

# Arsenate and Arsenite Adsorption and Desorption Behavior on Coprecipitated Aluminum:Iron Hydroxides

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Although arsenic adsorption/desorption behavior on aluminum and iron (oxyhydr)oxides has been extensively studied, little is known about arsenic adsorption/desorption behavior by bimetal Al:Fe hydroxides. In this study, influence of the Al:Fe molar ratio, pH, and counterion ( $\text{Ca}^{2+}$  versus  $\text{Na}^+$ ) on arsenic adsorption/desorption by preformed coprecipitated Al:Fe hydroxides was investigated. Adsorbents were formed by initial hydrolysis of mixed  $\text{Al}^{3+}/\text{Fe}^{3+}$  salts to form coprecipitated Al:Fe hydroxide products. At Al:Fe molar ratios  $\leq 1:4$ ,  $\text{Al}^{3+}$  was largely incorporated into the iron hydroxide structure to form a poorly crystalline bimetal hydroxide; however, at higher Al:Fe molar ratios, crystalline aluminum hydroxides (bayerite and gibbsite) were formed. Although approximately equal  $\text{As}^{\text{V}}$  adsorption maxima were observed for 0:1 and 1:4 Al:Fe hydroxides, the  $\text{As}^{\text{III}}$  adsorption maximum was greater with the 0:1 Al:Fe hydroxide.  $\text{As}^{\text{V}}$  and  $\text{As}^{\text{III}}$  adsorption decreased with further increases in Al:Fe molar ratio.  $\text{As}^{\text{V}}$  exhibited strong affinity to 0:1 and 1:4 Al:Fe hydroxides at pH 3–6. Adsorption decreased at pH  $> 6.5$ ; however, the presence of  $\text{Ca}^{2+}$  compared to  $\text{Na}^+$  as the counterion enhanced  $\text{As}^{\text{V}}$  retention by both hydroxides. There was more  $\text{As}^{\text{V}}$  and especially  $\text{As}^{\text{III}}$  desorption by phosphate with an increase in Al:Fe molar ratio.

## Introduction

Arsenic is toxic to animals and plants, and thus, its introduction to water by natural processes or human activities is of potential health, environmental, and ecological concern. In aqueous systems, inorganic arsenic exists in the 3+ and 5+ oxidation states as the respective oxyanions  $\text{H}_3\text{AsO}_3^\circ$  and  $\text{H}_3\text{AsO}_4^\circ$  and their hydrolysis species. The predominant arsenic speciation is strongly influenced by the redox potential and pH (1).  $\text{As}^{\text{V}}$  is usually dominant under oxidizing conditions, compared to  $\text{As}^{\text{III}}$  under reducing conditions. The  $\text{pK}_a$  values indicate that inorganic  $\text{As}^{\text{III}}$  exists predominately as  $\text{H}_3\text{AsO}_3^\circ$  ( $\text{pK}_{a1} = 9.2$ ,  $\text{pK}_{a2} = 12.1$ , and  $\text{pK}_{a3} = 12.7$ ) and inorganic  $\text{As}^{\text{V}}$  as  $\text{H}_2\text{AsO}_4^{2-}$  and  $\text{HASO}_4^{2-}$  ( $\text{pK}_{a1} = 2.3$ ,  $\text{pK}_{a2} = 6.9$ , and  $\text{pK}_{a3} = 11.5$ ) in natural aqueous environments (2).

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The distribution of arsenic is controlled by iron and aluminum hydroxides in most oxidized environments; therefore, arsenic adsorption by these minerals has been studied extensively. Adsorption of arsenic by iron and aluminum hydroxides is impacted by pH;  $\text{As}^{\text{V}}$  retention on ferrihydrite is usually maximum at pH 3–5, compared to the  $\text{As}^{\text{III}}$  retention maximum at approximately pH 8–10 (3, 4).  $\text{As}^{\text{V}}$  is readily adsorbed by aluminum hydroxides, whereas  $\text{As}^{\text{III}}$  is considerably less readily adsorbed (5). The  $\text{As}^{\text{V}}$  adsorption maximum on amorphous aluminum hydroxide occurs at approximately pH 4–4.5 (6).

The distinctive chemical and physical properties of coprecipitated Al:Fe hydroxides have been recognized relative to those of the pure end member aluminum and iron hydroxides (7). For example, when  $\text{Al}^{3+}$  and  $\text{Fe}^{3+}$  salts were coprecipitated at a 1:1 molar ratio at pH 8, an increase in point of zero charge, higher surface area, better retention of Zn, and reduced retention of Cd and Ag were observed compared to those of iron hydroxide alone (7). Retention of phosphate and selenite was unaffected by the presence of coprecipitated Al in the same study.

An understanding of the adsorption/desorption behavior of arsenic by coprecipitated Al:Fe is important in both natural environmental and water-treatment settings. In soils, the majority of iron (hydr)oxides are Al-substituted (8); therefore, arsenic retention by Al-substituted iron hydroxide needs to be resolved to fully understand arsenic retention in soil. In water treatment, coprecipitation of Al and Fe during coagulation processes might be advantageous for arsenic removal and waste management compared to the traditional coagulation processes with Al or Fe alone. Iron hydroxide is usually considered to be a superior arsenic adsorbent compared to aluminum hydroxide (9–11); however, iron hydroxide and adsorbed arsenic in contaminated water-treatment residual can transform into soluble forms due to redox processes involving Fe (12). Coprecipitated Al:Fe hydroxides might be advantageous for waste management since the rate of reductive dissolution of iron hydroxide is usually slower when Al is substituted within iron hydroxides. For example, a bacterial reductive-dissolution study comparing Al-substituted goethite and pure goethite indicated a slower rate of dissolution when Al was substituted in goethite (13). An increase of Al substitution in hematite and goethite also decreased the rate of reductive dissolution by dithionite (14). Furthermore, arsenic removal was enhanced during concurrent coprecipitation of  $\text{As}^{\text{V}}$  with Fe and Al at a 1:1 Al:Fe molar ratio compared to either Fe or Al alone at circumneutral pH (15). An improved understanding of arsenic adsorption/desorption behavior by coprecipitated Al:Fe hydroxides is needed to fully assess the potential utility of these phases for arsenic treatment and waste management. Here we examine  $\text{As}^{\text{V}}$  and  $\text{As}^{\text{III}}$  adsorption/desorption by preformed coprecipitated Al:Fe hydroxides as affected by Al:Fe molar ratio and pH. The effect of counterion ( $\text{Ca}^{2+}$  versus  $\text{Na}^+$ ) on arsenic adsorption by Al:Fe hydroxides is also examined.

## Materials and Methods

**Synthesis of Ferrihydrite and Coprecipitated Al:Fe Hydroxides.** A series of Al:Fe hydroxides was prepared at 0:1 (0% Al), 1:4 (20% Al), 1:2.3 (30% Al), 1:1.5 (40% Al), 1:1 (50% Al), and 1:0 (100% Al) Al:Fe molar ratios. Mixtures of  $\text{Fe}(\text{NO}_3)_3$  and  $\text{Al}(\text{NO}_3)_3$  solutions (0.1 M total Al + Fe) were hydrolyzed using 1 M NaOH with vigorous stirring. The products were adjusted to pH 7.5 and dialyzed against deionized water. The point of zero charge (pzc) of each

product was determined by the point of zero salt effect (PZSE) method from the intersection of batch acid–base titration curves using 0.0001, 0.01, and 1 M NaCl ionic strength buffers (16). X-ray diffraction patterns of powder samples of hydroxides were obtained using a Philips diffractometer with graphite-monochromated Cu K $\alpha$  radiation.

The 0:1 and 1:4 Al:Fe hydroxides used to investigate the effect of counterion were prepared by hydrolyzing Fe(NO<sub>3</sub>)<sub>3</sub> and Al(NO<sub>3</sub>)<sub>3</sub> solutions (0.004 M total Al + Fe) to pH 7.5 using either colloid-free saturated Ca(OH)<sub>2</sub> or 0.1 M NaOH.

**Arsenic Analysis.** Arsenic was analyzed by flow-injection hydride-generation flame-atomic-absorption spectrometry (FI-HG-FAAS) (17). The arsenic detection limit was 0.5  $\mu\text{g L}^{-1}$  with a 95% confidence level. The samples were centrifuged and filtered through 0.2  $\mu\text{m}$  nominal pore-size membrane filters prior to analysis.

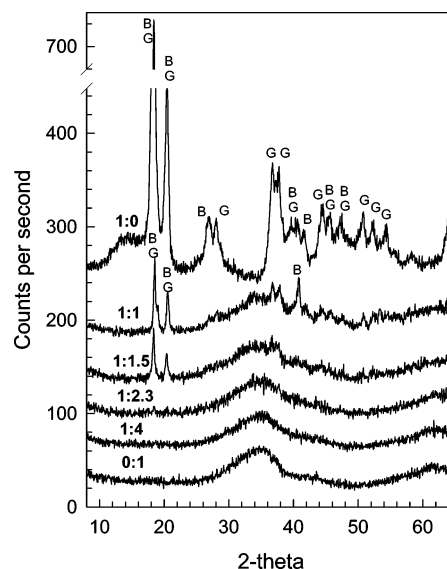
**Arsenic Adsorption Isotherms.** Adsorption isotherms of As<sup>V</sup> and As<sup>III</sup> on 0:1, 1:4, 1:1, and 1:0 Al:Fe hydroxides were obtained as batch experiments at pH 5 and 8 with the Al + Fe concentration fixed at 267  $\mu\text{M}$  as Al:Fe hydroxide and arsenic concentrations ranging from 3 to 133  $\mu\text{M}$ . The pH values of individual samples were adjusted by adding HCl or NaOH. The samples were allowed to react for 24 h on a reciprocating platform shaker.

The arsenic adsorption behavior was evaluated using the Langmuir adsorption maximum ( $b$ ) and binding constant ( $K_L$ ) from each isotherm, calculated by linear regression analysis of the Langmuir function  $C/q = (1/K_L b) + (C/b)$ , where  $C$  is the final dissolved arsenic concentration (mM) following 24 h of reaction and  $q$  is the amount of arsenic adsorbed by Al:Fe hydroxide ( $\text{mol}_{\text{As}} \text{mol}_{\text{Al+Fe}}^{-1}$ ). The last two data points in each isotherm were not included in the Langmuir calculations.

**Arsenic Adsorption Envelopes.** Adsorption envelopes of As<sup>V</sup> and As<sup>III</sup> on 0:1, 1:4, 1:1, and 1:0 Al:Fe hydroxides in 0.1 M NaCl were obtained as batch experiments at an As:(Al + Fe) molar ratio of 1:20 (13.4  $\mu\text{M}$  As and 267  $\mu\text{M}$  Al + Fe). The pH values of individual samples were adjusted between 3 and 11 using HCl or NaOH, and samples were allowed to react for 24 h on a reciprocating platform shaker. Upon centrifugation, the final pH values of the supernatant solutions were obtained.

**Arsenic Desorption Envelopes.** Arsenic desorption with phosphate as the desorbing ligand was studied at a 7500:1:20 P:As:(Al + Fe) molar ratio to ensure a large excess of phosphate with respect to both total arsenic and Al:Fe hydroxide surface site concentration. Arsenic was first adsorbed by 0:1, 1:4, 1:1, and 1:0 Al:Fe hydroxides in 0.1 M NaCl at a 1:20 As:(Al + Fe) molar ratio (26.7  $\mu\text{M}$  As and 534  $\mu\text{M}$  Al + Fe) for 24 h at pH 5.2 for As<sup>V</sup> and at pH 8.5 for As<sup>III</sup>. As<sup>III</sup> desorption from 1:0 Al:Fe hydroxide was not studied due to negligible adsorption of As<sup>III</sup>. Subsamples were taken from each suspension before phosphate addition to determine the amount of arsenic adsorbed. Desorption envelopes were obtained in batch experiments by adding 10 mL of 0.2 M sodium phosphate solution (pH was preadjusted to obtain a range of pH values from 3 to 11) to 10 mL of arsenic-adsorbed Al:Fe hydroxide suspensions (final concentrations 13.35  $\mu\text{M}$  As, 267  $\mu\text{M}$  Al + Fe, and 0.1 M sodium phosphate). Deionized water was added to a separate arsenic-adsorbed Al:Fe hydroxide suspension as a control. Each sample was allowed to react for 24 h on a rotary platform shaker. The samples were centrifuged, and the pH values of the supernatant solutions were obtained. The amount of desorbed arsenic was calculated relative to the amount of arsenic adsorbed prior to the desorption experiment.

**Arsenate Adsorption as Affected by the Counterion.** Adsorption envelopes of As<sup>V</sup> on 0:1 and 1:4 Al:Fe hydroxides, which had previously been prepared with Ca<sup>2+</sup> and Na<sup>+</sup> as



**FIGURE 1.** XRD patterns of the 0:1 (0% Al), 1:4 (20% Al), 1:2.3 (30% Al), 1:1.5 (40% Al), 1:1 (50% Al), and 1:0 (100% Al) coprecipitated Al:Fe hydroxides, obtained using graphite-monochromated Cu K $\alpha$  radiation. Major peaks attributable to bayerite and gibbsite are indicated as B and G, respectively.

the counterion, were obtained using Ca(NO<sub>3</sub>)<sub>2</sub> or NaNO<sub>3</sub> ionic strength buffers, respectively. The As:(Al + Fe) molar ratio was 1:10 (13.4  $\mu\text{M}$  As and 133.5  $\mu\text{M}$  Al + Fe), and the concentrations of Ca and Na were fixed at 100, 10, and 1 mM to examine the effect of counterion concentration. The pH values of separate samples were adjusted by adding HNO<sub>3</sub> or NaOH to obtain a pH range of 3–11 for the adsorption envelopes. Samples were reacted and analyzed as discussed above.

## Results and Discussion

**Properties of Al:Fe Hydroxides.** The 1:4 (20% Al) Al:Fe hydroxide resulted in an XRD pattern almost identical to that of the 0:1 Al:Fe hydroxide (two-line ferrihydrite) (Figure 1) (8). This result indicates that the Al<sup>3+</sup> was largely incorporated into the ferrihydrite structure as a solid solution, up to approximately a 1:4 Al:Fe molar ratio. Peaks at  $2\theta = 18.8$  and  $20.3^\circ$ , indicative of crystalline aluminum hydroxides, appeared as a trace in the 1:2.3 Al:Fe hydroxide and as distinct bands in the 1:1.5 Al:Fe hydroxide. These peaks were considerably more evident upon aging of the 1:2.3 Al:Fe molar ratio sample for 1 month at 4  $^\circ\text{C}$  but were not observed upon aging of the 1:4 molar ratio sample (Supporting Information Figure 1). Bayerite and gibbsite were identified as products at Al:Fe molar ratios  $\geq 1:2.3$ , although broad background peaks indicative of poorly crystalline hydroxide were also evident with these phases (Figure 1). In subsequent discussions, 0:1 (two-line ferrihydrite), 1:4 (20% Al-substituted ferrihydrite), 1:1 (mixture of crystalline aluminum hydroxides and poorly crystalline aluminum and iron hydroxides), and 1:0 (mixture of crystalline and poorly crystalline aluminum hydroxides) samples were used to represent the range of Al:Fe hydroxide mineralogy.

The pzc values of the 0:1, 1:4, 1:1, and 1:0 Al:Fe hydroxides were pH 7.6, 8.2, 8.7, and 8.9, respectively, indicating greater pzc with increasing Al:Fe molar ratio (Supporting Information Figure 2). The pzc of pristine gibbsite is pH 9.5–10, and that of ferrihydrite is pH 7–9, as reported by previous researchers (8, 18). Coprecipitated 1:1 Al:Fe hydroxide was previously observed to have a pzc of 9.1, as determined by electrophoresis (7).

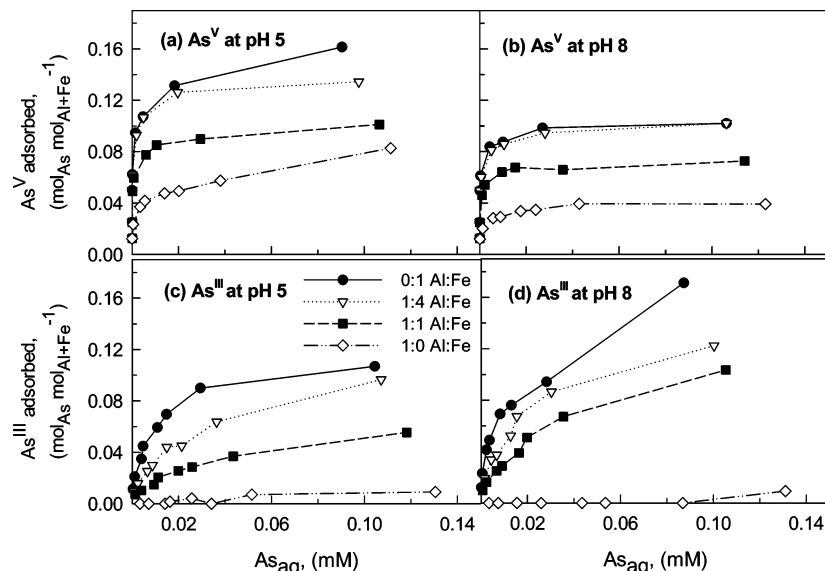


FIGURE 2. Adsorption isotherms of arsenic on the 0:1, 1:4, 1:1, and 1:0 Al:Fe hydroxides (267  $\mu\text{M}$  Al + Fe) in 0.1 M NaCl: (a)  $\text{As}^{\text{V}}$  at pH 5, (b)  $\text{As}^{\text{V}}$  at pH 8, (c)  $\text{As}^{\text{III}}$  at pH 5, and (d)  $\text{As}^{\text{III}}$  at pH 8.

TABLE 1. Binding Constants ( $K_L$ ), Adsorption Mixima ( $b$ ), and Correlation Coefficients ( $r^2$ ) of the Langmuir Function for Adsorption of  $\text{As}^{\text{V}}$  and  $\text{As}^{\text{III}}$  by Al:Fe Hydroxides

pH	adsorbent	$\text{As}^{\text{V}}$			$\text{As}^{\text{III}}$		
		$K_L$ ( $\text{mmol}_{\text{As}} \text{L}^{-1}$ )	$b$ ( $\text{mol}_{\text{As}} \text{mol}_{\text{Al+Fe}}^{-1}$ )	$r^2$	$K_L$ ( $\text{mmol}_{\text{As}} \text{L}^{-1}$ )	$b$ ( $\text{mol}_{\text{As}} \text{mol}_{\text{Al+Fe}}^{-1}$ )	$r^2$
5	0:1 Al/Fe	23298	0.1073	0.9985	288	0.0812	0.9574
	1:4 Al/Fe	15691	0.1062	0.9968	159	0.0577	0.9560
	1:1 Al/Fe	6219	0.0846	0.9971	104	0.0377	0.9168
	1:0 Al/Fe	1376	0.0505	0.9971			
8	0:1 Al/Fe	14266	0.0876	0.9996	565	0.0843	0.9824
	1:4 Al/Fe	9713	0.0858	0.9989	200	0.0785	0.9050
	1:1 Al/Fe	3422	0.0680	0.9982	145	0.0598	0.8828
	1:0 Al/Fe	910	0.0358	0.9957			

**Arsenic Adsorption Isotherms.**  $\text{As}^{\text{V}}$  adsorption isotherms with the 0:1 and 1:4 Al:Fe hydroxides were similar up to approximately 0.02 mM  $\text{As}^{\text{V}}_{\text{aq}}$ , but  $\text{As}^{\text{V}}$  adsorption was generally lower with further increases in Al:Fe molar ratio (Figure 2a,b). At both pH 5 and 8 with the 0:1 and 1:4 Al:Fe hydroxides,  $\text{As}^{\text{V}}_{\text{aq}}$  concentrations were less than 5  $\mu\text{g L}^{-1}$  (0.066  $\mu\text{M}$  As) at As adsorption up to 0.05  $\text{mol}_{\text{As}} \text{mol}_{\text{Al+Fe}}^{-1}$ , compared to the 1:1 Al:Fe hydroxide, which maintained this low of arsenic concentration in solution only at adsorbed  $\text{As}^{\text{V}}$  concentrations less than 0.025  $\text{mol}_{\text{As}} \text{mol}_{\text{Al+Fe}}^{-1}$ . In general, Langmuir  $\text{As}^{\text{V}}$  adsorption maxima ( $b$ ) decreased as Al:Fe molar ratio was increased, except in the case of  $\text{As}^{\text{V}}$  adsorption with the 0:1 and 1:4 Al:Fe molar ratio hydroxides (Table 1). Langmuir binding constant ( $K_L$ ) decreased with increasing Al:Fe molar ratio, indicating a decrease in relative  $\text{As}^{\text{V}}$  bonding strength with increasing Al:Fe molar ratio.

The lower  $\text{As}^{\text{V}}$  adsorption with 1:1 and 1:0 Al:Fe hydroxides is partially attributable to the lower concentration of surface-adsorption sites associated with bayerite and gibbsite components. Bayerite and gibbsite are relatively inert because all of the  $\text{OH}^-$  groups on the planar surfaces and half of the  $\text{OH}^-$  groups at the crystal edges are doubly coordinated to two surface structural  $\text{Al}^{3+}$ , charge satisfied, and probably unavailable for ligand exchange (18).

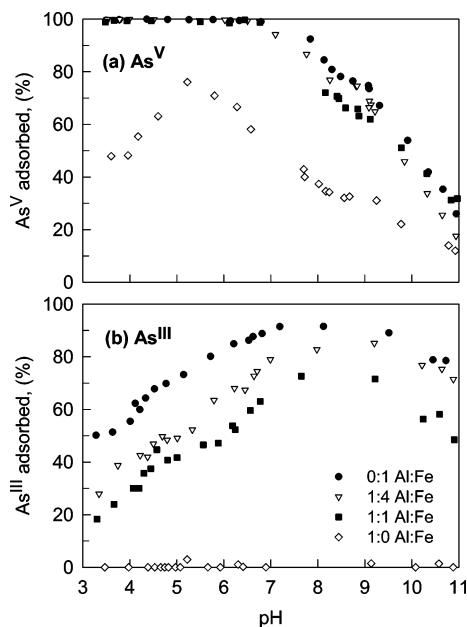
$\text{As}^{\text{III}}$  was not quantitatively adsorbed by any of the Al:Fe hydroxides, and adsorption decreased with increasing Al:Fe molar ratio at all  $\text{As}^{\text{III}}_{\text{aq}}$  concentrations.  $\text{As}^{\text{III}}$  adsorption on the 1:0 Al:Fe hydroxide was negligible under any condition (Figure 2c,d). The Langmuir  $\text{As}^{\text{III}}$  adsorption maximum ( $b$ )

decreased as Al:Fe molar ratio was increased, with a prominent reduction in  $b$  for 1:4 Al:Fe hydroxide compared to 0:1 Al:Fe hydroxide that was not observed for  $\text{As}^{\text{V}}$  (Table 1).  $\text{As}^{\text{III}}$  adsorption was higher at pH 8 compared to pH 5, which is opposite the trend observed for  $\text{As}^{\text{V}}$ . Langmuir binding constants ( $K_L$ ) decreased with increasing Al:Fe molar ratio.

The substantial decrease in  $\text{As}^{\text{III}}$  retention at a higher Al:Fe molar ratio and the negligible  $\text{As}^{\text{III}}$  adsorption by 1:0 Al:Fe hydroxide indicate that  $\text{As}^{\text{III}}$  retention on Al:Fe hydroxides must be attributable to adsorption at Fe surface sites. The weak affinity for  $\text{As}^{\text{III}}$  to gibbsite and amorphous aluminum hydroxide and a relatively slow kinetics of  $\text{As}^{\text{III}}$  adsorption by gibbsite have been reported previously (19, 20).

**Arsenic Adsorption Envelopes.**  $\text{As}^{\text{V}}$  adsorption on 0:1, 1:4, and 1:1 Al:Fe hydroxides followed similar trends with respect to pH (Figure 3a); maximum and approximately quantitative adsorption occurred at pH 3–7.  $\text{As}^{\text{V}}$  adsorption decreased gradually at pH > 7. Maximum  $\text{As}^{\text{V}}$  adsorption on ferrihydrite at pH < 7 has been reported previously (3, 4).  $\text{As}^{\text{V}}$  was never quantitatively adsorbed by 1:0 Al:Fe hydroxide, with a maximum of 76% of the added  $\text{As}^{\text{V}}$  adsorbed at pH 5.2. The pH ranges of maximum  $\text{As}^{\text{V}}$  adsorption were not appreciably affected by differences in pzc among 0:1, 1:4, and 1:1 Al:Fe hydroxides (pH at pzc = 7.6, 8.2, and 8.7, respectively).

$\text{As}^{\text{III}}$  adsorption decreased substantially with increasing Al:Fe molar ratio, and  $\text{As}^{\text{III}}$  adsorption by the 1:0 Al:Fe hydroxide was negligible across the entire pH range (Figure

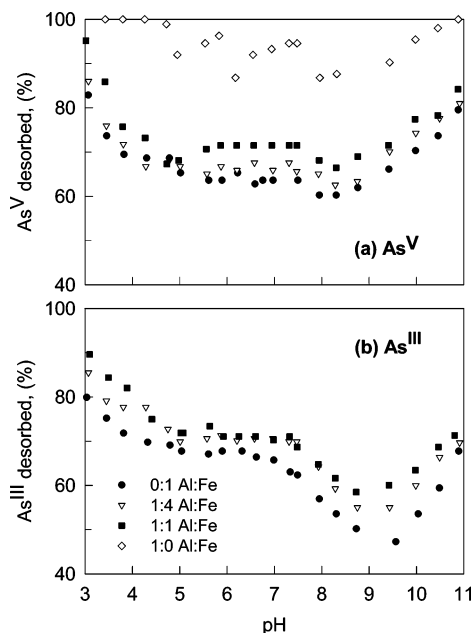


**FIGURE 3.** Adsorption envelopes of arsenic by 0:1, 1:4, 1:1, and 1:0 Al:Fe hydroxides (13.4  $\mu\text{M}$  As and 267  $\mu\text{M}$  Al + Fe) in 0.1 M NaCl at an As:(Al + Fe) molar ratio of 1:20 with (a) As<sup>V</sup> and (b) As<sup>III</sup>. The pH values are the final pH values measured upon 24 h of reaction.

3b). Maximum As<sup>III</sup> adsorption was observed at pH 7–9 with the 0:1, 1:4, and 1:1 Al:Fe hydroxides. An As<sup>III</sup> adsorption maximum in this pH range has previously been reported for ferrihydrite (3, 4). At pH 8, the 0:1, 1:4, and 1:1 Al:Fe hydroxides adsorbed 92%, 83%, and 72%, respectively, of the initially added As<sup>III</sup>. The pH ranges of maximum As<sup>III</sup> adsorption were also not appreciably affected by differences in pzc of 0:1, 1:4, and 1:1 Al:Fe hydroxides.

At pH < 7, As<sup>V</sup> adsorption is likely predominantly attributable to ligand exchange with surface OH<sub>2</sub> rather than surface OH<sup>−</sup> groups, since the surface OH<sub>2</sub> group is more conducive than the charged OH<sup>−</sup> group to desorption from a positively charged surface. As<sup>V</sup> adsorption around pH 7 might also involve an intermediate step in which H<sup>+</sup> dissociation from As<sup>V</sup> ( $\text{p}K_{\text{a}_2} = 6.9$ ) facilitates protonation of Al:Fe hydroxide surface OH<sup>−</sup> to form OH<sub>2</sub>. The optimal As<sup>III</sup> adsorption at pH 7–9 might be at least partially attributable to an intermediate protonation of Al:Fe hydroxide surface OH<sup>−</sup> sites at pH values near the  $\text{p}K_{\text{a}_1}$  of H<sub>3</sub>AsO<sub>3</sub><sup>°</sup> (9.2). Enhanced retention of an oxyanion around its  $\text{p}K_{\text{a}}$  values is a well-recognized phenomenon (21).

Decreased As<sup>V</sup> and As<sup>III</sup> retention at pH > 7 and pH > 9, respectively, is also likely due to increased electrostatic repulsion between negatively charged arsenic species and the Al:Fe hydroxide surface. The difference in the pH range of maximum As<sup>V</sup> adsorption of the 1:0 hydroxide compared with the Al:Fe hydroxides (Figure 3a) is likely influenced by the solubility of aluminum hydroxide. Aluminum hydroxide is subject to enhanced dissolution at low pH (i.e., pH < 4.5) (22), which likely contributed to the decreased As<sup>V</sup> adsorption. A similar trend in As<sup>V</sup> adsorption by amorphous aluminum hydroxide as a function of pH was observed by Anderson et al. (6). The sharp decrease in As<sup>V</sup> adsorption by the 1:0 Al:Fe hydroxide at pH > 5.2 could be partially due to an increased electrostatic repulsion between As<sup>V</sup> species and the aluminum hydroxide. Though the measured pzc of the 1:0 Al:Fe hydroxide was pH 8.9, a specifically adsorbed anion can shift the pzc of the hydroxide surface to lower pH values, making the surface charge at a given pH more negative (23). For example, the isoelectric point decreased from pH 8.5 to



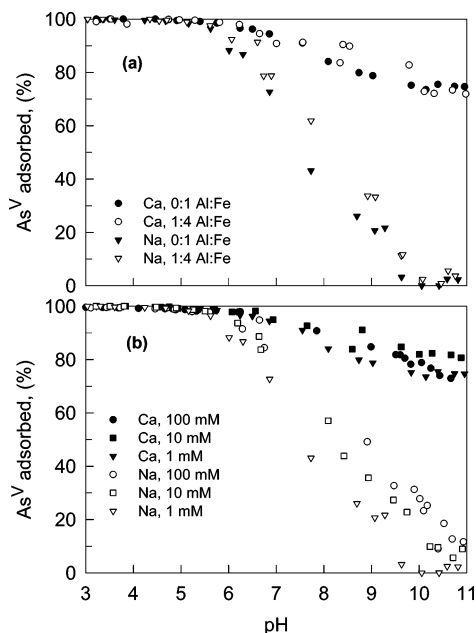
**FIGURE 4.** Desorption envelopes of arsenic from 0:1, 1:4, 1:1, and 1:0 Al:Fe hydroxides with sodium phosphate at a 7500:1:20 P:As:(Al + Fe) molar ratio (267  $\mu\text{M}$  Al + Fe) with (a) As<sup>V</sup> and (b) As<sup>III</sup>. The pH values are the final pH values measured upon 24 h of reaction.

pH 4.6 as increasing amounts of As<sup>V</sup> were added to amorphous aluminum hydroxide (6). The pzc of As<sup>V</sup>-treated ferrihydrite was at pH 6.1 compared to that of ferrihydrite at pH 8.5 (24). The pzc of the other hydroxides would also have been lowered due to As<sup>V</sup> adsorption; however, a sharp decrease in adsorption was not observed, probably because of the higher concentration of adsorption sites per unit weight of adsorbent with the poorly crystalline Fe-containing hydroxides (0:1, 1:4, and 1:1 Al:Fe hydroxides).

**Arsenic Desorption Envelopes.** More As<sup>V</sup> and As<sup>III</sup> were desorbed by phosphate with increasing Al:Fe molar ratio (Figure 4). Both As<sup>V</sup> and As<sup>III</sup> were more readily desorbed from Al surface sites than from Fe sites, which is substantiated by the almost total desorption of As<sup>V</sup> from the 1:0 Al:Fe hydroxide across the entire pH range. Greater desorption from Al<sup>3+</sup> sites was the most noticeable with As<sup>III</sup> and is attributable to the weak affinity and probable outer-sphere bonding of As<sup>III</sup> by aluminum (hydr)oxides (19, 20, 25).

The 0:1, 1:4, and 1:1 Al:Fe hydroxides followed almost identical desorption trends with pH for both As<sup>V</sup> and As<sup>III</sup>. Although appreciable As<sup>III</sup> and As<sup>V</sup> were retained across the entire pH range with 0:1, 1:4, and 1:1 Al:Fe hydroxides, desorption was greatest at low and high pH extremes (Figure 4). Minimum As<sup>V</sup> and As<sup>III</sup> desorption was observed at approximately pH 8 and 9.5, respectively. The pH of minimum As<sup>III</sup> desorption corresponded with the pH of maximum As<sup>III</sup> adsorption by Al:Fe hydroxide (Figure 3b) and the  $\text{p}K_{\text{a}_1}$  of H<sub>3</sub>AsO<sub>3</sub><sup>°</sup> (9.2). As<sup>V</sup> desorption was similar among Al:Fe hydroxides across the pH range of 5–8, with the lowest As<sup>V</sup> desorption at pH 8. Greater metal hydroxide solubility at the pH extremes (22) and an accelerated rate of ligand exchange at these pH values could lead to enhanced As<sup>V</sup> and As<sup>III</sup> desorption (23). Additionally, increased As<sup>V</sup> and As<sup>III</sup> desorption at pH < 5 could be partially attributable to a stronger competition by phosphate due to strong phosphate adsorption at this pH (26). During the 24 h reaction with deionized water, 0%, 0.1%, 0.3%, and 1.2% of As<sup>V</sup> and 2.7%, 3.7%, and 9.1% of As<sup>III</sup> were desorbed from 0:1, 1:4, 1:1, and 1:0 Al:Fe hydroxides, respectively (As<sup>III</sup> desorption from the 1:0 Al:Fe





**FIGURE 5.** Adsorption envelopes of As<sup>V</sup> as affected by Ca and Na at a 1:10 As:(Al + Fe) molar ratio (13.4  $\mu$ M As and 133.5  $\mu$ M Al + Fe) with (a) 0:1 and 1:4 Al:Fe hydroxides in 1 mM Ca or Na and (b) 0:1 Al:Fe hydroxide in 100, 10, and 1 mM Ca or Na. The pH values are the final pH values measured upon 24 h of reaction.

hydroxide was not determined due to its negligible original adsorption). Both As<sup>V</sup> desorption and As<sup>III</sup> desorption were achieved via ligand exchange by phosphate. In the absence of the exchange ligand, i.e., in deionized water, desorption of As<sup>V</sup> and As<sup>III</sup> was considerably lower.

**Arsenate Adsorption as Affected by Counterion.** Retention of As<sup>V</sup> by 0:1 and 1:4 Al:Fe hydroxides decreased more rapidly as pH was increased above 7 in the presence of Na compared to Ca (Figure 5a). With the Ca system, approximately 70% of As<sup>V</sup> remained on the 0:1 and 1:4 Al:Fe hydroxides at pH 11, compared to negligible As<sup>V</sup> remaining on the Al:Fe hydroxides with Na<sup>+</sup> as the counterion. Enhanced retention of arsenic by soil and aluminum and iron hydroxides in the presence of Ca has been reported previously (27–30). Maximum As<sup>V</sup> adsorption on 0:1 and 1:4 Al:Fe hydroxides was obtained at pH 3–5 with both counterions at a 1:10 As:(Al + Fe) molar ratio (Figure 5a), compared to the maximum As<sup>V</sup> adsorption at pH 3–7 in the previous adsorption envelopes conducted at a 1:20 As:(Al + Fe) molar ratio in 0.1 M NaCl (Figure 3a). The narrower pH range of maximum As<sup>V</sup> retention here is attributable to the higher As:(Al + Fe) molar ratio. Adsorption maxima of As<sup>V</sup> were also greater in 100 mM Ca compared to Na at both pH 5 and pH 8, on the basis of the As<sup>V</sup> adsorption isotherms with 0:1 and 1:4 Al:Fe hydroxides (Supporting Information Figure 3). As<sup>III</sup> adsorption by 0:1 and 1:4 Al:Fe hydroxides was also enhanced at pH > 8.5 in the presence of Ca (Supporting Information Figure 4).

There was no consistent effect of Ca concentration on As<sup>V</sup> adsorption; however, As<sup>V</sup> adsorption increased slightly with increasing Na concentration at pH > 7.5 (Figure 5b). This Na concentration effect is attributable to a diffuse double-layer phenomenon, by which increased Na concentration would result in reduced repulsive potential between the negatively charged hydroxide surface and the negatively charged oxyanion at pH > 7.5.

Strong retention of As<sup>V</sup> at pH > 5 in the presence of Ca compared to Na is likely attributable to reduced repulsive potentials in the presence of the divalent counterion Ca<sup>2+</sup>.

The more rapid decay in electrical potential with distance from the surface with the divalent Ca<sup>2+</sup> system compared to the monovalent Na<sup>+</sup> system would result in reduced repulsive potential between the negatively charged hydroxide surface and the negatively charged As<sup>V</sup> species (21). Adsorption of Ca<sup>2+</sup> might also contribute to a reduced negative charge on the Al:Fe hydroxide surface and hence provide conditions more favorable for As<sup>V</sup> adsorption compared to conditions with the Na<sup>+</sup> system (29). Another possible explanation for the impact of Ca on enhanced As<sup>V</sup> retention is Ca–As<sup>V</sup> precipitation. Ca–As<sup>V</sup> precipitation is favored at alkaline pH (31), and increased As<sup>V</sup> retention in cement-treated sludge containing Ca–As<sup>V</sup> solid at pH 9.5–12 has been reported (32). Although Ca–As<sup>V</sup> precipitation could explain greater As<sup>V</sup> retention in the presence of Ca, this process is not likely playing a significant role in the current study. If Ca–As<sup>V</sup> precipitation were controlling As<sup>V</sup> retention, an increase in pH and Ca concentration should have favored increased Ca–As<sup>V</sup> precipitation and resulted in greater As<sup>V</sup> retention; however, this phenomenon was not observed. The gradual and continuous decrease in As<sup>V</sup> retention with increasing pH suggests that surface charge is a major factor impacting the retention of As<sup>V</sup> (29). Enhanced PO<sub>4</sub><sup>3−</sup> adsorption by goethite at pH > 7 in the presence of Ca has also been observed under conditions where Ca–PO<sub>4</sub> precipitation is not favored (33). Spectroscopic evidence will be required to verify the mechanism of enhanced As<sup>V</sup> retention in the presence of Ca<sup>2+</sup>.

**Environmental Implications.** Differences in As<sup>V</sup> and As<sup>III</sup> adsorption as affected by Al:Fe molar ratio of the hydroxide were observed. When the majority of Al<sup>3+</sup> was substituted in the ferrihydrite structure, i.e., without evidence of separate aluminum hydroxide phases, the difference in As<sup>V</sup> adsorption compared to that by pure iron hydroxide was negligible. As<sup>V</sup> adsorption decreased as Al:Fe molar ratio increased once the maximum Al substitution in iron hydroxide was achieved. In contrast, As<sup>III</sup> adsorption decreased with an increase in Al content, even when the Al appeared to be quantitatively substituted in the ferrihydrite structure.

In soils, where iron (hydr)oxides often have appreciable Al substitution, As<sup>III</sup> might not be retained to the same extent as that observed with pure iron hydroxides, as shown by the decrease in As<sup>III</sup> retention and increase in As<sup>III</sup> desorption with an increase in Al:Fe molar ratio. On the contrary, Al substitution in iron hydroxides might not be a limiting factor for As<sup>V</sup> adsorption in soils, although As<sup>V</sup> on Al sites might be retained less strongly compared to that on Fe sites on the basis of the results of the desorption study.

In water treatment, equally efficient As<sup>V</sup> removal could potentially be achieved using either 0:1 or 1:4 Al:Fe hydroxides. At greater than 1:4 Al:Fe molar ratio, removal of As<sup>V</sup> might not be as effective, due to crystalline aluminum hydroxide formation. As<sup>III</sup> might be less effectively removed using 1:4 Al:Fe hydroxide compared to 0:1 Al:Fe hydroxide due to the negligible As<sup>III</sup> adsorption at Al surface sites. Use of Ca(OH)<sub>2</sub> instead of NaOH for hydrolysis will likely improve As<sup>V</sup> removal and As<sup>V</sup> retention at waste disposal sites with both 0:1 and 1:4 Al:Fe systems. Under reduced conditions as might occur at a waste disposal site, reduction of Fe<sup>III</sup> to Fe<sup>II</sup> and As<sup>V</sup> to As<sup>III</sup> would be expected. Although Al<sup>III</sup> is not redox sensitive, aluminum hydroxides might be less effective for arsenic removal and waste management due to the weak affinity of As<sup>III</sup> for aluminum hydroxides. Arsenic:adsorption-site ratio might be initially greater with the Fe<sup>III</sup> system; however, a decrease in reactive surface sites would be expected over time due to reductive dissolution of iron hydroxides. Although Al:Fe hydroxides will not retain As<sup>III</sup> as efficiently as iron hydroxides, the available Fe-site:arsenic ratio might be higher over time in a mixed Al:Fe system compared to the Fe system due to slower rate of reductive

dissolution when Al is in the structure of iron hydroxides (13, 14). Therefore, Al:Fe hydroxides could potentially be advantageous in a reduced environment as might exist at a waste disposal site. The rate of reductive dissolution and products of Al:Fe reduction in the presence of arsenic must be investigated to understand the probable fate of arsenic.

## Acknowledgments

This research was supported in part by a grant from the American Water Works Association, Project Number 2820. Additional support was obtained from the USGS through a grant by the Texas Water Resources Institute. We thank Dr. B. K. Biswas and Dr. G. N. White for assistance in arsenic analysis and XRD analysis, respectively. We acknowledge Dr. Scott Fendorf for helpful comments.

## Supporting Information Available

XRD of aged 1:4 and 1:2.3 Al:Fe hydroxides (Figure 1), pzc data (Figure 2), As<sup>V</sup> adsorption isotherms (Ca versus Na) (Figure 3), and As<sup>III</sup> adsorption envelopes (Ca versus Na) (Figure 4). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Received for review May 15, 2006. Revised manuscript received October 27, 2006. Accepted October 31, 2006.

ES061160Z