Arsenate and Arsenite Removal by Zerovalent Iron: Effects of Phosphate, Silicate, Carbonate, Borate, Sulfate, Chromate, Molybdate, and Nitrate, Relative to Chloride

CHUNMING SU*,† AND ROBERT W. PULS‡

*ManTech Environmental Research Services Corp.,
919 Kerr Research Drive, Ada, Oklahoma 74821-1198, and
U.S. Environmental Protection Agency, National Risk
Management Research Lab, 919 Kerr Research Drive,
Ada, Oklahoma 74821-1198*

Batch tests were performed to evaluate the effects of inorganic anion competition on the kinetics of arsenate (As(V)) and arsenite (As(III)) removal by zerovalent iron (Peerless Fe^0) in aqueous solution. The oxyanions underwent either sorption-dominated reactions (phosphate, silicate, carbonate, borate, and sulfate) or reduction-dominated reactions (chromate, molybdate, and nitrate) with Peerless Fe^0 in the presence of As(V) or As(III), relative to chloride. Pseudo-first-order rate equations were found to describe satisfactorily both As(V) and As(III) removal kinetics in the presence of each competing anion. Of the oxyanions tested for Peerless Fe^0 in the pH range from 7 to 9, phosphate caused the greatest decrease in As removal rate (7.0×10^{-3} to 18.5×10^{-3} h^{-1}) relative to chloride (34.9×10^{-3} to 36.2×10^{-3} h^{-1}). Silicate, chromate, and molybdate also caused strong inhibition of As removal, followed by carbonate and nitrate, whereas borate and sulfate only caused slight inhibition to As(III) removal. Present results show that Peerless Fe^0 may be an excellent permeable reactive barrier medium for a suite of mixed inorganic contaminants. The anion competing effects should be considered when designing permeable reactive barriers composed of zerovalent iron for field applications to remediate As(V) and As(III).

Introduction

A recent column study (*1*) and a batch test (*2*) have shown that zerovalent iron (Fe^0) removes both arsenate (As(V)) and arsenite (As(III)) from aqueous solution; thus, it may potentially be used to remediate As(V) and As(III) in groundwater via surface sorption and/or precipitation. This is encouraging since Fe^0 also has been reported to degrade many chlorinated hydrocarbon solvents effectively via reductive dehalogenation (*3–6*) and to immobilize other redox sensitive inorganic contaminants (CrO_4^{2-}, TcO_4^-, UO_2^{2+}, MoO_4^{2-}) from aqueous solution (*7–12*); removal rates decreased as follows: $CrO_4^{2-} > TcO_4^- > UO_2^{2+} \gg MoO_4^{2-}$ (*10*). The removal mechanism appears to be reductive

precipitation. Previous research has resulted in a relatively thorough understanding of the surface reactions, kinetics and mechanisms, contaminant product fate, and the effects of geochemical enhancements in systems of Fe^0 with chromate as the contaminant (*7–9*). Although As(V) should be reduced to As(III) by Fe^0 at low pH and low Eh conditions, both As(V) and As(III) can also be sorbed on the corroded Fe^0 surface. The sorption of both As(V) and As(III) may predominate over the redox reactions in the Fe^0 system under certain experimental conditions such as near neutral to alkaline pH and slightly reducing conditions. Previous studies have shown that both As(V) and As(III) are immobilized by Fe^0 and that surface sorption seems to be a major immobilization mechanism under alkaline pH and moderate Eh conditions (*2*).

Su and Puls (*2*) compared four types of Fe^0 used to remove both As(V) and As(III) in 0.01 M NaCl. Among them, the Fisher electrolytic Fe^0 showed the fastest As immobilization kinetics, followed by Peerless Fe^0 and Master Builders Fe^0 (the two behaved similarly), whereas the Aldrich Fe^0 was the least reactive.

Zerovalent iron corrodes in aqueous solution by forming corrosion products such as magnetite and maghemite on the Fe^0 surface (*13, 14*), thus affecting the behavior of the metal–contaminant interaction. Furthermore, anion competition between arsenate/arsenite and other anions may decrease the effectiveness of arsenic removal by zerovalent iron. Previous studies show that phosphate decreases both As(V) and As(III) sorption by ferrihydrite, depending strongly on pH and phosphate concentration (*15*). The inhibiting effect of phosphate on As(V) sorption is greater at high pH than at low pH; whereas, the opposite trend is observed for As(III). Desorption of already-sorbed As(V) and As(III) on amorphous ferric hydroxide and goethite by phosphate also showed the above trend toward pH and phosphate concentration (*15*). Application of phosphate fertilizers to lead arsenate-contaminated soils increased soil arsenic solubility and downward mobility (*16*). Sulfate was reported not to influence As(V) sorption by ferrihydrite but resulted in a considerable decrease in As(III) sorption below pH 7, with the largest decrease at the lowest pH (*15*). Sorbed As(V) by ettringite [$Ca_6Al_2(SO_4)_3(OH)_{12} \cdot 26H_2O$] was also not desorbable in the presence of concentrated sulfate and high ionic strength solutions (*17*). On the contrary, sulfate was found to decrease both As(V) and As(III) sorption on hydrous ferric oxide in the pH range of 4–7 (*18*). The release of As from a sandstone aquifer was found to be strongly and positively related to the bicarbonate concentration in the leaching solution (*19*). In the late Pleistocene-Recent alluvial aquifers of the Ganges Plain in Bangladesh and west Bengal, where groundwater is contaminated with naturally occurring arsenic, concentrations of As correlated with concentrations of bicarbonate and were uncorrelated with concentrations of dissolved iron. The relations suggest that the As in groundwater beneath the Ganges Plain is derived by reductive dissolution of Fe oxyhydroxides in the sediment that is driven by microbial metabolism of sedimentary organic matter (*20*).

There has been no systematic study on the influence of common anions in groundwater such as phosphate, silicate, carbonate, and sulfate on the kinetics of retention of inorganic As(V) and As(III) by Fe^0. Furthermore, at some sites the groundwater is contaminated with chromate, molybdate, nitrate, or borate (high in fly ash), in addition to As(V) and As(III). The influence of each of these anions needs to be evaluated in order to ensure an adequate thickness of the

* Corresponding author phone: (580)436-8638; fax: (580)436-8501; e-mail: su.chunming@epa.gov.
† ManTech.
‡ U.S. EPA.

permeable reactive barrier (PRB) iron wall to intercept the plume of contaminated groundwater.

The objectives of this study were to investigate the influence of competing anions such as phosphate, silicate, carbonate, borate, sulfate, chromate, molybdate, and nitrate, on As(V) and As(III) removal by Peerless Fe^0, compared to that of chloride, and to infer the potential limitations of Fe^0 as subsurface PRB medium in remediation of As contamination in groundwaters that contain significant amounts of competing anions.

Experimental Section

Peerless Fe^0 (Peerless Metal Powders & Abrasive, Detroit, MI) was chosen in the test because a previous study (2) has shown that it is effective in removing arsenic and that it is commercially available in large quantities at relatively low price compared to Fisher electrolytic Fe^0. Furthermore, Fisher electrolytic Fe^0 is much more reactive with water than Peerless Fe^0 and generates large amounts of hydrogen gas. Both facts make Fisher electrolytic Fe^0 unfavorable for field applications. Peerless iron had a surface area of $2.53 \pm 0.44 \ m^2 \ g^{-1}$ ($n = 2$). Surface areas were determined by BET N_2 sorption analysis on a Coulter SA 3100 surface area analyzer (Coulter Co., Hialeah, FL).

Stock solutions (1000 mg As L^{-1}) were prepared from reagent grade $Na_2HAsO_4 \cdot 7H_2O$ (Aldrich) for As(V) and $NaAsO_2$ (Baker) for As(III). Working solutions (generally 2 mg As L^{-1} in 0.01 M NaCl) were prepared fresh for each batch test. One gram of Peerless Fe^0 was added to a 50-mL polypropylene copolymer centrifuge tube (with a measured, capped volume of 41.64 ± 0.17 mL, $n = 10$) that was filled without a headspace with an anion solution that also contained As(V) or As(III) at 2 mg As L^{-1}.

Specifically, separate batch tests were performed for each anion using solutions of 2 mg As(V) L^{-1} in solutions of NaH_2PO_4 (0.1 mM, pH 5.44 not adjusted, and 1.0 mM, pH 5.46 not adjusted), Na_2SiO_3 (1 mM, pH 10.12 not adjusted, and pH 7.73 adjusted with HCl), $NaHCO_3$ (1.0 mM, pH 7.38 not adjusted, and 100 mM, pH 8.21 not adjusted), H_3BO_3 (1.0 mM, pH 5.96 not adjusted, and pH 7.88 adjusted with NaOH), Na_2SO_4 (1.0 mM, pH 6.42 not adjusted), K_2CrO_4 (0.1 mM, pH 5.37 not adjusted, and 1.0 mM, pH 4.67 not adjusted), Na_2MoO_4 (0.1 mM, pH 6.03 not adjusted, and 1.0 mM, pH 6.09 not adjusted), $NaNO_3$ (1.0 mM, pH 5.84 not adjusted), and NaCl (10 mM, pH 6.41 not adjusted). Similar anion solutions were also used for the As(III) tests. Four replicates were prepared for each anion with the Peerless Fe^0 and either As(V) or As(III). The centrifuge tubes were covered with aluminum foil to prevent light exposure and placed on a reciprocating shaker at a shaking frequency of 50 oscillations per minute at 23 °C. No attempt was made to adjust the pH once the reaction was initiated. At time periods (including 0.5 h centrifugation time) preset at 2, 4, 8, 12, 24, 48, 72, 96, and 120 h, the suspension was centrifuged, and 20 mL of supernatant solution was filtered through a 0.1 μm membrane and then analyzed for total As. The pH and Eh were determined for the remaining supernatant solutions containing the iron solids with an Orion ion analyzer (Orion Research Inc., Boston, MA) by using a combination pH electrode and a Pt electrode, respectively. The Eh readings are reported relative to the standard hydrogen electrode. The As concentration data were fitted to the pseudo-first-order reaction equations to calculate the reaction rates. The half-lives of As in solution were estimated from the rate equations and normalized to 1 m^2 surface area of zerovalent iron per mL of solution.

Total dissolved As, Si, Mo, Cr, B, Fe, and Mn were determined by inductively coupled plasma−atomic emission spectrometry (ICP-AES) for samples with total As > 0.1 mg L^{-1} and by graphite furnace−atomic absorption spectrometry
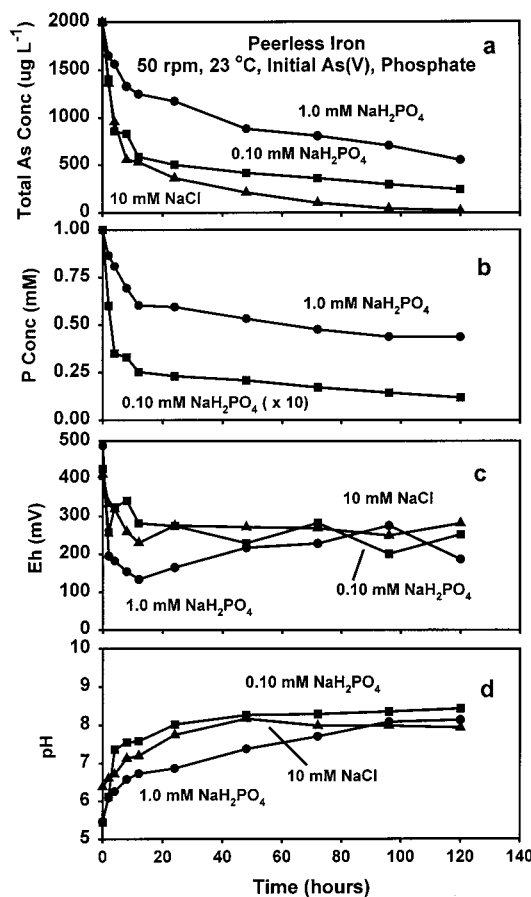

FIGURE 1. Kinetics of As(V) removal by Peerless Fe^0 in 0.10 mM or 1.0 mM NaH_2PO_4 relative to 10 mM NaCl: (a) total As concentration; (b) phosphate concentration; (c) Eh; and (d) pH.

(GF-AAS) for lower concentration As samples. Speciation of As(V) and As(III) was accomplished by ion chromatography−hydride generation−atomic fluorescence spectrometry (IC-HG-AFS) for the starting As(V) and As(III) solutions and for some selected samples. The detection limit of ICP-AES for As was 0.033 mg L^{-1}. The detection limit for arsenic speciation using IC-HG-AFS for both As(V) and As(III) was 0.005 mg L^{-1}. The detection limit of total As using GF-AAS was 0.001 mg L^{-1}, and the quantitation limit of As was 0.003 mg L^{-1}.

Orthophosphate was determined using ammonium molybdate and antimony potassium tartrate under acidic conditions to form an antimony−phosphomolybdate complex which is then analyzed by flow injection analysis colorimetry (USEPA, Method 365.1). Sulfate was determined using Waters capillary electrophoresis method N-601. Carbonate was determined by acid titration. The dissolved nitrate plus nitrite were determined by hydrazine reduction using flow injection analysis colorimetry (USEPA, Method 353.1). In this method, nitrate is reduced to nitrite with hydrazine sulfate. The nitrite (reduced nitrate plus original nitrite) is then determined by diazotizing with sulfanilamide followed by coupling with N-(1-naphthyl)ethylenediamine dihydrochloride. Nitrite alone is determined by substituting deionized water for the hydrazine reagent. Ammonium was determined by the automated phenate colorimetric method (USEPA, Method 350.1).

Results and Discussion

Effects of Phosphate and Silicate. Relative to chloride at 10 mM, which is considered a nonspecific anion in solid−liquid interfacial reactions, the presence of phosphate at either 0.1 or 1.0 mM caused a significant decrease in both
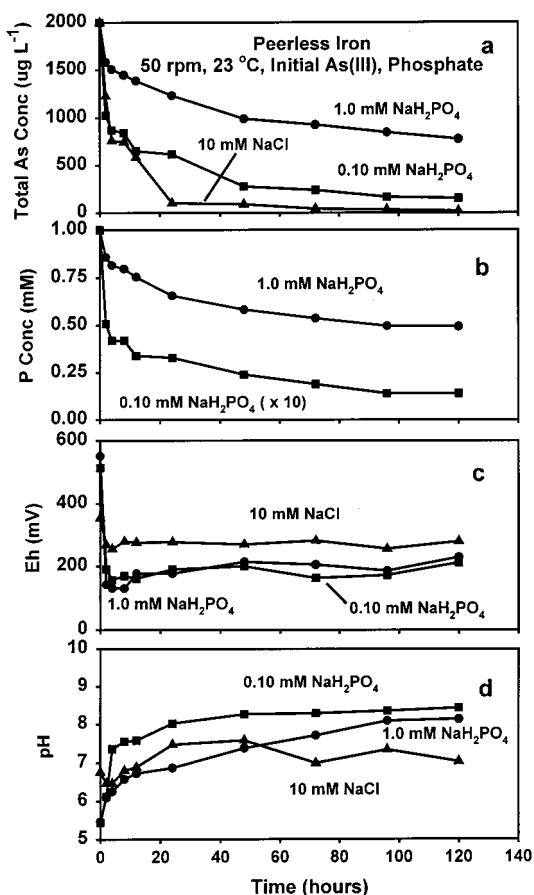
FIGURE 2. Kinetics of As(III) removal by Peerless Fe[0] in 0.10 mM or 1.0 mM NaH_2PO_4 relative to 10 mM NaCl: (a) Total As concentration; (b) phosphate concentration; (c) Eh; and (d) pH.

As(V) removal kinetics (Figure 1) and As(III) removal kinetics (Figure 2). Phosphate decreased both As(V) and As(III) removal by Peerless Fe[0] to a greater degree at 1.0 mM NaH_2-PO_4 (P:As ratio 37:1) than at 0.1 mM NaH_2PO_4 (P:As ratio 3.7:1) at each time interval (Figures 1a and 2a). Arsenic concentration decreased exponentially with time. Pseudo-first-order reaction kinetics was found to describe the data well with correlation coefficient (r^2) values ranging from 0.82 to 0.96.

Table 1 lists the pseudo-first-order rate constants (k) and their surface-area-normalized rate constants (k_{SA}), the cal-

culated half-lives ($t_{1/2}$), and normalized half-lives ($t_{1/2-N}$, for 1 m^2 mL^{-1}) for As(V) removal by Peerless Fe[o] as affected by anions. Table 2 shows the anion effects on As(III) removal by the Peerless Fe[0]. Although it is a common practice to use the initial surface area of iron to normalize the calculations of rate constants, it is acknowledged that a bias may be introduced due to possible increase in surface area with increasing time. We think the surface area change within a 72 h time frame should be comparable among different treatments; therefore, it still is valid to make comparisons between different anions.

As expected, phosphate was also removed by the Peerless Fe[0] (Figures 1b and 2b). This can be advantageous in that the Peerless Fe[0] could treat a mixed contaminant plume of both As and phosphate; however, excess phosphate will reduce the effectiveness of the PRB iron wall for As remediation. Phosphate is a known inner-sphere complex-forming anion that is strongly sorbed to mineral surfaces or is coprecipitated to form discrete solid phases on mineral surfaces (21−23). The suppression of As(V) sorption by phosphate has been reported to occur in soils (24−26), iron oxides (27, 28), and clay minerals (29). The present study also shows the same effect in the Fe[0] system.

Surface complexation is an important mechanism for As(V) and As(III) removal by iron oxides (30−37), which form a passivation layer on Fe[0] (13, 14). Arsenate predominately forms inner-sphere bidentate surface complexes with goethite (30) and ferrihydrite (31, 32). Three different surface complexes were reported to form on goethite: a monodentate complex, a bidentate−binuclear complex, and a bidentate−mononuclear complex (33). Spectroscopic studies support inner-sphere complexation of both As(V) and As(III) on goethite (34−36) and As(V) on hydrous iron oxides (37).

The Eh generally decreased initially and approached steady state with positive values (Figures 1c and 2c). The positive Eh values for Peerless Fe[0] were in contrast with those for Fisher electrolytic Fe[0] that gave negative (−400 mV) Eh values within a few hours in 0.01 M NaCl (6). The Eh values may be regarded as qualitative parameters that are not amenable to quantitative interpretation. The Peerless Fe[0] has already been slightly oxidized, as it appeared rusty when received. In the Peerless Fe[0]/anion systems, the redox potential is thought to be a mixed potential involving dissolved oxygen, the Fe[0]/Fe^{2+} couple, the Fe^{2+}/Fe^{3+} couple, and oxyanion species. The Eh measurements in the batch tests may not be relevant to a PRB field situation where biological activities also influence redox reactions.

TABLE 1. Correlation Coefficients (r^2), Pseudo-First-Order Rate Constants (k), and Their Surface-Area-Normalized Rate Constants (k_{SA}) for As(V) Removal by Peerless Fe[0] as Affected by Anions

anions	initial pH[a]	reaction pH[b]	r^2	$k \times 1000$ (h^{-1})[c]	k_{SA} (h^{-1} m^{-2} mL)[c]	$t_{1/2}$ (h)[c]	$t_{1/2-N}$ (h)[c]
10 mM NaCl	6.41 ± 0.02	7.50 ± 0.59	0.951	34.9 ± 2.0	0.572 ± 0.033	19.9 ± 1.1	1.21 ± 0.07
1.0 mM Na_2SO_4	6.42 ± 0.02	8.74 ± 0.35	0.900	32.9 ± 3.5	0.539 ± 0.058	21.3 ± 2.5	1.30 ± 0.15
0.1 mM NaH_2PO_4	5.44 ± 0.00	7.79 ± 0.71	0.898	13.7 ± 1.2	0.224 ± 0.020	50.8 ± 4.4	3.10 ± 0.27
1.0 mM NaH_2PO_4	5.46 ± 0.01	7.09 ± 0.73	0.909	9.07 ± 0.79	0.149 ± 0.013	76.9 ± 6.7	4.69 ± 0.41
1.0 mM Na_2SiO_3	7.73 ± 0.05	7.74 ± 0.24	0.841	11.6 ± 1.0	0.189 ± 0.016	60.0 ± 5.1	3.66 ± 0.31
1.0 mM Na_2SiO_3	10.12 ± 0.00	9.98 ± 0.11	0.850	0.70 ± 0.07	0.012 ± 0.001	987 ± 91	60.2 ± 5.6
1.0 mM H_3BO_3	5.96 ± 0.01	6.98 ± 0.13	0.820	40.5 ± 3.4	0.664 ± 0.055	17.1 ± 1.4	1.04 ± 0.09
1.0 mM H_3BO_3	7.88 ± 0.02	7.82 ± 0.17	0.909	30.2 ± 2.1	0.495 ± 0.034	23.0 ± 1.6	1.40 ± 0.10
1.0 mM $NaHCO_3$	7.38 ± 0.00	8.41 ± 0.27	0.917	26.7 ± 2.6	0.437 ± 0.043	26.3 ± 2.7	1.60 ± 0.17
100 mM $NaHCO_3$	8.21 ± 0.00	8.61 ± 0.16	0.922	26.6 ± 1.1	0.435 ± 0.018	26.2 ± 1.1	1.59 ± 0.07
0.1 mM K_2CrO_4	5.37 ± 0.01	8.59 ± 0.87	0.855	17.0 ± 1.9	0.279 ± 0.030	41.1 ± 4.3	2.51 ± 0.26
1.0 mM K_2CrO_4	4.67 ± 0.03	7.28 ± 1.44	0.894	7.50 ± 0.49	0.123 ± 0.008	92.8 ± 6.1	5.66 ± 0.37
0.1 mM Na_2MoO_4	6.03 ± 0.00	8.62 ± 0.22	0.902	18.6 ± 1.3	0.305 ± 0.021	37.3 ± 2.5	2.28 ± 0.15
1.0 mM Na_2MoO_4	6.09 ± 0.01	9.20 ± 0.11	0.918	12.9 ± 1.0	0.211 ± 0.017	76.9 ± 6.2	4.69 ± 0.38
1.0 mM $NaNO_3$	5.84 ± 0.02	8.10 ± 0.62	0.876	21.1 ± 1.6	0.346 ± 0.027	33.1 ± 2.5	2.02 ± 0.15

[a] The initial pH is the pH of the electrolyte solutions before contacting the iron ($n = 2$). [b] Reaction pH is the average pH for 36 pH values measured at time intervals of 2, 4, 8, 12, 24, 48, 72, 96, and 120 h ($n = 4$ for each time interval). [c] $n = 4$.

TABLE 2. Correlation Coefficients (r^2), Pseudo-First-Order Rate Constants (k), and Their Surface-Area-Normalized Rate Constants (k_{SA}) for As(III) Removal by Peerless Fe[0] as Affected by Anions

anions	initial pH[a]	reaction pH[b]	r^2	$k \times 1000$ (h^{-1})[c]	k_{SA} (h^{-1} m^{-2} mL)[c]	$t_{1/2}$ (h)[c]	$t_{1/2-N}$ (h)[c]
10 mM NaCl	6.65 ± 0.02	7.00 ± 0.43	0.962	36.2 ± 0.5	0.594 ± 0.008	19.1 ± 0.3	1.17 ± 0.02
1.0 mM Na$_2$SO$_4$	6.14 ± 0.02	8.29 ± 0.45	0.842	30.2 ± 0.4	0.495 ± 0.007	22.9 ± 0.3	1.40 ± 0.02
0.1 mM NaH$_2$PO$_4$	5.76 ± 0.01	7.85 ± 0.50	0.892	18.5 ± 0.4	0.304 ± 0.006	37.4 ± 0.8	2.28 ± 0.05
1.0 mM NaH$_2$PO$_4$	5.19 ± 0.01	7.10 ± 0.72	0.888	7.00 ± 0.04	0.115 ± 0.001	98.9 ± 0.6	6.03 ± 0.04
1.0 mM Na$_2$SiO$_3$	7.94 ± 0.01	7.54 ± 0.28	0.873	14.2 ± 1.5	0.233 ± 0.024	49.3 ± 5.2	3.01 ± 0.32
1.0 mM Na$_2$SiO$_3$	10.01 ± 0.03	10.02 ± 0.05	0.865	1.95 ± 0.13	0.032 ± 0.002	358 ± 23	21.8 ± 1.4
1.0 mM H$_3$BO$_3$	6.03 ± 0.04	6.61 ± 0.19	0.915	31.8 ± 0.3	0.521 ± 0.004	21.8 ± 0.2	1.33 ± 0.12
1.0 mM H$_3$BO$_3$	8.12 ± 0.01	7.99 ± 0.04	0.942	26.5 ± 0.5	0.434 ± 0.009	26.2 ± 0.5	1.60 ± 0.03
1.0 mM NaHCO$_3$	7.96 ± 0.01	8.31 ± 0.15	0.860	27.7 ± 0.4	0.454 ± 0.007	25.0 ± 0.4	1.53 ± 0.02
100 mM NaHCO$_3$	8.21 ± 0.01	8.57 ± 0.12	0.908	25.8 ± 0.1	0.422 ± 0.001	26.9 ± 0.1	1.64 ± 0.01
0.1 mM K$_2$CrO$_4$	5.32 ± 0.01	8.57 ± 0.35	0.887	20.5 ± 0.0	0.336 ± 0.000	33.8 ± 0.0	2.06 ± 0.00
1.0 mM K$_2$CrO$_4$	4.56 ± 0.02	7.01 ± 1.55	0.894	11.0 ± 0.1	0.181 ± 0.002	62.8 ± 0.7	3.83 ± 0.05
0.1 mM Na$_2$MoO$_4$	6.72 ± 0.06	8.60 ± 0.27	0.839	21.0 ± 0.9	0.344 ± 0.015	33.1 ± 1.4	2.02 ± 0.09
1.0 mM Na$_2$MoO$_4$	6.95 ± 0.01	9.21 ± 0.16	0.870	14.9 ± 0.6	0.244 ± 0.010	46.7 ± 2.0	2.85 ± 0.12
1.0 mM NaNO$_3$	7.12 ± 0.02	8.16 ± 0.61	0.843	15.1 ± 1.4	0.247 ± 0.022	46.4 ± 4.2	2.83 ± 0.26

[a] The initial pH is the pH of the electrolyte solutions before contacting the iron ($n = 2$). [b] Reaction pH is the average pH for 36 pH values measured at time intervals of 2, 4, 8, 12, 24, 48, 72, 96, and 120 h ($n = 4$ for each time interval). [c] $n = 4$.

The initial pH was the pH of the electrolyte solutions before contacting the iron ($n = 2$) and did not show significant change over time without the Peerless Fe[0] (data not shown). The reaction pH and sample standard deviation were calculated for the 36 pH values measured at time intervals of 2, 4, 8, 12, 24, 48, 72, 96, and 120 h (four replicates at each time interval). They provide a reasonable representation of the pH value distribution during the experiment. Ideally, the experiment would be conducted at constant pH using a pH-stat titrator; however, the large number of samples to be tested and the long duration tests for each anion called for a more practical approach. Fortunately, most of the oxyanions showed some degree of pH buffering and worked reasonably well for our purpose. The pH values showed gradual increase with increasing time but were less than 8.5 at 120 h (Figures 1d and 2d). The pH increase is expected because of water decomposition by Fe[0] (2, 3, 6) and because of sorption reactions of As(V), As(III), and phosphate, which release OH$^-$ groups from sorbents as a result of ligand exchange (21–23).

The effect of silicate (metasilicate ions hydrolyze instantly to form orthosilicate ions and silicic acid molecules) at 1.0 mM on As(V) removal by Peerless Fe[0] was pH-dependent (Figure 3a) in that an initial pH of 10.12 was far more effective in decreasing As(V) removal than an initial pH of 7.73. The Eh values for the two silicate solutions in contact with Peerless Fe[0] with different pH values showed convergence at 120 h (Figure 3c). Less than 10% of added As(V) was removed from 1.0 mM silicate at an initial pH 10.12, and the pH was constant throughout the test (Figure 3d). Silicate was also removed by the Peerless Fe[0] with greater removal at an initial pH of 7.73 than at an initial pH of 10.12 (Figure 3b). It is well-known that sorption of silicate increases with increasing pH from 4 to 9 and then decreases with increasing pH above 10 in soils, iron oxide minerals, and carbonate minerals (38–40). Sorption of silicate on ferrihydrite as studied by X-ray photoelectron spectroscopy (XPS) shows the presence of monomeric silicate or small units of polymerized silica at low solution silicate concentrations and the presence of Si-rich precipitate at high silicate concentrations (41).

Arsenate, phosphate, and silicate are all tetrahedral anions. All form inner-sphere complexes with the functional groups at the surfaces of iron oxides. Competition for sorption sites decreases the sorption of either anion when both are present compared to either anion alone. Zerovalent iron acted as a favorable sorbent for both phosphate and silicate; however, excess phosphate and silicate in groundwater may cause incomplete removal of As(V) and As(III). Other materials high in soluble silicate such as fly ash should not be mixed with
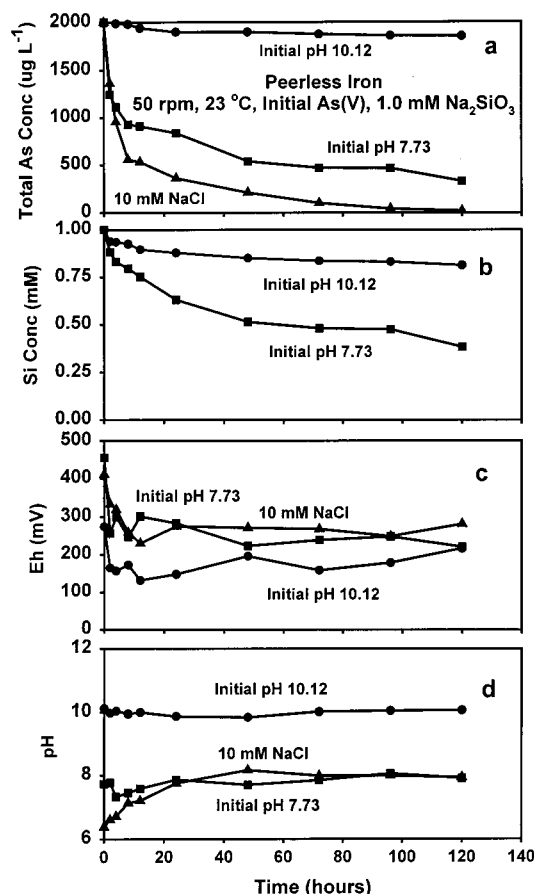

FIGURE 3. Kinetics of As(V) removal by Peerless Fe[0] in 1.0 mM Na$_2$SiO$_3$ (initial pH 7.73, or 10.12) relative to 10 mM NaCl: (a) total As concentration; (b) Si concentration; (c) Eh; and (d) pH.

zerovalent iron. Alternatively, excess iron must be used to ensure the complete removal of arsenic in the presence of strong competing anions.

Effects of Carbonate, Borate, and Sulfate. The presence of bicarbonate at either 1.0 mM or 100 mM noticeably decreased pseudo-first-order rate constants for As(V) removal by the Peerless Fe[0] (Table 1) and for As(III) removal (Table 2), relative to 10 mM NaCl. There was no significant difference between kinetic suppression of the two concentrations of bicarbonate. Carbonate has been reported to form a protonated and a nonprotonated inner-sphere monodentate
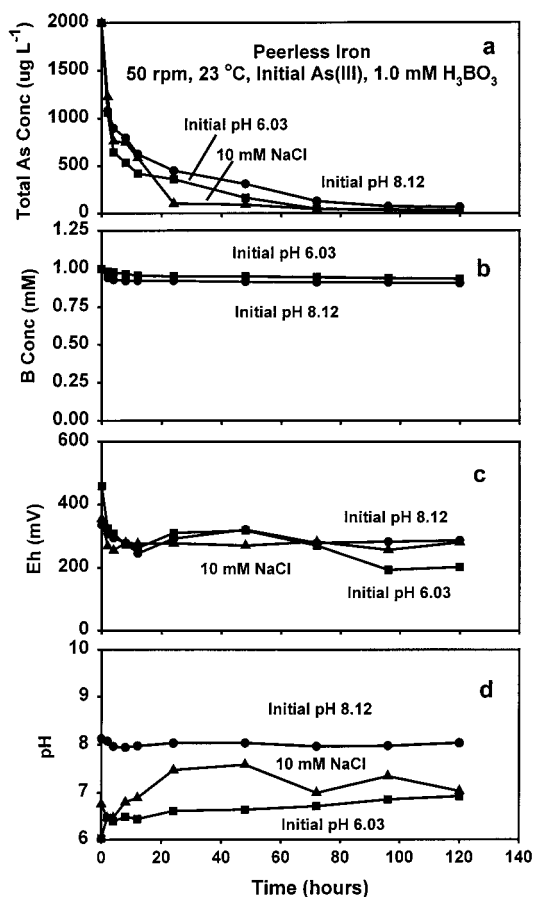
FIGURE 4. Kinetics of As(III) removal by Peerless Fe⁰ in 1.0 mM H₃BO₃ (initial pH 6.0, or 8.1) relative to 10 mM NaCl: (a) total As concentration; (b) B concentration; (c) Eh; and (d) pH.

FIGURE 5. Kinetics of As(III) removal by Peerless Fe⁰ in 0.10 mM or 1.0 mM K₂CrO₄ relative to 10 mM NaCl: (a) total As concentration; (b) Cr concentration; (c) Eh; and (d) pH.

surface complex with amorphous iron oxides in an attenuated total reflectance−FTIR study (*42*). The carbonate solution chemistry may be important to arsenic geochemistry, as is demonstrated by a recent study that found that As release from sandstone aquifer containing arsenic sulfide minerals, such as orpiment (As_2S_3) and realgar (AsS), is strongly and positively related to the bicarbonate concentration in the leaching solution (*19*). Furthermore, several arseno−carbonate complexes were proposed as stable in groundwater, including $As(CO_3)_2^-$, $As(CO_3)(OH)_2^-$, and $AsCO_3^+$ (*19*). More evidence comes from another recent study of the late Pleistocene-Recent alluvial aquifers of the Ganges Plain in Bangladesh and India, where concentrations of As in groundwater correlate positively with concentrations of bicarbonate and are uncorrelated with concentrations of dissolved iron (*20*). It was concluded that arsenic released by oxidation of pyrite, as water levels are drawn down and air enters the aquifer, contributes negligibly to the problem of As pollution. It was proposed that As release beneath the Ganges Plain is derived by reductive dissolution of iron oxyhydroxides in the sediment, which is driven by microbial degradation of sedimentary organic matter (*20*). It is obvious that more studies are required to confirm the existence of above-mentioned arseno−carbonate complexes and to explore other possible types of complexes that involve arsenate/arsenite and carbonate.

Borate shows maximum sorption on hematite, goethite, and amorphous iron oxide in the pH range from 7 to 8 (*43*), and it forms an inner-sphere complex with iron oxides (*44*). Borate at 1.0 mM at an initial pH value of 6.0 or 8.1 decreased As(III) removal by Peerless Fe⁰ (Figure 4a) with more decrease in As(III) removal at pH 8.1 than at pH 6.0, relative to 10 mM
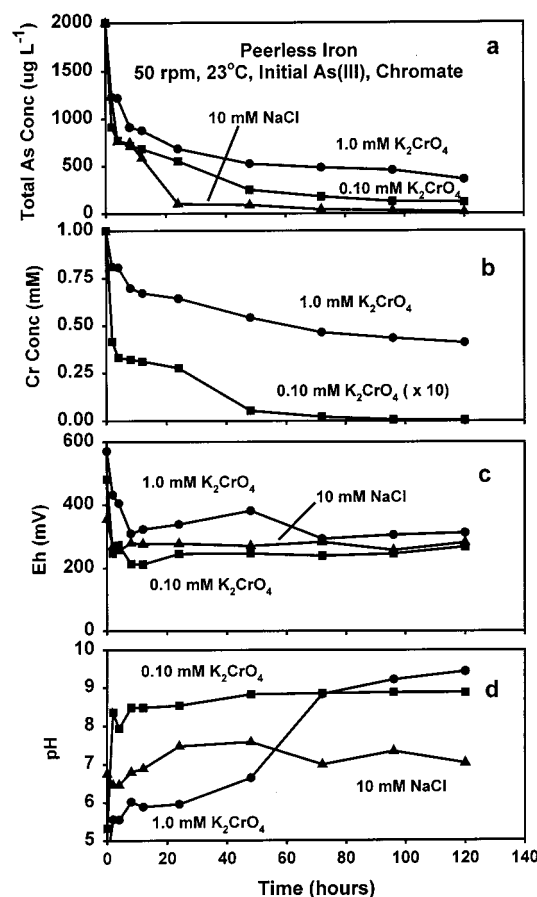
NaCl. Borate had a less inhibiting effect on As(V) removal kinetics than on As(III). This is in contrast with the behavior of phosphate and silicate that exhibited a greater inhibition effect on As(V) removal kinetics than on As(III) (Tables 1 and 2). This may be explained by the configuration of the molecular structures of these species. The tetrahedral structure of arsenate, phosphate, and silicate could have produced more competition between them for the surface functional groups on Peerless Fe⁰. Arsenite and H_3BO_3 (predominant form of boron at pH < 9.24, as H_3BO_3 + H_2O = $B(OH)_4^-$ + H^+, pK_a = 9.24) are trigonal in molecular structure in solution; therefore, more competition may be expected between $H_2AsO_3^-$ and H_3BO_3 for sorption as the two species share similar sorption sites. Concentrations of boron showed only slight decrease with increasing time (0.91 mM for the initial pH 8.1, and 0.94 mM for the initial pH 6.0, at 120 h) (Figure 4b). The Eh values were generally greater than 190 mV (Figure 4c). The pH of the solutions containing boron were much better buffered than the 10 mM NaCl solution (Figure 4d).

Sulfate did not significantly decrease As(V) removal by Peerless Fe⁰ (Table 1) but noticeably decreased As(III) removal (Table 2). Disagreement in the literature on the effects of sulfate on As(V) and As(III) sorption may have derived from different experimental conditions. Decreased sorption of both As(V) and As(III) on hydrous ferric oxide were reported in the presence of sulfate from pH 4 to 7 (*18*). Sorbed As(V) on ettringite [$Ca_6Al_2(SO_4)_3(OH)_{12} \cdot 26H_2O$] was not desorbable in the presence of 10 mM sulfate at alkaline pH (10−12.5) (*17*). In the zerovalent iron system, the reaction pH is generally greater than pH 7; thus, the sulfate effect may be diminished at alkaline pH conditions.
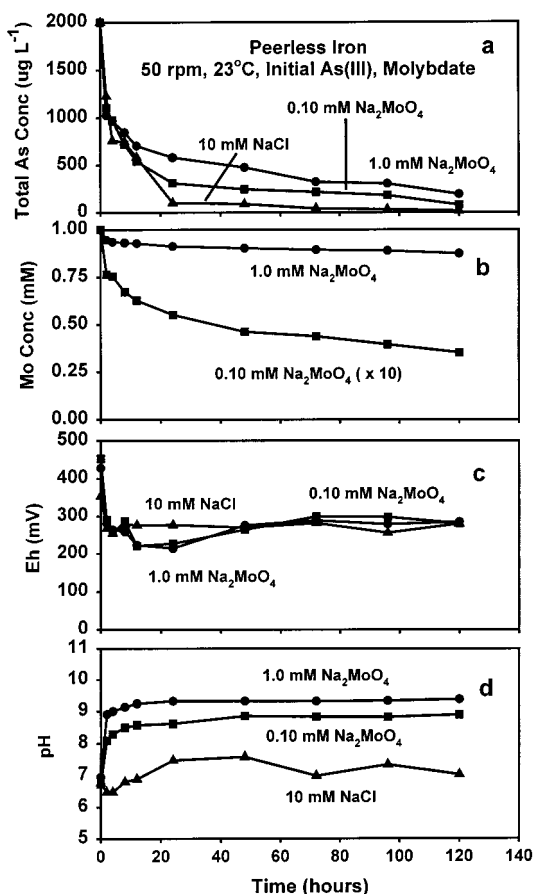
FIGURE 6. Kinetics of As(III) removal by Peerless Fe⁰ in 0.10 mM or 1.0 mM Na_2MoO_4 relative to 10 mM NaCl: (a) total As concentration; (b) Mo concentration; (c) Eh; and (d) pH.

Effects of Chromate, Molybdate, and Nitrate. These three anions are redox-sensitive and underwent reduction on Peerless Fe⁰ in the presence of As(V) or As(III). The presence of K_2CrO_4 caused greater inhibition of As(III) removal at 1.0 mM K_2CrO_4 than at 0.1 mM (Figure 5a and Table 2). A similar trend was also observed for As(V) (Table 1). Concomitantly, the concentration of total Cr decreased over time with 59% removal of added Cr for an initial 1.0 mM (24.5 μmol of total Cr removal) and 100% removal of added Cr for an initial 0.1 mM K_2CrO_4 (4.2 μmol of total Cr removal) at 120 h (Figure 5b). The Eh was generally greater than 200 mV (Figure 5c), but significantly higher pH was observed after 72 h for the 1.0 mM than the 0.1 mM K_2CrO_4 due to a greater chromate reduction that consumes more hydrogen ion for the 1.0 mM than the 0.1 mM K_2CrO_4 (Figure 5d). It has been shown that chromate is reduced by Fe⁰ to form a mixed Fe, Cr hydroxide (7−9).

The presence of 1.0 mM Na_2MoO_4 decreased As(III) removal rate to a greater degree than the presence of 0.1 mM Na_2MoO_4 (Figure 6a and Table 2). Concurrently, the concentration of total Mo decreased over time with 13% removal of Mo for an initial 1.0 mM (5.2 μmol of total Mo removal) and 65% removal of added Mo for an initial 0.1 mM Na_2MoO_4 (2.7 μmol of total Mo removal) at 120 h (Figure 6b). No significant difference was found in Eh for the two Mo concentrations (Figure 6c), but significantly higher pH was observed for the 1.0 mM than with the 0.1 mM Na_2MoO_4 due to a greater molybdate reduction that consumes more hydrogen ion for the 1.0 mM than the 0.1 mM Na_2MoO_4 (Figure 6d). Based on thermodynamic calculations, it was proposed (10) that the MoO_4^{2-} in the Fe⁰ system is reduced to Mo^{3+} which then precipitates as $Mo(OH)_3$. The presence

of other valence state (Mo^{4+}, Mo^{5+}) molybdenum-containing solids may also be possible and spectroscopic methods such as XPS may be useful for their detection.

Nitrate has been shown to be reduced by Fe⁰ to form predominantly NH_4^+ and a small amount of NO_2^- (45−47). Nitrate reduction by Fe⁰ is dependent on pH, more so than chromate reduction. Although less than 10% of added nitrate at 1.0 mM was degraded to mostly NH_4^+ and a trace amount of NO_2^- in the presence of As(V) or As(III) (data not shown), the removal rate of As(V) (Table 1) and of As(III) (Table 2) were significantly decreased with 1.0 mM nitrate relative to 10 mM NaCl, but to a lesser degree than with 1.0 mM chromate or molybdate. The presence of 1.0 mM nitrate is not uncommon in many contaminated groundwater resources, thus its impact on arsenic removal by a PRB iron wall should not be completely ignored.

Considerations for Field Applications. This study shows that Fe⁰ is effective in removing both As(V) and As(III) from solution when no competing anions were present. Not only can Fe⁰ degrade chlorinated solvents but also this study shows that it also can immobilize a variety of inorganic contaminants, including phosphate, chromate, and molybdate, and can degrade nitrate. It is a potentially cost-effective PRB medium for in situ site remediation of contaminated groundwater resources. The inner-sphere complex-forming phosphate, silicate, and molybdate compete strongly with As(V) and As(III) for sorption sites, whereas sulfate and chloride do not compete effectively. The implications from the oxyanion tests are that an excess amount of PRB materials may be needed for in situ remediation of arsenic in groundwater that commonly contains large amounts of dissolved silicate and possibly also contains phosphate, chromate, or molybdate.

Literature Cited

(1) Lackovic, J. A.; Nikolaidis, N. P.; Dobbs, G. M. *Environ. Eng. Sci.* **1999**, *17*, 29−39.
(2) Su, C.; Puls, R. W. *Environ. Sci. Technol.* **2001**, *35*, 1487−1492.
(3) Gillham, R. W.; O'Hannesin, S. F. *Ground Water* **1994**, *32*, 958−967.
(4) Johnson, T. J.; Scherer, M. M.; Tratnyek, P. G. *Environ. Sci. Technol.* **1996**, *30*, 2634−2640.
(5) Roberts, A. L.; Totten, L. A.; Arnold, W. A.; Burris, D. R.; Campbell, T. J. *Environ. Sci. Technol.* **1996**, *30*, 2654−2659.
(6) Su, C.; Puls, R. W. *Environ. Sci. Technol.* **1999**, *33*, 163−168.
(7) Puls, R. W.; Paul, C. J.; Powell, R. M. *Appl. Geochem.* **1999**, *14*, 989−1000.
(8) Powell, R. M.; Puls, R. W.; Hightower, S. K.; Sabatini, D. A. *Environ. Sci. Technol.* **1995**, *29*, 1913−1922.
(9) Pratt, A. R.; Blowes, D. W.; Ptacek, C. J. *Environ. Sci. Technol.* **1997**, *31*, 2492−2498.
(10) Cantrell, R. W.; Kaplan, D. I.; Wietsma, T. W. *J. Haz. Mater.* **1995**, *42*, 201−212.
(11) Del Cul, G. D.; Bostick, W. D. *Nucl. Technol.* **1995**, *109*, 161−162.
(12) Gu, B.; Liang, L.; Dickey, M. J.; Yin, X.; Dai, S. *Environ. Sci. Technol.* **1998**, *32*, 3366−3373.
(13) Oblonsky, L. J.; Ryan, M. P.; Isaacs, H. S. *Corros. Sci.* **2000**, *42*, 229−241.

(14) Nagayama, M.; Cohen, M. *J. Electrochem. Soc.* **1962**, *109*, 781−790.

(15) Jackson, B. P.; Miller, W. P. *Soil Sci. Soc. Am. J.* **2000**, *64*, 1616−1622.

(16) Peryea, F. J.; Kammereck, R. *Water, Air, Soil Pollut.* **1997**, *93*, 243−254.

(17) Myneni, S. C. B.; Traina, S. J.; Logan, T. J.; Waychunas, G. A. *Environ. Sci. Technol.* **1997**, *31*, 1761−1768.

(18) Wilkie, J. A.; Hering, J. G. *Colloid. Surf.* **1996**, *107*, 97−110.

(19) Kim, M.; Nriagu, J.; Haack, S. *Environ. Sci. Technol.* **2000**, *34*, 3094−3100.

(20) Nickson, R. T.; McArthur, J. M.; Ravenscroft, P.; Burgess, W. G.; Ahmed, K. M. *Appl. Geochem.* **2000**, *15*, 403−413.

(21) Hingston, F. J. A review of anion adsorption. In *Adsorption of inorganics at solid−liquid interfaces*; Anderson, M. A., Rubin, A. J., Eds.; Ann Arbor Science: Ann Arbor, MI, 1981; pp 51−90.

(22) Sposito, G. *The chemistry of soils*; Oxford University Press: New York, 1989; p 131.

(23) McBride, M. B. *Environmental chemistry of soils*; Oxford University Press: New York, 1994; p 136.

(24) Barrow, N. J. *Soil Sci.* **1974**, *117*, 28−33.

(25) Livesey, N. T.; Huang, P. M. *Soil Sci.* **1981**, *131*, 88−94.

(26) Roy, W. R.; Hassett, J. J.; Griffin, R. A. *Soil Sci. Soc. Am. J.* **1986**, *50*, 1176−1182.

(27) Manning, B. A.; Goldberg, S. *Soil Sci. Soc. Am. J.* **1996**, *60*, 121−131.

(28) Jain, A.; Loeppert, R. H. *J. Environ. Qual.* **2000**, *29*, 1422−1430.

(29) Manning, B. A.; Goldberg, S. *Clays Clay Miner.* **1996**, *44*, 609−623.

(30) Lumsdon, D. G.; Fraser, A. R.; Russell, J. D.; Livesey, N. T. *J. Soil Sci.* **1984**, *35*, 381−386.

(31) Waychunas, G. A.; Rea, B. A.; Fuller, C. C.; Davis, J. A. *Geochim. Cosmochim. Acta* **1993**, *57*, 2251−2269.

(32) Manceau, A. *Geochim. Cosmochim. Acta* **1995**, *59*, 3647−3653.

(33) Grossl, P. R.; Sparks, D. L. *Geoderma* **1995**, *67*, 87−101.

(34) Sun, X.; Doner, H. E. *Soil Sci.* **1996**, *161*, 865−872.

(35) Fendorf, S.; Eick, M. J.; Grossl, P.; Sparks, D. L. *Environ. Sci. Technol.* **1997**, *31*, 315−320.

(36) Manning, B. A.; Fendorf, S. E.; Goldberg, S. *Environ. Sci. Technol.* **1998**, *32*, 2383−2388.

(37) Myneni, S. C. B.; Traina, S. J.; Waychunas, G. A.; Logan, T. J. *Geochim. Cosmochim. Acta* **1998**, *62*, 3285−3300.

(38) McKeague, J. A.; Cline, M. G. *Can. J. Soil Sci.* **1963**, *43*, 83−96.

(39) Hingston, F. J.; Posner, A. M..; Quirk, J. P. *J. Soil Sci.* **1972**, *23*, 177−192.

(40) Sigg, L.; Stumm, W. *Collid. Surf.* **1980**, *2*, 101−117.

(41) Vempati, R. K.; Loeppert, R. H.; Dufner, D. C.; Cocke, D. L. *Soil Sci. Soc. Am. J.* **1990**, *54*, 695−698.

(42) Su, C.; Suarez, D. L. *Clays Clay Miner.* **1997**, *45*, 814−825.

(43) Goldberg, S.; Glaubig, R. A. *Soil Sci. Soc. Am. J.* **1985**, *49*, 1374−1379.

(44) Su, C.; Suarez, D. L. *Environ. Sci. Technol.* **1995**, *29*, 302−311.

(45) Zawaideh, L. L.; Zhang, T. C. *Water Sci. Technol.* **1998**, *38*, 107−115.

(46) Till, B. A.; Weathers, L. J.; Alverez, P. J. J. *Environ. Sci. Technol.* **1998**, *32*, 634−639.

(47) Huang, C. P.; Wang, H. W.; Chiu, P. C. *Water Res.* **1998**, *32*, 2257−2264.