



## Effects of Mn(II) on the sorption and mobilization of As(V) in the presence of hematite

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### ABSTRACT

In this study, the effects of Mn(II) on the sorption and mobilization of As(V) by synthetic hematite were investigated. Our results showed that As(V) removal by hematite was evidently dependent on pH, and simultaneous addition of Mn(II) and As(V) into hematite suspension resulted in more removal of As(V) via electrostatic attraction at pH 4.0, 7.0 and 8.3. However, in Mn(II) pre-loaded system, the removal percentages of As(V) at pH 8.3 decreased by 17.0%, 20.7% and 26.7% after 24 h at the aging time of 2, 12 and 36 h, respectively. The concentrations of the released As(V) after the addition of 1 mM Mn(II) were 23.6, 12.9 and 7.0  $\mu\text{M}$  at pH 8.5 in 2, 3 and 4 g L<sup>-1</sup> hematite suspension, respectively. But Ca<sup>2+</sup> did not show such an effect under similar experimental conditions. Abiotic oxidation of Mn(II) on hematite played an important role in As(V) mobilization. The growing thin layer of Mn(III, IV) (hydr)oxides (MnO<sub>x</sub>) formed on hematite would take up the sorption sites pre-occupied by As(V) and resulted in the release of the adsorbed As(V) back into solution. This study enriched our understanding on As(V) fate in the coexistence of iron oxides and Mn(II).

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### 1. Introduction

Arsenic is a toxic contaminant in natural aquatic environments and its toxicity derives from arsenic's affinity to proteins, lipids, and other cellular components [1]. Due to its acute toxicity, the World Health Organization (WHO) has revised the guidelines for maximum contaminant level (MCL) of 10  $\mu\text{g L}^{-1}$  for arsenic in drinking water [2]. In oxygen-rich environments, arsenate [As(V)] is a predominant inorganic species and primarily exists as H<sub>2</sub>AsO<sub>4</sub><sup>-</sup> and HAsO<sub>4</sub><sup>2-</sup> in natural aquatic environments since the pK<sub>a</sub> values for arsenic acid are pK<sub>a1</sub> = 2.3, pK<sub>a2</sub> = 6.8, and pK<sub>a3</sub> = 11.6 [3].

The common oxides of manganese, iron and aluminum are important sorbents for immobilizing arsenic in natural ecosystems [3–7]. The extent of arsenic sorption is strongly influenced by pH and the presence of other dissolved substances that interact with mineral surfaces or arsenic itself [3–9]. When natural organic matter (NOM) and As(V) were mixed together with hematite ( $\alpha\text{-Fe}_2\text{O}_3$ ), NOM dramatically delayed the equilibrium time and reduced the sorption capacity of As(V) [4]. Competition between arsenic and other anion sorbates (i.e. phosphate, silicate, sulfate,

chloride, carbonate, bicarbonate) has also been studied in previous works [5,6,8,10]. As(V) sorption on hydrous ferric oxides (HFO) decreased from 95% to about 80% at pH 4.0 in the presence of phosphate [5]. Although carbonate increased As(V) sorption on hematite in the air-equilibrated systems at pH 4 and 6, and at pH 8 after 3 h of reaction, suppressed As(V) sorption was also observed in the air-equilibrated system in the early stages of the reaction at pH 8 [6]. Cations such as Zn<sup>2+</sup>, Ca<sup>2+</sup> and Mg<sup>2+</sup> can enhance the sorption capacity to As(V) [10–12]. Gräfe et al. [11] indicated that As(V) sorption on goethite ( $\alpha\text{-FeOOH}$ ) increased by 29% at pH 4.0 and by more than 500% at pH 7.0 in the presence of Zn(II). Mn(II) is ubiquitous in aquatic environments and its effect on As(V) sorption has not been studied yet.

The adsorbed arsenic can be mobilized in aquatic environments, in which processes such as oxidation, reduction, dissolution and desorption might occur [1,13,14]. Microbes contribute to the mobilization of arsenic adsorbed on iron (hydr)oxides via mediating redox reactions involving As(III) and As(V) or through dissimilatory reduction of insoluble Fe(III) to soluble Fe(II) [15–18]. NOM and anions such as OH<sup>-</sup>, CO<sub>3</sub><sup>2-</sup>, SiO<sub>4</sub><sup>4-</sup> and PO<sub>4</sub><sup>3-</sup> also accelerate the desorption of As because of competition for sorption sites [1]. However, to the best of our knowledge, there is no published work focusing on the effect of Mn(II) on the mobilization of As(V) adsorbed on iron (hydr)oxides. Previous studies have demonstrated surface catalytic oxidation of Mn(II) on iron

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oxides in the pH range of 7.0–9.0, and heterogeneous oxidation rate of Mn(II) depended on mineral species and increased with the order of  $\gamma$ -FeOOH >  $\alpha$ -FeOOH >  $\text{SiO}_2$  >  $\delta$ - $\text{Al}_2\text{O}_3$  [19,20]. Junta and Hochella [21] revealed that the top and base of steps on minerals were the most reactive sites for initiating the oxidation reaction of Mn(II), and once the initially adsorbed Mn(II) was oxidized to  $\text{MnO}_x$ , it became the most reactive sites for continuing the oxidation process, resulting in more  $\text{MnO}_x$  formation on iron oxides.

In the present study, hematite was selected as a representative iron oxide since it is widely distributed in nature and is an important natural mineral for the sink of trace toxic metal pollutants [4,22,23]. The objectives of this study were to investigate the effects of Mn(II) on the sorption and mobilization of As(V) in the pH range of 4.0–9.0, which is often found in natural aquatic environments. Three parts of experiments were therefore designed: (i) the kinetics of As(V) sorption on hematite in the absence and presence of Mn(II); (ii) the effect of Mn(II) aging (that means Mn(II) pre-loaded on hematite for a long time) on As(V) sorption on hematite; (iii) the effect of Mn(II) on the mobilization of As(V) adsorbed on hematite.

## 2. Experimental

### 2.1. Chemicals

Chemicals of analytical grade or higher purity were used without further purification.  $\text{NaH}_2\text{AsO}_4 \cdot 7\text{H}_2\text{O}$  (Merck, purity > 99.0%) and  $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$  (Tianjin Bodi Chemical Co., Ltd., PR China, purity > 99.0%) were used as As(V) and Mn(II) sources, respectively. Stock solutions of As(V) ( $5 \text{ g L}^{-1}$ ) and Mn(II) (0.2 M) were prepared by dissolving the respective salt in deionized water.

### 2.2. Synthesis and characterization of hematite

Hematite was synthesized by following the method of Schwertmann and Cornell [24]. A beaker containing 1000 mL of 0.002 M  $\text{HNO}_3$  was brought into a  $98^\circ\text{C}$  vacuum oven overnight. After a brief removal from the oven, 8.08 g of  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  were added with vigorous stirring. The bottle was then returned to the oven immediately and held at  $98^\circ\text{C}$  for 7 days. The sediment was centrifuged and then washed three times with deionized water. The solid was then dried at  $50^\circ\text{C}$  in a vacuum oven for characterization. Morphology of the synthetic hematite was characterized by high-resolution analytical transmission electron microscopy (TEM, Fei Tecnai G2 F20). Fourier transform infrared (FT-IR) spectrum in KBr pellet was conducted on an American Nicolet NEXUS FT-IR spectrometer. Mineralogical composition and purity for synthetic hematite was confirmed using X-ray diffraction (XRD, Rigaku D/max 2200/PC). Fig. 1 shows the XRD pattern of synthetic hematite, in which all diffraction peaks are in good agreement with rhomb-centered hexagonal (rch) hematite (JCPDS Card No. 33-0664). No other peaks were observed, indicating that the as-synthesized sample consists of high-purity, well crystallized hematite nanoparticles. The diameter of the synthetic hematite was about 20–30 nm as shown in TEM analysis (Fig. 2a). The two dominant bands at about  $464 \text{ cm}^{-1}$  and  $545 \text{ cm}^{-1}$  in Fig. S1 also indicated the characteristic peaks of crystalline hematite [24], and  $3427 \text{ cm}^{-1}$  and  $1630 \text{ cm}^{-1}$  bands suggested the stretching vibration of hydroxyl groups and bending vibration of water molecules, respectively [25]. Specific surface area of synthetic hematite was  $40.1 \text{ m}^2 \text{ g}^{-1}$  as determined by BET- $\text{N}_2$  sorption method. The pH of point of zero charge ( $\text{pH}_{\text{pzc}}$ ) of synthetic hematite in 0.1 M NaCl solution was 8.9, as determined by potentiometric titration under the atmosphere of pure  $\text{N}_2$  [26].

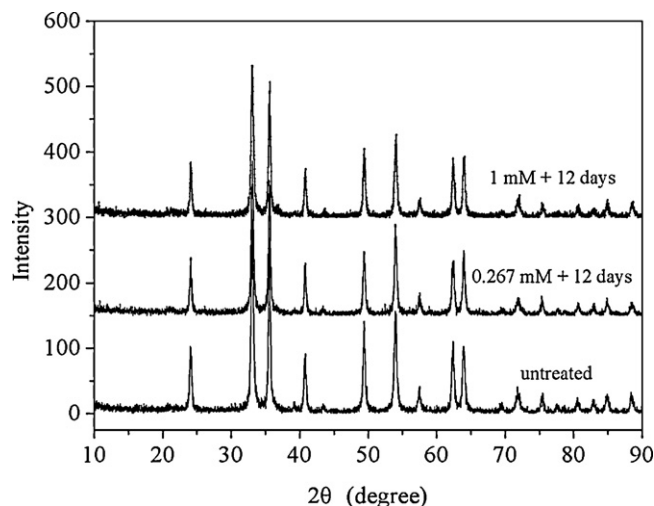


Fig. 1. XRD analysis of synthetic hematite untreated and treated with 0.267 and 1 mM Mn(II) for 12 days at pH 8.3. Hematite concentration was  $2 \text{ g L}^{-1}$  with working volume 150 mL in 0.1 M NaCl at  $25 \pm 0.1^\circ\text{C}$ .

### 2.3. Batch experiments

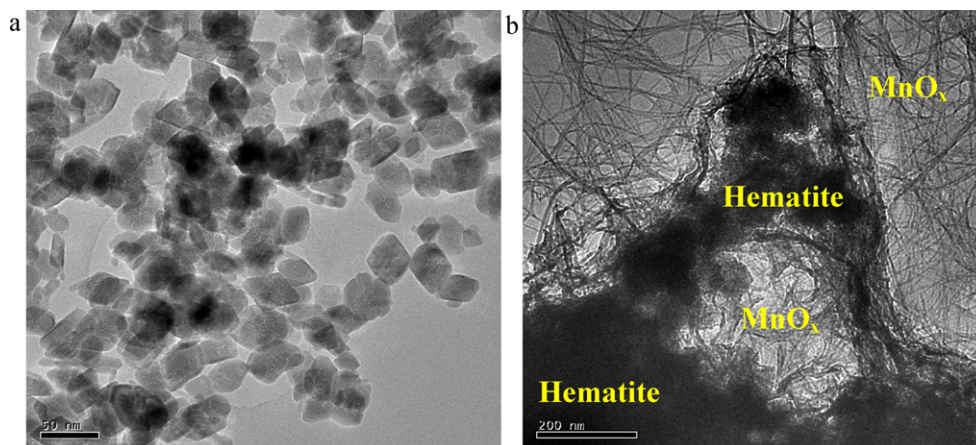
Compared with dry solid powder, the as-synthesized hematite in wet format could offer a greater surfaces area, owing to their good dispersion and little aggregation characters in water solution. The concentrated hematite was therefore used in all batch experiments. However, concentration of hematite was still expressed in dry weight. The ratio of wet weight to dry weight was determined by placing measured weights of wet samples in the vacuum oven at  $50^\circ\text{C}$  to constant value, and its ratio in the present study was  $17.6 \text{ mL g}^{-1}$  for hematite. Different pH values were maintained with different buffer solutions. Mixture of acetic acid and sodium acetate were only used at pH 4.0 [14 mM acetic acid + 8.3 mM sodium acetate]. Mixture of MOPS (3-morpholinopropane-1-sulfonic acid), sodium borate and/or boric acid were used at pH 7.0, 8.3 and 8.5 [(pH 7.0, 6 mM MOPS + 1.8 mM sodium borate), (pH 8.3, 2 mM MOPS + 4.7 mM sodium borate + 0.67 mM boric acid), and (pH 8.5, 2 mM MOPS + 5 mM sodium borate)].

#### 2.3.1. Sorption of As(V) on hematite in the absence and presence of Mn(II)

Individual sorption of As(V) and simultaneous sorption of As(V) and Mn(II) by hematite were investigated. Hematite was hydrated in 50 mL of 0.1 M NaCl solution at pH 4.0, 7.0 and 8.3 for 4 h to reach equilibrium before the addition of As(V) and Mn(II). After that, 100 mL solution contained As(V) mixed thoroughly with the hydrated hematite suspension with the identical pH values. Mn(II) stock solution was then immediately added into the suspension. The concentrations of Mn(II) and As(V) were 0.267 mM and hematite was  $2 \text{ g L}^{-1}$ , respectively. Samples were then placed on a shaker at 140 rpm. During the experiments, 1.3 mL samples were taken out regularly and centrifuged at 13,000 rpm for 5 min. The supernatant was used to determine the concentration of As(V) and the average value was recorded.

#### 2.3.2. Effect of Mn(II) aging on As(V) sorption on hematite

To investigate the effect of Mn(II) aging on As(V) sorption in the presence of hematite, different intervals (i.e. 2, 12 and 36 h) of pre-loaded Mn(II) on hematite at pH 8.3 was prepared, followed by the addition of As(V). Both concentrations of Mn(II) and As(V) were 0.267 mM. Samples were placed on a shaker with the same operational conditions as mentioned above. The supernatant was



**Fig. 2.** TEM analysis of (a) synthetic hematite and (b) hematite after the treatment of Mn(II). MnO<sub>x</sub> formed on hematite with 1 mM Mn(II) at pH 8.3. Initial concentration of hematite was 2 g L<sup>-1</sup>.

used to determine the concentration of As(V) and/or Mn(II) and the average value was recorded.

### 2.3.3. Mn(II) oxidation on hematite

The following experiments were conducted to confirm the oxidation of Mn(II) on hematite. A series of flasks of hematite were hydrated in 15 mL of 0.1 M NaCl solution at pH 8.3 for 4 h to reach equilibrium before the addition of Mn(II). Fifteen mL Mn(II) solution was then mixed thoroughly with the hydrated hematite suspension with the identical pH value, and the final Mn(II) was 0.267 or 1 mM. Samples were placed on a shaker with the same operational conditions as mentioned above. During the experiment, four flasks were taken out regularly and centrifuged at 4200 rpm for 5 min. The pellets were used to determine the content of Mn(III) and the average value was recorded.

### 2.3.4. Effect of Mn(II) on the adsorbed As(V) on hematite

In order to explore the effect of Mn(II) on the mobilization of As(V) adsorbed on hematite, As(V) was first adsorbed on hematite at pH 8.5 for 24 h to ensure that equilibrium was reached before the addition of Mn(II). The concentrations of hematite and Mn(II) were considered, and the values were 2, 3 and 4 g L<sup>-1</sup> for hematite, and 0.267 and 1 mM for Mn(II), respectively. In order to make a comparison, the same concentrations of Ca(II) were added to the As(V) pre-loaded systems to replace Mn(II).

In this study, all kinetic experiments were conducted in duplicate in the dark to prevent the photochemical oxidation of Mn(II). Temperature was controlled at 25 ± 0.1 °C with P<sub>O<sub>2</sub></sub> = 0.21 atm.

### 2.4. Analysis of metal concentration and characterization of hematite treated with As(V) and/or Mn(II)

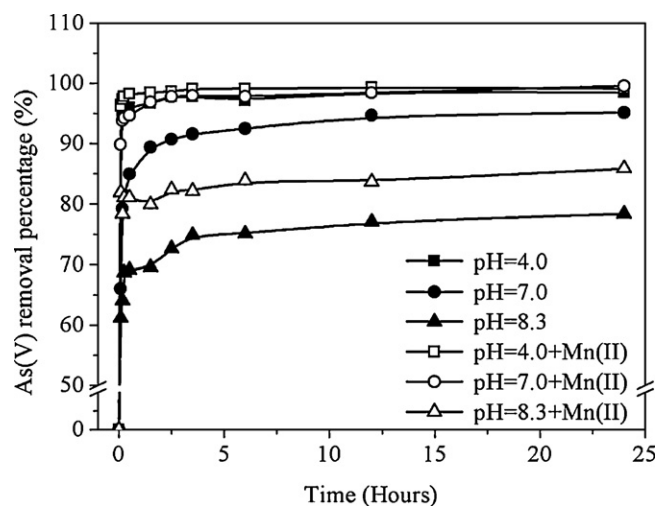
As(V) concentration was determined by molybdate-blue method [27]. No interference of buffers to the measurement of As(V) was observed, and detection limit for As(V) in the present study was 0.005 mg L<sup>-1</sup>. Mn(II) in solution was measured at λ = 257.61 nm by ICP-AES (Varian 715). The determination of Mn(III) was determined by monitoring the concentration of pyrophosphate-Mn(III) complex [28,29]. Pellets after centrifugation in the Mn(II) oxidation experiments were washed with deionized water to remove residual Mn(II) adsorbed on hematite and then the pellets were dissolved with 10 mL of 0.1 M Na<sub>4</sub>P<sub>2</sub>O<sub>7</sub>·10H<sub>2</sub>O (pH = 7.4) in a 50 mL centrifuge tube. The tubes were sonicated for 1 h and then placed on a shaker at 200 rpm and 25 ± 0.1 °C for 5 h. Afterwards, samples were centrifuged at 4200 rpm for 5 min and the absorbance of supernatants

was measured at the wavelength of 480 nm. Control experiment without the addition of Mn(II) was also conducted and showed insignificant formation of color complex even after 120 h (data not given), which indicated that interference of Fe(III) from ligand dissolution of hematite at pH 8.3 initiated by pyrophosphate could be neglected. Mineralogical composition for hematite treated with As(V) and/or Mn(II) was confirmed with XRD analysis.

## 3. Results and discussion

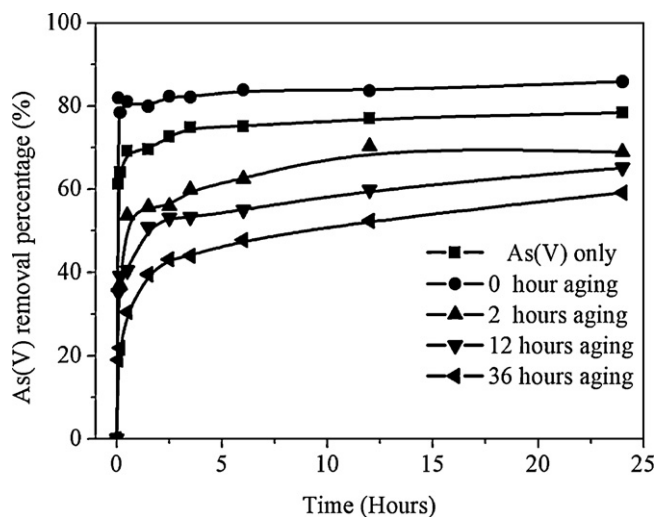
### 3.1. Sorption of As(V) on hematite in the absence and presence of Mn(II)

In the binary system containing arsenate and hematite in the absence of Mn(II), sorption of As(V) on hematite was evidently dependent on pH, with more As(V) removed at lower pH (Fig. 3). The removal percentages of As(V) were 98.5%, 95.1% and 78.4% at pH 4.0, 7.0 and 8.3 after 24 h, respectively. It could be explained by As(V) speciation and the abundance of positively charged sorption sites on hematite [23]. The aqueous As(V) exists predominantly as H<sub>2</sub>AsO<sub>4</sub><sup>-</sup> and HAsO<sub>4</sub><sup>2-</sup> considering the pH range used in this study. These two anionic species were expected to adsorb strongly on the



**Fig. 3.** Sorption of As(V) on synthetic hematite in the absence and presence of Mn(II). Initial As(V) and Mn(II) concentrations were both 0.267 mM and hematite was 2 g L<sup>-1</sup> with working volume of 150 mL in 0.1 M NaCl at 25 ± 0.1 °C.





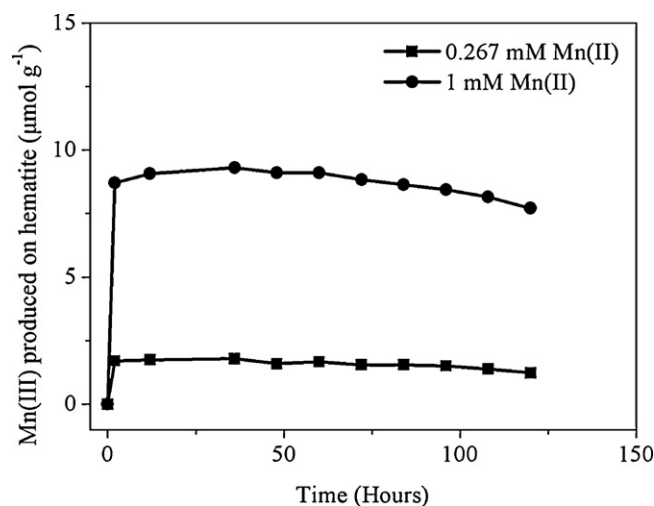
**Fig. 4.** Influence of Mn(II) aging on the sorption of As(V) at pH 8.3. Initial As(V) and Mn(II) concentrations were both 0.267 mM and hematite was  $2 \text{ g L}^{-1}$  with working volume of 150 mL in 0.1 M NaCl at  $25 \pm 0.1^\circ \text{C}$ . Control experiments in the absence of Mn(II) [As(V) only] and simultaneous addition of As(V) and Mn(II) (0 h aging) were also conducted.

positively charged hematite surface via electrostatic attraction as circumstantial pH was lower than the  $\text{pH}_{\text{pzc}}$  (8.9) of hematite. Arai et al. [6] also found that arsenate sorption on hematite decreased with the increase of pH from 4.0 to 8.0.

As Mn(II) was added simultaneously with As(V) into hematite suspension, more As(V) could be removed at all pH values compared with the system in the absence of Mn(II) (Fig. 3). The removal percentages of As(V) in the simultaneous sorption system were 99.1%, 99.6% and 85.9% at pH 4.0, 7.0 and 8.3 after 24 h, respectively (Fig. 3). Compared with the individual sorption of As(V) on hematite, the removal percentages increased by 0.6%, 4.5%, and 7.5% in the presence of Mn(II) at pH 4.0, 7.0 and 8.3 after 24 h, respectively. The presence of divalent cation could contribute to the increased positive charges on metal oxide surfaces and hence provided conditions more favorable for As(V) sorption compared to the system without divalent cation. It could be therefore explained that more positive charges carried by Mn(II) on hematite at higher pH contributed to the increased sorption of the anionic As(V). Gräfe et al. [11] also observed that  $\text{Zn}^{2+}$  increased the sorption of As(V) on goethite at pH 4.0 and 7.0. Masue et al. [12] demonstrated that  $\text{Ca}^{2+}$  enhanced As(V) retention on iron hydroxides only at  $\text{pH} > 5$ . The formation of Mn(II)–As(V) precipitate such as  $\text{Mn}_3(\text{AsO}_4)_2 \cdot 8\text{H}_2\text{O}$  ( $K_{\text{sp}} = -28.7$ ) crystalline was also possible at pH 8.3 as calculated with the software of Visual MINTEQ ver 2.61 (Table S1). However, no other peaks observed in XRD results suggested that such a precipitate could be avoided at this pH (Fig. S2). Therefore,  $\text{Mn}_3(\text{AsO}_4)_2 \cdot 8\text{H}_2\text{O}$  precipitate should not contribute to the high removal percentage of As(V) at pH 8.3.

### 3.2. Sorption of As(V) on Mn(II) pre-loaded hematite

Although positive charges carried by Mn(II) could enhance the sorption of As(V) on hematite at pH 8.3 in the simultaneous sorption process, a negative effect of the pre-loaded Mn(II) on As(V) sorption was detected (Fig. 4). Sorption capacity of As(V) on hematite was inverse to the aging time of Mn(II) on hematite, and less As(V) was removed after longer aging time of Mn(II). The removal percentages of As(V) at pH 8.3 were 68.9%, 65.2% and 59.2% at the aging time of 2, 12 and 36 h after 24 h, respectively (Fig. 4). The decreased removal percentages of As(V) at the aging time of 2, 12 and 36 h were therefore 17.0%, 20.7% and 26.7%, respectively. Considering



**Fig. 5.** Oxidation of Mn(II) on synthetic hematite at pH 8.3. Initial Mn(II) concentration was 0.267 or 1 mM and hematite was  $2 \text{ g L}^{-1}$  with working volume of 30 mL in 0.1 M NaCl at  $25 \pm 0.1^\circ \text{C}$ .

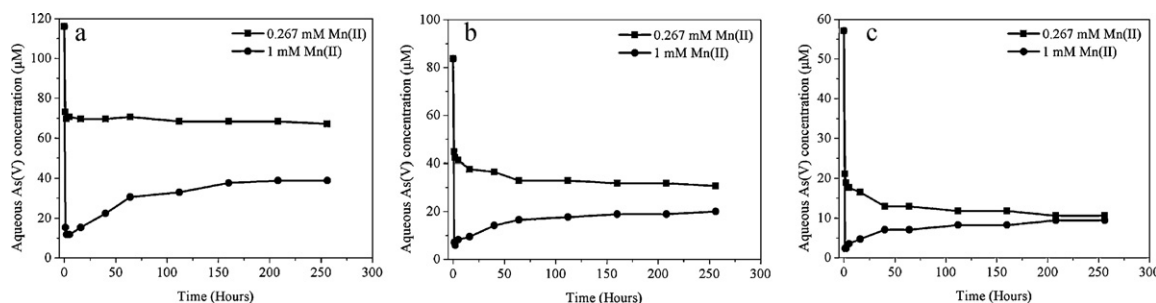
nearly all Mn(II) could adsorb on hematite in a short time (Fig. S3), the formation of  $\text{Mn}_3(\text{AsO}_4)_2 \cdot 8\text{H}_2\text{O}$  precipitate in solution could be excluded (Table S2).

Hematite surface has been proven to accelerate the abiotic oxidation of Mn(II) in oxic environments [21,30]. The initial reaction expected during the oxidation kinetic experiments in this study was:



where  $>\text{SOH}$  was a reactive surface site on hematite. The Mn(III) oxyhydroxide phase could be further oxidized to an Mn(IV) solid phase.

More production of Mn(III) on hematite and dark red color observed in 1 mM Mn(II) system suggested that higher concentration of Mn(II) promoted more oxidation of Mn(II) in the presence of hematite at the same intervals (Fig. 5 and Fig. S4). The rapid increase of Mn(III) in the first 2 h suggested that oxidation of Mn(II) on hematite could take place within a short period of time (Fig. 5). Interestingly, Mn(III) production decreased slowly on hematite after reaching the maximum value, suggesting that Mn(III) was an intermediate product in the oxidation of Mn(II) and it was subsequently transformed into Mn(IV). Murray et al. [31] suggested the occurrence of abiotic oxidation of Mn(II) to Mn(IV) via a two-step process in which solid phase Mn(III)-bearing (hydr)oxides were initially formed and then underwent slower disproportionation to Mn(IV) oxides. It could be therefore inferred that Mn(II) adsorbed on hematite first, and then a fraction of the adsorbed Mn(II) was oxidized to Mn(III, IV) (hydr)oxides. Although the occurrence of Mn(III) on hematite surfaces was almost comparable at 2, 12 and 36 h in 0.267 mM Mn(II) system (Fig. 5), the amount of total  $\text{MnO}_x$  should increase with the increase of reaction time due to the subsequent transformation of Mn(III) to Mn(III, IV) (hydr)oxides. Junta and Hochella [21] suggested that on the surface of hematite,  $\text{MnO}_x$  occurred as a layer of protocrystallites growing horizontally along the  $\{001\}$  surface and the surface could become entirely coated with a thin layer of precipitate within two days at pH 8.0 and 4 ppm Mn(II) solution. However, previous studies suggested that manganese oxides did not favor the sorption of As(V) compared with iron oxides [1,32,33]. It could be therefore deduced that Mn(II) aging promoted the production of  $\text{MnO}_x$  on hematite, which would take up the potential sorption sites for As(V) sorption and resulted in a decrease of As(V) removal.



**Fig. 6.** Aqueous As(V) concentration on different loadings of hematite [(a)  $2 \text{ g L}^{-1}$ , (b)  $3 \text{ g L}^{-1}$  and (c)  $4 \text{ g L}^{-1}$ ] in the presence of Mn(II) at pH 8.5. Initial As(V) was  $0.267 \text{ mM}$  and Mn(II) was  $0.267$  and  $1 \text{ mM}$  with working volume of  $150 \text{ mL}$  in  $0.1 \text{ M NaCl}$  at  $25 \pm 0.1 \text{ }^\circ\text{C}$ .

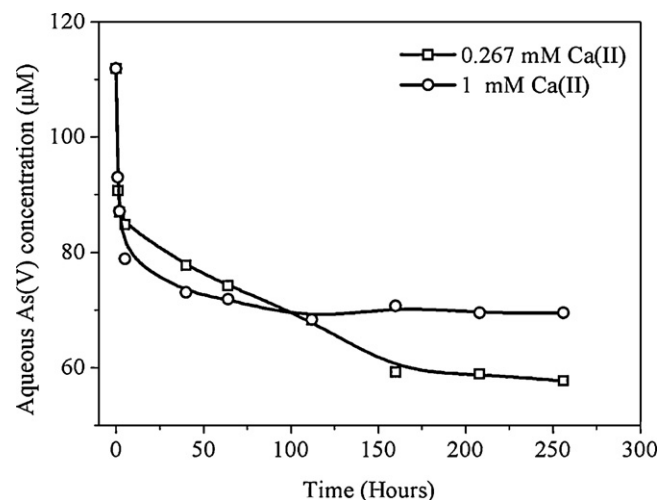
In order to determine the  $\text{MnO}_x$  precipitation formed on hematite, TEM analysis was conducted. Fiber-like  $\text{MnO}_x$  precipitation was found on the hematite surface when exposed to  $1.0 \text{ mM}$  Mn(II) at pH 8.3, and the hematite particles were aggregated together due to the presence of  $\text{MnO}_x$  (Fig. 2b). Murray and co-workers [31] also found similar morphology of  $\text{MnO}_x$  in their study. XRD results supported the amorphous characters of  $\text{MnO}_x$  precipitation formed on hematite when they were exposed to  $0.267$  and  $1 \text{ mM}$  Mn(II) at pH 8.3 for 12 days, since no significant change was found in XRD patterns compared with hematite in the absence of Mn(II) (Fig. 1). Longer time of reaction could result in the transformation of amorphous  $\text{MnO}_x$  to crystalline  $\text{MnO}_x$  as  $\beta\text{-MnOOH}$  was the primary product in heterogeneous oxidation of Mn(II) on hematite surfaces in aerated solutions containing  $26.7 \text{ ppm}$  Mn(II) at pH 8.15 after one month [21]. Considering the short time of Mn(II) reaction with hematite in the present study, amorphous  $\text{MnO}_x$  should be the primary product.

### 3.3. The effect of Mn(II) on the mobilization of the adsorbed As(V) on hematite

The concentrations of aqueous As(V) were  $116.0$ ,  $83.6$  and  $57.1 \text{ } \mu\text{M}$  after As(V) was adsorbed by  $2$ ,  $3$  and  $4 \text{ g L}^{-1}$  hematite for  $24 \text{ h}$  at pH 8.5, respectively (Fig. 6). In all systems, aqueous As(V) decreased in the first hour with the addition of  $0.267$  and  $1 \text{ mM}$  Mn(II), which was attributed to the electrostatic attraction of Mn(II) adsorbed on hematite and anionic As(V) (Fig. 6). In the second stage ( $1\text{--}256 \text{ h}$ ), a slow increase of As(V) was found in  $1 \text{ mM}$  Mn(II) system while such an observation was not detected in  $0.267 \text{ mM}$  Mn(II) system (Fig. 6). After  $256 \text{ h}$ , aqueous As(V) increased from  $15.3$ ,  $7.1$  and  $2.4 \text{ } \mu\text{M}$  to  $38.9$ ,  $20.0$  and  $9.4 \text{ } \mu\text{M}$  as for  $2$ ,  $3$  and  $4 \text{ g L}^{-1}$  hematite, respectively (Fig. 6).

The mobilization of the adsorbed As(V) in the presence of Mn(II) after the first hour could be attributed to the abiotic oxidation of Mn(II) on hematite. The growing thin layer of  $\text{MnO}_x$  formed on hematite would take up the sorption sites pre-occupied by As(V) and resulted in the release of the adsorbed As(V) into solution. The significant mobilization of the adsorbed As(V) after the first hour in  $1 \text{ mM}$  Mn(II) system than that in  $0.267 \text{ mM}$  Mn(II) system could be due to more  $\text{MnO}_x$  formed on hematite in the former system, which has been confirmed in Fig. 5. The concentrations of released As(V) from  $1 \text{ h}$  to  $256 \text{ h}$  were  $23.6$ ,  $12.9$  and  $7.0 \text{ } \mu\text{M}$  in  $2$ ,  $3$  and  $4 \text{ g L}^{-1}$  hematite suspension after the addition of  $1 \text{ mM}$  Mn(II), respectively (Fig. 6). Higher concentration of hematite provided more potential sites for the sorption of As(V), which resulted in a less mobilization of the adsorbed As(V).

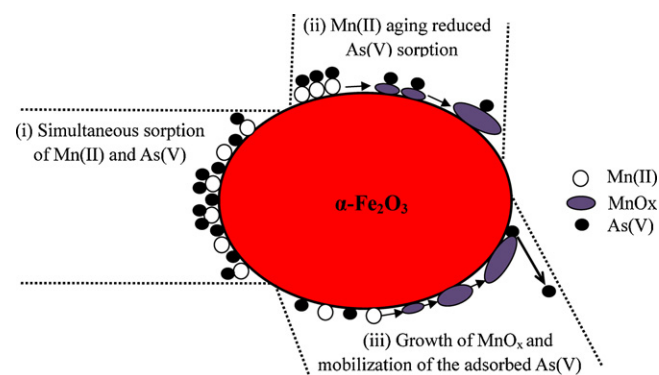
In order to further confirm the mobilization of the adsorbed As(V),  $\text{Mn}^{2+}$  was replaced by  $\text{Ca}^{2+}$  to test its effect on the mobilization of As(V) adsorbed on hematite. Fig. 7 showed that  $\text{Ca}^{2+}$  did not show an mobilization effect on the adsorbed As(V) under similar experimental conditions, and the aqueous As(V) reduced



**Fig. 7.** Aqueous As(V) concentration on hematite suspension in the presence of  $0.267$  and  $1 \text{ mM}$  Ca(II) at pH 8.5. Initial As(V) was  $0.267 \text{ mM}$  and hematite was  $2 \text{ g L}^{-1}$  with working volume of  $150 \text{ mL}$  in  $0.1 \text{ M NaCl}$  at  $25 \pm 0.1 \text{ }^\circ\text{C}$ .

slowly in the presence of  $0.267$  and  $1 \text{ mM}$   $\text{Ca}^{2+}$  after a rapid decrease in the first hour. The decrease of aqueous As(V) was due to the electrostatic attraction of Ca(II) and anionic As(V). In addition, the formation of Ca(II)–As(V) precipitate such as  $\text{Ca}_3(\text{AsO}_4)_2 \cdot 4\text{H}_2\text{O}$  could be excluded at pH 8.5 (Table S3).

XRD results excluded the formation of crystalline  $\text{Mn}_3(\text{AsO}_4)_2 \cdot 8\text{H}_2\text{O}$  formed on hematite surfaces (Fig. S5), and



**Fig. 8.** The mechanism of the effects of Mn(II) on the sorption and mobilization of As(V) in the presence of hematite. (i) Simultaneous sorption of Mn(II) and As(V) on hematite occurred firstly, and positive charges carried by the adsorbed Mn(II) could enhance the sorption of As(V) on hematite; (ii) the growth of  $\text{MnO}_x$  on hematite via abiotic oxidation of the adsorbed Mn(II) reduced sorption of As(V) on hematite; (iii) the growth of  $\text{MnO}_x$  on hematite resulted in the release of a fraction of the adsorbed As(V) on hematite.

the rapid removal of As(V) in the first hour as shown in Fig. 6 could be due to sorption but not precipitation.

### 3.4. The mechanism of Mn(II) on the sorption and mobilization of As(V)

On the basis of the above results, the potential mechanism of Mn(II) on the sorption and mobilization of As(V) in the presence of hematite was proposed (Fig. 8). Sorption of Mn(II) and As(V) on hematite occurred first, followed by the abiotic oxidation of Mn(II) on hematite. Although the adsorbed Mn(II) could enhance the sorption capacity of As(V) on hematite via electrostatic attraction, the growing  $\text{MnO}_x$  on hematite via abiotic oxidation of the adsorbed Mn(II) reduced further sorption of As(V) on hematite. In addition, the newly formed  $\text{MnO}_x$  could take up the sorption sites on which As(V) pre-occupied and then resulted in the release of the adsorbed As(V) into solution.

## 4. Conclusion

The present study revealed that Mn(II) played an important role in the sorption and mobilization of the aqueous and the adsorbed As(V) in aquatic environments. The results suggested that mechanisms involved in the sorption and mobilization of As(V) are different, depending upon how Mn(II) and As(V) are introduced into hematite suspension. Simultaneous addition of Mn(II) and As(V) into hematite suspension resulted in the increased removal of As(V) via electrostatic attraction at all pH values. However, the growing  $\text{MnO}_x$  on hematite via abiotic oxidation of the adsorbed Mn(II) reduced further sorption of As(V) on hematite and the removal percentages of As(V) decreased with longer time of Mn(II) aging in Mn(II) pre-loaded system. In the mobilization of the adsorbed As(V) on hematite, the aqueous As(V) increased from 15.3, 7.1 and 2.4  $\mu\text{M}$  at 1 h to 38.9, 20.0 and 9.4  $\mu\text{M}$  at 256 h on 2, 3 and 4  $\text{g L}^{-1}$  hematite suspension after the addition of 1 mM Mn(II), respectively. However,  $\text{Ca}^{2+}$  did not show such an effect on the adsorbed As(V) on hematite under similar experimental conditions. Therefore, the mobilization of As(V) in the presence of Mn(II) could therefore be attributed to the abiotic oxidation of Mn(II) on hematite. Considering the pH of natural aquatic environments is often in the range of 4.0–9.0 and the coexistence of As(V), Mn(II) and iron oxides under such conditions [18,34,35], the synergistic effect of Mn(II) on arsenate sorption and mobilization could occur.

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## Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jhazmat.2012.03.032.

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