

EQUILIBRIUM STUDY FOR ADSORPTION OF ARSENITES AND ARSENATES FROM AQUEOUS SOLUTIONS BY APPLICATION OF MODIFIED NATURAL INORGANIC MATERIALS

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Abstract: Two raw materials were investigated to provide a cheap and efficient arsenic removal from drinking water supply. For this purpose, studied materials were modified by insertion of iron within the materials' structure and substitution of calcium and magnesium ions with sodium ions in order to improve the sorptive and ion-exchange properties. White tuff from Strmos region and the commercially available Zeofit were the materials considered within our study. Simulations were performed on prepared solutions of arsenic added to water samples from the water supply in Skopje. Obtained results suggest that the Zeofit material produced better results regarding arsenic adsorption at various initial arsenic concentrations. The white tuff from Strmos is effective only at lower initial concentrations of arsenic. Regarding the equilibrium study on investigated systems for both materials, implemented models produced a good fit when applied to As⁵⁺ systems. The Strmos material did not produce satisfactory fitting results to implemented equilibrium models for the As³⁺ systems.

Keywords: arsenic removal, adsorption, adsorbent modification, modeling, equilibrium study

Introduction

High quality drinking water supply is an essential precondition for human health, quality of life and any type of further development. Some analysis of the drinking water supply in Macedonia indicate a presence of arsenic, with significant quantities detected in surface and underground waters in the region of Kumanovo, eastern part of the country (Sveti Nikole, Probistip, Stip, Kocani, Vinica, Radovis and Strumica), Kavadarci and Gevgelija region. An increased presence of arsenic, and therefore a constant concern, is located in the geothermal water bodies in Kocani and the Kozuf region and some mineral water bodies and rivers, such as Bosavica, Dosnica, Konska River and Anska River. For the forthcoming period, this problem will become a growing concern issue.

Considering presented facts and concerning issues, general criteria imposed by the WHO [1] and EU Directives [2] are adopted in Macedonia and implemented within the legal regulative that defines the water supply quality, where the maximal permitted concentrations (MPC) regarding arsenic presence is 10 µg/l [3].

Arsenic represents a highly reactive element that occurs in several oxidation states (-3, 0, +3 and +5). Most common natural forms of arsenic are arsenite acids (H₃AsO₃, H₃AsO₃⁻, H₃AsO₃²⁻), arsenate acids (H₃AsO₄, H₃AsO₄⁻, H₃AsO₄²⁻), arsenates, arsenates, methyl-arsenic acid, dimethyl-arsenic acid, arsine etc. As(III) represents a strong acid agent that creates complexes with oxygen and nitrogen, whereas As(V) represents a mild acid agent that creates sulfide complexes. Inorganic arsenic forms are very common within water springs and is mobilization prone at oxidizing and reduction conditions like most of the metalloids. The two most present forms are the arsenite (AsO₃³⁻) and arsenate (AsO₄³⁻), or As(III) and As(V) respectively. As(V) or arsenate forms are As₄³⁻, HAsO₄²⁻, H₂AsO₄⁻, whereas As(III) or arsenite forms are As(OH)₃, As(OH)₄⁻, AsO₂OH²⁻ и AsO₃³⁻. As(V) forms are dominant and stable in aerobic conditions, and As(III) forms are dominant and stable in mildly anaerobic environment, such as underground water bodies [4].

According to presented reasons, an arsenic removal is a necessity regarding drinking water treatment systems. Several removal techniques can be employed for arsenic removal, such as coagulation and flocculation with iron based salts [5]. This research is focused on the application of a specific filter material that, along with the mechanical treatment of drinking water, possesses active arsenic adsorption properties at lower initial arsenic concentrations, present in previously treated effluents.

Materials and methods

Two commercially available materials were used within the experimental studies of this research: white opalized tuff from Strmos mine and Zeofit material obtained from Rankovce mine in Palanka region. The chemical characterization of the investigated raw materials as potential adsorbents is presented in Table 1.

Table 1. Chemical characterization of used raw materials

Parameter	Strmos	Palanka
LOI	1.97	4.38
Al ₂ O ₃	2.98	19.25
CaO	0.18	4.29
Cr ₂ O ₃	0.00	0.00
Fe ₂ O ₃	0.10	5.00
K ₂ O	0.08	2.82
MgO	0.00	0.70
Mn ₂ O ₃	0.01	0.11
Na ₂ O	0.00	2.79
P ₂ O ₅	0.02	0.22
SO ₃		
SiO ₂	93.62	59.00
SrO	0.02	0.12
TiO ₂	0.53	0.76
ZnO	0.01	0.01
Total	99.52	99.45

The characterization of the investigated materials also included the analysis of mineral constituents, performed through XRD mineralogical analysis, and is presented in Table 2.

Table 2. XRD analysis of investigated raw materials

	Strmos	Palanka
Quartz	5.5	0.3
Cristobalite+Tridymite	82	4.6
Feldspads	4	56.1
Fe(OH) ₃		5.4
Clays	5.4	8.1
Calcite		1.5
Gypsum	2.5	-
TiO ₂	0.6	-
Amorphous	*	24
Total	100	100

The analysis of the obtained mineralogical composition suggests that the raw material from Strmos has a dominant SiO_2 mass with an appropriate crystal composition (Quartz, Tridymite and Cristobalite) in crypto-crystal phase, whereas the Palanka material has a dominant feldspads mass with traces of free carbonates, free iron in forms of oxides and hydroxides, clay and a certain amount of amorphous phase SiO_2 .

A physical-chemical analysis of the composition of the drinking water from Skopje water supply system is given in Table 3. Presented values of the investigated parameters represent an average value of several analyses performed in the Center for Sanitary Control laboratories within the public enterprise "Water Supply and Sewage" Skopje. This water supply was used for preparation of experimental solutions.

Table 3. Physical-chemical composition of used water

Parameter	MPC*		Result
	From	To	
Temperature			15.9
Odor		0.00	None
Taste			None
Turbidity*		1.50	0.380
Conductivity*		1,000.00	539.000
pH*	6,50	9.50	7.350
COD (permanganate)*		8.00	2.210
Total hardness*			17.520
Dry residue105°C		1,000.00	315.200
Alkalinity - p		0.00	0.000
Alkalinity - m	30,00	120.00	59.160
Ammonia*		0.50	0.000
Nitrites*		0.10	0.000
Nitrates*		50.00	6.920
Chlorides*		250.00	8.260
Sulphates		250.00	9.600
Silicates		20.00	11.070
Hydrocarbonates			360.510
Manganese		0.05	0.000
Iron		0.20	0.020
Calcium		200.00	99.600
Magnesium		50.00	15.550
Sodium		200.00	7.600
Potassium		12.00	1.030
Chromium (total)*		0.05	0.010
Copper		0.10	0.000
Zinc		3.00	0.020
Aluminium		2.00	0.020
Nickel		0.02	0.010

MPC* - maximal permitted concentration according to the "Rulebook for water safety", published by the Official Gazette of R. Macedonia 46/2008

An operating solution with concentration of 1 g/l was used for preparation of experimental solutions with concentrations of 20, 30, 40 and 90 $\mu\text{g/l}$ of As(III) and As(V) by utilization of the following salts [6], provided by FLUKA Riedel-de-Haen - Germany:

- Sodium arsenite (As^{+3}), NaAsO_2 , p.a.
- Disodium meta-arsenate (As^{+5}), $\text{Na}_2\text{HAsO}_4 \cdot x\text{H}_2\text{O}$, p.a.

Modification

An acid treatment was implemented for the raw material modification and for the chemical reaction in buffer solutions for application of an iron hydroxide layer. The iron hydroxide represents a macromolecule and the porous structure of the raw material is convenient for its insertion, as well as for the introduction of sodium ions as a neutralizing effect and as a component for the stabilization of the material. The procedures of acid-base treatment, especially regarding the insertion of the iron, are achievable even at room temperature, according to the literature data. On the other hand, best results are obtained at operating temperatures of 65-70 °C. For this procedure, the following chemicals were used: 4% HCl, 0.1 M FeCl₃, acetate buffer with pH 3.6 (composed of 0.2 M CH₃COONa and 0.2 M CH₃COOH), 4% NaOH, 4% NaCl and de-ionized water (for preparation of adequate solutions and material washing) [7-13].

The modified materials were subjected to a chemical analysis to determine the effect on the material and obtained results are presented in Table 4.

Table 4. Chemical analysis of the modified material

Parameter	Strmos	Palanka
LOI	3.36	7.74
Al ₂ O ₃	2.71	15.95
CaO	0.14	2.96
Cr ₂ O ₃	0.01	0.01
Fe ₂ O ₃	4.18	9.32
K ₂ O	0.09	2.13
MgO	0.00	0.38
Mn ₂ O ₃	0.00	0.04
Na ₂ O	0.31	2.48
P ₂ O ₅	0.16	0.14
SO ₃		
SiO ₂	87.27	57.70
SrO	0.07	0.09
TiO ₂	0.92	0.66
ZnO	0.00	0.02
Total	99.22	99.66

The analysis was performed according to the same procedure and on the same instrument as in the case of the raw material using the analyzer XRF ARL 9900 XP Thermo ARL. An AAS - Perkin Elmer AA 700/800 with a graphite furnace was used to determine the presence of arsenic within our experimental work at wavelength of 193.7 nm. These analyses were conducted in the Center of sanitary control, Public enterprise "Water Supply and Sewage" Skopje.

Experimental procedure

Experiments were performed using magnetic stirrers on a boron-silicate laboratory glass. The experimental procedure was conducted as follows: 5 g of the material (fraction <0.63 mm) was added in 2 l of solution with different initial concentrations of As, 20, 30, 40 and 90 µg/l in the form of As³⁺ and As⁵⁺. Adsorption was performed at room temperature and 750 rpm in a laboratory glass of 2000 ml. At predefined time sequences, a 5 ml sample was collected and filtrated through "black" filter paper. Then the sample was placed in a 10 ml cuvette followed by 150 µl concentrated HNO₃ as conserver. Prepared samples were used to determine the total amount of arsenic.

Results and discussion

Effect of initial arsenic concentration

Figure 1 presents the dependency of arsenic removal percentage from the initial arsenic concentration in the solution at constant values for adsorption time. From presented results it can be concluded that modified materials from Palanka region have a similar efficiency of arsenic removal regardless of the arsenic form (III or V), whereas modified materials from Strmos tuff produce better results regarding arsenic removal at lower initial concentrations of arsenic within the analyzed samples.

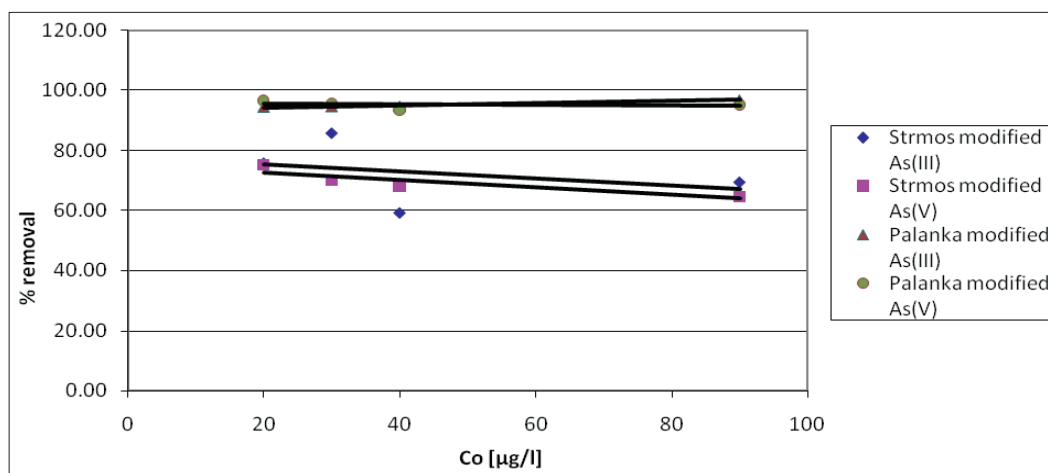


Figure 1. Effect of initial arsenic concentration on the adsorption efficiency of As^{3+} and As^{5+} by hydrous ferric oxide modified materials ($C_0 = 20, 30, 40$ and $90 \mu\text{g/l}$; $\text{pH}=7.35$; mass of adsorbent (fraction of $< 0.63 \text{ mm}$) = 2.5 g/L ; $T = 22^\circ\text{C}$; $\tau = 420 \text{ min}$)

Effect of adsorption time

Figure 2 presents the dependency of adsorbent capacity from the adsorption time at constant initial concentration of arsenic. The analysis of obtained results suggests that Palanka material produces almost equal adsorption capacity for As^{3+} and As^{5+} , whereas Strmos material has a greater adsorption capacity for As^{5+} . Regarding the adsorption kinetics, the Palanka material produced greater initial adsorption rate, followed by slower diffusive adsorption. The Strmos material, especially in the case of As^{5+} adsorption process, produces a relatively uniform adsorption rate.

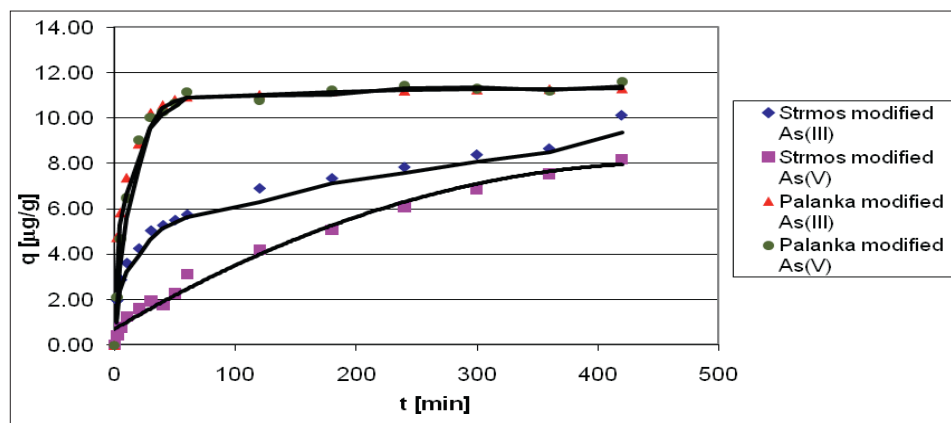


Figure 2. Effect of initial arsenic concentration on the adsorption efficiency of As^{3+} and As^{5+} by hydrous ferric oxide modified materials ($C_0 = 30 \mu\text{g/l}$; $\text{pH}=7.35$; mass of adsorbent (fraction of $< 0.63 \text{ mm}$) = 2.5 g/L ; $T = 22^\circ\text{C}$; $\tau = 420 \text{ min}$)

Freundlich and Langmuir equilibrium adsorption isotherms

Freundlich's equilibrium model equation

$$\log q^* = \log K_F + \frac{1}{n} \log C^*$$

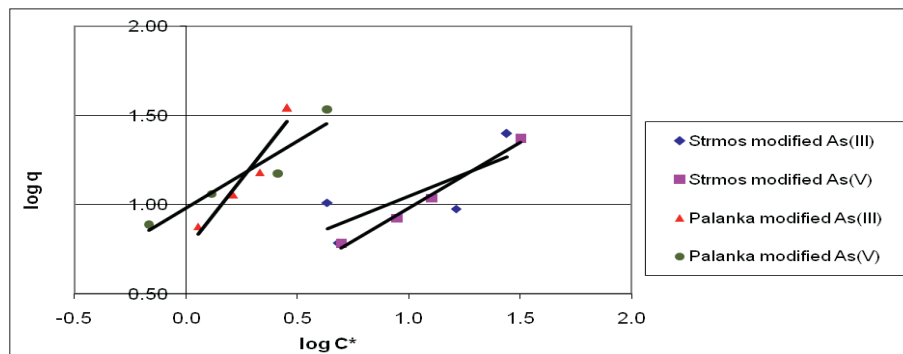


Figure 3. Freundlich - equilibrium adsorption isotherms for As³⁺ and As⁵⁺ adsorption on hydrous ferric oxide modified materials from Strmos (C₀ = 20,30,40 and 90 μg/l; pH=7.35; mass of adsorbent (fraction of < 0.63 mm) = 2.5 g/L; T= 22°C; τ = 420 min)

Langmuir's equilibrium model equation

$$1. \frac{C^*}{q^*} = \frac{1}{q_m} + \frac{C^*}{q_m K^*} \quad 2. \frac{1}{q^*} = \frac{1}{q_m} + \frac{1}{q_m K^*} \quad 3. q^* = q_m - \frac{q^*}{K^*}$$

Presented three forms of the model are equivalent and used depending on the obtained data and the specific case study.

The boundary adsorption capacity of the solid phase, q_m, is related to the Langmuir equilibrium constant, K_L, through the equation:

$$K_L = q_m K$$

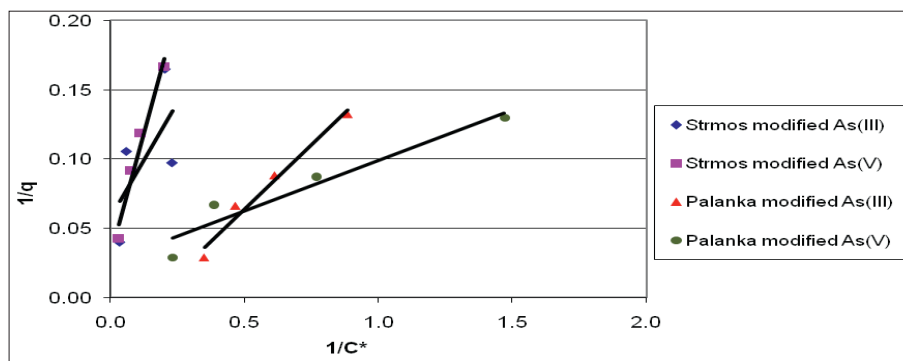


Figure 4. Langmuir - equilibrium adsorption isotherms for As³⁺ and As⁵⁺ adsorption on hydrous ferric oxide modified materials from Strmos (C₀ = 20,30,40 and 90 μg/l; pH=7.35; mass of adsorbent (fraction of < 0.63 mm) = 2.5 g/L; T= 22°C; τ = 420 min)

Table 5. Calculated coefficient values for the model equation

		Freundlich constants			Langmuir constants			
		n	K _F	R ²	q _m	K	K _L (q _m K)	R ²
Strmos	As ³⁺	2.0028	1.7262	0.5895	17.4216	0.1723	3.0017	0.4189
	As ⁵⁺	1.3508	1.2696	0.9917	33.5570	0.0418	1.4027	0.9691
Palanka	As ³⁺	0.6319	2.1132	0.9294	34.7222	0.1551	5.3854	0.9747
	As ⁵⁺	1.3373	2.6629	0.9085	38.4615	0.3571	13.7346	0.9257

Obtained results and model coefficients regarding the equilibrium study on investigated systems for both materials, implemented models produced a good fit when applied to As^{5+} systems. The Strmos material did not produce satisfactory fitting results to implemented equilibrium models for the As^{3+} systems.

Legend:

q_m – The boundary adsorption capacity of solid phase ($\mu\text{g/g}$)

C_0 – Concentration of arsenic in solution before adsorption ($\mu\text{g/L}$)

C^* – Equilibrium concentration of arsenic in solution after adsorption ($\mu\text{g/L}$)

n – Specific constant

K – Specific constant

K_F – Freundlich's equilibrium constant

K_L – Langmuir's equilibrium constant

Conclusions

- Modified materials from Palanka region have a similar efficiency of arsenic removal regardless of the arsenic form (III or V) and initial concentration, whereas modified materials from Strmos tuff produce better results regarding arsenic removal at lower initial concentrations of arsenic within the analyzed samples.
- Regarding the adsorption kinetics, the Palanka material produced greater initial adsorption rate, followed by slower diffusive adsorption. The Strmos material, especially in the case of As^{5+} adsorption process, produces a relatively uniform adsorption rate.
- Implemented models produced a good fit to the equilibrium equations when applied to As^{5+} systems for the Palanka and Strmos materials.
- The Strmos material did not produce satisfactory fitting results to implemented equilibrium models for the As^{3+} systems

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