

Arsenic(V) Removal by Sulfate Modified Iron Oxide-Coated Sand (SMIOCS) in a Fixed Bed Column

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A novel granular media developed by the coating of iron, barium and sulfur on quartz sand surface has been demonstrated to be an effective sorbent for removal of arsenic(V) from a 0.01 M NaNO₃-spiked distilled water system in laboratory-scale tests. The results of fixed bed studies indicate that arsenic(V) removal is dependent on pH, the size of sorbent and influent arsenic concentrations. The particle size of media has shown significant differences in reactor breakthrough times in similar experimental conditions. The removal of As(V) may be explained using the surface complexation theory. The presence of alkalinity (250–260 mg/L as CaCO₃) and hardness (200 mg/L as CaCO₃) slightly increases reactor breakthrough time for similar experimental conditions without alkalinity and hardness. Desorption studies using 0.2 M NaOH as elutant resulted in nearly 92% recovery of arsenic(V). A theoretical model based on two parameters has shown good correlation with observed experimental data generated during depth variation studies.

Key words: adsorption, arsenic(V), fixed bed, media, model, desorption

Introduction

The presence of arsenic (As) in groundwater has been reported to be extremely detrimental to humans (Poin-tus et al. 1994). Arsenic contamination in natural water is a worldwide problem (Welch et al. 2000). High arsenic concentrations have been reported in some groundwater in Bangladesh and West Bengal (India) and certain other parts of Indian subcontinents. In Bangladesh it is a specific problem in drinking water supplies (Karim 2000). Fossil fuel burning, agricultural activities, volcanic actions and weathering processes also contribute significant flux of arsenic to various sectors of the environment. Common symptoms are 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. The epidemiological studies in Chile have shown that long-term human exposures to arsenic can cause skin, liver, lung, kidney and gallbladder cancer (Smith 1998a). Due to the carcinogenic properties of arsenic, the World Health Organization (WHO) has recommended a provisional guideline value of 0.01 mg/L for arsenic in drinking water (WHO 1993).

Methods for removing arsenic from water include adsorption-coprecipitation with hydrolyzing metals, such as aluminum or iron(III) (Herring et al. 1996). Ion

exchange can also be used but the high cost of resins and regeneration makes it a less appropriate technology for rural applications. Coagulation with iron salts is perhaps the most effective method for large-scale treatment plants but excess sludge handling makes this process much more difficult. 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 technologies such as coating of Fe oxides onto the sand surface to effectively remove/recover trace heavy metals have been used by many researchers (Edward and Benjamin 1989; Bailey et al. 1992). Arsenic(V) is removed more effectively than arsenic(III) due to the neutral status of the latter at normal water pH (Ferguson and Gavis 1972). In the reduced environment arsenite has also shown a strong affinity for sulfur. Therefore, when hydrogen sulfide is present, the removal of arsenic as orpiment or metal sulfides often occurs (Hounslow 1980). Arsenate also forms stable solids (BaHAsO₄) and Ba₃(AsO₄)₂ in the presence of Ba⁺² at near neutral pH (Robin 1985).

The present study was carried out to assess the uptake potential of sulfate modified iron oxide-coated sand (SMIOCS) as an adsorbent for arsenic(V). The study also includes characterization of media and determination of breakthrough time under various conditions of synthetic water during column studies. The breakthrough time forecasting using two parameter models and a regeneration study has also been included.

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Materials and Methods

SMIOCS Preparation

The SMIOCS was prepared using quartz sand from a local quarry in the Yamuna river basin, near Allahabad, India. This quartz sand was soaked in an acid solution (1.0 M HCl) for 24 h then rinsed with distilled water and dried at 105°C. The geometric mean sizes of sand were 324, 498 and 716 μm . The oxide 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 5 N 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 of 0.5 M $\text{Fe}_2(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ solution was then added and the mixture was mixed on a shaker at 30 strokes/min for 10 min. Quartz sand (500 g) was added to this mixture and it was mixed for an additional 30 min on the shaker. The beaker was then kept in an oven at 105°C for 24 h. After 24 h the heated sand was washed with distilled water till the supernatant was clear. The washed sand was dried again in an oven at the same temperature. These procedures yielded slightly red coloured sand which was used for further experiments.

Characterization of SMIOCS

The total coated iron on the sand surface and its resistance to acid and alkali was determined as per Kuan et al. (1998). The total coated barium and sulfur were determined by dissolving 5.0 g SMIOCS in 50 mL conc. HNO_3 for 24 h. The suspension from all of these experiments was filtered by Whatman-42 ashless filter paper and the contents were determined by ICP-AES (model 8440 PlasmaLab, GBC, Australia). The surface area of quartz and coated sand was measured by the BET method using the model Micromeritics (ASAP-2000 model, U.S.A.).

Column Studies

Adsorption experiments were conducted in a number of fixed-bed columns (glass columns) in down-flow mode employing distilled water with 0.01 M NaNO_3 ionic strength solution using arsenic(V) as adsorbate. Three columns of identical internal diameter, of 15 mm each with media depths of 200, 400 and 600 mm were used to generate data for models used in this study. The packed sorbent bed was supported on 50-mm glass wool at the bottom of the column. The influent concentration was maintained constant at 1.0 mg/L except influent concentration variation studies. The influent flow rate was 1.56 $\text{m}^3/\text{m}^2/\text{h}$ in all studies using a peristaltic pump (Watson Marlow, U.S.A.). The samples were collected at different time intervals and analyzed for arsenic concentration. The column was allowed to run until 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 Johnson and Pilson (1972). The method allows for routine analysis of As(V) by spectrophotometric measurement of arsenic-molybdenum blue complexes. For measurement of arsenic(V), two 40-mL aliquots of the sample were taken into each of two 125-mL Erlenmeyer flasks. One millilitre of 1 N hydrochloric acid solution and two drops of 50% saturated solution of potassium iodate were added successively to each of the aliquots with thorough mixing after each addition. Fifteen minutes were allowed for oxidation of As(III) to As(V) if trace quantities of As(III) were present in the sample. Thereafter, 4 mL of mixed reagent were added to each of the aliquots with thorough mixing. The mixed reagent is 125 mL of 5 N sulphuric acid (H_2SO_4) solution and 37.5 mL of 0.032 M ammonium molybdate $[(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}]$ solution mixed thoroughly. Then 75 mL of 0.1 M ascorbic acid ($\text{C}_6\text{H}_8\text{O}_6$) and 12.5 mL of 0.0082 M potassium antimonyl tartrate $[\text{K}(\text{SbO})\text{C}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}]$ solution were added successively with thorough mixing after each addition. This reagent was prepared fresh as required. The total content of the flasks was then transferred to 50-mL test tubes and these test tubes were placed for 2 h in a water bath at 50°C for development of blue colour. The absorbance was taken at 865 nm by using a spectrophotometer (Spectronic 20 Genesys, U.S.A.). Blanks were run, by the above procedure, along with the samples, and all the samples were analyzed in duplicate. The minimum detection limit was 4 $\mu\text{g}/\text{L}$ As. Samples which were not analyzed on the same day of adsorption experiments were preserved using 1000 mg/L ascorbic acid and stored in acid-washed high density polyethylene (HDPE) containers at 2°C. All samples were analyzed within seven days of experimentation.

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 coated sand increases by more than two times as compared to plain sand of the same size. The measured BET surface area of this media is quite less in comparison to activated carbon and activated alumina. This is not uncommon as BET methods always underestimate surface areas of particles (Smith 1996). The obtained result of this study is just near to reported N_2 -BET surface areas of IOCS (5.0 m^2/g) in the literature (Stenkamp and Benjamin 1992). The presence of barium and sulfur along with iron on the media surface can also be seen in Table 1. The presence of Fe and Ba on media may also play an important role for the removal/immobilization of arsenate [As(V)] from water. Davis (2000), after conducting experiments on typical

TABLE 1. Physical and chemical characteristics of plain quartz sand and SMIOCS

No.	Characteristics	Plain sand	SMIOCS
1.	Size	498 μm	≅498 μm
2.	Diameter of particle	≅0.5 mm	≅0.5 mm
3.	Surface area, BET (m ² /g) (size = 0.498 mm)	1.79	3.74
4.	Surface area, BET (m ² /g) (size = 0.324 mm)	—	7.89
5.	Surface area, BET (m ² /g) (size = 0.716 mm)	—	2.95
6.	Fe salt used for coating (%)	—	4%
7.	Total iron on coated sand (mg/g)	—	1.91
8.	Total barium on coated sand (mg/g)	—	0.126
9.	Total sulfur on coated sand (mg/g)	—	0.47
10.	Acid resistance at pH ≅ 1.0	0.02%	45.67%
11.	Alkali resistance at pH ≅ 12.67	—	0.94%

water distribution systems at neutral pH, reported a log K_{sp} value of -5.51 ± 0.02 for barium hydrogen arsenate ($BaHAsO_4$). Thus, barium which is normally absent in natural water, if made available artificially even in traces, can play a major role for arsenic(V) immobilization from groundwater. The presence of Ba may form insoluble solids, i.e., $Ba_3(AsO_4)_2$ with As(V) as log K_{sp} of these solids are negative (Essington 1988). After sieve analysis, not more than 8% size variation was observed due to oxide coating. The properties that are more relevant for design of fixed bed columns are tabulated in Table 2.

Column Adsorption Model

In this study, the two-parameter model proposed by Lin and Huang (2000) has been used to describe the change in As(V) concentrations in the adsorption column. In the adsorption column, the entering aqueous solution flows through the stationary bed of media, and some of the As(V) in aqueous solution is adsorbed on the active sites while others pass through the bed. The fraction of As(V) being adsorbed is denoted A, and the fraction remaining in the aqueous solution and passing through the stationary bed is P. The rate of decrease in the As(V) is given by:

$$-\frac{dA}{dt} = kAP \tag{1}$$

where k is the proportionality constant. It is noted in the above equation that $P = 1 - A$. Although nonlinear, this equation can be integrated within the initial condition of $A = A_a$ at $t = t_a$

$$\ln \left[\frac{A(1 - A_a)}{A_a(1 - A)} \right] = k(t_a - t) \tag{2}$$

which is the same as

$$\ln \left[\frac{P_a(1 - P)}{P(1 - P_a)} \right] = k(t_a - t) \tag{3}$$

For 50% As(V) adsorption, $P_a = 0.5$, the adsorption time, t_a , is denoted as τ and equation 3 becomes

$$P = \frac{1}{1 + \exp[k(\tau - t)]} \tag{4}$$

or

$$t = \tau + \frac{1}{k} \ln \left(\frac{P}{1 - P} \right) \tag{5}$$

The As(V) fraction P that passes through the adsorption column is equal to C/C_o with C being the As(V) concentration in the aqueous solution at time, t, and C_o being the inlet concentration. According to equation 5 a plot of adsorption time, t, versus $\ln[C/(C_o - C)]$ yields a straight line with intercept and slope of the straight line equal to τ and $1/k$, respectively. Alternatively, τ can also be obtained at the adsorption time when $\ln[C/(C_o - C)]$ is zero because by definition, τ is the adsorption time when C is half of C_o . With the help of τ and $1/k$ entire breakthrough can be established.

Equation 4 of the model Lin and Huang (2000) can be changed to:

$$\ln \left(\frac{C_o}{C} - 1 \right) = k\tau - k t \tag{6}$$

Equation 6 is similar to the model by Bohart and Adams (1920) as given in equation 7:

$$\ln \left(\frac{C_o}{C} - 1 \right) = \frac{Kq_o}{v} x - KC_o t \tag{7}$$

TABLE 2. Properties of SMIOCS media for fixed bed column studies

Sr. no.	Media properties	Value
1.	Apparent density (dry) (g/cm ³)	1.48
2.	Apparent density (wet) (g/cm ³)	1.43
3.	Specific gravity (g/cm ³)	2.51
4.	Porosity	0.33
5.	Diameter of particle (mm)	0.5

where C_0 is the influent solute concentration (mg/L); C_e is the effluent solute concentration (mg/L); K is the rate constant (mL/min mg); q_0 is the adsorption capacity (mg/g); x is the depth of bed (cm); v is the linear flow velocity of feed to bed (mL/cm²); and t is the service time of column under the above condition (h).

As $V = Qt$, $Q = vA$ and the mass of adsorbent $M = Ax$, where Q is the volumetric flow rate (mL/min), M is the mass of adsorbent (g) and A is the section area of bed (cm²). The model of Bohart and Adams can be rewritten as:

$$\ln\left(\frac{C_0}{C} - 1\right) = \frac{Kq_0}{Q}M - KC_0t \tag{8}$$

The model developed by Thomas (1948) also has the same form as equation 8. However, the model proposed by Lin and Huang (2000), which may have been a modified form of the Bohart and Adams model, has been used in this paper to predict breakthrough time of experimental data.

Using the plots in Fig. 1 for various depths of column the model parameters could be obtained. Table 3 lists the model parameters obtained as a function of media depth. Based on these model parameters, the predicted As(V) breakthrough curves are compared with the experimental ones in Fig. 2. It is apparent that predicted and experimental breakthrough curves show a good correlation (coefficient of correlation >0.98 for all least square linear regression plots).

Effect of Initial As(V) Concentrations

Figure 3 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 separate fixed bed experiments. As indicated in Fig. 3, 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 exhaus-

TABLE 3. Parameters for As(V) adsorption by SMIOCS

Bed depth (cm)	k (1/h)	τ (h)
20	0.07569	36.27
40	0.0833	58.00
60	0.1115	69.45

tion time. The breakthrough time was about 5 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. The proportional relationship of solid and liquid phase loading for heavy metal adsorption is certainly not unusual (Reed et al. 1996).

Effect of Media Sizes

The breakthrough data on three different media sizes are presented in Fig. 4. The figure shows that 0.324 mm geometric mean size media is able to treat a considerably higher number of bed volumes to both breakthrough and exhaustion. It may be due to more surface area of smaller particles. The measured surface area of 0.324-mm particle size media was twice that of 0.498 mm (Table 1). At breakthrough the obtained solid phase loadings for the 0.324, 0.498 and 0.716 mm size particles were 0.120, 0.065 and 0.033 mg/g, respectively. These loadings also provide significant information that smaller sized particles have more adsorption capacity than larger sized particles. The solid phase loading and bed volume treated prior to breakthrough are also of the same order of magnitude as column adsorption capacities for metals by a synthesized hybrid iron oxide adsorbent (Gao et al. 1995).

Effect of Initial Solute pH

Figure 5 illustrates the effect of solution pH on breakthrough capacity of media. It can be seen from the fig-

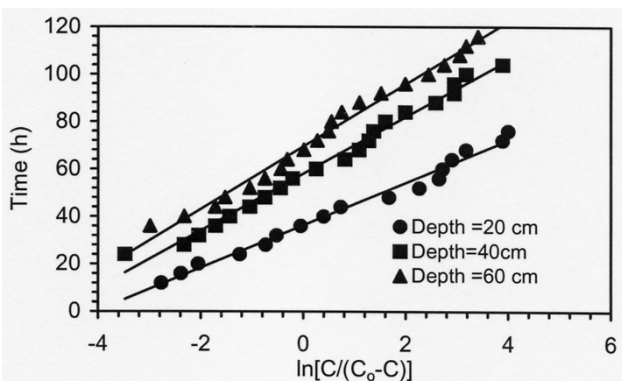


Fig. 1. Linear plots of t versus $\ln[C/(C_0 - C)]$ for As(V) adsorption on SMIOCS.

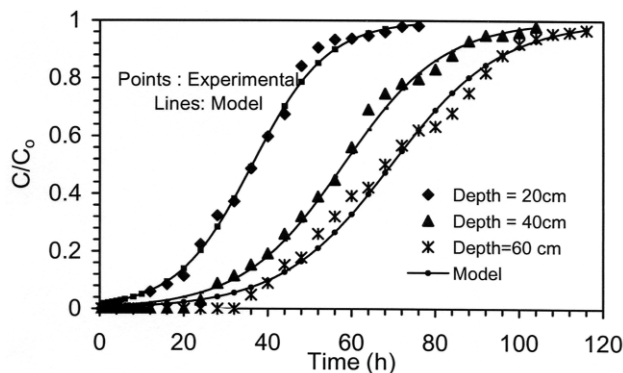


Fig. 2. Comparison of observed and predicted breakthrough curves of As(V) adsorption on SMIOCS at various media depths.

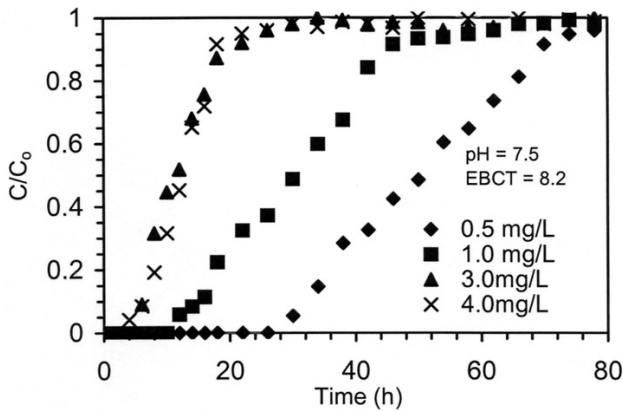


Fig. 3. Breakthrough curves of As(V)-spiked distilled water system with ionic strength of 0.01 M NaNO₃ for different As(V) influent concentrations.

ure, that studied influent pH has little effect on adsorptive capacity of As(V) in the fixed bed except at pH 9.5, where some adsorption capacity reduction was observed. When influent pH was set at 4.0, the effluent pH was initially at 7.3 and increases to 8.04 till breakthrough and after that it fluctuates between 7.4 and 7.65. It reflects that a OH⁻ ion was released during FBR operation. When influent pH was 7.5, the effluent pH at the initial stage varied from 7.59 to 8.57 till breakthrough and after breakthrough it ranges from 7.36 to 7.72 till bed exhaustion. Similarly, when influent pH was 9.5 the effluent pH at the initial stage varied from 7.68 to 9.05 till breakthrough and after breakthrough it varied from 8.68 to 7.68 till bed exhaustion (unpublished data). The solid phase loading at exhaustion, q_e , a factor that is also reflected in bed volume treated at exhaustion at influent pH (pH_i) 4.0 is ~1.5 times that for pH_i 9.5. Also, the solid phase loading, q_e , at pH_i 4.0 is approximately equal to that of pH_i 7.5.

Removal Mechanisms

The removal mechanism is based on the surface complexation theory of Smith (1998b). SMIOCS, when placed in solution, a hydrous oxide layer forms over time on the surface of the media, probably in heterogeneous fashion, the nature of which is impacted to some degree by solution conditions. As a result, the media is assumed to have oxide on the hydroxylated surface sites in the solution such as $>SOH_2^+$ and $>SOH$ representing positive and neutral charged sites. Since Fe is present on the coated sand surface, these surface sites may be $>FeOH_2^+$ and $FeOH^{+2}$. The surface complexation model has three central features. The number of exchangeable surface hydroxyl groups limits the extent of adsorption, which is a function of surface area. All absorbing species (including protons) compete for available surface sites; the effect of pH on adsorption thus drives from the acid-

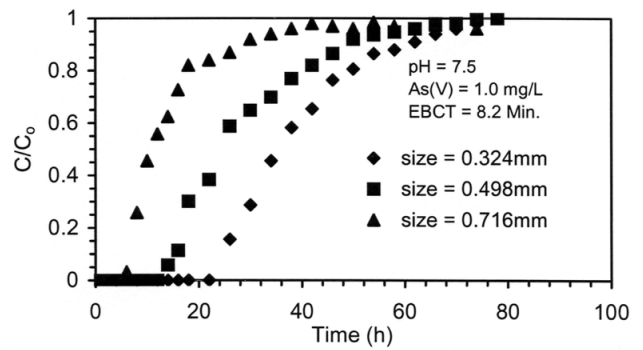
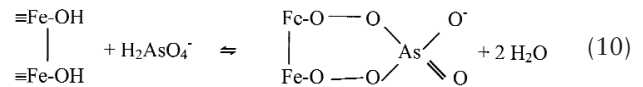


Fig. 4. Breakthrough curves of As(V)-spiked distilled water system with ionic strength of 0.01 M NaNO₃ for different media sizes.

base reactions both of oxide surface and adsorbing species. The reaction of As(V) with oxide surface can be explained with the help of the surface complexation theory. If S-OH corresponds to $\equiv Fe-OH$, then attachment of As(V) on the $\equiv Fe-OH$ surface may be presented by following equation:



Here, site $\equiv Fe-OH$ acts as a Lewis acid and the arsenate anion acts as a Lewis base, and due to the exchange of OH⁻, the mechanism is known as ligand exchange mechanism.

Effect of Alkalinity and Hardness

An alkalinity of 250 to 260 mg/L as CaCO₃ and hardness of 200 mg/L as CaCO₃ was spiked in a distilled water system during column studies. The results are presented in Fig. 6. The figure shows that presence of alkalinity and hardness has little effect on breakthrough time (it slightly increases breakthrough time of the reactor). The formation of Ca₃(AsO₄)₂ in the excessive presence of Ca⁺⁺ may

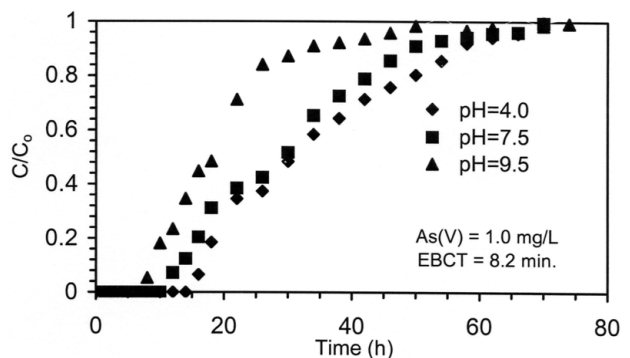


Fig. 5. Breakthrough curves of As(V)-spiked distilled water system with ionic strength of 0.01 M NaNO₃ at different pH.

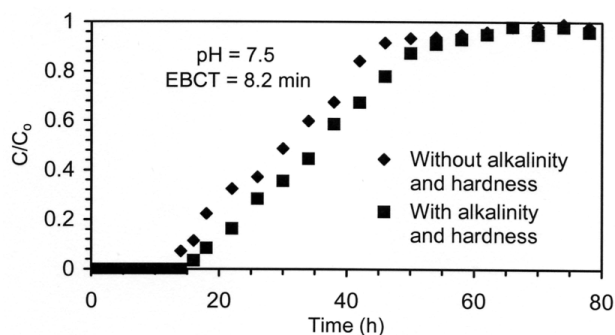


Fig. 6. Breakthrough curves of As(V)-spiked distilled water system with ionic strength of 0.01 M NaNO₃ for influent As(V) concentration of 1.0 mg/L.

be one of the reasons. Meng et al. (2000) have also reported similar results and gave a reason, i.e., that the presence of Ca⁺⁺ neutralizes and reduces negative surface charges of media thus paving a way for higher removal of As(V). Min et al. (1998) have also reported similar results that Ca-Fe beads were quite effective for removing As(V) from solution in comparison to Fe beads only.

Desorption of Arsenic from Media

After bed exhaustion ($C/C_0 \geq 0.95$), 0.2 M NaOH was passed through the bed in up-flow direction at a flow rate of 9.2 mL/min (3.124 m³/m²/h). The concentration of As(V) was monitored as shown in Fig. 7. The figure shows that the desorption cycle took nearly 3 h, after which further regeneration was negligible. The maximum concentration of As(V) obtained at a contact time of 1.5 h, was 5.7 mg/L. The eluent was collected in a 2.0-L PVC beaker. The flow of 9.2 mL/min for 3 h, yielded 1.656 L of elutant having an As(V) concentration of 5.12 mg/L. After passing 2.0 L of 0.2 M NaOH in upward flow mode the column was backwashed by distilled water until the effluent and influent pH were comparable. The time required for completing the regen-

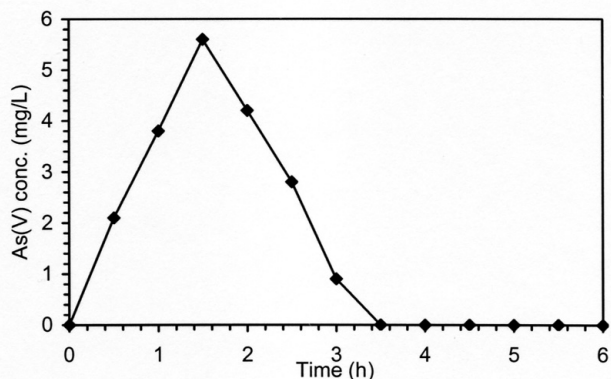


Fig. 7. Desorption profile of As(V) from the spent sorbent using 0.2 M NaOH in a fixed bed reactor.

eration process was 12 h and out of 9.936 mg As(V) adsorbed, 9.12 mg (92%) As(V) could be desorbed. Therefore, NaOH could be used as elutant for the desorption of As(V) from the SMIOCS media. The SMIOCS media has shown negligible alkali resistance (Table 1), therefore, it has the least chance of losing its basic characteristics (coatings). Singh et al. (1992) also used NaOH as an eluting agent for arsenic in their studies.

Conclusions

This study demonstrated that SMIOCS could be an effective media for arsenic(V) removal from water in a fixed bed reactor. A simple two parameter model showed good correlation between the observed and predicted curves. The results show that smaller sized particles have more adsorption capacity than larger sized particles and the presence of alkalinity and hardness slightly increases breakthrough time of the reactor. The media showed higher solid phase loading in acidic pH than in alkaline pH. Sodium hydroxide (NaOH) proves to be an efficient elutant for desorption of As(V) from SMIOCS in the column studies by counter flow (up flow) process.

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Received: August 3, 2005; accepted: January 30, 2006.