

## Removal of arsenite by Fe(VI), Fe(VI)/Fe(III), and Fe(VI)/Al(III) salts: Effect of pH and anions

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### ABSTRACT

The removal of arsenate and arsenite from drinking water poses challenges, especially when arsenite is present in a significant amount. The removal of arsenite by  $K_2FeO_4$ ,  $K_2FeO_4/FeCl_3$ , and  $K_2FeO_4/AlCl_3$  salts was studied at pH 6.5 and at an initial As concentration of  $500 \mu g As(III) L^{-1}$ . The arsenite removal in Fe(VI)/Fe(III) and Fe(VI)/Al(III) systems was also examined as a function of pH (6.0–8.0). Arsenite was first oxidized by Fe(VI) to arsenate, which was subsequently removed through adsorption by Fe(III) or mixed Fe(III)–Al(III) oxy/hydroxide phases. Fe(VI)/Al(III) salts had higher removal efficiency of arsenite than Fe(VI) and Fe(VI)/Fe(III) salts. A molar ratio of 6(3/3):1 for Fe(VI)/Al(III) to As(III) decreased arsenite concentration from 500 to  $1.4 \mu g L^{-1}$  at pH 6.5. Arsenite removal increased with a decrease in pH from 8.0 to 6.0 and exhibited less pH dependence in the Fe(VI)/Al(III) system than in the Fe(VI)/Fe(III) system. Aluminum chloride salts performed better than  $FeCl_3$  and  $FeCl_3/AlCl_3$  salts (Fe:Al = 1:1) in removing As(V) from water. Effect of anions (phosphate, silicate, bicarbonate, nitrate, and sulfate) on the arsenite removal by Fe(VI)/Al(III) salts at pH 6.5 was examined. Phosphate, silicate, and bicarbonate ions interfered with the removal of arsenite in water. Nitrate and sulfate had none to minimal effect on arsenite removal. Fe(VI)/Al(III) salts showed a potential for removing arsenite below the current drinking water standard ( $10 \mu g L^{-1}$ ).

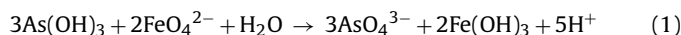
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### 1. Introduction

Arsenic is a common contaminant in groundwater worldwide and according to the World Health Organization (WHO), a long-term exposure of arsenic could reach epidemic proportions [1]. Serious health concerns include cancer of the lung, skin, kidney, bladder, and colon and digestive and neurological disorder. The drinking water standard for arsenic at  $10 \mu g L^{-1}$  was instituted by the WHO, European Union, Japan, and recently by the US Environmental Protection Agency [2]. In natural waters, arsenic is primarily present in inorganic forms as arsenious acid ( $H_3AsO_3$ ) of trivalent arsenite [As(III)] and as oxyanions ( $H_2AsO_4^-$  and  $HAsO_4^{2-}$ ) of pentavalent arsenate [As(V)]. Arsenate is the predominant species in oxygenated water and arsenite is more prevalent under moderately reducing conditions common in groundwater. However, both forms usually coexist in either environment because of their slow redox transformations. The challenges in removing both As(V) and As(III) below the drinking water standard of  $10 \mu g L^{-1}$  and recent arsenic contamination of groundwater in Bangladesh, India, and Vietnam have fueled the need of an effective, efficient, and fea-

sible method for the removal of both arsenic species, particularly arsenite.

The arsenic removal from drinking water is usually performed by coagulation with ferric salts or alum followed by filtration. [3,4]. However, this method cannot effectively remove arsenic if As(III) is present in significant amount. Arsenite has very little affinity for aluminum hydroxides [5]. Both arsenite and arsenate have shown strong affinities for iron oxyhydroxides; however, arsenite sorption is weaker than arsenate at  $pH < 7.0$  [6]. The competitive effect of arsenate on arsenite sorption on iron oxyhydroxides was more pronounced than the effect of arsenite on arsenate sorption [7]. Because of the higher toxicity and mobility of As(III) than As(V), co-occurrence of As(III) and As(V) and their different sorption behavior towards metal oxy/hydroxides, the oxidation of As(III) to As(V) is needed to achieve an effective removal of arsenic from water through adsorption of As(V) onto metal oxyhydroxides. Of the several possible chemical oxidants [8,9], ferrate [Fe(VI)] has recently received increasing attention because of its environmentally-friendly properties and strong oxidizing power [10]. Fe(VI) oxidizes arsenite to arsenate in less than a second in natural water conditions Eq. (1) [11].



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Iron(III) hydroxide produced from the reduction of Fe(VI) Eq. (1) subsequently coagulates arsenate. Fe(VI) thus performs a dual function and has an advantage over other oxidants [12]. Additionally, Fe(VI) can also disinfect the water and will not give chlorinated disinfected by-products [13].

There have been some reports on the removal of arsenite by ferrate in water [9,11]. However, there is no information available on the use of Fe(VI)/Al salts for arsenite removal and the effect of pH and various anions on the removal efficiency. In the present work, a systematic study on the removal of arsenite by  $K_2FeO_4$  with and without Fe(III) and Al(III) chloride salts was performed to determine which of the system suitable for removing arsenite efficiently at a low dose. The effect of pH on arsenite removal by Fe(VI)/Fe(III) and Fe(VI)/Al(III) salts was also evaluated. A combined use of Fe(VI) and  $AlCl_3$  gave better removal performance than that of Fe(VI) and  $FeCl_3$ . Therefore, the effect of phosphate, silicate, bicarbonate, nitrate, and sulfate ions on the removal of arsenite was carried out in the mixed solution of Fe(VI)/Al(III) salts.

## 2. Materials and methods

### 2.1. Materials

All chemicals used were analytical grade and were used without further purifications. High purity deionized water (18.2 M $\Omega$  cm) was prepared using the Barnstead water purification system and was used to prepare all solutions. Ferrate(VI) as the potassium salt ( $K_2FeO_4$ ) was prepared according to the method of Thompson et al. [14]. The purity of  $K_2FeO_4$  was >98%. A molar absorption coefficient,  $\epsilon_{510nm} = 1150 M^{-1} cm^{-1}$ , was used for the calculation of Fe(VI) concentrations at pH 9.0 [15].

Stock solutions of arsenite and arsenate containing 1000 mg  $As L^{-1}$  were prepared using  $NaAsO_2$  and  $Na_2HAsO_4 \cdot 7H_2O$ , respectively and were stored at 4 °C in the refrigerator. Secondary stock solution of 100 mg  $As L^{-1}$  was prepared on the day of experimentation by diluting the primary stock solution with deionized water. An arsenite solution at an initial experimental concentration of 500  $\mu g As(III) L^{-1}$  was prepared by spiking a secondary stock solution into a 0.01 M NaCl solution in order to provide a constant background ionic strength. A solution of Fe(VI) was prepared by adding the  $K_2FeO_4$  salt to water and was always prepared fresh before its addition to arsenite solutions. Solutions of Fe(III) and Al(III) at 0.1 M concentrations were also prepared fresh using  $FeCl_3 \cdot 6H_2O$  and  $AlCl_3 \cdot 6H_2O$  salts, respectively. Solutions of phosphate, silicate, bicarbonate, nitrate, and sulfate were prepared from  $Na_2HPO_4$ ,  $Na_2SiO_3 \cdot 9H_2O$ ,  $NaHCO_3$ ,  $NaNO_3$ , and  $Na_2SO_4$  salts, respectively. The pH of the silicate solution was adjusted to 7.8 by adding HCl in order to achieve silicate as  $H_4SiO_4$  and  $H_3SiO_4^-$  species, which are generally present in natural water samples [16].

### 2.2. Methods

Batch-scale experiments were conducted by transferring 20 mL of 500  $\mu g As(III) L^{-1}$  (6.67  $\mu M$ ) arsenite solutions to 60-mL polyethylene bottles followed by the addition of Fe(VI) solution at various concentrations ranging from 33.4 to 123  $\mu M$ . After adding Fe(VI) solution, the samples were shaken at 240 rpm using a rotary shaker (VWR DS-500) for about 10 min. The pH of the samples was adjusted to 6.5 using HCl. The samples were agitated for 24 h on a rotary shaker. The final pH was measured and the samples were filtered through 0.20  $\mu m$  pore size surfactant-free cellulose acetate membrane filters. The arsenite analysis was performed immediately after filtration and the remainder of the sample was stored at 4 °C for further analysis.

In arsenite removal efficiency experiments using Fe(VI)/Fe(III) and Fe(VI)/Al(III) salts, the Fe(VI) concentrations in mixed solutions were varied to obtain molar ratios of As(III) to Fe(VI) in the range 1.0–3.0. This corresponds to Fe(VI) concentrations of 6.7–20  $\mu M$ . After 10 min of mixing time on a rotary shaker, solutions of Fe(III) and Al(III) chloride salts were added separately in varied concentrations ranging from 6.7 to 127  $\mu M$ . The pH was subsequently adjusted to the desired pH with the addition of KOH. The samples were agitated for 24 h using a rotary shaker. The final pH was measured and the samples were filtered using 0.20  $\mu m$  pore size membrane filters.

Similar batch experiments were conducted to investigate the effect of phosphate, silicate, bicarbonate, nitrate, and sulfate on arsenite removal by Fe(VI)/Al(III) salts at pH 6.5. The experimental set-up was the same as for the above arsenite removal studies except that 20 mL of 500  $\mu g As(III) L^{-1}$  arsenite solutions were spiked separately with various concentrations of phosphate (0.1–1.0 mg  $P L^{-1}$ ), silicate (1.0–10.0 mg  $Si L^{-1}$ ), bicarbonate (10–750 mg  $HCO_3^- L^{-1}$ ), nitrate (1–10 mg  $N L^{-1}$ ), and sulfate (1–50 mg  $SO_4^{2-} L^{-1}$ ) prior to addition of Fe(VI).

### 2.3. Arsenic speciation analyses

Arsenic analysis was performed using an atomic absorption spectrophotometer (Analyst 300 AA, PerkinElmer Corporation, Norwalk, CT, USA) coupled with a flow injection analysis system (FIAS-100) and a graphite furnace system (HGA-850). The flow injection analysis system was equipped with an electrically heated quartz cell. An electrodeless discharge lamp was used as a radiation source. The FIAS-100 was used to analyze arsenite concentrations and total arsenic [ $As(III) + As(V)$ ] concentration <10  $\mu g L^{-1}$ , while the HGA-850 was used to determine total arsenic concentration >10  $\mu g L^{-1}$ . The analytical parameters for the FIAS system were as follows: carrier gas, argon; cell temperature, 900 °C; sample loop, 500  $\mu L$ ; carrier solution, 10% HCl; reducing agent, 0.03%  $NaBH_4$  in 0.05% NaOH (arsenite), and 0.25%  $NaBH_4$  in 0.05% NaOH (arsenite + arsenate). Prior to the determination of total arsenic by FIAS, the samples were reacted with KI and ascorbic acid for at least 1 h before analysis to ensure that all arsenate was converted into arsenite. The method detection limits for total arsenic and arsenite were 0.1 and 0.5  $\mu g L^{-1}$ , respectively. During the analysis by the graphite furnace system, 5  $\mu L$  of Pd–Mg–citric acid matrix modifier was used. The method detection limit for total arsenic by graphite furnace was 1  $\mu g L^{-1}$ . Arsenate concentrations were determined from the difference between total arsenic and arsenite concentrations.

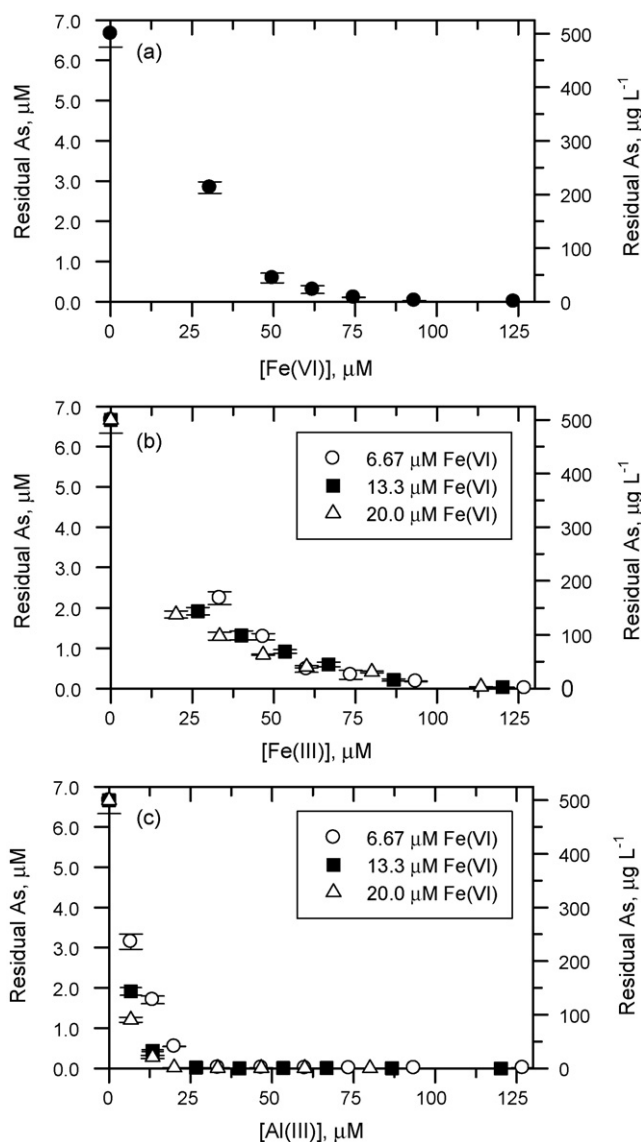
### 2.4. Surface area determinations

Samples of Fe(III), and Fe(III)–Al(III) oxy/hydroxides were synthesized at pH 6.5 using  $K_2FeO_4/FeCl_3$  and  $K_2FeO_4/AlCl_3$  salts, respectively, using a similar procedure as was used for arsenite removal, but no arsenite was present in the solution. The surface areas of the samples were determined using Beckman Coulter SA3100 Surface Area Analyzer utilizing the gas sorption technology. The samples were outgassed at 78 °C for 150 min. Nitrogen gas was used as the adsorbate. The surface area was calculated using the Brunauer–Emmett–Teller (BET) method.

## 3. Results and discussions

### 3.1. Arsenic removal study

The results of the arsenite removal by Fe(VI), Fe(VI)/Fe(III), and Fe(VI)/Al(III) salts are shown in Fig. 1. In the combination system, Fe(VI) was added to arsenite solutions [500  $\mu g As(III) L^{-1}$ ] at three concentration levels, i.e., 6.67, 13.3, and 20.0  $\mu M$  (equivalent



**Fig. 1.** Removal of arsenite by Fe(VI) (a), Fe(VI)/Fe(III) salts (b), and Fe(VI)/Al(III) salts (c) at pH 6.5. Initial arsenic concentration =  $500 \mu\text{g As(III)} \text{L}^{-1}$ .

to As(III):Fe(VI) molar ratios of 1:1, 1:2, and 1:3, respectively) followed by the addition of Fe(III) or Al(III) chloride solutions. Fe(III) or Al(III) concentration varied from 6.67 to  $126.7 \mu\text{M}$ . The final pH was  $6.5 \pm 0.1$ . The speciation analysis of residual arsenic in the solution detected only arsenate. This suggests that Fe(VI) oxidized the initially added arsenite to arsenate Eq. (1), followed by the adsorption of arsenate by Fe(III) or mixed Fe(III)–Al(III) oxy/hydroxide phases.

When only Fe(VI) was used, the concentration of residual As in solution decreased sharply with increasing amounts of Fe(VI) (Fig. 1a) and  $\sim 75 \mu\text{M Fe}$  in  $\text{FeO}_4^{2-}$  was required to reduce the initial arsenite concentration [ $500 \mu\text{g As(III)} \text{L}^{-1}$ ] to less than  $10 \mu\text{g L}^{-1}$  ( $0.13 \mu\text{M}$ ). Comparatively, about  $100 \mu\text{M Fe}$  in  $\text{FeO}_4^{2-}$ – $\text{FeCl}_3$  mixture was needed to achieve the residual arsenic level  $< 10 \mu\text{g L}^{-1}$  (Fig. 1b). It seems that iron(III) oxy/hydroxide precipitated from Fe(III), produced from the reduction of Fe(VI), has higher adsorption capacity for arsenic than that precipitated directly from Fe(III) chloride salt. Other studies also support such advantageous properties of removing contaminants by Fe(III) precipitates, produced from Fe(VI) ion [17,18].

In combination systems, at all three Fe(VI) concentrations used, Al(III) chloride was found more effective than Fe(III) chloride in

decreasing arsenic to below  $10 \mu\text{g L}^{-1}$  (Fig. 1b and c). A comparison of Fig. 1b and c shows that in the Fe(VI)/Al(III) system, arsenic solution concentrations decreased sharply with increasing Al concentrations, while it decreased relatively slowly with increasing Fe(III) concentrations in the Fe(VI)/Fe(III) system. These results suggest that the Fe(III)–Al(III) oxy/hydroxide phases provided more surface sites for arsenic adsorption than did the Fe(III) oxy/hydroxide phases. This could be attributed to the smaller particle size of the Fe(III)–Al(III) oxy/hydroxide precipitates than Fe(III) oxy/hydroxide precipitates leading to higher surface area and more adsorption sites available for arsenic retention. This observation was confirmed by determining the surface areas of the precipitates. The specific surface area values were determined as 250 and  $336 \text{m}^2 \text{g}^{-1}$  for Fe(III) oxy/hydroxides and Fe(III)–Al(III) oxy/hydroxides, respectively. The Fe(III)–Al(III) oxy/hydroxides precipitates with larger surface area were thus able to remove arsenic at a lower dose than the Fe(III) oxy/hydroxides precipitates with smaller surface area.

The required concentrations of Fe(VI) and a coagulant to remove arsenite below drinking water standard ( $10 \mu\text{g L}^{-1}$ ) under different conditions are given in Table 1. At all Fe(VI) concentrations, the required amounts of Al(III) were much lower than that of Fe(III) to reduce the As level to below  $10 \mu\text{g L}^{-1}$ . Interestingly, the molar amount of a combination of Fe(VI) and a coagulant remains constant to decrease As  $< 10 \mu\text{g L}^{-1}$ . These molar concentrations were found to be 133 and  $40.0 \mu\text{M}$  for Fe(VI)/Fe(III) and Fe(VI)/Al(III) salts, respectively (Table 1).

In order to gain a better understanding of As removal by Fe–Al oxy/hydroxides, additional experiments were performed separately on the removal of arsenate by Fe(III), Al(III), and an equimolar mixture of Fe(III)/Al(III) chloride salts at pH 6.5 (Fig. 2). The results in Fig. 2 indicate that  $\text{AlCl}_3$  was more effective for arsenate removal than  $\text{FeCl}_3$ , and  $\text{FeCl}_3$ – $\text{AlCl}_3$  salt solution, and the removal efficiencies were in the following order  $\text{AlCl}_3 > \text{FeCl}_3$ – $\text{AlCl}_3 > \text{FeCl}_3$ . This order is also demonstrated in Table 1 at two different molar ratios of As(V) to coagulant. A molar ratio of 1:4 was not sufficient to achieve the residual concentration of As below  $10 \mu\text{g L}^{-1}$ . A molar ratio of 1:6 was needed for  $\text{AlCl}_3$  and  $\text{FeCl}_3$ – $\text{AlCl}_3$  salts to obtain As levels  $< 10 \mu\text{g L}^{-1}$ . These results are consistent with the results obtained in the arsenite removal by Fe(VI)/Al(III) salts solutions (Table 1). These results suggest that arsenate has a higher sorption affinity

**Table 1**  
Removal of As under different conditions at pH 6.5.

Removal of As(III) by oxidant, Fe(VI) and coagulant		
Fe(VI) ( $\mu\text{M}$ )	Coagulant ( $\mu\text{M}$ )	Residual As ( $\mu\text{g L}^{-1}$ )
0.00	0.00	500
75	–	6.9
6.67	125 $\text{FeCl}_3$	0.7
6.67	33.4 $\text{AlCl}_3$	1.4
13.3	120 $\text{FeCl}_3$	2.6
13.3	26.7 $\text{AlCl}_3$	1.5
20.0	113 $\text{FeCl}_3$	3.4
20.0	20.0 $\text{AlCl}_3$	1.5
Removal of As(V) by coagulant		
Molar ratio 1:4 [As(V):coagulant]		
	0.0 $\mu\text{M FeCl}_3/\text{AlCl}_3$	500
	26.7 $\mu\text{M FeCl}_3$	150
	26.7 $\mu\text{M AlCl}_3$	16.2
	13.3 $\mu\text{M FeCl}_3 + 13.3 \mu\text{M AlCl}_3$	59.6
Molar ratio 1:6 [As(V):coagulant]		
	0.0 $\mu\text{M FeCl}_3/\text{AlCl}_3$	500
	40.0 $\mu\text{M FeCl}_3$	82.8
	40.0 $\mu\text{M AlCl}_3$	1.0
	20.0 $\mu\text{M FeCl}_3 + 20.0 \mu\text{M AlCl}_3$	2.5

Initial arsenic concentration =  $500 \mu\text{g As L}^{-1}$  ( $6.67 \mu\text{M}$ ).

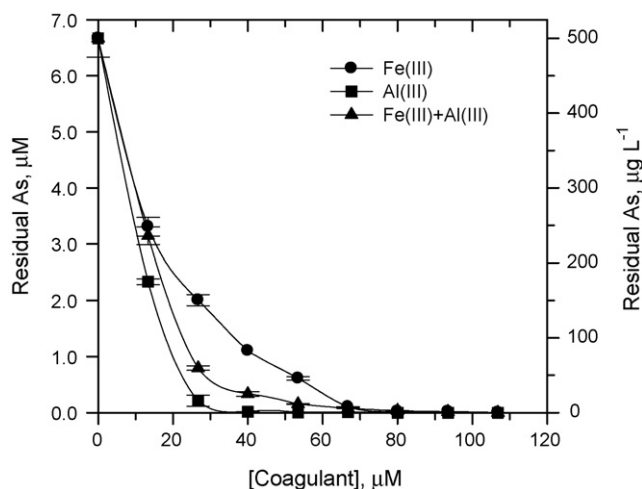


Fig. 2. Removal of arsenate by Fe(III), Al(III), and Fe(III)/Al(III) (Fe:Al = 1:1) salts at pH 6.5. Initial arsenic concentration =  $500 \mu\text{g As(V)} \text{L}^{-1}$ .

for aluminum oxy/hydroxide phases than for iron oxy/hydroxide phases.

The literature reveals inconsistencies as to whether Al(III) or Fe(III) or Fe(III)–Al(III) salts are the most effective for arsenate removal. Previous studies [5,19] have reported that alum and ferric chloride were equally efficient in removing As(V) at pH < 7.5 but Fe(III) salts were more effective than alum at pH > 7.5. However, other researchers [3,20] have found that ferric chloride was a much more effective coagulant than alum in removing arsenate at pH ≤ 7. In a recent report, a mixed Fe(III)–Al(III) reagent at Al:Fe = 1:1 molar ratio yielded better arsenate removal efficiency than individual Fe(III) or Al(III) salt solution [21]. More recently, in the study on the adsorption and desorption of arsenate on presynthesized coprecipitated Al(III)–Fe(III) hydroxides, approximately an equal amount of arsenate was adsorbed at molar ratios of Al:Fe ≤ 1:4, but arsenate adsorption decreased with an increase in Al:Fe molar ratios > 1:4 [22].

The differences in the results could be attributed to having different experimental conditions in various studies [19–22]. In our work, we used membranes with a pore size of  $0.20 \mu\text{m}$ , while in most of the previous studies,  $0.45 \mu\text{m}$  pore size membrane filters were applied. Aluminum hydroxide flocs with sorbed arsenic can pass through  $0.45 \mu\text{m}$  pore size membranes and decrease arsenic removal by alum coagulation [19]. This is consistent with our observation and specific surface area data that the Al oxy/hydroxide flocs are smaller in size than the Fe oxy/hydroxide flocs.

There is a general speculation about the health concern of aluminum in drinking water at concentrations  $> 100 \mu\text{g L}^{-1}$ , the maximum contaminant level for aluminum in drinking water. The residual aluminum concentrations in solutions were analyzed using graphite furnace technique by atomic absorption spectrophotometer and were found to be  $< 20 \mu\text{g L}^{-1}$  over the experimental pH range (6.0–8.0) of this study (data not shown).

### 3.2. Effect of pH

Effect of pH on arsenite removal by Fe(VI)/Al(III) and Fe(VI)/Fe(III) salts are shown in Fig. 3. In both the systems, the residual arsenic concentration in solution decreased with a decrease in pH. However, arsenite removal in Fe(VI)/Fe(III) system showed a greater dependence on pH than in the Fe(VI)/Al(III) system. Analysis of the data in Fig. 1b and c suggests that there are fewer surface sites on the Fe(III) oxy/hydroxide surface than on the Fe(III)–Al(III) oxy/hydroxide surface. This would cause a stronger competition

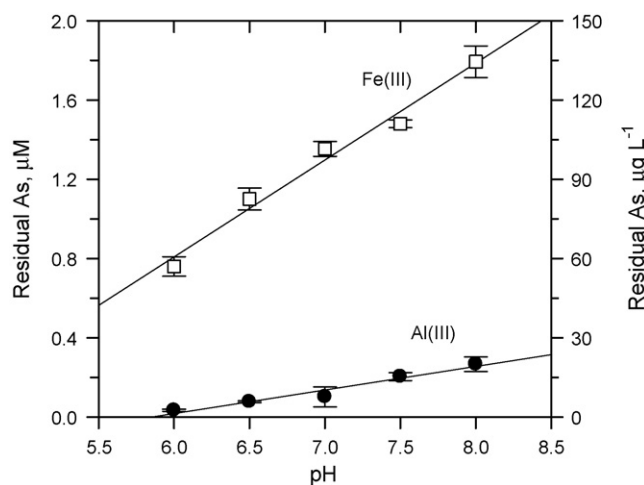


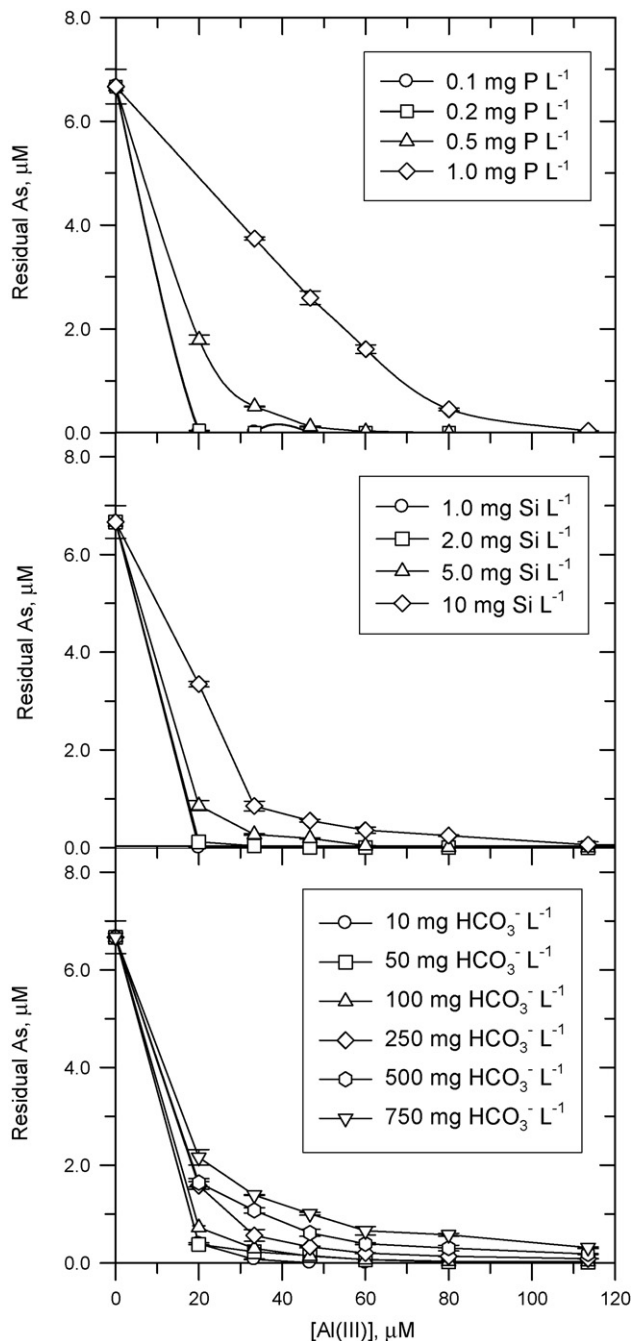
Fig. 3. Effect of pH on arsenite removal by Fe(VI)/Fe(III) and Fe(VI)/Al(III) salts.  $[\text{Fe(VI)}] = [\text{Fe(III)}] = [\text{Al(III)}] = 20 \mu\text{M}$ . Initial arsenic concentration =  $500 \mu\text{g As(III)} \text{L}^{-1}$ .

between arsenate and hydroxyl ions during the adsorption of arsenate on the Fe(III) oxy/hydroxide surface than on the Fe(III)–Al(III) oxy/hydroxide surface to yield results similar to those of Fig. 3. Furthermore, the differences in the point of zero charge (PZC) values of Fe(III) hydroxide and Fe(III)–Al(III) hydroxide could also contribute to this varied pH effect on arsenite removal. The PZC values of Fe hydroxides and Fe–Al hydroxides (Fe:Al = 1:1) are 7.0–8.5 and 8.7–9.1, respectively [22,23]. Thus, the latter would be relatively more positively charged than the former at the experimental pH of 6.5 in our study. This leads to more favorable conditions for arsenate removal in the Fe(VI)/Al(III) than in the use of Fe(VI)/Fe(III) system.

### 3.3. Effect of anions

The influence of phosphate, silicate, and bicarbonate ions on arsenite removal by the Fe(VI)/Al(III) chloride salts at pH 6.5 is shown in Fig. 4. The presence of phosphate at  $0.1$  and  $0.2 \text{ mg L}^{-1}$  had a negligible effect on arsenic removal. This implies that either there were enough sites available for both arsenate and phosphate to adsorb simultaneously or there were some specific sites that preferentially adsorbed phosphate. However, phosphate at  $\geq 0.5 \text{ mg L}^{-1}$  (equivalent to P/As molar ratio of  $\geq 2.4$ ) adversely affected arsenic removal resulting in higher residual dissolved arsenic concentration (Fig. 4a). At  $0.5$  and  $1.0 \text{ mg PL}^{-1}$ , arsenite removal reduced to 73 and 30%, respectively. Hence, higher dose of Al salts would be required in the presence of phosphate, for example, 47 and  $114 \mu\text{M}$  Al were needed to reduce arsenite concentration from 500 to  $< 10 \mu\text{g L}^{-1}$  in the presence of  $0.5$  and  $1.0 \text{ mg PL}^{-1}$ , respectively, as compared to  $20 \mu\text{M}$  Al in the absence of phosphate.

Silicate at  $\leq 2 \text{ mg Si L}^{-1}$  had no significant effect on arsenite removal, but resulted in a noticeable reduction at concentrations  $> 2 \text{ mg Si L}^{-1}$  (Fig. 4b). In the presence of 5 and  $10 \text{ mg Si L}^{-1}$  (equivalent to Si to As ratio = 27 and 53, respectively), arsenite removal decreased to 87 and 50%, respectively. Such effects of silicate have been reported for adsorption of arsenic onto iron hydroxides [24,25]. Silicate has been reported to hinder hydrolysis of Fe(III) salts at a concentration of  $5 \text{ mg Si L}^{-1}$ , which could have also contributed to the reduction in As removal [24]. Like phosphate, silicate also appears to compete with arsenate for sorption sites. However, the results of the current study indicate that silicate is not as competitive as phosphate with arsenate. For example, silicate at  $1 \text{ mg Si L}^{-1}$  had no significant effect on arsenite removal, whereas phosphate at  $1 \text{ mg PL}^{-1}$  reduced arsenite removal more than 50%. Arsenate and phosphate have similar pK values, but pK values of silicic acid differ ( $\text{pK}_1 = 9.46$  and  $\text{pK}_2 = 12.56$ ) [16]. At the initial



**Fig. 4.** Effect of phosphate, silicate, and bicarbonate on removal of arsenite by Fe(VI)/Al(III) salts at pH 6.5. Fe(VI) = 20  $\mu\text{M}$  and initial arsenic concentration = 500  $\mu\text{g As(III) L}^{-1}$ .

pH of 7.8, uncharged species,  $\text{Si(OH)}_4$  would be present predominantly, which may not be strongly preferred by positively charged Fe(III)–Al(III) oxy/hydroxide surface at pH 6.5. This results in less influence of silicate than phosphate on the removal of As in the Fe(VI)/Al(III) system. The results indicate that if silicate is present at 5 and 10  $\text{mg Si L}^{-1}$ , 60 and 114  $\mu\text{M Al}$  are required in addition to 20  $\mu\text{M}$  ferrate to achieve effective removal of arsenite.

Bicarbonate also had an effect on arsenite removal, but the magnitude of the effect was much less than that observed with phosphate and silicate even when bicarbonate was present at concentrations about 2–3 orders of magnitude higher than that of phosphate and silicate (Fig. 4c). Although the reduction in arsenic removal increased with increasing bicarbonate concentration from

10 to 750  $\text{mg L}^{-1}$ , the reduction of arsenic removal was much smaller compared with the increase in bicarbonate concentration. In the presence of bicarbonate at 10, 50, 100, and 500  $\text{mg L}^{-1}$  (corresponding to As to C molar ratios of 1:24, 1:123, 1:246, and 1:1227), arsenite removal was reduced to 94, 94, 89, and 75%, respectively. It is important to note that even at an As:C molar ratio 1:>1000, 75% As removal was observed. These results indicate that arsenic has a much greater affinity for Fe(III)–Al(III) oxy/hydroxide surface than bicarbonate and these two ions apparently do not adsorb on Fe–Al oxy/hydroxide surface by the same mechanism. Similar effects of bicarbonate on arsenate removal by nanoscale zerovalent iron at pH 7 were observed [26]. Bicarbonate ions have been reported to form inner-sphere monodentate complexes with surface functional groups of Fe and Al hydroxides [27]. Phosphate and silicate ions also form inner-sphere complexes and compete strongly with arsenic on Fe or Al oxy/hydroxide surfaces. This suggests that some mechanism other than competition between arsenic and bicarbonate ions contribute to the reduction in arsenic removal.

Table 2 shows the effect of nitrate and sulfate ions on arsenite removal by Fe(VI)/Al(III) salts at pH 6.5. Nitrate ions at concentrations ranging from 1 to 10  $\text{mg N L}^{-1}$  showed a negligible effect on the arsenite removal efficiency. However, arsenite removal was slightly affected by  $\text{SO}_4^{2-}$  ions in the concentration range from 1 to 50  $\text{mg SO}_4^{2-} \text{ L}^{-1}$ . At Fe(VI) and Al(III) concentration of 20  $\mu\text{M}$  each, the residual As concentration increased from 2.5 to 11  $\mu\text{g As L}^{-1}$  with an increase in sulfate concentration from 1 to 50  $\text{mg SO}_4^{2-} \text{ L}^{-1}$ . As evident in Table 2, a higher dose of 33  $\mu\text{M Al(III)}$  was required to decrease the arsenic concentration to <10  $\mu\text{g L}^{-1}$  in the presence of 50  $\text{mg SO}_4^{2-} \text{ L}^{-1}$  as compared to a dose of 20  $\mu\text{M Al(III)}$  in the absence of sulfate. Overall, the results of having none to minimal effects of nitrate and sulfate on the adsorption of arsenate onto Fe(III)–Al(III) oxy/hydroxide phase indicate that Fe(VI)/Al(III) can efficiently remove arsenic under natural water conditions.

Finally, the removal of arsenic from a drinking water sample, spiked with 500  $\mu\text{g L}^{-1}$  arsenite was sought. This drinking water is supplied by the City of Tallahassee in Florida. The composition of the drinking water was: pH 7.5, hardness 156  $\text{mg L}^{-1}$  as  $\text{CaCO}_3$ , phosphate <0.5  $\text{mg P L}^{-1}$ , silicate 13  $\text{mg Si L}^{-1}$ , and dissolved organic carbon <1.0  $\text{mg C L}^{-1}$ . After adding Fe(VI) into the sample, different amounts of Al(III) salt solution were added and the pH of the sample was adjusted to 6.5. The concentrations of remaining As in filtered samples were determined. As shown in Fig. 5, the removal of As could be achieved using  $\sim 100 \mu\text{M Al(III)}$ , similar to results obtained in solution containing Si (see Fig. 4). To see the effect of natural organic matter (NOM) in water on the removal of As, Suwannee River NOM at a concentration of 4  $\text{mg C L}^{-1}$  was added into the arsenite spiked drinking water sample. The remaining concentrations of As in the filtered sample are shown in Fig. 5. At a low concentration of Al(III), NOM spiked sample (4  $\text{mg C L}^{-1}$ ) showed a lower reduction in the concentration of As compared with the sample having <1  $\text{mg C L}^{-1}$ . However, no significant differences between

**Table 2**

The effect of nitrate and sulfate on the removal of arsenite by Fe(VI) and aluminum chloride at pH 6.5.

[Al] ( $\mu\text{M}$ )	Residual arsenic ( $\text{mg L}^{-1}$ )						
	Nitrate ( $\text{mg N L}^{-1}$ )			Sulfate ( $\text{mg SO}_4^{2-} \text{ L}^{-1}$ )			
	1.0	5.0	10	1.0	10	20	50
20.0	1.8	1.6	1.3	2.5	6.3	7.8	11
33.3	0.3	0.3	0.2	0.5	1.0	1.5	3.0
46.7	0.2	0.1	0.1	0.4	0.7	0.9	1.9
60.0	0.1	0.1	<0.1	0.3	0.3	0.6	1.0
80.0	0.1	0.1	<0.1	0.3	0.2	0.4	0.7
113	0.1	0.1	<0.1	0.4	0.3	0.4	0.3

Initial arsenic concentration = 500  $\mu\text{g As(III) L}^{-1}$  (6.67  $\mu\text{M}$ ); [Fe(VI)] = 20  $\mu\text{M}$ .

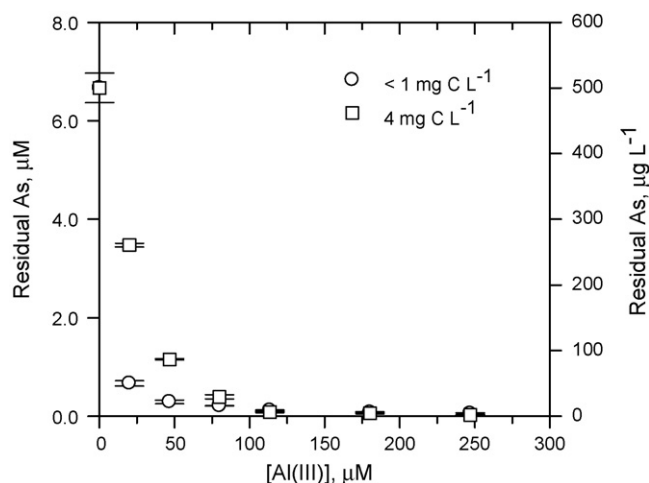


Fig. 5. Effect of NOM on the removal of arsenite in drinking water by Fe(VI)/Al(III) salts at pH 6.5. Fe(VI) = 20  $\mu\text{M}$  and initial arsenic concentration = 500  $\mu\text{g As(III) L}^{-1}$ .

samples with and without NOM were observed for removal of As at Al(III) concentration >100  $\mu\text{M}$ . It seems that at low concentrations of Al(III), functional groups present in organic matter compete with arsenic for sorption sites resulting in less sites available for arsenic removal. At higher Al(III) concentrations (>100  $\mu\text{M}$ ), sufficient sorption sites are available for removal of arsenic in the water samples containing NOM at 4  $\text{mg C L}^{-1}$ .

#### 4. Conclusions

Fe(VI)/Al chloride salts were more effective and efficient than Fe(VI) or Fe(VI)/Fe(III) chloride salts in reducing arsenite concentration from 500  $\mu\text{g As(III) L}^{-1}$  to <10  $\mu\text{g As L}^{-1}$ . A molar ratio of 6(3/3):1 for Fe(VI)/Al(III) to As(III) reduced arsenite concentration from 500 to 1.45  $\mu\text{g L}^{-1}$  at pH 6.5. Aluminum chloride salts performed better than  $\text{FeCl}_3$  and  $\text{FeCl}_3/\text{AlCl}_3$  salts (Fe/Al = 1:1) in removing As(V) from water. The optimum Al(III) to As(V) molar ratio was 6:1 for effectively removing As(V) from 500 to below 10  $\mu\text{g L}^{-1}$  at pH 6.5. If both arsenite and arsenate are present concurrently in water, Fe(VI)/Al chloride salts are suitable for efficient removal of arsenic. Phosphate, silicate, and bicarbonate ions interfered with arsenite removal by Fe(VI)/Al(III) salts at pH 6.5 but the magnitude of interference was different for each ion. Nitrate and sulfate had negligible effect on arsenite removal. Overall, Fe(VI)/Al chloride salts demonstrated potential in removal of arsenite and arsenate from drinking water below the current drinking water standard (10  $\mu\text{g L}^{-1}$ ).

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#### References

- [1] M. Bissen, F.H. Frimmel, Arsenic – a review. Part I: occurrence, toxicity, speciation, and mobility, *Acta Hydrochim. Hydrobiol.* 31 (2003) 9–18.
- [2] United States Environmental Protection Agency, Federal Register, National primary drinking water regulations; arsenic and clarification to compliance and new source contaminants monitoring, final rule, 66 (2001) 6976–7066.
- [3] R.C. Cheng, S. Liang, H.-C. Wang, M.D. Beuhler, Enhanced coagulation for arsenic removal, *J. Am. Water Works Assoc.* 81 (9) (1994) 79–90.
- [4] J.G. Hering, P.-Y. Chen, J.A. Wilkie, M. Elimelech, S. Liang, Arsenic removal by ferric chloride, *J. Am. Water Works Assoc.* 88 (4) (1996) 155–167.
- [5] J.G. Hering, P.-Y. Chen, J.A. Wilkie, M. Elimelech, Arsenic removal from drinking water during coagulation, *J. Environ. Eng.* 123 (1997) 800–807.
- [6] K.P. Raven, A. Jain, R.H. Loeppert, Arsenite and arsenate adsorption on ferrihydrite; kinetics, equilibrium, and adsorption envelopes, *Environ. Sci. Technol.* 32 (1998) 344–349.
- [7] A. Jain, R.H. Loeppert, Effect of competing anions on the adsorption of arsenate and arsenite by ferrihydrite, *J. Environ. Qual.* 29 (2000) 1422–1430.
- [8] G. Ghurye, D. Clifford, As(III) oxidation using chemical and solid-phase oxidants, *J. Am. Water Works Assoc.* 96 (1) (2004) 84–96.
- [9] V.K. Sharma, P.K. Dutta, A.K. Ray, Review of kinetics of chemical and photocatalytic oxidation of arsenic(III) as influenced by pH, *J. Environ. Sci. Heal. A* 42 (2007) 997–1004.
- [10] V.K. Sharma, F. Kazama, H. Jiangyong, A.K. Ray, Iron(VI) and iron(V): environmentally-friendly oxidants and disinfectants, *J. Water Health* 3 (2005) 45–58.
- [11] Y. Lee, I.-H. Um, J. Yoon, Arsenic(III) oxidation by iron(VI) (ferrate) and subsequent removal of arsenic(V) by iron(III) coagulation, *Environ. Sci. Technol.* 37 (2003) 5750–5756.
- [12] C. Li, X.Z. Li, N. Graham, N.Y. Gao, The aqueous degradation of bisphenol and steroid estrogens by ferrate, *Water Res.* 42 (2007) 109–120.
- [13] J.Q. Jiang, Research progress in the use of ferrate(VI) for the environmental remediation, *J. Hazard. Mater.* 146 (2007) 617–623.
- [14] G.W. Thompson, G.W. Ockerman, J.M. Schreyer, Preparation and purification of potassium ferrate(VI), *J. Am. Chem. Soc.* 73 (1951) 1279–1281.
- [15] J.D. Rush, B.H.J. Bielski, Pulse radiolysis of alkaline Fe(III) and Fe(VI) solutions. Observation of transient iron complexes with intermediate oxidation states, *J. Am. Chem. Soc.* 108 (1986) 523–525.
- [16] J.E. Schenk, J.W. Walter, Chemical interactions of dissolved silica with iron(II) and (III), *J. Am. Water Works Assoc.* 2 (1968) 199–212.
- [17] J.Q. Jiang, S. Wang, A. Panagouloupoulos, The exploration of potassium ferrate(VI) as a disinfection/coagulant in water and wastewater treatment, *Chemosphere* 63 (2006) 212–219.
- [18] M.E. Potts, D.R. Churchwell, Removal of radionuclides in wastewaters utilizing potassium ferrate(VI), *Water Environ. Res.* 66 (1994) 107–109.
- [19] L.S. McNeill, M. Edwards, Predicting As removal during metal hydroxide precipitation, *J. Am. Water Works Assoc.* 89 (1) (1997) 75–86.
- [20] K.N. Scott, V. Green, H.D. Do, S.J. McLean, Arsenic removal by coagulation, *J. Am. Water Works Assoc.* 87 (4) (1995) 114–126.
- [21] R.G. Robins, P. Singh, R.P. Das, Coprecipitation of arsenic with Fe(III), Al(III) and mixtures of both in chloride system, In: R.G. Reddy, V. Ramachandran (Eds.), *Arsenic metallurgy*, TMS Annual Meeting, San Francisco, California, 2005, pp. 113–128.
- [22] Y. Masue, R.H. Loeppert, T.A. Kramer, Arsenate and arsenite adsorption and desorption behavior on coprecipitated aluminum:iron hydroxides, *Environ. Sci. Technol.* 4 (2007) 837–842.
- [23] P.R. Anderson, M.M. Benjamin, Surface and bulk characteristics of binary oxide suspensions, *Environ. Sci. Technol.* 24 (1990) 692–698.
- [24] P.J. Swedlund, J.G. Webster, Adsorption and polymerization of silicic acid on ferrihydrite, and its effect on arsenic adsorption, *Water Res.* 33 (1999) 3413–3422.
- [25] X. Meng, S. Bang, G.P. Korfiatis, Effects of silicate, sulfate and carbonate on arsenic removal by ferric chloride, *Water Res.* 34 (2000) 1255–1261.
- [26] S.R. Kanel, B. Manning, L. Charlet, H. Choi, Removal of arsenic(III) from groundwater by nanoscale zerovalent iron, *Environ. Sci. Technol.* 39 (2005) 1291–1298.
- [27] C. Su, D.L. Suarez, In situ infrared speciation of adsorbed carbonate on aluminum and iron oxides, *Clays Clay Miner.* 45 (1997) 814–825.