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EFFECTS OF SILICATE, SULFATE, AND CARBONATE ON ARSENIC REMOVAL BY FERRIC CHLORIDE

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Abstract—Effects of silicate, sulfate, and carbonate on the removal of arsenite [As(III)] and arsenate [As(V)] by coprecipitation with ferric chloride were studied. Silicate significantly decreased As(III) removal when Si concentration was higher than 1 mg/l and the pH was greater than 5. The removal of As(V) was decreased moderately by silicate in 0.04 M KNO₃ solution. Addition of Ca²⁺ and Mg²⁺ to the KNO₃ solution reduced the adverse effect of silicate on As(V) removal. In the presence of 10 mg/l Si and at a pH of approximately 6.8, the adsorption capacity of ferric hydroxide for As(V) and As(III) was reduced from 864 and 116 µg/mg to 274 and 23 µg/mg Fe, respectively. Sulfate and carbonate had a negligible effect on the removal of As(III) and As(V). The triple layer model was used with site binding reactions to describe As(III) and As(V) removal by ferric hydroxide in the presence of silicate. The results obtained in the present study suggest that silicate in natural water can significantly decrease the efficiency of As(III) removal by coagulation treatment with ferric chloride. © 2000 Elsevier Science Ltd. All rights reserved

Key words—arsenic, coprecipitation, adsorption, coagulation, silicate, sulfate, anions, model

INTRODUCTION

Elevated arsenic concentrations are found in some natural waters due to oxidative weathering and dissolution of As-containing minerals (Bagla and Kaiser, 1996; Brown and Fan, 1994; Chen *et al.*, 1994; Korte and Fernando, 1991). Arsenic is also a common pollutant in groundwater and industrial wastewater. While As(V) is the predominant species in oxygenated waters (Ferguson and Gavis, 1972), As(III) can be prevalent in groundwater (Chen *et al.*, 1994; Korte and Fernando, 1991). Studies on long-term human exposure show that arsenic in drinking water is associated with liver, lung, kidney, and bladder cancers, as well as skin cancer (Wu *et al.*, 1989). To minimize these risks, the US Environmental Protection Agency has been considering more stringent arsenic regulations than the current maximum contaminant level of 50 µg/l arsenic for drinking water (Reid, 1994; USEPA, 1993).

Batch adsorption and coprecipitation tests are commonly used to study the removal of arsenic by ferric chloride (Fuller *et al.*, 1993). In adsorption experiments, arsenic solution is added to a suspension containing preformed and aged ferric hydroxide precipitate. Coprecipitation tests are conducted

by addition of ferric chloride to arsenic solutions. In coprecipitated solids, As(V) densities can be as high as 0.7 mol/mol of Fe and As(V) removal can be completed in a few minutes because As(V) is coordinated by ferric hydroxide sites before crystallite growth and coagulation processes can proceed (Fuller *et al.*, 1993). Extended X-ray absorption fine structure (EXAFS) (Manning *et al.*, 1998; Waychunas *et al.*, 1993) and Fourier transform IR spectroscopy (Sun and Doner, 1996) have shown that As(V) and As(III) form inner sphere surface complexes with iron hydroxide sites in coprecipitated and adsorbed solids. No ferric arsenate and any other As-bearing surface precipitate are observed in the precipitates (Waychunas *et al.*, 1993).

The adsorption of cations and anions onto metal oxides and hydroxides has been described successfully by surface complexation models (Davis and Leckie 1978, 1980; Stumm *et al.*, 1976). A few researchers have used the models to study the competitive effect of co-occurring solutes on heavy metal adsorption (Van Geen *et al.*, 1994; Wilkie and Hering, 1996). These theoretical models include surface complexation reactions of adsorbates with surface hydroxyl groups and electrical double layer effects. One of the surface complexation models is the triple layer model (TLM) (Hayes and Leckie, 1987), which is used to simulate the formation of inner and outer sphere surface complexes by placing the adsorbed ions in different planes in the electrical

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layer. In this study, TLM was used to describe the adsorption of As(III) and As(V) in the presence of silicate. Monodentate and inner sphere surface complexes were considered for the adsorption of As(V), As(III), and silicate in the model calculations.

The surface complexation models are usually applied to well-defined oxide systems with low adsorption densities since uniform surface sites are assumed. At high adsorption densities, significant amount of adsorbates can be associated with less reactive surface sites. The Langmuir and Freundlich equations are commonly used to describe solute adsorption on oxides, soils, and sediments over a wide range of surface coverage (Stumm, 1992). In this study, the Langmuir equation was used to determine the adsorption capacity of ferric hydroxide. Effect of silicate on As(V) and As(III) removal by ferric chloride was quantified by comparing arsenic adsorption capacity in suspensions with and without the presence of silicate.

Adsorption of As(V) and As(III) oxyanions by ferric hydroxide may be adversely affected by anions such as silicate, sulfate, carbonate, and natural organic matter. It has been reported that the adsorption of silicate decreases the adsorption of SO_4^{2-} , SeO_3^{2-} , PO_4^{3-} , and CrO_4^{2-} by ferric hydroxide but has no obvious effect on cation adsorption (Anderson and Benjamin, 1990; Goldberg, 1985; Meng and Letterman, 1996; Zachara *et al.*, 1987). Only a few studies have been conducted to investigate the effects of sulfate and organic matter on arsenic adsorption (Hering *et al.*, 1997; Wilkie and Hering, 1996; Xu *et al.*, 1991). No research results on the effects of silicate on arsenic removal by ferric hydroxide have been reported in the literature. Silicate in natural water is mainly derived from the weathering of minerals and is constantly dissolving and precipitating over a large part of the earth's surface (Iler, 1979). Silicate species are common oxyanions in natural water, with concentration ranging from 0.45 to 14 mg/l Si (Clesceri *et al.*, 1989). An understanding of silicate competition will benefit the development of effective treatment processes for arsenic removal. In the present work, the effects of silicate, sulfate, and carbonate on As(III) and As(V) removal by coprecipitation with ferric chloride were investigated over a wide pH range and at different anion concentrations.

EXPERIMENTAL METHODS

A background electrolyte of 0.04 M KNO_3 prepared by dissolving reagent grade KNO_3 (Fisher, Pittsburgh, PA) in distilled-deionized (DI) water, was used in the coprecipitation experiments. All chemicals used in the experiments were reagent grade. Fe(III) stock solution containing 2000 mg/l Fe(III) and 0.1% HCl was prepared from $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (Fisher) and trace metal grade HCl (Fisher). $\text{As}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ (Aldrich, Milwaukee, WI) was dissolved in DI water to prepare primary stock solution containing 1000 mg/l As(V). Secondary stock solution of 10 mg/l As(V) was prepared every week by dilution of the primary

stock solution with DI water. NaAsO_2 (Fisher) and $\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O}$ (Fisher) stock solutions containing 1000 mg/l As(III) and Si, respectively, were prepared every two weeks. Speciation analysis with disposable cartridges (Meng and Wang, 1998) indicates that a negligible amount of As(III) in the stock solution was oxidized to As(V). The cartridges packed with 2.5 g of selective aluminosilicate adsorbent completely removed As(V) and did not adsorb As(III) in a pH range 4 to 9. As(III) was separated from As(V) by passing 50 ml of sample through a cartridge at a flow rate of 60 ± 20 ml per minute using a syringe.

Batch experiments were conducted to study the removal of As(V) and As(III) with ferric chloride under an N_2 atmosphere or in ambient air. After the electrolyte solution in a 1-l glass or polypropylene beakers was purged with N_2 or air for approximately 30 min, As(III) or As(V) stock solution was added to the electrolyte solution to reach the desired arsenic concentrations. Initial arsenic concentration varied from 50 to 1400 $\mu\text{g/l}$. Small amounts of silicates (i.e. less than 0.1 mg/l Si) dissolved from the glass beakers, had a negligible effect on the removal of arsenic. When effects of competing ions were investigated, sulfate (Na_2SO_4 , Fisher) or silicate stock solution, was added to the solution. Coprecipitation experiments were conducted by adding 1 or 3 mg/l Fe(III) to the solutions. The solution pH was adjusted with KOH and HNO_3 in a range 3 to 11 while the solution was purged with N_2 or air. At designated pH values, 60 ml of the solution was transferred to 125-ml polypropylene bottles. After the samples in the capped bottles were mixed for 1 h to reach equilibrium, the equilibrium pH was measured and the suspensions were centrifuged at 16,750 g for 7 min or filtered through a 0.4- μm pore size membrane filter. Kinetic experiments indicate that arsenic removal reached equilibrium within 1 h. The same procedures were used to test silicate removal by coprecipitation with ferric chloride in 0.04 M KNO_3 solution purged with air. Si and Fe(III) concentration in the coprecipitation system was 500 $\mu\text{g/l}$ and 15 mg/l, respectively. Most of the experiments were repeated more than twice.

Soluble arsenic concentrations in filtered and centrifuged samples were determined using a Zeeman Furnace Atomic Absorption Spectrometer (AAS) (Varian SpectrAA-400). During AAS analysis, 20 μl water samples and 5 μl palladium-citric acid modifier were injected in a partitioned graphite tube. The relative standard deviation of the measurements was normally less than 10% when arsenic concentration in the samples was greater than 2 $\mu\text{g/l}$. The

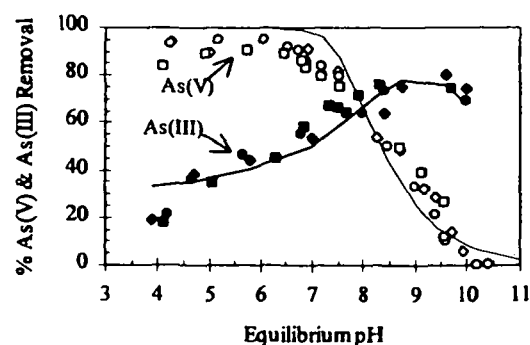


Fig. 1. Removal of As(V) and As(III) in the 0.04 M KNO_3 solution under N_2 (\diamond , \blacklozenge) and in air (\circ , \bullet), and in 0.04 M KNO_3 -sulfate solutions. " \square " 250 mg/l SO_4 in As(V) system; " \blacksquare " 18 mg/l SO_4 in As(III) system; As(V) = 100 $\mu\text{g/l}$ or 1.3 μM , Fe(III) = 1 mg/l or 17.8 μM (in As(V) system); As(III) = 50 $\mu\text{g/l}$, Fe(III) = 3 mg/l (in As(III) system).

Table 1. Surface reactions used in the model calculations

Surface reactions	Equilibrium expressions	log K
Surface ionization (inner sphere)		
(1) $\text{SOH} \cdot \text{H}^+ \rightleftharpoons \text{SOH}_2^+$	$K_{a,1} = \exp(F\Psi_0/RT)[\text{SOH}][\text{H}^+]$	5.1 ^a
(2) $\text{SOH} \rightleftharpoons \text{SO}^- + \text{H}^+$	$K_{a,2} = \exp(-F\Psi_0/RT)[\text{SO}^-][\text{H}^+]/[\text{SOH}]$	-10.7 ^a
Electrolyte adsorption (outer-sphere)		
(3) $\text{SOH} + \text{K}^+ \rightleftharpoons \text{SO}^-\text{K} + \text{H}^+$	$K_K = \exp(F\Psi_0 - \Psi_0/RT)[\text{SO}^-\text{K}][\text{H}^+]/[\text{SOH}][\text{K}^+]$	-9.0 ^a
(4) $\text{SOH} + \text{NO}_3^- + \text{H}^+ \rightleftharpoons \text{SOH}_2^+\text{NO}_3$	$K_{\text{NO}_3} = \exp(F\Psi_0 - \Psi_0/RT)[\text{SOH}_2^+\text{NO}_3]/[\text{SOH}][\text{H}^+][\text{NO}_3^-]$	6.9 ^a
Inner sphere surface complexes		
(5) $\text{SOH} + \text{H}_3\text{AsO}_4 \rightleftharpoons \text{SAso}_4^- + \text{H}_2\text{O} + 2\text{H}^+$	$K^{(5)} = \exp(-2F\Psi_0/RT)[\text{SAso}_4^-][\text{H}^+]^2/[\text{SOH}][\text{H}_3\text{AsO}_4]$	0.6 ^b
(6) $\text{SOH} + \text{H}_3\text{AsO}_3 \rightleftharpoons \text{SHAsO}_3^- + \text{H}_2\text{O} + \text{H}^+$	$K^{(6)} = \exp(-F\Psi_0/RT)[\text{SHAsO}_3^-][\text{H}^+]/[\text{SOH}][\text{H}_3\text{AsO}_3]$	-3.1 ^b
(7) $\text{SOH} + \text{H}_3\text{AsO}_3 + \text{K}^+ \rightleftharpoons \text{SHAsO}_3^-\text{K} + \text{H}_2\text{O} + \text{H}^+$	$K^{(7)} = \exp(F\Psi_0 - \Psi_0/RT)[\text{SHAsO}_3^-\text{K}][\text{H}^+]/[\text{SOH}][\text{H}_3\text{AsO}_3]$	-2.1 ^b
(8) $\text{SOH} + \text{H}_4\text{SiO}_4 + \text{K}^+ \rightleftharpoons \text{SH}_2\text{SiO}_4\text{K} + \text{H}_2\text{O} + \text{H}^+$	$K^{(8)} = \exp(F\Psi_0 - \Psi_0/RT)[\text{SH}_2\text{SiO}_4\text{K}][\text{H}^+]/[\text{SOH}][\text{H}_4\text{SiO}_4]$	-2.1 ^b

^aFrom Davis and Leckie (1978).

^bBest-fit constants determined with model simulations of the experimental data.

method detection limit (MDL) was 0.7 µg/l arsenic. Spike recovery and matrix-matching standards were used to check the accuracy of the arsenic analysis for solutions containing high concentrations of sulfate and silicate.

RESULTS AND DISCUSSION

Arsenic removal in sulfate and carbonate systems

The results in Fig. 1 show the removal of As(V) and As(III) by ferric hydroxide in N₂, air, and sulfate systems. When pH was decreased from 10 to 6, As(V) removal increased from 0 to 95%. In contrast to As(V) removal, As(III) removal increased from 20 to 80% when pH was increased from 4 to 9.5. A maximum As(III) removal occurred at approximately pH 9.5. The maximum adsorption pH value was similar to the first dissociation constant of H₃AsO₃ (pK₁ = 9.2).

The curves in Fig. 1 were calculated with the TLM using reactions 5–7 in Table 1 for the formation of adsorbed As(V) and As(III) species. Surface reactions including surface protolysis and electrolyte binding (reactions 1–4 in Table 1) were always considered in TLM calculations of As(V), As(III), and silicate adsorption. TLM calculations of the surface reactions and distribution of aqueous As(V), As(III), and silicate species were made using the MINTEQA2 program (David and Allison, 1988). The best-fit values of the formation constants (log K in Table 1) for the surface complexes were determined by fitting TLM calculated adsorption values to the experimental data in the N₂ systems. The modeling results indicate that As(V) and

As(III) were associated with ferric hydroxide in SAso₄⁻, SHAsO₃⁻, and SHAsO₃⁻-K⁺ species. (S denotes ferric hydroxide sites.)

Thermodynamic calculations using the aqueous equilibrium constants in Table 2 indicate that when pH values are between 2.2 and 11.6, HAsO₄²⁻ and H₂AsO₄⁻ are the predominant species in water (Fig. 2). AsO₄³⁻ becomes the predominant aqueous species when pH is greater than 11. However, the modeling results in Fig. 1 suggest that As(V) was adsorbed through the formation of SAso₄²⁻ complex at pH values less than 10. Since the SAso₄²⁻ complex gave better model fitting to the observed data than SHAsO₄⁻ and SH₂AsO₄ species, only SAso₄²⁻ complex was used in the model calculations of As(V) adsorption. It is possible that the chemical bonds between adsorbed As(V) and the ferric ions on the hydroxide surface enhanced protonation of arsenic acid. Davis and Leckie (1980) reported that adsorbed anions were more easily protonated than dissolved anions.

The predominate aqueous As(III) species is H₃AsO₃ when the pH is less than 9.2 (Fig. 2). On the other hand, the modeling results indicate the formation of SHAsO₃⁻, which is attributed to the enhanced protonation of arsenious acid. When SHAsO₃⁻-K⁺ species was included in the TLM calculations for As(III) adsorption, model description of the experimental data was improved in a high pH range. Similar surface species were used to model the adsorption of selenite onto ferric hydroxide (Hayes *et al.*, 1988). The surface potential of ferric hydroxide decreased with increasing pH.

Table 2. Surface parameters and aqueous equilibrium constants

Surface		Aqueous ^a	
Surface site concentration	0.9 mmol/l mmol Fe ^b	pK ₁ (H ₃ AsO ₃)	2.2
Site density (sites/nm ²)	11.4 ^b	pK ₂ (H ₂ AsO ₄)	6.8
Capacitance C1 (µF/cm ²)	140 ^c	pK ₃ (HAsO ₄)	11.6
Capacitance C2 (µF/cm ²)	20 ^c	pK ₁ (H ₃ AsO ₃)	9.2
		pK ₂ (H ₂ AsO ₄)	12.1
		pK ₃ (HAsO ₄)	13.4

^aFrom David and Allison (1988).

^bFrom Meng and Letterman (1993).

^cFrom Davis and Leckie (1978).

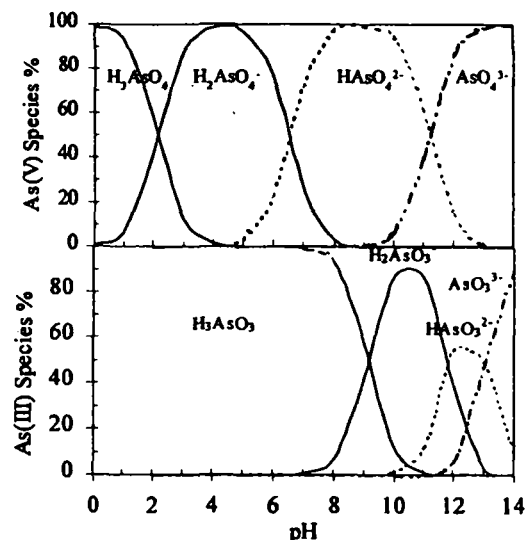


Fig. 2. Distribution of As(V) and As(III) species as a function of pH. Ionic strength = 0.04 M.

When pH was greater than the point of zero charge of the ferric hydroxide (i.e. $pH_{PZC} = 7.9$) (Davis and Leckie, 1978), the particle surface became negatively charged. It is possible that K^+ cations were attracted to the negatively charged surface species, $SHAsO_3^-$, and provided charge compensation in the high pH range. Experimental results show that when KNO_3 concentration increased from 0.001 to 0.04 M, As(III) removal increased slightly, which can be attributed to the effect of K^+ .

Effects of carbonate on As(V) and As(III) removal were evaluated by comparing the amounts of arsenic removal in the KNO_3 solutions purged with N_2 or air (Fig. 1). Total carbonate content in the suspensions purged with air was approximately 0.01 mM. The removal of the arsenic species under N_2 atmosphere and in ambient air was essentially identical, indicating that carbonate species had a negligible effect on arsenic removal in a pH range 4 to 9.5. Fuller *et al.* (1993) also reported that the

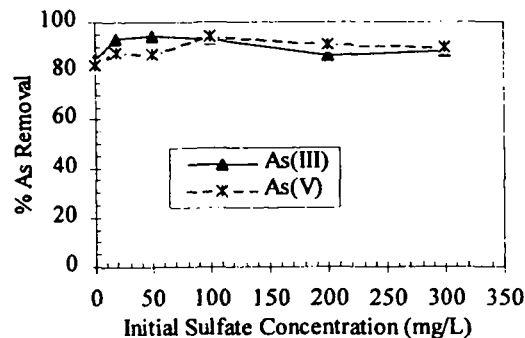


Fig. 3. Removal of arsenic by coprecipitation with ferric chloride as a function of initial sulfate concentration. 0.04 M KNO_3 solution; equilibrium $pH = 6.8 \pm 0.1$; initial As(III) = 100 $\mu g/l$, Fe = 5 mg/l (in As(III) system); initial As(V) = 300 $\mu g/l$, Fe = 1 mg/l (in As(V) system).

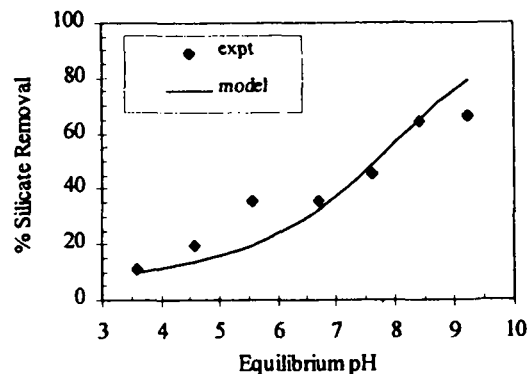


Fig. 4. Model simulation of silicate removal by ferric hydroxide in 0.04 M KNO_3 solution. Initial silicate = 500 $\mu g/l$ Si (18.8 μM); Fe(III) = 15.0 mg/l (268 μM).

presence of carbonate species had no effect on the adsorption of As(V) by ferric hydroxide.

The results in Fig. 1 also show that when sulfate was added to 0.04 KNO_3 solutions, the removal of As(V) and As(III) was not affected in a pH range 4 to 10. The negligible effect of sulfate is further demonstrated by the experimental data in Fig. 3. The equilibrium pH of the suspensions in Fig. 3 was 6.8 ± 0.1 . When the sulfate concentration was increased from 0 to 300 mg/l, no apparent change in As(V) and As(III) removal was observed. The results suggest that sulfate binding affinity for ferric hydroxide was much weaker than As(V) and As(III).

Silicate effect on arsenic removal

The adsorption behavior of silicate onto ferric hydroxide was similar to As(III) (Fig. 4) since both chemicals are present as weak acids in water. The first dissociation constant, pK_{1} , of H_2SiO_3 is 9.9 (David and Allison, 1988). When the pH was increased from 3.5 to 9.2, silicate removal increased from 11 to 66% (Fig. 4). Similar to As(III) removal, silicate removal increased when the surface potential decreased. The results indicate that the chemical binding affinity of As(III) and silicate for the surface sites overcame the electrostatic repulsion between the anions and the charged surface. The reaction of silicate with ferric hydroxide sites and the formation constant were determined by fitting TLM calculated adsorption values to the experimental data in Fig. 4. The modeling curve in Fig. 4 was calculated using reaction 8 and the best-fit formation constant in Table 1.

In addition to adsorption on ferric hydroxides, silicate can interact with Fe(II) to form soluble polymers and highly dispersed colloids that are not removed by filtration (Iler, 1979; Robinson *et al.*, 1992). Effects of silicate and sulfate on precipitation of ferric hydroxide are illustrated in Fig. 5. When the pH was between 4 and 10, less than 30 $\mu g/l$ Fe remained soluble in the 0.04 M KNO_3 solution.

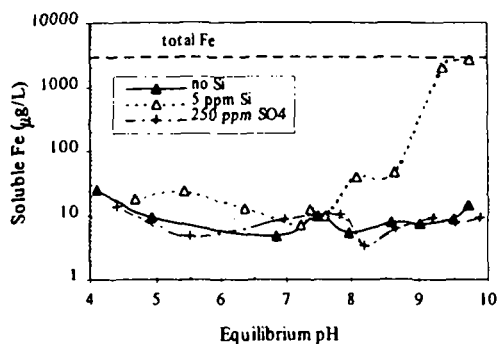


Fig. 5. Effects of silicate and sulfate on precipitation of ferric hydroxide. 0.04 M KNO₃, total Fe=3 mg/l, As(III)=50 µg/l.

The addition of 250 mg/l SO₄²⁻ to the KNO₃ solution did not increase the soluble iron concentration. In the presence of silicate, the soluble iron concentration increased significantly in the high pH range. When the silicate concentration was 5 mg/l Si and the pH was increased from 8.6 to 9.4, soluble iron concentration increased from 47 to 2040 µg/l. When the pH was between 4 and 8.6, greater than 97% of the iron formed hydroxide precipitates in the silicate solution. Therefore, the increased iron solubility can cause significant reduction in arsenic removal only at a pH greater than 8.6.

The results in Fig. 6 show the removal of As(V) and As(III) as a function of silicate concentration at pH 6.8. When the silicate concentration was increased from 0 to 1 mg/l Si, no significant change in arsenic removal was observed. The removal of As(III) and As(V) decreased from approximately 90 to 45% when the silicate concentration was increased from 1 to 10 mg/l. Silicate concentration in natural water varies from 0.45 to 14 mg/l Si (Clesceri *et al.*, 1989), which may significantly reduce the amount of arsenic removed by coagulation treatment with ferric chloride.

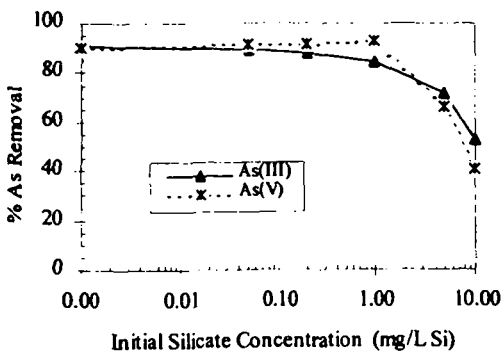


Fig. 6. Effect of silicate on arsenic removal by ferric hydroxide in 0.04 M KNO₃ solution. Equilibrium pH=6.8 ± 0.2; initial As(III)=100 µg/l, Fe=5 mg/l (in As(III) system); initial As(V)=300 µg/l, Fe=1 mg/l (in As(V) system).

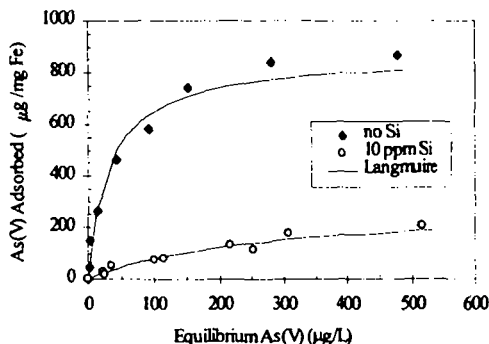


Fig. 7. As(V) adsorption isotherms in 0.04 M KNO₃ and 0.04 M KNO₃-10 mg/l Si solutions. Fe=1 mg/l; equilibrium pH=6.8 ± 0.1.

The adsorption isotherms in Figs 7 and 8 show the effects of silicate on the adsorption capacity of ferric hydroxide. The Langmuire equation (Stumm, 1992) was used to determine the adsorption capacity and to calculate the curves in the figures. At a pH of 6.8, ferric hydroxide had an As(V) adsorption capacity of 864 µg/mg Fe (i.e. 645 µmol/mmol Fe), corresponding to 72% of the Fe-OH site density (i.e. 0.9 mmol/mmol Fe, Table 2). The lower adsorption capacity compared to the surface site density was attributed to the formation of bidentate surface complexes and electrostatic repulsion. Formation of SAsO₄²⁻ complexes at high surface coverage significantly decreased the surface potential and prevented further As(V) adsorption. In the presence of 10 mg/l Si, As(V) adsorption capacity was reduced from 964 to 274 µg/mg Fe. The significant reduction in As(V) adsorption capacity was due to strong association of silicate with ferric hydroxide, which reduced the surface site available for As(V). In addition, the formation of SH₂SiO₄⁻K⁺ (Reaction 8 in Table 1) reduced surface potential, therefore, increasing electrostatic repulsion between As(V) and the negatively charged surface sites.

Ferric hydroxide had a much lower adsorption capacity for As(III) than for As(V) due to lower binding affinity of As(III) for ferric hydroxide.

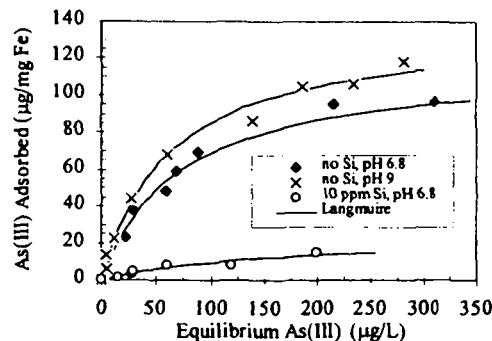


Fig. 8. As(III) adsorption isotherms in 0.04 M KNO₃ and 0.04 M KNO₃-10 mg/l Si solutions. Fe=3 mg/l; equilibrium pH=6.8 ± 0.1.

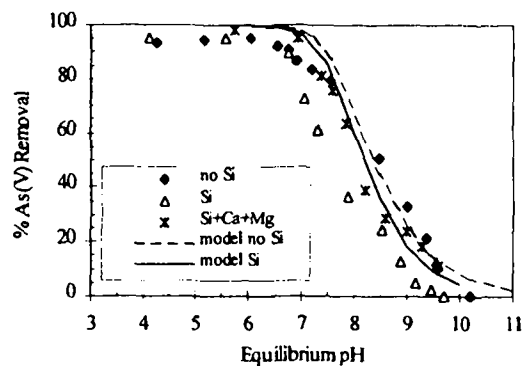


Fig. 9. Effects of silicate on As(V) removal and model predictions of As(V) removal. In all systems: initial As(V) = 100 ppb, Fe(III) = 1 ppm. In labeled systems: Si = 4.5 mg/l, Ca^{2+} = 18 mg/l, Mg^{2+} = 7 mg/l.

When equilibrium pH values were 9.2 (i.e. near optimum pH for As(III) removal) and 6.8, the As(III) adsorption capacity was 137 and 116 $\mu\text{g}/\text{mg}$ Fe, respectively (Fig. 8). When 10 mg/l Si was added to the KNO_3 solution at a pH of 6.8, As(III) adsorption capacity was reduced from 116 to 23 $\mu\text{g}/\text{mg}$ Fe. The results indicate that when silicate content in water was high, the removal of As(III) by coprecipitation with ferric chloride was not effective. The adsorption capacity determined with the Langmuire equation was a conditional maximum adsorption density. While total site density of ferric hydroxide was a constant, the adsorption capacity varied with the types of adsorbates and the composition of water.

The results in Fig. 9 show the effects of silicate on As(V) removal in a pH range 4 to 10. When the pH was greater than 7, As(V) removal decreased in the presence of 4.5 mg/l Si. As(V) removal was not affected by silicate when the pH was less than 6.8. The adverse effect of silicate was coincident with increased silicate adsorption in the high pH range (Fig. 4). In the presence of Ca^{2+} and Mg^{2+} the adverse affect of silicate was reduced, which can be

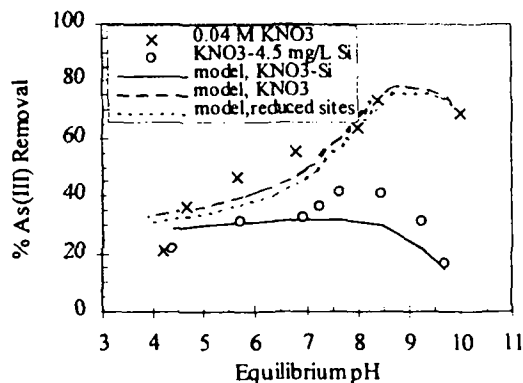


Fig. 10. Effects of silicate on As(III) removal and model predictions of As(III) removal in KNO_3 -silicate system. Initial As(III) = 50 ppb; Fe(III) = 3 ppm.

attributed to neutralization of the negative surface charges.

As(V) removal in the presence of silicate was calculated with the TLM and compared with the experimental data in Fig. 9. Surface species SAsO_4^{2-} and $\text{SH}_2\text{SiO}_4^- \text{K}^+$ with the best-fit formation constants determined in the single anion systems (reactions 5 and 8 in Table 1) were used to calculate the As(V) adsorption curves. The modeling calculation predicted the adverse effect of silicate on As(V) removal. However, agreement between the calculated and observed As(V) removal in the presence of silicate was poor.

The removal of As(III) was significantly reduced by silicate over a wide pH range (Fig. 10). The magnitude of silicate effects became greater when the pH was increased from approximately 4 to 9.5. At a pH of 8.5, As(III) removal decreased from approximately 75% in 0.04 M KNO_3 solution to 40% in the KNO_3 solution containing 4.5 mg/l Si. When the pH was greater than 8.6, the reduced As(III) removal in the 4.5 mg/l Si solution could be attributed in part to a lesser amount of ferric hydroxide precipitated (Fig. 5). In the presence of Ca^{2+} and Mg^{2+} , As(III) removal was also reduced significantly (data are not presented).

Surface species SHAsO_3^- , $\text{SHAsO}_3^- \text{K}^+$ and $\text{SH}_2\text{SiO}_4^- \text{K}^+$ with the best-fit formation constants (reactions 6, 7, and 8 in Table 1) were used to predict As(III) removal in a 4.5 mg/l Si system. The calculated curve agreed reasonably well with the experimental data (Fig. 10). Adsorption of silicate reduced the amount of Fe-OH sites available for As(III) and decreased the surface potential, Ψ_0 . Modeling results suggested that when the pH was increased from 4.4 to 9.7, the amount of Fe-OH sites occupied by adsorbed silicate increased from 5.4 to 15.2%. The surface potential decreased from -51 to -77 mV when 4.5 mg/l of Si was added to the KNO_3 solution at a pH of 8.5. Both competitive and Coulombic interactions caused by silicate adsorption can reduce As(III) adsorption.

To determine the predominant interaction reducing As(III) adsorption, model calculations were performed to evaluate the effect of surface site reduction on As(III) removal. When the concentration of the surface sites was reduced by 5.4 to 15.2% in a pH range 4.4 to 9.7, calculated As(III) removal in the KNO_3 solution was only reduced slightly (see line 'model, reduced sites' in Fig. 10). Therefore, it appears that silicate decreased As(III) removal, mainly by decreasing the surface potential and increasing electrostatic repulsion for As(III) species.

CONCLUSIONS

Silicate significantly reduced the removal of As(III) by coprecipitation with ferric chloride when Si concentration was higher than 1 mg/l. The

removal of As(V) was reduced moderately by silicate in a 0.04 M KNO₃ solution. At the lower pH and in the presence of Ca²⁺ and Mg²⁺, the effect of silicate on As(V) removal was not significant. The TLM can be used to qualitatively predict the effects of silicate on As(III) and As(V) removal. The adsorption of silicate on ferric hydroxide increased the electrostatic repulsion for the arsenic anions and reduced the concentration of the surface sites available to arsenic. At pH values greater than 8.6 and at a silicate concentration of 5 mg/l Si, silicate hindered the precipitation of ferric hydroxide. Sulfate and carbonate were found to have a negligible effect on the removal of As(V) and As(III) with ferric hydroxide.

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