Mobilization and re-adsorption of arsenate on ferrihydrite and hematite in the presence of oxalate

Bo Yu\textsuperscript{a}, Shao-Yi Jia\textsuperscript{a}, Yong Liu\textsuperscript{b}, Song-Hai Wu\textsuperscript{a}, Xu Han\textsuperscript{c,d,e,∗}

\textsuperscript{a} School of Chemical Engineering and Technology, Tianjin University, Tianjin, P.R. China
\textsuperscript{b} School of Chemistry and Chemical Engineering, Tianjin University of Technology, Tianjin, PR China
\textsuperscript{c} State Key Laboratory of Hollow Fiber Membrane Materials and Processes, Tianjin Polytechnic University, Tianjin, PR China
\textsuperscript{d} School of Environmental and Chemical Engineering, Tianjin Polytechnic University, Tianjin, PR China
\textsuperscript{e} Key Laboratory of Systems Bioengineering, Ministry of Education, Tianjin University, Tianjin, PR China

\textbf{HIGHLIGHTS}

- Mobilization of pre-loaded As(V) was found on iron oxides in the presence of oxalate.
- Re-adsorption of As(V) was significant in ferrihydrite system.
- Insignificant re-adsorption of As(V) was found in hematite system.
- There was an inhibitory effect on the dissolution with the increase of As(V) loading.
- Mathematical model was firstly set up to describe As(V) mobilization.

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\textbf{ABSTRACT}

In this study, mobilization and re-adsorption of arsenate on 2-line ferrihydrite and hematite in the presence of oxalate was investigated. Our results showed that arsenate could be mobilized during the dissolution of ferrihydrite and hematite. After reaching the maximum values, the released arsenate could re-adsorb on the residual ferrihydrite, whereas such an observation was not significant in hematite system. More reactive sites exposed during the dissolution of ferrihydrite could contribute to the re-adsorption of the released arsenate at pH 3.0, while the insignificant re-adsorption of arsenate on hematite could be explained by the inhibitory adsorption effect of oxalate on arsenate. Although dissolution rates of iron oxides decreased with the increase of arsenate on both ferrihydrite and hematite, dissolution rate was mainly determined by the reactivity of iron oxides, and ferrihydrite showed a higher reactivity than hematite in the presence of oxalate. Mathematical model proposed in our study further indicated that arsenate loading showed a more significant effect on arsenate mobilization in hematite system, while it was more effective in arsenate re-adsorption in ferrihydrite system.

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1. Introduction

Arsenic is a ubiquitous contaminant in nature, and primarily exists in inorganic forms as oxyanions of trivalent arsenite and pentavalent arsenate in aquatic environments [1]. It may cause cardiovascular disease and cancers of the liver, bladder and lung to human beings [2,3]. The WHO (World Health Organization) guideline for arsenic in drinking water was therefore reduced in 1993 from 50 to 10 μg L\textsuperscript{−1} [4]. Iron oxides, such as ferrihydrite, lepidocrocite, magnetite, goethite and hematite, are probably the most important adsorbents for the immobilization of arsenic in sandy aquifers owing to their great abundance and strong binding affinities to arsenic [5,6]. Environmental arsenic problems are always correlated with the mobilization of arsenic caused by natural weathering process, biological activities, geochemical reactions, volcanic emissions and other anthropogenic activities [7]. It is clear that mobilization of arsenic in ground water is mainly controlled by the dissolution of iron oxides [8].

Previous studies suggested that Fe(III) reducing bacteria played important roles in the reductive dissolution of iron oxides, which leads to the release of the immobilized arsenic [9]. On the other hand, abiotic dissolution of iron oxides may also contribute to the mobilization of arsenic. It has been reported that abiotic dissolution of iron oxides consists of different mechanisms, such as protonated, ligand-promoted, reductive and photochemical dissolution.
Oxalate is commonly found in natural water and has a great contribution to both reductive and ligand-promoted dissolution of iron oxides. The concentration of oxalate in natural waters always ranges from 2.5 × 10⁻⁵ to 4.0 × 10⁻³ M as mentioned in previous study [12]. As oxalate adsorbs onto the surface of iron oxides, surface complex of [Fe(II)-C₂O₄]⁻ forms followed by electron transfer between Fe(III) and C₂O₄²⁻, which subsequently results in the formation of Fe(II) and semi-stable state surface complexes. Fe(III) can also be directly released through ligand-promoted dissolution as Fe(II)–C₂O₄²⁻. Without the electron transfer process [10,12,13].

If arsenic is immobilized on the surface of iron oxides, it will be released into solution, accompanied with the release of dissolved iron. Under anaerobic conditions, the released Fe(II) initiates various transformation pathways of iron oxides, which may further change the immobilization of the dissolved arsenic [14]. In aerobic environment, Fe(II) will be oxidized to Fe(III) which may form amorphous iron oxides afterwards and contributes to the re-adsorption of the dissolved arsenic. However, little attention has been paid to the ligand-promoted and the reductive dissolution of iron oxides under aerobic conditions. In addition, the amount of reductants was always enough that iron oxides would be completely dissolved in previous studies, and pre-loaded arsenic was therefore fully released into solution [15]. If only a fraction of iron oxides is dissolved, the remained iron oxides may also contribute to the re-adsorption of the released arsenic and the amount of pre-loaded arsenate may also influence to the mobilization and re-adsorption of arsenate on iron oxides. Besides, mathematic model is a valuable tool to further evaluate the kinetic mechanism of the mobilization and re-adsorption of arsenate in the presence of iron oxides.

In order to elucidate the mobilization and re-adsorption of arsenate during the ligand-promoted and the reductive dissolution of iron oxides by oxalate under aerobic conditions, the objectives of this study were therefore: (i) to compare reactivities of ferrihydride and hematite in the mobilization and re-adsorption of arsenate; (ii) to investigate the amount of pre-loaded arsenate on iron oxides in the mobilization and re-adsorption of arsenate under different pHs; (iii) to propose rate expressions to model kinetics in the mobilization and re-adsorption of arsenate in the presence of ferrihydride and hematite.

2. Experimental

2.1. Synthesis and characterization of iron oxides

Hematite and 2-line ferrihydrite were synthesized following the procedures in Schwertmann and Cornell [16]. Two-line ferrihydrite was prepared by the addition of NaOH solutions into Fe(NO₃)₃ solution. Fe(NO₃)₃·9H₂O 20 g was dissolved in 250 mL distilled water with the addition of 160 mL 1 M NaOH to bring the pH to 7–8. The last 60 mL was added dropwise with constant monitoring pH and vigorous stirring. In preparation of hematite, a beaker containing 1000 mL of 0.002 M HNO₃ was brought into a 98 °C vacuum oven overnight. After that, 8.08 g Fe(NO₃)₃·9H₂O was added with vigorous stirring. The bottle was then held at 98 °C for 7 days. Both of the synthesized ferrihydrite and hematite were centrifuged and washed three times with distilled water. The solid was then freeze dried for further characterization. XRD analysis results showed that the as-synthesized ferrihydrite and hematite samples consisted of high-purity nanoparticles (Fig. S1). The average diameters of the synthesized particles were about 8–10 nm for ferrihydrite and 30–40 nm for hematite as shown in TEM analysis (Fig. S5). Specific surface area of ferrihydrite and hematite were 210 and 40 m² g⁻¹, respectively as determined by BET-N₂ adsorption method. Point of zero charge (PZC) of the synthesized ferrihydrite and hematite was 7.8 and 8.9, respectively as determined by potentiometric titration.

The synthesized ferrihydrite and hematite were stored in distilled water. As the final pH of the titration was about 7–8 during the synthesized procedure of ferrihydrite, pH of the stored ferrihydrite suspension was 6.8, whereas pH of the stored hematite suspension was 2.3 due to its acidic synthesized procedure. As a comparison, part of hydrated hematite particles were centrifuged and stored in neutral pH solution. Hematite used in our experiments was the acid-stored hematite, which has been stored in acidic pH for at least 3 months. Compared with dry solid powder, the synthesized iron oxides in wet format could offer a greater surface area owing to their good dispersion and little aggregation characters in solution. The concentrated ferrihydrite and hematite were therefore used in all batch experiments. However, concentration of iron oxides was still expressed in dry weight. The ratios of wet weight to dry weight for ferrihydrite and hematite were 10.8 and 17.6 g L⁻¹, respectively.

2.2. Effect of pH on the adsorption of arsenate

Adsorption of arsenate on ferrihydrite and hematite was investigated at pH 3.0, 7.5 and 11.0. Both ferrihydrite and hematite were hydrated in 100 mL 0.1 M NaCl solution at pH 3.0, 7.5 and 11.0 by using 0.5 M HCl solution and 0.5 M NaOH solution, for 12 h to reach equilibrium before the addition of arsenate. After that, 50 mL 0.1 M NaCl solution containing measured amount of arsenate was mixed thoroughly with the hydrate suspension and the identical pHs. Initial concentration of arsenate was 20 mg L⁻¹, and concentrations of ferrihydrite and hematite were 0.1 g L⁻¹ and 0.5 g L⁻¹ respectively to make a comparable surface area of these two iron oxides in the experiments. The suspension was then placed on a shaker at 150 rpm for 24 h and the supernatant obtained after centrifugation was used to determine the concentration of arsenate. All experiments were conducted in duplicate at 25 °C.

2.3. Effect of oxalate on the adsorption of arsenate

Individual adsorption of arsenate and simultaneous adsorption of arsenate and oxalate on hematite were investigated. Hematite was hydrated in 100 mL 0.1 M NaCl solution at pH 3.0 for 12 h to reach equilibrium before the addition of arsenate and oxalate. In the simultaneous adsorption, 50 mL 0.1 M NaCl solution with arsenate and oxalate was mixed thoroughly with the hydrated hematite at pH 3.0. Another 50 mL 0.1 M NaCl solution only contained arsenate was also prepared at pH 3.0 for the individual adsorption of arsenate. After the thorough mixing, the initial concentration of arsenate was 15 mg L⁻¹, and the initial concentration of oxalate was 0.5 and 1 mM for the competitive adsorption. The shaker was employed to maintain the suspension well dispersive at 150 rpm. During the experiment, 1.0 mL samples were taken out regularly and centrifuged at 12,000 rpm for 5 min, and the supernatant was used to determine the concentration of arsenate and the average value was recorded.

2.4. Dissolution of iron oxides and mobilization of arsenate

Both ferrihydrite and hematite were hydrated in the 100 mL of 0.1 M NaCl solution with the addition of measured amount of arsenate at pH 3.0, 7.5 and 11.0 by using 0.5 M HCl solution and 0.5 M NaOH solution. In iron oxides dissolution, 1 mM oxalate in 50 mL of 0.1 M NaCl with the identical pHs was mixed with the above suspension. During the experiment, 1.0 mL samples were taken out regularly and centrifuged at 12,000 rpm for 5 min, and the supernatant was used for the determination of arsenate, Fe(II) and total Fe concentrations.
Although interference and Fe(III) was determined by the molybdate-blue method [17] and the detection limit for arsenate in this present study was 0.005 mg L$^{-1}$. Fe(II) concentration was determined by a modified ferrozine method [18], and in order to eliminate the interference of Fe(III) in Fe(II) measurement, 0.05 M NaF was added to mask Fe(III) in Fe(II) determination. Total Fe was determined by reducing total Fe(III) to Fe(II) and then Fe(II) was measured by ferrozine method without the addition of NaF solution. Ferrozine reagent and ammonium acetate buffer solution were then mixed and allowed 10 min for full color development. The absorbance was measured at the wavelength of 562 nm.

2.6. Analytical methods

Morphology of the synthesized iron oxides was characterized by high-resolution analytical transmission electron microscopy (TEM, Fei Tecnai G2 F20). Mineralogical composition and purity for synthesized iron oxides was confirmed using X-ray diffraction (XRD, Rigaku D/max 2200/PC).

3. Results and discussions

3.1. Effect of pH on the initial adsorption of arsenate

Adsorption of arsenate on ferrihydrite and hematite was evidently dependent on pH with more arsenate adsorbed at lower pH (Fig. 1). The fraction of the adsorbed arsenate on ferrihydrite was 83.5% at pH 3.0, 50% at pH 7.5 and 25% at pH 11.0, whereas it was 60% at pH 3.0, 30% at pH 7.5 and 17.5% at pH 11.0 for hematite. Although the specific surface area of hematite was controlled as large as that of ferrihydrite, the adsorbed arsenate still decreased by 23.5% at pH 3.0, 20% at pH 7.5 and 7.5% at pH 11.0 owing to its lower reactivity. It has been reported that arsenate adsorption on iron oxides always decreased with the increase of pH [19–21].

3.2. Dissolution of iron oxides

Dissolution of iron oxides was monitored by measuring aqueous Fe(II) and Fe(III) at pH 3.0, but such a method was not effective at pH 7.5 and 11.0 due to the rapid oxidation of Fe(II) followed by Fe(III) hydrolysis under aerobic conditions. Total released Fe from ferrihydrite increased rapidly at the beginning and began to level off at 28.3 mg L$^{-1}$ after 1 h at pH 3.0 (Fig. 2a). Compared with ferrihydrite, dissolution of hematite was much slower, which lasted over 60 h before reaching equilibrium as compared to 1 h as the ferrihydrite (Fig. 2a and b). Two dissolution stages were found in the dissolution of hematite, with a fast dissolution within the first 10 h and a slow one until the curve leveled off after 60 h (Fig. 2b). The final concentrations of Fe(II) released from ferrihydrite and hematite at pH 3.0 were 2.9 and 0.68 mg L$^{-1}$, respectively, whereas final concentrations of total Fe were 28.3 and 12.3 mg L$^{-1}$, respectively (Fig. 2a and b).

Iron oxides could be dissolved by oxalate through reductive and ligand-promoted process. Difference between these two processes was the electron transfer process. Oxalate would firstly adsorb onto the surface of iron oxides by forming complex of [Fe(III)-C$_2$O$_4$]$^{2-}$ before dissolution in both reductive and ligand-promoted process [10]. Subsequently, there would be an electron transfer between Fe(III) and C$_2$O$_4$]$^{2-}$ in reductive process, which subsequently results in the formation of Fe(II) and semi-stable state surface complexes [10]. Fe(III) can also be directly released in ligand-promoted process as Fe(III)-C$_2$O$_4$]$^{2-}$ without the electron transfer process [10,12,13]. Considering the slow oxidation rate of Fe(II) at pH 3.0 under aerobic condition, it could be deduced that reductive and ligand-promoted dissolution were both involved in our study, and the ligand-promoted dissolution was predominant, as shown in Fig. 2a and b.

A suite of the synthesized iron oxides has been investigated to compare reactivities of different iron oxides in the reductive dissolution [22–25], and effects of both ascorbic acid concentration and crystal properties on the overall dissolution rate could be expressed by the general rate law [22,26]}

\[
\frac{df}{dt} = -k_m \frac{f}{m_0} g(C)
\]

where $f$ is the overall rate of dissolution (mol s$^{-1}$), $m$ is the amount of undissolved crystals (mol), $t$ is the time (s), $k$ is the rate constant (s$^{-1}$), and $m_0$ is the initial mass of crystals (mol). $f/m_0$ is a function of the remaining fraction of mineral mass and $g(C)$ is a function of the ascorbic acid concentration. As suggested in previous studies, ferrihydrite showed the highest reactivity, and the rate constants of Fe for ferrihydrite, lepidocrocite and goethite were 4.2–7.6 x 10$^{-4}$, 1.2–1.9 x 10$^{-5}$ and 1.1–5.4 x 10$^{-6}$ s$^{-1}$, respectively [15,24].

The kinetics of the dissolution of ferrihydrite and hematite could be estimated by fitting the data with the rate expression, modified from Eq. (1) as described previously [22]:

\[
\frac{df}{dt} = \frac{m}{m_0} = -k \left( \frac{m}{m_0} \right)^r
\]

where $f$ is the overall dissolution rate (mg L$^{-1}$ s$^{-1}$), $m_0$ is the maximum of the released total Fe (mg L$^{-1}$), and $m$ is the difference between the maximal and the released total Fe (mg L$^{-1}$) at time $t$ (s). The parameter $k$ stands for the kinetic constant, and $r$ is the constant related to the mineral reactivity, crystalline structure and aggregated degree. Parameters of $k$ and $r$ were estimated by MATLAB at pH 3.0 to measure rate changes of the dissolution, and results were shown in Table 1. Fig. 3 compared reactivities of ferrihydrite and hematite, showing the rate expression of the iron oxides in terms of $\log(f/m_0)$ versus $-\log(m/m_0)$. The rate expression resulted in a straight line where the value of $\log(f/m_0)$ at $\log(m/m_0)$ equals the kinetic constant $k$, and the slope of the line corresponds to the constant $r$. Although kinetic constants were different due to different arsenate loading on iron oxides, insignificant difference was found in the same oxides loaded with different amount of arsenate. The higher $\log(f/m_0)$ values of ferrihydrite than that of hematite at the same values of $-\log(m/m_0)$ suggested higher reactivity of ferrihydrite than hematite in the presence of oxalate.
Arsenate had an inhibitory effect on the dissolution of iron oxides, and the initial dissolution rate decreased slightly with the increase of arsenate loading (Table 1 and Fig. 2c and d). The kinetic constants of ferrihydrite and hematite dissolution decreased from $4.0 \times 10^{-5}$ to $1.3 \times 10^{-3}$ s$^{-1}$ and from $3.9 \times 10^{-5}$ to $2.9 \times 10^{-5}$ s$^{-1}$ with the increase of initial arsenate-loaded capacities from 50 to 160 mg g$^{-1}$ and from 7 to 24 mg g$^{-1}$, respectively (Table 1). This suggested that arsenate occupied the adsorption sites and decreased the oxalate adsorption on iron oxides [27,28]. Moreover, $r$ was 1.1–1.5 for ferrihydrite and was 3.0–5.0 for hematite (Table 1). The adsorption of oxalate by forming bidentate mononuclear surface complexes with $\equiv$Fe–OH group on iron oxides was the first and key step in both reductive and ligand-promoted dissolution [10,12,13]. Other binuclear surface complexes, especially phosphate, borate and sulfate also showed inhibitory effects on the dissolution of iron oxides [29,30].

### 3.3. Mobilization of arsenate during the dissolution process

#### 3.3.1. Kinetics of arsenate released from iron oxides

The mobilization of arsenate during the dissolution of ferrihydrite and hematite was shown in Fig. 4. In Fhy-1, Fhy-2 and Fhy-3, the mobilized arsenate increased rapidly and reached the maximum values at 6.7, 3.5 and 1.0 mg L$^{-1}$ within 40 min at pH 3.0, respectively. After that, arsenate decreased and began to level off after reaching 5.3, 2.6 and 0.4 mg L$^{-1}$ after 2 h at pH 3.0 as to Fhy-1, Fhy-2 and Fhy-3, respectively (Fig. 4a). This indicated the re-adsorption of arsenate on ferrihydrite. The re-adsorption of arsenate was also significant at high pH of 7.5 and 11.0 in ferrihydrite system (Fig. 4a). However, this was insignificant in hematite system. The released arsenate from Hem-1, Hem-2 and Hem-3 leveled off after 2 h, and reached 5.7, 1.6 and 0.8 mg L$^{-1}$ at pH 3.0, respectively (Fig. 4b).

#### Table 1

Regression results of dissolution of ferrihydrite and hematite in the presence of arsenate.

<table>
<thead>
<tr>
<th>Species</th>
<th>As(V) adsorption (mg g$^{-1}$)</th>
<th>Reactivity</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$k$ (s$^{-1}$)</td>
</tr>
<tr>
<td>Fhy-1</td>
<td>160</td>
<td>$1.3 \times 10^{-3}$</td>
</tr>
<tr>
<td>Fhy-2</td>
<td>100</td>
<td>$2.4 \times 10^{-3}$</td>
</tr>
<tr>
<td>Fhy-3</td>
<td>50</td>
<td>$4.0 \times 10^{-3}$</td>
</tr>
<tr>
<td>Hem-1</td>
<td>24</td>
<td>$2.9 \times 10^{-5}$</td>
</tr>
<tr>
<td>Hem-2</td>
<td>12</td>
<td>$3.8 \times 10^{-5}$</td>
</tr>
<tr>
<td>Hem-3</td>
<td>7</td>
<td>$3.9 \times 10^{-5}$</td>
</tr>
</tbody>
</table>

Fhy and Hem represent ferrihydrite and hematite, respectively. Parameters of rate laws for iron oxides were obtained by data fitting with Eqs. (2) and (3). $k$, $k_1$, and $k_2$ are rate constants, and $r$, $r_1$, and $r_2$ are constants related to the mineral reactivity, crystalline structure and aggregated degree.
Changes of arsenate in Fig. 4 could be due to the mobilization and re-adsorption of arsenate during the dissolution of iron oxides. During the dissolution process, arsenate was incorporated into these precipitates by adsorption onto existing surface of iron oxides, rather than by the formation of FeAsO₄ (Table S1). Oxalate could complex with Fe atoms and drag them out from the surface of iron oxides, and arsenate would not be released until the Fe atoms that held arsenate were dissolved [15]. The further decrease of arsenate in solution suggested the re-adsorption of the released arsenate on iron oxides. Given little Fe(III) hydrolysis at pH 3.0, secondary minerals formed in both iron oxide systems could be neglected (Fig. S5e and f). It could be therefore deduced that more reactive sites exposed after the dissolution of iron oxides could contribute to the re-adsorption of the released arsenate in ferrihydrite system [27]. At high pHs of 7.5 and 11.0, Fe(III) hydrolysis could lead to the formation of amorphous iron oxides, which had a contribution to the re-adsorption of arsenate on ferrihydrite (Fig. 4). However, due to the insignificant difference found in the morphology of ferrihydrite and amorphous iron oxides, secondary minerals could not be detected at pH 7.5 and 11.0 in TEM analysis (data not shown).

The insignificant re-adsorption of arsenate on hematite at pH 3.0 could be explained by the inhibitory effect of oxalate and no secondary minerals formed in the dissolution process (Fig. 5c and d). As the reactive sites were exposed in the dissolution process, oxalate and arsenate in solution would compete for the sorption sites. Considering the significant higher concentration of oxalate than that of the released arsenate in solution, re-adsorption of the released arsenate could be inhibited. In order to further confirm the competitive adsorption of oxalate and arsenate on iron oxides, hematite was used due to its low reactivity in the dissolution process. Individual adsorption of arsenate on hematite was compared with the simultaneous adsorption of arsenate and oxalate at pH 3.0. Arsenate removal percentage was 86.7% in the absence of oxalate when the initial concentration of arsenate was 15 mg L⁻¹, however it decreased to 72.3% and 59.7% in the presence of 0.5 and 1 mM concomitant oxalate, respectively (Fig. 6). This suggested that the presence of oxalate significantly inhibited the adsorption of arsenate. The inhibitory effect was due to the similar adsorption mechanisms of arsenate and oxalate. Arsenate adsorbed onto the surface of iron oxides by forming bidentate mononuclear edge-sharing complexes, bidentate binuclear corner-sharing complexes and monodentate mononuclear complexes [31–34]. The Fe–O–As coordinative bond had a great contribution to the formation of these surface complexes. Similarly, oxalate connected with iron oxides by forming Fe–O–C coordinative bond and was adsorbed by the formation of bidentate mononuclear surface complexes [28,35]. All these surface complexes would occupy Fe atoms on the surface of iron oxides, which resulted in the competitive adsorption of oxalate and arsenate. Previous studies also suggested that organic ligands could inhibit the adsorption of trace elements in anionic form, such as arsenate and selenite, they would compete for sorption sites on metal oxides [28,36].

In order to understand the morphological changes during the dissolution of iron oxides, TEM analysis was also carried out. Given the smaller particle size of ferrihydrite, no difference could be found in ferrihydrite under pH 3.0 in the presence or the absence of oxalate (Fig. S5e and f). Similar results were also found in the reductive dissolution of 7 nm hematite by ascorbic acid [37]. It was interesting to notice the differences between the acid-stored and the newly prepared hematite. Dot- and line-shaped defects on the surface or inside the hematite particles under acidic conditions suggested dissolution of hematite (Fig. 5a). The dissolution was
initiated at defects on hematite surface, and then extended toward the center of hematite particles. These defects could increase the surface area of the oxide and contribute to the increased adsorption capacity of arsenate. Compared with hematite particles stored in the acidic solution, the newly synthesized hematite showed less defects, and the arsenate adsorbed fraction decreased by 20% at pH 3.0, 4.0% at pH 7.5 and 4.5% at pH 11.0 (Fig. 1). Although dissolution of hematite could provide more surface area for the re-adsorption of arsenate, the presence of oxalate was the main cause for the effective inhibition of arsenate re-adsorption as mentioned above.

The dissolution mechanism of hematite could also be used to explain the slow release of Fe in hematite system as shown in Fig. 2b and d. Considering the defects were more easily to be etched than the smooth facets of hematite particles, the initial fast release of dissolved iron was followed by a slow release stage (only the first 80 h as shown in Fig. 2b and d). As shown in Fig. 5c and d, the outline of particles became rounded and smooth and the etching effect was more significant at dot-shaped defects. The increase of line-shaped defects and fragments of hematite particles after the dissolution process revealed that dissolution of hematite was

Fig. 5. TEM analysis of iron oxides before and after the dissolution at pH 3.0. (a) Acid-stored hematite before dissolution, (b) newly-prepared hematite, (c) and (d) acid-stored hematite after dissolution, (e) ferrihydrite before dissolution, and (f) ferrihydrite after dissolution.
initiated at defects and the dissolution rate would not slow down until defects became smooth. Echigo et al. [37,38] also suggested that the dissolution rate of hematite by ascorbic acid slowed down and was mainly controlled by shape-preserving dissolution after reactive sites such as defects and sharp edges were consumed.

3.3.2. Mathematical modeling of arsenate mobilization in the dissolution process

Mathematical model is a valuable tool to further evaluate the kinetic mechanism of the mobilization of arsenate, and pseudo-first-order, pseudo-second-order and intraparticle diffusion models have been set up to describe arsenate adsorption kinetics so far [39]. In order to model the kinetics of arsenate mobilization in the dissolution of iron oxides, we proposed the following rate expression:

\[
\frac{R}{c_0} = \frac{dc}{dt} = k_1 \left( \frac{m}{m_0} \right)^{r_1} - k_2 \left( \frac{m}{m_0} \right)^{r_2}
\]

(3)

In this expression, the mobilization rate of arsenate is expressed by the difference between arsenate mobilization and re-adsorption rates. \( R \) is the overall mobilization rate of arsenate (mg L\(^{-1}\) s\(^{-1}\)), \( c \) is the amount of mobilized arsenate (mg L\(^{-1}\)), and \( c_0 \) is the maximum value of the mobilized arsenate (mg L\(^{-1}\)). The parameters \( k_1 \) and \( k_2 \) are kinetic constants for mobilization and adsorption rates respectively, while \( r_1 \) and \( r_2 \) are the constants related to the mineral reactivity, crystalline structure for the release and re-adsorption of arsenate, respectively.

After combining Eqs. (2) and (3), we could get:

\[
\frac{R}{J} = \frac{dc}{dt} = -c_0 k_1 \left( \frac{m}{m_0} \right)^{r_1} - k_2 \left( \frac{m}{m_0} \right)^{r_2} + c_0 k_2 \left( \frac{m}{m_0} \right)^{r_2}
\]

(4)

Eq. (4) revealed that the difference between mobilization and re-adsorption of arsenate was dependent on iron oxides dissolution. All these parameters were estimated by MATLAB at pH 3.0, since dissolved Fe was insignificant at high pHs of 7.5 and 11.0. As shown in Table 1, \( k_1 \) changed from \( 3.3 \times 10^{-3} \) to \( 1.1 \times 10^{-2} \) s\(^{-1}\) and \( k_2 \) changed from \( 1.5 \times 10^{-4} \) to \( 5.6 \times 10^{-4} \) s\(^{-1}\) with the decreased arsenate loading in ferrihydrite system. In hematite system, \( k_1 \) changed from \( 2.9 \times 10^{-4} \) to \( 1.7 \times 10^{-3} \) s\(^{-1}\) with the decreased arsenate loading, \( r_2 \) was not available due to \( k_2 = 0 \) as for hematite. Parameter \( k_1 > k \) meant the release rate of arsenate was higher than the dissolution rate and it suggested that mobilization of the pre-loaded arsenate followed surface-mobilization mechanism. Fig. 7 showed the difference of arsenate mobilization on ferrihydrite and hematite in terms of \( c/c_0 \) versus \( m/m_0 \), using arsenate data calculated by Eq. (4). It indicated that the effect of arsenate loading was more significant in arsenate mobilization process in hematite system, while it was more effective in arsenate re-adsorption process in ferrihydrite system.

4. Conclusion

The present study revealed that reactivities of iron oxides played important roles in the mobilization and re-adsorption of arsenate in the presence of oxalate. Dissolution of ferrihydrite and hematite by oxalate was primarily controlled by the ligand-promoted dissolution, although reductive and ligand-promoted dissolution were both involved in this process. Dissolution of hematite was initiated at dot- and line-shaped defects and the dissolution rate would not slow down until defects became smooth. However, no morphological change could be found on ferrihydrite in the dissolution process. Although dissolution rates of iron oxides decreased with the increase loading of arsenate on both ferrihydrite and hematite, dissolution rate was mainly determined by reactivities of iron oxides, and ferrihydrite showed a higher reactivity than hematite in the presence of oxalate.

Re-adsorption of arsenate was detected after arsenate mobilization reached maximum values in ferrihydrite system, whereas such an observation was not significant in hematite system. Considering no secondary minerals detected in ferrihydrite and hematite systems at pH 3.0, more reactive sites exposed during the dissolution of ferrihydrite could contribute to the re-adsorption of the released arsenate. The insignificant re-adsorption of arsenate on hematite was due to the competition between oxalate and arsenate for the sorption sites, which were exposed in the dissolution process. Mathematic model proposed in our study further indicated that the effect of arsenate loading was more significant in arsenate mobilization process in hematite system, while it was more effective in arsenate re-adsorption process in ferrihydrite system. Considering the extensive distribution of oxalate in aquatic environments, and the importance of iron oxides as carriers to immobilize arsenic in nature, arsenic mobilization and re-adsorption could be initiated by oxalate. Mathematic model of arsenate mobilization proposed...
in this study could also help us to predict the fate and transport of arsenate under the dissolution conditions.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jhazmat.2013.09.010.

References