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REMOVAL OF As, Cr AND Cd BY ADSORPTIVE FILTRATION

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ABSTRACT

The US Environmental Protection Agency (USEPA) recently introduced more stringent arsenic regulations by lowering the maximum contaminant level (MCL) to 10 μg l^{-1} (ppb) arsenic in drinking water. During the present study, an iron solution injection sand filtration process was designed and tested to selectively remove arsenic (As(V)), chromate (Cr(VI)) and cadmium (Cd(II)) from aqueous solutions down to trace level. Bench scale sand columns with a chemical feeding system were used to conduct the filtration study. The filtration results demonstrate that As(V) could be removed by ferric solution-treated sand filters from 2,000 μg l^{-1} (ppb) down to less than 5 μg l^{-1} (ppb) using two sand filters connected in series (two stage filtration). During the filtration, ferric concentrations in the first and second filters were maintained at 5 and 2 ppm, respectively, through a continuous injection scheme. Bench scale filtration results suggest that Cr(VI) could also be effectively removed by injection of ferrous solution into the sand columns. Similar ferric treatment of the sand columns also significantly increased Cd(II) removal. Batch adsorption experimental results suggest that when solution pH is lower than 8, arsenate can be removed by iron-treated sand. Arsenate-saturated sand can be regenerated using a high pH (pH > 12) solution. Scanning Electron Microscope (SEM) and energy dispersive x-ray (EDX) studies suggest that very little amount of Fe on the sand surface was dissolved when the sand was regenerated using a dilute NaOH solution (pH = 13).

KEYWORDS: water; arsenic; iron; ferric; chromium; cadmium; wastewater; pH; effluent; treatment; adsorption; silica; sand.

INTRODUCTION

Conventional treatment processes currently applied for the removal of heavy metals from the liquid phase, are generally based on a chemical precipitation and coagulation approach (Dupont, 1986; Eary and Rai, 1988; Cheng *et al.*, 1994). These processes generate large amounts of sludge and they are considered to be ineffective, especially for the treatment of large quantities of dilute aqueous streams, such as wastewater discharges and the solution generated during pump-and-treat process at contaminated sites (Sandesara, 1978). Furthermore, the precipitation-based treatment techniques may not provide the ultimate solution to the wastewater treatment problem because of increasingly stringent discharge standards. On the other hand, the sand filtration technology is not effective in removing toxic trace elements, especially arsenic and chromate, mainly because sand filter media have very low sorptive capacity. However, if the filter sand surface is coated with iron or aluminum hydroxides, the adsorption capacity of the filter media can be significantly enhanced (Meng, 1993). Consequently, a technically sound yet cost effective filtration technology can be developed to selectively remove trace toxic contaminants from wastewater.

Column studies (Benjamin, 1992; Jarog *et al.*, 1992; Edwards and Benjamin, 1989) have shown that cationic metals (i.e. Cu, Cd, Zn and Pb) can be removed effectively by sand and granular activated carbon coated with ferric oxide. However, during these processes, sand and activated carbon have to be coated periodically prior to their placement in the filter, through what is known to be a time-consuming procedure. Moreover, the adsorption capacity of the ferric oxide coating is much less than fresh ferric hydroxide precipitates. These technologies are not yet proven at full-scale treatment plants (Edwards, 1994).

In addition to the adsorptive filtration process, a number of other treatment technologies, such as microfiltration (Martin *et al.*, 1991), and adsorption and magnetic filtration (Chen *et al.*, 1991), have also been studied. The microfiltration process (Martin *et al.*, 1991) includes precipitation and filtration in two steps. The main difference between this process and the traditional precipitation and filtration treatment is that heavy metal precipitates are removed directly through a membrane filter, thus eliminating the coagulation step. However, this process carries the same disadvantages as the conventional precipitation-based treatment methods. In the adsorption and magnetic filtration process (Chen *et al.*, 1991), heavy metals are adsorbed onto fine magnetite particles coated with ferrihydrite. The magnetite particles are then collected using a magnetic filter. Finally, the magnetite particles are regenerated by metal desorption and reused. The main advantage of the magnetic-based treatment technique is that a minimal volume of sludge byproduct is generated. However, the magnetic-based treatment is known to be an expensive and time-consuming alternative. Recent studies on long-term human exposure show that arsenic in drinking water is associated with liver, lung, kidney, and bladder cancers in addition to previously documented skin cancer (Wu *et al.*, 1989). The US Environmental Protection Agency (USEPA, 2003) recently introduced more stringent arsenic regulations by lowering the maximum contaminant level (MCL) to 10 $\mu g\ l^{-1}$ (ppb) arsenic in drinking water to minimize these risks (USEPA, 2003). Overall, the removal of anions, such as As and Cr(VI), from solution is more difficult than that of cationic heavy metals.

In the present study, an iron injection-sand filtration process for selective removal of As, Cr, and Cd is investigated. The technology involves continued injection of small amounts of iron solution into the packed-bed sand filter during filtration. The advantage of this technique is the continuous formation of iron hydroxide in the filter. Therefore, any adverse effect of co-existing substances, such as oil and grease, could be eliminated. Moreover, adsorptive filtration is capable of removing As, Cr, and Cd over a wider pH range, and to much lower levels than precipitation-based processes. Moreover, existing conventional sand filters can be easily modified to iron injection filters.

MATERIALS AND METHODS

Filter sand with effective size of 0.35-0.60 mm and uniformity coefficient of 1.2-1.6 was obtained from Ricci Bros. Sand Co., Inc. in Port Norris, New Jersey. All the chemicals, including $FeSO_4 \cdot 7H_2O$, $Fe(NO_3)_3 \cdot 7H_2O$, $FeCl_3 \cdot 6H_2O$, As_2O_5, K_2CrO_4, $Cd(NO_3)_2$, NaOH, and HNO_3, were reagent grade. Silica (Cab-O-Sil M5) particles with a specific surface area of 200 $m^2\ g^{-1}$ were supplied by Cabot Corp., Tuscola, IL. Tap water was used for preparing artificially contaminated influent solutions.

Two sand filters were fabricated using PVC pipes. The two filter systems can be operated separately as well as in series. Figure 1 is a schematic diagram of the single stage pilot filter system. Smaller sand columns were also used for filtration tests. The dimensions and operation parameters of both sand filters are listed in Table 1. The bed height, filtration rate and backwash flow rate are similar to those for conventional sand filters. During the filtration tests, the effluent solution was collected every 0.1 to 20 l and analyzed for metal concentrations, pHs, and turbidity. Filter pressures were also recorded.

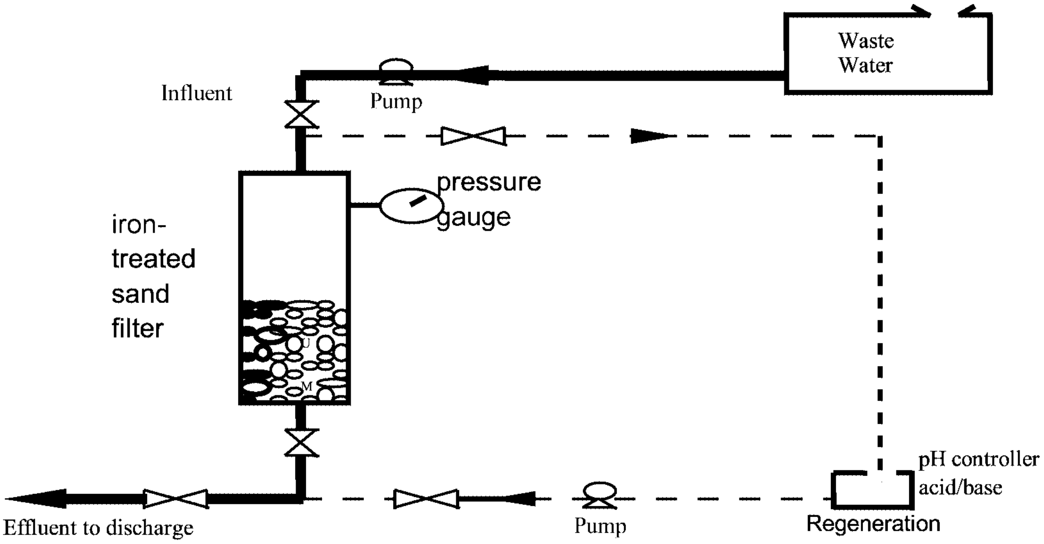

Figure 1. Single stage pilot filtration system

Batch adsorption experiments were performed to determine the optimum conditions of filtration and regeneration. They involved adding As_2O_5 stock solution to SiO_2 and $Fe(OH)_3$ suspensions. After pH adjustment, the suspensions were shaken at 25 °C for 2 h. The equilibrium pH of the suspensions was then measured and samples of solution obtained by centrifugation were analyzed for soluble As using an Inductively Coupled Plasma Emission Spectrometer or Zeeman Graphite Furnace Atomic Absorption Spectrometer according to standard analytical methods. Finally, selected sand samples were viewed under the SEM-EDX to obtain information on the stability of the Fe adsorptive coating.

RESULTS AND DISCUSSION

Bench scale filtration results (Dermatas and Meng, 1996) showed that the removal of As(V) by sand filtration was dramatically enhanced when the sand columns were treated with ferrous sulfate or ferric nitrate solutions. Based on these results, pilot scale tests were conducted to establish the optimum conditions for As(V) removal using continuous injection of ferric nitrate solution. The conditions tested include one influent As(V) concentration 2,000 $\mu g\ l^{-1}$ (ppb), six ferric levels in filter solution (i.e. 0.5, 1, 2, 5, 10 and 40 mg l^{-1} (ppm)), and different solution pHs. Saturated filters were regenerated using dilute sodium hydroxide solution (pH = 13), and used during filtration tests.

The As(V) filtration results presented in Figure 2 depict the treatment of a 2,000 $\mu g\ l^{-1}$ (ppb) As(V) solution using a two-stage pilot filtration system. Ferric concentrations for the first and second filters were 5 and 2 mg l^{-1} (ppm), respectively. High As(V) concentration at the beginning of the filtration step was caused by a high pH of 8 due to the remaining regeneration solution in the filter. As(V) concentrations were reduced to less than 30 $\mu g\ l^{-1}$ (ppb) by the first filter. After 200 pore volumes of solution were treated, effluent As(V) concentrations started to increase. It was found that the effluent As(V) concentrations were related to effluent Fe content. When the As(V) concentrations were less than 30 $\mu g\ l^{-1}$ (ppb), the Fe concentrations were below 70 $\mu g\ l^{-1}$ (ppb). The Fe concentrations increased to more than 100 $\mu g\ l^{-1}$ (ppb) when the As(V) concentrations were higher than 100 $\mu g\ l^{-1}$ (ppb). It is possible that fine $Fe(OH)_3$ colloids carried adsorbed As(V) passing through the filter.

Table 1. Dimensions and parameters of filtration systems

	Sand Depth, in	**Filtration rate, gal $ft^{-2}\cdot min^{-1}$**	**Bed Volume, l**	**Pore volume, l**
Bench scale column	24	3	3.8	1
Small sand column	7	0.08	0.36	0.1

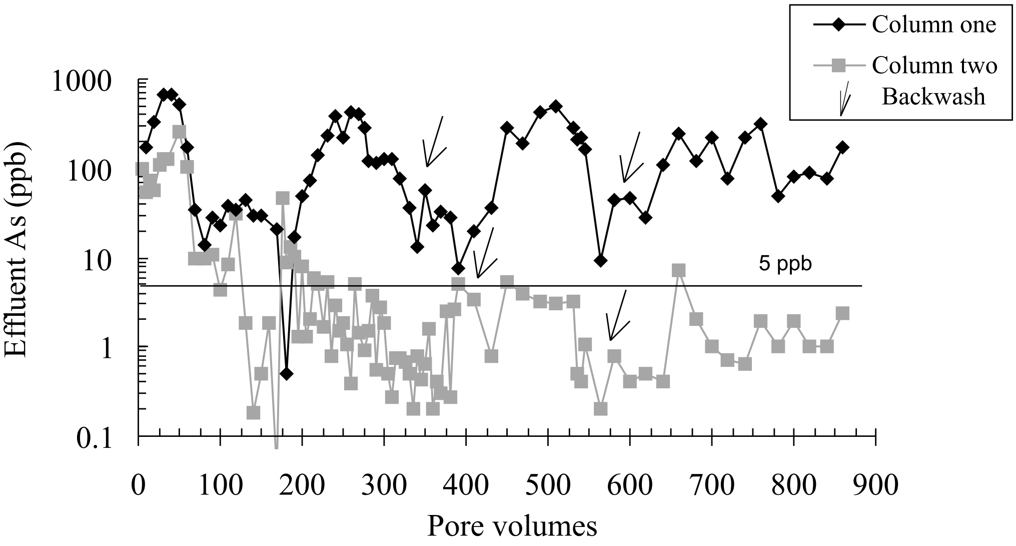

Figure 2. As(V) removal from a 2,000 μg l^{-1} (ppb) influent solution using a two-stage filtration system, Fe concentration was 5 mg l^{-1} (ppm) for the first filter, and 2 mg l^{-1} (ppm) for the second filter

Despite high fluctuations in effluent concentrations from the first filter, most of the time As(V) concentrations coming out of the second filter were kept below 5 μg l^{-1} (ppb).

During filtration, each filter was back washed two times with 10 to 18 litters of tap water due to a flow rate decrease. After sedimentation of the backwash solution for the first filter, 200 to 500 ml of sludge with less than 10% of solid was collected. The total As(V) content of the sludge was between 1,070 and 11,560 mg l^{-1} (ppm). The high As(V) concentration in the sludge might suggest most of the As(V) retained in the filter was associated with $Fe(OH)_3$ precipitates that could be removed from the filter with backwash. In this case if all the $Fe(OH)_3$ precipitates can be removed by backwash, filtration capacity of the filter will be completely recovered. The supernatant As(V) concentration was approximately 0.4 mg l^{-1} (ppm). Therefore, the supernatant can be pumped into the second filter for As(V) removal. The amount of sludge collected for the second filter was much less than that collected for the first one. Overall, more than 99.7% of As(V) removal was attained when the 2,000 μg l^{-1} (ppb) As(V) solution was treated using the two-stage pilot filtration system that was continuously treated with ferric solution. Less than one liter of settled sludge was produced when more than 800 litters of the As(V) solution were treated.

Moreover, bench scale experiments were also conducted to test chemicals that could be used to enhance chromate removal during sand filtration. The chemicals tested include $FeSO_4{\cdot}7H_2O$ and $FeCl_3{\cdot}6H_2O$ solutions. During filtration, chromate solution ([Cr(VI)] = 2 mg l^{-1} (ppm)) was passed through treated as well as untreated sand columns. The experimental results in Figure 3 show that for the untreated sand column, Cr breakthrough occurred when one pore volume of the sand bed passed through the column. These results suggest that, as expected, the untreated sand filter has negligible affinity to retain Cr(VI). Conversely, when 3 ml of 1% $FeSO_4{\cdot}7H_2O$ solution was injected into the sand bed, approximately 5 pore volumes of As solution were filtered before breakthrough took place. However, injection of 3 ml of 1% $FeCl_3{\cdot}6H_2O$ solution did not enhance Cr(VI) removal by the sand column.

The results indicate that the enhanced Cr(VI) removal by the $FeSO_4{\cdot}7H_2O$ treated sand column was due to reduction of Cr(VI) to Cr(III) species by Fe(II) ions, and subsequent adsorption or precipitation of Cr(III) in the column. The reaction for chromate reduction by Fe(II) is represented as follows:

$$CrO_4^{2-} + 3Fe^{2+} + 8H_2O \rightarrow$$
$$\rightarrow Cr(OH)_3 + 3Fe(OH)_3 + 4\,H^+ \qquad (1)$$

A reduction kinetics experiment conducted in our laboratory indicated that more than 99% of the

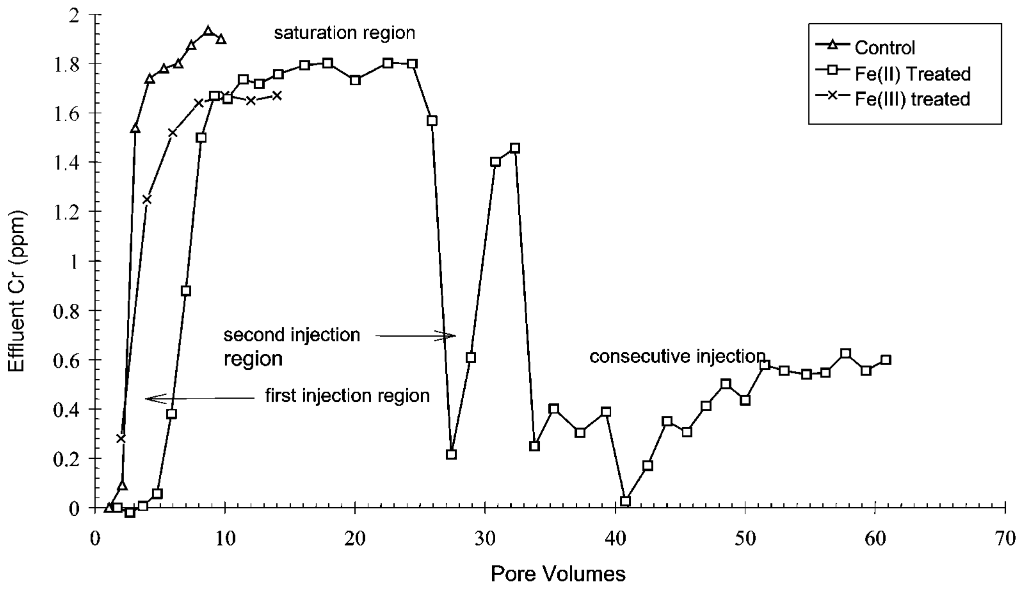

Figure 3. Comparison of Cr(VI) removal by plain sand and iron treated sand columns, influent Cr(VI) concentration: 2 mg l^{-1} (ppm)

Cr(VI) was reduced to Cr(III) at neutral pH within a few minutes.

The results in Figure 3 also show that when additional doses of $FeSO_4 \cdot 7H_2O$ solution were injected consecutively to the Cr-saturated sand column, following Cr breakthrough, low Cr effluent was continuously produced. Pilot scale tests will be conducted to find optimum conditions for Cr(VI) removal using ferrous treated filters.

Cadmium, (Cd(II)) adsorption by $Fe(OH)_3$ increases dramatically when solution pH increases from 6 to 8 (Meng, 1993). Therefore, in this pH region Cd(II) removal by ferric treated sand column is very sensitive to pH change. Figure 4 shows effluent Cd(II) concentration and pH changes when a 1% ferric nitrate ($Fe(NO_3)_3 \cdot 7H_2O$) solution was injected into a bench scale sand column. At the beginning of filtration, 2 ml of ferric solu-

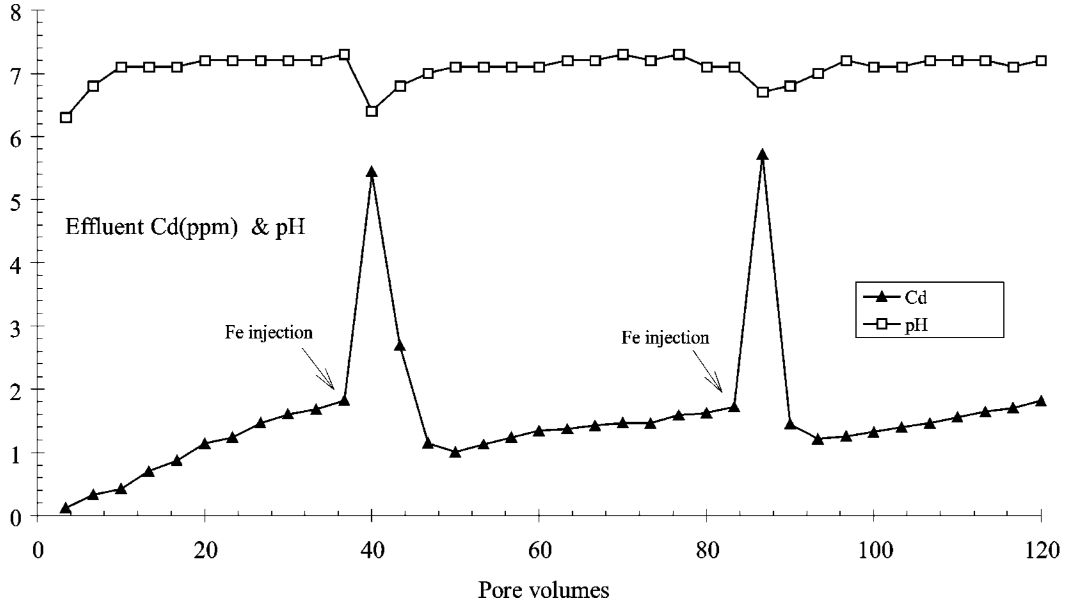

Figure 4. Effect of ferric solution injection on effluent pH and Cd concentration, bench scale column test results, influent Cd concentration: 2 mg l^{-1} (ppm)

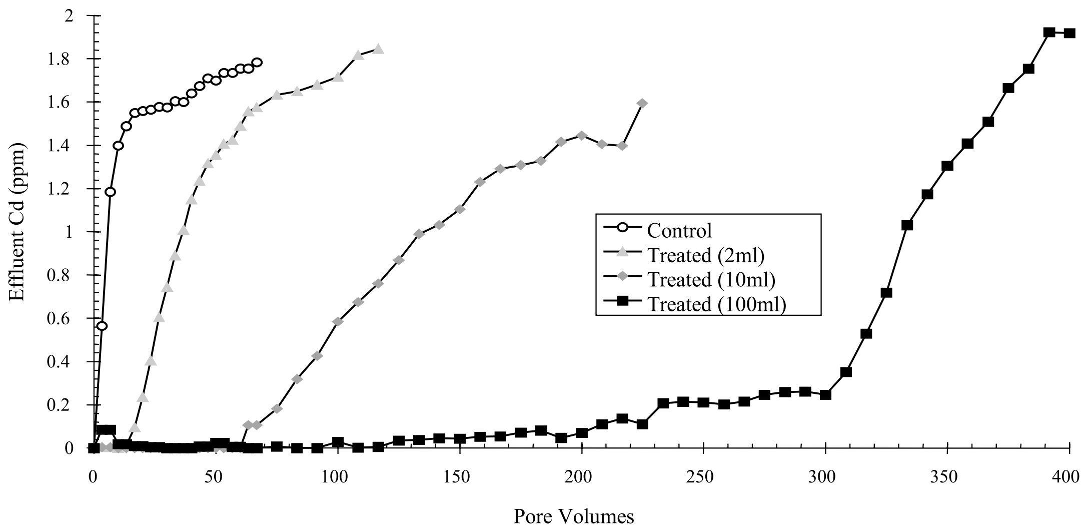

Figure 5. Cd break through curves for bench scale sand columns treated with different amounts of ferric solution, effluent pH =7.8; influent Cd concentration: 2 mg l^{-1} (ppm)

tion was injected into the column, and then cadmium nitrate solution ([Cd] = 2 mg l^{-1} (ppm)) was passed through the column. When effluent Cd(II) concentration reached 1.8 mg l^{-1} (ppm) at 38 pore volumes, another 2 ml of the ferric solution was injected, which decreased effluent pH to 6.4 and increased Cd(II) concentration to 5.4 mg l^{-1} (ppm). The results suggest that a high pH should be maintained in order to remove Cd(II) from the solution. In order to improve Cd removal, both influent solution pH and the pH of the ferric solution were adjusted to 7.8 using sodium hydroxide solution. Figure 5 shows Cd break through curves for sand columns treated with different amounts of the ferric solution at the beginning of filtration. The pore volumes of Cd solution treated by the sand columns increased significantly when amount of ferric solution injected into the column increased. When 100 ml of the ferric solution was added into the column, approximately 300 pore volumes of Cd solution were treated before Cd started to break through.

Batch adsorption experiments were conducted with suspensions of fine silica (SiO_2) particles, fresh $Fe(OH)_3$ precipitates, and their mixture. The purpose of these tests was to elucidate the optimum pH of solution conditions for which both the adsorption and the regeneration steps would be effective. Amorphous silica particles, rather than sand, were used during the adsorption tests because a uniform suspension can be prepared using the fine particle and because a small amount of fine particles can provide a large surface area for adsorption. Total As(V) concentration in the suspension was 20 mg l^{-1} (ppm). The percent removal of As(V) by the silica and $Fe(OH)_3$ is plotted in Figure 6 as a function of equilibrium solution pH. Silica particles did not show obvious adsorption tendencies for As(V) between a pH of 4 and 13. On the other hand, As(V) was completely removed by the $Fe(OH)_3$ when pH was lower than 9. A computer program simulation of the adsorption data using a triple-layer surface complexation model (Meng, 1993) suggest that arsenate species were adsorbed on the $Fe(OH)_3$ surface sites through the formation of outer-sphere complexes (i.e. $FeOH_2^+$-$HAsO_4^{2-}$, $FeOH_2^+$-$H_2AsO_4^-$). $FeOH_2^+$ represents positively charged $Fe(OH)_3$ surface sites. The negligible arsenate uptake by the silica was due to low affinity of silinol site, SiOH, for the anion and strong electrostatic repulsion between the negatively charged surface and the anion. When pH was higher than 2, silica surface is negatively charged. On the other hand, the $Fe(OH)_3$ surface is positively charged when pH is lower than 8, which favors anions adsorption (Meng, 1993).

Arsenate adsorption by a 5 mM of $Fe(OH)_3$ suspension and a suspension containing 1 g l^{-1} silica and 5 mM of $Fe(OH)_3$ is compared in Figure 7. Arsenate uptake by the mixed oxides was less than that by the $Fe(OH)_3$ suspension. This was mainly caused by the competition of dissolved silicate

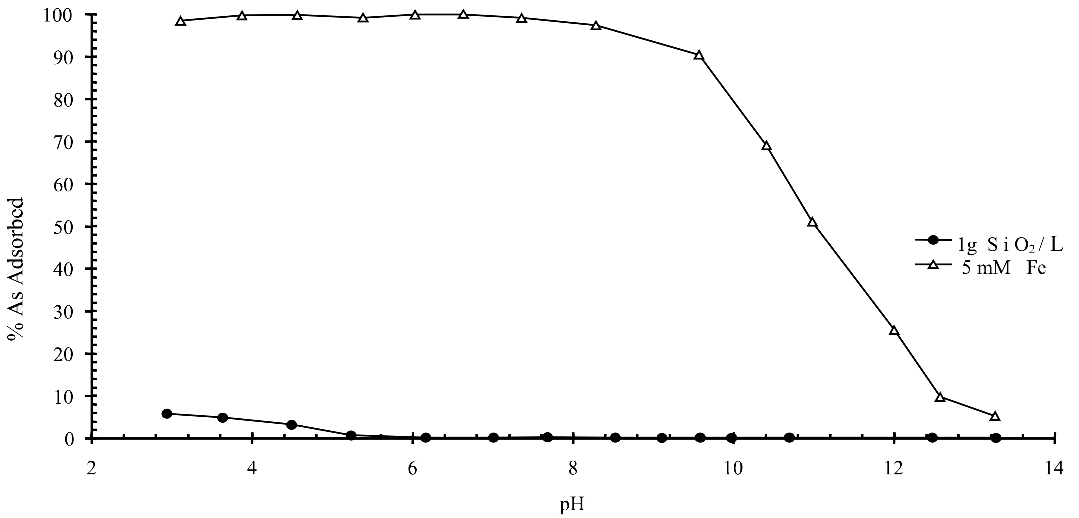

Figure 6. As(V) adsorption by SiO_2 and $Fe(OH)_3$ suspensions

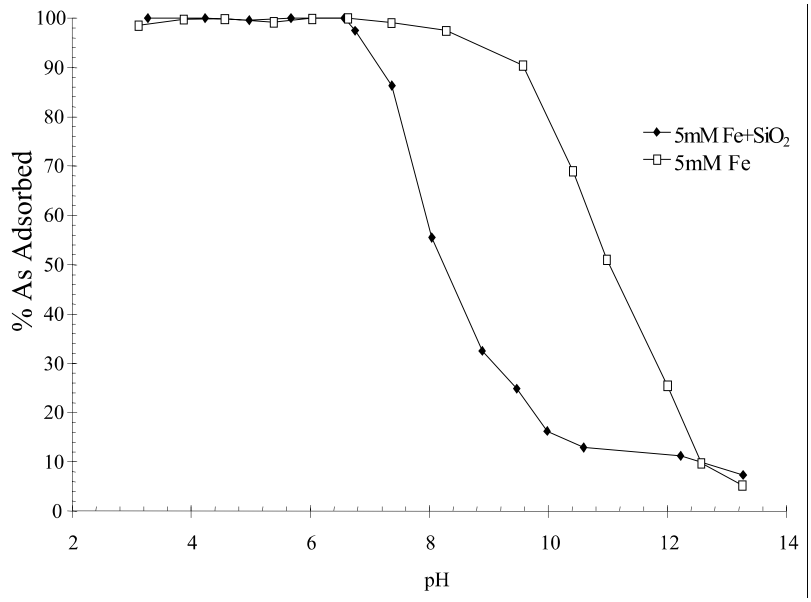

Figure 7. Comparison of As(V) adsorption by $Fe(OH)_3$ and $Fe(OH)_3/SiO_2$ mixtures

species and arsenate ions for the FeOH surface sites. Approximately 10 mg l^{-1} (ppm) of dissolved SiO_2 were detected in the mixed suspension. During filtration, much less silica should be dissolved from the sand in the filter because sand is much more inert than the amorphous silica particles.

Overall, the adsorption experimental results suggest that when solution pH is lower than 8, arsenate can be removed by iron-treated sand. Arsenate-saturated sand can be regenerated using a high pH (pH > 12) solution.

SEM-EDX techniques were used to examine clean sand as well as the sand that was used for more than 10 filtration and regeneration cycles. The surfaces of clean sand and used sand taken from the filter before and after base-regeneration looked similar under the microscope. However, both used and regenerated sand surfaces contained much higher Fe atoms than the clean sand surface (Table 2). No As was detected on the used sand surface because the EDX analysis is not sensitive enough to measure element contents of less than 1%. The similar Fe atom content for used versus base-regenerated sand surface suggests that

Table 2. Chemical composition of sand surface

	Si atom %	Fe atom %
Clean sand	98.3	1.7
Used sand	80.5	19.5
Base-regenerated sand	80.6	19.4

very little amount of Fe on the sand surface was dissolved when the sand was regenerated using a dilute NaOH solution (pH = 13).

CONCLUSIONS

The iron injection-sand filtration process could effectively reduce As(V) concentration from 2,000 μg l^{-1} (ppb) to less than 5 under the normal filtration rate conditions used for conventional sand filters. The process could attain very low sludge to treated water volume ratios, especially for influent solutions with low As(V) content. No pH adjustment was needed when wastewater pH was between 4.5 and 7. A two-stage filtration was necessary to reduce As(V) concentration from 2,000 μg l^{-1} (ppb) to less than 5 μg l^{-1} (ppb). The saturated filters could be regenerated by backwash with water. Ferrous solution should be used to remove Cr(VI) during the iron injection-sand filtration process. In order to remove Cd(II) through the adsorptive filtration process, solution pH should be higher than 7. Batch adsorption experimental results suggest that when solution pH is lower than 8, arsenate can be removed by iron-treated sand. Arsenate-saturated sand can be regenerated using a high pH (pH > 12) solution. SEM-EDX techniques used to examine clean sand as well as the sand that was used for more than 10 filtration and regeneration cycles showed that very little amount of Fe on the sand surface was dissolved when the sand was regenerated using a dilute NaOH solution.

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