

STUDY OF ADSORPTION/DESORPTION OF ARSENATE ON/FROM GOETHITE-COVERED QUARTZ SAND UNDER FLOW REGIME OF OPERATION

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ABSTRACT: The main aim of this article was to assess adsorption/ desorption of arsenate under a continuous regime of operation of a filter filled with goethite-covered quartz sand. The results showed that at constant experimental conditions (temperature, arsenate concentration, and pH), the arsenate adsorption depends mainly on the filter's height and the flow rate of the inlet solution injection into the filter. The following parameters: efficiency of arsenate adsorption, equilibrium uptake, adsorbent exhaust rate, as well as the rate constant of adsorption and bed sorption capacity were determined by breakthrough curves and the applied Adams-Bohart model. the pH of desorption solution played a paramount role in the arsenate desorption, as the process was very efficient at slightly alkaline conditions in comparison to the desorption's efficiency at slightly acidic pH.

Keywords: arsenate, goethite, breakthrough curves, Adams-Bohart model

ИЗСЛЕДВАНЕ АДСОРБЦИЯ/ДЕСОРБЦИЯ НА АРСЕНАТНИ ЙОНИ ВЪРХУ/ОТ КВАРЦОВ ПЯСЪК, ПОКРИТ С ГЪОТИТ ПРИ ПРОТОЧЕН РЕЖИМ НА РАБОТА

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РЕЗЮМЕ: Основната цел на настоящата статия е оценка на сорбцията/десорбцията на арсен при проточен режим на работа на филтър, състоящ се от кварцов пясък, покрит с гьотит. Получените резултати показват, че при постоянни условия на средата (температура, концентрация на арсен, pH), сорбцията на арсен зависи основно от височината на филтъра и скоростта на постъпване на разтвора във филтъра. Показателите ефективност на сорбция, равновесно натоварване, скорост на изтощение, както и скоростната константа и сорбционен капацитет на филтъра, са определени посредством кривите на сорбция на арсен и приложения модел на Адамс-Бохарт. pH на десорбиращия разтвор, от своя страна, има ключова роля по отношение на десорбцията на арсенатните йони от филтъра, като процесът е значително по-ефективен при слабоалкални условия в сравнение с ефективността, установена при слабокисели условия.

Ключови думи: арсен, гьотит, криви на сорбция, модел на Адамс-Бохарт

Introduction

The natural weathering of arsenic-bearing minerals and discharge of arsenic-containing wastes from petroleum refining, melting of base metal sulphide ores are the main reasons for the elevated concentrations of pollutants in surface and subsurface waters.

Arsenic occurs in natural waters both in organic and inorganic forms, as the arsenite, As(III), and arsenate, As(V), are the major inorganic arsenic species. Arsenite is the chemically dominant form in reducing environments, whereas, arsenate dominates at oxidising conditions. Arsenate is a chemical similar to phosphate which enhances its transport and accumulation of the pollutants in the organisms under exposure to the pollutant (Sharma, Sohn, 2009).

Numerous methods for arsenic removal from aquatic environments have been studied including ion exchange, precipitation, coagulation, membrane filtration, flocculation, ozone oxidation, biological treatment, electrochemical treatment, and adsorption (Choong et al., 2007). Adsorption is evolving as one of the most applicable method for the arsenic removal from water because of the wide range of commercial and low-cost adsorbents (activated carbon, oxides, hydrotalcite, metal-based methods, biosorbents, soils and

constituents, industrial by-products/ wastes, etc.) that could be used (Mohan, Pittman, 2007).

The previous studies have shown that goethite possesses higher adsorption capacity and it adsorbs arsenate more efficiently from slightly acidic to slightly alkaline waters in comparison to hematite (Zheleva et al., 2016). The higher efficiency of that process is based on the inner sphere complex formation between adsorbate and the mineral surface (Manning et al., 1998).

The main aim of this article is to test the capability of goethite-covered quartz sand to adsorb arsenate from slightly alkaline spring water under a continuous regime of operation of a filter column and to determine the value of some important parameters about that treatment.

Materials and methods

The experiments about the arsenic removal from studied spring water by means of adsorption were performed in the column type reactor. The experimental set-up consisted of a feed vessel (1), a peristaltic pump (2), a column (4), and a vessel collecting treated solutions (4) (Fig. 1). The columns' height for all experiments was 10 cm. In each column, two zones were distinguished – an adsorption and a supporting

zone. The adsorption zone occupied the central part of the column and it consisted of goethite-covered quartz sand (dominant particle size minus 0.315 mm – 81%). The supporting zones, situated in the inlet and outlet point of the column, consisted of glass wool.

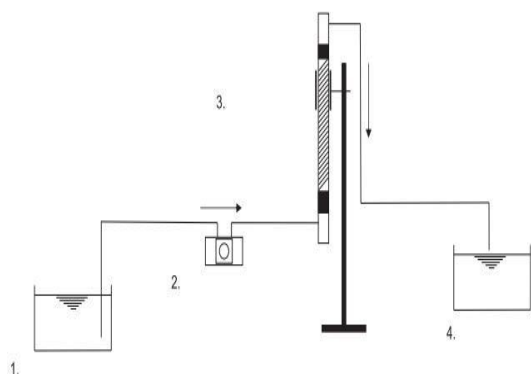


Fig. 1. Scheme of the experimental set up used in these experiments

The surface of quartz sand was preliminary cleaned and activated by means of treatment with 4N HCl at conditions of agitation at a temperature of 70°C. The residual acidic solution was separated and the quartz sand was washed three times with distilled water. The goethite was deposited on the quartz sand by means of its mixing with $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and the serial alteration of chemical ferrous oxidation (by means of H_2O_2 addition) and the ferric iron precipitation (by means of NaOH addition). As a result of that treatment, the colour of quartz sand changed from snow white to yellow-brown. Each column was filled with the relevant amount of goethite-covered-quartz-sand. After their preparation, the adsorption zone in each column was washed with the amount of distilled water equal to three times the column's operating bed volume.

The ration between the adsorption and supporting zone changed in some experiments which had an effect on the adsorption zone bed height. The working volume of the adsorption zone in each column (so-called bed volume) was determined before the start of each experiment by means of an upward injection of water until all pores filled up with water.

The columns operated in an upward continuous regime which provided for the optimal contact between the goethite-covered-quartz-sand and the treated solution. The spring water with slightly alkaline pH, spiked preliminary with arsenate (as K_2HAsO_4), was used as a model solution in this study (Table 1). The temperature during the experiment was in the range of 25–27°C.

Table 1. Chemical content of water being treated

Index	Value
Na, mg/L	50
K, mg/L	1.6
Ca, mg/L	3.2
F, mg/L	2.4
Cl, mg/L	5.3
SO_4 , mg/L	20.5
CO_3 , mg/L	24.0
HCO_3 , mg/L	65.5
H_2SiO_3 , mg/L	50.6
As, mg/L	0.025
pH	8.95

Two types of experiments regarding the arsenate adsorption on goethite-covered-quartz-sand were carried out. Firstly, the effect of adsorption's zone height in the column on the arsenate adsorption was studied. In that case, the flow rate applied to all columns was identical. In the second set of experiments, the arsenate adsorption was studied in dependence on the column's flow rate. The adsorption zone height of columns was constant in that case. The kinetic parameters of arsenate adsorption on goethite-covered-quartz-sand at flow regime of operation were determined and assessed by means of Adams-Bohart model:

$$t = N_0 \cdot Z / C_i \cdot V - (1 / K \cdot C_i) \cdot \ln [(C_i / C_b) - 1]$$

where:

C_i is the initial arsenic concentration ($\mu\text{g/L}$), C_b is the breakthrough arsenic concentration ($\mu\text{g/L}$), t is the time of breakpoint (hour), N_0 is the sorption capacity of sorbent ($\mu\text{g/L}$), Z is the bed height of column (cm), V is the linear velocity (cm/min) and K is the rate constant ($\text{L/mg} \cdot \text{min}$). From the slope and intercept of the respective iso-removal line, the adsorption capacity (N_0) and the rate constant of adsorption (K) were calculated.

The following parameters were measured during the experiments: pH and the arsenate concentration in effluents. The samples from effluent solutions were stored in a refrigerator until the arsenic determinations. pH was measured daily. Based on the collected data for each column, the relevant parameters were determined: a breakthrough point; total amount of solutions being injected into the column to the breakthrough point (V_{eff}), point of the column exhaustion, total amount of arsenic entered the column until the moment of breakthrough point (m_{total}), the total amount of adsorbed arsenic (q_{total}), equilibrium amount of adsorbed arsenic (q_{eq}), the efficiency of arsenic removal (%), and adsorbent exhaustion rate.

The desorption experiments were also carried out in a continuous regime of operation with filter columns, characterised with an equal bed height of goethite-covered quartz sand and to which the same flow rate during the period of arsenate adsorption have been applied. The arsenate desorption was carried out with arsenic-free spring water as the main solution, which was spiked with 75 $\mu\text{g/L}$ HPO_4^{3-} (added as Na_2HPO_4). The effect of pH was studied by the addition of sulphuric acid (or sodium hydroxide) to the above-mentioned solution with an aim to study the desorption process at acidic (or alkaline pH). The flow rate of desorption solutions to the columns was 0.176 L/24h. The effluent solutions were collected in plastic vessels. pH was measured daily. The samples from effluent solutions were stored in a refrigerator until the arsenic determinations. The arsenic concentration was measured by means of a spectrophotometer MERCK SQ22 at 820 nm and 20 mm cuvette (Johnson, Pilson, 1971).

Results and discussion

The main advantages of the pollutant removal by means of sorption are: the process carried out without significant changes in the water chemistry and the high percent of the pollutant removal is combined with a lower residence time of waters being treated. For that reason, the methods based on

adsorption processes are preferred into practice for the treatment of waters polluted by one or two compounds presented in lower concentrations as a rule.

Effect of the bed height on the arsenate adsorption

The experiments were carried out with an upward injection of arsenate-containing spring water into the column as the measured pollutant's concentration in the effluents was related to the duration of the experiment. The arsenate adsorption on the goethite-covered quartz sand was a very efficient process at the very beginning of the experiment which resulted in its zero concentration in the column's effluent. As the volume of the solution being treated increased and the arsenic adsorption continued, the arsenic concentration in the effluents gradually rose. Finally, the adsorption zone reached the column's top and the arsenic concentration in effluents was almost equal to the concentration in the inlet solution. Several parameters about the arsenate adsorption on goethite-covered quartz sand were determined. Time for arsenic breakthrough concentration – the time when the arsenic concentration in effluents reached 10 µg/L (which is the arsenic permissible concentration for drinking water; it meant that the efficiency of the pollutant removal at this time of the column's operation was about 60%), a column exhaustion time referred to the moment when only about 10% of the inlet arsenic concentration (around 2–2.5 µg/L) sorbed on goethite during the column operation.

The bed height of goethite-covered quartz sand in the filter column had a strong effect on the arsenate adsorption, the appearance of the arsenic breakthrough concentration and the time of filter's exhaustion. For example, the time for arsenic breakthrough concentration for 1.8 cm bed height was at 13 days since the start of column operation and 30 days for 4.0 cm bed height, respectively (Table 2). These results were logical having in mind that shorter bed height of goethite-covered quartz sand directly determined the smaller number of binding sites on which the arsenate adsorption could take place. The effect of bed height of goethite-covered quartz sand on the arsenic breakthrough curves is depicted in Figure 2.

The rate of arsenate adsorption was strongly dependent on several factors like pH, ambient temperature and the arsenic concentration. With the main aim to make the comparison between variants easier, the temperature (in the range 25–27°C) and the arsenic concentration (25 µg/L, i.e. 2.5 times higher than the element's permissible concentration for drinking water) during the experiments were constant. However, the pH of treated spring waters had a significant effect on the arsenate adsorption. That effect was determined by the Point of Zero Charge of goethite ($PZC_{\text{goethite}} = 5.35$) and the slightly alkaline pH (8.95, Table 1) of the spring waters being treated. At these conditions, the goethite possessed slightly dominant negative surface charge which detained to some extent the arsenate adsorption because of the repulsive force acted between ions with identical charge. At such conditions, the arsenate adsorption on goethite-covered quartz sand took place by means of a ligand exchange mechanism which involved the exchange of aqueous ligand for a surface hydroxyl group:

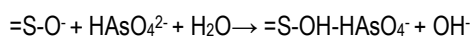


Table 2. Characteristics of the experiment about the effect of height of goethite-covered quartz sand in the columns on the arsenic adsorption

Index	Height of goethite-covered quartz sand in the column, cm		
	1.8	2.7	4.0
Arsenic in inlet solution, µg/ L	25.0		
Flow rate, L/ 24 h	0.33		
Applied bed volumes per 24 h	9.4	6.3	3.25
Time of arsenic breakthrough concentration, days	13	21	30
A column exhaustion time, days	16	25	34

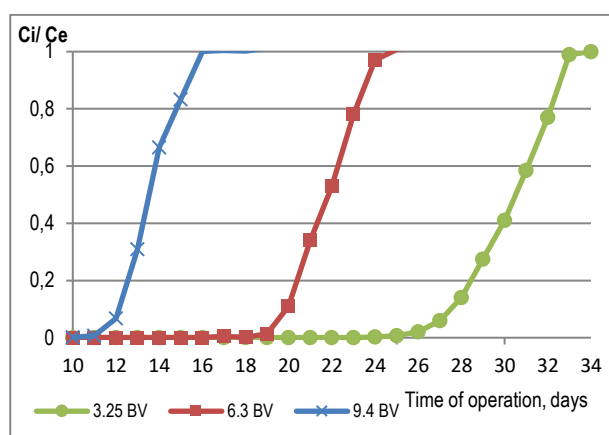


Fig. 2. Effect of the bed height of goethite-covered quartz sand in the column on the arsenate adsorption (flow rate 0.33 L/ 24 h, initial arsenic concentration 25 µg/ L, temperature 25–27°C)

That process led to the release of hydroxyl ion into the solution which maintained the slightly alkaline pH of the column effluents (8.32–8.40) for the largest bed height of goethite-covered quartz sand (4.0 cm).

The effluents from the goethite-covered quartz sand with the shortest bed height (1.8 cm) was with almost neutral (pH 7.62–7.86) especially when the duration of column operation was near its breakthrough time. It was evident that the decreasing of effluent's pH was due to the deprotonation of near-surface situated hydroxyl groups of goethite.

The arsenic adsorbed in the filter columns strongly depended on the bed height (Table 3) – the adsorbed amount steadily increased from 107.8 µg for 1.8 cm bed height to 258 µg for bed with 4.0 cm height, respectively. However, the equilibrium arsenic content (q_{eq}) in the whole column was in a narrow range. The efficiency of arsenic adsorption was the highest (94.7%) for a bed with 4 cm height. The higher bed height of goethite-covered quartz sand combined with a constant flow rate of inlet spring water determined a smaller value for bed volumes being treated per day. It meant, that the treated solution remained longer in the filter column which enhanced the contact and adsorption between the binding sites of goethite-covered quartz sand and arsenate ions. For that reason, the rate of adsorption zone movement in the

Table 3. Parameters characterising the arsenic adsorption on goethite-covered quartz sand under a continuous regime of operation in dependence on the bed height

Index	Height of goethite-covered quartz sand in the column, cm		
	1.8	2.7	4.0
V _{eff} , L	4.95	7.59	10.9
Q _{total} , µg	107.76	167.1	258
M _{total} , µg	123.75	189.75	272.3
q _{eq} , µg/ g	3.59	3.71	3.77
Efficiency of the arsenic adsorption, %	87.1	88.1	94.7
Adsorbent exhaustion rate, kg/ L	0.0061	0.0059	0.0062
Breakthrough capacity (Q _{50%}), µg As/ g adsorbent	3.71	3.76	3.66
Rate of adsorption zone movement in the column U _z , cm/ 24 h	0.071	0.024	0.0045

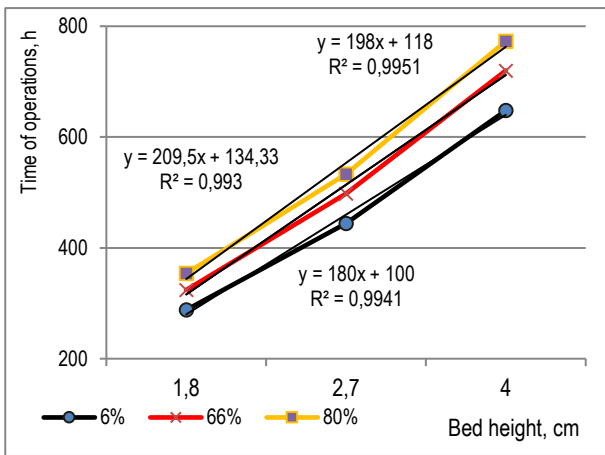


Fig. 3. Bohart-Adams model for 6, 66, and 80% breakthrough at different bed heights and constant inlet arsenic concentration (25 µg/ L) and flow rate (0.33 l/ 24 h)

column steadily decreased from 0.071 to 0.0045 cm/ 24 h when the bed height increased from 1.7 to 4.0 cm. However, the determined equilibrium arsenic content (q_{eq}) was quite lower in comparison to the values determined by other researchers (Kundu, Gupta, 2005). It is well-known that the slightly alkaline pH of waters being treated as well as the significantly higher concentrations of anions (sulphate, hydrocarbonate, silicate, (Table 1) hinders the arsenate adsorption (Genc-Fuhrman et al., 2005).

Data modelling about the arsenic adsorption from the operation of the laboratory filter column was carried out by Bohart-Adams mathematical model (Bohart, Adams, 1920) and bed depth service time approach proposed by Hutchins (1973). The data from each column operation was assessed by means of determination of three different points of arsenic isoremoval from the spring waters being treated, i.e. at 1.5, 10, and 20 µg/L breakthrough concentration in effluents (Table 4). So, for each arsenic isoremoval percent, the Bohart-Adams model was simplified to the equation

$$t = a \cdot x + b \text{ where } a = \text{slope's line} = N_0/C_i \cdot V \text{ and } b = \text{intercept} = 1/ KC_i \cdot \ln((C_i/ C_e) - 1).$$

The relationship between the bed depth versus time of the operation for the three isoremovals is depicted in Figure 3. It is evident that these lines were almost parallel to each other and the horizontal distance between them was 0.12 cm (so-called height of exchange zone). The results showed clearly that the rate of arsenic adsorption under continuous way of operation (K_{BA}) and the adsorption capacity of goethite-covered quartz sand (N₀) decreased significantly at longer columns' service operation (Table 4). That trend was logical having in mind that the higher number of binding sites of sorbent have been already occupied at such conditions which determined the higher breakthrough arsenic concentration in the effluents.

Table 4. Bohart-Adams model constants for the arsenic adsorption on goethite-covered quartz sand

Iso-removal, %	Breakthrough concentration µg/L	N ₀ , µg/ L	K, L/µg.h	R ²
6	23.5	373.1	-0.0011	0.9941
60	10.0	410.4	0.0001	0.9951
80	5.0	434.2	0.0004	0.9930

Table 5. Comparison between the measured and predicted breakthrough times (in hours) at 60% arsenic removal using Bohart-Adams model constants

Index	Height of the adsorption zone, cm		
	1.8	2.7	4.0
Flow rate: 0.33 L/24 h			
Measured	312	504	720
Predicted	474	650	910

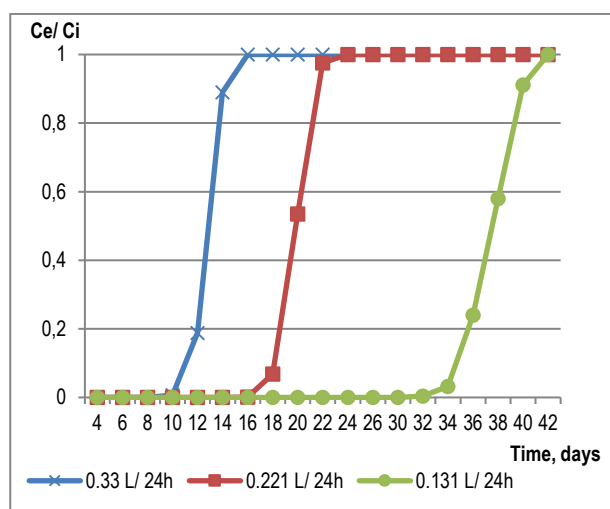
The results included in Table 5 revealed that the values of measured breakthrough time at 60% arsenic concentration were 25% averagely lower than the values predicted by the Bohart-Adams model. The main reason was probably the insufficient bed height being used in those experiments. It is shown that the model could be used roughly for designing other column operation experiments over a range of flow rate or arsenic concentration. There are other models too, i.e. Thomas, Yoon-Nelson that could be used in modelling of the data about the arsenate adsorption in a continuous regime of operation.

Effect of the flow rate on the arsenate adsorption

The flow rate of a column operation has a crucial effect on factors as volumes of water being treated and a residual arsenic concentration lower than permissible concentration, are needed to be combined at a pilot or industrial scale. In that experiment, the arsenic inlet concentration and the bed height were constant to all columns and only the flow rate of spring waters being treated distinguished from one variant to other (Table 6). The breakthrough curves are shown in Figure 3. The applied flow rate varied between 0.131–0.33 L/24 h which related to 3.7 to 9.4 bed volumes of spring waters treated per day. That range of bed volumes meant that the residence time which water spent into the filter column varied 2.5 times. So, the arsenate ions and the binding sites of goethite-covered quartz sand had different contact times to react with each other.

Table 6. Characteristics of the experiment about the effect of flow rate on the arsenic adsorption

Index	Applied flow rate, L/24 h		
	0.33	0.221	0.131
Arsenic in inlet solution, $\mu\text{g/L}$	25.0		
Height of the adsorption zone, cm	1.8		
Volume of solutions being treated, L	5.30		
Applied bed volumes per 24 h	9.4	6.3	3.7
Time of operation until 100 % arsenic breakthrough, days	16	24	40

Fig. 3. Breakthrough curves of arsenic for varying flow rates (L/24 h) at a bed height of 1.8 cm and 25 $\mu\text{g/L}$ inlet concentration of arsenic

As a result, the lower the flow rate was, the higher the residence time of waters into the column was and arsenates removed more efficiently by adsorption of goethite-covered quartz sand. At higher flow rate, the arsenic left the column before the equilibrium between the adsorbate and adsorbent took place. For example, the time for arsenic breakthrough concentration steadily increased from 13.4 to 36.7 days due to the decreasing of the water's flow rate (Table 7). The value of rate constant of arsenate adsorption (K) increased gradually at a higher flow rate of spring waters (Table 8). However, the value of sorption capacity of goethite-covered quartz (N_0) sand was higher at the lowest tested flow rate which was an indication that the process of arsenate adsorption was rate-dependent. For that reason, the equilibrium arsenic content (q_{eq}) and maximum adsorption capacity (q_0) of goethite-covered quartz sand were 3.97 $\mu\text{g/g}$ and 4.04 $\mu\text{g/g}$ for 0.131 L/24 h. At all tested flow rates, the value for the maximum adsorption capacity (q_0), predicted by Adams-Bohart model, was close to the experimentally determined values of the equilibrium arsenic content (q_{eq}). However, we must keep in mind that some review shows that the maximum adsorption capacity determined by Adams-Bohart Model usually underestimate the value in comparison to other models applied to continuously operated experiments (Podder, Mjumder, 2018).

Table 7. Parameters characterising the arsenic adsorption on goethite-covered quartz sand under a continuous regime of operation in dependence on the applied flow rate

Index	Applied flow rate, L/24 h		
	0.33	0.221	0.131
V_{eff} , L	4.95	5.08	5.11
Q_{total} , μg	108.61	111.72	119.03
m_{total} , μg	131.25		
q_{eq} , $\mu\text{g/g}$	3.62	3.72	3.97
Efficiency of the arsenic adsorption, %	82.7	85.1	90.7
Adsorbent exhaustion rate, kg/L	0.0061	0.0059	0.00587
Breakthrough capacity ($Q_{50\%}$), $\mu\text{g As/g adsorbent}$	3.56	3.65	3.90
Time for arsenic breakthrough concentration, days	13.4	20.6	36.7

Table 8. Bohart-Adams model constants for the arsenic adsorption on goethite-covered quartz sand under a continuous regime of operation in dependence on the applied flow rate

Flow rate, L/24h	N_0 , $\mu\text{g/L}$	K , L/ $\mu\text{g}\cdot\text{h}$	q_{eq} , $\mu\text{g/g}$	q_0 , $\mu\text{g/g}$	R^2
0.33	21.22	0.0936	3.62	3.69	0.9856
0.221	21.74	0.0589	3.72	3.78	0.9326
0.131	23.23	0.0369	3.97	4.04	0.981

Although the experiments were carried out until 100% arsenic breakthrough, the process of arsenic removal from the spring water was very efficient. For example, at the highest tested flow rate, 0.33 L/24h, the efficiency of arsenic removal was higher than 82%.

Arsenate desorption from goethite-covered quartz sand under a continuous regime of operation

The arsenate desorption from goethite-covered quartz sand was carried out with phosphate containing water whose concentration was three times higher than the arsenic concentration in the waters being treated. The results suggested that the arsenate adsorption on goethite-covered quartz sand led to the formation of a covalent bond. For example, the total amount of desorbed arsenic was 13.3 μg , when the desorption solution was with slightly alkaline pH, which related to 11.2% of efficiency (Fig. 4). When the pH of the above-mentioned desorption solution decreased to 5.00, almost the same amount of arsenic desorbed from the sorbent. If the pH decreased further to pH 3.00, additional 4.9 μg arsenic desorbed just in a few cycles and the final percent of desorption reached 13.0% (Fig. 5).

Arsenate desorbed most efficiently when the pH of the desorbing solution increased above 8.5. In that case, the percent of desorption reached 55.2% (Fig. 6). A ligand exchange process between adsorbed arsenate and hydroxyl anions was the mechanism and the decreasing pH of effluents to values in the range 7.6–7.8 evidenced it. Further alkalisation of desorption solution to 9.5–10.0 led to the release of 12.5 μg additionally and the total arsenate desorption reached 65.8%.

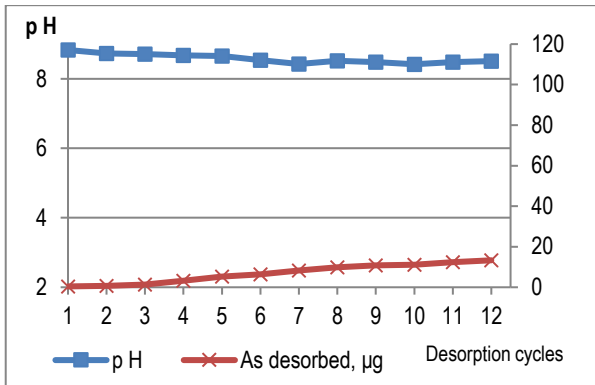


Fig. 4. Arsenic desorption from goethite-covered quartz sand by HPO_4^{2-} -spiked spring water in a continuous regime of operation

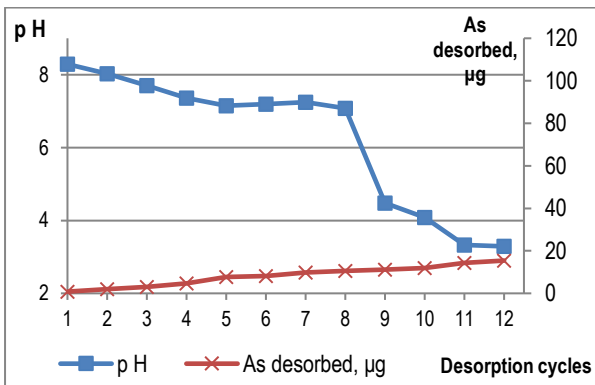


Fig. 5. Arsenic desorption from goethite-covered quartz sand by HPO_4^{2-} -spiked spring water at acidic pH in a continuous regime of operation

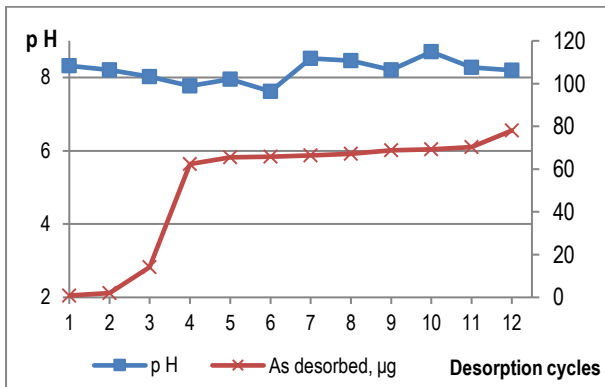


Fig. 6. Arsenic desorption from goethite-covered quartz sand by HPO_4^{2-} -spiked spring water at alkaline pH in a continuous regime of operation

Conclusions

1. The equilibrium content of adsorbed arsenates on goethite-covered quartz sand in a filter column, operated in flow regime, was in the range of 3.5–3.9 $\mu\text{g/g}$. The bed height of the adsorption zone and the applied flow rate had a crucial effect on the efficiency of the pollutant removal.

2. There is a need to test other widely applied column adsorption kinetic models such as Thomas, Yoon-Nelson, etc., to the experimental data to predict the arsenic breakthrough curves and for estimating the column kinetic parameters.

3. The arsenate desorbed more efficiently under a continuous regime of operation at alkaline in comparison to acidic pH. It revealed that the ligand exchange mechanism played the main role in sorption/ desorption process of arsenate on/ from goethite-covered quartz sand.

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