Keywords: *Hydrothermal carbonization, glucose, iron(II)sulfate, hydrochars, thin films*

Abstract

Hydrothermal carbonization (HTC) of biomass is a simple, low cost method especially suitable for wet biomass. HTC is performed by heating wet biomass or organic precursors in an aqueous medium under a self-generated pressure and part of the carbon forms as carbonized solids known as hydrochars. The hydrochars can be refined into renewable and sustainable functional materials with industrial applications in for example water treatment, CO₂ capture, gas separation, energy storage, and the production of platform chemicals [1]. HTC of simple sugars often leads to spherically shaped hydrochar particles, rich in carboxyl surface functional groups, and aldehydes. Metal salts and oxides catalyses the HTC reactions and results in the production of structurally modified hydrochars with specific industrial applications. HTC in the presence of inorganic salts and oxides is significantly influenced by pH, temperature, metal concentration [2].

In this study, we studied the effect of the concentration of iron(II) sulfate on the structural features of the hydrochars. As is shown in Figure 1, a) hydrochars with a gold shine was derived. A shiny piece of hydrochar was chosen for the cross sectional view. SEM images (figure. 1, b) show a 150 nm thin film, which is deposited on an assembly of spherically shaped hydrochars. Interestingly, the assembly of hydrochars is structured and the spherical particles grow in size with respect to the thin film membrane. We speculate that the thin film is polymerized chain of small particles of hydrochars and that the color is interference thin film colour as it was shown by XPS that there is no trace of iron in the thin film. To the best of our knowledge, the formation of golden like and structured hydrochars has not been reported in the open literature.

The importance of hydrochars derived in the catalytic presence of iron ions or iron oxides is that, first, a reproducible low cost method to derive thin membranes with potential application in water treatment, catalysis loading and gas separation seems to be possible. Second, the formation of the membrane on top of the spherical hydrochar particles may indicate aspects of the catalytic reaction networks being active.

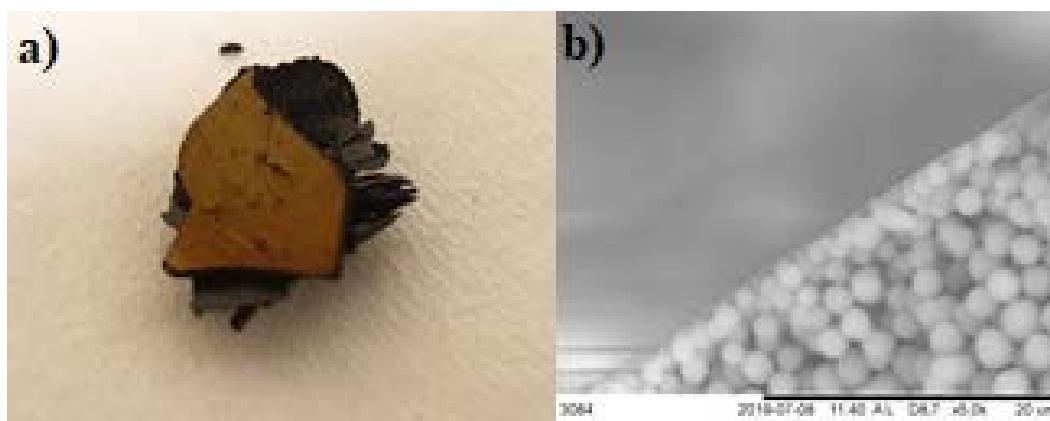


Fig. 1. a) Shiny piece of hydrochar b) SEM cross section of a piece of hydrochar, as shown in the cross section view.

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Biomass based carbon materials for gas storage and separation

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Keywords: biomass; hydrothermal carbonization, global warming, CO₂ adsorption

Abstract

Global warming is a matter of great concern around the world. With an increase of about 40% in the atmospheric concentration since the industrial revolution, CO₂ represents the primary cause of the greenhouse effect. The main sources of CO₂ are represented by human activities, contributing with more than 80% of the atmospheric CO₂ in urban areas.¹ Over the time, several technologies have been developed to decrease the CO₂ concentration, such as absorption using alkaline solvents, membrane-separation, conversion/adsorption using a wide range of adsorbents, like zeolites, metal organic frameworks and activated carbons.² But despite all the efforts devoted to minimizing it, recent studies reported an increase of CO₂ emission from 280ppm, in 1750, up to 406 ppm in 2017. Therefore, finding new ways to diminish the CO₂ content in the atmosphere is still a topic of great interest. Porous carbon materials have attracted a lot of attention, due to their multiple applications, such as catalysis, adsorption processes for water and air depollution, energy storage and production. In particular, CO₂ capture *via* physical adsorption represents an eco-friendly alternative to the traditional amine-based absorption processes.³ Herein we present the synthesis of porous carbon materials starting from different biomass precursors, such as palm date, guava seeds and winged beans. The bio-inspired adsorbents have been prepared *via* hydrothermal carbonisation (HTC) and have been used for CO₂ capture. Following the HTC, different activation methods have been employed in order to boost the porosity of the pristine carbons. The resulted materials have been characterized using different characterization techniques and have been tested for CO₂ adsorption. The N₂ sorption isotherms revealed the presence of porous carbons with large pore volume and considerable high surface area, in between 950 m²/g and 2800 m²/g. SEM micrographs were in good agreement with surface area measurements, showing the formation of porous carbon spheres. The preliminary tests, for CO₂ uptake, presented good adsorption capacities in STP (0°C and 1bar), reaching a maximum of about 5.47 mmol/g. Overall, the experimental results showed that HTC is a useful tool for the development of porous carbon materials derived from sustainable resources, such as biomass feedstock. The resulted hydrochar presented high potential for gas storage applications, with an increase in the adsorption activity after chemical activation.

Acknowledgement: This project has received funding from the European Union's Horizon 2020 research and innovation program under the Marie Skłodowska-Curie grant agreement No 721991.

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Macroscopic rods of self-assembled monodispersed colloidal hydrochar and related templated SiC and Cu₇Si₂

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Keywords: colloidal hydrochar, monodisperse, self-assembly, templating

Abstract

Self-aggregation of monodisperse particles of hydrochar (diameter 100 - 200 nm) was studied in relation to colloid chemistry, which is important for the use of the associated and macroscopically large colloidal structures for the production of other materials. One such example was explored. With the help of design of experiments, the hydrothermal synthesis of hydrochar particles from glucose was optimized so that highly monodisperse hydrochar particles were obtained. After purification by dialysis or centrifugation and precipitation / dissolution, these particles showed the expected electrostatic stability in dispersion. These dependencies applied to both pH conditions and ionic strength and were studied by analyzing the zeta potential and salt-induced precipitation and sedimentation. This type of hydrochar particles is negatively charged due to acid groups on the external surface. Macroscopically large and rod-like particles of hydrochar were formed by evaporation of water within glass or polypropylene vials when the dispersions were appropriately electrostatically stabilized (not at too low of a pH), and the pH could not be very high either. These large and rod-like particles consisted of closely packed smaller hydrochar particles and could be pyrolyzed into a carbon material without a qualitative change in the shape of the macroscopically sized rods or change in the shape of the underlying small particles. As an example of how these rod-like particles can be used to make other materials, we used them as templates for a reactive alloy. A Cu-Si alloy was melted and let to react and wet in-situ pyrolyzed hydrochar at 1300 °C, and composite of Cu₇Si₂-SiC/Carbon was formed, which later was calcined into a Cu₇Si₂-SiC material. The Si atoms reacted with the C atoms which in turn led to that the carbon particles were wetted by the reactive alloy. The shape of the carbon particles was maintained at the high temperatures used. Transmission, scanning electron microscopy, and X-ray diffraction were used to study the shape, composition, and structures of the formed materials. Further studies of monodisperse particles of hydrochar are justified from a perspective of colloidal chemistry and physics but also in relation to how self-aggregated particles can be used for the synthesis of materials other than Cu₇Si₂ and SiC. Studies of applications of the templated Cu₇Si₂ and SiC in, for example, catalysis may also be justified.

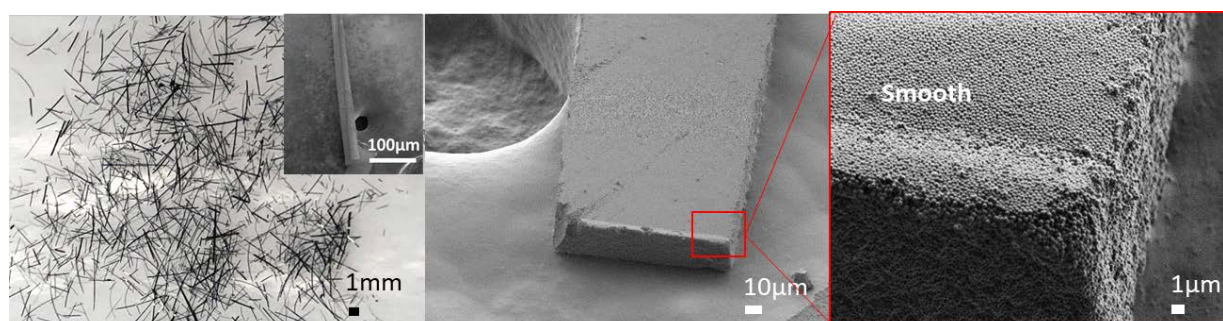


Fig. 1. a) Photograph and the insert SEM image display the rod morphology of the highly monodispersed colloidal hydrochar self-assembly b) SEM image shows the smooth surface and edge-cutting end of the self-assembly and c) Well-arranged particles on one of the smooth faces, and two rough faces of the self-assembly.

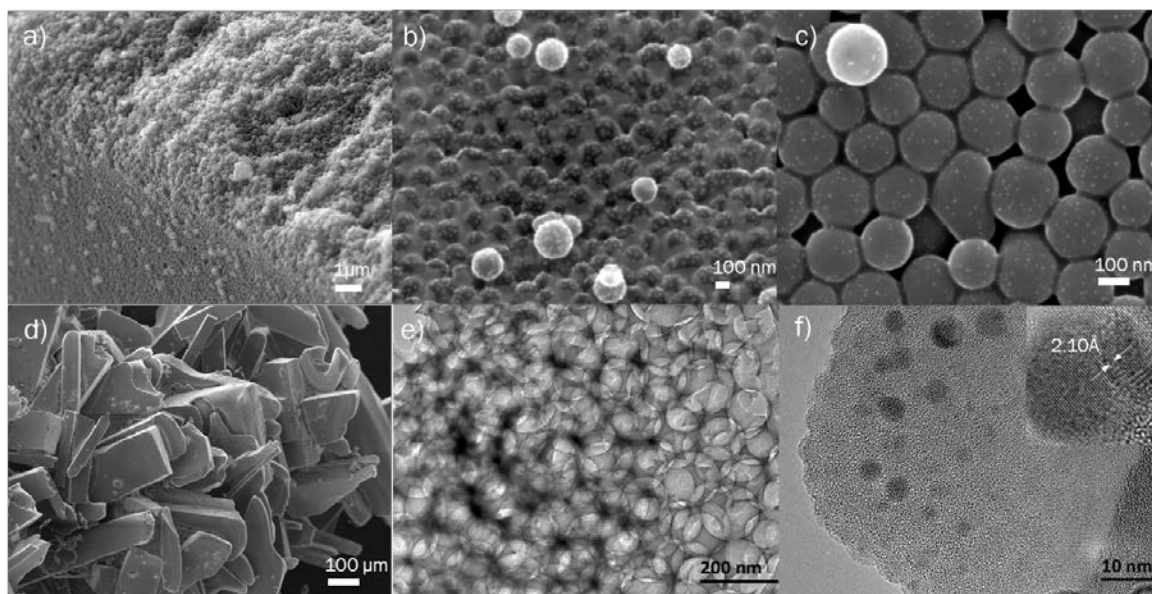


Fig. 2. a) b) and c) SEM images of sample SiC-Cu-1.5 which consisted of pyrolyzed hydrochar that had been reactively infiltrated with a Cu-Si alloy. d) SEM image of the calcined sample, SiC-Cu-1.5c, e) and f) TEM images of sample SiC-Cu-1.5c, and the insert is the HRTEM image of a copper particle observed in Si-Cu-1.5c. A d-CH0.5: alloy (mass) of 1:1.5 were used.

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Influence of slow pyrolysis conditions on the adsorption of organic dyes from water

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Keywords: *char, slow pyrolysis, auger reactor, adsorption, water decontamination.*

Abstract

The contamination of water by organic compounds such as dyes is very harmful for the environment and the biosphere, and it can be challenging to remove these contaminants, especially if concentrations are very low. Adsorption using porous materials such as activated carbons is an effective process for the removal of those contaminants, however, the production of these materials is often unsustainable. Therefore, there is a need to produce suitable adsorbent materials from more sustainable sources such as waste biomass and with less resource-consuming processes. Char, the carbonaceous solid material produced by pyrolysis, can be produced with suitable features for adsorption and therefore become a replacement for the current adsorbent options. Wheat straw was used as biomass feedstock in a slow pyrolysis process, producing char in a continuous manner inside a screw reactor (300 g/h). Process conditions such as pyrolysis temperature (400 to 600 °C), solid residence time (3 to 10 min), and utilization of carrier gas (none, N₂, or CO₂) were tested. Different feedstock pre-treatments were also investigated to study their influence on the solid products' properties and on their methylene blue adsorption performance. Pre-treatment consisted of varying moisture content (0.1, 50 or 75 wt.%), and wet impregnation with 0.1 or 1.0 M KOH solutions. The char products were characterized in terms of their proximate and ultimate analyses, surface chemical functionalities with FTIR, surface area, and pH (in H₂O suspension). Methylene blue adsorption tests were carried out using an initial dye concentration of 100 mg/L, adsorbent mass of 25 mg, operating temperature of 50 °C, and a 3 h contact time.

The adsorption performance decreased substantially for the chars produced at higher pyrolysis temperatures: the ones produced at 400 °C achieved up to 96 % of dye removal, while the ones produced at 500 and 600 °C obtained at most 78 and 65 % removal, respectively. This was connected to the greater proportion of surface functionalities present on the surface of the chars produced at lower temperatures, which was verified by FTIR analysis. For example, at a temperature of 600 °C, the solid products showed practically no IR manifestation in the region corresponding to carbonyl bond vibrations (C=O stretching, 1750-1650 cm⁻¹), with reductions in other IR regions as well. Analyses of the char's pH (in H₂O) found that the chars become more basic when produced at higher pyrolysis temperature, which can be related to the loss of chemical functionalities and increase in aromaticity on the surface. The increase in basicity led to poorer adsorption of the cationic dye from aqueous solution. The surface areas determined by nitrogen porosimetry were below 10 m²/g for all the produced chars, and so the adsorption mechanism was not attributed to interactions of the dye with the char's porosity. The adsorption performance showed different trends with solid residence time depending on the pyrolysis temperature applied. When the feedstock's moisture content was raised (50 and 75 wt.%), the adsorption performance suffered a slight improvement, for both pyrolysis temperatures of 400 and 600 °C. The chars produced at 400 °C with increased moisture contents had higher IR manifestation in some regions, mainly corresponding to C=C and C-H_n bond vibrations (1800-1300 cm⁻¹), and also C-O bond vibrations (1150-1050 cm⁻¹). These changes were not verified for the chars produced at 600 °C. The elemental analyses found that the chars produced at 400 °C with increased feedstock moisture content had higher oxygen proportion than the chars from feedstock with normal moisture content. This change did not occur for the chars produced at 600 °C, which corroborates the findings from FTIR. KOH impregnation of the feedstock led to solid products with even higher removal of the dye (up to 99 %), for the lowest concentration tested of 0.1 M KOH. A further increase in KOH concentration did not further improve the adsorption performance, which is hypothesized to be connected to the pH value and basicity of the chars, which became too high. The chars produced from slow pyrolysis experiments using a CO₂ atmosphere have not been tested for methylene blue adsorption. The effect of pre-treating the feedstock can thus lead to improved adsorption performance and to the possibility of tailoring char products for specific adsorbent applications.

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Production of biomass-derived activated carbons for bio-oil and biogas upgrading

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Keywords: Activated carbons, biochar, steam and dry reforming, biogas upgrading, K_2CO_3

Abstract

Thanks to their versatility to be adapted to specific applications (e.g., liquid purification, electrochemistry, soil remediation and catalysis) activated carbons are considered promising candidates to address environmental issues related to global warming and pollution. Nevertheless, the current main drawback is that the production of activated carbons is still partly based on fossil fuels, which do not meet sustainability criteria [1,2]. An alternative is the use of biochar, an organic charred solid obtained from the thermal degradation of biomass, as a promising precursor of advanced carbon materials. Depending on the producing conditions, the pristine biochar does not have the appropriate textural properties, since its porosity is mainly restricted to narrow micropores. Thus, an activation step is required to expand the initial surface area and pore size distribution.

The main advantage of biochar activation process is that it is possible to tune the textural features of the starting biochar by properly adjusting the activation conditions, mainly temperature, type and/or concentration of activation agent, as well as pressure. One of the most interesting fields of application of activated biochars is the upgrading of the pyrolysis vapors, usually performed via steam or dry reforming [3,4], in which the activated biochar is employed as catalyst support or as catalyst itself. Keeping in mind all the above, the main objective of this study was to perform a preliminary investigation about the effects of several activation conditions on the textural properties and the catalytic activity of the resulting activated biochars. Firstly, chemical activation with K_2CO_3 was performed at different pressures (0.10–1.00 MPa) and mass impregnation ratios (1:1–3:1). Physical activation with CO_2 was then performed at different temperatures (700–850 °C) and pressures (0.10–1.00 MPa). To objectively assess the effects of the activation conditions on the textural properties (specific area and pores volume) of activated biochars, a two-level factorial design of experiments (with two factors and three replicates at the center point) was adopted for both chemical and physical activations. For chemical activation, the analyzed factors were the absolute pressure and the impregnation ratio of K_2CO_3 to raw biochar, whereas in the case of physical activation, the temperature and the absolute pressure were the studied factors. To the best of our knowledge, even though both activation procedures are widely reported in the literature, a statistical approach of the influence of the activating parameters was never reported so far. The most promising activated biochars were finally tested as catalysts and as support for a metallic active phase for steam and dry reforming of pyrolysis oil under different conditions of temperature and residence time. Their performance was evaluated in terms of conversion of liquid into gas, product selectivity and resistance to deactivation. Besides their employment in catalysis processes, activated carbons are also widely used as adsorbent in biogas cleaning applications. In particular, among all the several methods for biogas upgrading, pressure swing adsorption (PSA) is the most promising due to its relatively low cost and energy consumption [5]. Therefore, the last aim of the present study was to assess the performance in pressure swing CO_2 adsorption under dynamic conditions of an adsorbent bed composed of the previously produced activated carbons.

Acknowledgement: This project has received funding from the European Union's Horizon 2020 research and innovation program under the Marie Skłodowska-Curie grant agreement No 721991.

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Heterogeneous transformation of CO₂ to methanol – Structural study of the support

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Keywords: *heterogeneous, catalysis, methanol, adsorption, environmental*

Abstract

Carbon dioxide is emitted to the atmosphere as a side product in several industrial processes and, seeing that global warming has become such a pressing matter, it would be best if it could instead be captured and stored. Or, potentially even better, captured and transformed in order to give it a use which could even lead to negative emissions of CO₂. In this project, we research the prospect of capturing CO₂ by chemisorption on amine-rich sorbents and subsequently transforming it to CH₃OH by catalytic hydrogenation. Methanol can be used in many different ways, a main one being as fuel. Amongst its advantages we find that it is easier to transport and store than CH₄ in regions that lack natural gas pipelines and it can be used as an additive directly with other liquid fuels.

In this respect, commercially available mesoporous silica has been modified with aminated polymers and then a homogeneous ruthenium catalyst has been immobilised on it. These materials have two main functions: one is the capturing of CO₂ (the aminated polymer part is the one involved in this process) and the other one is the catalytic transformation of this pre-concentrated CO₂ (where the ruthenium will play its part). Structural chemistry studies of these modified supports have been performed using various techniques, mainly solid-state ¹³C NMR, in order to understand how the CO₂ is being captured and if it can be tuned for optimising the transformation process. Along the structural studies, the activity of these materials has also been tested using a homemade batch reactor set-up in which the hydrogenation occurs. The final prospect after finding a working system is the implementation of biomass-derived supports for a more renewable cycle.

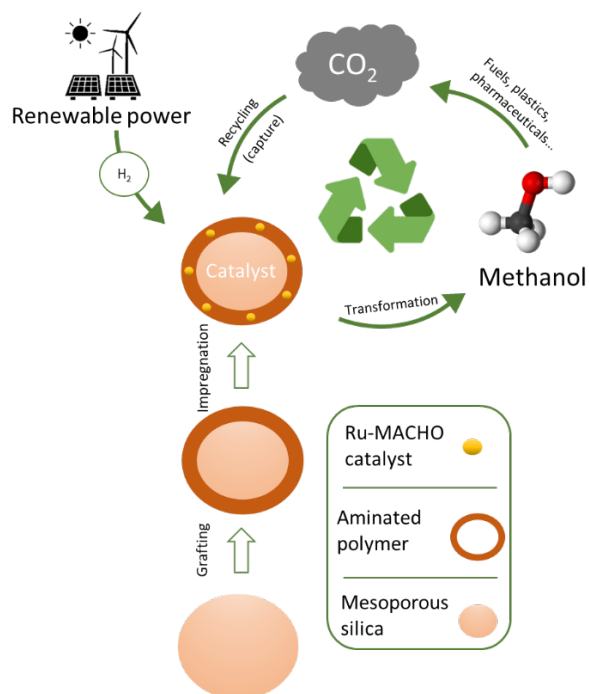


Fig. 1. Graphic representation of the aim of the project.

Acknowledgement: This project has received funding from the European Union's Horizon 2020 research and innovation program under the Marie Skłodowska-Curie grant agreement No 721991.

Sequential biochar systems

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Keywords: *Biochar systems, Recycling, Wastewater filtration, Gas filtration, Biochar economics*

Abstract

The last decade saw an immense increase in biochar research and it is now feasible to enhance the efficiency of biochar by deliberately tailoring its properties for specific applications. However, engineered biochars still face harsh competition from traditional materials such as activated carbons and are yet to be seen as being economically competitive. While there have been significant advancements in improving specific biochar properties, less attention has been given to the development of comprehensive biochar systems to maximize the economic value of biochar beyond single use applications. We argue that the perception of biochar solely as a material is a rather narrow perspective on its multiple characteristics. In contrast, the view of biochar as a carrier for environmental services enables a more flexible conceptualization of biochar systems. We developed the concept of sequential biochar systems to simultaneously maximize economic competitiveness and environmental gain by utilizing a stepwise sequence of different applications. A recycling intervention between each step allows for the properties of the material to be manipulated and optimized for the subsequent application. This essentially reverses the idea of engineering biochar for certain applications as each application phase requires tailoring of a certain specific characteristic. The economic focus of our concept is based on distributing initial production costs over several users, and associated risks over several applications. By focusing on a service-based approach, we illustrate how a sequential biochar system can efficiently reduce the biochar price for users without lowering the actual production and feedstock costs. We present results of an experimental validation of the concept based on a sequence of wastewater and gas filtration applications which highlights the potential to increase the revenue of biochar over its lifecycle. Additionally, the results show that while designing biochar for certain applications, a simultaneous focus on both the application as well as the recycling of the material can give a more comprehensive picture of the overall requirements for further optimization of biochar systems.

Acknowledgement: This project has received funding from the European Union's Horizon 2020 research and innovation program under the Marie Skłodowska-Curie grant agreement No 721991.

Aqueous phase hydrogenolysis of glycerol over Ni/AC catalysts

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Keywords: *glycerol, in situ hydrogen, Ni/AC catalysts, fixed bed reactor*

Abstract

Nowadays, the production of biodiesel originates glycerol as by-product, for every 10 tons of biodiesel generates around 1 ton of glycerol. The use of glycerol has several advantages for instance, the benefits of its valorisation contribute the economic viability of biodiesel industries [1]. Considering this, several processes have been investigated to promote the glycerol valorisation [1,2]. Hence, the challenge of this project is the glycerol conversion to value-added products.

The present work studied aqueous phase hydrogenolysis (APH) of glycerol over Ni/AC catalysts without external hydrogen addition, where AC is a commercial activated carbon. Three catalysts based on Ni/AC were prepared through incipient wetness impregnation method by changing the Ni content (5%, 10% and 15%). These catalysts were tested during 3 h at 34 absolute bar and 227 °C. The fresh and used catalysts were characterized by several method such as ICP-OES, N₂-physisorption, H₂-TPR, among others. This work will examine the effect of the Ni content on the physicochemical characteristics of Ni/AC catalysts and during the APH of glycerol. Fig. 1 shows the biodiesel production cycling towards value-added products from glycerol as by-product.

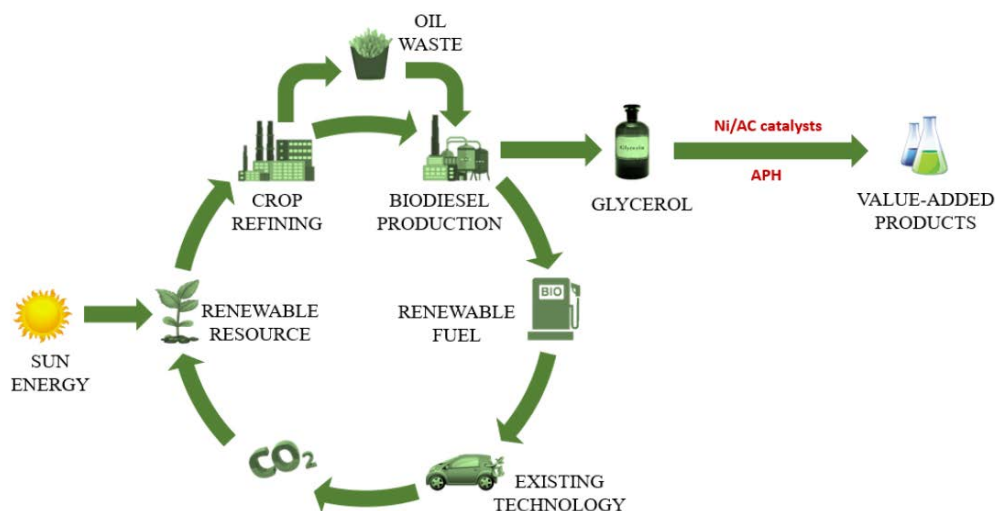


Fig. 1. Biodiesel production cycling towards value-added products from glycerol as by-product.

Acknowledgements: The authors wish to express their gratitude to the AEI/FEDER, UE (project CTQ2017-86893-R). The authors acknowledge the funding from the Aragón Government (ref. T22_20R), co-funded by FEDER 2014-2020 “Construyendo Europa desde Aragón”.

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Adsorption of propylene glycol on activated carbon: kinetics experiments

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Keywords: *Activated carbon, Propylene glycol, kinetics, adsorption, glycerol*

Abstract

Propylene glycol (PG) is an increasing demanded compound due to its antifreeze properties, applications in food and pharmaceutical industry and as raw material for unsaturated polyester resins manufacture [1]. Its production by catalytic pressure aqueous processing of glycerol is being investigated by using glycerol produced in biodiesel production process, decreasing its production cost [2, 3]. Separation from the exit stream is critical due to compound's high dilution. Due to all this, adsorption by Norit GAC 1240 W activated carbon is studied as a sustainable separation process. Batch adsorption experiments were performed to analyse the adsorption kinetics of PG from aqueous solutions by activated carbon. This study is needed in perspectives of conducting fixed-bed experiments, providing information about the adsorption mechanism and rate-controlling step in adsorption process enabling the prediction of the breakthrough curves. The experiments were conducted in 50 mL beakers containing 14 mL aqueous solution with PG at concentrations of 10, 50 or 100 g/L. Activated carbon previously dried was added to the mixture and stirred using an orbital shaker at 160 rpm. As equilibrium is reached in less than 30 minutes, solutions were filtered and analysed in a Total Organic Carbon Analyser at different times in order to have a good resolution in the results. In literature there is a non-agreement about organic compounds kinetics on activated carbon, finding that, despite many studies find pseudo-second order model as the most accurate to their experimental data, some find other models as the most accurate. Thus, the experimental data obtained were evaluated by pseudo-second order model, Weber-Morris intraparticle diffusion model, and linear driving force model [4-6]. As a result, pseudo-second order model was found as the model which better fits the experimental data, having a RR^2 value of 0.997 and a rate constant value of 0.56 kg AC/(min mol PG) and an equilibrium concentration value of 0.775 mol PG/ kg AC at 10 g/L concentration. As concentration is raised, diffusion models are less accurate with the experimental points, meanwhile pseudo-second order model keeps a RR^2 value higher than 0.99. However, it was also found that Weber-Morris intraparticle diffusion model, and linear driving force model had also a good RR^2 value (higher than 0.94 in both models) at 10 g/L, implying that PG adsorption onto activated carbon is probably limited by both film and intraparticle diffusion, especially at low concentrations [5].

Acknowledgements: The authors wish to express their gratitude to the AEI/FEDER, UE (project CTQ2017-86893-R). The authors acknowledge the funding from the Aragón Government (ref. T22_20R), co-funded by FEDER 2014-2020 "Construyendo Europa desde Aragón".

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Hydrothermal carbon as metal-free catalyst and electrocatalyst

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Keywords: hydrothermal carbon, metal-free, catalyst, electrocatalyst

Abstract

Carbon materials have been prepared by hydrothermal carbonization of both glucose and cellulose precursor under different temperatures and times of hydrothermal treatment. To favor the hydrolysis of cellulose also diluted HCl was added during synthesis. [1] The surface area of cellulose derived materials depended very much on the hydrothermal conditions of temperature, HCl concentration and time of hydrothermal treatment. For carbons derived from glucose or from cellulose under the milder conditions, lower values of surface area are attained (~ 143 m²/g). The surface area is also low for the harsher conditions of cellulose treatment (215 °C and 5M HCl). The surface area is thus maximized for cellulose derived carbons treated under conditions of intermediate strength, as e.g. 195 °C, HCl 2M, 40 h. The morphology of carbons derived from glucose and cellulose is very different (Figure 1). Glucose forms spheres of regular size about ~ 500 nm diameter (Figure 1a) while cellulose exhibits a mixture of fibrous forms and spheres (Figure 1b), strongly depending on the preparation conditions. In a second step, the carbon materials were treated with sulfuric acid at different temperatures (100-150°C), ending up in the covalent attachment of sulfonic groups and the carbon oxidation creating acidic oxygenated surface groups such as carboxylic groups. The sulfonation of cellulose led to higher values of sulfonic group loading but lower total acidity (Table 1). The sulfonated carbons have been used as heterogeneous acid catalyst in several reactions such as esterification of palmitic acid with methanol [2] or acetalization of glycerol to solketal [3]. The different carbons led to different TOF values, in spite of the identical nature of the sulfonic sites, being the less active cellulose-carbons prepared for the longer hydrothermal treatment times.

In a different application field, hydrothermal carbons were also doped with S and N by introducing thiophene and pyrrolic precursors, respectively. The doped carbons were tested as metal-free electrocatalyst in the oxygen reduction reaction, achieving very high selectivity to the production of water peroxide [4].

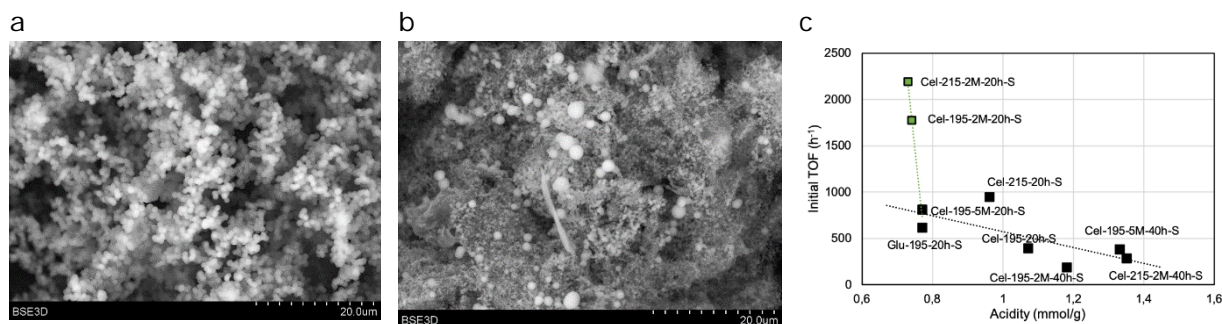


Fig. 1. SEM images of hydrothermal carbons prepared from glucose (a) and from cellulose (b). (c) Initial TOF in acetalization of glycerol.

Table 1. Characterization and preparation conditions of sulfonated hydrothermal carbon

Entry	Precursor	Temp. (°C)	Time (h)	Additive	S.Area CO ₂ (m ² /g)	SO ₃ H (mmol/g)	Total acidity (mmol/g)
1	Glucose	195	20	-	142	0.77	5.4
2	Cellulose	195	20	HCl 2M	208	1.07	4.4
	Cellulose	195	40	HCl 2M	386	1.18	4.3
3	Cellulose	215	20	HCl 2M	279	0.76	2.4
4	Cellulose	215	20	HCl 5M	104	-	-

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Synthesis of porous carbon materials from nanocellulose

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Keywords: nanocellulose, pyrolysis, hierarchical porous carbon

Abstract

Porous carbon materials with a hierarchical structure encompassing macro, meso- and micropores are highly desired for absorption and catalytic applications.¹ They are usually prepared by physical or chemical activation of biomass precursors requiring high temperatures and chemicals. This method does not allow a precise control over the porous structure. Starting from synthetic precursors such as resorcinol and formaldehyde, polymeric aerogels are produced, which can be converted into mesoporous-microporous carbon by pyrolysis at high temperature.² However, these synthetic precursors are not natural and expensive to prepare. Here, we have tackled the preparation of hierarchical porous carbons using nanocellulose as building blocks. Nanocellulose was synthesized as one of the two types of crystalline allomorphs as described previously.³ We have prepared different nanocellulose aerogels by previous gelation and subsequent freeze drying. The aerogels have been pyrolyzed under different temperatures. We have characterized the texture of carbon aerogel produced by N₂ physisorption and SEM, and the composition unraveled by elemental analysis. At the end, we have disclosed how the different pyrolysis parameters affect the carbon yield and porous texture. The hierarchical porous carbons have excellent prospects to be used as metal-free catalyst or catalyst support.

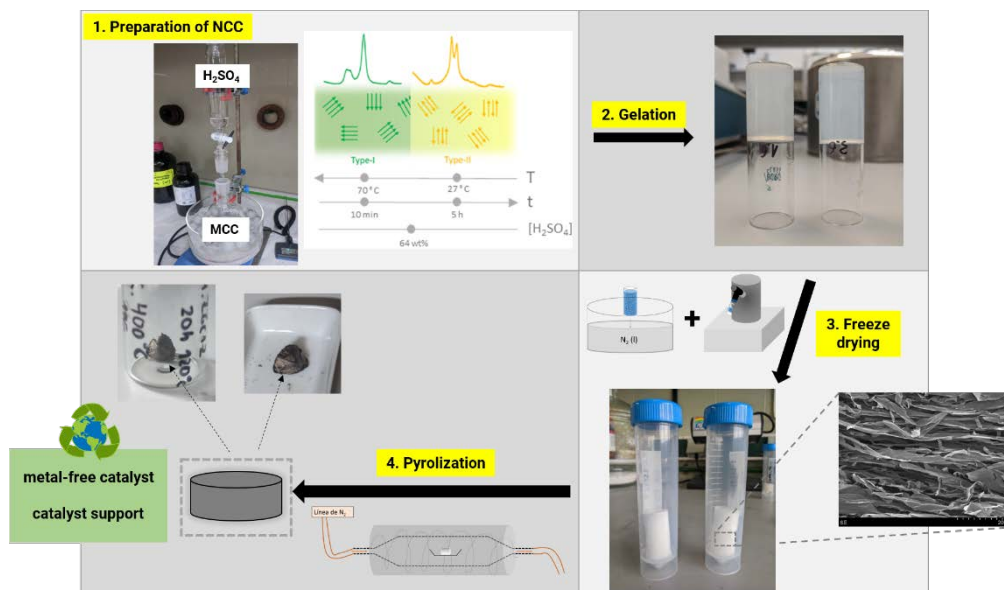


Fig. 1. Scheme of the preparation of the pyrolyzed nanocellulose aerogels.

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Turkish hazelnut shells as precursor of sustainable CO₂ adsorbent

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Keywords: CO₂ capture, activated carbon, biomass, adsorption

Abstract

The carbon dioxide (CO₂) capture and storage are indispensable for reducing greenhouse gas emissions. Post-combustion capture is one of the most promising technologies to capture CO₂ because it can be retrofitted to any facility with an acceptable footprint. Adsorption-based technologies are appealing for CO₂ capture mainly due to the ease of the regeneration and the benign character of solid sorbents. To date, the greatest research efforts have aimed at improving efficient adsorbents with higher working capacity for CO₂, higher selectivity, and better impurity tolerance [1]. Among the alternative methodologies in adsorbent production, valorization of agricultural residues is an efficient way in terms of a sustainable circular economy. Besides, valorizing the agricultural residues in porous carbon materials contributes to the reduction of the overall cost of carbon capture since they are ubiquitous and inherently of low-cost. It may also provide a further benefit for more cost-effective waste management [2]. In post-combustion CO₂ capture literature, there are many studies that address the use of waste materials as precursors of adsorbents; the current study puts for the first time on evaluating the performance of hazelnut shells. The targets are to develop an activated carbon from hazelnut shells with suitable textural development in terms of microporosity and surface area to enhance the adsorption capacity, and to investigate its potential use for CO₂ capture under post-combustion capture conditions with particular emphasis on the thermal energy requirements for regeneration.

The hazelnut shells-based activated carbon (HS-AC) was produced by single-step physical activation with CO₂ as activating agent. Textural characterization of the HS-AC was accomplished through N₂ adsorption at -196 °C and CO₂ adsorption at 0 °C. Thereby, the activation with CO₂ led to the development of a highly microporous carbon from hazelnut shells. The pure CO₂ and N₂ adsorption isotherms were also measured at temperatures of 30, 50, and 70 °C, and at pressures up to 120 kPa. The resulting data were fitted with the temperature-dependent Toth and Sips models. The pure component isotherm parameters were used to predict the binary adsorption data using the ideal adsorbed solution theory (IAST). The results obtained by IAST showed that at post-combustion capture conditions, namely low CO₂ partial pressure and low temperature, adding N₂ gas to the mixture does not change the CO₂ uptake performance of HS-AC significantly. To determine the pore size distribution of the HS-AC sample, CO₂ and N₂ isotherms were analyzed by the NLDFT and QSDFT models, respectively, and a major contribution of pores below 0.7 nm was confirmed. According to the NLDFT, 52% of the total narrow micropore volume was comprised of pores with sizes below 0.36 nm, which is desirable for CO₂ capture under typical post-combustion conditions. The isosteric heats of adsorption of CO₂ and N₂ on the HS-AC sample were calculated as 28 kJ/mol and 17 kJ/mol, respectively, by fitting the Sips equation to the pure adsorption isotherms and applying the Clausius–Clapeyron equation. The isosteric heat values calculated imply a highly microporous structure of adsorbent—in agreement with the pore size distribution analysis—and stronger interaction of CO₂ with HS-AC than that of N₂. The thermal energy requirement was calculated by summation of the sensible heat required to heat the adsorbent and the isosteric heat of desorption, assuming a temperature swing adsorption process. Considering hard coal combustion for the production of the thermal energy required for regeneration, the net CO₂ uptake of HS-AC was calculated to be between 0.016 – 0.064 kg CO₂/kg adsorbent; which in turn would result in energy savings of up to 677 kJ/kg adsorbent. The dynamic performance of the HS-AC was evaluated with breakthrough experiments feeding a CO₂/N₂ gas mixture, representative of post-combustion flue gas, to a fixed-bed adsorption set-up and the results revealed that HS-AC has fast adsorption and desorption kinetics, which is very crucial in rapid swing adsorption processes. Future research will address the adsorption performance of HS-AC in adsorption-desorption cycles that will be optimized by designed accordingly and where the results obtained in the current study will be the cornerstone.

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Carbon-nanoparticles hybrids as electrodes in electrochemical energy storage systems

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Keywords: *Energy storage, nanomaterials, non-toxic*

Abstract

Energy storage systems will play an essential role in reducing fossil fuel consumption and greenhouse gas emissions by providing solutions to store energy produced from renewable sources and implement electrical mobility.

Graphite is the conventional material used to fabricate standard rechargeable batteries and supercapacitors. Nonetheless, it has some limitations such as limited intrinsic capacity, lithium-ion insertion capacity, and specific capacitance. Additionally, graphite, together with lithium and cobalt, characteristic materials used in Li-ion batteries, are limited resources, especially since Europe depends on importation and external supply.

In this sense, UNIZAR is leading the European project NOEL: Innovative Nanostructured Electrodes for Energy Storage Concepts preparing new functionalized carbons with non-toxic nanoparticles to be used as electrode materials for batteries and supercapacitors, in collaboration with the National Institute of Chemistry (NIC) in Slovenia and the Poznan University of Technology (PUT), Poland. The presence of nanoparticles on the carbon surface can bring interesting features like higher surface/volume ratio, which can increase the contact area between electrode and electrolyte, more ion adsorption sites, smaller distances for ion or electron transport and better accommodation of the mechanical strain and structural distortion [1].

Novel heteroatom doped microporous and mesoporous carbons decorated with nanoparticles have been prepared for their use as electrodes in batteries and supercapacitors.

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Studying carbons derived from urban pruning waste as additives in Li-ion battery anodes

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Keywords: *pruning, waste, carbon, anode, battery*

Abstract

The research of anodic materials which could be substituted to graphite and improve its properties leads to a considerable effort for creating novel carbons. Most of carbon materials tested as carbon anodes in Li-ion batteries are obtained from precursors, which are, either, directly or indirectly related to the petroleum products or fossil fuels such as graphite and most the preparation methods rely on special equipment, special reagents or complex process control. Previous results have shown that the use of carbon materials obtained from waste as additives in Li-ion anodes is a promising alternative to the cyclability of Li-ion cells [1]. However, further studies are needed to understand the role of the different properties of biocarbons as additives in Li-ion batteries.

For synthesizing novel carbon material as a viable product, it is necessary to select a precursor, which is not derived from fossil fuels or related to petroleum products and with high availability and abundance in the earth. One interesting waste source for that purpose is urban pruning waste. Each year, different types of trees must be pruned to remove old, dead or broken leaves producing a huge amount of tons of waste in the cities. These large amounts of waste can be converted into biocarbons, which is a high-value material with energy and environmental applications [2].

In this work, biocarbons obtained from pruning waste with different microporosity have been developed in order to study the effect of this type of porosity on the role of biocarbons as additives in graphite based lithium-ion battery anodes.

For that, in the first step different properties of pruning waste first characterized in terms of volatile matter, ash content and water and elemental and inorganic composition.

Previously to biocarbons production the thermal behavior of pruning waste under different carbonization and activation conditions were performed by thermogravimetric analysis. From this study, the optimum conditions were determined for experimental carbon production processes.

After that, a carbonization process was performed in order to obtain a biocarbon which was physically activated with CO₂ under different activation times in order to produce carbons with different microporosity.

Different properties of the carbons obtained were measured, such as porosity by N₂ adsorption isotherms at -196 °C, density and ash content. Finally, the carbons obtained were processed for their integration as additives in graphite based anodes and were electrochemically characterized.

The results obtained shows that the carbonization/activation process of pruning waste gives a series of micro-mesoporous carbons with the same mesoporosity but with different micropores volume and pore size distribution making them suitable for the study of the role of microporosity of these additives on the performance of anode materials. The use of these obtained materials as an additive in carbon anode materials show a clear effect of the micropore volume and pore size distribution on the processing and performance of Li-ion anode materials.

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Biomass Based Activated Nitrogen Doped Carbons for Energy Applications

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Keywords: *biomass, activated carbons, porous structure, fuel cells, supercapacitors*

Abstract

The goal of this research is synthesis of nanoporous activated carbons with high specific surface on the base of wood charcoal and Kraft pulping residues, their structural modification with nitrogen, and determination of nitrogen content depending on synthesis conditions and carbonaceous precursor. The obtained carbons were tested as candidates for application as oxygen reduction (ORR) cathode in the low-temperature fuel cells and as electrodes in supercapacitors.

Alder wood char, cellulose, black liquor and fine cellulose sludge were used as precursors. Activated carbons (AC) were obtained using chemical activation method with NaOH at 700 °C in argon. Nitrogen was introduced into AC using DCDA solution in DMF, doping was performed at 800 °C for 1 hour in argon. The following tests were performed: porosity (liquid nitrogen adsorption at 77K), elemental composition, XPS, Raman spectroscopy, RDE electrochemical measurements, cyclic voltammetry, impedance spectroscopy.

It is demonstrated that content of introduced nitrogen depends on oxygen content in the structure of carbonaceous precursor. The ORR activity of the carbon materials in the case of activated doped wood char and black liquor was comparable with commercial 20% Pt/C catalyst. Electrocatalytic properties of the synthesized N-doped wood-derived carbon catalysts may be associated with the highly developed surface area, micro- and mesoporosity, as well as structural qualities of the biomass based carbon materials, high percentage of pyridinic nitrogen and lack of stacking defects of graphene layers.

Application of above mentioned carbons as electrodes in supercapacitors was tested in TEA-TFB /acetonitrile electrolyte in the potential range up to 4V. The systems have shown high gravimetric capacitance 180F/g and good stability.

The results of this study prove that nitrogen doped activated carbons on the base of biomass are promising materials for application in fuel elements for oxygen reduction, and are excellent candidates as electrodes in supercapacitors.

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Biochar from greenhouse waste: Production, characterization and evaluation for its potential use in the horticultural growing media

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Keywords: *Biochar production, co-pyrolysis, plastic, biochar characterization, growing media*

Abstract

Protected agriculture plays a vital role in increasing productivity. Thus, farmers are increasingly practicing greenhouse agriculture. As a result, substantial amount of biomass waste mixed with plastics are being generated; i.e., spent growing media wrapped with plastics (SGP). Separating plastics out of the organic waste further complicates its treatment. Introducing a solid product (i.e., char) valorized out of this waste, which could be used as a growing medium ingredient back in the greenhouse agriculture, benefits the farmers as well as the environment due to waste valorization. Within this context, the potential of co-pyrolysis to valorize SGP waste was examined in this study. The focus was on the solid product obtained through slow co-pyrolysis, which is char. In a first experiment, biochars were produced through co-pyrolysis of plastic grow bags and spent growing medium waste in different ratios using a retort type mini pyrolysis set-up to identify the impact of the low level of plastic incorporation into the feedstock material on biochar properties. Then, biochars were produced through co-pyrolysis of biomass and plastics under different pyrolysis production temperatures using a bench-scale pyrolysis-batch unit at UKBRC to identify the impact of production conditions on biochar physicochemical properties. After initial screening, biochars were produced at a larger scale using the pilot-scale pyrolysis-continuous unit at UKBRC using SGP at 550 °C. These biochars were used to assess their potential as a substitute for peat use in horticultural growing media. Produced biochar samples were characterized for elemental (C, H, N, S, nutrients, and potentially toxic elements), proximate analysis, thermogravimetric analysis, FT-IR, and phytotoxicity. In order to assess the potential of produced biochars to substitute peat in horticultural growing media, seven growing medium formulations were prepared using peat, perlite, and biochar in different ratios. Formulated growing mediums were characterized in terms of physicochemical properties such as particle size distribution, bulk density, water-holding capacity, air-filled porosity, pH, EC, and nutrient contents. Phytotoxicity of formulated mediums was assessed through a germination assay. Then, a plant growth experiment was carried out to assess the impact of formulated growing mediums on flower quality and plant growth parameters of Marigold. According to the results obtained, the inclusion of biochar significantly increased plant growth parameters compared to peat and perlite containing control media. Results obtained from this study suggest that spent growing medium waste together with plastic grow bags offer great potential as a feedstock for biochar production and inclusion of biochar had positive effects on plant germination and growth that might compete with the control. In terms of technical performance, biochar could effectively replace 23% to 35% of use in horticultural growing media without compromising growth performance. The findings of this study will be beneficial for commercial growers to valorize their spent growing media waste together with plastic grow bags while reducing the harmful impact of plastics on the environment. Moreover, it will help to reduce the pressure on peatlands due to horticultural extraction of peat and greenhouse gas emissions associated with degraded peatlands.

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Role of biochar in the implementation of a phytomanagement strategy on soils presenting polymetallic pollution

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Keywords: Biochar, Phytomanagement, Metal(loid)s, Mining technosol.

Abstract

Soil contamination is an important issue worldwide, particularly the pollution by metals and metalloids since they are not degradable and accumulate in soils for long period of time. Moreover, metal(loid) polluted soils often lack vegetation, due to extreme conditions (acidic pH, low nutrient and organic matter content), and thus are subjected to wind erosion and water leaching, endangering surrounding areas. In order to remediate such polluted soils, phytomanagement process can be applied. This process is defined as the manipulation of the soil-plant system in order to recover or stabilize the metal(loid)s and produce biomass of economic value [1]. The success of phytomanagement will depend on the amendment and plant selected. In phytomanagement, biochar, a carbon based amendment, has shown good results in term of soil condition amelioration and stabilization of metal(loid)s [2]. Such amelioration allowed plant establishment and growth. However, the benefits will depend on the biochar origin and characteristics; In order to have an economic value of the remediation process, tree species, such as *Salix*, which produce high biomass in short time, are a good option. Previous studies showed that, on an amended contaminated soil, *Salix* were able to grow and accumulate metal(loid)s mainly in their roots, allowing the utilization of its aerial biomass [3, 4].

with the goal of remediation a former mine technosol, highly contaminated by arsenic and lead, using phytomanagement, laboratory mesocosm experiments were set up in order to determine the most appropriate biochar and plant species. Biochars of different feedstock origin and harboring diverse particle size were tested [5]. In addition, the effect of the plant part used for biochar production was evaluated. Several *Salicaceae* species were also tested. In *fine*, a biochar made from hardwood biomass and having a particle size of 0.5-1 mm was applied to the field for an *in situ* experiment, at a rate of 2% (w:w) and five willow species were implanted, *Salix purpurea*, *Salix triandra*, *Salix alba*, *Salix viminalis*, and an native *Salix*. Soil samples were taken before and after biochar application and after six months, for physico-chemical analysis. Moreover, microscopic analysis were realized on the samples in order to study the localization of the metal(loid)s. Plants were monitored for metal(loid) accumulation. Results showed that biochar increased soil pH, organic matter content and nutrient availability, and immobilized Pb. The microscopic analysis showed that part of the Pb was immobilized on the biochar surface as $PbCO_3$ [6]. Regarding the plants, *Salix triandra* showed the best biomass production, with lower Pb concentration in the leaves. The evaluation of the arsenic distribution showed a more complex behavior, which will be explained. This *in situ* experiment will be monitored for several years to assess long-term biochar effect.

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Biochar from agro residues in adsorption tests for water treatment

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Keywords: biochar, flax shives, bark, biochar production and characterization, adsorption

Abstract

Biochar is considered as a complementary, cheaper alternative material for commercial active carbon with a lower environmental impact when produced from locally sourced agriculture residues. Numerous studies are on-going, demonstrating the adsorption capacities of various biochars towards a wide range of pollutants (1).

This study explores the potential of biochar from bark and flax shives (the woody core in flax-grasses used for fibers) as an adsorbent for medicine and pesticide residues among other pollutants. The biochars are produced in a co-production process with bio-energy in an auger pyrolysis unit at 400 and 670°C under gasification conditions using a mixture of nitrogen and steam. A series of adsorption tests was carried out, to assess the potential of removing pollutants from water by biochar as a sorbent. A first series of experiments were done using Carbamazepine, as an example for a medicine present in waste water and on Methylene Blue, which is a medicine, a dye and a substance often used to characterize the adsorption potential of materials. Concentrations of Carbamazepine used in water ranged from 1 to 10 mg/L and concentration of Methylene Blue in water ranged from 1 to 20 mg/L. The adsorption equilibrium was represented with Langmuir and Freundlich isotherm models. The adsorption of pollutants on both biochars followed the Langmuir isotherm model ($R = 0.99$). Maximum adsorption values for q_m reached 0.8 and 1.5 mg/g on bark and flax biochar respectively for carbamazepine and 4 and 7.5 mg/g on bark and flax biochar respectively for methylene blue. Figures 1 and 2 show the results on the equilibrium data and removal efficiencies for the tested biochars on Carbamazepine. Biochars produced at 670 C showed the higher adsorption values, indicating the larger surface area of the biochar is important. The flax shives showed much higher adsorption capacities than the bark biochars for both temperature levels. The surface chemistry characterization of the biochars, before and after the adsorption tests is ongoing and will be presented. Biochar obtained from flax shives seems like a promising alternative for active carbon as a sorbent for pollutants found in wastewater and stormwater. Further optimization of the biochar is needed to increase the potential.

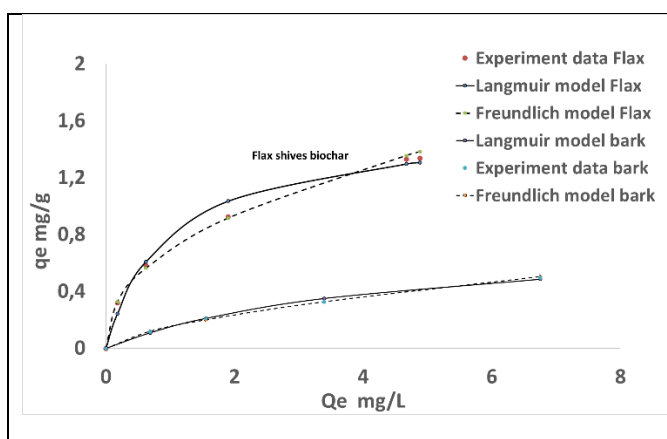


Fig. 1. Adsorption equilibrium for the biochars

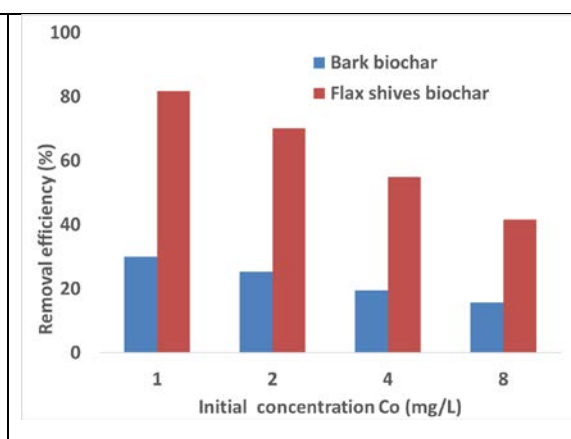


Fig. 2. Adsorption efficiency of the biochars for Carbamazepine

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Examining samarium sorption in biochars and carbon-rich materials for water remediation: batch vs. continuous-flow methods

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Keywords: Biochar, activated carbon, samarium, sorption, water remediation

Abstract

Batch and continuous-flow experiments were used to assess the viability of using carbon-rich materials as sorbents for the removal of samarium (Sm) from aqueous solutions. Biochars derived from castor meal (CM); eucalyptus forest residues (CE); sugarcane bagasse (SB); and green coconut pericarp and charcoal fines (CF) were examined and compared with two commercial activated carbons (AC1, AC2). The main aim was to recommend the most suitable materials for the removal of rare earth elements (REE), here represented by Sm, from contaminated waters, and to suggest the best laboratory approach to rapidly test sorption capacities of candidate materials.

Batch experiments revealed great K_d values, within the range of 10^4 - 10^5 L kg⁻¹, for all tested materials, whereas the maximum sorption capacities (derived from the fitting of sorption data to the Langmuir equation) ranged between 1 and 37 mg Sm/g of material. Continuous-flow experiments, which better simulate a real water treatment situation, permitted to obtain maximum sorption capacities by mass balance and by data fitting to Thomas and Yan models. CF exhibited the greatest sorption capacity at every stage of the sorption process besting the commercial activated carbons, while CM was established as the best biochar for Sm sorption, competing with AC2 but not with AC1. It was observed that samarium sorption in all materials, except AC2, was governed, to some extent, by a cation exchange mechanism. As shown in Figure 1, maximum sorption capacities derived from Langmuir fitting of the sorption isotherms correlated well with maximum sorption capacities obtained from continuous-flow experiments. Both laboratory methods were confirmed to be suitable to determine the maximum samarium sorption capacity of the materials under the conditions used.

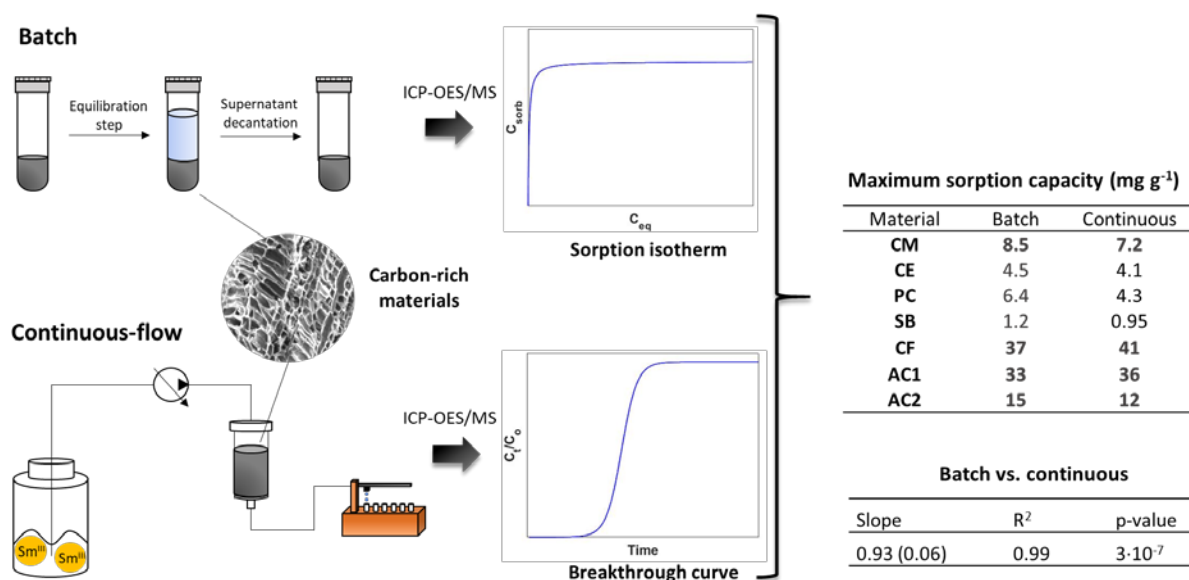


Fig. 1. Scheme of the strategy and main results obtained.

Comparative analysis of biochars to be used in greenhouse gas abatement and first trends of their application to pig manure

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Keywords: *biochar, muffle furnace, greenhouse gas abatement, manure*

Abstract

Greenhouse gas reduction has been a widely researched topic over the last few decades. In terms of abatement technologies, the options are many and varied but one material which is getting more and more attention is biochar. The role of biochar as a regulator of greenhouse gas (GHG) emissions from soil has been well established, while its application in manure management has been less well researched. Considerable uncertainties remain regarding operational setting and efficacy. This study attempts to explore the production and utilization of biochar produced from five feedstock sources to mediate reductions in greenhouse gas emissions for manure management systems. Slow pyrolysis, at temperatures of 450 - 750 °C with a heating rate of 7.5 °C min⁻¹ and a residence time of 20 minutes, was used to produce biochars in a muffle furnace. The biochars and feedstocks were then analysed using pH, TGA, BET, SEM and ICP in order to establish appropriate protocols for the optimal production and application of biochar in GHG-manure management. Results indicate that drying as a pre-treatment in production does not increase the biochar yield if calculated on a dry matter basis. At the same time, the yield is decreasing with increasing treatment temperatures. It was also observed that thermal treatment increases the pH of the tested materials irrespective of whether they were fresh or pre-dried, making the biochars more alkaline than the original materials. Additionally, rising process temperatures have led to a decrease in volatile matter content for all materials used, whereas the surface area and the fixed carbon content increased. Furthermore, it was found that the none biochars produced from the five feedstocks contained traceable amounts of arsenic or cadmium making the biochars non-toxic and suitable to be used in the environment. Based on the biochar yield results it can be concluded that drying is not necessary in an attempt to make the process less emission-intensive. Focussing on the biochar properties, a reduction of volatile matter content and an increase of the fixed carbon content with rising treatment temperatures have resulted in more stable biochars due to a reduced amount of volatiles and a higher amount of fixed carbon, which is favouring biochars produced at higher temperatures. Preliminary emission trials were performed by mixing pig manure from a farrowing system with different amounts of biochar (0.25, 0.5, 1% w/v). No clear trend in the reduction of emissions through the addition of biochar to manure was found yet. Though the amount of NH₄ measured in the manure after the trials was less in the samples exposed to biochar.

HTC as promising route for enhancing thermal insulation in bioarchitecture

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Keywords: *thermal insulation, hydrothermal carbonization, biomass, bioarchitecture*

Abstract

Sustainable construction is considered an attractive and constantly expanding eco-friendly methodology for bioarchitecture. It is above all about looking for acoustic and thermal insulation materials that are environmentally sustainable in order to build more comfortable and economic buildings, that use less energy during their useful life.

A sector that is receiving much interest is the use of biomass and other biological materials as building products, due to their excellent physical and mechanical properties [1]. Although dried biomass has been used in blends with other materials, like gypsum or concrete, carbon materials can offer some advantages related to their porous structure. In this field, recent studies have found promising results with activated carbons, but literature offers scant references on the use of hydrochars (HCs) regarding this application, despite their potential advantages during pressing processes, owing to the content of natural binders [2], that might have additional benefits regarding their mechanical strength.

This work aimed to evaluate the mechanical and thermal insulating properties of biomass (water hyacinth) and derived HCs, by blending them with gypsum. Water hyacinth was selected because it is a high priority invasive weed that is currently considered as a severe threat for ecosystems in many countries. Among their different fractions, stem was selected for this work, due to its sponge-like structure, since the air confined into its cavities might act as thermal insulating medium.

Longips type B1 controlled construction gypsum (G, EN13279-1:2009) was used as a matrix and blended with dry particles of water hyacinth stem (WHS) or HCs prepared from them (HC_WHS) as reinforcement to develop bio-based composites (P_WHS or P_HC_WHS). Three different sizes of reinforcement were studied, as well as different loads of reinforcement/G, making sure that in all cases an overall water quantity of 0.62 cm³ per g of the reinforcement/G mixture was used. The mixture was poured into a circular 60 mm aluminum mould 40 mm high, and pressed using a rigid plastic cylinder. The biopanelled were characterized in terms of helium and bulk density, mechanical strength and thermal conductivity.

The results showed that adding biomass/HC to the G resulted in a large decrease in density (up to 5 times lower). Keeping a similar trend, thermal conductivity values decreased with the addition of biomass or HC, reaching a drop in this parameter that was more dramatic in the case of biomass, which in turn showed a better insulating potential. The better mechanical performance of HCs demonstrated that, the improvement in binding associated to previous hydrolysis was very beneficial. Despite HCs involved a lower thermal insulation in relation to biomass blends (conductive coefficients of 0.403 versus 0.221 W/mK) they might be more interesting in real applications.

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The effect of biomass-derived carbon materials on the recovery of metals from mining tailings by hydrometallurgical processes

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Keywords: *biochar, leaching, sulphide ore.*

Abstract:

Traditionally, mineral extraction created negative impacts on the environment and the surrounding human population. One of these impacts is the generation of tailings. Tailings and mine spoil waste with no market value for the mining companies must be stored on tailings dams. However, there are various social and environmental effects of the tailings storage, resulting in the contamination of water due to acid mine drainage, the aerial dispersion by wind erosion that can contain toxic metal, the degradation of the associated soils and ecosystems and the major environment disasters caused by the failure of the mining waste dams. The recent adoption of the Circular Economy Strategy by European Union (EU) considers the wastes as a resource related with the new concept of urban mining. Only in Europe, there are between 150000 and 500000 landfill sites representing in some cases, an environmental problem but also a significant potential reserve of raw materials.

The physical, chemical and mineralogical properties of tailings considerably changes with the ore type and the way the mineral was processed. However, some mining wastes, as those generated during flotation processes of sulfidic ores, could contain significant amounts of valuable metals, particularly where the efficiency of separation and flotation technologies used some decades ago to concentrate target minerals were not as good as those currently available. The presence of low-grade minerals hinders metal extraction by traditional pyrometallurgical processes but the hydrometallurgical technology is limited by the low leaching rates of metal sulfides like chalcopyrite. Several research have been performed on chalcopyrite leaching adding pyrite [1] or iron powder [2], nanosized silica [3] and more recently, coal and activated carbon [4].

The main objective of the present work is to study the effect of different biomass-derived carbon materials on metal leaching from different mining tailings samples. Experimental results showed that some biomass-derived carbon materials could improve the leaching rate of Cu or Zn on sulfuric acid solutions. The catalytic effect greatly depends on the carbon material properties, the pH of the leaching solution and the concentration of oxidants.

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Copper and zinc leaching from complex sulphide ore: The effect of biomass-derived activated carbon as catalyst

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Keywords: *biomass, activated carbon, leaching, sulphide ore.*

Abstract

Chalcopyrite (CuFeS_2) is the most abundant copper-bearing resource, accounting for appropriately 70% of the known reserves in the world [1, 2]. However, chalcopyrite and other copper sulphides such as enargite, bornite or covelite are usually found in deposits with grades around 0.4-0.5% copper. The exploitation of these reserves is in the limit of economically viable by traditional flotation methods followed by pyrometallurgical processes. The hydrometallurgical route would be more interesting for complex and low-graded sulphide ores. Nevertheless, chalcopyrite is refractory in sulfuric media and has a slow dissolution rate in aqueous solutions.

In order to accelerate the kinetics of chalcopyrite leaching in acidic sulfuric media, the effects of several species have been investigated. Several research have been performed by adding pyrite [3], iron powder [4], nanosized silica [5] and more recently, coal and activated carbon [6].

The main objective of the present work is to study the effect of one biomass-derived activated carbon on Cu and Zn leaching from a concentrate sample from the massive sulphide deposits of the Iberian Pyrite Belt (Spain). The biomass-derived activated carbon used here was produced by physical activation (with CO_2 at 700 °C and at an absolute pressure of 1.0 MPa) of wheat straw pellets-derived char (which was produced by slow pyrolysis at a highest temperature of 500 °C and atmospheric pressure).

The catalytic effect of biomass-derived activated carbon greatly depends on the pH of the leaching solution and temperature. More than 90 wt% of Cu and Zn could be recovered after leaching with sulfuric/ferric solution during 96 hours at 90°C. Best results were obtained with ratios of sample/activated carbon of 1/0.5 and 1/0.25 w/w.

Acknowledgment: The authors acknowledge for funding to Spanish Ministerio de Economía y Competitividad with reference RTI2018-096695-B-C31.

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The use of magnetic biochars as catalysts in the lixiviation of metals from mining tailings

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Keywords: *magnetic, biochar, metal, leaching*

Abstract:

Sulphide minerals usually contain significant amounts of valuable metals and/or metalloids, but it is well known that its metallurgical extraction by conventional pyro-metallurgical routes is not very economically suitable [1]. Since the low efficiency of hydrometallurgical operations with sulphide minerals makes it a costly process, there is a need to develop low-cost technologies and processes to treat them in acidic sulphuric media. Some new applications have been investigated focused on the kinetics acceleration of sulphide minerals weathering in leaching procedures [2]. Among them, the addition of carbon materials as catalyst or catalyst support [3] have also revealed to improve, not only the leaching kinetics course of sulphide minerals in sulphate media but also the metal extraction rate.

The most carbon materials used as catalyst in previous studies were commercial activated carbon or carbon black powders, with low information available on their physicochemical properties. Furthermore, they are actually considered to be relatively expensive, and their use could significantly raise the cost of hydrometallurgy industrial processes. For this reason, main objective of the present work is to study the use of magnetic biochars as catalysts in the leaching of metals from mining tailings with high content on sulphide minerals.

The catalyst addition ratio; thermochemical conditions used in biochar fabrication (pyrolysis or hydrothermal carbonization), mine tailing properties, temperature and leaching time played an important role in the leaching behavior of metals. Compared to the control, increments higher than 65% of copper leached were obtained.

Acknowledgment: The authors acknowledge for the funding of Spanish Ministerio de Economía y Competitividad with reference RTI2018-096695-B-C31.

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