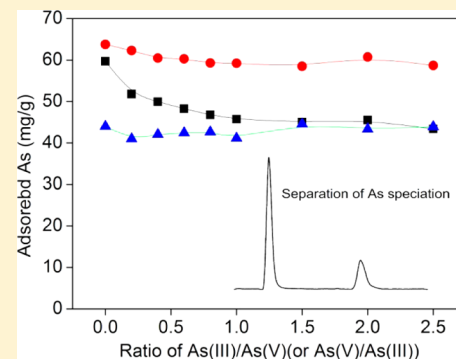


Closer Look at As(III) and As(V) Adsorption onto Ferrihydrite under Competitive Conditions

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ABSTRACT: Batch experiments were conducted in order to investigate the competitive interaction of arsenite (As(III)) and arsenate (As(V)) onto ferrihydrite as a function of initial pH, adsorbent dosage, concentration of coexisting ligands, and order of addition. The pH generally had a great impact on adsorption under both single ion and competitive conditions. However, the amount of As(V) in solution was the controlling factor of adsorption behavior, and As(III) more or less outcompeted As(V) across the pH scale from 4 to 10. Under competitive conditions, i.e., both species were present at the same time, As(III) and As(V) were adsorbed almost equally up to a pH of 5 at an adsorbent dosage of 0.5 g/L and up to a pH of 6 at an adsorbent dosage of 1 g/L. This was contrary to the theoretical prediction that As(V) should adsorb more strongly than As(III) at pH values below the point of zero charge (pzc) of ferrihydrite of about 7 to 8. At low pH, As(V) impedes the adsorption of As(III) but to lesser degree than As(III) impedes As(V) adsorption at a pH above 6. The effect of As(III) on the adsorption of As(V) increased with an increase in pH, and the adsorption of As(V) was almost absent at pH 9 at an adsorbent dosage of 1 g/L and at pH 8 at an adsorbent dosage of 0.5 g/L. In the range of ferrihydrite dosages from 0.2 to 1.6 g/L, As(III) was adsorbed preferentially over As(V) under the availability of less adsorbent. The order of anion addition also had significant effects on their competitive adsorption behavior: the first species was always more favored to compete for the adsorbing sites than when the two species were added to the suspensions simultaneously.



1. INTRODUCTION

Arsenic (As), a natural metalloid, is present in virtually every part of the environment, including the atmosphere, soil, rocks, water, and food, which can have an impact on human health, something that has been recognized as a global problem.^{1–3} Trivalent As (As(III)) and pentavalent As (As(V)) are regularly detected in groundwater, and both species are known to exist. Exposure to inorganic arsenic (As(III) or As(V)) affecting the lungs, skin, liver, kidney, and blood vessels was recognized to be a risk for human. As(V) and more toxic As(III) must be removed from drinking water when concentrations are above what is considered safe for human consumption.^{4,5} Among a number of techniques, such as chemical precipitation, ion exchange, filtration, and reverse osmosis, adsorption is considered to be an inexpensive, simple, safe, and versatile method for the removal of As.⁶ In nature, adsorption onto the mineral ferrihydrite seems to be the main mechanism for controlling the fate and transport of As.⁷ Thus, numerous studies quantified As(V) and As(III) adsorption behavior on iron oxides and hydroxides, such as ferrihydrite, goethite, and hematite.^{8–11} Up to a pH of about 7 to 8, the surface of ferrihydrite is mainly positively charged, and theoretically the adsorption of the As(V) oxyanion, HAsO_4^{2-} , should be favored over that of the neutrally charged As(III) complex, H_3AsO_3 . There is, however, a discrepancy between theoretical considerations and experimental observations. Several studies concluded that As(V) adsorption is pH-dependent whereas As(III) adsorption is less affected by pH.^{12–15} Dixit and

Hering¹¹ pointed out that the sorption of As(V) onto HFO and goethite was more favorable than that of As(III) below pH 5 to 6. Jain and Loeppert¹⁶ observed that As(V) was better adsorbed than As(III) on ferrihydrite at low pH and at a low initial concentration, while the opposite occurred at a high initial arsenic concentration. Raven et al.⁹ reported that As(V) adsorption was greater than As(III) adsorption at a lower pH whereas As(III) adsorption was greater at a higher pH or at high arsenic concentrations.

As(V) mainly formed inner-sphere complexes on hydrous ferric oxide (HFO), whereas As(III) was retained by a combination of inner- and outer-sphere surface complexes.^{17–19}

The presence of competing anions, such as sulfate, bicarbonate, silicate, selenium, and antimony, significantly affects As adsorption.^{20–22} For example, phosphate is a major competitor for both As(V) and As(III).²³ Similarly, the presence of As(III) might influence the adsorption of As(V) and vice versa. Most research into As adsorption involved only single-component adsorption of either As(III) or As(V). Only a few studies concerning the competitive adsorption of As(III) and As(V) exist. Jain and Loeppert¹⁶ also found that in the dual-anion system at equimolar As concentrations of $\leq 156 \text{ mg} \cdot \text{L}^{-1}$ each, As(V) influenced the retention of As(III) in the pH range of 4 to 10 more pronouncedly than As(III) influenced

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the retention of As(V). Goldberg²⁴ reported that the presence of As(III) had no competitive effect on As(V) adsorption, and the influence of As(III) adsorption on As(V) was minor and apparent only for kaolinite and illite.

To understand better the competition between As(III) and As(V) for adsorption sites on ferrihydrite, a set of experiments were carried out for the individual species, i.e., either As(III) or As(V) was present or both species were present at the same time. The objectives of this work were to evaluate (1) the individual and competitive adsorption of As(V) and As(III) within a wide range of pH (4–10) at different adsorbent dosages; (2) the competition as a function of adsorbent dosages; (3) the effect of increasing concentrations of As(III) on the removal of As(V) and vice versa; and (4) the order of species addition on competitive adsorption.

2. MATERIALS AND METHODS

2.1. Materials. Distilled deionized water (DDI) with a resistivity of better than 18 M Ω -cm was used to prepare all of the solutions. Stock solutions of As(V) and As(III) (1000 mg/L) were prepared by dissolving of Na₂HAsO₄·7H₂O (Sigma-Aldrich, Spain) and As₂O₃ (Sigma-Aldrich, Spain) in the DDI water and 4% NaOH solution, respectively. To maintain a relatively constant ionic strength, all working As solutions were freshly prepared with a background electrolyte concentration of 0.01 M NaCl. Other reagents used, such as HCl, NaOH, and NaCl, were at least analytical grade.

Ferrihydrite was synthesized according to the method of Schwertmann and Cornell²⁵ by adding dropwise and under constant stirring a 1 M solution of KOH (Sigma-Aldrich, Germany) to 500 mL of 0.2 M Fe(NO₃)₃·9H₂O (Alfa Aesar, Germany) until the pH increased to 7.4 \pm 0.1 and ferrihydrite started to precipitate. The precipitate was then washed with DDI water, freeze dried, ground, and stored in polyethylene bags in the refrigerator. X-ray diffraction analysis of the material confirmed two-line ferrihydrite (Figure 1), and

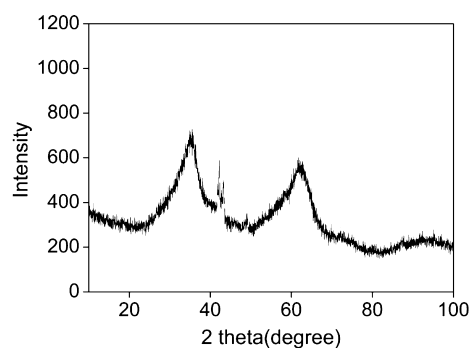


Figure 1. X-ray diffraction pattern of the synthesized ferrihydrite.

the surface area of freeze-dried ferrihydrite was 120 m²/g, as analyzed by the BET (Brunauer–Emmett–Teller) method. The discrepancy between this value and the theoretically possible value may due to the aggregation of the nanoparticles.²⁵

2.2. Experimental Procedure. The experiments of As(III) and As(V) adsorption were carried out in 50 mL polyethylene vials. A solution of As(III) or As(V) of known concentration or their mixture in equal concentrations was pipetted into vials in contact with 0.5 or 1 g/L adsorbent (molar ratio of Fe/As corresponding to 8.48 or 16.96). The vials were capped and shaken in a Rotoshake (RS12/RS8) at 20 rpm at room temperature for 24 h. Kinetics experiments were carried out and 24 h reaction time was adequate to reach equilibrium. The pH of the suspension was adjusted using HCl or NaOH at the beginning, and once the experiment approached equilibrium, the final pH was measured to assess the change in pH during the experiment. The suspensions were filtered with a syringe filter with a pore size of 0.45 μ m, and the supernatant was then analyzed for total As or As

speciation. Arsenic speciation was measured, and As(V) was undetectable in the supernatant of As(III) adsorption. In addition, dissolved iron was negligible, indicating that the oxidation of As(III) did not occur. Similarly, previous studies also reported that no oxidation occurred within 72 h,²⁶ and Manning et al.¹⁴ found no heterogeneous oxidation of As(III) to As(V) on goethite using spectroscopy (XANES). In addition, Zhao et al.²⁷ showed that As(III) oxidation on ferrihydrite did not occur at low Fe/As ratios. The oxidation of dissolved As(III) to As(V) by atmospheric oxygen is unlikely because the reaction vessels were capped, oxygen diffusion was slow, and the As concentrations were sufficiently high.²⁸ Therefore, the oxidation and reduction of As is not a disturbing factor in our competitive adsorption experiments.

To study the effect of the adsorbent dosage on adsorption, a series of 50 mL As solutions containing As(III), As(V), or a mixture of both species were equilibrated with increasing amounts of adsorbent (0.2 to 1.6 g/L) for 24 h in a shaker at pH 6.

To investigate the competitive effect of As(III) on the adsorption of As(V) at pH 4 and vice versa at pH 4 and 9, the competition during adsorption was evaluated by varying the individual concentrations of As(V) and As(III). A mixture of As solution, with the concentration ratio of As(III)/As(V) (or As(V)/As(III)) from 0 to 2.5, was brought into contact with 1 g/L adsorbent, and the residual arsenic species were determined after 24 h.

Experiments with the simultaneous and sequential addition of As(V) and As(III) were carried out for a series of initial As concentrations. During the simultaneous addition experiments, a mixture of both species with equal concentrations was brought into contact with 25 mg of ferrihydrite at the same time. The mixture was then shaken for 48 h. During the sequential addition experiments, As(III) was first added to 25 mg ferrihydrite and then shaken for 24 h. The same concentration of As(V) was then added after 24 h and shaken for an additional 24 h. In another experiment, the order was reversed: As(V) was added first and shaken for 24 h, and then As(III) was added and shaken for another 24 h. The supernatants of all experiments were analyzed for As speciation.

2.3. Analytical Methods. As species were separated by liquid chromatography (LC) using a Hamilton PRP-X100 column, and the concentrations were determined by hydride generation atomic fluorescence spectroscopy (HG-AFS) on a PSA analytical Millennium System, which was directly coupled to the LC system. The detection limits of this method for As(III) and As(V) are 0.17 and 0.38 μ g/L,^{29,30} respectively, with a precision of \pm 2%. The flow rate was 1.5 mL/min, and a 20 mM phosphate buffer (H₆NO₄P, Fluka, India) was used as the mobile phase. The pH of the mobile phase was adjusted to 6 with ammonia. A detailed description of the analytical procedures can be found elsewhere.³¹

The total As concentration was measured by inductively coupled plasma–optical emission spectrometry (ICP-OES) on an Optima 7300 DV instrument. On the basis of at least three repeat measurements, the analytical precision was estimated to be between 2 and 3% and the detection limit was 0.02 mg/L.

3. RESULTS

3.1. Effect of Initial pH. Figures 2 and 3 show the relationship between the initial solution pH and the percentage of As adsorbed under single and competitive conditions at different ferrihydrite dosages. The As(V) adsorption efficiency is clearly dependent on pH, with a higher adsorption capacity at lower pH, decreasing with increasing pH. A different trend was observed for As(III) adsorption, which was more or less constant over a wide pH range. The shapes of the As(V) adsorption edges in the presence of As(III) were similar to those observed without As(III), and the influence of As(III) on As(V) adsorption was negligible under acidic conditions. Competition between the two species was demonstrated by the change in adsorption behavior relative to the availability of adsorption sites. In Figure 2 at a ferrihydrite dosage of 1 g/L,

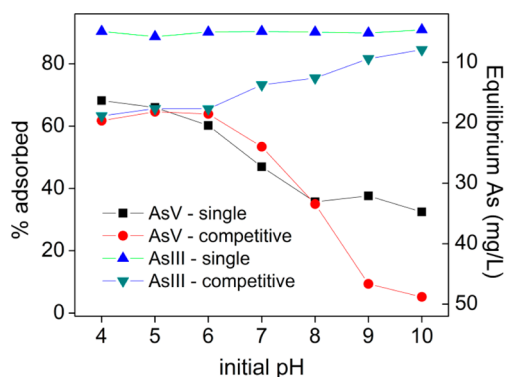


Figure 2. Percent adsorption of As(III) and As(V) onto ferrihydrite as a function of initial pH in single and competitive adsorption experiments (single adsorption, concentration of each As species, 50 mg/L; competitive adsorption, As(III) and As(V), 50 mg/L each; initial pH range from 4 to 10; adsorbent dosage, 1 g/L).

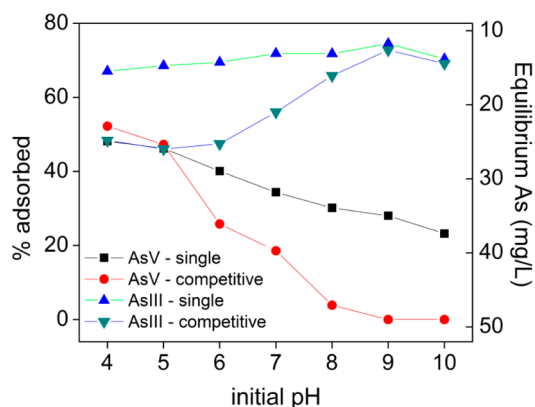


Figure 3. Percent adsorption of As(III) and As(V) onto ferrihydrite as a function of initial pH in single and competitive adsorption experiments (single adsorption, concentration of each As species, 50 mg/L; competitive adsorption, As(III) and As(V), 50 mg/L each; initial pH range from 4 to 10; adsorbent dosage, 0.5 g/L).

As(V) adsorption remained relatively constant until a pH of 6, while at a ferrihydrite dosage of 0.5 g/L, adsorption decreased at pH greater than 5. The presence of As(V) always had an inhibitory impact on the adsorption of As(III) over a wide pH range (4–10) at each ferrihydrite dosage studied. The inhibitory effect on As(III) adsorption by As(V) is stronger at low pH than at high pH. The quantities of As(III) adsorbed decreased under competitive conditions compared to those adsorbed when As(III) was added alone. For example, at a ferrihydrite dosage of 1 g/L and at pH 4, 90.4% of As(III) was adsorbed in the single-species system but only 63.3% of As(III) was adsorbed in the presence of As(V).

3.2. Effect of Adsorbent Dosage. The adsorption capacity can be affected by the quantity of adsorbent, particularly under competitive conditions. The dependence of As adsorption on the adsorbent dosage from 0.2 to 1.6 g/L is shown in Figure 4 as the removal of the two As species from solution, i.e., adsorption, increased with increasing ferrihydrite dosage. Compared to the adsorption of a single species, at a ferrihydrite dosage of less than 0.4 g/L, less As(III) was adsorbed under competitive conditions, whereas As(V) adsorption was negligible. Both As(III) and As(V) uptake under competitive conditions was lower than their respective adsorption during single-species experiments; i.e., the individual

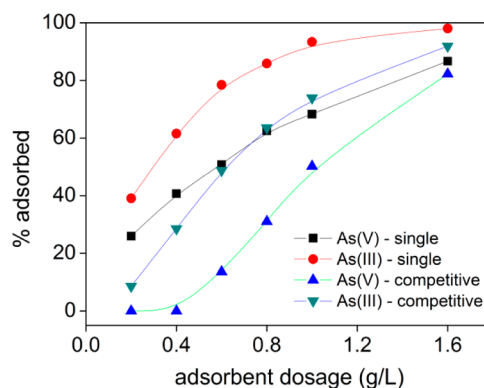


Figure 4. Effect of adsorbent dosage on the removal of As(V) and As(III) in single and competitive adsorption experiments (single adsorption, concentration of each As species, 50 mg/L; competitive adsorption, As(III) and As(V), 50 mg/L each; pH 6; adsorbent dosage, 0.2 to 1.6 g/L).

adsorption percentages of As(V) and As(III) were 68.3 and 93.4% at a ferrihydrite dosage of 1 g/L, while their adsorption percentages under competitive conditions were 50.2 and 73.9%, respectively. Competition was weaker with increasing ferrihydrite dosage; i.e., the inhibitory extent on As(III) adsorption by As(V) was around 26 versus 6.25% at a ferrihydrite dosage of 0.8 versus 1.6 g/L. This suggests that the competition increases with a decreasing number of adsorption sites and could be considered for site heterogeneity on the surface of ferrihydrite.

3.3. Effect of Increasing Concentration of As(III) (or As(V)) on the Adsorption of As(V) (or As(III)).

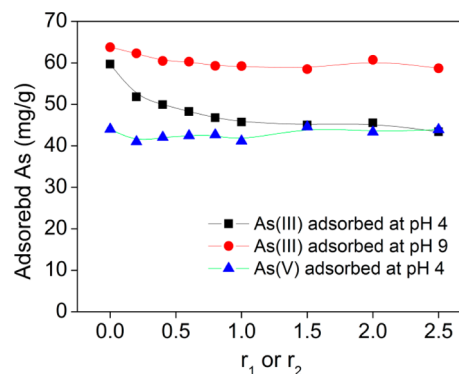


Figure 5. As(III) adsorption behavior under increasing concentrations of As(V) (As(V)/As(III) concentration ratio $r_1 = 0$ to 2.5; pH 4 or 9) and As(V) adsorption behavior under increasing concentrations of As(III) (As(III)/As(V) concentration ratio $r_2 = 0$ to 2.5; pH 4).

presents the amount of As(III) adsorbed on ferrihydrite at pH 4 and 9 in the presence of increasing concentrations of As(V). The adsorption of As(V) at low pH 4 under the condition of increasing concentration of As(III) is shown in Figure 5. The initial concentration ratio of competing and objective ions (As(V)/As(III) = r_1 or As(III)/As(V) = r_2) ranged from 0 to 2.5.

The amount of As(III) adsorption decreased gradually with an increase in r_1 from 0 to 2.5 at both pH values, i.e., from 59.7 to 43.4 mg/g at pH 4 and from 63.8 to 58.7 mg/g at pH 9. The decline in As(III) adsorption was larger under acidic conditions than under alkaline conditions. The adsorption envelope stayed the same up to an r_1 of 1.5. Comparatively, the quantities of As(V) adsorbed remained practically constant at pH 4 for r_2

ranging from 0 to 2.5. Therefore, the adsorption of As(III) was disturbed in the presence of As(V) and decreases as the abundance of As(V) increases. The adsorption of As(V) was irrespective of the presence of increasing concentrations of As(III).

3.4. Influence of the Order of Addition. The competitive adsorption experiments with As(III) and As(V) added simultaneously and sequentially were conducted at pH 5. Figures 6 and 7 show the amounts of As(V) and As(III)

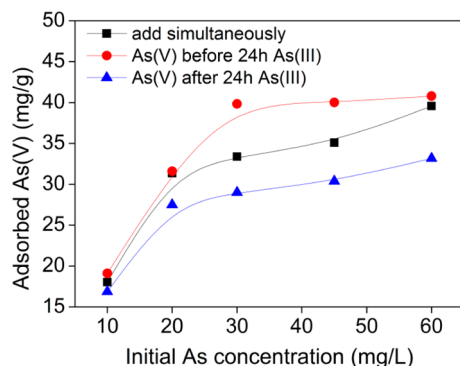


Figure 6. Adsorption behavior of As(V) under competitive conditions as a function of exposure order (pH value 5; adsorbent dosage 0.5 g/L; As(V) added 24 h before As(III); As(III) added 24 h before As(V); and the two species added simultaneously).

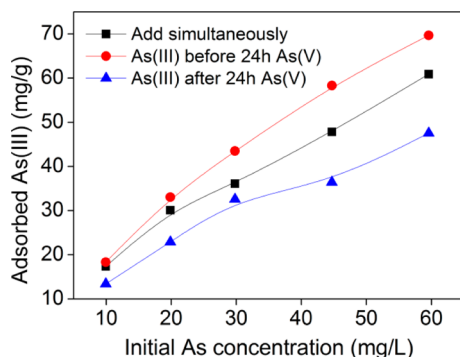


Figure 7. Adsorption behavior of As(III) under competitive conditions as a function of exposure order (pH value 5; adsorbent dosage 0.5 g/L; As(III) added 24 h before As(V); As(V) added 24 h before As(III); and the two species added simultaneously).

adsorbed at different initial As concentrations when the competing species were added (a) at the same time, (b) 24 h before, and (c) 24 h later. The results show that the order of addition had a significant influence on the amount of either As(III) or As(V) adsorbed in the experiments with both species present at the same time. The overall amount of arsenic adsorbed increased with the initial As concentrations.

Most arsenic was adsorbed when the main species were added to ferrihydrite 24 h prior, while the smallest amount of arsenic was adsorbed when the competing species were added 24 h prior (Figures 6 and 7). The amount of arsenic adsorbed was between these two values, when both the main and competing species were added at the same time. In other words, when As(III) and As(V) were added simultaneously, the ability of As(V) to prevent the adsorption of As(III) was slightly greater than that in the As(V) before As(III) systems whereas lower than those in the As(III) before As(V) systems. However, compared to the order of addition affecting either

As(III) or As(V) adsorbed, it did not have a considerable influence on the total amounts of As(III) and As(V) adsorbed (Figure 8). It is evident that the first As species was always

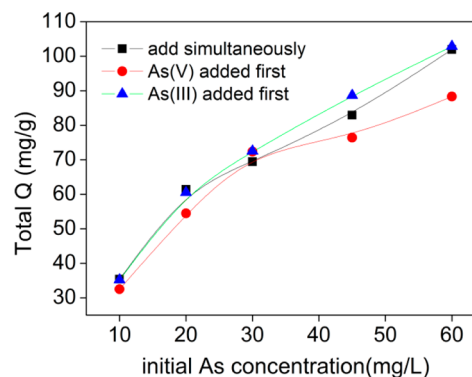


Figure 8. Total amounts of As(V) and As(III) adsorbed onto ferrihydrite under competitive conditions as a function of exposure order (pH value 5; adsorbent dosage 0.5 g/L; As(III) added 24 h before As(V); As(V) added 24 h before As(III); and the two species added simultaneously).

more favored to compete for the adsorption sites than when the species were added simultaneously. This is particularly true once the conditions get more and more competitive.

4. DISCUSSION

4.1. Arsenic Adsorption Behavior under Varying pH.

The solution pH is an important control for the distribution of the As species, which in turn strongly affects the adsorption. The adsorption of As(V) was favored at low pH and decreased considerably with increasing pH, while the pH had a minor influence on As(III) adsorption, which corresponds to their adsorption behavior under competitive conditions (Figures 2 and 3). The dependence of As(V) adsorption on pH may be caused by (1) electrostatic attraction and (2) the formation of inner-sphere complexes by ligand exchange.¹⁸ Specific adsorption may occur between uncharged species H_3AsO_3^0 and HFO .^{8,32} It was reported that the mechanism of adsorption of As(III) may be a complexation reaction rather than a surface potential.³³ Contrary to theoretical considerations, As(III) showed a higher affinity than As(V) even at low pH in our single adsorption experiments. Contrary to theoretical considerations, As(III) showed a higher affinity than As(V) even at low pH in our single adsorption experiments. A study by Chakravarty et al.³⁴ showed that ferruginous manganese ore was an efficient adsorbent for both arsenic species but showed a higher adsorption for As(III). Similar findings were observed by others who reported that As(III) was adsorbed more strongly than As(V) on ferrihydrite at high As concentrations of $13.3 \text{ mol}_{\text{As}} \text{ kg}_{\text{fer}}^{-1}$ and $3.47 \text{ mol}_{\text{As}} \text{ kg}_{\text{fer}}^{-1}$.^{9,16} At low As concentrations, the adsorption of As(III) was approximately equal to that of As(V).⁹ In this study, the As(III) adsorption was already stronger at a lower As concentration of $0.67 \text{ mol}_{\text{As}} \text{ kg}_{\text{fer}}^{-1}$ than those reported by Raven et al., which should be caused by a lower surface area of the ferrihydrite used in this study of $120 \text{ m}^2/\text{g}$, and hence fewer adsorption sites. The effect is identical to that of increasing the As concentration in solution. The final pH of As(V) adsorption drifted 1 to 2 units to higher pH compared to the initial pH. HAsO_4^{2-} is the predominant dissolved species in the pH range of 3 to 6, and the adsorption of As(V) is supported by the existence of H^+ . No addition of

H^+ may contribute to the lower adsorption of As(V). The pH variation during the adsorption should attract attention in case it is useful in explaining the adsorption mechanism which is still unknown.

4.2. Competitive Interaction between As(III) and As(V). Under competitive adsorption conditions, As(III) and As(V) were adsorbed in almost equal amounts up to a pH of 5 at a adsorbent dosage of 0.5 g/L and up to a pH of 6 at an adsorbent dosage of 1 g/L (Figures 2 and 3). This finding was contrary to the common belief that As(V) is more strongly adsorbed than As(III) at a pH below its point of zero charge (approximately 7 to 8). At the same time, As(V) affects the adsorption of As(III) but to a lesser degree: as the pH increases, As(III) is more strongly adsorbed (Figures 2 and 3). This is even more pronounced as adsorption conditions become more competitive: the ferrihydrite dosage decreases to 0.5 g/L (Figure 3), which demonstrates the greater affinity of As(III) for ferrihydrite across the whole pH spectrum studied.

The potential of As(III) to outcompete As(V) under competitive conditions is further demonstrated in Figures 4 and 5. Compared to As(V), As(III) was adsorbed preferentially at lower ferrihydrite dosages at a pH below the PZC during competitive adsorption, which is in agreement with the result that As(III) generally showed a higher affinity for adsorption onto ferrihydrite than did As(V). Only when there was virtually no more competition with abundant adsorption sites for both species at a high ferrihydrite dosage was As(V) adsorbed almost as much as As(III) (Figure 4). These findings are consistent with studies that reported that the adsorption of As(V) on goethite and ferrihydrite can be lessened by the presence of As(III) at high pH values, while the adsorption of As(III) was influenced by As(V) over a wide range of pH.^{16,35}

The inhibitory effect on the adsorption of As(III) by As(V) is stronger at low pH, the value of which ranged approximately from the pK_1 to the pK_2 of As acid (H_3AsO_4 , $pK_1 = 2.3$, $pK_2 = 6.8$). This may be ascribed to the fact that As(V) was more strongly retained on ferrihydrite by electrostatic attraction in this pH range, while As(III) may be loosely bound on the surface sites and can be partially replaced by As(V). It was reported that As(III) was less strongly adsorbed than As(V) on goethite.²³ As pointed out by Jain et al.,³⁶ the uncharged As(III) species would likely be less retained on the surface of ferrihydrite than the negatively charged As(V) species. Another explanation according to Arai et al.³⁷ is that As(V) forms inner-sphere complexes regardless of the pH and ionic strength and that As(III) forms inner-sphere complexes at low pH but together with outer-sphere complexes with increasing pH. The inner-sphere complex of As(V) may affect the formation of inner-sphere As(III) complexes on ferrihydrite at low pH.

4.3. Mechanism of Arsenic Adsorption under Competitive Conditions. Anions could be adsorbed on the adsorbents through nonspecific and/or specific adsorption. It has been shown that the electrostatic interaction, surface complexation and specific adsorption are the main adsorption mechanisms for the adsorption of arsenic on iron oxides.³⁸ During competitive adsorption with sufficient As(III) and As(V) present in solution, both As(III) and As(V) were adsorbed onto ferrihydrite (Figure 3). We found that As(III) continued to be strongly adsorbed when the adsorption sites were not available for excess As(V) at high pH. Moreover, the total amount of As(III) and As(V) adsorbed in the competitive adsorption experiments was significantly larger than either As species adsorbed but lower than the sum total of each As

species adsorbed when added alone. The oxide surface contains adsorption sites which are accessible to both species where competitive adsorption could take place and adsorption sites which are species-exclusive.³⁹ It is pointed out that the iron oxides have two types of surface sites, one of which is accessible to both As(V) and phosphate and one type for phosphate only.⁴⁰ The competitive adsorption between As(III) and As(V) may take place only for sites accessible to both species.

The sequence of contact with ferrihydrite had a significant effect on the adsorption of either arsenic species (Figures 6 and 7). If added in sequence, either As(III) first or As(V) first, the species which was added first can occupy the adsorption sites more successfully. During simultaneous addition, the two species may be expected to compete for some sites directly, but during sequential addition, the first species must be desorbed before the second ion can be adsorbed. Previous studies also reported that the order of anion addition affected the adsorption of phosphate and As(V) on the surfaces of goethite.^{41,42} The results may indicate that only a small fraction of the adsorbed arsenic is desorbed and replaced by the competing ions added later. It is evidence that both As(III) and As(V) adsorption are dominated by forming stable surface complexes (inner-sphere complexes) on HFO.

4.4. Implication for As(III) and As(V) Mobility in the Environment. The relative affinity for the adsorption of As(III) and As(V) onto ferrihydrite depends on the pH of the solution, the adsorbent dosage, and competing ions. In single systems, As(III) was adsorbed more favorable than was As(V) over the studied pH ranges. However, As(V) was adsorbed to a similar extent as As(III) at low pH under competitive conditions (Figures 2 and 3). The presence of As(V) would decrease the affinity of As(III) on the surface of HFO.

These results have some implications for the mobility of As in the environment. The general recognition that As(III) is more soluble and mobile than As(V),⁵ due to As(III) weakly adsorbed on iron oxides, is one-sided and oversimplified. The greater affinity of As(III) for adsorption onto ferrihydrite suggests that the existence of iron hydroxides in the soil must exert an inhibitory effect on its mobility. In the aquatic system, As(V) may compete for the surface sites of HFO, and thus some As(III) may desorb. Thus, the presence of As(V) would enhance the mobility of As(III), and As(III) may be slightly more agile than As(V) under acidic aqueous conditions.

5. CONCLUSIONS

The dependence of As(V) adsorption on pH and the independence of As(III) adsorption with respect to pH were observed in both single and competitive adsorption experiments. Contrary to the theoretical prediction that As(V) should adsorb more strongly than As(III) at pH values below the point of zero charge (pzc) of ferrihydrite of about 7 to 8, As(III) more or less outcompeted As(V) across the pH scale from 4 to 10. At low pH, As(V) impedes the adsorption of As(III) but to a lesser degree than As(III) impedes As(V) adsorption at a pH above 6, which is below the PZC of ferrihydrite. The effect of As(III) on the adsorption of As(V) increased with an increase in pH, and the adsorption of As(V) was almost absent at a pH of 8 to 9. The decrease of adsorbed As(III) was higher at low pH ranging from pK_1 to pK_2 for arsenate acid and lower with increasing pH. The decrease in adsorbed As(III) also depended on the concentrations of coexisting As(V). The order of species addition had a significant effect on their competitive adsorption

because each arsenic species could occupy the adsorption sites successfully when in contact with ferrihydrite first.

The results confirm that there was competition during the simultaneous adsorption of As(III) and As(V). It is inferred that the competition is limited on some adsorption sites which are common to both As(V) and As(III). Ferrihydrite displays an inhibitory effect on As(III) mobility in the environment, although the presence of As(V) enhances the mobility of As(III) and As(III) may be slightly more mobile than As(V) under acidic conditions.

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Notes

The authors declare no competing financial interest.

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REFERENCES

- (1) Jones, F. T. A Broad View of Arsenic. *Poult. Sci.* **2007**, *86*, 2–14.
- (2) Bissen, M.; Frimmel, F. H. Arsenic – a Review. Part 1: Occurrence, Toxicity, Speciation, Mobility. *Acta Hydrochim. Hydrobiol.* **2003**, *31*, 9–18.
- (3) Smedley, P. L.; Kinniburgh, D. G. A Review of the Source, Behaviour and Distribution of Arsenic in Natural Waters. *Appl. Geochem.* **2002**, *17*, 517–568.
- (4) Ahmed, M. F.; Ahuja, S.; Alauddin, M.; Hug, S. J.; Lloyd, J. R.; Pfatt, A.; Pichler, T.; Saltikov, C.; Stute, M.; Van Geen, A. Ensuring Safe Drinking Water in Bangladesh. *Science* **2006**, *314*, 1687–1688.
- (5) Basu, A.; Saha, D.; Saha, R.; Ghosh, T.; Saha, B. A Review on Sources, Toxicity and Remediation Technologies for Removing Arsenic from Drinking Water. *Res. Chem. Intermed.* **2014**, *40*, 447–485.
- (6) Gallegos-Garcia, M.; Ramirez-Muniz, K.; Song, S. Arsenic Removal from Water by Adsorption Using Iron Oxide Minerals as Adsorbents: A Review. *Miner. Process. Extr. Metal. Rev.* **2012**, *33*, 301–315.
- (7) Pichler, T.; Veizer, J.; Hall, G. E. M. Natural Input of Arsenic into a Coral-Reef Ecosystem by Hydrothermal Fluids and Its Removal by Fe(III) Oxyhydroxides. *Environ. Sci. Technol.* **1999**, *33*, 1373–1378.
- (8) Pierce, M. L.; Moore, C. B. Adsorption of Arsenite and Arsenate on Amorphous Iron Hydroxide. *Water Res.* **1982**, *16*, 1247–1253.
- (9) Raven, K. P.; Jain, A.; Loeppert, R. H. Arsenite and Arsenate Adsorption on Ferrihydrite: Kinetics Equilibrium, and Adsorption Envelopes. *Environ. Sci. Technol.* **1998**, *32*, 344–349.
- (10) Mamindy-Pajany, Y.; Hurel, C.; Marmier, N.; Roméo, M. Arsenic(V) Adsorption from Aqueous Solution onto Goethite, Hematite, Magnetite and Zero-Valent Iron: Effects of pH, Concentration and Reversibility. *Desalination* **2011**, *281*, 93–99.
- (11) Dixit, S.; Hering, J. G. Comparison of Arsenic(V) and Arsenic(III) Sorption onto Iron Oxide Mineral: Implications for Arsenic Mobility. *Environ. Sci. Technol.* **2003**, *37*, 4182–4189.
- (12) Maiti, A.; DasGupta, S.; Basu, J. K.; De, S. Batch and Column Study: Adsorption of Arsenate Using Untreated Laterite as Adsorbent. *Ind. Eng. Chem. Res.* **2008**, *47*, 1620–1629.
- (13) Kundu, S.; Gupta, A. K. Adsorptive Removal of As(III) from Aqueous Solution Using Iron Oxide Coated Cement (IOCC): Evaluation of Kinetic, Equilibrium and Thermodynamic Models. *Sep. Purif. Technol.* **2006**, *51*, 165–172.
- (14) Manning, B. A.; Fendorf, S. E.; Goldberg, S. Surface Structures and Stability of Arsenic(III) on Goethite: Spectroscopic Evidence for Inner-Sphere Complexes. *Environ. Sci. Technol.* **1998**, *32*, 2383–2388.
- (15) Jeong, Y.; Fan, M.; Singh, S.; Chuang, C. L.; Saha, B.; Van Leeuwen, J. H. Evaluation of Iron Oxide and Aluminum Oxide as Potential Arsenic(V) Adsorbents. *Chem. Eng. Process.* **2007**, *46*, 1030–1039.
- (16) Jain, A.; Loeppert, R. H. Effect of Competing Anions on the Adsorption of Arsenate and Arsenite by Ferrihydrite. *J. Environ. Qual.* **2000**, *29*, 1422–1430.
- (17) Waychunas, G. A.; Rea, B. A.; Fuller, C. C.; Davis, J. A. Surface Chemistry of Ferrihydrite: Part I. EXAFS Studies of the Geometry of Coprecipitated and Adsorbed Arsenate. *Geochim. Cosmochim. Acta* **1993**, *57*, 2251–2269.
- (18) Goldberg, S.; Johnston, C. T. Mechanisms of Arsenic Adsorption on Amorphous Oxides Evaluated Using Macroscopic Measurements, Vibrational Spectroscopy, and Surface Complexation Modeling. *J. Colloid Interface Sci.* **2001**, *234*, 204–216.
- (19) Ona-Nguema, G.; Morin, G.; Juillot, F.; Calas, G.; Brown, G. E., Jr. EXAFS Analysis of Arsenite Adsorption onto Two-Line Ferrihydrite, Hematite, Goethite, and Lepidocrocite. *Environ. Sci. Technol.* **2005**, *39*, 9147–9155.
- (20) Bullough, F.; Weiss, D. J.; Dubbin, W. E.; Coles, B. J.; Barrott, J.; SenGupta, A. K. Evidence of Competitive Adsorption of Sb(III) and As(III) on Activated Alumina. *Ind. Eng. Chem. Res.* **2010**, *49*, 2521–2524.
- (21) Jeong, Y.; Fan, M.; Van Leeuwen, J.; Belczyk, J. F. Effect of Competing Solutes on Arsenic(V) Adsorption Using Iron and Aluminum Oxides. *J. Environ. Sci. (Beijing, China)* **2007**, *19*, 910–919.
- (22) Manning, B. A.; Goldberg, S. Modeling Competitive Adsorption of Arsenate with Phosphate and Molybdate on Oxide Minerals. *Soil Sci. Soc. Am. J.* **1996**, *60*, 121–131.
- (23) Stachowicz, M.; Hiemstra, T.; Van Riemsdijk, W. H. Multi-Competitive Interaction of As(III) and As(V) Oxyanions with Ca²⁺, Mg²⁺, PO₄³⁻, and CO₃²⁻ Ions on Goethite. *J. Colloid Interface Sci.* **2008**, *320*, 400–414.
- (24) Goldberg, S. Competitive Adsorption of Arsenate and Arsenite on Oxides and Clay Minerals. *Soil Sci. Soc. Am. J.* **2002**, *66*, 413–421.
- (25) Schwertmann, U.; Cornell, R. M. *Iron Oxides in the Laboratory: Preparation and Characterization*, 2nd ed.; Wiley-VCH: Weinheim, Germany, 2008.
- (26) Oscarson, D. W.; Huang, P. M.; Defosse, C.; Herbillon, A. Oxidative Power of Mn(IV) and Fe(III) Oxides with Respect to As(III) in Terrestrial and Aquatic Environments. *Nature* **1981**, *291*, 50–51.
- (27) Zhao, Z.; Jia, Y.; Xu, L.; Zhao, S. Adsorption and Heterogeneous Oxidation of As(III) on Ferrihydrite. *Water Res.* **2011**, *45*, 6496–6504.
- (28) Johnson, D. L.; Pilson, M. E. The Oxidation of Arsenite in Seawater. *Environ. Lett.* **1975**, *8*, 157–171.
- (29) Gomez-Ariza, J. L.; Sanchez-Rodas, D.; Beltran, R.; Corns, W.; Stockwel, P. Evaluation of Atomic Fluorescence Spectrometry as a Sensitive Detection Technique for Arsenic Speciation. *Appl. Organomet. Chem.* **1998**, *12*, 439–447.
- (30) Wu, D.; Pichler, T. Simultaneous Speciation Analysis of As, Sb and Se Redox Couples by SF-ICP-MS Coupled to HPLC. *Anal. Methods* **2014**, *6*, 5112–5119.
- (31) Price, R. E.; Amend, J. P.; Pichler, T. Enhanced Geochemical Gradients in a Marine Shallow-Water Hydrothermal System: Unusual Arsenic Speciation in Horizontal and Vertical Pore Water Profiles. *Appl. Geochem.* **2007**, *22*, 2595–2605.
- (32) Bowell, R. J. Sorption of Arsenic by Iron Oxides and Oxyhydroxides in Soils. *Appl. Geochem.* **1994**, *9*, 279–286.
- (33) Pokhrel, D.; Viraraghavan, T. Arsenic Removal from an Aqueous Solution by Modified A. Niger Biomass: Batch Kinetic and Isotherm Studies. *J. Hazard. Mater.* **2008**, *150*, 818–825.
- (34) Chakravarty, S.; Dureja, V.; Bhattacharyya, G.; Maity, S.; Bhattacharjee, S. Removal of Arsenic from Groundwater Using Low Cost Ferruginous Manganese Ore. *Water Res.* **2002**, *36*, 625–632.
- (35) Kanematsu, M.; Young, T. M.; Fukushi, K.; Green, P. G.; Darby, J. L. Arsenic(III, V) Adsorption on a Goethite-Based Adsorbent in the Presence of Major Co-Existing Ions: Modeling Competitive

Adsorption Consistent with Spectroscopic and Molecular Evidence. *Geochim. Cosmochim. Acta* **2013**, *106*, 404–428.

(36) Jain, A.; Raven, K. P.; Loeppert, R. H. Arsenite and Arsenate Adsorption on Ferrihydrite: Surface Charge Reduction and Net OH⁻ Release Stoichiometry. *Environ. Sci. Technol.* **1999**, *33*, 1179–1184.

(37) Arai, Y.; Elzinga, E. J.; Sparks, D. L. X-ray Absorption Spectroscopic Investigation of Arsenite and Arsenate Adsorption at the Aluminum Oxide-Water Interface. *J. Colloid Interface Sci.* **2001**, *235*, 80–88.

(38) Guo, H.; Stüben, D.; Berner, Z. Adsorption of Arsenic(III) and Arsenic(V) from Groundwater Using Natural Siderite as the Adsorbent. *J. Colloid Interface Sci.* **2007**, *315*, 47–53.

(39) Hingston, F. J.; Posner, A. M.; Quirk, J. P. Competitive Adsorption of Negatively Charged Ligands on Oxide Surfaces. *Discuss. Faraday Soc.* **1971**, *52*, 334–342.

(40) Zeng, H.; Fisher, B.; Giammar, D. E. Individual and Competitive Adsorption of Arsenate and Phosphate to a High-Surface-Area Iron Oxide-Based Sorbent. *Environ. Sci. Technol.* **2008**, *42*, 147–152.

(41) Hongshao, Z.; Stanforth, R. Competitive Adsorption of Phosphate and Arsenate on Goethite. *Environ. Sci. Technol.* **2001**, *35*, 4753–4757.

(42) Liu, F.; De Cristofaro, A.; Violante, A. Effect of pH, Phosphate and Oxalate on the Adsorption/desorption of Arsenate on/from Goethite. *Soil Sci.* **2001**, *166*, 197–208.