

Article

Efficiency of Modified Natural Clinoptilolite Tuff for As(III) and As(V) Uptake from Model Polluted Water

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Abstract: Granular and powdery clinoptilolite tuff samples from Beli Plast, Eastern Rhodopes, Bulgaria, were coated with metal hydroxides (Fe, Al, Fe-Mg) by two-step alkalization. The prepared sorbents were tested for As(III) and As(V) uptake from a modeled water solution with an arsenic concentration of 44 µg/L. The granular sorbent was used in the sorption columns and showed a high efficiency of arsenic purification from slightly polluted waters. The calculated maximum sorption capacity for the optimal conditions is 32.9 µg/g. The adsorption proceeds according to the Langmuir model. The mechanism of adsorption is most likely inner-sphere complexation. The sorbents' complete regeneration was achieved by NaOH treatment. The results of the experiments show good possibilities for obtaining water with an arsenic concentration ranging from below the limit of detection to 3.8 µg/L, which is a significantly lower value than the permitted value of 10 µg/L and close to the national environmental quality standard for shallow waters. The high efficiency shows Fe- or Mg,Fe-coated clinoptilolite sorbents. The sorbents are highly efficient in purifying 400 liters of water with an initial concentration of 44 mg/L of either arsenate or arsenite per 1 kilogram of sorbent at a rate of 2.4–2.0 L/h/kg. The powdered sorbents used in a batch system under “static” conditions showed a much higher adsorption capacity than the granular one. Such sorbents are more suitable for small quantities of water with a high concentration of arsenic.



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1. Introduction

Arsenic contamination of water is a global problem. Arsenic is an element with transition metal properties and can occupy cationic and anionic positions within compounds [1]. Arsenic reacts quickly to changes in environmental conditions and easily changes its oxidation state. In aqueous solutions, depending on the Eh–pH conditions, arsenic forms different arsenite and arsenate oxyanions [2].

Most natural waters have pH values between 5.5 and 9. Under these conditions, the compounds H_3AsO_3^0 for As(III) and H_2AsO_4^- and HAsO_4^{2-} for As(V) are stable [3]. Arsenic acid H_3AsO_4^0 is stable in strongly acidic environments (pH < 2) and is not characteristic of natural underground and surface waters. Under oxidizing conditions at pH = 2 ÷ 6.9, the arsenate oxyanion H_2AsO_4^- is stable. As the pH increases to 11.5, the dominant oxyanion becomes HAsO_4^{2-} . Complete dissociation to AsO_4^{3-} in natural conditions is rare because extremely high pH values are required [3].

In reducing conditions for most natural waters, the arsenite form (H_3AsO_3^0) is dominant at pH up to 9. As the pH values increase, it dissociates to H_2AsO_3^- and HAsO_3^{2-} . The dissociation is completed in situations with pH values above 13.5.

The ecological problems arise depending on the mobilization of arsenic species under the influence of natural processes—reactions in natural waters, biological activity, volcanic

emissions, etc. Some anthropogenic factors—the mining industry, the burning of fossil fuels, and the use of arsenic-containing pesticides—cause a local increase in the concentration of arsenic in water.

Based on continued research on the effects of inorganic arsenic on human health, the World Health Organization in 1993 reduced the permissible concentration of arsenic for safe water from 50 µg/L to 10 µg/L [4]. Various methods for removing arsenic from low- and high-contaminated waters have been developed and tested to meet the new requirements [2,5]. Two of the most widely used, developed, and studied methods for arsenic removal are coagulation and flocculation and adsorption and chemisorption. The efficiency of coagulation and flocculation method was investigated considering various factors such as the type of coagulant and the existing arsenic species [6–8], solubility [9], amount of coagulant [10–12], pH [11,13,14], etc. The adsorption and chemisorption of various arsenic species are processes of even higher research interests. The adsorption ability of different adsorbents such as alumina, activated carbon, carbon molecular sieves, various modified zeolites, polymer adsorbents, and silica gel has been widely studied [15–36].

In Bulgaria, contamination with arsenic has been noted in water sources (Poibrene village), soils (Pirdop aria), and mine and industrial wastewater. The pollution of the Ogosta dam in NW Bulgaria is one of the biggest problems connected with As-contamination in the country. The dam collects the waters of the Chiprovksa River, which passes through the Chiprovksa ore zone, uniting the decommissioned Fe-ore deposit Martinovo, Pb-Zn-Ag deposit Chiprovtsi, and Au-deposits Govejda and Kopilovtsi [37]. The pollution is due to the runoff of mine waters in the tributaries of the Chiprovksa River and to the Mechi dol, Chiprovtsi, and Golyam Bukovets tailings deposits. The sources, mechanisms of pollution, and their effect on the environment (soils, groundwater, etc.) are the subject of intensive research [38–40]. The average content of As in the waters of the Ogosta dam is 42–45 mg/L. Depending on the distance from the arsenic sources, the As concentrations vary from 18 to 103 mg/L [41].

The present work aims to develop a suitable solution for reducing the arsenic contamination of waters with low and high concentrations of arsenic. The uptake efficiency of natural zeolite (clinoptilolite) rocks coated with pure Fe and Al hydroxides, oxo-hydroxides, and Mg-Fe layered double hydroxide (LDH) for arsenite and arsenate adsorption in dynamic conditions (sorption column) and static conditions (constant volume system) was studied. The adsorption method with coated zeolitized tuff is chosen because of the physicochemical properties (chemical, physical, and structural stability, and high specific surface) of zeolites and zeolitized tuffs and the large deposits of clinoptilolite tuffs in Bulgaria, which predetermines the relatively low cost of this type of sorbent.

2. Materials and Methods

2.1. Materials

The stock solution of As(III) was prepared under laboratory conditions by dissolving NaAsO₂ in 1 L of tap water to obtain a solution of As(III) with 4 mg/L concentration. By diluting with distilled water, 20 L of solution with a 44 mg/L As(III) concentration was prepared. Half of this solution (10 L) was oxidized with H₂O₂ to give an As(V) solution with 44 mg/L concentration. A solution with arsenite and arsenate content (As(III): As(V) = 1:1) is prepared by mixing equal volumes of the two mono-anionic solutions. All chemical reagents used were with grade “pure for analysis”.

The rock material used for sorbent preparation is clinoptilolite tuff from the Beli Plast deposit, Eastern Rhodopes, Bulgaria. The mineral composition of the rock includes 80–88% clinoptilolite, 3–10% montmorillonite and celadonite, and 2–8% α-cristobalite.

2.2. Sorbent Preparation Method

Four clinoptilolite tuff (Cpt) 200 g samples (fraction up to 2.5 mm) were used. One sample was tested as a direct sorbent. The other three samples were coated with oxy-

hydroxides and hydroxides of iron (Fe-Cpt), aluminum (Al-Cpt), and magnesium-iron LDH (Mg,Fe-Cpt).

The sorbents Fe-Cpt and Al-Cpt were prepared by soaking 200 g of clinoptilolite tuff with 80 mL of 1 M $\text{Fe}(\text{NO}_3)_3$ or 2M AlCl_3 solution for 30 min under vigorous stirring. After supernatant decantation, the solid samples were treated with 150 mL of 1 M NaOH solution. After alkalization, the entire coating procedure was repeated with 40 mL of 1M $\text{Fe}(\text{NO}_3)_3$ or 2M AlCl_3 and alkalization with 60 mL of 1M NaOH to obtain a sufficiently dense layer of Fe or Al oxy-hydroxides and hydroxides, containing approximately 0.03 g of tri-valent cation per gram of zeolite.

The sorbent Mg,Fe-Cpt was prepared by wetting 200 g clinoptilolite tuff with a 120 mL mixed solution of 1M $\text{Fe}(\text{NO}_3)_3$ and 1M MgCl_2 with ratio Fe:Mg = 2.5:1. The particles remained in the solution for 30 min under continuous vigorous stirring. After the solid phase separation phase, an alkalization with 200 mL of 1M NaOH for 5 h follows.

After the last alkalization, all three obtained samples were washed until pH 8.5 of the wash water, and dried for 12 h at room temperature.

All three sorbents were prepared by sieving into two different sizes: granular with a size range of 0.5–2.5 mm (denoted as Fe-Cpt, Al-Cpt, and Mg,Fe-Cpt) and powder with a size less than 0.5 mm (Fe-Cpt-f, Al-Cpt-f, and Mg,Fe-Cpt-f).

2.3. Adsorption Study

2.3.1. Arsenic Uptake from Aqueous Solution under Dynamic Conditions in a Sorption Column

Two sorption columns were constructed using burettes with a volume of 25 mL and a diameter of 10 mm (for sorption column I) and 0.8 mm (for sorption column II). A glass cotton filter with a thickness of 15 mm for sorption column I and 8 mm for sorption column II is placed in the lower part of the burettes (Figure 1).

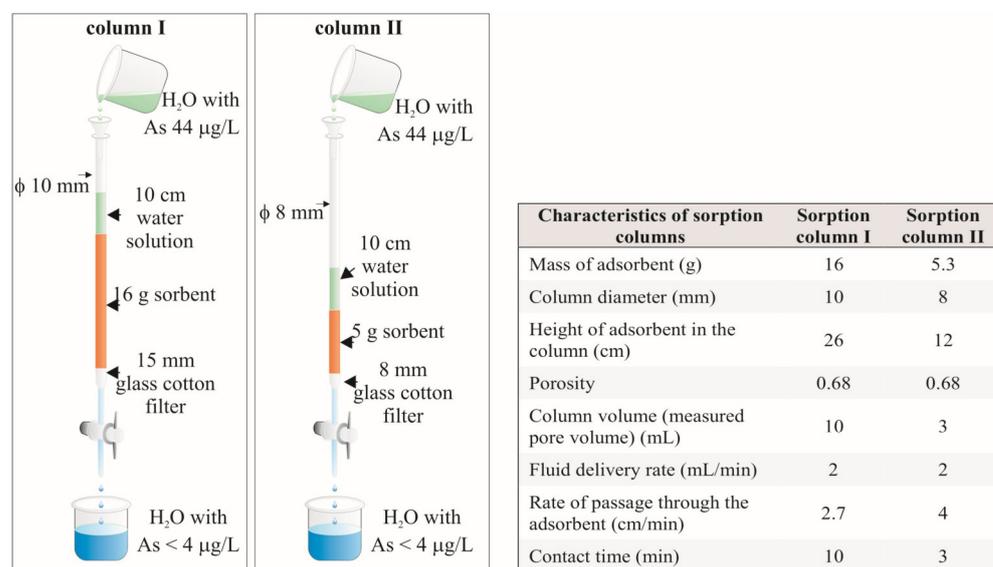


Figure 1. Scheme and main characteristics of sorption columns.

During the experiments, a constant water column with a height of about 10 cm is maintained over the sorbent to prevent the column from drying.

An amount of 1.92 L of solution with an arsenic content of 44 $\mu\text{g}/\text{L}$ was passed through sorption column I, and 4 L of the same solution through sorption column II. The arsenic concentration in outflow was monitored after a certain number of 1 mL volume doses (one dose = 1 mL).

2.3.2. Arsenic Uptake from Aqueous Solution under Static Conditions in a Constant Volume System

To study the sorption activity in static conditions, the fine fraction (<0.5 mm) was used to avoid the possible dusting of the granular fraction under the conditions of the experiment, which would lead to contamination of the system with uncoated zeolite tuff particles. The experiment with adsorbents Fe-Cpt-f, Mg,Fe-Cpt-f, and Al-Cpt-f follows this procedure: 1 g of each sorbent was placed in 300 mL of As(III) solution with a concentration of 44 µg/L and stirred with an electromagnetic stirrer. The adsorption efficiency was studied depending on the time—30 min, 60 min, 90 min, and 450 min.

2.3.3. Co-Precipitation

The experiment was carried out with solutions with an As(III) or As(V) concentration of 4 mg/L following the procedure. To 50 mL of these solutions, 5 mL of 1M Fe(NO₃)₃ or 1 mL of 1M AlCl₃ and 1M NaOH were added until complete precipitation. After the completion of each precipitation, the pH was measured, and the resulting slurries were filtered, and supernatant analyzed for arsenic content.

The experiment was repeated by adding 0.1 g of micronized clinoptilolite tuff (size fraction < 20 µm) to the solutions to accelerate the flocculation. The pH after complete precipitation was determined, followed by filtration of the precipitate and supernatant analyses for arsenic content.

2.3.4. Elution of Arsenic from the Spent Sorbents

The extraction elution of the adsorbed arsenic from Fe-Cpt was carried out by wetting 4 g of the spent sorbent with 1 M NaOH. After 1 h, 12 mL of distilled water was passed through the wetted sorbent in the column. The As concentration of outflow was determined by electrothermal atomic absorption spectrometry.

2.3.5. Data Analysis Methods

Adsorption data were analyzed using Langmuir and Freundlich adsorption isotherms. The isotherms relate the amount adsorbed per unit mass of adsorbent (S) to the equilibrium concentration of the adsorbate in the liquid phase (C_e).

Langmuir isotherm

The Langmuir model assumes that the maximum adsorption occurs when a saturated monolayer of solute molecules is present on the surface of the adsorbent is saturated with a monolayer of solute molecules. In this case, the adsorption energy is constant, and there is no migration of the adsorbed molecules in the surface plane.

The mathematical equation that describes the Langmuir isotherm is:

$$S = \frac{S_m K_L C_e}{1 + K_L C_e}, \quad (1)$$

where S_m and K_L (Langmuir constants) indicate the maximum adsorption capacity (S_m) and the energy referred to as the heat of adsorption (K_L), respectively.

Freundlich isotherm

The Freundlich model is an empirical expression that considers the adsorbent surface heterogeneity and describes the exponential distribution of adsorption sites and their energies.

The mathematical equation that gives the Freundlich isotherm is:

$$S = K_f C_e^N, \quad (2)$$

where K_f and N are Freundlich constants that indicate the adsorption capacity and adsorption intensity, respectively.

Freundlich isotherms are more widely used, but unlike the Langmuir model, do not provide information on monolayer adsorption capacity.

2.4. Methods for Characterization

The phase composition of the sorbents was investigated by powder X-ray diffraction (XRD) analysis. The powder XRD patterns were recorded on a diffractometer D8 Advance, Bruker. Filtered Co-K α radiation was used in the range 2Θ 4–80°, step 0.02° 2Θ , and exposure time per step 1.5 s. The specialized software Diffrac.EVA version 5.2.0.5 was used for qualitative and semi-quantitative phase composition determination. The morphology and chemical composition of covering layers were investigated by Scanning Electron Microscope (SEM) JEOL—model JSM-6010PLUS/LA fitted with energy dispersive spectrometer (EDS).

Determination of As-content in starting and purified water solutions was carried out by electrothermal atomic absorption spectrometry (ETAAS). Electrothermal atomic absorption measurements were carried out on a Perkin-Elmer (Norwalk, CT, USA) Zeeman 3030 spectrometer with an HGA-600 graphite furnace. The light source was an electrodeless discharge lamp for As. The spectral bandpass for all analytes was 0.7 nm. Pyrolytic graphite-coated tubes with pyro-coated platforms were used as atomizers. Sample aliquots of 20 μ L were injected into the graphite furnace using autosampler AS-70. All measurements were carried out with at least three replicates and the values measured were based on integrated absorbance. For low arsenic concentration electrothermal atomic absorption spectrometry was used (ETAAS)—palladium was applied as a modifier, 20 μ L sample injection volume, temperature program: drying 130 °C (hold 20 s), pretreatment 800 °C (hold 30 s), atomization 2300 °C (hold 3 s), area of absorbance signal was used for arsenic quantification. For higher arsenic concentrations above 60 μ g/L atomic emission spectrometry with inductively coupled plasma was used—(ICP-OES, VISTA MPX AXIAL, VARIAN, Australia); wavelength: 188.979 nm and 193.696 nm.

3. Results and Discussion

3.1. Sorbent Characterization

The used zeolitized tuffs are mainly composed of well-walled plate clinoptilolite crystals with dimensions of 20–30 μ m (Figure 2a). After treatment with Fe-, Al-, or Fe- and Mg- salts, and subsequent alkalization with NaOH, the minerals from the clinoptilolite tuff are covered by a dense layer of nano-sized crystals (Figure 2b).

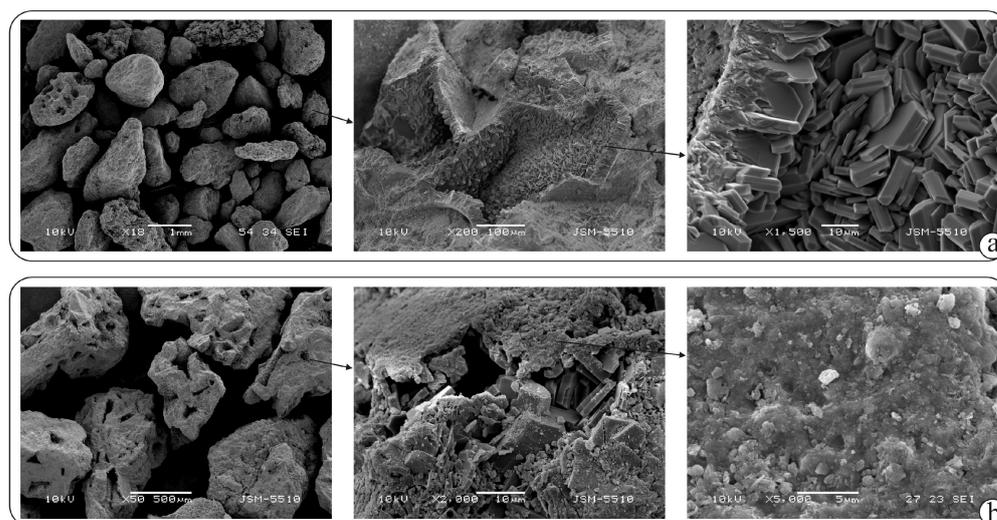


Figure 2. SEM micrographs of: (a) clinoptilolite tuff particles; (b) coated with Fe hydroxides clinoptilolite tuff particles.

The phase identification of the newly formed hydroxides and oxo-hydroxides is complicated due to the nanoscale of the synthesized hydroxides. According to Scherer's equation for the dependence of the intensities of X-ray reflections on the size of the crystallites (Equation (3)), when the size of the crystals decreases to nanoscales, the X-ray reflections become low intensive and broaden.

$$\tau = \frac{k\lambda}{\beta \cos\theta} \quad (3)$$

where τ —volume average size of crystallites in the given direction; k —constant between 0.87 and 1; λ —wavelength of X-ray radiation; and β —integral half-width of the line, measured in radians (2θ).

The recorded X-ray amorphous nature of covering layers in XRD patterns of sorbents (Figure 3b–d) suggests the formation of crystallites with sizes of several unit cells.

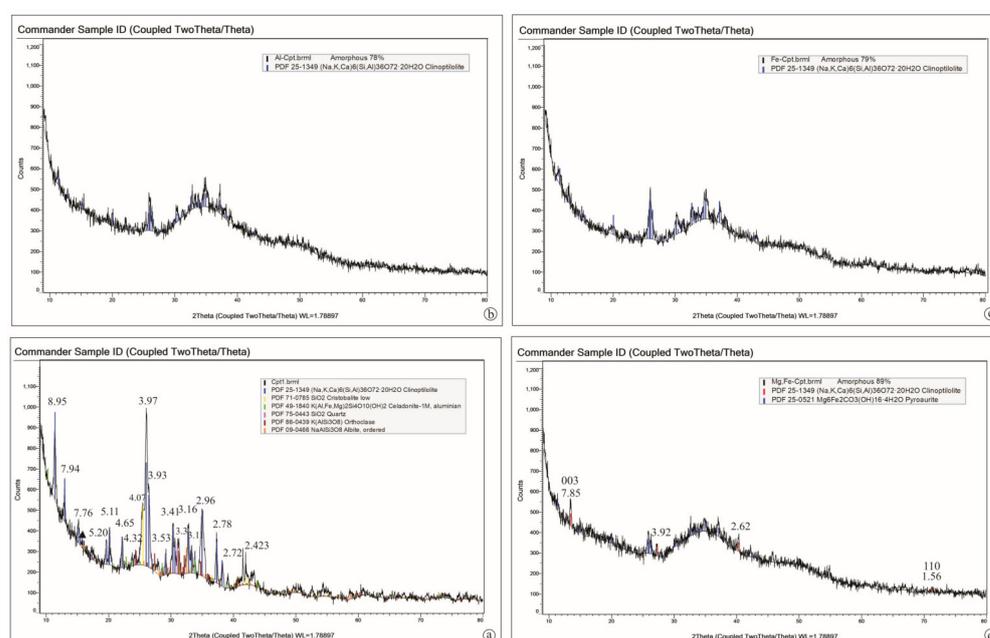


Figure 3. Powder XRD patterns of: (a) clinoptilolite tuff (Cpt), (b) covering layer of Al-Cpt, (c) covering layer of Fe-Cpt, (d) covering layer of Mg,Fe-Cpt.

The chemical composition, determined by EDS, shows presence only of Fe or Al and O in covering layers of Cpt-Fe and Cpt-Al sorbents, respectively. The obtained ratio of the Fe:O and Al:O in different parts of the covering layers is 2:1 or 3:1, which implies forming of Fe (or Al)-oxyhydroxides and Fe (or Al)-hydroxides, respectively (Figure 4a,b).

The obtained Mg,Fe-Cpt sorbent possesses a covering layer with quite different morphology—plate crystals typical for layered hydroxides are visible at some places (Figure 4c). The XRD analysis reveals a formation of doubled layer hydroxide mineral—pyroaurite ($\text{Mg}_6\text{Al}_2(\text{OH})_{16}(\text{CO}_3)\cdot 4\text{H}_2\text{O}$) (Figure 3d). The calculated d-spacing values for pyroaurite 003 and 110 indicate the formation of pyroaurite with a Mg:Fe ratio of 3:1, which is higher than the initial ratio. The obtained ratio Mg:Fe in plate crystals varies from 3.1:1 to 3.4:1. The residual part of Fe forms Fe-oxy-hydroxides and Fe-hydroxides, which are detectable in some parts of covering layers (Figure 4c).

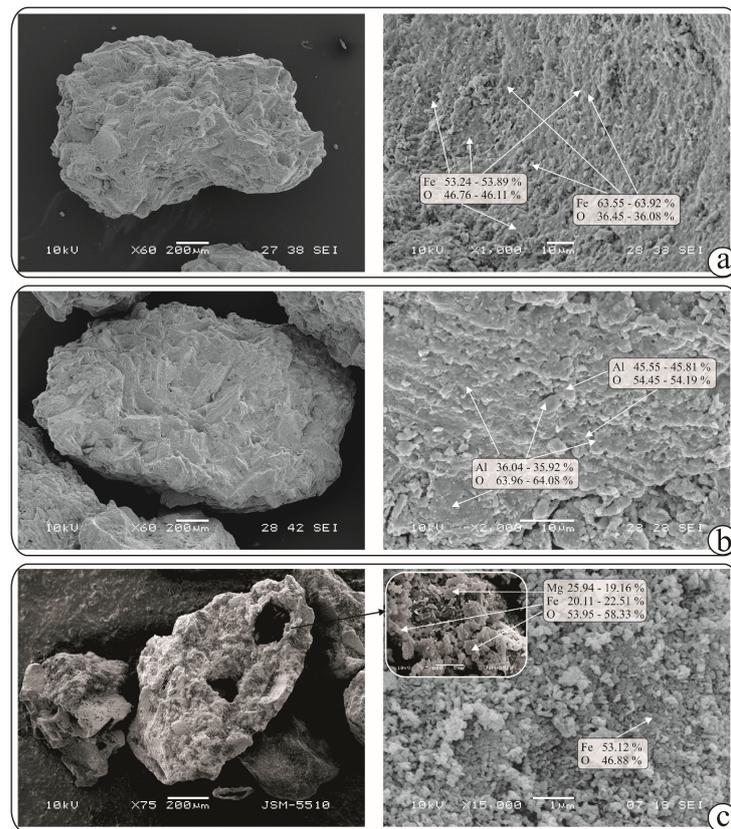


Figure 4. SEM micrographs of sorbents and chemical composition of cover layer: (a) Fe-Cpt, (b) Al-Cpt, (c) Mg,Fe-Cpt.

3.2. Adsorption in Sorption Columns

3.2.1. Adsorption of As(III) in a Sorption Column

The sorption properties of the unmodified clinoptilolite tuff were tested to determine its effect on arsenic adsorption. The unmodified clinoptilolite tuff (sorbent Cpt) showed a poor adsorption efficiency of 5% for dissolved As(III) in the first 100 mL of the solution. Moreover, the volume of the passed solution increases, causing the proceeding desorption of As(III). The initially recorded adsorption may be associated with the clay minerals in the composition of the clinoptilolite tuff. Since the amount of retained arsenite is negligibly small, the sorption efficiency of unmodified clinoptilolite tuff is insignificant, and its influence on the overall process is imperceptible.

The obtained data of the As(III) adsorption on the three different sorbents point to good performance of the sorbents. In the first third of the experiment, all three sorbents showed 100% absorption of the amount of As supplied. The main differences in the efficiency of the sorbents are in the total amount of As adsorbed. For example, Al-Cpt sorbent acts very well in the first 500 mL of the solution passed through the sorption column I, where its efficiency is about 100%. After passing the following 140 doses (1.42 L), a slight decrease in the adsorbed amount (57.23 μg) compared to the supplied initial amount (62.48 μg) is observed (91.6% degree of sorption efficiency) (Table 1).

Table 1. Results of As(III) adsorption by granular sorbents in sorption column I.

Amount of Water with As(III) (44 µg/L) Passed through the Column			As(III) Content in Supplied Water (µg)	As(III) Concentration in Outflow (µg/L)	Adsorbed As(III) in the Sorbent			
Total Volume (L)	Column Volume (Number)	Top-Up Volume (mL)			(%)	(µg)	(µg/g)	
Al-Cpt								
0.02	2	20	0.88	<dl	100	0.88	0.055	
0.10	10	80	3.52	<dl	100	3.52	0.220	
0.50	50	400	17.6	<dl	100	17.6	1.100	
1.00	100	500	22.0	2.1	90.45	19.9	1.244	
1.92	192	920	40.48	3.8	90.61	36.68	2.293	
			84.48			78.58	4.912	
Fe,Mg-Cpt								
0.02	2	20	0.88	<dl	100	0.88	0.055	
0.10	10	80	3.52	<dl	100	3.52	0.220	
0.50	50	400	17.6	<dl	100	17.6	1.100	
1.00	100	500	22.0	<dl	100	22.0	1.375	
1.92	192	920	40.48	3.8	90.61	36.68	2.293	
			84.48			80.68	5.043	
Fe-Cpt								
0.02	2	20	0.88	<dl	100	0.88	0.055	
0.10	10	80	3.52	<dl	100	3.52	0.220	
0.50	50	400	17.6	<dl	100	17.6	1.100	
1.00	100	500	22.0	<dl	100	22.0	1.375	
1.92	192	920	40.48	<dl	100	40.48	2.530	
			84.48			84.48	5.280	

dl: detection limit of the method.

Unlike the Al-containing sorbent, the Fe-Mg-Cpt sorbent shows about 100% efficiency for a twice-higher outflow volume. Moreover, the sorbent active component (trivalent Fe^{3+} cation) is about 2.5 times less than that in the other two sorbents. LDHs have layered structures made up of positively charged hydroxide layers for the compensation of which exchangeable anions are placed in the interlayer space [42,43]. The observed activity of the sorbent could be attributed to the isomorphic substitution of interlayer anions of Mg,Fe-LDH by the arsenite anions. The compensating anion is probably the hydroxyl group because of the high alkalinity of the synthesis. According to XRD data, the d_{003} value after the adsorption experiment slightly increases ($d_{003} = 7.92 \text{ \AA}$ compared to $d_{003} = 7.85 \text{ \AA}$ of the starting sample). The arsenite ion is larger than the hydroxyl one and can induce an increase in the d_{003} value. Because the obtained result suggests a possible ion exchange of the interlayer anion. Due to the small size of the particles, however, the registered X-ray reflections are low intensive and broadened which makes their precise measurement difficult and introduces significant errors. Therefore, the evidence for anion exchange is not very reliable.

The highest efficiency of As(III) adsorption was obtained for Fe-Cpt sorbent. After passing the entire amount of water (1.92 L), the concentration of As(III) in the effluent spent solution remained below the limit of analytical method detection. The uptake efficiency of the sorbent is assumed to be about 100% for the entire experiment.

For determination of the complete adsorption capacity of the sorbent, a new sorption column (sorption column II) was constructed. The amount of sorbent in this column is three times lower than that of sorption column I. The reduced amount of sorbent determines a threefold smaller dose, which provides a threefold higher amount of solution passing per gram of sorbent for the same experimental time. On the other hand, the reduced dose causes a reduction in the contact time between the solution and the sorbent.

The results show that during the experiment, the amount of adsorbed As(III) decreases, and the sorbent reaches almost complete exhaustion. According to the obtained data, the adsorbed amount of arsenic approaches 100% of the supplied amount at the middle of the experiment while at the end of the experiment, the adsorption gradually decreases (Figure 5).

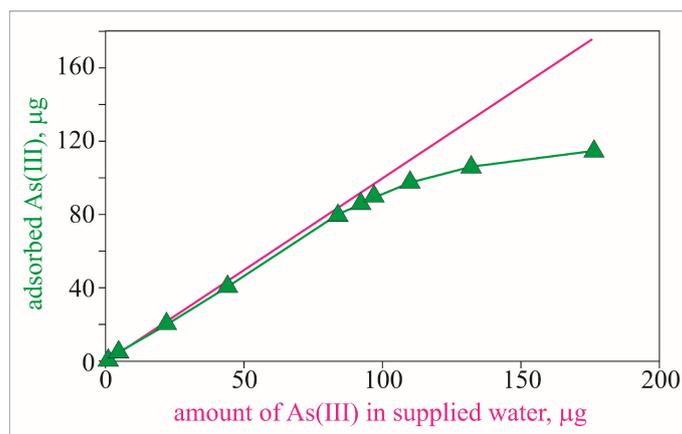


Figure 5. Ratio of the adsorbed amount of As(III) to the amount of As(III) in the supplied water.

The behavior of the adsorption concerning the amount of outflow (Figure 6) shows that up to the passage of about 700 doses, the efficiency of the adsorbent is close to 95%, as 87.04 µg of arsenic is adsorbed from 92.4 µg of supplied As (Table 2). Within these 700–715 doses, the concentration of arsenic in the effluent spent solution is below the permissible value of 10 µg/L for drinking water.

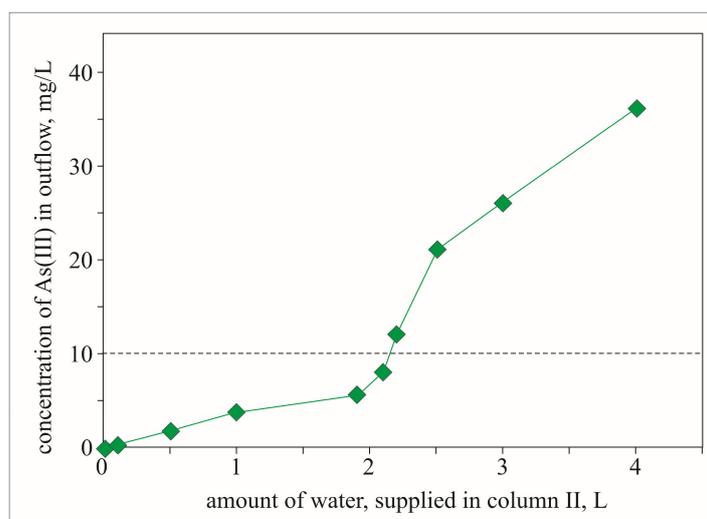


Figure 6. As(III) concentration in the outflow in column II.

The estimated amount of adsorbed arsenic is about 17 µg/g (Table 2), indicating a relatively good efficiency of the sorbent. The sorption capacity of similar sorbents varies from about 9 mg/g [17] to 75.4 µg/g [44], corresponding to the specific characteristics of the sorbents and adsorption conditions (for example, the value of 75.4 µg/g is reached at pH = 3). The results obtained by us (17 µg/g) are most comparable with the data for a similar sorbent (22 µg/g) used in similar conditions at three times longer contact time [29]. In the following 633 doses, the efficiency of the sorbent decreases until it is almost completely exhausted. Within this volume, only 24% of the total amount of arsenic (114.14 µg) is adsorbed.

Table 2. Results of As(III) adsorption by granular Fe-Cpt sorbent in sorption column II.

Amount of Water with As(III) (44µg/L) Passed through the Column			As(III) Content in Supplied Water		As(III) Concentration in Outflow (µg/L)	Adsorbed As(III)		
Total Volume (L)	Dose (Number)	Top-Up Volume (mL)	Between Measurements (µg)	To Reached Volume (µg)		Between Measurements (µg)	To the Particular Sample (µg)	Per Sorbent Unit (µg/g)
0.02	7	20	0.88	0.88	0 *	0.88	0.88	0.166
0.10	33	80	3.52	4.40	0.3 *	3.50	4.38	0.826
0.50	167	400	17.6	22.0	1.85 *	16.86	21.24	4.008
1.00	333	500	22.0	44.0	3.8	20.08	41.32	7.796
1.90	633	900	39.6	83.6	5.6	38.5	79.82	15.060
2.10	700	200	8.80	92.4	7.9	7.22	87.04	16.423
2.20	733	100	4.40	96.8	12	3.20	90.24	17.026
2.50	833	300	13.2	110	21	6.90	97.14	18.328
3.00	1000	500	22.0	132	26	9.00	106.14	20.026
4.00	1333	1000	44.0	176	36	8.00	114.14	21.536

* Values are calculated by interpolation between 0–3.8 µg/L.

3.2.2. Adsorption of As(V) in a Sorption Column

Based on the observed adsorption data (Table 3), it can be concluded that the sorbents Fe-Cpt and Mg,Fe-Cpt retained their high extraction efficiency for the adsorption of As(V)—100% and 92.9%, respectively. Unlike the two Fe-containing sorbents, the Al-Cpt sorbent has a very low uptake efficiency (64.75%). In contrast to the adsorption of As(III), after the 10th dose (100 mL of aqueous solution passed through the column), the concentration of arsenate ions in the effluent waste solution exceeded the maximum permissible concentration of 10 µg/L.

Table 3. Results of As(V) adsorption by granular sorbents in sorption column I.

Amount of Water with As(V) (44µg/L) Passed through the Column			As(V) Content in Supplied Water (µg)	As(V) Concentration in Outflow (µg/L)	Adsorbed As(V) in the Sorbent		
Total Volume (L)	Dose (Number)	Top-Up Volume (mL)			(%)	(µg)	(µg/g)
Al-Cpt							
0.02	2	20	0.88	<dl	100	0.88	0.055
0.10	10	80	3.52	13	70.45	2.48	0.155
0.50	50	400	17.6	14	68.18	12.00	0.750
1.00	100	500	22.0	15	65.91	14.50	0.906
1.92	192	920	40.48	17	61.36	24.84	1.553
			84.48			54.7	3.419
Fe,Mg-Cpt							
0.02	2	20	0.88	<dl	100	0.88	0.055
0.10	10	80	3.52	<dl	100	3.52	0.220
0.50	50	400	17.6	<dl	100	17.6	1.100
1.00	100	500	22.0	2.1	90	19.9	1.244
1.92	192	920	40.48	3.9	90	36.58	2.286
			84.48			78.48	4.905
Fe-Cpt							
0.02	2	20	0.88	<dl	100	0.88	0.055
0.10	10	80	3.52	<dl	100	3.52	0.220
0.50	50	400	17.6	<dl	100	17.6	1.100
1.00	100	500	22.0	<dl	100	22.0	1.375
1.92	192	920	40.48	<dl	100	40.48	2.530
			84.48			84.48	5.280

dl: detection limit of the method.

3.2.3. Adsorption of As(III) + As(V) in a Sorption Column

In agreement with the established high efficiency in mono-anion solutions, Fe-cpt sorbent also performs very well in mixed solutions (Table 4). The experimental data showed

a high efficiency of the sorbent (adsorbed 84.41 μg out of 84.48 μg sold, which is close to 90%, similar to that of As(III) adsorption.

Table 4. Results of As(III) + As(V) adsorption by granular Fe-Cpt sorbent in sorption column I.

Amount of Water with As(III) + As(V) (44 $\mu\text{g/L}$) Passed through the Column			As Content in Supplied Water (μg)	Concentration of As in Outflow ($\mu\text{g/L}$)	Adsorbed As in the Sorbent			
Total Volume (L)	Dose (Number)	Top-Up Volume (mL)			(%)	(μg)	($\mu\text{g/g}$)	
Fe-Cpt								
0.02	2	20	0.88	<dl	100	0.88	0.055	
0.10	10	80	3.52	<dl	100	3.52	0.220	
0.50	50	400	17.6	<dl	100	17.60	1.100	
1.00	100	500	22.0	<dl	100	22.00	1.375	
1.92	192	920	40.48	4.1	90	36.41	2.276	
			84.48			80.41	5.026	

dl: detection limit of the method.

3.2.4. Data Analysis

In the analysis of adsorption data from aqueous solutions, the Langmuir and Freundlich isotherms are most commonly used. Langmuir (K_L) and Freundlich (K_f) constants are indicators of sorption capacity. In both models, the amount adsorbed per unit mass of adsorbent (S) relates to the equilibrium concentration of the adsorbate in the liquid phase (C_e). The amount of adsorbed arsenic was calculated using the formula:

$$S = \frac{(C_i - C_e)V}{m} \quad (4)$$

where C_i is the initial and C_e is equilibrium concentration of As(III) ($\mu\text{g/L}$); V is the volume passed (L) and m is the mass of adsorbent (g).

The linear form of the Langmuir equation allows the calculation of the adsorption parameters:

$$\frac{1}{S} = \frac{1}{S_m} + \frac{1}{S_m K_L} \frac{1}{C_e} \quad (5)$$

The Langmuir constants can be determined graphically by plotting the reciprocal values of the equilibrium concentration of the adsorbate in the solution ($\frac{1}{C_e}$) on the abscissa, and the reciprocal values of the adsorbed amount per gram of adsorbent ($\frac{1}{S}$) on the ordinate (Figure 7).

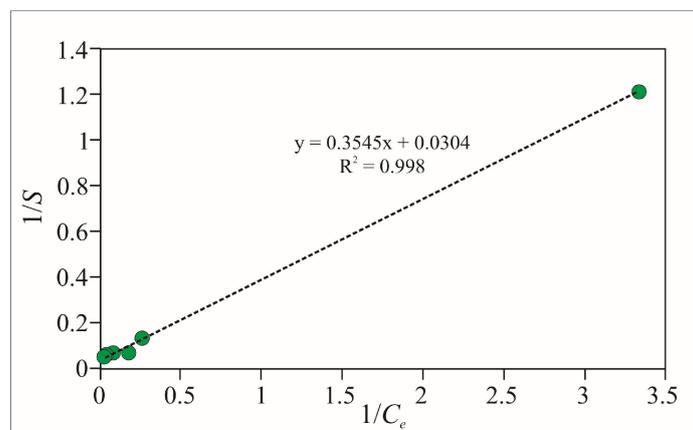


Figure 7. Linear form of the Langmuir isotherm for Fe-Cpt sorbent.

The calculated values of the coefficients for As(III) are for Fe-Cpt $K_L = 0.0858 \text{ L}/\mu\text{g}$ and $S_m = 32.90 \mu\text{g/g}$; for Al-Cpt $K_L = 0.0558 \text{ L}/\mu\text{g}$ and $S_m = 21.98 \mu\text{g/g}$; and for Mg,Fe-Cpt $K_L = 0.0496 \text{ L}/\mu\text{g}$ and $S_m = 24.75 \mu\text{g/g}$.

The correlation factor R^2 for all three sorbents is close to one (0.998, 0.996, and 0.97 for Fe-Cpt, Al-Cpt, and Mg,Fe-Cpt, respectively), which indicates that the adsorption of arsenite ions very well fits to the Langmuir model. The calculated value for $K_L = 0.0858$ L/ μ g for Fe-Cpt is in good agreement with the literature data [25,32–35] for similar adsorbents (Fe-OH-coated various zeolites and other natural materials). The calculated maximum adsorption capacity (32.9 mg/g) was less than the capacity (79 mg/g) of Fe-treated activated carbon [25] but greater than that for the goethite (25 mg/g) and is comparable with data published by other authors [17,30,35,36]. The results for adsorption of arsenate are as the data obtained for Fe-coated sorbents.

The Freundlich model assumes non-uniformity of adsorption sites. This heterogeneity is assumed to be due to both the presence of adsorption sites with different energies and a consequence of the action of repulsive forces between adsorbed atoms and molecules.

The logarithmic equation represents the linear form of the mathematical equation of the Freundlich isotherm:

$$\log(S) = \log(K_f) \cdot N \log(C_e), \quad (6)$$

where K_f and N are Freundlich constants. K_f is an index of adsorption capacity and N being an index of adsorption intensity. The coefficients can be calculated from the $\log(C_e)$ to $\log(S)$ plot, where K_f is (the perpendicular/horizontal projection of the line onto the abscissa), and N reflects the slope of the line.

From the constructed graph for the studied Fe-Cpt adsorbent (Figure 8), the values of the two constants were calculated: $K_f = 5.689$ and $N = 0.396$.

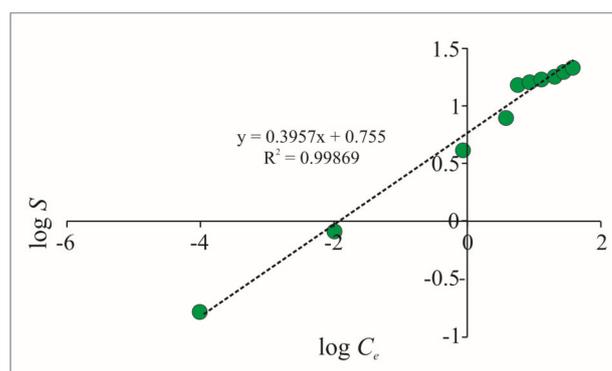


Figure 8. Linear form of the Freundlich isotherm for Fe-Cpt sorbent.

The greater the value of the Freundlich constant K_f , the greater the assumed activity of the adsorption sites. The mathematical constant N is an empirical constant that depends on the nature of the adsorption sites. Values of $N > 1$ suggest adsorption in non-equivalent adsorption sites. For values of $N < 1$, the Freundlich model approaches the Langmuir model for homogeneity of adsorption sites.

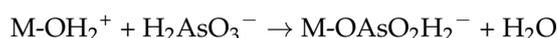
The obtained correlation factor is $R^2 = 0.9869$, which gives reason to assume that the Freundlich isotherm is also applicable to characterize the studied adsorption process. The obtained values for K_f and especially for N ($N < 1$), however, indicate that the adsorption in the present experiment follows the Langmuir model. These results correspond to the studies of many authors who assume that the isotherms related to the adsorption of anions reflect pseudo-Langmuir sorbate/sorbent relationships; i.e., there is one dominant mode of adsorption binding, most commonly through ligand exchange, resulting in complexation.

3.2.5. Binding Mechanisms

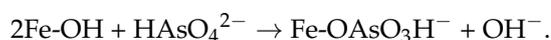
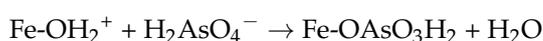
Since the active surface of the sorbents is composed of iron or aluminum hydroxides and oxyhydroxides, the adsorption of arsenic proceeds with the formation of complexes with the cations from the active surface [24].

The starting As(III) solution has a measured pH of 6.8, indicating a neutral to slightly acidic nature of the solution. In the range of pH values 6–9, As(III) is mainly represented by the neutral form of arsenic acid H_3AsO_3^- , but a small amount of dissociated arsenite ions (H_2AsO_3^-) is also probably present.

For the present study, the adsorption of As(III) most likely takes place by the mechanism of inner-sphere binding, as for the H_3AsO_3^0 a reaction takes place between a basic and an acidic species with the formation of complexes, and for the monovalent H_2AsO_3^- ions—at the expense of protonated hydroxyl groups:



Under the conditions of the experiment with a solution of As(V) (pH 6.9), the dominant ions of arsenic are H_2AsO_4^- and HAsO_4^{2-} [2]. The mechanisms of inner- and outer-sphere connection can be described by reactions:



The analysis of the obtained Langmuir and Freundlich isotherms shows that the adsorption follows the Langmuir model, proceeding on equivalent adsorption sites with inner sphere complex formation. The results of the arsenic rehabilitation of spent sorbent support such an assumption. The elution results show complete recovery of the adsorbed arsenic with a small amount of NaOH (20 g spent sorbent was washed with 100 mL 0.1M NaOH). The X-ray powder XRD patterns of the NaOH-treated spent sorbents were identical to the starting ones. Because the formation of arsenites or arsenates was not registered, the base-acid reaction proceeds, resulting in the formation of iron hydrogen arsenite complexes. The results of the reuse of the sorbents determined adsorption efficiency as of the initial samples, which indicates that the regeneration is complete, and the sorbents have preserved their qualities.

3.3. Arsenic Uptake from a Constant Volume System (Batch System) Static Condition

Adsorption of arsenic in a constant volume system has a very high efficiency (Table 5). The amount of adsorbed arsenic in the batch system from the sorbents Al-Cpt-f, Fe-Mg-Cpt-f, and Fe-Cpt-f is much greater than the amount of retained arsenic on the corresponding granular sorbents for the same amount of As(III) or As(V) solution (300 mL). Some authors [17,44] have established similar differences in arsenic adsorption in the two different systems. The high efficiency of the constant volume systems is due to the long contact time between the sorbents and the solutions (in the present study—7 h 30 min) on the one hand, and on the other hand, due to the small sizes of the sorbents, which provide a large adsorption surface. The static experiment was performed with the fine fraction obtained as a waste product after the sieving of the coated sorbents.

Table 5. Results of the adsorption of As(III) and As(V) in a constant volume system (batch system).

Sorbent	Concentration of As(III) ($\mu\text{g/L}$) in the Solution after				Amount of Adsorbed As(III) at the End ($\mu\text{g/g}$)	Concentration of As(V) ($\mu\text{g/L}$) in the Solution after				Amount of Adsorbed As(V) at the End ($\mu\text{g/g}$)
	30 min	60 min	90 min	450 min		30 min	60 min	90 min	450 min	
Al-Cpt-f	4.2	3.0	<dl	<dl	132	11	7.2	4.5	<dl	132
Fe,Mg-Cpt-f	3.6	2.1	<dl	<dl	132	5	3	<dl	<dl	132
Fe-Cpt-f	<dl	<dl	<dl	<dl	132	<dl	<dl	<dl	<dl	132

dl: detection limit of the method.

Despite the good adsorption characteristics, the method in a batch system is not suitable for the treatment of large amounts of water. Its disadvantage is related to the fact that the installations would take up a lot of space, and continuous stirring is required, which is

associated with additional energy consumption. The need for suspension flocculation and filtration is also the disadvantage of adsorption in a constant volume system. However, the method could be used for the purification of solutions with a high arsenic concentration, such as technological waste products, solutions obtained during the regeneration of sorbents from sorption columns, etc.

3.4. Arsenic Uptake by Precipitation Reactions

In the present study, the experiments of precipitation of aluminum or iron oxyhydroxides in aqueous solutions with 4200 µg/L As(III) and As(V) solutions without or with the addition of a small amount of clinoptilolite tuff (fraction < 20 µm) were carried out.

The results show that the reactions in the presence of iron cations work better than in the presence of aluminum cations. After the precipitation experiment with iron salts, the As(III) or As(V) concentration of supernatant solutions is 3 µg/L. The results of precipitation reactions with Al salts show quite worse performance for arsenite and arsenate uptake. The concentration of As(III) and As(V) in aqueous solution is 400 µg/L and 450 µg/L, respectively. In the experiment with the addition of a micron fraction of clinoptilolite tuff, the adsorption is worse (concentration of As(III) in the supernatant solution was 600 µg/L for reactions with Al and 5 µg/L for reactions with Fe, respectively) but flocculation of the suspension was accelerated five times. The results for As(V) uptake by precipitation reactions are in the same range—the concentration of As(III) in the solution was 550 µg/L for reactions with Al and 3 µg/L for reactions with Fe, respectively.

4. Conclusions

The adsorption with the granular sorbents shows good possibilities for obtaining water with an arsenic concentration below the permissible value of 10 µg/L for drinking water. The determined efficiency of the Fe-containing sorbents for arsenite and arsenate uptake from wastewater with 44 mg/L concentration is 400 L of water per kg sorbent with the rate of 2–2.4 L/h/kg.

The powdered sorbent showed a much higher adsorption capacity than the granular one in the batch system. As this requires further processing of flocculation and filtration, it is more suitable for small quantities of water with a very high concentration of arsenic.

For waters with high concentrations of arsenic, the extraction method by precipitation reactions is most effective and suitable.

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