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Adsorption of arsenites and arsenates from aqueous solutions by application of modified natural inorganic materials - a kinetic study

Two commercially available adsorbents, white tuff from Strmos region and a material with a commercial name Zeofit obtained from Palanka region, were investigated as possible raw materials for adsorption of arsenites and arsenates from aqueous solutions. These raw materials were modified through chemical insertion of iron within the basic material structure and ionic substitution of calcium and magnesium ions with sodium ions in order to improve the sorptive and ion-exchange properties of studied raw materials. Obtained results from the experimental study of the adsorption of arsenic ions from simulated aqueous solutions suggest that the Zeofit material produced better results than the white tuff material, which showed satisfactory adsorption efficiency only at lower arsenic ions concentrations. Drinking water from the water supply system in Skopje was used for preparation of the studied arsenic ions solutions. Performed kinetic study and resulting kinetic models for both materials, generated a kinetic model of first order for the white tuff material, whereas the Zeofit material adsorption kinetics indicated a pseudo-second order.

Keywords: adsorption, adsorbent modification, modeling, kinetic 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, Kanska 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 (H_3AsO_3 , H_3AsO_3^- , $\text{H}_3\text{AsO}_3^{2-}$), arsenate acids (H_3AsO_4 , H_3AsO_4^- , $\text{H}_3\text{AsO}_4^{2-}$), 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 (AsO_3^{3-}) and arsenate (AsO_4^{3-}), or As(III) and As(V) respectively. As(V) or arsenate forms are As_4^{3-} , HAsO_4^{2-} , H_2AsO_4^- , whereas As(III) or arsenite forms are $\text{As}(\text{OH})_3$, $\text{As}(\text{OH})_4^-$, $\text{AsO}_2\text{OH}^{2-}$ и AsO^{3-} . 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 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

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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 an analysis of mineral constituents, performed through XRD mineralogical analysis, is presented in Table 2.

Table 2 - XRD analysis of investigated raw materials

Parameter	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 SiO₂ 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 SiO₂.

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 analysis 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 µg/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}), $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$, 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 FeCl_3 , acetate buffer with pH 3.6 (composed of 0.2 M CH_3COONa and 0.2 M CH_3COOH), 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_2O_3	2.71	15.95
CaO	0.14	2.96
Cr_2O_3	0.01	0.01
Fe_2O_3	4.18	9.32
K_2O	0.09	2.13
MgO	0.00	0.38
Mn_2O_3	0.00	0.04
Na_2O	0.31	2.48
P_2O_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 $\mu\text{g/l}$ in the form of As^{3+} and As^{5+} . 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 HNO_3 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.

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.

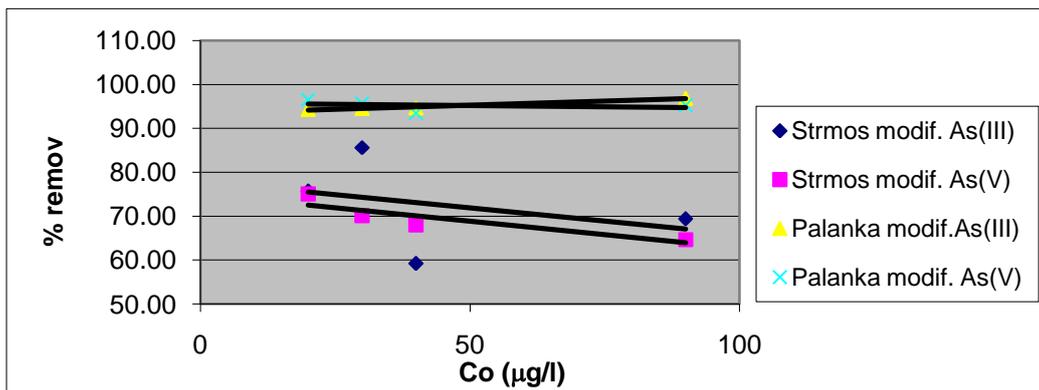


Figure 1 - Effect of initial arsenic concentration on the adsorption efficiency of As^{3+} and As^{5+} by hydrous ferric oxide modified materials ($C_o = 20, 30, 40$ and $90 \mu\text{g/l}$; $\text{pH} = 7.35$; mass of adsorbent (fraction of $< 0.63 \text{ mm}$) = 2.5 g/L ; $T = 22^\circ\text{C}$; $t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

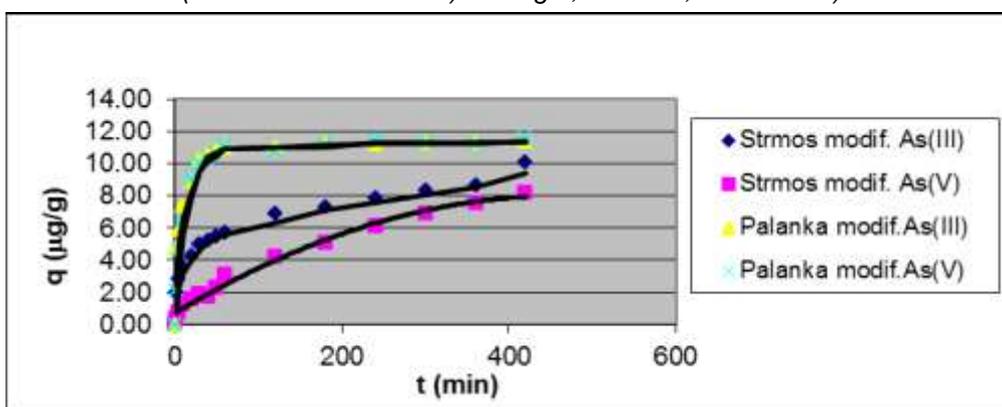


Figure 2 - Effect of initial arsenic concentration on the adsorption efficiency of As^{3+} and As^{5+} by hydrous ferric oxide modified materials ($C_o = 30 \mu\text{g/l}$; $\text{pH} = 7.35$; mass of adsorbent (fraction of $< 0.63 \text{ mm}$) = 2.5 g/L ; $T = 22^\circ\text{C}$; $t = 420 \text{ min}$)

Kinetic models

The basic empirical model that describes the kinetics of many processes as well as the adsorption kinetics represents a step function:

$$R = k_t t^m$$

or its logarithmic form:

$$\ln R = \ln k_t + m \ln t$$

where R is adsorption efficiency (%), t is adsorption (contact) time, k_t and m are model constants.

Kinetics model of first order

$$\ln C_t = \ln C_o - k_1 t$$

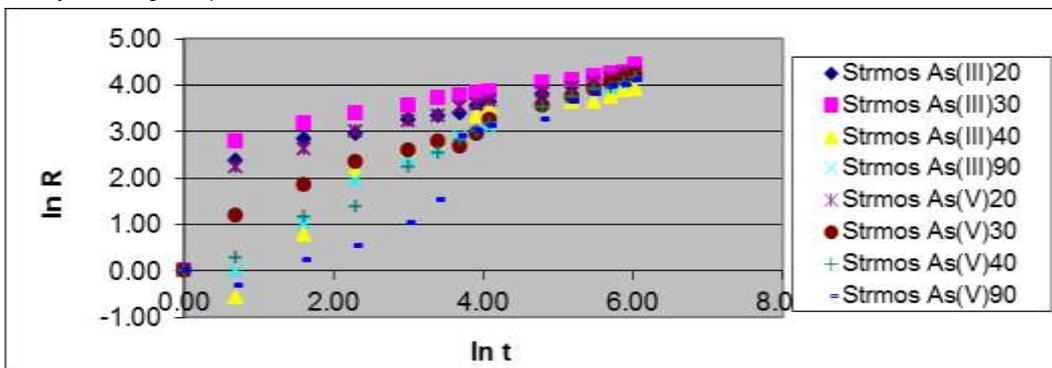


Figure 3 - $\ln R = f(\ln t)$ for the kinetics of As^{3+} and As^{5+} adsorption on hydrous ferric oxide modified materials from Strmos ($C_o = 20, 30, 40$ and $90 \mu\text{g/l}$; $\text{pH} = 7.35$; mass of adsorbent (fraction of $< 0.63 \text{ mm}$) = 2.5 g/L ; $T = 22^\circ\text{C}$; $t = 420 \text{ min}$)

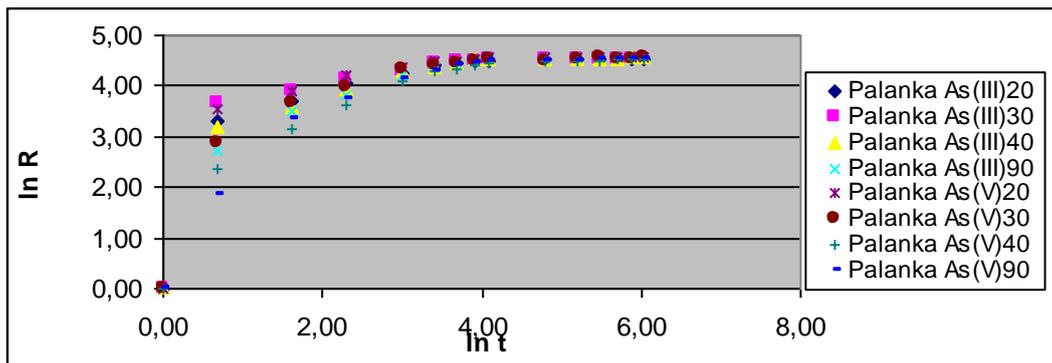


Figure 4 - $\ln R = f(\ln t)$ for the kinetics of As^{3+} and As^{5+} adsorption on hydrous ferric oxide modified materials from Palanka ($C_o = 20, 30, 40$ and $90 \mu\text{g/l}$; $\text{pH} = 7.35$; mass of adsorbent (fraction of $< 0.63 \text{ mm}$) = 2.5 g/L ; $T = 22^\circ\text{C}$; $t = 420 \text{ min}$)

Kinetics model of pseudo-second order

$$\frac{dq_t}{dt} = k_{ads} (q_c - q_t)^2, \quad t = 0; \quad q_c = 0$$

where k_{ads} is the constant of equilibrium state kinetics of pseudo-second order (g/mgmin), q_c is the adsorption capacity in equilibrium state (mg/g) and q_t is quantity of adsorbed arsenic on the adsorbent surface area at adsorption time t (mg/g).

After modification of the presented equation:

$$\frac{1}{q_t} = \frac{1}{h} + \frac{1}{q_e} t$$

where $h = k_{ads} q_e^2$ is the initial adsorption rate (mg/g min).

The values for q_e and k_{ads} are calculated from the slope and the cut-off from the linear graphical relation t/q_t versa t .

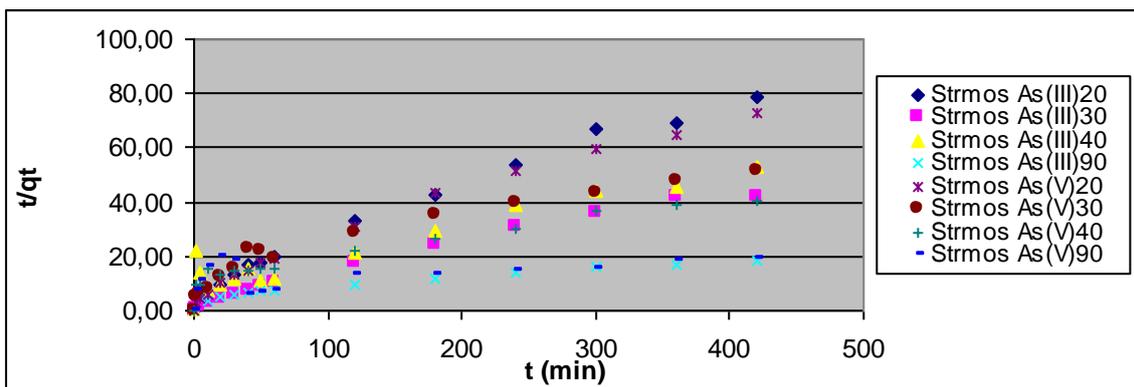


Figure 5 - Graphical relation t/q_t versa t for the As^{3+} and As^{5+} adsorption kinetics on hydrous ferric oxide modified materials from Strmos ($C_o = 20, 30, 40$ and $90 \mu\text{g/l}$; $\text{pH} = 7.35$; mass of adsorbent (fraction of $< 0.63 \text{ mm}$) = 2.5 g/L ; $T = 22^\circ\text{C}$; $t = 420 \text{ min}$)

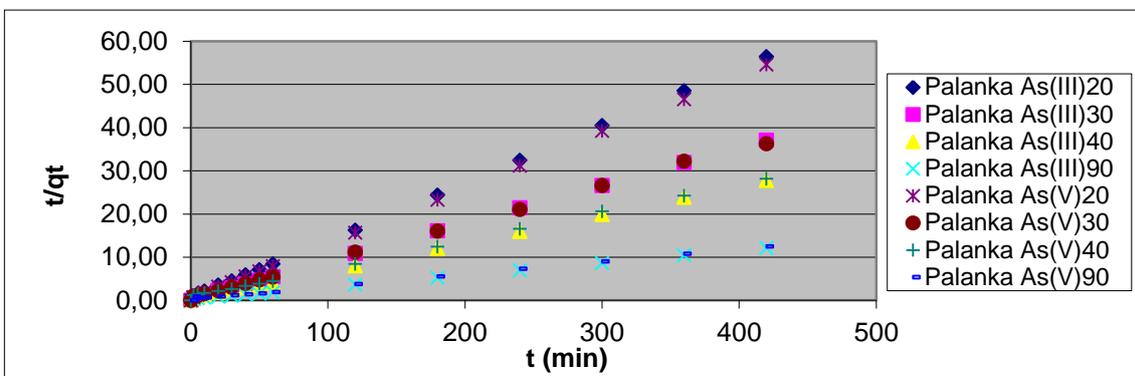


Figure 6 - Graphical relation t/q_t versa t for the As^{3+} and As^{5+} adsorption kinetics on hydrous ferric oxide modified materials from Palanka ($C_o = 20, 30, 40$ and $90 \mu\text{g/l}$; $\text{pH} = 7.35$; mass of adsorbent (fraction of $< 0.63 \text{ mm}$) = 2.5 g/L ; $T = 22^\circ\text{C}$; $t = 420 \text{ min}$)

Table 5 - Calculated coefficient values for the first order model equation for the Strmos material

Strmos	Step 1 (0-10 min)			Step 2 (10-420 min)		
	m	K_T	R^2	m	K_T	R^2
As ³⁺ 20	1.6981	-0.3624	0.8107	0.3244	0.3519	0.9898
As ³⁺ 30	1.8883	-0.2711	0.7766	0.2508	0.4529	0.9871
As ³⁺ 40	0.5391	-0.4713	0.4162	0.4445	0.1183	0.9137
As ³⁺ 90	0.6636	-0.7690	0.8097	0.5899	-0.1949	0.9947
As ⁵⁺ 20	1.5713	-0.3839	0.8020	0.3362	0.3508	0.9943
As ⁵⁺ 30	1.1210	-0.8179	0.9383	0.5384	-0.0218	0.9754
As ⁵⁺ 40	0.7321	-1.0841	0.9567	0.6788	-0.7435	0.9644
As ⁵⁺ 90	0.1730	-0.7945	0.2454	0.9324	0.0969	0.8823

Table 5a - Calculated coefficient values for the first order model equation for the Palanka material

Palanka	Step 1 (0-10 min)			Step 2 (10-420 min)		
	m	K_T	R^2	m	K_T	R^2
As ³⁺ 20	2.1936	-0.1897	0.7634	0.0972	0.6032	0.7050
As ³⁺ 30	2.3012	-0.1212	0.7215	0.0857	0.6112	0.6743
As ³⁺ 40	2.1215	-0.2069	0.7556	0.1197	0.5926	0.6310
As ³⁺ 90	2.1023	-0.3449	0.8582	0.1500	0.5755	0.6836
As ⁵⁺ 20	2.3135	-0.1487	0.7482	0.0721	0.6216	0.6633
As ⁵⁺ 30	2.2012	-0.3150	0.8526	0.1065	0.5998	0.6533
As ⁵⁺ 40	0.8521	-2.0000	0.9994	0.1848	0.5476	0.7162
As ⁵⁺ 90	2.0476	-0.8074	0.9797	0.1575	0.5662	0.6918

Presented results in Table 5 and Table 5a suggest that the Strmos material adsorption produces a better fit regarding the first order kinetics in the diffusion stage than the Palanka material.

Table 6 - Calculated coefficient values for the pseudo-second order model equation for the Strmos material

Strmos	Step 1 (0-420 min)			
	q_e	K_{ads}	$h=k_{ads} q_e^2$	R^2
As ³⁺ 20	5,3792	0,213529	6,1787	0.9798
As ³⁺ 30	9,4877	0,030827	2,7749	0.9782
As ³⁺ 40	9,2764	0,106055	9,1263	0.9069
As ³⁺ 90	27,5482	0,005866	4,4515	0.9297
As ⁵⁺ 20	5,8411	0,189137	6,4531	0.9766
As ⁵⁺ 30	9,1075	0,125986	10,4500	0.9004
As ⁵⁺ 40	12,5471	0,066373	10,4490	0.9182
As ⁵⁺ 90	46,7290	0,004535	9,9018	0.2628

Table 6a - Calculated coefficient values for the pseudo-second order model equation for the Palanka material

Palanka	Step 1 (0-420min)			
	q_e	K_{ads}	$h=k_{ads} q_e^2$	R^2
As ³⁺ 20	7,5245	0,009843	0,5573	0.9999
As ³⁺ 30	11,4025	0,002299	0,2989	0.9999
As ³⁺ 40	15,3374	0,001301	0,3061	0.9997
As ³⁺ 90	35,4610	0,000164	0,2061	0.9996
As ⁵⁺ 20	7,7700	0,005842	0,3527	0.9999
As ⁵⁺ 30	11,5741	0,003565	0,4776	0.9994
As ⁵⁺ 40	34,4828	0,000248	0,2954	0.9982
As ⁵⁺ 90	15,2672	0,002984	0,6955	0.9992

Based on the obtained results regarding the model coefficients for the pseudo-second order kinetics, the Palanka material adsorption process produces a better fit to the experimental data than the Strmos material.

Legend:

R - adsorption efficiency (%)

q - adsorption capacity ($\mu\text{g/g}$)

q_e - equilibrium state amount of adsorbed arsenic ($\mu\text{g/g}$)

q_t - amount of adsorbed arsenic on the adsorbent surface at time t ($\mu\text{g/g}$).

t - adsorption (contact) time (min),

q_e – Boundary adsorption capacity of the solid ($\mu\text{g/g}$)

h – initial adsorption rate ($\mu\text{g/g min}$) - $h = k_{\text{ads}} q_e^2$

C^* – arsenic equilibrium concentration in the solution ($\mu\text{g/L}$)

m – model constant

K_t – model constant

K_{ads} – constant of the equilibrium state reaction rate of pseudo-second order ($\mu\text{g/gmin}$)

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.
- The Strmos material adsorption produces a better fit regarding the first order kinetics in the diffusion stage than the Palanka material
- The Palanka material adsorption process produces a better fit regarding the pseudo-second order kinetics than the Strmos material

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ИЗВОД

АДСОРПЦИЈА АРСЕНИТА И АРСЕНАТА ИЗ ВОДЕНИХ РАСТВОРА ПРИМЕНОМ МОДИФИКОВАНИМ ПРИРОДНИХ НЕОРГАНСКИХ МАТЕРИЈАЛА-КИНЕТИЧКА СТУДИЈА

Два комерцијално доступна адсорбента, бели туф из региона Стрмош и материјала са комерцијалним именом Зеофит добијеним из региона Паланке, испитивани су као могућа сировина за адсорпцију арсенита и арсената из водених раствора. Ове сировине су модификоване хемијским убацавањем гвожђа у основну структуру материјала и јонском изменом калцијума и магнезијума са натријум јона у циљу побољшања сорпционе и јоноизмењивачке особине испитиваног материјала. Добијени резултати експерименталног истраживања за адсорпцију арсенових јона из моделних водених раствора сугеришу да Зеофит показује боље резултате од материјала бели туф, који је показао задовољавајуће резултате само при нижим концентрацијама арсена. Извршена кинетичка студија за оба материјала дају кинетички модел из првог реда за материјал бели туф, док за Зеофитом добија се кинетички модел из псеудо - другог реда.

Кључне речи: адсорпција, модифицирање адсорбента, моделовање, кинетичка студија

Оригинални научни рад

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