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E. A. Deliyanni[a]; D. N. Bakoyannakis[a]; A. I. Zouboulis[a]; E. Peleka[a]
[a] Chemical Technology Department, School of Chemistry, Aristotle University, Thessaloniki, Greece

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Removal of Arsenic and Cadmium by Akaganeite Fixed-Beds

E. A. Deliyanni,[*] D. N. Bakoyannakis, A. I. Zouboulis, and E. Peleka

Chemical Technology Department, School of Chemistry,
Aristotle University, Thessaloniki, Greece

ABSTRACT

The possibility of using a packed-bed (in column configuration) of akaganeite to remove oxyanions like As(V) and cations like Cd from aqueous solutions was the aim of the present study. Synthesized akaganeite was used in two forms, i.e., in fine powder (of nanocrystals) and in the form of grains (as granular). The main examined parameters were: 1) the quantity of sorbent in the column and 2) the presence (or not) of ionic strength. The bed depth-service time (BDST) model was applied to the sorption results to model the column operation. The removal efficiency of As(V) anions by the sorptive column was found to

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[*] Correspondence: E. A. Deliyanni, Chemical Technology Department, School of Chemistry, Aristotle University, GR-54006 Thessaloniki, Greece; Fax: +3031-997759; E-mail: elndbak@chem.auth.gr.

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be higher than that of Cd cations. The presence of increased ionic strength caused a serious increase of removal efficiency for the case of arsenic anions. Granular akaganeite was less effective in all cases, but still, it remained a good adsorbent.

Key Words: Akaganeite; Adsorption; Column; Arsenic; Cadmium.

INTRODUCTION

The control and removal of contaminants produced by the technological activities of humans has become an important issue recently, due to increased significance of related pollution aspects and to water scarcity. Arsenic is a contaminant in the groundwater and drinking water of some regions. It is famous for its high toxicity and its ability to induce skin cancer with long-term ingestion.[1] Cadmium belongs to heavy metals that regulate indirectly the potential reuse of treated liquid wastes. It is also known for its high toxicity.[2]

Specific studies dealing with the performance of novel inorganic sorptive materials have been performed, as for example, the examination of adsorption behavior of cadmium and zinc on natural and activated bentonite[3] and the evaluation of cadmium and lead removal by zeolites.[4] The most common technique for arsenic removal is coagulation with ferric salts followed by filtration.[5] Another technique, more simple but less effective, is the adsorption on activated alumina in fixed bed reactors. Alum as coagulant is less effective than any ferric salt.[6]

Hydrous oxides and oxyhydroxides has been found recently to control trace elements removal,[7] although their use has been limited, mostly due to competition from the commercially available in several phases, particle sizes, and surface areas, oxides of aluminum[8] or active carbon.[9] These oxyhydroxides are available only as fine powders or are generated in aqueous suspensions as a hydroxide floc or gel. In these forms, they retain their desirable sorptive properties for trace elements, but are limited to reactor configurations that incorporate large sedimentation basins or filtration units for subsequent separation. Under such conditions, the separation and regeneration of these materials can be difficult. These disadvantages can be overcome if the oxide is available in granulated form, thereby, permitting its use in fixed-bed design. In addition, the comparative insolubility of iron oxides permits their use under greater extremes of pH than most other oxide materials. Such a characteristic is important for regeneration, and for the removal of anionic and cationic contaminants, for which simple pH adjustment is often sufficient.[10]

The design advantages of granular forms of iron oxide have been recognized for some time. Edwards and Benjamin[11] used quartz grains and ferric nitrate as starting materials, resulting in a product that contained one to 2% iron and could be used and regenerated in a packed-bed design. Theis et al.[10] used granular iron oxide for the sorption of aqueous cadmium and chromate ions. Jekel and Driehaus[12–14] prepared granular ferric hydroxide as adsorbent, for arsenic removal. Lehmann et al.[15] used a packed-bed (column configuration) of synthetic granulated goethite for the sorption of chromate and zinc ions from dilute aqueous solutions.

In practical cases, the concept of fixed-bed absorbers is expressed graphically by the ''breakthrough'' curve concept. Various similar approaches have been followed,[9] such as the length of unused bed, the empty bed residue time, and the bed depth-service time model (denoted hereafter as BDST) that is applied in the present investigation. The later correlates the service time of sorptive column with other design parameters and it was originally developed for adsorption studies of activated carbon.[16] It has been used for the modeling of biosorption data,[17,18] for the adsorption of metal ions on silica gels,[19] and for the adsorption of zinc and chromium ions on goethite fixed-beds.[15]

The preparation of akaganeite nanocrystals by an advantageous innovative technique involving the precipitation of Fe(III) chloride salt from aqueous solution using ammonium carbonate as precipitating agent has been recently presented.[20] Granular akaganeite was also prepared in this study to be tested for its efficiency for arsenate and cadmium removal, too. The scope of this study was to evaluate the performance of an adsorptive column configuration based on a promising material, since it retained its high surface area and was crystalline for a long time, even after its regeneration. On the other hand, the starting reagents are cheap and common, so the sorbent can be characterized as a low-cost and easily available sorbent. Arsenate and cadmium ions existing in many wastewaters were selected for examination. Experimental and theoretical results were presented for the sorption of aqueous arsenate and cadmium ions in aqueous solutions onto akaganeite nanocrystals and granular akaganeite fixed beds, so that an appropriate comparison to be made; the effect of ionic strength was also examined.

EXPERIMENTAL

Preparation of the Sorbent

The sorbent used for the fixed-bed column operation was akaganeite, and was prepared in the laboratory in two forms, i.e., fine powder (nanocrystals) and granular. For the preparation of powder akaganeite, aqueous solutions of iron(III) chloride and ammonium carbonate, as precipitating agent, were used for the hydrolysis process. The final pH of the suspension after hydrolysis (measured with a Crison microPH 2002 instrument) was adjusted to 8. The chloride ions present in the suspension were slowly removed by osmosis and the resulting cake on the membrane was freeze-dried in a bench freeze dryer (DF1, Thermovac). After the freeze-drying process, the obtained material appeared as ultrafine powder.[20]

For the preparation of granular akaganeite, the same procedure as above was followed, but after the resulting cake was isolated from the mother liquor, it was gradually frozen (duration 24 h) from room temperature to $-15°C$ in an isolated chamber. The granules produced were dried at room temperature.[15]

Chemicals

All chemicals were reagent grade and they were used without further purification. All solutions were prepared with distilled water and all glassware was cleaned by soaking in 10% HCl and rinsed with deionized water. The arsenate stock solution was prepared from the dissolution of disodium hydrogen arsenate, $Na_2HAsO_4 \cdot 7H_2O$ and the initial pH value was adjusted to 7. The cadmium stock solution was prepared from the dissolution of the respective nitrate salt, $Cd(NO_3)_2 \cdot 4H_2O$ and the initial pH value was adjusted to 8. The pH was adjusted by addition of nitric acid (0.1 M) or sodium hydroxide solution (0.1 M), and ionic strength by the addition of KNO_3.

Procedure

The laboratory set-up for the column tests consisted of a Watson-Marlow (model 101 U/R) peristaltic pump and a vertical plastic column having an inner diameter of 1.5 cm and height of 10 cm. A fixed-bed of akaganeite nanocrystals or akaganeite granules was formed in the column containing a predetermined mass of sorbent (2.5, 5, or 10 g), which corresponded to 1.2, 2.4, and 4.8 cm of bed height, respectively. The sorbent was added to the column under the influence only of gravity, i.e., without the application of any additional pressure. The porosity of the resulted bed was calculated as 60.6% and its bulk density as $0.53\ g\ mL^{-1}$, according to the volumetric method.[21]

All experiments were performed at room temperature in an upflow-operating mode using a volumetric flowrate of $40\ mL\ s^{-1}$; under these conditions, the sorptive bed was not fluidized. Coarser filter media are generally recommended for upflow filters than that commonly used in conventional downflow filters.[22] Liquid samples were taken at different times from the column outlet to determine the residual concentrations of As(V) ions by the molybdenum blue method using a double-beam UV-visible spectrophotometer (Hitachi, model U-2000), or Cd cations by atomic absorption spectophotometry (Perkin Elmer Model 2380, using a C_2H_2/O_2-flame) respectively, according to the appropriate standard method.

RESULTS AND DISCUSSION

Column Experiments

Column experiments were conducted using solutions with initial pH values of 7.5 for arsenate and for cadmium ions as well. At this pH range, most of the natural waters and soils exist.[23]

The pH range of column outlet samples for all the experiments performed was found to be 6.0 (first sample taken) in the case of arsenate and 6.5 in the case of cadmium, increasing gradually with progressing of serving time and exhaustion of sorbent, toward pH values close to the initial ones. This pH lowering can be attributed to the release of H^+ due to the sorption of ions.[24] As long as the procedure is going on, the sorptive material is exhausted, so the H^+ release is eliminated and the outlet pH remains stable.

The experimental results, expressed typically with the breakthrough curve concept, i.e., treated volume vs breakthrough (ratio of the column outlet concentration to the initial metal concentration, $C_{outlet}/C_{initial}$, expressed as percentage), are presented in Figures 1 and 2 for arsenate and Figure 3 for cadmium ions. In the insets, the iso-removal lines of treatment volume vs the respective quantity of sorbent are also presented, at breakthrough points of 20, 35, and 50%.

In all cases, it is obvious that the mass increase from 2.5 to 10 g of akaganeite results in a better removal efficiency. The term removal efficiency and/or adsorption may be used in the present study with the meaning of quantitative comparison between service volume, until the same breakthrough level in the column outlet can be achieved, for the different experimental conditions applied.

The increase of the treated volume, indicating increase of the metal uptake, with the increase of sorbent mass from 2.5 to 10 g of akaganeite, was due to the increase in the surface area of adsorbent, which provided more binding sites for the adsorption.[25]

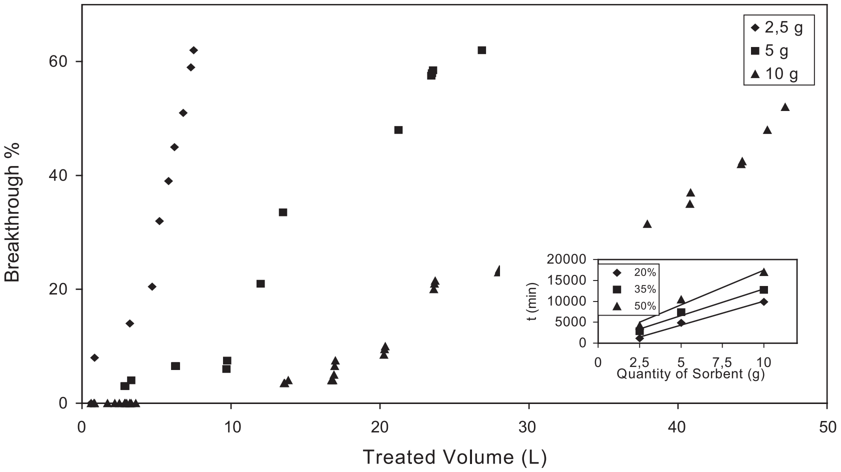

Figure 1. Breakthrough curves for different sorbent quantities (2.5, 5, and 10 g). Sorbent: nanostructured akaganeite. Solution: 10 mg L^{-1} As(V), pH = 7.5, I = 0.1 = M KNO_3.

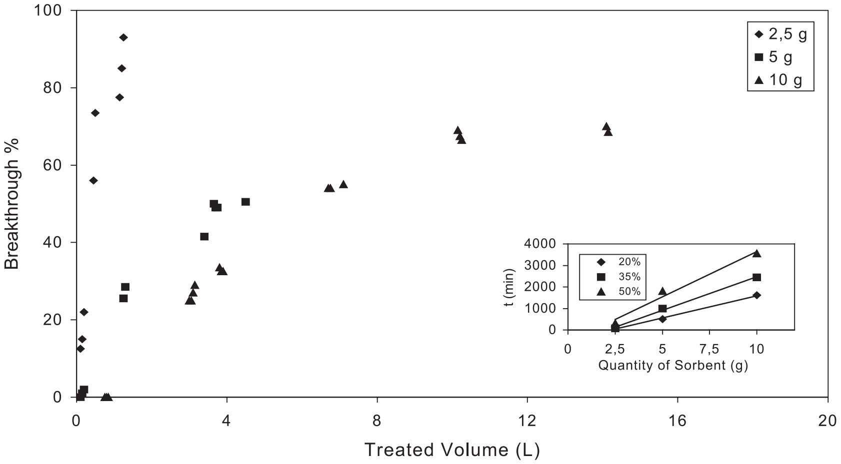

Figure 2. Breakthrough curves for different sorbent quantities (2.5, 5, and 10 g). Sorbent: granular akaganeite. Solution: 10 mg L^{-1} As(V), pH = 7.5, I = 0.1 = M KNO_3.

Akaganeite was examined as a sorbent in the form of ultrafine powder (nanostructured) with a crystalline size of 3 to 6 nm and a surface area of 330 m^2g^{-1}, and in a granulated form with a surface area of 230 m^2g^{-1}.

From Figures 1 and 2, it is concluded that granulated akaganeite is a poorer sorbent compared to nanostructured akaganeite since at a breakthrough 50% and for sorbent mass of 10 g, the treated volume is 12 L and 30 L, respectively. Smaller aggregates of particles will have a shorter diffusion path, thus allowing the adsorbate to penetrate deeper into the adsorbent elementary particle more quickly, resulting in a higher rate of adsorption. In addition, the total external surface area per unit volume for all smaller particles inside the column will be larger, providing more external surface for initial mass transfer to take place.[26]

In the presence of ionic strength, the pronounced affinity of akaganeite for the adsorption of anionic arsenate species was found to increase further. Nanostructured akaganeite presented higher removal efficiency than granular akaganeite but in the presence of ionic strength, both of the sample types presented nearly the same affinity.

In Figure 4, the breakthrough curves for sorbent mass of 10 g are presented for all the experimental cases, expressed in bed volumes, for comparison. From the breakthrough curves for arsenate and cadmium ions, it is obvious that the removal efficiency of both the sample types for anionic arsenate species were more pronounced than that of cationic cadmium species. This can be explained by the help of the chemical

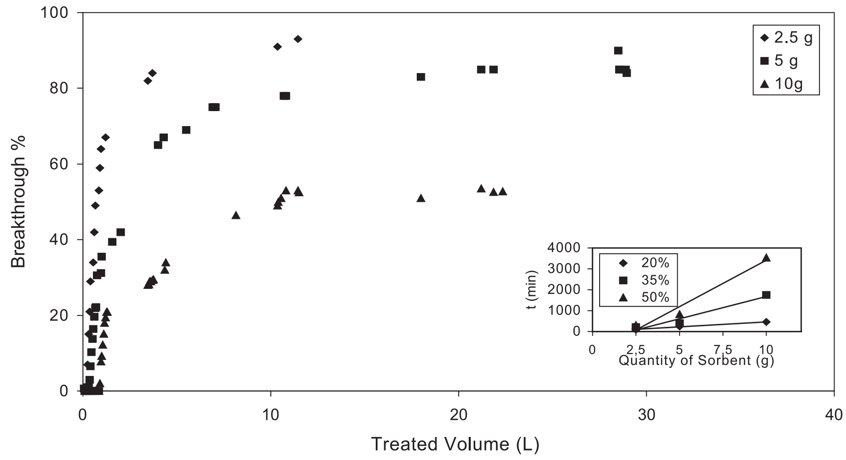

Figure 3. Breakthrough curves for different sorbent quantities (2.5, 5, and 10 g). Sorbent: granular akaganeite. Solution: 10 mg L^{-1} Cd, pH = 8, I = 0.

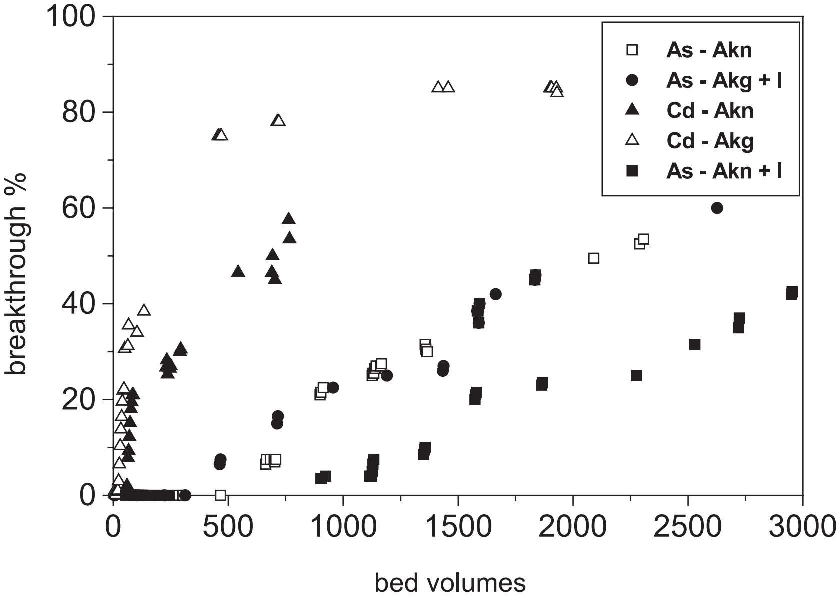

Figure 4. Breakthrough curves for sorbent mass of 10 g for all the experimental cases, expressed in bed volumes.

speciation of arsenate and cadmium in aqueous solutions of different pH. In Figure 5a, the chemical speciation is presented for an aqueous solution containing arsenate anions by using the Mineql + program (1994).[27] This is a convenient chemical equilibrium modeling system, which can be used to perform calculations on aqueous systems with moderate ionic strength at ambient temperatures. The main species for a single As(V) solution in the considered pH value are $HAsO^{4-}$ and $H_2AsO_4{}^{2-}$. In the considered pH range, the main species for a single Cd(II) aqueous solution are divalent cadmium, as can be seen from Figure 5b, which presents the aqueous species for a solution containing Cd(II) cations. At the outlet pH values (about 6), the surface of the akaganeite particles was positively charged, since the pzc of akaganeite is 7.3,[28] so the negatively charged arsenate ions were more easily adsorbed than the positively charged cadmium ions.

From Figure 4, it is obvious that bed volumes can be treated for arsenate and for cadmium ions. These results can be considered as satisfactory regarding the applicability of the method, as they were obtained without any pretreatment of the solution (i.e., pH adjustment). Since there are no studies regarding the removal of arsenic in fixed beds, the direct comparison of the obtained results with other research findings is not

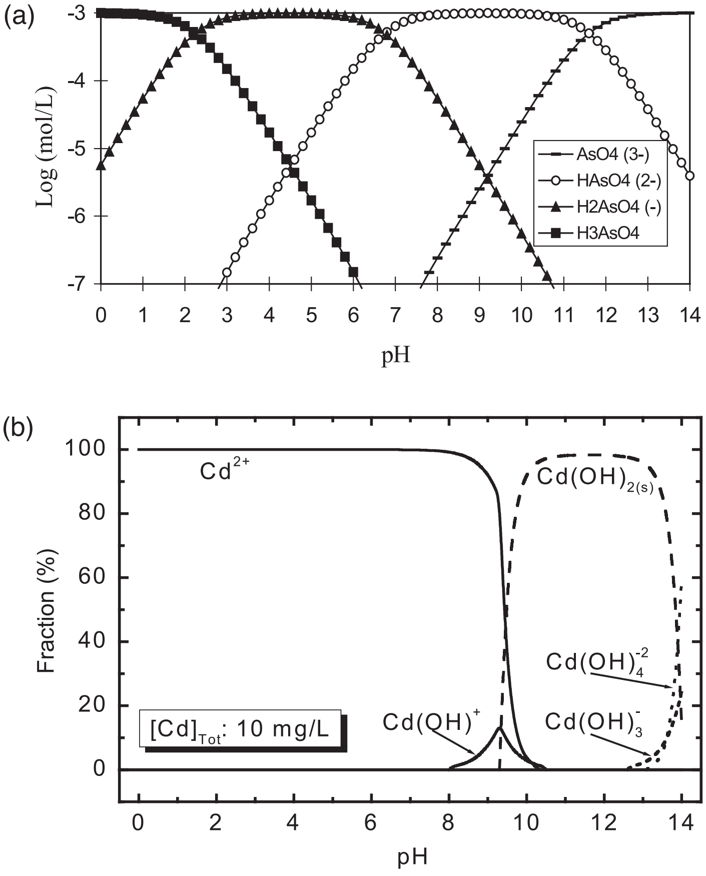

Figure 5. (a) Speciation of arsenate (b) Speciation of cadmium(II).

possible. In filter tests, an adsorption density was found to be in the range of 1 mmol As g^{-1} Fe at an residual concentration of 10 mg L^{-1} and pH 7, for GFH, an adsorbent resembling akaganeite,[13] which presented a specific capacity of more than 30,000 bed volumes, for g of adsorbent. For nanostructured akaganeite, the adsorption density was found to be 2.85 mmol As g^{-1} Fe at a residual concentration of 10 mg L^{-1} and pH 7.5,[28] and from column experiments, breakthrough of 50% can be reached at a specific capacity of about 2000 bed volumes.

Removal of Cd from aqueous solutions by using Darco 12–20 mesh granular activated carbon for 50% breakthrough presented a specific capacity of 91.5 pore volumes (i.e., about 3.6 L treated volume),[24] while for the same conditions and the same amount of sorbent, akaganeite presented a specific capacity of about 750 bed volumes (12 L treated volume).

Modeling of Column Operation

For a given set of experimental conditions, during operation of a fixed-bed adsorption column, the service time of the system could be related to the bed depth. The initial solute concentration fed to column was desired to be reduced in the final effluent to a predetermined value, usually imposed by the respective environmental regulation or laws. At the beginning of sorbing operation, when the sorbent material is still unused, the exit concentration is actually lower than the permitted one. As sorption proceeds and the sorbent material is being gradually saturated, the effluent concentration increases and reaches the so-called breakthrough point.

When sizing adsorptive columns, the main aim is the ability to predict the service time until the column effluent exceeds a predefined solute concentration. The BDST model relates the service time of a fixed-bed with the height of adsorbent material in the bed, hence, with its mass, as mass is directly proportional to the bed height. The measurement of sorbent mass is more precise than the determination of the respective volume, especially for the case of granules. Therefore, sorbent quantity is being preferably used, instead of the bed height. The following equation was proposed[19] to describe the BDST model:

$$t = \frac{q_o}{C_o V} M - \frac{1}{kC_o} \ln[(C_o/C_t) - 1] = aM + b$$

where t is the service time (min), q_o the adsorption capacity (mol/g), C_o the initial concentration of adsorbate (mM), V the applied flowrate (L/min), M the mass of sorbent inside the column (g), k the rate constant of adsorption (L/min/mol), and C_t the respective effluent concentration of adsorbate (mM) at time t.

From the iso-removal lines, i.e., the plots of t vs M (see Figures 1 through 3), regarding column operation under constant experimental conditions (except a sorbent dosage), the main parameters of BDST equation can be calculated. From the slope (a) of the respective lines the adsorption capacity (q_o) can be calculated, while from the intercept (b) the rate constant of adsorption (k) can be found. Usually, the 50% breakthrough curve between t and M must result in a straight line passing through the origin, since an assumption inherent in the BDST model is that the breakthrough curve from 0 to 50% breakthrough is of a similar shape to the curve from 50 to 100% breakthrough.[25] From the breakthrough curves of the insets of Figures 1 through 3, it is concluded that in most cases, the respective straight line at 50% breakthrough is passing through the origin, confirming the reliability of the BDST model.

The advantage of the BDST model is that the necessary quantity of sorbent for a preselected service time period can be directly calculated until a desirable breakthrough concentration is achieved, using the obtained parameters from the respective linear equation ($t = aM + b$).

In Table 1, the summarized results of these calculations are presented. The maximum adsorption capacities (q_o of the Langmuir isotherm equation) from batch experiments, for arsenate and cadmium ions sorbed onto akaganeite were found to be 1.79 mmol As g^{-1} Ak[28] and 0.125 mmol Cd g^{-1} Ak, respectively.

The calculated adsorption capacities from the application of the BDST equation at 50% breakthrough were found to be substantially lower. This can be attributed to the fact that sorption at 50% breakthrough is far from

Table 1. Summarized results of BDST model calculations.

	Species	Breakthrough point	k (L/min/mol)	q_o (mmol/g)	Correlation coefficient, r^2
Ak_n	As(V)	20	0.892	0.209	0.999
		35	0.463	0.343	0.998
		50	*	0.395	0.998
$Ak_n + I$	As(V)	20	0.779	0.353	0.988
		35	0.279	0.396	0.980
		50	*	0.512	0.970
Ak_{gr}	As(V)	20	2.250	0.065	0.978
		35	1.020	0.094	0.982
		50	*	0.133	0.987
$Ak_{gr} + I$	As(V)	20	1.015	0.186	0.980
		35	0.285	0.275	0.981
		50	*	0.316	0.927
Ak_n	Cd(II)	20	42.460	0.010	0.991
		35	1.033	0.045	0.951
		50	*	0.095	0.967
Ak_{gr}	Cd(II)	20	68.970	0.38E-3	0.964
		35	19.076	0.78E-3	0.942
		50	*	1.49E-3	0.995

Where: Ak_n = the nanostructured akaganeite, $Ak_n + I$ = the nanostructured akaganeite at solutions with ionic strength of 0.1 = M KNO_3, Ak_{gr} = the granular akaganeite, and $Ak_{gr} + I$ = the granular akaganeite at solutions with ionic strength of 0.1 = M KNO_3.
*At 50% breakthrough, k cannot be calculated.

Table 2. Adsorption capacities from the application of the BDST model on sorption of toxic ions.

q_o (mmol g^{-1})		Reference
0.0031	Adsorption of zinc cations at pH = 3.5	[15]
0.0109	Adsorption of zinc cations at pH = 5	[15]
0.297	Adsorption of chromic anions at pH = 3.5	[15]
0.138	Adsorption of chromic anions at pH = 5	[15]
4.89	Adsorption on silica gel at pH = 5.15	[26]
0.45	Adsorption of zinc cations on water fern azola at pH = 4	[17]

reaching the equilibrium stage, depending on addition of sorbent in the column, therefore, the sorbent rarely becomes totally exhausted.

Since any other application of the BDST for sorption of arsenate and cadmium ions onto akaganeite has not been reported, to the best of our knowledge, a comparison was made for goethite, another surging material with a surface area of 130 m^2g^{-1}. Hence, in Table 2, results are presented for the adsorption capacities from the application of the BDST for sorption of toxic ions. Akaganeite presented a greater adsorption capacity than that of goethite, although the pH of the treated solution in the case of goethite was adjusted to 3.5 or 5, which certainly is not typical of the natural waters.

CONCLUSION

A sorption process as an alternative removal technique was proposed and examined to evaluate the removal efficiency of a new adsorbent. Akaganeite was used in two forms, i.e., in nanocrystals and in granules. The BDST model was fitted to the experimental results. From the obtained breakthrough curves, the following were concluded:

1. In all cases, the sorbent mass increase resulted in a better removal efficiency.
2. Nanostructured akaganeite presented higher removal efficiency than granular akaganeite.
3. The effect of ionic strength was positive, as was expected from batch experiments, for the case of arsenate.
4. The removal efficiency of akaganeite (both nanostuctured and granular) for anionic arsenate was more pronounced than that of cationic cadmium species.

From the obtained breakthrough curves and from the calculation of BDST model parameters, the following classification of removal efficiency can be depicted:

$$\begin{aligned} \mathrm{As(V)}_{\mathrm{Akn-I=0.1}} &> \mathrm{As(V)}_{\mathrm{Akg-I=0.1}} > \mathrm{As(V)}_{\mathrm{Akn-I=0}} \\ &> \mathrm{As(V)}_{\mathrm{Akg-I=0}} > \mathrm{Cd(II)}_{\mathrm{Akn-I=0}} > \mathrm{Cd(II)}_{\mathrm{Akg-I=0}} \end{aligned}$$

where $\mathrm{Ak_n}$ denoted the nanostuctured akaganeite, $\mathrm{Ak_g}$ the granular akaganeite, and I the ionic strength in presence of KNO_3. The BDST model, finally, was found to be a simple but effective methodology for designing and controlling the removal of toxic ions from water.

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