

ADSORPTION/ DESORPTION OF ARSENATE ON/ FROM GOETHITE AND HEMATITE

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ABSTRACT. Arsenic migrates in environment as anions and for that reason its mobility is not strong dependent on pH and redox conditions in the ecosystems. The main aim of this article was to study adsorption/ desorption processes of arsenates on the surface of crystalline ferric iron oxides (goethite and hematite) as the main mechanism to decrease the exposure of aquatic organisms to that pollutant. Adsorption and desorption isotherms as well as the relevant kinetic rate constants, determined by pseudo- first and pseudo-second order equation rate, were the main parameters for the adsorbents evaluation. The results shown that point of zero charge (PZC) of the relevant type iron oxide and the pH of treated waters were the key factors governing arsenate adsorption.

Keywords: arsenate, goethite, hematite, adsorption, point of zero charge (PZC), kinetic

АДСОРБЦИЯ/ ДЕСОРБЦИЯ НА АРСЕНАТНИ ЙОНИ ВЪРХУ/ ОТ ГЪОТИТ И ХЕМАТИТ

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РЕЗЮМЕ. Арсенът мигрира в околната среда под формата на аниони и поради тази причина неговата мобилност не е силно зависима от pH и редукционните условия на екосистемите. Главната цел на статията бе да изследва адсорбцията/ десорбцията на арсенатни йони върху повърхността на кристалинни железни окиси (гъотит и хематит), като основен механизъм за намаляване експозицията на водни организми към този замърсител. Основните параметри за оценка на двата адсорбента бяха съответните адсорбционни и десорбционни изотерми, както и скоростните константи, определени чрез съответните уравнения от псевдо-първи и псевдо-втори ред. Резултатите показваха че точката на нулев заряд на съответния железен окис и pH на замърсените води бяха ключовите фактори, управляващи адсорбцията на арсена.

Introduction

Mining and mineral processing industries as well as application of As-containing compounds as biocides in agriculture and chemicals against materials' corrosion are the main sources of pollution with arsenic of environment. Arsenic in dependence on the local conditions (pH and Eh) is presented as arsenite and arsenate in soluble form and because of their net negative charge arsenic is highly mobile. Because of the chemical similarity between arsenate and phosphate, the organisms in an exposure adsorb and accumulate it easily. In that case, different kind of toxic symptoms are evolved which strength is determined by the exposure duration as well as the pollutant concentration (Sharma and Sohn, 2009).

A lot of mechanisms and different kind of active and passive systems being used into the practice for treatment of arsenic contaminated waters. At acidic pH, beside of arsenic, some heavy metals, toxic elements, iron, aluminium, etc., are also presented in wastewater and their treatment is based usually on the waters neutralization combined with oxidative or reductive processes (Vogel and Johnson, 1998; Altun, M. et al., 2014). However, the operation costs are higher and higher residence time is usually needed to be applied. In waters with slightly acidic or alkaline pH, arsenic is the only pollutants and in that case water treatment relied usually on sorption processes on suitable sorbents (Mohan and Pittman, 2007).

Iron is the most common metal on Earth and it is presented by huge variety of minerals in dependence on the local environmental conditions. For that reason, these minerals played a key role in the transformation of the inorganic and organic pollutants in the contaminated ecosystem and by that way they determined indirectly the exposure of organism to the relevant compound presented in biotope.

Taking in consideration the relevant kinetic and sorption data about arsenate removal from waters with slightly acidic to slightly alkaline pH by some crystalline ferric iron (hydro)oxides (goethite and hematite) and how effectively the pollutant eluted and desorbed from their surface were the main aim of this article.

Materials and methods

Goethite (γ -FeOOH) and hematite (α -Fe₂O₃) as wide-spread crystalline ferric iron oxides in environment were used as sorbents of arsenate in this study. Goethite was formed as a result of bacterial oxidation of ferrous iron at acidic pH by means of mesophilic chemolithotrophic bacteria (*Acidithiobacillus ferrooxidans*, *Leptospirillum ferrooxidans*). Hematite formed by means of heating of preliminary acidified solution of Fe(NO₃)₃ for 7 days till the bright, red precipitate formation. It was separated by centrifugation, washed several times and dried to constant weight (Penners & Koopal, 1986).

The chemical content and main properties of both iron oxides are presented in Table 1. The active and exchangeable acidity of both minerals were determined in distilled water and 1M KCl, respectively, at 1:2.5 ratio solid and aqueous phase (APHA, 1995). The point of zero charge (PZC) was determined by potentiometric titration of a series of suspensions of the relevant type iron oxide in 0.01 – 1.0 M KCl with standard solutions of HCl or NaOH (Marcano-Martinez and McBride, 1989).

A spring waters with slightly alkaline pH was used as a model solution in this study (Table 2). Aliquots of that water were spiked preliminary with arsenate stock solution (1 000 mg/ L arsenic as K_2HAsO_4) to its final concentration within the range of 750 - 800 $\mu\text{g/ L}$. Diluted solution of sulfuric acid was used to correct pH within the range of neutral to slightly acidic value.

Batch tests for arsenate sorption on the crystalline ferric iron (hydro)oxides were carried out in polypropylene beakers (500 ml) at very low pulp density (0.5-1.0 %). Overhead stirrer FALCAT-M equipped with a tephlon propeller was used for the suspension stirring at 220 rpm. The temperature during the test was constant (20 °C) and it was maintained by means of a JULABO water bath. Water samples were taken at equal intervals by means of plastic syringes equipped with a micropore filter (0,45 μm). The transparent solutions were stored in a refrigerator (at temperature below 4 °C) till arsenic determination. Arsenic concentration was measured by means of spectrophotometer MERCK SQ22 at 820 nm and 20 mm cuvette (Johnson and Pilson, 1971). Each sorption experiment was carried out triple. pH measurement were carried out by WTW pH-meter equipped with combined pH-glass electrode.

Ferric iron oxides was separated from solutions by means of centrifugation (15 000 rpm, 10 minutes) at the end of relevant sorption experiment. The adsorbent was washed with distilled waters and then dried to the constant weight. Already dried iron oxides were mixed having in mind pH at which the relevant sorption experiment have been carried out. By that way, the sufficient amount of the relevant type iron oxide were collected to carry out the desorption experiments. These experiments were realized at the same conditions at which the experiments for arsenate sorption were carried out. 0.1 M HCl and 0.1 M NaOH were the desorption solutions used in the study.

The percentage of arsenate sorption/ desorption (D) was calculated by means of the equation:

$$D, \% = (C_0 - C_e / C_0) \times 100, \quad (1)$$

where

C_0 and C_e are equilibrium concentration of arsenate in solution at the start and at the end of sorption experiment (in mg/L), or equilibrium concentration of arsenate on ferric iron oxide at the start and at the end of desorption experiment (in mg/ g), respectively.

The kinetics of arsenate sorption/ desorption on/ from crystalline ferric iron oxides was evaluated by means of pseudo-first and pseudo-second order rate equations (Lagergren, 1898; Ho et al., 2000).

Table 1.

Data about the chemical content and the main properties of goethite and hematite used for arsenate sorption experiments

Index	γ -Goethite	α -Hematite
Fe, %	98.3	99.6
Al, %	1.5	0.01
Cu, %	0.010	< 0.005
Zn, %	0.008	< 0.005
pH (H ₂ O)	4.55	4.56
Free acidity, mmol/ L	15.6	21.2
pH (KCl)	4.76	6.52
Total acidity, mmol/ L	54.2	5.8
Point of zero charge (PZC)	5.35	7.75

Table 2.

Data about the spring water used as background solutions for arsenate sorption on crystalline iron oxides

Concentration, mg/ L	Value
Na	45.7
K	1.7
Ca	5.4
Mg	0.3
F	4.5
Cl	6.4
SO ₄	24.5
CO ₃	15
HCO ₃	67.2
HSiO ₃	0.9
H ₂ SiO ₃	47.9
Properties	
pH	8.88
TDS, mg/ L	219.3

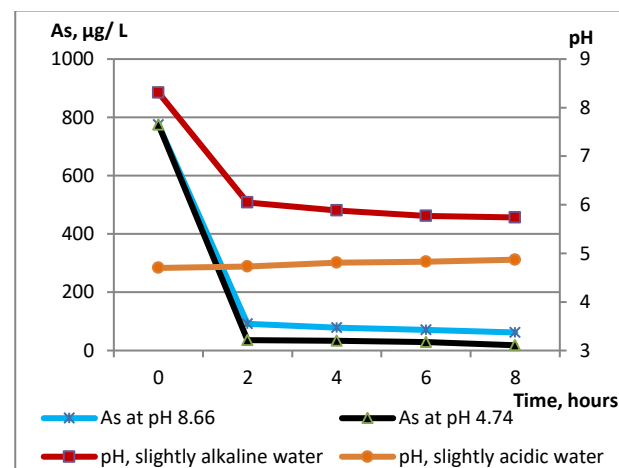


Fig.1. Arsenate sorption on goethite from waters with slightly alkaline and slightly acidic pH

A Langmuir equation was employed to analyze the arsenate sorption/ desorption in dependence on the background solution:

$$D_e/q_e = 1/K_d.D_m + D_e/D_m, \quad (2)$$

where

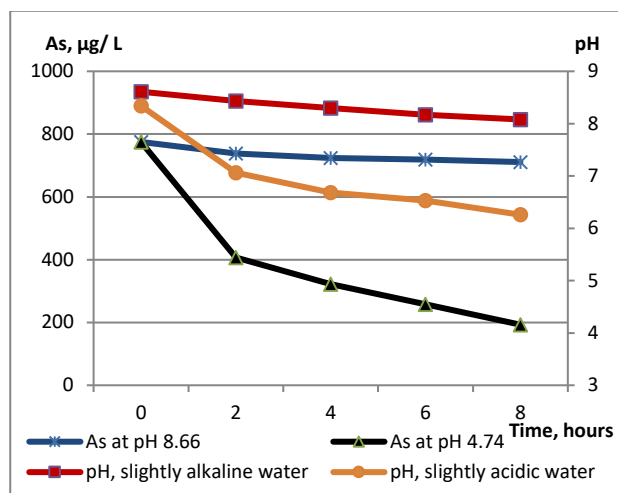


Fig.2. Arsenate sorption on hematite from waters with slightly alkaline and slightly acidic pH

D_e – amount of arsenate sorbed (desorbed) on (from) ferric iron oxide, mmol/L; D_m – maximum content of arsenate that could be sorbed (desorbed) at the relevant experimental conditions, mmol/ kg ferric iron oxide; q_e – content of sorbed (desorbed) arsenate, mmol/kg ferric iron oxide; K_d – sorption (desorption) constant, L /kg.

A Lineweaver-Burk regression method was applied to calculate D_m and K_d .

Results and discussion

Hematite and goethite were characterized by higher content of iron (above 97 %) as some non-ferrous metals as zinc and copper as well as aluminium as impurities were detected in the goethite (Table 1). The pH values of both minerals in distilled water were slightly acidic. The exchangeable acidity of goethite was almost ten times higher than the acidity determined for hematite. Point of zero charge (PZC) was 5.35 and 7.75 for goethite and hematite, respectively.

Arsenate sorption on hematite and goethite was studied at a broad spectrum of pH of one and the same model solution. The final results revealed that at all studied pH range arsenic sorbed on goethite quite faster and effectively than sorption on hematite (Figure 1, 2). For example, the arsenic concentration at the end of experiment with goethite with slightly alkaline water (pH 8.66) was 62 µg/ L, while in experiment with hematite it was 711 µg/ L. At the end of the experiment with slightly acidic water (pH 4.74), the residual concentration of arsenic was 18 and 193 µg/ L when goethite and hematite was used as sorbent, respectively. For both sorbents, lowering of model solution pH determined the better sorption of arsenic on the surface of iron minerals. However, the percentage of arsenic removal was in the range of 91.7-97.6 in all experiments with goethite, while the values about the pollutant removal by hematite were in the range of 5.2-74.3. It could be explained by the surface properties of both minerals and the point of zero charge chiefly. Its value for goethite was 5.35 (Table 1) and when the surround solution was with lower pH a surface positive charge emerged on the minerals surface which greatly enhanced the arsenate attraction and sorption on

Table 3.

Constants and correlation coefficient of Langmuir isotherm of arsenate sorption on goethite in dependence on the model solutions pH

pH of model solution	Isotherm parameters		
	q_{max} , µg/ g	K_d , L/ g	R^2
8.66	313.6	11.09	0.9962
7.33	325.2	12.64	0.9893
6.33	377.6	16.44	0.9922
4.74	402.3	40.67	0.9827

Table 4.

Constants and correlation coefficient of Langmuir isotherm of arsenate sorption on hematite in dependence on the model solutions pH

pH of model solution	Isotherm parameters		
	q_{max} , µg/ g	K_d , L/ g	R^2
8.66	7.04	0.055	0.9758
7.33	13.18	0.89	0.9896
6.33	61.4	1.37	0.9795
4.74	64.4	2.89	0.9909

the relevant mineral surface. For that reason, the highest percentage of arsenic sorption was determined when the model solution was with slightly acidic pH (4.74). However, arsenic removal by goethite was quite efficient process even in the experiments with neutral and slightly alkaline waters. At such conditions, the goethite surface charge was negative and theoretically arsenic sorption have to be retarded significantly due to the repulsion between the same charged surfaces. However, considerable reduction of arsenic sorption wasn't noticed. The reason was the higher surface area and higher exchangeable acidity of goethite which enabled significant part of water alkalinity to be consumed and pH to be buffered within the range of 4.87-5.74 in all experiments (Figure 1). For example, the surface area of goethite varied in the range of 45 – 54 m²/ g (Grossl, and Sparks.1995; Manning et al., 1998). These processes weren't manifested so significantly during the sorption experiments with hematite because of its lower surface area and exchangeable acidity. Its surface area is in the range of 4.9-6.0 m²/ g (Ramos-Tejada et al., 2003.). For that reason, pH in experiments with slightly alkaline and neutral waters changed insignificantly and the efficiency of arsenate sorption depended on the hematite's PZC (Figure 2).

All data from sorption experiments were modeled by Langmuir equation which is still one of more oftenly used into the practice. The relevant constants and correlation coefficients for arsenate sorption on goethite and hematite which had been determined by Langmuir isotherms, are presented in Table 3 and Table 4, respectively. Their values confirmed preliminary results about arsenate sorption on both sorbents. For example, the maximum sorption capacity (q_{max}) of goethite towards the pollutant steeply increased from 313.6 to 402.3 µg/ g with the lowering pH from 8.66 to 4.74 (Table). At the same time, the distribution coefficient (K_d) increased almost fourfold to maximum value of 40.67 L/ g. R-squared value of the isotherms were with an acceptable significance (0.98-0.99). The relevant constants describing arsenic sorption on hematite were considerably lower. For example, the highest value of K_d (at pH 4.74) was 14.1 times lower than the value determined at the same conditions with goethite. It revealed also that despite

Table 5.

Kinetic of arsenate sorption on goethite in dependence on the pH of model solutions evaluated by means of pseudo-first order and pseudo-second order rate equations

pH	Equation parameters			
	Pseudo-first-order equation		Pseudo-second-order equation	
	k_1, min^{-1}	$q_e, \mu\text{g/g}$	$k_2, \text{g} \cdot \mu\text{g}^{-1} \cdot \text{min}^{-1}$	$Q_e, \mu\text{g} \cdot \text{g}^{-1}$
8.66	$5.08 \cdot 10^{-3}$	346.1	0.936	373.1
7.33	$5.17 \cdot 10^{-3}$	349.8	0.0898	376.6
6.33	$7.50 \cdot 10^{-3}$	353.0	0.0842	378.4
4.74	$2.04 \cdot 10^{-3}$	376.9	0.0809	404.8

Table 6.

Kinetic of arsenate sorption on hematite in dependence on the pH of model solutions evaluated by means of pseudo-first order and pseudo-second order rate equations

pH	Equation parameters			
	Pseudo-first-order equation		Pseudo-second-order equation	
	k_1, min^{-1}	$q_e, \mu\text{g/g}$	$k_2, \text{g} \cdot \mu\text{g}^{-1} \cdot \text{min}^{-1}$	$Q_e, \mu\text{g} \cdot \text{g}^{-1}$
8.66	$5.06 \cdot 10^{-3}$	6.49	16.23	7.14
7.33	$4.73 \cdot 10^{-3}$	11.73	12.60	12.60
6.33	$6.60 \cdot 10^{-3}$	49.55	0.751	52.6
4.74	$4.95 \cdot 10^{-3}$	126.37	0.321	133.3

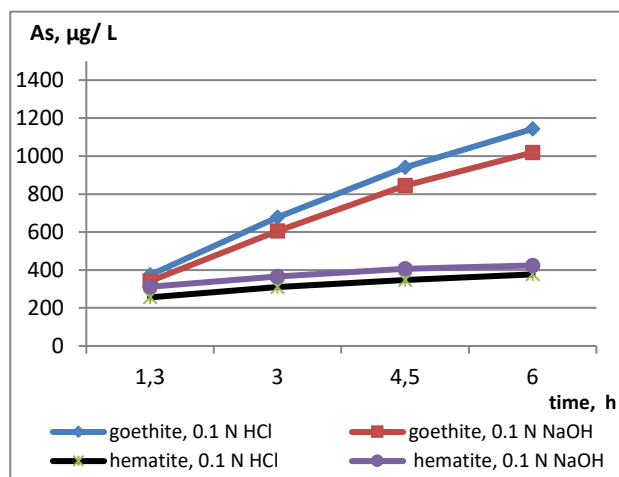


Fig.3. Arsenate desorption from hematite and goethite in dependence on the desorption solution

of conditions favouring the arsenate sorption, the process have been retarded significantly and for that reason q_{max} barely reached 64.4 $\mu\text{g/g}$.

Data from batch tests was evaluated by means of pseudo-first and pseudo-second order equations rates. It allowed not just to determine the rate constants for the relevant experimental conditions but also to reveal mechanisms which have been involved in sorption of arsenate on goethite and hematite. The arsenate sorption on goethite as well as the sorption on hematite at pH 4.74 revealed that two separate phases, fast and slow phase, have been manifested. The fast phase carried out during the first two hours from the beginning of the experiment when significant part of arsenate (62-96 %) from the model solution removed. It was determined by the higher number of surface-situated reactive groups with higher free

energy which sorbed arsenate with higher rate. For example, the rate constants (k_1 (min^{-1}) and k_2 ($\text{g} \cdot \mu\text{g}^{-1} \cdot \text{min}^{-1}$)) of arsenate sorption on goethite and hematite at pH 4.74 were 0.0308 and 0.295, and $7.97 \cdot 10^{-3}$ and 0.614, respectively. The slow phase carried out during the rest of batch test and the arsenate sorbed with significant lower rate. The freely accessible reactive groups on the sorbent surface had been saturated during the first phase and it was the main reason for the second phase occurrence. During that phase, the process carried out by the reactive groups which weren't exposed on the mineral's surface and for that reason a longer period of time was needed for sorption on them (Smith, 1999). The average values of the rate constants of pseudo-first and pseudo-second order equation rates of the arsenate sorption on goethite and hematite are shown in Table 4 and Table 5, respectively. These values are significantly lower in comparison to the relevant values determined for the fast phase of process. These results are with significant importance for the practice. They revealed that if the arsenate removal from polluted waters is carried out continuously by means a filter filled with iron hydroxides with higher surface area, the rate of sorption process will be very high and the residual pollutant concentration could be maintained below the relevant permissible levels.

By means of the relevant rate equations, arsenate equilibrium concentration (q_e) on the relevant sorbent was determined. Its value for all experiments were higher when pseudo-second order equation rate was applied in comparison to the value determined by the pseudo-first equation rate. When the model solution pH was 4.74 equilibrium concentration of arsenate (q_e) on both sorbents reached its maximum values (Tables 4 and 5). R-squared values calculated from the relevant experimental data revealed that kinetic of arsenate sorption on hematite and goethite was described considerably better by pseudo-first order equation rate than the pseudo-second order equation. It mean that arsenate removal by means of goethite and hematite was connected probably with formation of the pollutant monolayer on surface of relevant sorbent (Mok and Wai, 1994.).

In dependence of the compounds being sorbed and conditions at which the sorption process have been carried out, each sorbent has maximum sorption capacity. When this sorption capacity is reached, a regeneration of sorption's surface is needed to be applied. It is achieved usually by diluted solutions of acids or bases and the main mechanisms of the compound desorption are acidolysis and anion exchange, respectively. In this study, arsenate desorption from goethite and hematite were realized by means of 0.1N HCl and 0.1 N NaOH. These experiments were realized with goethite and hematite on which surface arsenate had been sorbed at slightly acidic pH 4.8-5.0. The initial content of arsenate was 714 $\mu\text{g/g}$ and 448 $\mu\text{g/g}$ for goethite and hematite, respectively. Total duration of desorption experiment was 6 hours and when the process was realized at acidic pH, 91.5 % and 48.1 % of arsenate from goethite and hematite, respectively, had desorbed. At alkaline conditions, 81.5 % and 51.4 % of arsenate had desorbed from the same sorbents (Figure 3).

The arsenate desorption from goethite and hematite carried out by two separate phases too. The fast phase lasted the first ninety minutes from the experiment beginning and between 38-69 % of arsenate had been desorbed from the

Table 6.

Kinetic of arsenate desorption from goethite and hematite in dependence on the desorption solution evaluated by means of pseudo-first order and pseudo-second order rate equations

Index	Equation parameters			
	Pseudo-first-order equation		Pseudo-second-order equation	
	k_1, min^{-1}	$q_e, \mu\text{g.L}^{-1}$	$k_2, \text{g} \cdot \mu\text{g}^{-1} \cdot \text{min}^{-1}$	$q_e, \mu\text{g.L}^{-1}$
Goethite				
0.1 N HCl	0.0074	196.2	0.3855	208.3
0.1 N NaOH	0.0075	173.4	0.4096	188.68
Hematite				
0.1 N HCl	0.0079	134.5	0.2651	144.9
0.1 N NaOH	0.0069	164.2	0.1687	176.9

relevant sorbent surface. In that case, the percentage of pollutant desorption from hematite was higher than the value determined for goethite. The R-squared values of the kinetic data revealed that arsenate desorption from both sorbents was described better by pseudo-first order rate equation ($R^2 = 0.97-0.99$) than pseudo-second ones ($R^2 = 0.86-0.93$). Arsenate desorption from goethite at acidic pH carried out with higher rate during the fast phase of the process. However, the process rate decreased during the second phase, while the rate of the pollutant desorption at alkaline pH increased during this period. For that reason, the average values of rate constant determined by pseudo-first equation rate were almost equal. However, arsenate equilibrium concentration (q_e) in both desorption solutions weren't equal as higher was the content in the solution with acidic pH. Arsenate desorption from hematite carried out with higher rate at alkaline pH during the both phases than the desorption rate determined at acidic pH.

Results from this study revealed that process of arsenate sorption/ desorption carried out with higher rates and intensity on/ from goethite surface in comparison to those determined for hematite. For that reason, goethite will be tested for arsenate removal from model solution by means of column experiments in future.

Conclusions

1. The results of batch tests revealed that arsenate sorption on goethite was significantly more efficient process than in the presence of hematite. The chemisorption was the main mechanism involved during the pollutant removal on the surface of both minerals.
2. Because of the higher surface area and PZC (5.35), goethite adsorbed arsenate very efficiently from model solution at acidic as well as slightly alkaline pH. These properties determined goethite as a suitable sorbent for arsenate containing in waters where it is the only pollutant.
3. Arsenate desorption from goethite carried out with higher rate at acidic pH as the sorbent's surface was restored almost completely.

References

- Altun, M., E.Sahinkaya, I.Durukan, S.Bektas, K.Komnitsas. 2014. Arsenic removal in a sulfidogenic fixed-bed bioreactor. *Journal of Hazardous Materials* 269, 31-37. j
- APHA. 1995. *Standard methods for examination of water and wastewater*. American Public Health Association, Washington, D.C.
- Grossl, P.R., D.L. Sparks. 1995. *Evaluation of contaminant ion adsorption/ desorption on goethite using pressure-jump relaxation kinetics*. *Geoderma* 67, 87-101.
- Ho, Y.S., Ng, J.C.Y., McKay, G., 2000. *Kinetics of pollutant sorption by biosorbents: Review*. *Separation and Purification Methods* 29, 189-232.
- Jonhson, D.L. and M.E.Q. 1971. *Spectrophotometric determination of arsenite, arsenate, and phosphate in natural waters*. *Analytica Chimica Acta* 58: 289-299.
- Lagergren, S., 1898. *About the theory of so called adsorption of soluble substances*. *Kungliga Svenska Vetenskapsakademiens Handlingar* 24-4, 1-39.
- Manning, B.A., S.E. Fendorf, S. Goldberg. 1998. *Surface structures and stability of arsenic(III) on goethite: spectroscopic evidence for inner-sphere complexes*. *Environmental Science & Technology*. 32, 2383-2388.
- Marcano-Martinez, E., McBride, M.B., 1989. *Comparison of the titration and ion adsorption methods for surface charge measurements in Oxisols*. *Soil Science Society of America Journal* 53, 1040 - 1045.
- Mohan, D. and C.U. Pittman. *Arsenic removal from water/ wastewater using adsorbents- A critical review*. *Journal of Hazardous Materials* 142, 1-53.
- Mok, W.M. and C.M.Wai. *Mobilization of arsenic in contaminated river waters*. In: Nriagu J.O. (ed.). *Arsenic in the environment. Part 1*. New York: Wiley, 1994. p. 99-117
- Penner, N.H.G. & Koopal, L.K.. 1986. *Preparation and optical properties of homodisperse hematite hydrosols*. *Colloids & Surfaces* 19, 337-349.
- Ramos-Tejada M.M. 2003. *Interfacial and rheological properties of humic acid/hematite suspensions*. *Journal of Colloid Interface Science*, 268, 85.
- Sharma, V. and M.Sohn. 2009. Aquatic arsenic: toxicity, speciation, transformation, and remediation. *Environment International* 35, 743-759.
- Smith, K.S. Metal sorption on mineral surfaces: an overview with examples relating to mineral deposits. In: *Reviews in Economic Geology. The Environmental Geochemistry of Mineral Deposits*. G.S.Plumlee & M.J.Logsdon (eds.). published by Society of Economic Geologists.
- Strawn, D.G. and D.L. Sparks. 2000. *Effects of soil organic matter on the kinetics and mechanisms of Pb (II) sorption and desorption in soil*. *Soil Science Society of American Journal* 64, 144-156.
- Vogel, C.M. and M.D.Johnson. 1998. *Arsenic remediation in drinking waters using ferrate and ferrous ions*. WRI technical completion report no. 307; 21.

The article has been recommended for publication by department "Engineering geocology".\