Arsenite and Arsenate Adsorption on Ferrihydrite: Kinetics, Equilibrium, and Adsorption Envelopes

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Because of its toxicity, arsenic is of considerable environmental concern. Its solubility in natural systems is strongly influenced by adsorption at iron oxide surfaces. The objective of this study was to compare the adsorption behavior of arsenite and arsenate on ferrihydrite, under carefully controlled conditions, with regard to adsorption kinetics, adsorption isotherms, and the influence of pH on adsorption. The adsorption reactions were relatively fast, with the reactions almost completed within the first few hours. At relatively high As concentrations, arsenite reacted faster than arsenate with the ferrihydrite, i.e., equilibrium was achieved sooner, but arsenate adsorption was faster at low As concentrations and low pH. Adsorption maxima of approximately 0.60 (0.58) and 0.25 (0.16) mol_{As} mol_{Fe}^{-1} were achieved for arsenite and arsenate, respectively, at pH 4.6 (pH 9.2 in parentheses). The high arsenite retention, which precludes its retention entirely as surface adsorbed species, indicates the likelihood that ferrihydrite was transformed to a ferric arsenite phase, although this possibility has yet to be confirmed by spectroscopic studies. The general trend at initial arsenic concentrations ≥ 0.27 mol_{As} kg^{-1} ferrihydrite within the pH range of 4–9 was increasing arsenite adsorption and decreasing arsenate adsorption with increasing pH. At initial As concentrations of 0.27–0.80 mol_{As} kg^{-1} ferrihydrite, the adsorption envelopes crossed at approximately pH 6–7.5, i.e., adsorbed arsenate concentrations were relatively greater than adsorbed arsenite concentrations at lower pH values whereas adsorbed arsenite was greater at higher pH. At the highest initial arsenic concentration of 13.3 mol_{As} kg^{-1} ferrihydrite, a distinct adsorption maximum was observed for arsenite adsorption at approximately pH 9.0, which corresponds closely to the first pK_a (9.2) of $H_3AsO_3^0$, whereas there was a continuous drop in arsenate adsorption with increasing pH from 3 to 11.

Introduction

Arsenic, which is toxic to man and other living organisms, presents potentially serious environmental problems throughout the world. The biogeochemistry of As has been reviewed by Ferguson and Gavis (*1*) and Korte and Fernando (*2*). Arsenate (as $H_2AsO_4^-$ and $HAsO_4^{2-}$) is the predominant As form in well-oxidized waters, while arsenite occurs predominantly as $H_3AsO_3^0$ and $H_2AsO_3^-$ in reduced environments, although because of the relatively slow redox transformations (*3*), both arsenite and arsenate are often found

in either redox environment. Arsenite is 25–60 times more toxic than arsenate and has been reported to be more mobile in the environment (*2*).

Adsorption is one of the reactions that controls the mobility and bioavailability of As. Arsenic adsorption has been studied using a variety of adsorbents, including phyllosilicates, silica, and hydrous oxides of Fe and Al, as reviewed by Korte and Fernando (*2*). There have been quite a few studies of the adsorption of arsenite and arsenate on iron oxides (*4*–*9*). The adsorption of arsenate and other anions have been reported to be dependent on the nature of the anion and the adsorbent surface (*4*). Arsenic adsorption has been observed to be more highly dependent on its oxidation state than on pH within the range of 5.5–7.5 (*5*). It has been reported that arsenate reacts with amorphous iron oxides much faster than arsenite (*6*). On the other hand, slow adsorption kinetics of arsenate on ferrihydrite has been reported to be due to a diffusion-controlled rate-determining step (*10*). The molecular structure of arsenate surface complexes adsorbed on iron oxides have been investigated using EXAFS, EDAX, and IR spectroscopic techniques (*11*–*16*). Recently, Sun and Doner (*17*) investigated the mode of bonding of arsenite and arsenate adsorbed on goethite using FTIR spectroscopy. Despite the high toxicity and the environmental relevance of arsenite, the reaction of arsenite with ferrihydrite has not received as much attention. The reason may be that it is generally assumed that arsenite is less strongly adsorbed than arsenate on the oxide surface. There is very little information on the kinetics of arsenite adsorption on ferrihydrite. Because of the slow redox transformation of arsenic, it is important to understand the reactions of arsenite and arsenate with iron oxides in comparable systems. Also, there are some conflicting results regarding the adsorption envelope of arsenite. Ferguson and Anderson (*5*) observed an increase in arsenite adsorption with increasing pH from 6 to 8, while Pierce and Moore (*6*) observed an adsorption maximum at pH 7.0 at the same approximate As to Fe molar ratio.

The objectives of this research were to study the kinetics and equilibria of the adsorption of arsenite and arsenate on ferrihydrite, at pH 4.6 and pH 9.2. In addition, the effect of pH on the adsorption of arsenite and arsenate was evaluated within the pH range of 3–11 at different As concentrations. Relatively high concentrations of As were used in order to achieve the adsorption maxima. The experimental pH values, during the kinetics and adsorption isotherm experiments, were selected to obtain equilibrating solutions with only one or two predominant As species. pK_a values of arsenious acid (H_3AsO_3) and arsenic acid (H_3AsO_4) are as follows: $pK_1 = 9.22$, $pK_2 = 12.13$, and $pK_3 = 13.4$; $pK_1 = 2.20$, $pK_2 = 6.97$, and $pK_3 = 11.53$, respectively (*18*). Hence at pH 4.6, $H_3AsO_3^0$ and $H_2AsO_4^-$ are the predominant dissolved arsenite and arsenate species, respectively. While approximately equal concentrations of $H_3AsO_3^0$ and $H_2AsO_3^-$ are present in arsenite solutions at pH 9.2, $HAsO_4^{2-}$ is the predominant dissolved arsenate solution species at the same pH. By minimizing the number of dissolved species, the number of possible adsorption reactions is reduced, and the overall system is simpler and more easily characterized.

Experimental Section

Ferrihydrite Synthesis. Two-line ferrihydrite was synthesized in the laboratory as described by Schwertmann and Cornell (*19*), with slight modifications. To 500 mL of a solution containing 40 g of $Fe(NO_3)_3 \cdot 9H_2O$, 310 mL of 1 M KOH was added at a fixed rate of addition of approximately

100 mL min^{-1}, during vigorous stirring with a magnetic stirrer. The pH of the suspension was then adjusted to 7.5 by the dropwise addition of 1 M KOH. Once the pH was stabilized at 7.5, the suspension was washed three times with 0.1 M NaCl and the sediment separated by centrifugation at $2500g$ for 10 min. The centrifugation sediment was resuspended in 0.1 M NaCl, adjusted to pH 7.5, diluted to 1 L final volume, and stored at 2 °C. The ferrihydrite concentration in the final suspension was approximately 10 g L^{-1}. The identity of the 2-line ferrihydrite was confirmed by powder X-ray diffraction using CuKα radiation at 35 kV and 15 mA from a Philips–Norelco diffractometer equipped with a graphite monochromator. The surface area of a freeze-dried sample was determined with a Quantasorb flow-through surface-area analyzer using the three-point BET method of N_2 gas adsorption at liquid N_2 temperature (20). The sample was degassed at 110 °C for 2 h with a continual stream of dry N_2 prior to surface area determination. The surface area of ferrihydrite was $202 \pm 6 \text{ m}^2 \text{ g}^{-1}$. The zero point of salt effect (ZPSE) of ferrihydrite was determined from the crossover point of acid–base titration curves obtained at three electrolytic concentrations using the method of Van Raij and Peech (21), and it was 8.5. Preliminary tests showed that the ferrihydrite transformed partially into goethite upon prolonged storage (>4 weeks at room temperature). Therefore, each batch of ferrihydrite was used in the adsorption studies within 10 days of its synthesis, at which time there was no evidence of goethite contaminants as determined by powder X-ray diffraction and diffuse reflectance FTIR spectroscopy of freeze-dried samples.

Adsorption Kinetics. Adsorption kinetics were evaluated, at pH 4.6 and 9.2, at initial As (arsenite or arsenate) solution concentrations of 0.534 and 26.7 mmol L^{-1} (corresponding to 0.267 and $13.3 \text{ mol}_{As} \text{ kg}^{-1}$ ferrihydrite). Preliminary adsorption experiments showed that these concentrations resulted in intermediate and nearly maximum As adsorption, respectively. The stock solutions of arsenite and arsenate were prepared in 0.1 M NaCl having As concentrations of 2.67 and 133 mmol L^{-1}. NaAsO$_2$ (Fisher) and Na$_2$HAsO$_4$·7H$_2$O (Sigma) were used as the arsenite and arsenate sources, repectively. Four hundred milliliters of a 2.5 g L^{-1} ferrihydrite suspension in 0.1 M NaCl was added to the 700-mL polyethylene reaction vessel. A combination pH electrode and a burette tip connected to an automatic titrator were introduced into the ferrihydrite suspension through perforations in the lid of the reaction vessel. With this experimental setup, pH was maintained constant using HCl or NaOH as the titrant during the reaction between arsenic and ferrihydrite. The system was purged with N_2 at a flow rate of 60 mL min^{-1} to minimize the effect of CO_2 on the adsorption reaction. An additional perforation, which was stoppered when not in use, was used to add As solution to the ferrihydrite suspension and to sample the ferrihydrite suspension during the adsorption reaction. The pH of the ferrihydrite suspension was adjusted to the desired pH and stabilized for 30 min before each kinetic run. Agitation was accomplished by means of a magnetic stirrer. One hundred milliliters of As stock solutions with preadjusted pH was then quickly added to the ferrihydrite suspension, as the automatic titrator was simultaneously switched on at the beginning of each kinetic run. Twelve milliliters of suspension was sampled with a syringe after 0.083, 0.167, 0.25, 0.33, 0.5, 0.67, 0.83, 1, 2, 3, 4, 6, 24, 48, 72, and 96 h of reaction. The sampled suspension was immediately filtered using a membrane filter (0.45-μm nominal pore size), and the filtrate was stored at 2 °C until analyzed. Duplicate kinetic runs were carried out for each treatment.

The adherence of the adsorption kinetic data to first order, second order, power function, simple Elovich, and parabolic diffusion equations (22) was tested graphically.

Adsorption Isotherms. Adsorption isotherms were obtained at pH 4.6 and pH 9.2 at initial As (arsenite or arsenate) solution concentrations of 0.267, 0.668, 1.33, 2.67, 6.67, 13.3, and 26.7 mmol L^{-1} (corresponding to 0, 0.133, 0.333, 0.667, 1.33, 3.33, 6.67, and $13.3 \text{ mol}_{As} \text{ kg}^{-1}$ ferrihydrite). The stock solutions of arsenite and arsenate were prepared in 0.1 M NaCl having As concentrations of 1.33, 3.33, 6.67, 13.3, 33.3, 66.7, and 133 mmol L^{-1}. The experimental setup was the same as for the kinetic studies, except that 60-mL reaction vessels containing 40 mL of a 2.5 g L^{-1} ferrihydrite suspension in 0.1 M NaCl were used. The pH of the ferrihydrite suspension, which was agitated with a magnetic stirrer, was adjusted to the desired pH before each experiment. Ten milliliters of As stock solution with preadjusted pH was then quickly added to the ferrihydrite suspension, as the automatic titrator was simultaneously switched on at the beginning of each run to keep the pH constant. Titration was continued for 20 min, as preliminary experiments showed that most of the adsorption reaction was complete, and pH drift was minimal after this time. Thereafter, the four perforations on the cap of the bottle were stoppered, and the bottle was shaken at 240 rpm on a rotary shaker. After 24 h, the pH of the suspension was readjusted. The suspension was then centrifuged at $2500g$, and the supernatant was passed through a membrane filter (0.45-μm nominal pore size) and stored at 2 °C until analyzed. For selected samples from both arsenite and arsenate experiments, the solid phases obtained after centrifugation and filtration were freeze-dried. Diffuse reflectance FTIR spectra of these freeze-dried samples were recorded to check for possible transformation between arsenite and arsenate species. The spectra did not give any evidence of transformation of arsenic species.

The adherence of the adsorption data to Freundlich, simple Langmuir, and Temkin equations (23) was tested graphically.

Arsenic Adsorption Envelopes. Adsorption envelopes were obtained for both arsenite and arsenate in 0.1 M NaCl at initial As solution concentrations of 0.534, 1.60, and 26.7 mmol L^{-1} (corresponding to 0.267, 0.800, and $13.3 \text{ mol}_{As} \text{ kg}^{-1}$ ferrihydrite, respectively). The stock solutions of arsenite and arsenate were prepared having As concentrations of 2.67, 8.00, and 133 mmol L^{-1}. Five milliliters of As stock solution and 20 mL of 2.5 g L^{-1} ferrihydrite suspension, each buffered at the appropriate ionic strength (0.1 M NaCl), were added to 40-mL centrifuge tubes and purged with N_2. A given amount of 0.1 M HCl or NaOH was added to the centrifuge tubes in order to obtain final supernatant pH values in the range of 3–11. The centrifuge tube was purged with N_2, capped, and placed on a reciprocating shaker for 24 h. After equilibration, the suspension was centrifuged, the pH of the supernatant was measured, and the supernatant was passed through a membrane filter (0.45-μm nominal pore size) and stored at 2 °C until analyzed.

Arsenic Analyses. Arsenic analyses were obtained using a 3100 EDS atomic absorption spectrophotometer (Perkin Elmer Corporation, Norwalk, CT), with an electrodeless discharge lamp (EDL) as the radiation source. The matrices of standards and test solutions were matched in terms of NaCl concentration. The flame technique was used for solutions with As concentrations $>0.1 \text{ mmol L}^{-1}$, at a wavelength of 193.7 nm and with the absorbance signal averaged over 10 s. The hydride generation technique was used for solutions with As concentrations $<0.1 \text{ mmol L}^{-1}$. Twenty milliliters of test solution, consisting of 10 mL of 12 M HCl and 10 mL of sample solution, was used for each determination. The sample solution was transferred into a stoppered 500-mL separatory funnel that was used as the reaction vessel. Six milliliters of 3% NaBH$_4$ solution in 1% NaOH was then injected into the reaction vessel. The released H$_3$As was transported through Tygon tubing in a 3.5 L min^{-1}
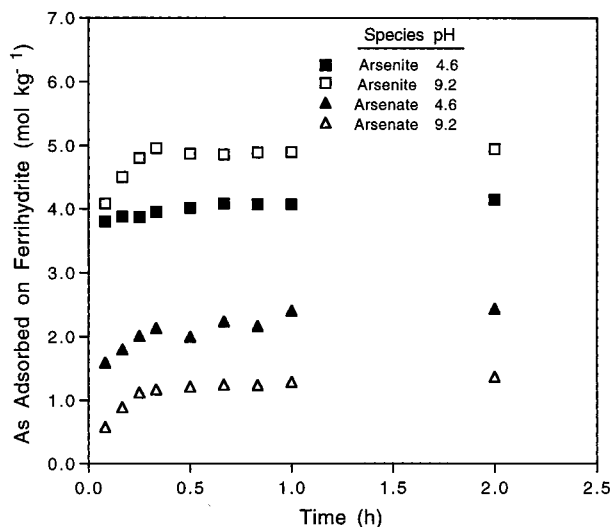
FIGURE 1. Kinetics of arsenite and arsenate adsorption by 2-line ferrihydrite in a 2 g L^{-1} suspension at pH 4.6 and pH 9.2 with an initial As addition of 13.3 mol_{As} kg_{fer}^{-1}.

FIGURE 2. Kinetics of arsenite and arsenate adsorption by 2-line ferrihydrite in a 2 g L^{-1} suspension at pH 4.6 and pH 9.2 with an initial As addition of 0.267 mol_{As} kg_{fer}^{-1}.

Ar stream to a quartz cell heated using a 5-cm burner head and centered in the optical beam of the spectrometer. The As atomized in the heated quartz cell was measured with 189.0 nm radiation. The absorbance peak area integrated over 45 s was used as the analytical signal. The As detection limit of the test solution was approximately 4.4 nmol L^{-1}. The accuracy of detection methods was ± 0.21 mg L^{-1} and ± 0.13 μg L^{-1} for flame and hydride generation techniques, respectively.

Results and Discussion

Adsorption Kinetics. With an initial arsenic solution concentration equivalent to 13.3 mol_{As} kg^{-1} ferrihydrite, arsenite adsorption was considerably faster, i.e., approximate equilibrium was achieved sooner than with arsenate. For example, after 2 h of reaction, arsenite adsorption was 99.7 and 98.3% of that at 96 h as compared to arsenate adsorption, which was only 79.6 and 83.4% of that at 96 h at pH 4.6 and 9.2, respectively (Figure 1). After 24 h, arsenate adsorption was 94.1 and 98.0% of that at 96 h, at pH 4.6 and 9.2, respectively. Fuller et al. (10) also reported the slow adsorption kinetics of arsenate on ferrihydrite after an initial rapid adsorption for 5 min. With an initial As solution concentration equivalent to 0.267 mol_{As} kg^{-1} ferrihydrite, after 1 h of reaction arsenate adsorption was 99.99 and 99.69% of that at 96 h as compared to arsenite adsorption, which was 99.55 and 99.96% of that at 96 h at pH 4.6 and 9.2, respectively (Figure 2). At this lower concentration of arsenic, arsenate adsorption equilibrium was more rapidly achieved at pH 4.6 (e.g., maximum adsorption occurred in less than 5 min) as compared to arsenite adsorption equilibrium, which was more rapidly achieved at pH 9.2. The different relative reaction rates at low and high initial As concentrations for arsenate adsorption could relate to previous EXAFS results (11–13), which have provided evidence that, at low surface coverage, arsenate is retained mainly by the formation of monodentate complexes on the iron oxide surface, and at high surface coverages 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 the predominantly monodentate reactions at low surface coverage. Similar EXAFS studies with arsenite have not been conducted. Our results are in general agreement with those of Pierce and Moore (6), who observed that the adsorption reaction was noticeably faster at low As concentrations and
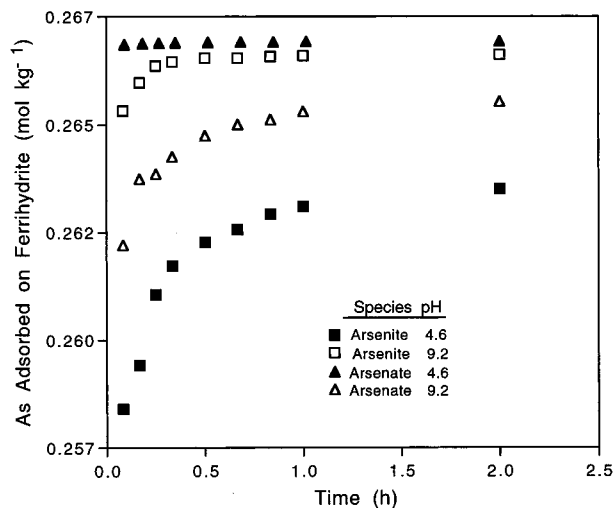
99% of the maximum observed arsenite and arsenate adsorption was complete within 4 h of reaction initiation. The conflicting results were obtained only at high pH. We observed that arsenite adsorption is faster than that of arsenate at pH 9.2, while Pierce and Moore (6) reported that arsenate adsorption was much faster than that of arsenite at pH 8.0 and pH 9.9. We do not have an explanation for this discrepency other than that it could be attributable to the different experimental conditions. In our studies, an adsorbent concentration of 2 g L^{-1}, a maximum As concentration of 26.6 mM and an ionic strength of 0.1 were used, compared to an adsorbent concentration of 0.00445 g L^{-1}, a maximum As concentration of 0.667 mM, and an ionic strength of 0.01 in the study of Pierce and Moore (6). Also, in their studies pH was not maintained constant during the experiment and final pH was considered as the experimental pH.

The As adsorption kinetic data in the current study were generally best described by the parabolic diffusion equation (Table 1). These results suggest that the reactions between arsenic and ferrihydrite were diffusion-controlled. Fuller et al. (10) reported that the time dependence of arsenate adsorption on ferrihydrite could be described by a general model for diffusion into a sphere if a subset of surface sites located near the exterior of aggregates is assumed to attain equilibrium rapidly. Orthophosphate diffusion into ferrihydrite particles has been verified by electron microprobe analysis (24); however, the diffusion of As into ferrihydrite particles has not been verified.

Adsorption Isotherms. Arsenite was generally adsorbed on ferrihydrite in larger amounts than arsenate at high As concentrations (Figure 3). At pH 4.6, only at As solution concentrations less than approximately 1 mol_{As} kg^{-1} ferrihydrite was arsenate adsorbed in equal or larger amounts than arsenite (Figure 4). At pH 9.2, arsenite was adsorbed in larger amounts than arsenate, even at the lowest As concentrations. The adsorption maxima for arsenate on the ferrihydrite corresponded to approximately 0.25 and 0.16 mol_{As} mol_{Fe}^{-1} at pH 4.6 and pH 9.2, respectively. In contrast, arsenite adsorption did not attain a maximum at either pH and at initial As concentrations in solution as high as 13.3 mol_{As} kg^{-1} ferrihydrite, and the highest observed adsorption density was about 0.60 mol_{As} mol_{Fe}^{-1} at each pH value. The highest adsorption density for arsenite exceeds the maximum number of surface sites (0.25 mol of sites per mol of Fe) (25) on hydrous iron oxides. Maximum adsorption densities of 0.25 and 0.11 mol_{As} mol_{Fe}^{-1} for arsenate were reported by

TABLE 1. Coefficients of Determination (r^2) for the Fit of the Time Dependence of Arsenite and Arsenate Adsorption on Ferrihydrite at pH 4.6 and pH 9.2 to Several Kinetic Models[a]

		arsenite		arsenate	
kinetic equation	linear plot[b]	pH = 4.6	pH = 9.2	pH = 4.6	pH = 9.2
first order	$\ln[1 - (As_t/As_\infty)]$ vs t	0.002	0.000	0.582	0.582
second order	$1/[1 - (As_t/As_\infty)]$ vs t	0.019	0.018	0.888	0.415
power function	$\ln(As_t)$ vs $\ln(t)$	0.262	0.169	0.916	0.688
simple elovich	As_t vs $\ln(t)$	0.258	0.165	0.949	0.825
parabolic diffusion	$(As_t/As_\infty)/t$ vs $t^{-0.5}$	0.904	0.930	0.947	0.977

[a] As was initially added at 13.3 mol kg^{-1} ferrihydrite. [b] Adapted from Sparks (1989); As_t, adsorbed As at time t. As_∞, adsorbed As at equilibrium. t, reaction time.
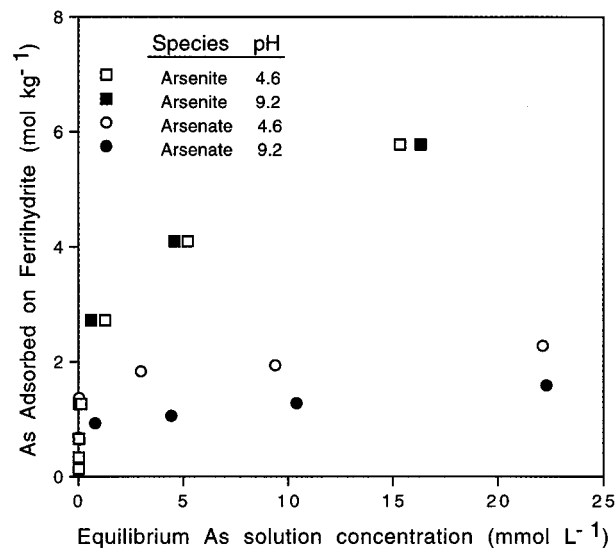

FIGURE 3. Adsorption isotherms for arsenite and arsenate by 2-line ferrihydrite in a 2 g L^{-1} suspension at pH 4.6 and pH 9.2.
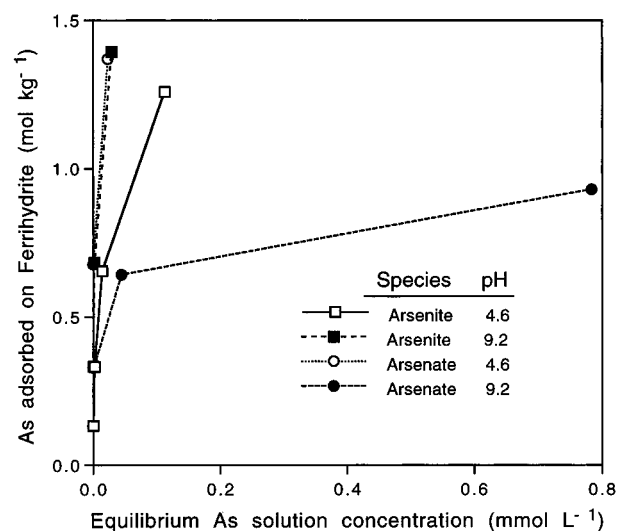

FIGURE 4. Adsorption isotherms for arsenite and arsenate by 2-line ferrihydrite in a 2 g L^{-1} suspension at pH 4.6 and pH 9.2 at low equilibrium As solution concentrations.

Fuller et al. (10) and Ferguson and Anderson (5), respectively. Pierce and Moore (6) reported extremely high adsorption maxima of approximately 5.0 mol$_{As}$ mol$_{Fe}^{-1}$ for both arsenite and arsenate. The extremely high adsorption densities in that study could be an experimental anamoly attributable to the high As to Fe ratios in solution, i.e., 15:1, used in their studies. Ferguson and Anderson (5) also reported that arsenite adsorption did not reach a state of saturation and observed a maximum adsorption density at 0.4 mol$_{As}$ mol$_{Fe}^{-1}$.

The different trends of adsorption isotherms for arsenite and arsenate suggest that something different than a strictly adsorption-controlled process might be occurring during arsenite adsorption. These very high arsenite retention levels preclude the possibility of its retention entirely as a surface-adsorbed monomeric species. It is possible that, upon reaction with arsenite, the ferrihydrite was reordered as a ferric arsenite phase, although this hypothesis would require verification by other means. On the contrary, recently Sun and Doner (17) have shown using FTIR spectroscopy that arsenite forms inner-sphere binuclear bridging complexes comparable to those with arsenate on the goethite surface.

Arsenate adsorption was higher at pH 4.6 than at pH 9.2 (Figures 3 and 4). At this pH the surface has a net positive charge that would attract $H_2AsO_4^-$ ions. At pH 9.2, the surface has a net negative charge and would tend to repulse the $HAsO_4^{2-}$ ions in solution. These electrostatic factors could influence both the kinetics and equilibrium of arsenate adsorption. At the lower equilibrium arsenite concentrations (Figure 4), adsorption at pH 9.2 was generally higher than at pH 4.6; however, at the higher equilibrium concentrations (Figure 3) approximately equivalent amounts of arsenite were adsorbed at pH 4.6 and pH 9.2. In the pH range of 4.6–9.2, neutral $H_3AsO_3^0$ ($pK_a = 9.2$) is the dominant As(III) species in solution. Therefore, the adsorption of As(III) would be less strongly influenced by the anion repulsion forces that would likely play an important role in the adsorption of As(V) species at high pH. Also, adsorption of neutral $H_3AsO_3^0$ would have less influence than the adsorption of negatively charged As(V) species on the total negative charge character of the ferrihydrite surface.

Overall, adsorption was best described by the Freundlich and Langmuir equations (Table 2), although these simple equations do not have any mechanistic implications (26).

Adsorption Envelopes. The adsorption envelopes for arsenite and arsenate at the lowest initial solution concentration equivalent to 0.267 mol$_{As}$ kg^{-1} ferrihydrite indicated adsorption of greater than 99.9% of the total arsenic added and corresponded to equilibrium As concentrations less than 40 μg L^{-1} throughout the pH range of 3.8–10 for arsenate and 5.5–10.5 for arsenite (Figure 5). The relatively strong retention of arsenite and arsenate in the presence of the 0.1 M NaCl ionic strength buffer suggests that each species was retained as an inner-sphere complex throughout the pH range of 4–10. With arsenite, there was a trend of increasing adsorption with increasing pH, with maximum adsorption corresponding to equilibrium-dissolved As concentrations of approximately 15 μg L^{-1} at pH 8.2–10. With arsenate, a different trend was observed, with a broad adsorption maximum at pH 3.8–7.4 corresponding to approximately 20 μg dissolved As L^{-1}. The adsorption envelopes crossed at approximately pH 7.5, i.e., at lower pH values arsenate was retained in larger amounts as compared to the greater retention of arsenite at pH >7.5. The reduction in adsorption of arsenite and arsenate at pH <4 and >10 is attributable to the increased solubility of ferrihydrite at these pH extremes

TABLE 2. Coefficients of Determination (r^2) for the Fit of Arsenite and Arsenate Adsorption Data on Ferrihydrite at pH 4.6 and pH 9.2 to Several Adsorption Isotherms

adsorption isotherm	linear plot[a]	arsenite		arsenate	
		pH = 4.6	pH = 9.2	pH = 4.6	pH = 9.2
Freundlich	ln(As$_A$) vs ln(As$_S$)	0.992	0.966	0.809	0.992
simple Langmuir	As$_S$/As$_A$ vs As$_S$	0.979	0.995	0.994	0.983
Temkin	As$_A$ vs ln(As$_S$)	0.799	0.916	0.976	0.956

[a] As$_A$, equilibrium adsorbed As; As$_S$, equilibrium As solution concentration.
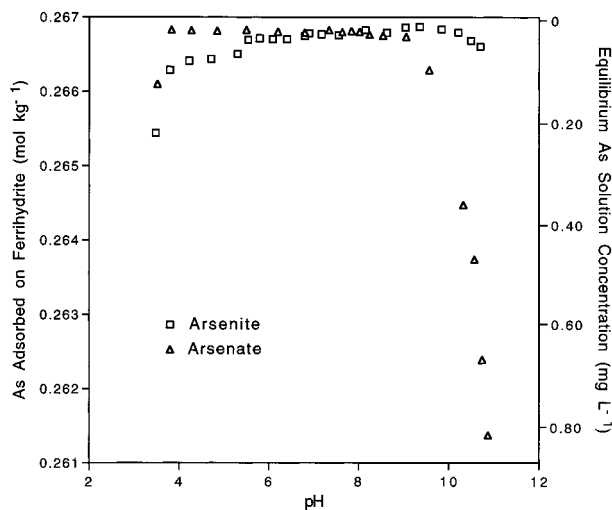
FIGURE 5. Adsorption envelopes for the reaction of arsenate and arsenite with 2-line ferrihydrite at 0.1 ionic strength following the addition of 0.267 mol$_{As}$ kg$_{fer}^{-1}$.
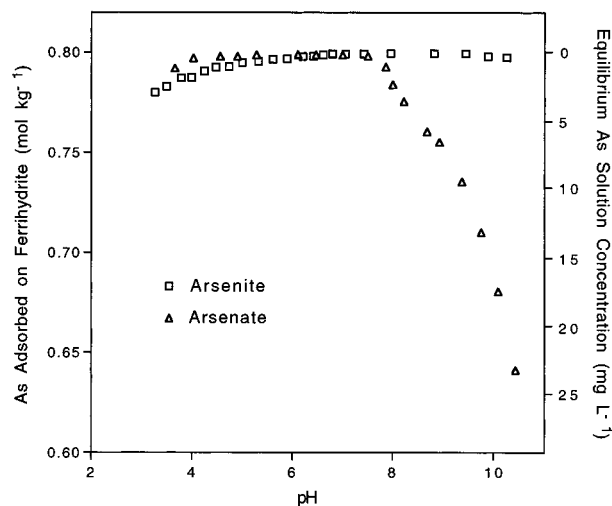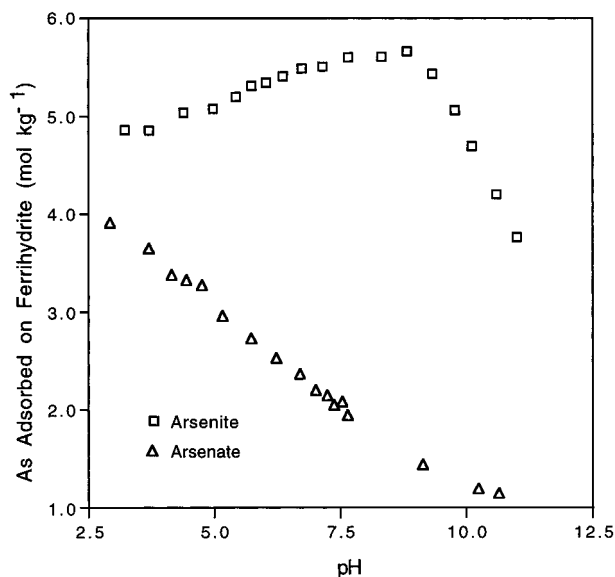

FIGURE 6. Adsorption envelopes for the reaction of arsenate and arsenite with 2-line ferrihydrite at 0.1 ionic strength following the addition of 0.80 mol$_{As}$ kg$_{fer}^{-1}$.

(27) and the resulting release of arsenic.

At the initial As solution concentration equivalent to 0.800 mol$_{As}$ kg^{-1} ferrihydrite, arsenate was adsorbed in larger quantities than arsenite below pH 7.0 whereas arsenite adsorption was significantly greater than arsenate above pH 7.0 (Figure 6). The adsorption envelopes exhibited broad adsorption maxima extending from approximately pH 6.8 to pH 9.4 for arsenite and from pH 5.2 to pH 7.0 for arsenate. In the latter case, there was a significant reduction in adsorption above pH 7.0, which coincided approximately with the second pK_a (6.9) of H$_3$AsO$_4$. Inflections or maxima in the adsorption envelopes of anions at pH values close to

FIGURE 7. Adsorption envelopes for the reaction of arsenate and arsenite with 2-line ferrihydrite at 0.1 ionic strength following the addition of 13.3 mol$_{As}$ kg$_{fer}^{-1}$.

their pK_a are a well-documented phenomenon (28). Arsenite adsorption did not decrease significantly until pH values were greater than 9.4.

At the highest initial solution concentration equivalent to 13.3 mol$_{As}$ kg^{-1} ferrihydrite, arsenite adsorption was higher than arsenate adsorption throughout the pH range of 3−11 (Figure 7). The amount of arsenate adsorbed by ferrihydrite decreased approximately linearly from 3.5 mol$_{As}$ kg^{-1} ferrihydrite at pH 4 to 1.2 mol$_{As}$ kg^{-1} at pH 10. The lower adsorption of arsenate at high pH values is attributable to an increased repulsion between the more negatively charged arsenate species and negatively charged surface sites. Since arsenite species have less negative charge character as compared to arsenate species at the same pH value, they do not exhibit as much repulsion, and as a result, the adsorption decreases less with increasing pH. At the highest initial arsenite solution concentration, a distinct adsorption maximum was observed at approximately pH 9. This adsorption maximum of the adsorption envelope was close to the first pK_a (9.2) of H$_3$AsO$_3^0$. The adsorption envelopes for arsenate obtained in this study were similar to those observed in the previous studies (4, 6, 9). Ferguson and Anderson (5) also reported that arsenite adsorption on iron oxide increased with an increase in the pH from 6 to 8. Pierce and Moore (6) reported adsorption envelopes of different shape for arsenite. At an initial As:Fe molar ratio of 1:0.74 in solution, they observed that arsenite adsorption decreased continuously with increasing pH from 4 to 10, while in our studies arsenite adsorption increased with increasing pH up to 9.0. Also, they observed adsorption maxima for arsenite at around pH 7.0 with an initial As:Fe molar ratio in the range of 0.014− 0.29 mol$_{As}$ mol$_{Fe}^{-1}$. In our studies, with a total As:Fe molar ratio of 0.028 and 0.083 mol$_{As}$ mol$_{Fe}^{-1}$, the adsorption maxima

occurred around pH 9.5. The disagreement might possibly be due to the different experimental conditions, as discussed earlier. The adsorption of arsenite on kaolinite, alumina, and bauxite was observed to increase with increasing pH from 4 to 9 (*29, 30*). Recently, Manning et al. (*31*) studied the adsorption of arsenite on kaolinite, illite, montmorillonite, and amorphous aluminum hydroxide as a function of pH and reported that maximum adsorption occurred in the pH range of 7.5−9.5.

The results of this study show that both arsenite and arsenate have strong affinities for ferrihydrite, and arsenite can be retained in much larger amounts than arsenate at high pH (approximately >7.5) or at high As concentrations in solution. Spectral evidence and structural data will be required to obtain molecular explanations for the high retention of arsenite by ferrihydrite.

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