Arsenate uptake and arsenite simultaneous sorption and oxidation by Fe–Mn binary oxides: Influence of Mn/Fe ratio, pH, Ca^{2+}, and humic acid

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ABSTRACT

Arsenate retention, arsenite sorption and oxidation on the surfaces of Fe–Mn binary oxides may play an important role in the mobilization and transformation of arsenic, due to the common occurrence of these oxides in the environment. However, no sufficient information on the sorption behaviors of arsenic on Fe–Mn binary oxides is available. This study investigated the influences of Mn/Fe molar ratio, solution pH, coexisting calcium ions, and humic acids have on arsenic sorption by Fe–Mn binary oxides. To create Fe–Mn binary oxides, simultaneous oxidation and co-precipitation methods were employed. The Fe–Mn binary oxides exhibited a porous crystalline structure similar to 2-line ferrihydrite at Mn/Fe ratios 1:3 and below, whereas exhibited similar structures to δ-MnO$_2$ at higher ratios. The As(V) sorption maximum was observed at a Mn/Fe ratio of 1:6, but As(III) uptake maximum was at Mn/Fe ratio 1:3. However, As(III) adsorption capacity was much higher than that of As(V) at each Mn/Fe ratio. As(V) sorption was found to decrease with increasing pH, while As(III) sorption edge was different, depending on the content of MnO$_2$ in the binary oxides. The presence of Ca^{2+} enhanced the As(V) uptake under alkaline pH, but did not significantly influence the As(III) sorption by 1:9 Fe–Mn binary oxide; whereas the presence of humic acid slightly reduced both As(V) and As(III) uptake. These results indicate that As(III) is more easily immobilized than As(V) in the environment, where Fe–Mn binary oxides are available as sorbents and they represent attractive adsorbents for both As(V) and As(III) removal from water and groundwater.

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1. Introduction

Arsenic, a naturally occurring element, is of environmental and public concern because of its high toxicity and carcinogenicity [1,2]. The presence of arsenic at elevated concentrations in natural environments (soils, sediments, and waters) is attributable to both natural processes and anthropogenic activities [3]. The toxicity, mobility, and bioavailability of arsenic are highly dependent on its oxidation state and chemical speciation [4]. In natural environments, arsenic is primarily present in inorganic forms and exists in two predominant species, arsenate [As(V)] and arsenite [As(III)]. As(V) is the major arsenic species under oxidizing conditions, while As(III) is the dominant arsenic species under reducing conditions. As(III) is considered to be more toxic [5], soluble, and mobile than As(V).

Although the concentrations of arsenic in the aquatic environment are controlled by different mechanisms including adsorption, redox processes, ion exchange, and dissolution/precipitation, the adsorption reactions occurring at surfaces of minerals (particularly metal oxides) play a very important role in its mobility and potential bioavailability [6,7]. Fe oxides are the most abundant metal oxides found in soils and sediments. Numerous investigations have focused on arsenic immobilization by natural and synthetic Fe oxides and hydroxides since they have a strong affinity for arsenic species [8–11]. Manganese is the 10th most abundant element in the earth's crust and second only to iron as the most common heavy metal [12]. Its oxides are very active components of natural environments and are also ubiquitous in soils and sediments. These metal oxides not only have the ability to adsorb arsenic but also effectively oxidize As(III) into As(V) in natural environments. Therefore, the retention and transformation of arsenic by Mn oxides have been studied extensively [13–17,7].

Mn and Fe are closely related in chemical properties and occur together in soils and sediments [18]. Deschamps and coworkers have observed that Mn and Fe enriched minerals could oxidize arsenite to arsenate and reacted better in arsenite uptake than that of arsenate [4,19]. In our previous studies [20,21], we encountered similar phenomena when a synthetic Fe–Mn binary oxide was used to adsorb both arsenate and arsenite from water. Our findings indicated that the Fe–Mn binary oxide was more effective in arsenic immobilization than both the pure Fe oxide and Mn oxide. Thus, the processes of arsenic sorption and oxidation at

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the interface of Mn and Fe enriched minerals/water may play an important role in the mobilization and transformation of As in the environment.

Previous studies on As sorption onto samples containing both Fe and Mn oxides are relatively few [4,19–21] and limited to one natural sample or a synthetic Fe–Mn binary oxide with a fixed Fe/Mn ratio. It is known that the ratios of Mn/Fe in Fe–Mn binary oxides vary largely in natural environments [22], and Fe–Mn binary oxides with different Mn/Fe ratios may differ greatly in arsenic uptake. Therefore, a detailed and inclusive study of arsenic sorption onto Fe–Mn binary oxides is necessary to better understand the fate and transport of arsenic in the natural environment. This research also has the ability to aid in the development of new adsorbents for arsenic removal in water treatment processes.

The objectives of this research are (1) to synthesize a series of Fe–Mn binary oxides with different Mn/Fe molar ratios and characterize them with a variety of techniques; (2) to investigate the arsenic sorption behaviors as affected by Mn/Fe molar ratio and solution pH; and (3) to study the influences of commonly occurring Ca^{2+} and humic acid on arsenic sorption.

2. Materials and methods

2.1. Materials

All chemicals are analytical grade and were used without further purification. Reaction vessels (glass) were cleaned with 1% HNO_3 and rinsed several times with deionized water before use. As(III) and As(V) stock solutions were prepared with deionized water using $NaAsO_2$ and $NaHAsO_4 \cdot 7H_2O$, respectively. Arsenic working solutions were freshly prepared by diluting arsenic solutions with deionized water.

2.2. Preparation of ferrihydrite and Fe–Mn binary oxides

A series of Fe–Mn binary oxides was synthesized at 0:1 (0% Mn), 1:9 (10% Mn), 1:6 (14.2% Mn), 1:3 (25% Mn), and 1:1(50% Mn) Mn/Fe molar ratios. The Fe–Mn binary oxide with a molar ratio of 1:3 was prepared according to a method slightly modified from that proposed by G.S. Zhang et al. [20]. Potassium permanganate ($KMnO_4$, 0.015 mol) and iron(II) sulfate heptahydrate ($FeSO_4 \cdot 7H_2O$, 0.045 mol) were dissolved in 200 mL of deionized water. Under vigorous magnetic stirring, the $FeSO_4$ solution was added into the $KMnO_4$ solution simultaneously with 3 M NaOH solution to keep the solution pH in a range between 7 and 8. After addition, the formed suspension was continuously stirred for 1 h, aged at room temperature for 4 h, and then washed repeatedly with deionized water until no sulfate could be detected. The suspension was then filtrated and dried at 65 °C for 24 h. The dry material was crushed and stored in a desiccator for later use. The synthesis of Fe–Mn binary oxides with Mn/Fe molar ratios of 1:9 and 1:6 was similar to that of 1:3 with the exception of the addition of $FeCl_3$ into the $FeSO_4$ solution. For the preparation of Fe–Mn binary oxide at 1:1 (50%) Mn/Fe molar ratio, 0.027 mol potassium permanganate ($KMnO_4$,) was dissolved in 200 mL of deionized water. Following the preceding steps, 0.045 mol iron(II) sulfate heptahydrate ($FeSO_4 \cdot 7H_2O$) and 0.018 mol manganese(II) chloride tetrahydrate ($MnCl_2 \cdot 4H_2O$) were dissolved in another 200 mL of deionized water. The just mentioned steps were comparable to that of the 1:3 ratio. Ferrihydrite was prepared using the following method: Under vigorous magnetic-stirring, sodium hydroxide solution (NaOH, 3 M) was added using a pipette, into the 0.2 M $FeCl_3$ solution to raise the solution pH to approximately 7.5. After addition, the formed suspension was continuously stirred for 1 h, aged at room temperature for 4 h, and then washed several times with deionized water.

2.3. Characterization

X-ray diffraction patterns of powder samples from Fe–Mn binary oxides were obtained using a D/Max-3A diffractometer with Ni-filtered copper Kα 1 radiation. Specific surface area, pore volume, and pore size distribution were measured by nitrogen adsorption–desorption isotherm using the BET method with a Micromeritics ASAP 2000 surface area analyzer.

The point of zero charge (pzc) of the Fe–Mn binary oxide was determined according to the slightly modified method described by D.G. Kinniburgh et al. [23], an inert electrolyte titration one. The Fe–Mn binary oxide powder was suspended in 0.01 M $NaNO_3$ for 24 h, after which the rate of pH change with time was very slow. Fifty milliliter of suspension was then adjusted to various pH values with NaOH or HNO_3 solution. After agitation for 60 min for equilibrium, the initial pH was measured; then, 1.5 g of $NaNO_3$ was added to each suspension to bring final electrolyte concentration to about 0.45 M. After an additional 3 h, the final pH was measured. The results, plotted as ΔpH (final pH – initial pH) against final pH, yielded the pzc as the pH at which ΔpH = 0.

2.4. Batch adsorption

Adsorption isotherms of arsenate and arsenite on 0:1, 1:9, 1:6, 1:3, and 1:1 Mn/Fe binary oxides were obtained using batch experiments at pH 7.0. Initial arsenic concentration varied from 5 mg/L to 40 mg/L. In each test, 10 mg of the adsorbent sample was loaded in the 150-mL glass vessel, and 50 mL of solution containing differing amounts of arsenic was then added to the vessel. In order to keep the pH level around 7.0, 0.1 M of NaOH or HNO_3 was added, accordingly. The vessels were shaken on an orbit shaker at 140 rpm for 24 h at 25 ± 1 °C. After the reaction period, all samples were filtered by a 0.45 μm membrane filter and analyzed for arsenic.

Adsorption envelopes of arsenate and arsenite on 0:1, 1:9, 1:6, 1:3, and 1:1 Mn/Fe binary oxides were obtained using batch tests. In each test, 10 mg of the adsorbent sample was loaded in the 150-mL glass vessel containing 50 mL of arsenic solution. The pH values of individual samples were adjusted every 4 h with dilute HNO_3 and/or NaOH solution to designated values in the range of 3–12 during the shaking process. The equilibrium pH was measured, and the supernatant was filtered through a 0.45 μm membrane after the solutions were mixed for 24 h.

The influence of calcium ions and humic acid on the sorption of arsenic was investigated by, respectively, adding lime nitrate and humic acid to 10 mg/L of arsenic solution. In each test, 10 mg of the adsorbent sample was loaded in the 150-mL glass vessel containing 50 mL of arsenic solution. The concentrations of Ca^{2+} were fixed at 1 and 10 mM, while the concentration of humic acid was fixed at 5 mg TOC/L. The pH values of individual samples were adjusted every 4 h with dilute HNO_3 and/or NaOH solution to designated values in the range of 3–12 during the shaking process. After reaction, samples were analyzed as described previously.

2.5. Analytical methods

Total arsenic (As(III) + As(V)) concentrations were determined using an inductively coupled plasma atomic emission spectroscopy machine (ICP-AES, Optima 2100 DV, Perkin Elmer Co.). Prior to analysis, the aqueous samples were acidified with concentrated HNO_3 in an amount of 1% and stored in acid-washed glass vessels. Selective As(III) analysis was performed using hydride generation–atomic fluorescence spectroscopy (HG–AFS) with AF-610A equipment (Beijing Ruili Analytical Instrument Co., Ltd. China). Five milliliter-filtered supernatant was transferred into 10 mL test tube, and 2 mL 0.5 mol L^{-1} citric acid was added as a carrying solution. The

solution was next diluted to 10 mL with deionized water (solution pH = 3.1) and was subsequently analyzed. All samples used in our analysis were analyzed within 24 h of collection.

3. Results and discussion

3.1. Characteristic of Fe–Mn binary oxides

X-ray diffraction patterns of prepared Fe–Mn binary oxides are illustrated in Fig. 1. The pattern of the oxide with a Mn/Fe molar ratio of 0:1, namely the pure Fe oxide, shows the poorly ordered 2-line ferrihydrite pattern with two broad peaks at 34.4° and 62.1°, according to d spacing of 0.260 and 0.149 nm, respectively [24,25]. The patterns of Fe–Mn binary oxides with Mn/Fe molar ratios of 1:9, 1:6, and 1:3 were almost identical to that of the 0:1 oxide. However, for 1:1 Fe–Mn binary oxide, the two peaks shifted to 37.3° and 66.7°, respectively, which are typical of the synthetic birnessite phase δ-MnO$_2$ [26]. Clearly, Fe–Mn binary oxides with lower MnO$_2$ content are similar to 2-line ferrihydrite in phase structure, while Fe–Mn binary oxides with higher MnO$_2$ content are similar to birnessite δ-MnO$_2$.

The results of BET surface area measurements of the Fe–Mn binary oxides are summarized in Supplementary material Table S1. It can be seen that the Fe–Mn binary oxides all contain a high surface area. However, with the exception of 1:3 Fe–Mn binary oxide, the surface areas of other Fe–Mn binary oxides were smaller than that of the pure Fe oxide, but the pore volumes overall were larger.

The values of point of zero charge of the 0:1, 1:9, 1:6, 1:3, and 1:1 Fe–Mn binary oxides were 7.4, 6.9, 6.4, 5.8, and 4.8, respectively, suggesting lower pzc value with increasing Mn/Fe molar ratio (Supplementary material Fig. S1). The pzc of ferrihydrite is pH 7–9 and that of MnO$_2$ is 2–3 [27,28]. Clearly, the pzc value lowered as MnO$_2$ content increased in the binary oxides, due to its lower pzc value. In our previous study [20], 1:3 Fe–Mn binary oxide was found to have a pzc of pH 5.9, as determined by potentiometric titration. This indicated that the obtained pzc values were reasonable in the present research.

3.2. Sorption isotherms

Arsenic sorption capacities of Fe–Mn binary oxides with different Mn/Fe molar ratios were evaluated using adsorption isotherms at pH 7.0 ± 0.1 (Fig. 2). Data from the adsorption isotherms were modeled using both Freundlich and Langmuir models (Freundlich type provided in Fig. 2). It was found that the Freundlich model was much more suitable for describing the adsorption behavior of arsenic on Fe–Mn binary oxides than the Langmuir model. The

Freundlich adsorption constants obtained from the isotherms are listed in Table 1.

As(V) adsorption increased with an increase in Mn/Fe molar ratio and reached a maximum of approximately 60 mg g^{-1} when the ratio was 1:6 and then reduced with further increases in Mn/Fe molar ratio. The As(V) adsorption capacity decreased to 40 mg g^{-1} at a Mn/Fe molar ratio of 1:1. This value is even lower than that of pure 2-line ferrihydrite. The higher As(V) adsorption with 1:9, 1:6, and 1:3 Fe–Mn binary oxides can be ascribed to their higher specific surface areas and pore volumes. Generally, adsorbents with a high specific surface area and big pore volume have a high adsorption capacity. Although adsorbents with a high specific surface area generally exhibit a high adsorption capacity, its adsorption ability is also influenced by the pore volume and components. Thus, the lower As(V) adsorption with 1:1 Fe–Mn binary oxide could be partially attributable to the presence of a high concentration of manganese dioxide, which has very low arsenic adsorption ability.

The trend of As(III) adsorption with the increase in Mn/Fe molar ratio was similar to that of As(V), except that the maximum adsorption capacity of 114 mg g^{-1} occurred at Mn/Fe molar ratio of 1:3. It should be noted that As(III) adsorption capacity was much higher than that of As(V) at each Mn/Fe molar ratio in this study, even for 0:1 Mn/Fe binary oxide, namely pure 2-line ferrihydrite. This is interesting because As(V) is generally considered to adsorb and react more strongly onto the solid phase than As(III). But some researchers have also found that the ferrihydrite had higher adsorption capacity toward As(III) than that of As(V), especially at high As equilibrium concentrations [8,10]. These results further confirm that the often-stated generalization that As(III) is more mobile in the environment than As(V) is too simplistic, when iron oxides are available as sorbents [10]. For other Fe–Mn binary oxides, the higher As(III) sorption capacities could be explained as follows. The presence of manganese dioxide in the binary oxides can influence As(III) sorption in two aspects. On the one hand, the introduced manganese dioxide may effectively oxidize As(III) to As(V). In addition, during As(III) oxidation, the reductive dissolution of MnO$_2$ resulted in the production of fresh adsorption sites at solid surface, which favored the adsorption of formed As(V) [21]. The As(III) uptake was, therefore, enhanced. Due to the low As(V) adsorption ability of manganese dioxide alone, the high concentrations present in the binary oxide were not beneficial to arsenic uptake. The increase in As(III) uptake due to the As(III) oxidation process cannot compensate for the loss in As(III) sorption as the presence of excessive manganese dioxide would lead to a decrease in the total amount of arsenic sorption.

These results indicate that there is an optimal range for Mn/Fe molar ratio and within this range, the Fe–Mn binary oxides would have much higher sorption capacities toward both As(V) and As(III). Moreover, the different sorption behaviors of As(III) on the surfaces of the Fe–Mn binary oxides are mainly due to the processes of As(III) oxidation.

3.3. Influence of solution pH on arsenic sorption

Fig. 3 demonstrates the effect of pH on arsenic sorption of Fe–Mn binary oxides. As(V) sorption on Fe–Mn binary oxides followed similar trends with respect to pH (Fig. 3a). It was clearly dependent on pH with the greatest adsorption occurring under acidic conditions and decreased with increases in solution pH. Many researchers have also observed similar pH effects for the sorption of As(V) onto iron oxides or iron-containing oxides [29,30]. Under the tested pH range (3–11), $H_2AsO_4^-$ and $HAsO_4^{2-}$ are dominant As(V) species in the solution. Lower pH is favorable for the protonation of sorbent surfaces. Increased protonation is thought to increase positively charged sites and enlarges the attracting force existing
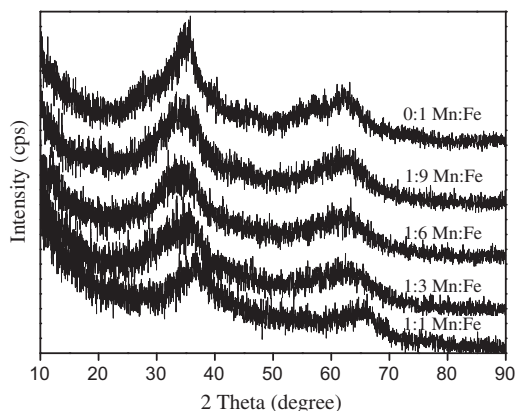

Fig. 1. XRD patterns of the Fe–Mn binary oxides containing different molar ratios of 0:1, 1:9, 1:6, 1:3, and 1:1.
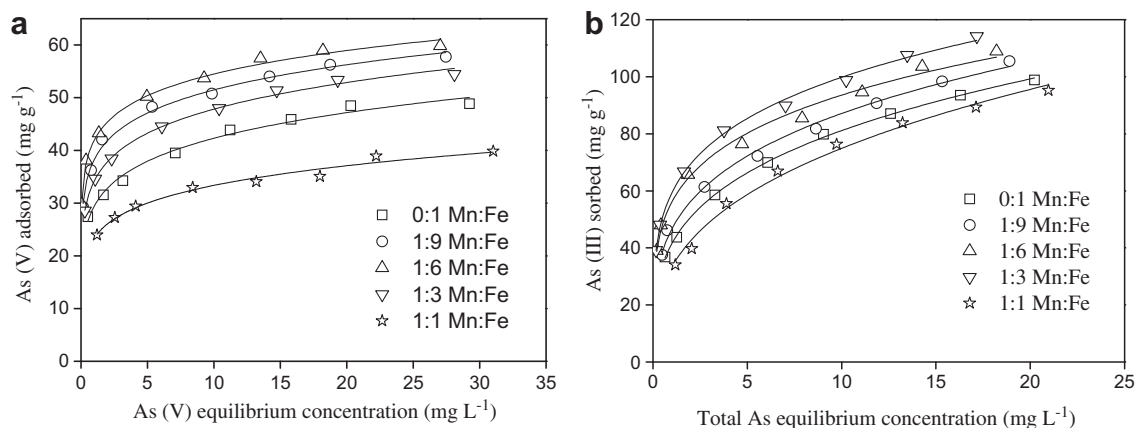
Fig. 2. Sorption isotherms of As(V) (a) and As(III) (b) on Fe–Mn binary oxides in 0.01 M NaNO₃ at pH 7.0.

Table 1
Freundlich isotherm parameters for As(V) and As(III) adsorption on Fe–Mn binary oxides at pH 7.0 ± 0.1.

Adsorbent	As(V)			As(III)		
	K_F (mg g^{-1})	$1/n$	R^2	K_F (mg g^{-1})	$1/n$	R^2
0:1 Mn/Fe	29.49	0.1569	0.985	41.55	0.2905	0.999
1:9 Mn/Fe	38.33	0.1281	0.992	46.66	0.2712	0.994
1:6 Mn/Fe	42.00	0.1132	0.995	56.10	0.2221	0.991
1:3 Mn/Fe	34.27	0.1449	0.992	59.40	0.2254	0.997
1:1 Mn/Fe	23.47	0.1529	0.975	33.35	0.3514	0.990

between the sorbent surface and arsenate anions, therefore, increasing the amount of adsorption in the lower pH region. With an increase in solution pH, the negatively charged sites gradually dominate, further enhancing repulsion effects, and the amount of adsorption is consequently dropped.

As(III) sorption on 0:1 Fe–Mn binary oxide increased gradually with the increasing solution pH and reached a maximum at a pH of approximately 8.8 (Fig. 3b), which is characteristic of As(III) adsorption [31]. Adsorption of weak acids by metal oxides usually reaches a maximum at pH values similar to pk_{a1} of the acid [32]. The pk_{a1} of arsenious acid is 9.2. The decrease in As(III) uptake at pH over 9 is likely attributable to increased electrostatic repulsion between negatively charged arsenite species and the oxide surface.

The trends of As(III) sorption on 1:3 and 1:1 Fe–Mn binary oxides with respect to pH are very similar to those of As(V), except for higher arsenic sorption capacity. This indicated that As(III) in the solution was almost oxidized to As(V) by these two oxides [20].

As(III) sorption on 1:9 and 1:6 Fe–Mn binary oxides followed similar trends with respect to pH, partially similar to that of 0:1,1:3 and 1:1 oxides, indicating that part of As(III) was converted to As(V). These results specify that the Fe–Mn binary oxide with high manganese dioxide content could oxidize As(III) more effectively.

3.4. Influence of calcium ions and humic acid on arsenic sorption

The influences of coexisting calcium ions on arsenic sorption for 1:9 and 1:3 Fe–Mn binary oxides were, respectively, investigated at two concentration levels (1 mM and 10 mM). The results are shown in Fig. 4. For As(V), the presence of Ca^{2+} ions enhanced the retention of As(V) on both 1:9 and 1:3 Fe–Mn binary oxides, especially when the solution pH was over 7.0. Increasing the concentration of present Ca^{2+} ions could further increase As(V) sorption. Similar results of Ca-induced enhancement in As(V) sorption at a higher pH have been reported for both clay minerals and oxides [27,33–35]. The high uptake of As(V) on the Fe–Mn binary oxide is most likely due to the participation of calcium ions in the adsorption process. It was believed that the adsorption of calcium ions resulted in a positive charged surface, which favored the adsorption of anionic species [33]. Another possible interpretation for the Ca-induced enhancement in As(V) sorption is the formation of CaHAsO₄ or Ca₃(AsO₄) precipitation, which is favored at alkaline pH levels [36].

The presence of Ca^{2+} ions influenced the sorption of As(III) on 1:3 Fe–Mn binary oxide in a similar way to that of As(V). It is not
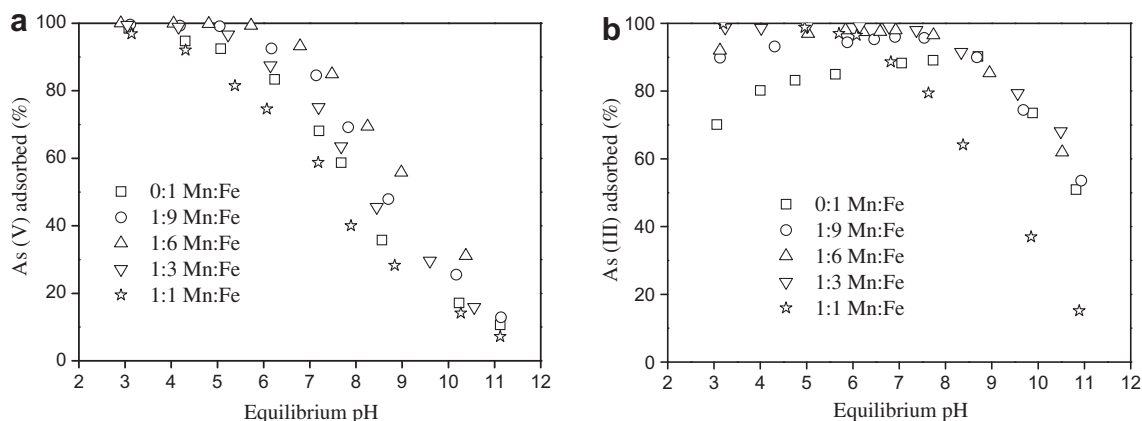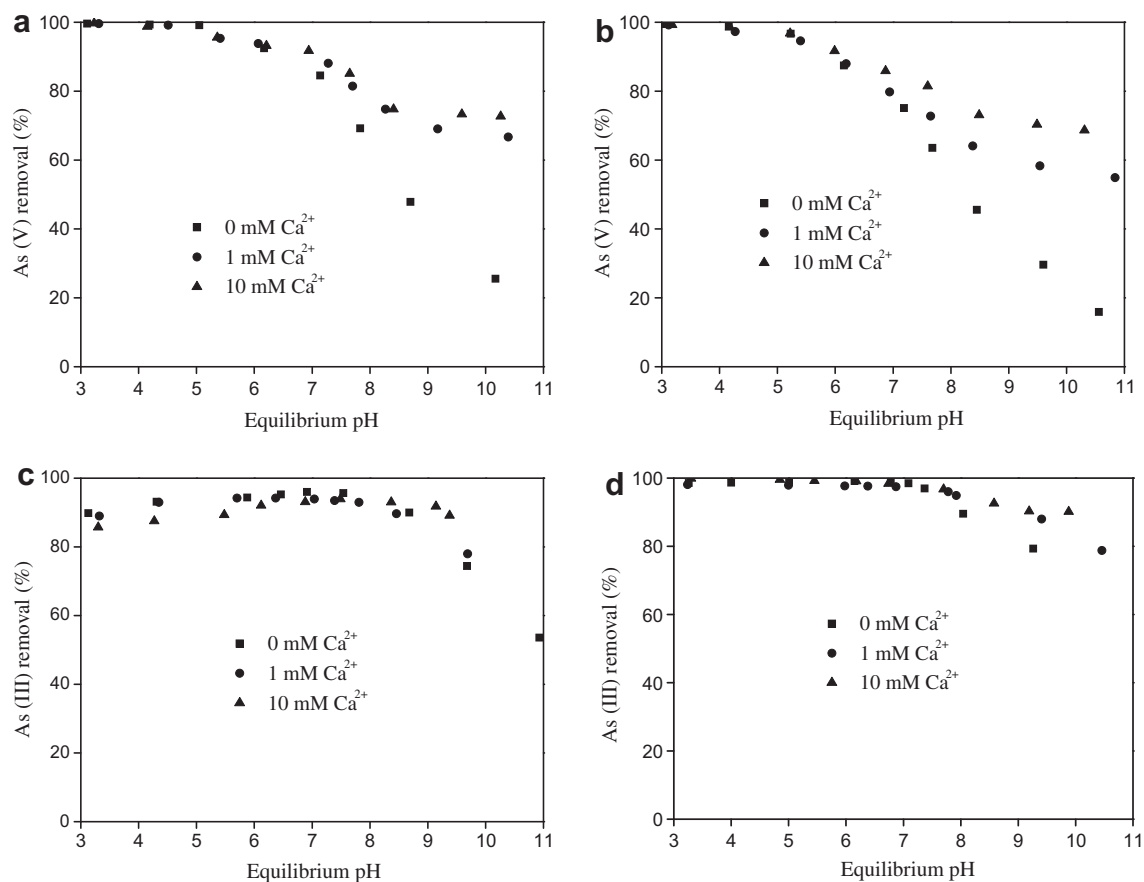

Fig. 3. Influence of solution pH on As(V) (a) and As(III) (b) sorption by Fe–Mn binary oxides in 0.01 M NaNO₃. Initial arsenic concentration: 10 mg/L; adsorbent content: 200 mg/L.

Fig. 4. Influence of calcium ions on sorption of As(V) by 1:9 Fe–Mn binary oxide (a), 1:3 Fe–Mn binary oxide (b) and As(III) by 1:9 Fe–Mn binary oxide (c), 1:3 Fe–Mn binary oxide (d). Initial arsenic concentration: 10 mg/L; adsorbent content: 200 mg/L.

a surprise since added As(III) can be completely oxidized to As(V) by this Fe–Mn binary oxide [20]. For the 1:9 Fe–Mn binary oxide, the presence of Ca^{2+} ions slightly increased the removal of As(III) at pH over 8.0, whereas the removal of As(III) at a pH below 6.0 only exhibited a small reduction. Evidently, due to the MnO_2 concentration in the 1:9 Fe–Mn binary oxide, added As(III) was partially oxidized to As(V) and largely presents in neutral H_3AsO_3 species at pH below 6.0. However, As(III) may form both inner- and outer-sphere surface complexes on Fe oxide [37] with outer-sphere complexes being sensitive to the change in ionic strength. The nitrate concentration increased with an increase in calcium ions, since calcium nitrate was used in this study, which could reduce the sorbed arsenic in outer-sphere complexes.

Natural organic matter, which is not only ubiquitous in natural aquatic and soil environments but also highly reactive toward metals and surfaces, may interfere with arsenic sorption on the surfaces of minerals and increase the mobility of arsenic. Therefore, the effect of present humic acid on arsenic sorption by the Fe–Mn binary oxides was studied. The results are shown in Fig. 5.

The presence of HA decreased arsenic sorption to both 1:9 and 1:3 Fe–Mn binary oxides. However, the reduction in arsenic sorption was not significant, with the only exception being As(III) to the 1:9 Fe–Mn binary oxide at a pH below 6.0. In a study where humic acid was pre-adsorbed onto Fe–Mn nodules, a decrease in both oxidation and sorption of As was observed due to reduced binding sites for As(III). A study conducted by Redman et al.
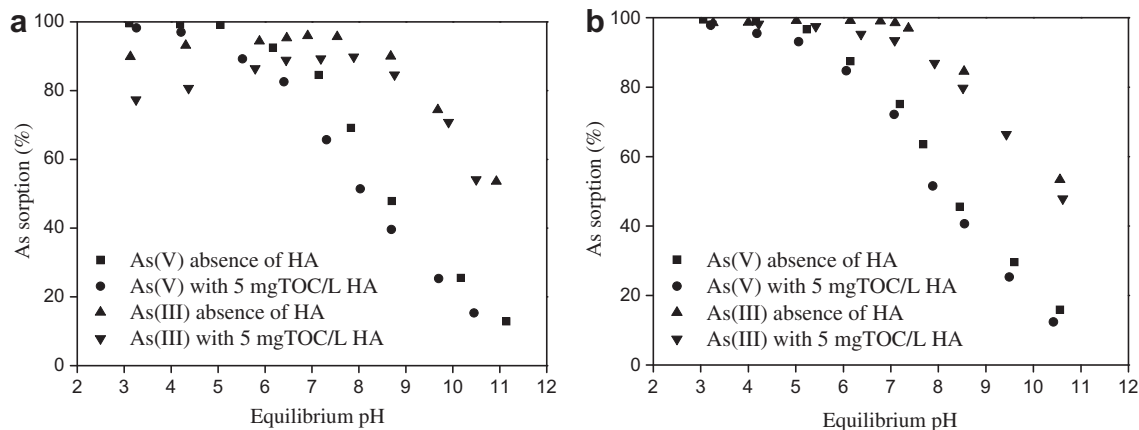
Fig. 5. Influence of HA on arsenic sorption by 1:9 (a) and 1:3 (b) Fe–Mn binary oxides. Initial arsenic concentration: 10 mg/L; sorbent content: 200 mg/L.

focused on the influence of NOM on arsenic removal using hematite [38]. Their research found that NOM dramatically delayed the attainment of sorption equilibrium and diminished the extent of sorption of both arsenite and arsenate when NOM and As were incubated together with hematite. The results indicated that the Fe–Mn binary oxide adsorbent was also effective for arsenic removal when natural organic matter was present.

4. Conclusions

Differences in As(V) retention, As(III) oxidation and sorption as affected by Mn/Fe molar ratio of the binary oxide were observed. The retention of As(V) increased with an increase in Mn/Fe molar ratio and reached maximum at approximately Mn/Fe 1:6. For As(III), a similar trend was observed except that the As(III) uptake maximum occurred at around Mn/Fe 1:3. Moreover, much more As(III) could be sorbed by the Fe–Mn binary oxides than As(V).

In sediments and soils where Mn and Fe (hydr)oxides often occur together, much more arsenic might be retained than that observed with pure iron (hydr)oxides because As(III) was more easily retained than As(V) on the basis of the results of the sorption study. These findings suggest that the frequent generalization of As(III) having higher mobility in the environment than As(V) is too simplistic, especially when Fe–Mn binary oxides are available as sorbents.

In water treatment, the introduction of manganese dioxide into (hydr)oxides could be noticeably favoring both As(V) and As(III) removal, especially As(III), which is usually more challenging to remove than As(V) using traditional techniques. Furthermore, the Mn/Fe molar ratio can be smoothly adjusted according to the As(III)/As(V) ratio in the water or groundwater, to make full use of the sorption and redox capacity of the Fe–Mn binary oxides. Due to their high uptake of both As(V) and As(III) and low cost, Fe–Mn binary oxides represent an attractive adsorbent for arsenic removal from water and groundwater.

Acknowledgments

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jcis.2011.09.058.

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