

# CHEMICAL SCIENCES

## NATURAL ZEOLITE CLINOPTILOLITE AS ADSORBENT FOR CLEANING WATERS FROM ARSENIC IONS

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### ABSTRACT

The article presents the results of researches the adsorption of As (III) in cationic ( $\text{As}^{3+}$ ) and in anionic ( $\text{AsO}_3^{3-}$ ) forms from water solutions on different adsorbents, obtained from natural zeolite Clinoptilolite (CL) of deposits of Georgia. The influence of various parameters such as effect of pH, contact time, initial arsenic concentration, temperature and sorbent dosage was studied. It was found that in the process of adsorption  $\text{As}^{3+}$  cations on zeolites are implemented in two mechanisms: ion exchange and donor-acceptor. Sorption of  $\text{As}^{3+}$  ions occurs by substitution of  $\text{H}^+$  ions in hydroxyl groups of zeolites, and by exchange the adsorbed ion with compensate cations of the zeolite. During the adsorption of the anionic form  $\text{AsO}_3^{3-}$ , physical adsorption predominates.

**Keywords:** natural zeolite, adsorption, arsenic ions.

### Introduction

Contamination of ground waters and soil by toxic compounds of arsenic, as well as their penetration to food chain became a serious health in recent years in many countries problem worldwide (Bangladesh, India, Vietnam, countries of Central and South America, Eastern Europe, etc.). The problem is very significant also for developed countries (Western Europe, USA) what is confirmed with recent tightening of documents regulating maximal permitted concentrations of arsenic and its compounds in drinking water, animal food and environment. Most of these countries do not have the significant deposits of arsenic minerals and have not been involved in production of this element and chemicals on its base.

In the mountainous areas of Western Georgia based on the local natural deposits of arsenic minerals, as well as those transported from Russia, several sites for mining arsenic ores and production of various chemicals on its base have been in operation since 1932. Due to the lack of appropriate systems for a safe deposition of industrial wastes and industrial-water

treatment plants the aquatic basin of the region, as well as soil and environment in general, have been contaminated with toxic arsenic compounds. Shortly before and after dissolution of the former Soviet Union these factories stopped operation without taking any care for toxic waste conservation. Some remains of toxic chemicals are still accessible for local population, tourists, domestic and wild animals, etc. Serious human health problem and environmental concerns related to a pollution of environment with arsenic and its toxic compounds is widely addressed in the scientific literature [1-5].

The toxic industrial remains are washed out into the rivers in Western Georgia by rains and snow waters and contaminate not only local water sources but are transported along the entire basins of rivers. The content of arsenic in the surface waters of Georgia ranges from 1.2-2.1  $\mu\text{g/l}$  (Table 1) [6]. Excessive amounts of arsenic are found in salty and polluted waters. The exception is the river Kvirila, arsenic in it is 1.6  $\mu\text{g/l}$ , and the reason for this is its adsorption on activated manganese.

Table 1.

## Arsenic content in surface waters of Georgia

N	River-Point	N	µg/l			% $\sum \cdot 10^{-3}$		
			Min.	Max.	Ave.	Min.	Max.	Ave.
1	Mtkvari-Minadze	4	1.60	6.60	3.40	0.70	4.40	1.83
2	Mtkvari-Akhaldaba	4	1.60	6.60	3.30	1.04	2.54	1.60
3	Mtkvari-Mtskheta	8	1.50	4.00	2.50	0.48	1.38	0.85
4	Faravani-Head	4	0.40	1.00	0.70	0.88	2.08	1.25
5	Faravani-Junction	6	0.50	3.30	1.30	0.67	2.20	1.00
6	Liakhvi-Confluence	3	1.20	1.30	1.40	0.39	0.76	0.53
7	Aragvi-Confluence	11	0.00	4.00	2.00	0.00	1.82	0.80
8	Vere-Confluence	4	1.60	3.30	2.40	0.16	0.37	0.27
9	Khrami-Confluence	4	1.60	11.60	5.80	0.29	2.23	1.42
10	Mashavera-Bolnisi	5	1.00	12.00	5.30	0.33	2.02	1.14
11	Rioni-Ambrolauri	8	0.80	8.00	4.40	0.42	4.40	2.50
12	Khobi-Head	3	0.00	0.70	0.30	0.00	0.88	0.27
13	Khobi-Confluence	11	0.00	1.50	0.70	0.00	1.00	0.47
14	Kodori-Confluence	6	1.50	2.70	2.00	1.00	2.00	1.53
15	Alazani-Kedi	5	2.60	6.00	3.40	0.63	1.35	0.87

It is worth to be considered, that these toxic compounds penetrate to major rivers (for example, r. Rioni) and carry their waters to Black Sea and this way may represent very serious over-regional environmental problem. The particularly high toxicity of arsenic compounds is evidenced by the fact that the previously established stringent requirements for the maximum permissible concentration of arsenic in water of 50 µg/l were later reduced to 10 µg/l. Therefore, this element requires special attention when assessing the quality of drinking and mineral waters.

The problem of cleaning the natural waters from arsenic is solved by using the ion-exchange and sorption methods. Among the various adsorbents natural zeolites are widely used. Natural zeolites are environmentally friendly and cost-effective sorbents, possessing ion-exchange and sorption properties.

It was shown earlier [7, 8] that modified forms of natural zeolite - Clinoptilolite possess high sorption capacity. The sorption properties of this material depended on type of Chemical and thermal treatment, pH, concentration of model solution and dispersion degree. It was concluded that for more complete removal of arsenic it is necessary to use sorbents that operate more efficiently for every form of As. The first step is to carry out extraction of  $AsO_3^{3-}$  and  $As^{3+}$ .

In submitted work study, we first compared the adsorption of As (III) in cationic ( $As^{3+}$ ) and in anionic ( $AsO_3^{3-}$ ) forms from water solutions on different adsorbents, obtained from natural zeolite Clinoptilolite (CL) of deposits of Georgia, in initial and modified forms.

#### Materials and methods

The samples were obtained by using different methods of treatment. The modification was carried out for increasing the adsorption capacity and activity of natural zeolites at 80°C according to the method changed by us, i.e. by means of combination of acid, thermal and alkali treatment in different sequence and variation of treatment time and concentration of solutions. Acid modification was carried out by treatment with 0.25, 0.5, 1.0 and 2.0 N hydrochloric acid in the same conditions, alkali treatment with 0.25 – 0.30 % KOH solutions with purpose to increase thermal and mechanical stability. Multiple ion-exchange of zeolites was carried out with transition metals' salt solutions in dynamic conditions after preliminary treatment.

The chemical composition of initial and modified samples was determined using conventional chemical analysis, AAS, flame spectrometry and flame photometry. The retention of structure was controlled by X-ray. The chemical content of some samples is given in table 2. Exchange degree of Fe was 6.32%.

Table 2.

#### The chemical content of initial and modified CL, %.

N	დასახელება	%								
		SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	CaO	MgO	Na <sub>2</sub> O	K <sub>2</sub> O	Fe <sub>2</sub> O <sub>3</sub>	TiO <sub>2</sub>	P <sub>2</sub> O <sub>5</sub> MnO
1	CL	56.66	13.35	7.09	0.34	1.78	1.74	2.75	0.56	0.12 0.12
2	DeCL	68.58	7.69	2.68	0.11	0.42	0.75	1.82	0.65	0.05 0.07
3	CL-H	59.74	13.35	5.99	1.13	0.73	1.74	2.40	0.53	0.12 0.18
4	FeDeCL	68.04	7.92	2.52	0.11	0.45	1.77	3.13	0.65	0.05 0.07

In carrying out the experiments and analysis, we used chemicals, reagents and standard solutions of ultrapure qualification, production companies Sigma-Aldrich, Perkin Elmer. The initial model solutions were prepared for trivalent Arsenic in cationic and anionic forms. Arsenic concentrations in the resulting solutions

were 0.1 g/l, which is further diluted to working concentrations.

Batch experiments were performed to remove As (III) from aqueous solution considering various parameters such as effect of pH, contact time, initial arsenic concentration, temperature and sorbent dosage. The

analysis of Arsenic ion in initial model and waste solutions was carried out by AA Spectroscopy on apparatus "Perkin Elmer" AAnalyst 200 using as the source of atomization flame mixture of air-acetylene and  $N_2O$  gas according to methodic, applied in [9]. Quantitative determination of Arsenic in the analyzed solutions was performed according to the obtained calibration graphs in mg/l. The dynamic exchange capacity value, coefficients of adsorption and distribution were calculated on the base of received data.

### Results and discussion

Iron oxides, oxyhydroxides, and hydroxides, including amorphous iron oxhydroxide (FeO-OH), goethite ( $\alpha$ -FeO-OH), and hematite ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>), are known to be promising adsorbents for removing both As (III) and As (V) from water [10-14]. To improve the absorption of arsenic from water, studies were carried out in according to [10] on the modification of natural zeolite CL with iron (III) and aluminum ions. The results of the experiments showed that the sorption of arsenic on the Fe-exchange zeolite can reach 100 mg/kg. However, Fe-exchange zeolite is inefficient for removing As from groundwater due to its high initial concentration (511  $\mu$ g/L), large amount of natural organic matter, and its low redox potential [10, 12].

Arsenite is more toxic than arsenate, while it is more difficult to be removed than arsenate; the As (III) removal was essentially due to a sorption coupled with oxidation process [14-16]. In this work, we studied the adsorption of ionic forms of arsenic on untreated, hydrogen, and iron forms of CL under dynamic conditions. Results showed that sorption properties of CL depend on type of chemical and thermal treatment, pH, Concentration of model solution and dose of adsorbents.

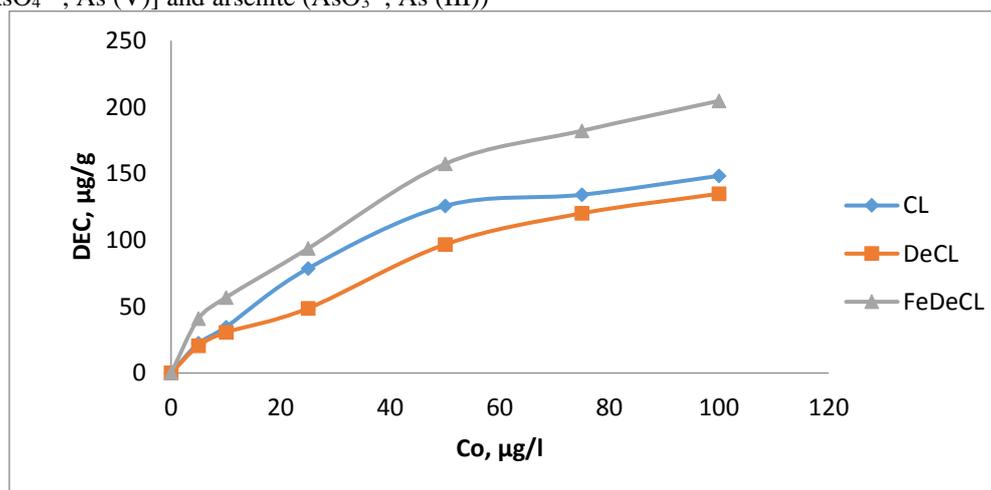
Sodium arsenate and arsenite solutions were used as model solutions, as the most common forms of arsenic. Arsenic is widespread in the environment as the arsenate [ $AsO_4^{3-}$ , As (V)] and arsenite ( $AsO_3^{3-}$ , As (III))

ions. Trivalent arsenic is 60 times more toxic than pentavalent arsenic. Inorganic arsenic compounds are 100 times more toxic than organic ones [11–15]. At the same time, arsenite is a more mobile and most toxic form of arsenic [11]. The initial concentration of arsenic in the prepared solutions was 0.1 g/l.

#### A) Influence of initial arsenic concentration

According to fig.1 the curves of dependence of dynamic exchange capacity (DEC) from concentration till 20-25 mg/l have had practically parallel ways for arsenic anions  $AsO_3^{3-}$  and arsenic cations ( $As^{3+}$ ), and then the saturation for  $AsO_3^{3-}$  was reached. But the saturation of DEC of arsenic cations ( $As^{3+}$ ) wasn't reached in the investigated area of concentrations. Thus, the dependence of the concentration of the solution DEC is more expressed for the cationic form of As (III). The authors of [16] showed that the adsorption of arsenate on the iron-containing adsorbent akaganeite proceeds at a high rate and amounts to 90% after 3 hours of stirring at pH=5 and an ionic strength of 0.1M  $KNO_3$ . After 15 hours, the maximum adsorption was 99%, and 24 hours was the time to reach the required equilibrium. Adsorption due to electrostatic processes usually proceeds in seconds. The adsorption of arsenic studied in this work was hours, which may indicate the specific adsorption of arsenic particles on the sorbent with the formation of arsenate  $FeAsO_4$ . The adsorption of both arsenate and arsenite on the studied zeolites reaches equilibrium in a matter of minutes, which indicates the ionic mechanism of the process.

In addition to the ion-exchange interaction is also possible the formation of strong bonds between the modified zeolite and absorbed cations, which has the donor-acceptor nature. May be the free d-orbitals of  $As^{3+}$  presented as acceptors. Donors can be groups with oxygen atoms, located on the surface of zeolite, and having an unshared electron pair.



B) Influence of adsorbent dose

The efficiency of arsenic removal increases with an increase in the amount of adsorbent (Fig. 2). The removal efficiency does not change significantly: from 97.5% ( $m = 0.1$ g) to 99.6% ( $m = 0.3$ g). Thus, even the smallest amount of sorbent  $m = 0.1$ g provides a very

high degree of purification, and the residual content of total arsenic is 2.9  $\mu$ g/l, which corresponds to the WHO standards for the concentration of arsenic in drinking water (10  $\mu$ g/l).

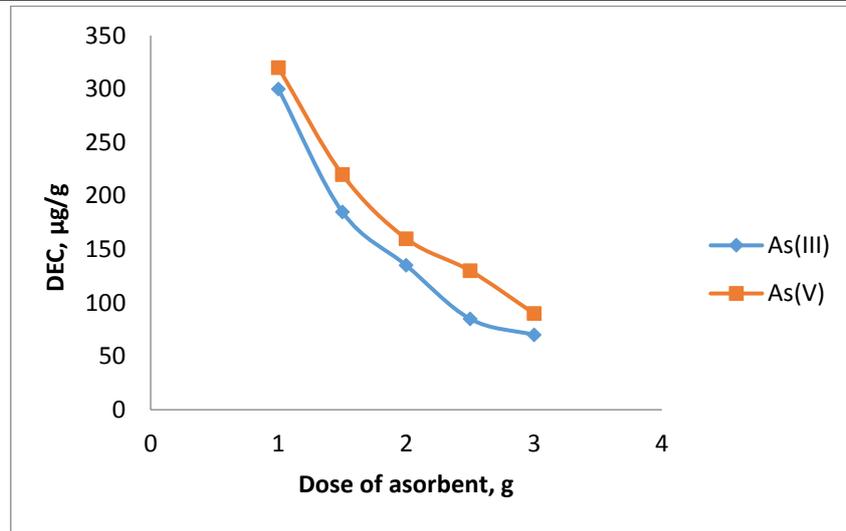


Fig.2. Dependence of dynamic exchange capacity (DEC) on mass of CL.  
C) Influence of pH

It is known that pH of solution plays the significant role in adsorption.

Under stationary conditions, the experiments were carried out according to the following scheme:

- The prepared model solution with a volume of 100 ml was placed in a flask with a volume of 250 ml;
- 0.5g of sorbent was added, the pH of the solution was determined and intensive shaking was carried out for 1 hour;
- The resulting suspension was settled and filtered through a paper filter;
- Determined the pH of the filtrate;
- Determined the adsorption characteristics.

The adsorption of arsenic on CL (GeO) at pH 2 to 12 was investigated for three different contact times. As shown in fig. 3 with longer contact time, better adsorption removal is observed; however, differences are mainly noted at pH values greater than 8.

It is known that in the pH range between 3 and 6, pentavalent arsenic is mainly in the form of  $\text{H}_2\text{AsO}_4^-$  [17, 18], while the divalent anion  $\text{HAsO}_4^{2-}$  dominates at pH values between 8 and 10.5. The authors of [18] also showed that the dependence of the absorption degree  $A$  on pH for arsenite is dome-shaped with a maximum in the region of pH=7, and sorption isotherms in the region of low sorbate concentrations were described by the Langmuir equation. At high ( $>33.4 \mu\text{mol/L}$ ) initial arsenite concentrations, the sorption isotherms were described by the Henry equation. Almost the same is the observed for arsenate. The maximum sorption of arsenite was  $\approx 1.0$ , and that of arsenate was  $\approx 1.5 \text{ mmol. g}^{-1}$ . The absorbed form of arsenite is  $\text{H}_2\text{AsO}_3^-$ , arsenate -  $\text{H}_2\text{AsO}_4^-$  and  $\text{HAsO}_4^{2-}$  [19].

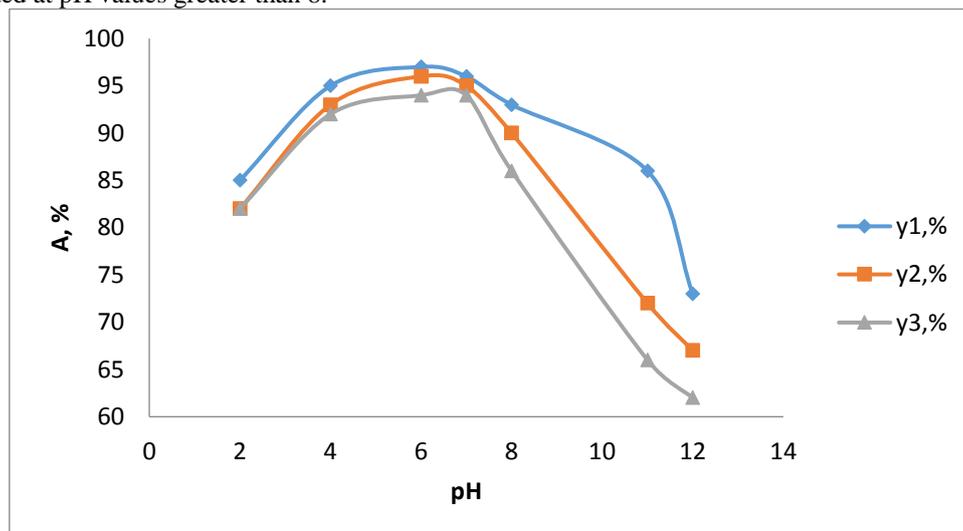


Fig.3. The dependence of As (III) adsorption on pH (initial concentration of As (III) -10 mg/l, contact time 1, 4, 20 hours and temperature -25°C)

D) Dependence on thermal pretreated of samples

An increase in the temperature of the preliminary heat treatment of the zeolite has a strong effect on the sorption of the  $\text{AsO}_3^{3-}$  anion, but not of the trivalent Arsenic cation (Fig. 4). Increasing the pre-calcination temperature above  $250^\circ\text{C}$  worsens their ion-exchange properties, and the higher is the temperature, the deeper is this process. The decrease in the ion-exchange capacity and, consequently, the number of ion-exchange centers with increasing temperature, in general, is in good correlation with the available X-ray and adsorption data [20; 21]. It is obvious that heat treatment, accompanied by the loss of zeolite water, causes the migration of ion-exchange cations of alkali and alkaline earth metals to inaccessible positions of channels B and C in CL and their strong fixation on the channel walls. These cations become inaccessible to large  $\text{AsO}_3^{3-}$  ions surrounded by a hydration shell, which may be the reason for the

decrease in DEC, while  $\text{As}^{3+}$  cations with a radius of 0.072 nm [22] are adsorbed on zeolite samples subjected to heat treatment at  $700^\circ\text{C}$ . The factor of compression of the zeolite lattice and a decrease in the volume of cavities as the result of calcination cannot be excluded. A sharp decrease in the ion-exchange capacity of the samples treated above  $400^\circ\text{C}$  should be associated with violations of the structure of zeolites and their amorphization. The cationic composition plays the most significant role in determining the thermal behavior of CL. The presences of cations such as K, which have a low surface or bulk charge density, increase the thermal stability of CL. In particular, the crystallinity of the K-exchange forms is the retained upon heat treatment at  $450^\circ\text{C}$  and slightly decreases at  $600^\circ\text{C}$ .

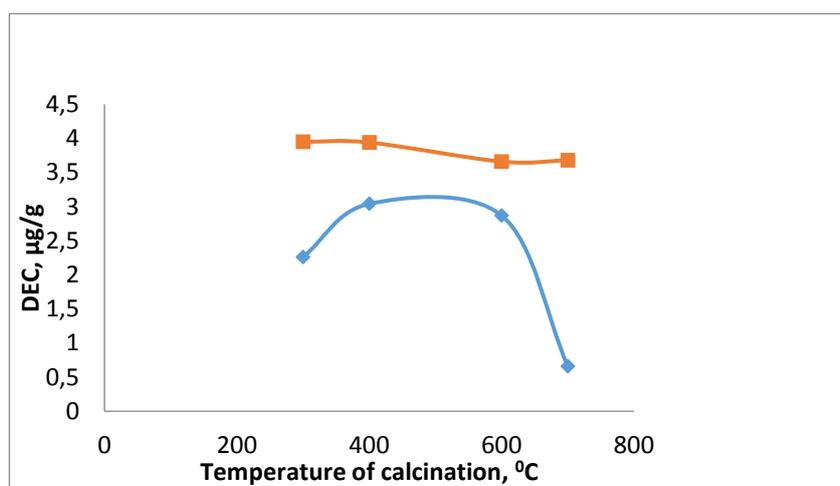


Fig.4. Dependence of DEC on temperature of pretreated calcination of CL

### Conclusion

The multicomponent crystal adsorbents were prepared to optimize the effectiveness of the elimination of As (III) from aqueous solution. Batch experiments were performed to remove As (III) from aqueous solution considering various parameters such as effect of pH, initial arsenic concentration, temperature, and sorbent dosage. The maximum sorption capacity of the surface was almost steady from pH= 4 to pH=9. In the process of adsorption  $\text{As}^{3+}$  cations on zeolites are implemented in two mechanisms: ion exchange and donor-acceptor. The ion-exchange mechanism supposes that sorption of  $\text{As}^{3+}$  ions from solutions by modified zeolites occurs by substitution of  $\text{H}^+$  ions in hydroxyl groups of zeolite, and by exchange the adsorbed ion with compensate cations of the zeolite -  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{K}^+$ ,  $\text{Na}^+$ . During the adsorption of the anionic form of  $\text{AsO}_3^{3-}$ , physical adsorption predominates.

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