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Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

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Online publication date: 08 July 2010

To cite this Article Vaishya, Rakesh Chandra and Gupta, Sudhir Kumar(2005) 'Modeling Arsenic(V) Removal from Water by Sulfate Modified Iron-Oxide Coated Sand (SMIOCS)', Separation Science and Technology, 39: 3, 645 — 666

To link to this Article: DOI: 10.1081/SS-120027999

URL: http://dx.doi.org/10.1081/SS-120027999

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SEPARATION SCIENCE AND TECHNOLOGY
Vol. 39, No. 3, pp. 645–666, 2004

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Modeling Arsenic(V) Removal from Water by Sulfate Modified Iron-Oxide Coated Sand (SMIOCS)

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ABSTRACT

The batch kinetics of arsenic(V) on a novel media developed by coating $BaSO_4$ and Fe on quartz sand, known as sulfate modified iron-oxide coated sand (SMIOCS), was investigated. Batch rate data were analyzed using active available site and chemical reaction rate models. The batch kinetic data were a better fit on an active, available site model as compared to a chemical reaction rate model. The media was characterized for certain chemical properties and surface area. The media showed alkali resistance with the presence of iron, barium, and sulfur on the surface. The Langmuir and Freundlich isotherm equations could be used to describe the partitioning

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DOI: 10.1081/SS-120027999 0149-6395 (Print); 1520-5754 (Online)
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behavior of system at different pH. The removal of As(V) on SMIOCS was pH dependent and maximum removal was observed in acidic pH range. The variation in ionic strength and chloride (Cl^-) concentration in the solute do not play a significant role in As(V) removal efficiency but major anions showed some reduction in As(V) removal efficiency. A very small concentration of silica drastically reduced arsenic removal efficiency. However, the presence of Ca^{2+} and Mg^{2+} as cations improved arsenic(V) removal efficiency. The fixed bed studies indicated that the breakthrough time for arsenic(V) removal is dependent on the initial influent arsenic concentrations. These results suggest that arsenate adsorption on SMIOCS media may play an important role for arsenic immmobilization.

Key Words: Arsenic(V) removal; Water; Sulfate modified iron-oxide coated sand.

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INTRODUCTION

Arsenic is of environmental concern because of its toxicity to plants, animals, and human beings. Water pollution due to arsenic contaminants has been, and continues to be, a specific problem of drinking water supplies in certain parts of Indian subcontinents.[1] A common symptom is depigmentation rashes on palms and soles of feet, which eventually develop gangrene and cancer. The other health effects e.g., skin and internal cancers, cardiovascular, and neurological effects have been attributed to arsenic uptake mainly from drinking water. Epidemiological studies in Taiwan have shown that long-term human exposure to arsenic can cause skin, liver, lung, kidney, and galbladder cancer.[2] The mobility and treatability of arsenic have become pressing concerns with the anticipated revision of drinking water standard currently $50-10\,\mu g/L$. Weathering of arsenic bearing minerals are major sources of arsenic contamination in the ground water supplies.

In the past, a variety of methods have been used for arsenic removal from water and wastewater. Coagulation using ferric chloride, ferric sulfate, or alum as a coagulant effectively removed As(V).[3] However, use of coagulation and flocculation is not feasible for small ground water supply schemes. Ion exchange can also be used, but high cost of resins and regeneration is likely to make it a less appropriate technology for rural applications. Therefore, adsorption using low cost adsorbents could prove to be a suitable alternative. This process also offers more reliable and more efficient removal of complex inorganic and organic metals that would not have been removed by conventional treatment methods.

Innovative technology, like coating of Fe oxides onto sand surface, to effectively remove and recover trace heavy metals has been used by many researchers.[4,5] The results from their studies confirm that the utilization of

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iron-oxide coated sand is feasible for metal ion removal from water. Pierce and Moore[6] successfully used ferrihydrite for the removal of arsenic from water and wastewater. In the reduced environment, arsenite has also shown strong affinity for sulfur. Therefore, when hydrogen sulfide is present, the removal of arsenic as orpiment or metal sulfides often occurs.[7] Arsenate also forms a stable solid ($BaHAsO_4$) in the presence of Ba^{2+} at near neutral pH range.[8] Ca^{2+} and Ba^{2+} ions form solids such as $Ca_3(AsO_4)_2$ and $Ba_3(AsO_4)_2$ in the presence of arsenate ions in natural systems. These solids have shown some control over arsenic immobilization in the aqueous environment.[5]

The research described here was designed to test the uptake potential of sulfate modified iron-oxide coated sand (SMIOCS) as an adsorbent for As(V). The study includes batch kinetic modeling, using active available site and chemical reaction rate models; characterization of media, and determination of sorption properties with respect to kinetic and isothermal studies. This study also includes the effect of pH and ionic strength variation and the presence of competitive anions/cations on the removal of As(V) by SMIOCS and column studies.

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MATERIALS AND METHODS

Sulfate Modified Iron-Oxide Coated Sand Preparation

The quartz sand used in this process was soaked in an acid solution (1.0-M HCl) for 24 hr, rinsed with distilled water, and dried at 105°C. The geometric mean size of sand was 498 μm. The coating was applied by taking 100 mL of 0.5-M $BaCl_2$ solution in a 1.0-L glass beaker. To this solution, 12 mL of 2.5 M H_2SO_4 was added drop by drop with simultaneous shaking of the beaker till a dense white floc of $BaSO_4$ was formed. In this solution, 100 mL 0.5-M $Fe(NO_3)_3 \cdot 9H_2O$ solutions were then added and mixture was mixed on horizontal shaker at 30 strokes/min for 10 min. Five hundred grams of quartz sand was added to this mixture and it was mixed for additional 30 min on the horizontal shaker. The beaker was kept in an oven at 105°C for 24 hr. The coated sand was washed with distilled water till the supernatent was clear. The washed sand was dried again in an oven at 105°C and kept in a capped bottle for further analysis. This procedure yielded slightly red colored sand.

Characterization of Sulfate Modified Iron-Oxide Coated Sand

The total coated iron on the sand surface and its resistance to acid and alkali are determined as per Kuan et al.[9] The total coated barium and sulfur

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were determined by dissolving 5.0 g of SMIOCS in 50 mL concentrated HNO_3^- for 24 hr. The suspension from all these experiments was filtered by Whatman-42 filter paper (ashless) and the contents were determined by ICP-AES (model-8440 Plasmalab), GBC, Australia. The surface area of quartz and coated sand was measured by BET method using model Micromeritics (ASAP-2000 model, USA). The pH_{zpc} of media was determined by the potentiometric titration method as described by Smith.[10]

Adsorption Studies

Batch Adsorption Kinetics

The batch sorption studies were carried out at room temperature (27 ± 1°C) in a rotary shaker at 44 ± 2 rpm. Media dose was 20 g/L (GM size = 498 μm) and ionic strength of synthetic water was adjusted to 0.01 M with $NaNO_3$. The reaction mixture consisted of total volume of 100 mL in 300 mL borosilicate glass bottles containing initial As(V) concentration of 0.5, 1.0, and 2.0 mg/L for kinetic studies. The bottles were removed from the shaker after the desired contact time (i.e., 0.5, 1, 2, 3, . . . , 8 hr) and supernatant was separated from adsorbent by Whatman-42 filter paper (ashless) and the filtrate was stored at 2°C until analyzed for arsenic(V) concentration. Samples in duplicate were used for some specific experiments. The pH of each solution was measured before and after each experiment. Drifting of pH was allowed during experimental studies. The desired initial pH of solution was achieved by the addition of 0.1-M HCl and 0.1-M NaOH. Arsenic(V) stock solution was prepared by the dissolution of di-sodium hydrogen arsenate ($Na_2HAsO_4 \cdot 7H_2O$) in distilled water. The pH of stock solution was kept at 3.5. Fresh stocks were prepared after 1 week. All chemicals were of anaytical reagent (AR) grade and were procured from E. Merck (India) Limited, Worli, Mumbai (India).

Isothermal Studies

The adsorption isotherms were obtained at different pH and sorbate concentrations to find out capacity of the media for arsenic removal. The sorbate concentration was varied from 0.5 to 3.5 mg/L keeping the dose of sorbent as 20 g/L and ionic strength as 0.01-M $NaNO_3$ in the solution. The initial pH of sorbate was adjusted to the desired pH before each experiment and mixing time was 8 hr. The pH drift during experimental studies was also measured. Equilibrium studies were also performed with 40 mg/L

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concentration of Ca^{2+} and Mg^{2+} ions. Other conditions were similar to the batch kinetic experiments.

Competitive Adsorption

Experiments were conducted for an initial As(V) concentration of 1.0 mg/L at pH 7.0 ± 0.1 (initial pH adjusted with NaOH and HCl) with concentration of foreign competing anions (SO_4^{2-}, CO_3^{2-}, HCO_3^- and Cl^-) and cation (Ca^{2+}) ranging from 0 to 300 mg/L, except silica ion Si(IV). Si(IV), concentration varied from 0 to 10 mg/L. The salts, i.e., $NaSO_4$, NaCl, Na_2CO_3, $NaHCO_3$, $CaCl_2$ and $Na_2SiO_3 \cdot 6H_2O$ were used for developing the required concentrations of SO_4^{2-}, Cl^{2-} CO_3^{2-}, HCO_3^-, Ca^{2+}, and Si^{4-} ions, respectively, in the aqueous environment. The ionic strength of 0.01-M $NaNO_3$ was maintained during experimentation.

Column Studies

Adsorption experiments were conducted in a number of fixed-bed reactors (glass columns) in a down-flow mode using distilled water with 0.01-M $NaNO_3$ ionic strength solution and arsenic as adsorbate. Four columns of identical internal diameter, of 15 mm each, with media depths of 200 mm were used to generate data. The packed sorbent bed was supported on 50 mm glass wool at the bottom of column. The influent concentration was maintained at different concentrations for this study. The influent flow rate was 1.56 $m^3/m^2/hr$ in all studies using a peristaltic pump (Watson Marlow, USA). The samples were collected at different time intervals and analyzed for arsenic concentration. Each column was allowed to run till the effluent concentration (C) reached more than 95% of influent concentration (C_0).

Sample Analysis

The analysis of As(V) was carried out as per the Johnson and Pilson[11] method. The absorbance was measured at 865 nm by using spectrophotometer (Spectronic 20 Genesys, USA). The minimum detection limit was 4 μg As. All samples were measured in duplicate.

Active Available Site Model

The present coated sand surface may be considered to consist of a number of chemically active sites.[12] The attachment of sorbate species occurs at these sites. So, the sorption capacity of sorbent for a specific sorbate is a

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function of 'available active sites.' The available sites can vary for the same sorbat–sorbent system under different environmental conditions like pH, temperature, and particle size.

The attachment of arsenic species from aqueous phase to active available site can be considered to occur in two steps. These are:

- Transfer of sorbate from aqueous phase to the active available site on the sorbent.
- Chemical complexation and ion exchange at these chemically active sites.

The following assumptions were made in the development of the proposed active available site mass transfer model.

- Both physisorption and chemisorption occur simultaneously.
- The Langmuir isotherm model fits the sorption equilibrium data well.
- The monolayer coverage parameter, Q_o in the Langmuir isotherm model, represents the saturation capacity of a sorbent. Thus, it is assumed that available active sites, $N_{\theta t}$ are proportional to the fractional monolayer coverage, i.e.,

$$N_{\theta t} \propto \frac{q}{Q_o} \tag{1}$$

- Here, Q_o is the Langmuir monolayer coverage parameter.
- Physisorption is accounted for, by considering the linear driving force approximation, i.e.,

$$\frac{dC}{dt} \propto (C - C_e) \tag{2}$$

- Chemisorption is a function of number of available active sites, $N_{\theta t}$.

The solid phase sorbate concentration can be obtained by applying mass balance for the sorbate, i.e.,

$$q = \frac{(C_0 - C)V}{m} \tag{3}$$

Considering that the Langmuir isotherm can describe the data and local equilibrium exists,

$$q = \frac{Q_o C}{1 + bC} \tag{4}$$

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Taking both physisorption and chemisorption into account, i.e., combining the concentration gradient, Eq. (2), with fractional surface coverage, $N_{\theta t}$ (chemisorption),

$$\frac{dC}{dt} \propto N_{\theta t}(C - C_e) \tag{5}$$

$$\Rightarrow \frac{dC}{dt} = -K_s N_{\theta t}(C - C_e) \tag{6}$$

Here, K_s is the active available site mass transfer coefficient (hr^{-1}). It is basically proportionality constant representing net mass transfer from aqueous phase to solid phase, and incorporates both, physisorption and chemisorption. The equation can be written as:

$$\left(\frac{1}{q}\right) = \left(\frac{1}{Q_o}\right) + \left(\frac{1}{C_e}\right) \cdot \left(\frac{1}{bQ_o}\right) \tag{7}$$

By combining Eqs. (1), (4), and (7), we get

$$\frac{dC}{dt} + \frac{bK_s C^2}{(1 + bC)} - \frac{bK_s C_e C}{(1 + bC)} = 0 \tag{8}$$

By using the technique of separation of variables, integrating Eq. (8), and putting boundary conditions, i.e., $t = 0$, $C = 0$, and at $t = \infty$, $C = C_e$, the linearized form of the equation obtained is as follows:

$$s \ln (C - C_e) + \ln C = (\ln C_0 + s \ln(C_0 - C_e)) + bK_s C_e t \tag{9}$$

where,

$$s = -(1 + bC_e) \tag{10}$$

Now, the overall mass-transfer coefficient can be obtained from Langmuir parameter, b, initial arsenic concentration C_0, and equilibrium arsenic concentration C_e. A plot of:

$$[s \ln (C - C_e) + \ln C] \text{ vs. } t$$

will yield a straight line of slope, $K_s C_e b$, from which the overall mass-transfer coefficient can be obtained.

Chemical Reaction Rate Model

The chemical reaction rate model[13] is based on mass law concept. The adsorption kinetics on oxide-coated sand may be treated as chemical

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reaction. This equation may be represented by a second-order reaction of the form:

$$\mathrm{M} + \mathrm{SS} \xrightarrow{K_R} [\mathrm{M} * \mathrm{SS}] \tag{11}$$

Where, M represents the dissolved metal contaminant, SS the available surface sites, M∗SS the adsorbed state, and K_R the reaction rate constant (l/h). The rate equation is expressed in terms of concentrations of respective reactants:

$$\frac{dC_M}{dt} = -k_R C_M C_{SS} \tag{12}$$

Employing, a Langmuir-type treatment, Eq. (12) can be rewritten entirely in terms of the liquid phase metal concentration

$$\frac{dC}{dt} = -K_R C(C - C_e) \tag{13}$$

$$\int \frac{dC}{C(C - C_e)} = -\int K_R\, dt \tag{14}$$

In Eq. (12), C_M is no longer used, since all concentrations refer to liquid phase metal concentration in mg/L. The rate expression in second order in C, $C - C_e$, represent an effective sorbent concentrations at time t, whereas, C_e is the equilibrium concentration of solution phase metal. C_e can be estimated from the equilibrium relationship and the sorbent dose used in the experiment. Integrating the left portion of Eq. (14), the rate constant K_R, may be determined by least squares linear regression of $\ln[(C - C_e)/C]$ vs. t. The slope of the line provides a value of $-K_R$, by putting in the value of C_e. The linear form of this equation is given below:

$$\ln\left(\frac{C - C_e}{C}\right) = -C_e K_R t + \ln\left(\frac{C_0 - C_e}{C_0}\right) \tag{15}$$

While this model yields a more realistic picture of the entire kinetic profile, it does not capture the rapid rate of adsorption during the early minutes of the experiment.

RESULTS AND DISCUSSION

Media Properties

The physical and chemical characteristics of plain quartz sand and SMIOCS are shown in Table 1. The table shows that the BET surface area of

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Table 1. Physical and chemical characteristics of plain sand and SMIOCS.

Number	Characteristics	Plain sand	SMIOCS
1	Size[a]	498 μm	≅ 498 μm
2	Diameter of particle	≅ 0.5 mm	≅ 0.5 mm
3	Surface area, BET (m^2/g)	1.79	3.74
4	Fe salt used for coating (%)	0	4%
5	Total amount of iron on coated sand (mg/g)	0	1.91
6	Total amount of barium on coated sand (mg/g)	0	0.126
7	Total amount of sulfur on coated sand (mg/g)	0	0.47
8	Acid resistance at pH ≅ 1.0	0.02%	45.67%
9	Alkali resistance at pH ≅ 12.67	0	0.94%
10	pH_{zpc}	—	8.2

[a] After sieve analysis, not more than 8% size variation was observed due to oxide coating.

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coated sand increases by more than two times as compared to plain sand of the same size. The presence of barium and sulfur along with iron on media surface can also be seen from Table 1.

Adsorption Kinetics

The arsenate adsorption kinetic data in the current study were fitted to active available site[12] and chemical reaction rate models.[13] The fitting of model was tested either by overlapping of experimental data points with model calculated values or by comparing quantitatively by normalized standard deviation Δq. The normalized standard deviation Δq was calculated by the following equation

$$\Delta q(\%) = 100 \times \sqrt{\frac{\sum [(q_{\mathrm{exp}} - q_{\mathrm{cal}})/q_{\mathrm{exp}}]^2}{(n-1)}} \tag{16}$$

where, q_{exp} is solid phase loading data obtained experimentally at time t, and q_{cal} is model calculated solid phase loading data at time t, and n is the number of data points.

Fitting of both reaction rate and active available site models were tested by overlapping of experimental data points with model calculated values and normalized standard deviations. It was quite difficult to judge a better-fit

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model based on overlapping of data points. However, based on the normalized standard deviation data, the active available site model was better described (Table 2). Since both models have shown similar trends, therefore, fitting of only active available site model curves with adsorption kinetic data are shown in Fig. 1. Table 2, also shows that the concentration of As(V) was increased from 0.5 to 2.0 mg/L, the rate of reactions were found to decrease. The different relative reaction rates at low and high initial arsenate concentrations could relate to previous extended x-ray absorption of fine structure (EXAFS) results,[14,15] which provide evidence that, at low surface coverage, arsenate is retained mainly by the formation of monodentate complexes on the iron oxide surface. At high surface coverage, arsenate binds to the surface mainly by the formation of bidentate binuclear and bidentate mononuclear complexes. It is possible that formation of the bidentate complexes at high surface coverage is slower than predominantly monodentate reactions at low surface coverage. The rate data of this study are in general agreement with those of Pierce and Moore,[6] who observed that the adsorption reaction was noticeably faster at low arsenic concentration. Figure 1 also shows that the adsorption rate increases rapidly initially and the maximum rate of adsorption is within 30 min and it decreases markedly from 0.5 to 8 hr. At 5 to 8 hr, the curve becomes flat. Fuller et al.[16] also reported similar findings of a slow rate of arsenate adsorption on ferrihydrite after an initial rapid adsorption. It can be seen from Fig. 1 that with an increase in As(V) concentration from 0.5 to 2 mg/L, the adsorption capacity of media increases from 0.024 to 0.072 mg/g.

The presence of Fe, Ba, and S on media may play some important role in the removal of arsenate from water. The insoluble solids like $Fe_3(AsO_4)_3$ and $Ba_3(AsO_4)_2$ may be formed with As(V) as $\log K_{sp}$ of these solids are negative.[17] Davis,[18] after conducting experiments on typical water distribution systems at neutral pH range, reported a $\log K_{sp}$ value of -5.51 ± 0.02 for barium hydrogen arsenate ($BaHAsO_4$). Since the barium was available on the coated media therefore, it may have played role for

Table 2. Kinetic parameter and normalized standard deviations for adsorption of As(V) on SMIOCS at 27 ± 1°C.

			Chemical reaction rate model $\ln[(C - C_e)/C]$ vs. t		Active available site model $[s \ln(C - C_e) + \ln C]$ vs. t	
C_0 (μg/L)	m (μg/L)	d_p (mm)	k_2 (mg/L hr)	Δq (%)	K_s (hr^{-1})	Δq (%)
0.5	20	0.498	4.27	141	4.37	138
1.0	20	0.498	4.17	4.34	4.59	4.34
2.0	20	0.498	0.58	5.67	0.97	5.49

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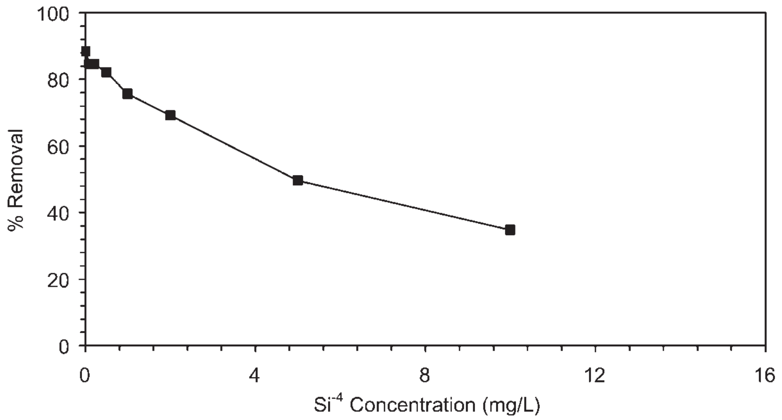
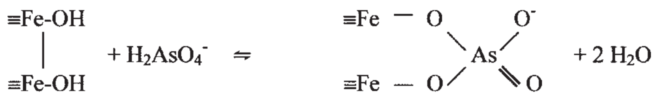


Figure 1. Fitting of AAS model for As(V) adsorption on SMIOCS at different initial As(V) concentrations in a distilled water system with an ionic strength of 0.01-M $NaNO_3$, media dose = 20 g/L, media size = 0.498 mm, and pH = 7.1 ± 0.1.

arsenic immobilization in the present study (see Table 1). The reaction of As(V) with oxide surface can also be explained with the help of the surface complexation theory. If surface sites correspond to ≡Fe–OH, then the attachment of an As(V) anion on ≡Fe–OH surface may be presented by following equation:



(1)

Here, site ≡Fe–OH acts as Lewis acid and arsenate anion acts as Lewis base and due to exchange of OH^-, the mechanism is known as ligand exchange mechanism.[19]

Isothermal Studies

pH Adsorption Edge

The pH adsorption edge equilibria data were obtained at three-different pH (see Fig. 2). For all three pH values, the shape of adsorption isotherms indicates that sorbate–sorbent interactions are of the favorable type. The Langmuir and Freundlich isotherm constants were determined using the linear form of the equations of both isotherms and optimization of data using the

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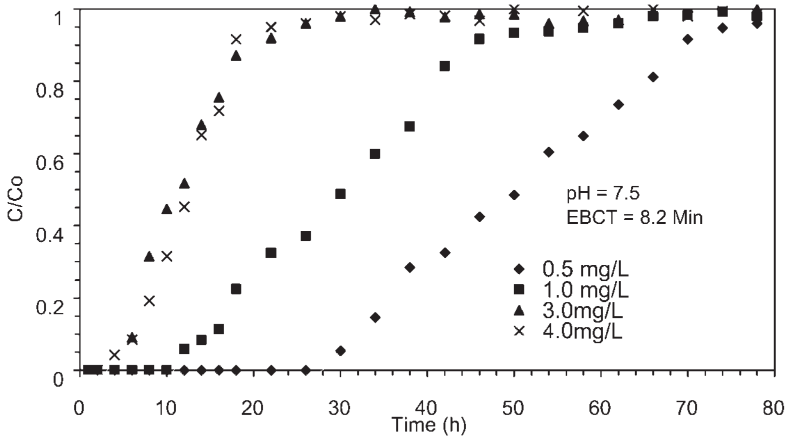

Figure 2. Equilibrium curve for As(V) adsorption on SMIOCS at different solute pH in a distilled water system with an ionic strength of 0.01-M $NaNO_3$, media dose $= 20\,g/L$ and media size $= 0.498\,mm$.

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least squares method. These constants are shown in Table 3. In the Freundlich isotherm model, the trends in sorption capacity are largely captured in the parameter K_F, while n reflects the steepness of the curve whether plotted on arithmetic or logarithmic scale. According to Treybal,[20] the value of $n > 1$, represents favorable sorption conditions. Apparently, the value of n for the present system is greater than one in all cases. However, significant differences have been shown by equilibrium curves with respect to pH. Table 3 shows that at pH 4.0 the monolayer adsorption capacity of media is 0.128 mg/g whereas, it reduces to 0.082 mg/g for pH 10.2.

The values of nonlinear regression coefficient (R^2) for different pH were larger than 0.92, indicating that both Freundlich and Langmuir isotherms successfully describe the partition behavior between water and media surface for arsenate. These correlation coefficients seem to indicate that these models of monolayer sorption do not match the sorption mechanism very well. The diffusion in the solid, or the limitation of diffusion to a thin layer, to a multilayer sorption, even if the sensibility of sorption mechanism to pH could induce significant variations, if the pH varies during metal ion uptake. These simple equations do not have any mechanistic implications, however, Matis et al.[21] reported that sorption of anions are typically pseudo-Langmuirian for all sorbate–sorbent ratios, indicating ligand exchange as the dominant binding site. Since the observed drift in pH during the present equilibrium studies may have been due to net release of OH^-, it indicates that both binuclear and

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Table 3. Langmuir and Freundlich model coefficients for As(V) adsorption on SMIOCS at different pH and cations concentrations.

	pH				
	4.0	7.2	10.2	7.2	7.2
Langmuir constants					
Q_o (mg/g)	0.128	0.117	0.082	0.200	0.149
b (L/mg)	2.66	2.64	3.19	1.70	3.10
R^2	0.95	0.94	0.95	0.92	0.92
Freundlich constants					
K_F [(mg/g)/(mg/L)$^{1/n}$]	0.095	0.079	0.051	0.123	0.116
$1/n$	0.355	0.450	0.547	0.529	0.476
R^2	0.94	0.92	0.99	0.93	0.99
pH_{drift}	6.95–7.25	7.35–7.42	7.43–8.2	7.25–7.55	7.02–7.69
Remarks	Without Ca^{2+} and Mg^{2+}	Without Ca^{2+} and Mg^{2+}	Without Ca^{2+} and Mg^{2+}	With Ca^{2+} = 40 mg/L	With Mg^{2+} = 40 mg/L

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monodentate surface complexation may be the dominant mechanism, as shown in the following equations with ligand exchange reaction, whereby, the anion displaces OH^- and/or H_2O from the media surface,[22] if surface sites corresponds to SS.

$$SS{-}OH + L^{z-1} \leftrightarrow SS - L^{(z-2)} + OH^- \qquad (18)$$

$$2SS{-}OH + L^{z-1} \leftrightarrow SS_2{-}L^{(z-2)-} + 2OH^- \qquad (19)$$

On the basis of net OH^- release, it can be postulated that either monodentate or bidentate bonding may take place. But the current x-ray adsorption and infrared spectroscopic evidence indicate that bidentate complexes are likely to dominate over monodentate complexes.[23] Jain et al.[24] also observed net release of OH^- from adsorption of arsenate by ferrihydrite at pH 4.6 and 9.2. The extent and nature of pH drift appears to be most affected by initial pH and arsenic in the solution. For same ionic background and dosage, pH drift is greater for pH 4.0 and minimum for pH 7.2. The trends of pH drift indicate that the presence of adsorbent may act as "buffer," driving the system toward its pH_{zpc} ($pH_{zpc} = 8.2$).

To measure uptake of arsenate onto SMIOCS at various pH ranging from 2 to 11, the effect of pH was also conducted (Fig. 3). Generally, in natural water, arsenate is present as anions. $H_2AsO_2^{2-}$ is dominant in the pH range 2 to 7, $HAsO_4^{2-}$ is important between pH 7 to 11 in the water. The obtained result can be interpreted with the help of pH_{zpc} (8.2) of media (see Table 1). Below pH_{zpc}, the media surface is positively charged and in

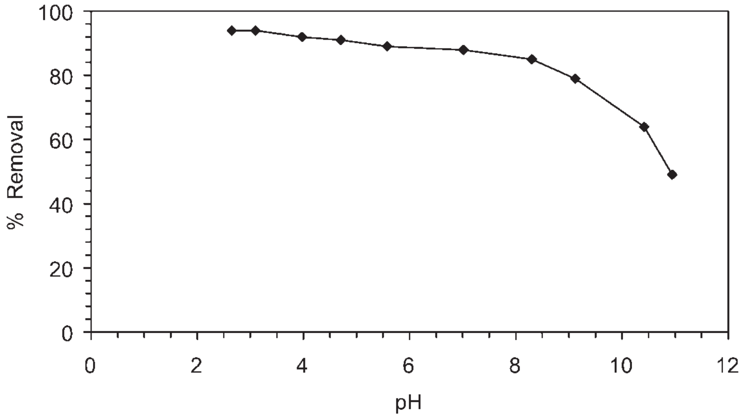

Figure 3. Effect of pH on As(V) removal by SMIOCS in a distilled water system with an ionic strength of 0.01 M $NaNO_3$, media dose = 20 g/L, media size = 0.498 mm, and initial As(V) = 1.0 mg/L.

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this pH range, species of arsenate is available as anion.[25] Therefore the adsorption of arsenate is expected to be electrostatically favored at pH less than pH_{zpc} of the media specially, when protonated species dominate. In the pH range of 2 to 7, adsorption of arsenate onto SMIOCS is through the formation of inner-sphere surface complexes and may be the dominant mechanism for As(V) removal.

Above pH 8.2, the positive potential charge on media reduces changes to negative charge, therefore, As(V) removal by SMIOCS starts decreasing. The significant decrease in As(V) removal by SMIOCS in the pH range 8.3 to 11 may be the result of repulsive forces between net negative charge on SMIOCS media ($>pH_{zpc}$) and arsenate species ($H_2AsO_4^-$ and $HAsO_4^{2-}$).

Effect of Ionic Strength

Figure 4 depicts the effect of ionic strength on arsenate adsorption. The figure shows that with the increase in ionic strength from 0.001 to 0.1-M, As(V) removal decreased from 92.7% to 85.4%. At pH 7.2, $HAsO_4^{2-}$ and $H_2AsO_4^-$ are the predominant species of As(V). The increase in the ionic strength of solution enhanced the availability of Na^+ in the solution. These ions may have developed a bond with arsenate species as $HAsO_4^{2-}{-}Na^+$ and $H_2AsO_4^-{-}Na^+$, thus decreasing the intensity of attraction toward positively charged media surface (below pH_{zpc}). However, the reduction in the removal efficiency was less ($<10\%$), therefore, it can be concluded that

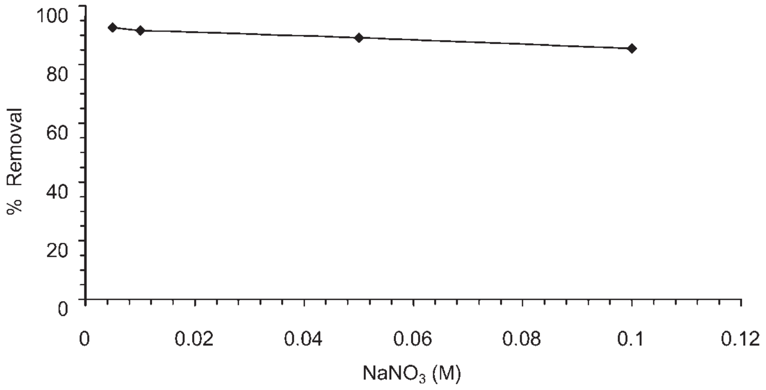

Figure 4. Effect of ionic strength on As(V) removal by SMIOCS in a distilled water system, media dose = 20 g/L, media size = 0.498 mm, pH = 7.1 ± 0.1, and initial As(V) = 1.0 mg/L.

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variation in ionic strength does not play a major role in As(V) removal by SMIOCS.

Effect of Competitive Ions

The effect of different anions on As(V) adsorption by SMIOCS is illustrated in Fig. 5. From the figure, it can be seen that with increasing $HCO_3{}^-$, $CO_3{}^{2-}$, $SO_4{}^{2-}$, and Cl^- concentrations from 0 to 300 mg/L, As(V) removal efficiency decreases from 90.4% to 68.8% for HCO_3^-; 90.4% to 82.4% for $CO_3{}^{2-}$ and 90.4% to 72.6% for $SO_4{}^{2-}$ ions, with the exception of Cl^-, which showned insignificant reduction in arsenic removal efficiency. The difference in the reduction of arsenic removal efficiency in the presence of $SO_4{}^{2-}$, $CO_3{}^{2-}$, and $HCO_3{}^{1-}$ may be due to their different complex formation characteristics with the oxide surface of media. The probable reaction of SO_4^{2-} and iron present at SMIOCS surface may be as follows:

$$2FeOH^{1/2-} + SO_4{}^{2-} + 2H^+ \leftrightarrow Fe_2O_2SO_2{}^- + 2H_2O \qquad (20)$$

McNeil and Edward[26] have observed that carbonate competes with arsenic for sorption sites on iron hydroxides. Kuan et al.[9] also reported that the presence of $HCO_3{}^-$ in the solute reduces the efficiency of Se(IV) and Se(VI) removal by aluminum oxide coated sand (AOCS) in pH range of 3 to 8.

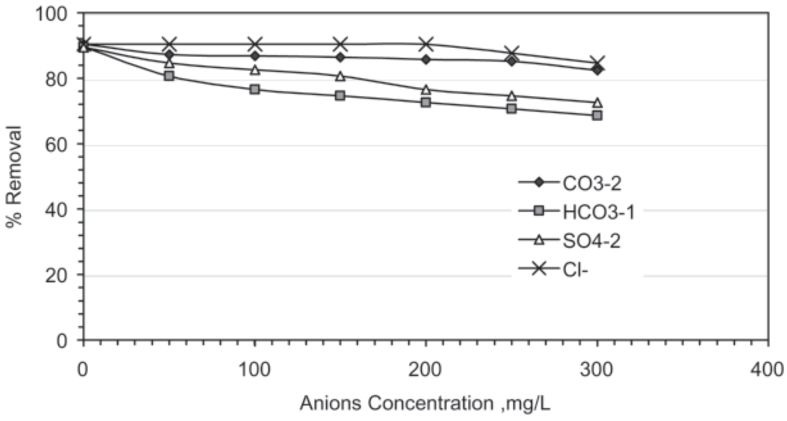

Figure 5. Effect of different anions on As(V) removal by SMIOCS in a distilled water system with an ionic strength of 0.01-M $NaNO_3$, media dose = 20 g/L, media size = 0.498 mm, pH = 7.1 ± 0.1, and initial As(V) = 1.0 mg/L.

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Effect of Ca^{2+} and Mg^{2+}

The presence of Ca^{2+} plays a significant role in the arsenic immobilization. As shown in Fig. 6, when the concentrations of Ca^{2+} increased along with combined concentration of HCO_3^-, CO_3^{2-}, SO_4^{2-}, and Cl^- from 0 to 300 mg/L in the solution, the removal efficiency of As(V) increases from 89% to 98.6%. Whereas, when combined concentrations of HCO_3^-, CO_3^{2-}, SO_4^{2-}, and Cl^- was increased from 0 to 300 mg/L in the absence of Ca^{2+}, As(V) removal efficiency decreased from 89% to 64%. Also, the monolayer sorption capacity of media increased from 0.128 mg/g to 0.2 and 0.149 mg/g for Ca^{2+} and Mg^{2+} ions, respectively, when, Ca^{2+} and Mg^{2+} concentration of 40 mg/L was maintained during isothermal studies at pH 7.2 (Table 3). The increase in sorption capacity in the presence of Mg^{2+} was less as compared to Ca^{2+}. The reason for this behavior may be the formation of $Ca_3(AsO_4)_2$ as insoluble solids and $Mg_3(AsO_4)_2$ as soluble solids in presence of excessive Ca^{2+} and Mg^{2+}.[26,27] Min and Herring[28] also reported that Ca–Fe beads were found to be quite effective for removing As(V) from solution as compared to Fe beads only. The presence of Ca^{2+} in the $Fe{-}CO_3^{2-}$ system improves removal efficiency of arsenic with respect to only $Fe{-}CO_3^{2-}$ system.[26] The surface complexation reactions may be used to represent complex formation with Ca^{2+}. If surface sites correspond to SS, then these reactions are as follows:

$$Ca^{2+} + 2SS{-}OH \leftrightarrow (SSO^-)_2{-}Ca^{2+} + 2H^+ \tag{21}$$

$$Ca^{2+} + SS{-}OH + H_2O \leftrightarrow SSO^-{-}Ca{-}OH^+ + 2H^+ \tag{22}$$

The adsorption of calcium on the media surface may increase the positive surface charge of the media. The resulting enhanced positive surface charge favors more anionic arsenic(V) species adsorption.[29]

Effect of Silica

Figure 7 shows the effect of Si on As(V) removal efficiency by SMIOCS. The removal efficiency decreased from 88.4% to 47.3% when the silicate concentration was increased from 0 to 10 mg/L in the solution. Stumm[19] reported that a very low concentration of inhibitors could often be effective because it may block the functional groups of active sorbent sites. The silicate concentration in natural water varies from 0.45 to 14 mg/L,[30] which may significantly reduce the amount of arsenic removed by adsorption processes. The significant reduction of As(V) adsorption capacity was due to a strong association of silicate with active sorption sites on the media surface. In addition, the formation of $SH_2SiO_4^-{-}Na^+$ may

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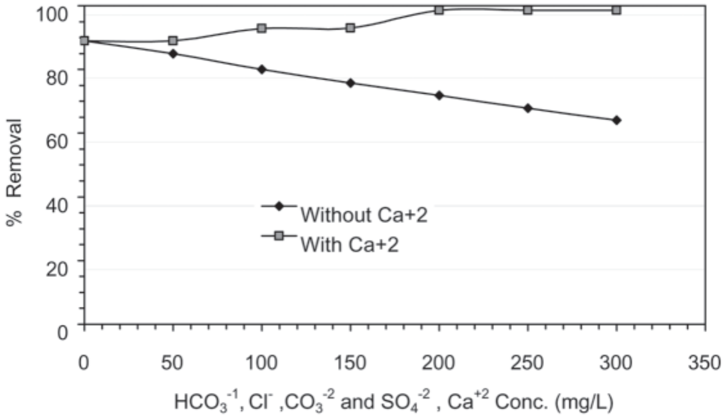

Figure 6. Combined anionic and Ca^{+2} effect of As(V) removal on SMIOCS in a distilled water system with an ionic strength of 0.01-M $NaNO_3$, media dose = 20 g/L, media size = 0.498 mm, pH = 7.1 ± 0.1, and initial As(V) = 1.0 mg/L.

have reduced the surface potential of media. Silicate also interacts with Fe(III) to form soluble polymers and highly dispersed colloids that are not removed by filtration.[31] The results indicate that when silicate content in water was high, the possibility for the removal of As(V) by co-precipitation and solid formation was reduced.

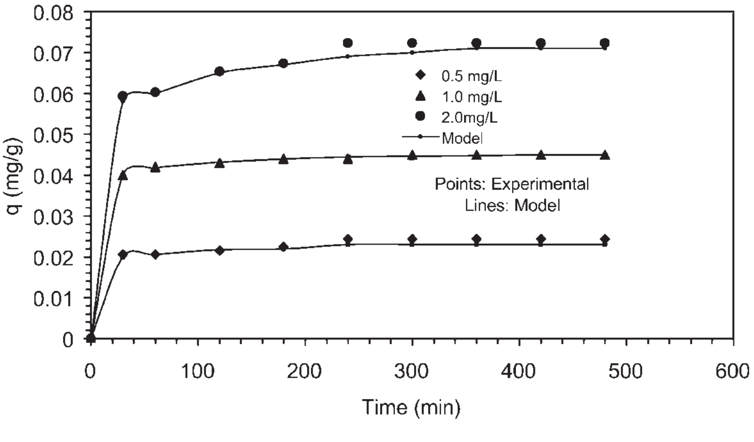

Figure 7. Effect of silica on As(V) removal by SMIOCS in a distilled water system with an ionic strength of 0.01-M $NaNO_3$, media dose = 20 g/L, media size = 0.498 mm, pH = 7.1 ± 0.1, and initial As(V) = 1.0 mg/L.

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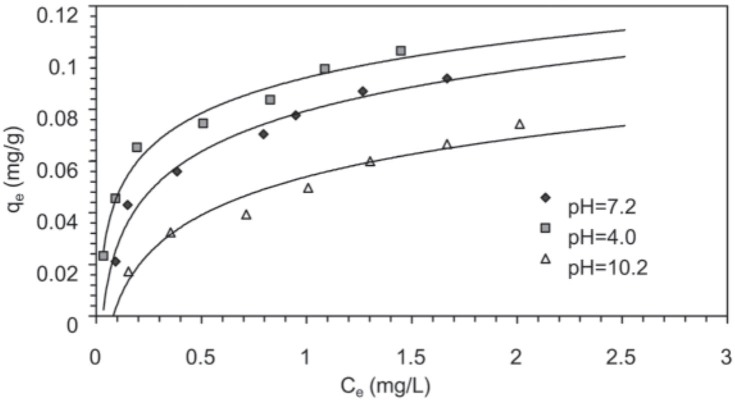

Figure 8. Breakthrough curves of an As(V) spiked distilled water system with an ionic strength of 0.01-M $NaNO_3$ for different As(V) influent concentrations.

Column Studies

Figure 8 illustrates the effect of influent concentration on breakthrough time. The influent concentration C_0 of As(V) was varied from 0.5 to 4.0 mg/L in a separate fixed bed experiment. As indicated in the figure, the bed volumes treated to both breakthrough ($C/C_0 \leq 0.05$ mg/L) and exhaustion ($C/C_0 \geq 0.95$) increases for decreasing C_0. The solid phase loading for $C_0 = 3.0$ and 4.0 mg/L are almost similar with respect to breakthrough and exhaustion time. Whereas, the breakthrough time was about five times for $C_0 = 0.5$ mg/L than $C_0 = 3.0$ and 4.0 mg/L. The solid phase loading at the breakthrough and exhaustion is also considerably less for higher initial As(V) concentrations.

CONCLUSION

Sulfate modified iron-oxide coated sand (SMIOCS) may be used an alternative media for the treatment of water containing arsenate along with anions and cation. The acidic and near neutral pH is most suited for arsenate removal from water.

NOMENCLATURE

b = constant in the Langmuir isotherm model (L/mg)
C = liquid phase concentration (mg/L)

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C_e = equilibrium liquid phase concentration (mg/L)
C_0 = initial liquid phase concentration (mg/L)
C_c = coefficient of correlation
d_p = average particle diameter (mm)
K_R = reaction rate mass-transfer coefficient (L/hr)
K_s = active available site model mass-transfer coefficient (hr^{-1})
K_F = Freundlich isotherm model constant (representing sorption capacity) $[(\mathrm{mg/g})/(\mathrm{mg/L})^{1/n}]$
$1/n$ = constant in the Freundlich isotherm model (representing intensity of sorption),
$N_{\theta t}$ = number of available active sites (proportional to Langmuir monolayer coverage factor)
m = mass of sorbent (g)
q = solid phase sorbate concentration at time t (mg/g)
Q_o = monolayer coverage factor for Langmuir model (mg/g)
t = time (hr)

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Received August 2002
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