

# Arsenite and arsenate leaching and retention on iron (hydr)oxide-coated sand column

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## Abstract

**Purpose** Arsenite and arsenate leaching from iron (hydr)oxides is one major parameter affecting the mobility of arsenic in the natural environment. In the process of arsenic transfer to groundwater, the retention capacity of arsenic by different iron (hydr)oxides needs to be investigated. The aim of this study is to determine the retention capacity of arsenite or arsenate from the ferrihydrite, lepidocrocite, or magnetite-coated sand column in the leaching process as well as the influence factors on leaching.

**Materials and methods** The leaching of arsenite and arsenate from columns loaded with ferrihydrite, magnetite, or lepidocrocite-coated quartz sand was examined, and the influence factors such as pH, phosphate, and humic acid (HA) contents on leaching and retention were also investigated.

**Results and discussion** The retention performance of As(III) and As(V) depended on the type of iron (hydr)oxides: ferrihydrite > magnetite > lepidocrocite. The retention capacities of As(III) and As(V) by amorphous ferrihydrite versus magnetite and lepidocrocite are 3.25, 5.63 (As(III)) and 1.75, 3.65 (As(V)) times higher. The retention capacity of arsenic is largely affected by the pH of leaching solutions. The retention of As(III) by ferrihydrite is efficient in near-neutral or slightly acidic environments. The addition of phosphate or HA significantly affected the leaching and retention. The addition of

phosphate severely inhibited the leaching and retention of As(III) and As(V) by ferrihydrite, and the inhibitory effect was more obvious along with the increase of phosphate concentration. The retention of As(III) and As(V) by ferrihydrite was significantly enhanced by the addition of low-dose HA but was inhibited by the addition of excessive HA.

**Conclusions** Retention performance of As(III) and As(V) from a ferrihydrite-coated sand column is greater than a magnetite- or a lepidocrocite-coated sand column, and the influence factors such as pH, phosphate, and HA affect the leaching and retention of As(III) and As(V). The results theoretically underlie the application of iron (hydr)oxide in arsenic pollution control.

**Keywords** Arsenate · Arsenite · Ferrihydrite · Iron (hydr)oxides · Leaching · Retention

## 1 Introduction

Arsenic (As), a known poison, is widely distributed in the environment because of its natural existence and anthropogenic use in both agriculture and industry to control a variety of insect and fungal pests (Ruokolainen et al. 2000; Leist et al. 2003). Arsenic is well-known for its high toxicity and strong carcinogenicity (United States Environmental Protection Agency 1997). At the end of the twentieth century, the revision of the maximum contaminant level (MCL) for arsenic in drinking water was reduced from 50 to 10 µg/l by the Environmental Protection Agency (USEPA) and World Health Organization (WHO) (Ghosh et al. 2006a). Arsenic pollution has been a long concern, and such incidents occur frequently in recent years, especially in waters and soils (Jain and Ali 2000; Smedley and Kinniburgh 2002; Swartz et al. 2004; Jaime et al. 2007; Amstaetter et al. 2010; Jia et al. 2012; Tuna et al. 2013).

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In China, arsenic resources are widely associated with ore in nonferrous polymetallic deposits. These arsenic-bearing solid residuals (ABSR) from waste tailings are discarded in the periphery of mining areas. After a series of weathering conditions such as accumulation, oxidization, leaching, and dissolution, the arsenic-containing waste rocks and tailings will release arsenic and thus pollute and harm the surrounding groundwater, farmlands, and eco-environment to different degrees.

The common valence states of As found in natural waters, As(V) and As(III), exist as arsenate (As(V), as  $H_2AsO_4^{x-3}$ ) and arsenite (As(III), typically as  $H_3AsO_3$ ) (Kocar et al. 2006). Both the redox states and chemical forms of arsenic are important because they determine its toxicity and environmental mobility (Keon et al. 2001; Hamon et al. 2004). Reduction from As(V) to As(III) for example leads to enhanced mobility and toxicity of the reduced species (Delaun et al. 1991; Dixit and Hering 2003; Oremland and Stolz 2005; Kulp et al. 2008). Removal of As(III) and As(V) by adsorption onto solid media is currently the most widely chosen treatment option, and it is effective to remove arsenic from water and soils (Ghosh et al. 2006b; Amstaetter et al. 2010). The adsorption of arsenite or arsenate is significantly associated with the oxides (hydroxides) of iron and aluminum and the clay content in soils (Douglas 1984; Raven et al. 1998). Arsenite or arsenate can be chemically adsorbed by specific iron (hydr)oxides to mainly form inner-sphere complexes (Pierce and Moore 1982; Dzombak and Morel 1990; Goldberg and Johnston 2001; Zhang et al. 2007a).

Iron (hydr)oxides ubiquitous in soil and groundwater environment are commonly used as absorbents and antioxidants to remove heavy metals and organic matter from water or soils, owing to their large specific surface areas, high surface energy, high chemical activity, high oxidizability, wide availability, high contents, and low costs (Pierce and Moore 1982; Manning, et al. 1998; Raven, et al. 1998; Silva, et al. 2007; Demetriou and Pashalidis 2012). Therefore, characterizing the retention of arsenic by iron (hydr)oxides helps to understand the arsenic removal mechanism and thus the removal from the environment. However, there is little research about the different leaching migration characteristics between As(III) and As(V) from representative minerals (e.g., lepidocrocite, ferrihydrite, and magnetite) or about the effects of iron (hydr)oxides on arsenic leaching. Therefore, in this study, we selected these three representative iron (hydr)oxides and determined the retention capacity of arsenite or arsenate from ferrihydrite, lepidocrocite, and magnetite-coated sand columns in the leaching process as well as the influence factors on leaching. This study theoretically underlies the alleviation of the arsenite and arsenate pollution from groundwater environment and restoration from environmental pollution.

## 2 Materials and methods

### 2.1 Materials

All chemicals were analytical grade and purchased from Beijing Chemical Co. (Beijing, China). The As(III) and As(V) stock solutions were prepared with deionized water using  $NaAsO_2$  and  $Na_2HAsO_4$ , respectively. Arsenic working solutions were freshly prepared by diluting arsenic solutions with deionized water.

Experimental quartz sand (Sinopharm Chemical Reagent Co., Ltd.; purity > 98 %; average particle size 500  $\mu\text{m}$ ; evenness index 1.25) was used as a packing medium in simulation of soils. To remove the surface metallic oxides, the quartz sand was soaked in 0.01 mol/l NaOH and HCl for 24 h in due order, washed with deionized water and then dried at 105 °C.

### 2.2 Preparation of iron (hydr)oxides

The iron oxides were prepared according to the method by Schwertmann and Cornell (2000) with modification.

$FeCl_3 \cdot 6H_2O$  (54.06 g) was dissolved in 2 l of twice-distilled water, which was held in a 3-l closed container at 40 °C for 8 days. During this period, the bright gold solution became lighter yellow and compact yellow precipitates. The pH dropped from 1.7 to ~1.2 (lepidocrocite,  $\gamma\text{-FeOOH}$ ). Then  $Fe(NO_3)_3 \cdot 9H_2O$  (40.00 g) was dissolved in 500 ml of distilled water and added with 330 ml of 1 mol/l KOH to bring the pH to 7.0–8.0. The last 20 ml of KOH was added dripped with constant checking of pH. Then, the mixture was stirred vigorously, centrifuged and then dialyzed rapidly until free from electrolytes (ferrihydrite,  $Fe_3HO_8 \cdot 4H_2O$ ).  $FeSO_4 \cdot 7H_2O$  (80.00 g) was soaked in 560 ml distilled water in a 1-l container. The container was placed in a water bath (90 °C) and a gas inlet for purge  $N_2$ . Then, 240 ml of solution containing 6.46 g  $KNO_3$  and 44.9 g KOH was dripped over about 5 min. After addition of this solution, the resulting mixture was heated over 30–60 min, cooled overnight, and the black precipitates were washed (magnetite,  $Fe_3O_4$ ). All the precipitates were dried in a vacuum drying box at 60 °C.

### 2.3 Column experiments

The quartz sand as-prepared (20.00 g) was slowly poured into a chromatographic column and tamped tightly to a filling height of 3.5 cm. This step was repeated five times and totally 100 g of quartz sand was filled in. Then, different amounts of an iron oxide sample were added into the column as per different dosage ratios.

About 1.00 g of an iron oxide (content 1 %) was added to the column. The pH 7 As(III) or As(V) stock solution was adjusted with 0.1 mol/l NaCl, 10 mg/l NaOH, and 10 mg/l HCl and then pumped from top to down into the packed

column. During the experiment, the surface level of the packed column was 2 cm above the top of the quartz sand. The leaching speed of the leaching solutions was regulated to 1.0 ml/min by adjusting the peristaltic pump. The automatic collector collected at an interval of 10 min.

Different amounts of NaCl were added to control the ionic strength at 0.1 or 0.01 mol/l; 10 mg/l NaOH and 10 mg/l HCl were added to control the pH at 3, 5, 7, 9, or 11; different amounts of  $\text{NaH}_2\text{PO}_4$  were added to control the molar ratio of As to  $\text{PO}_4^{3-}$  (mol/l:mol/l) at 1:0.1 or 1:10; different amounts of HA were added to control the concentration ratio of As to HA (mg/l:mg/l) at 1:0.1 or 1:1 in the As(III) or As(V) stock solution. The following steps are the same as the second paragraph in Section 2.3.

## 2.4 Analysis methods

The total arsenic concentration in a leaching solution was measured by an iCAP 6300 inductance-coupling plasma (ICP) emission spectrometer (Thermo Fisher Scientific; USA), following the procedure as described in previous studies (Gil et al. 2007; Lopes et al. 2009). Different forms of arsenic concentration in the solution after leaching were measured by a liquid chromatography-atomic fluorescence spectrometer (LC-AFS) model 9700 (Beijing Haiguang Instrument Co., Ltd.). Aqueous pH was measured by a PHS-3C pH meter and an E-201-C pH composite electrode (Shanghai INESA Scientific Instrument Co., Ltd).

The LC-AFS conditions were (Yun et al. 2010; Xiao et al. 2014): pH 5.92 phosphate buffer solution (PBS;  $\text{Na}_2\text{HPO}_4$  and  $\text{KH}_2\text{PO}_4$ ) as mobile phase; injection volume 100  $\mu\text{l}$ ; pumping flow 1.0 ml/min. To 5 % HCl as a load flow, 20 g/l alkaline  $\text{KBH}_4$  as a reductant was added and mixed to form a reductant  $\text{H}_2$ ; the separated substance reacted with  $\text{H}_2$  to form gaseous  $\text{AsH}_3$ . The AFS conditions were as follows: flow rate of carrier gas and shielding gas were 300 and 900 ml/min, respectively; main current=80 mA; auxiliary current=40 mA; negative high voltage=300 V; atomization temperature=200 °C; height of atomization device=10 mm.

All experimental data were compared by analysis of variance (ANOVA) and processed using the statistical software SPSS 19.0 of treatments and control samples.

## 2.5 Iron (hydr)oxides characterization

To determine the arsenic species adsorbed on the surface of the adsorbent after reaction with As(III) or As(V), we selected some samples and freeze-dried them for further analysis using scanning electron microscopy (SEM) and X-ray diffraction (XRD).

An S-4800 scanning electron microscope (SEM, Hitachi Ltd., Japan) and an XD-3 X-ray diffraction (XRD) analyzer (Beijing Purkinje General Instrument Co., Ltd.) were used to

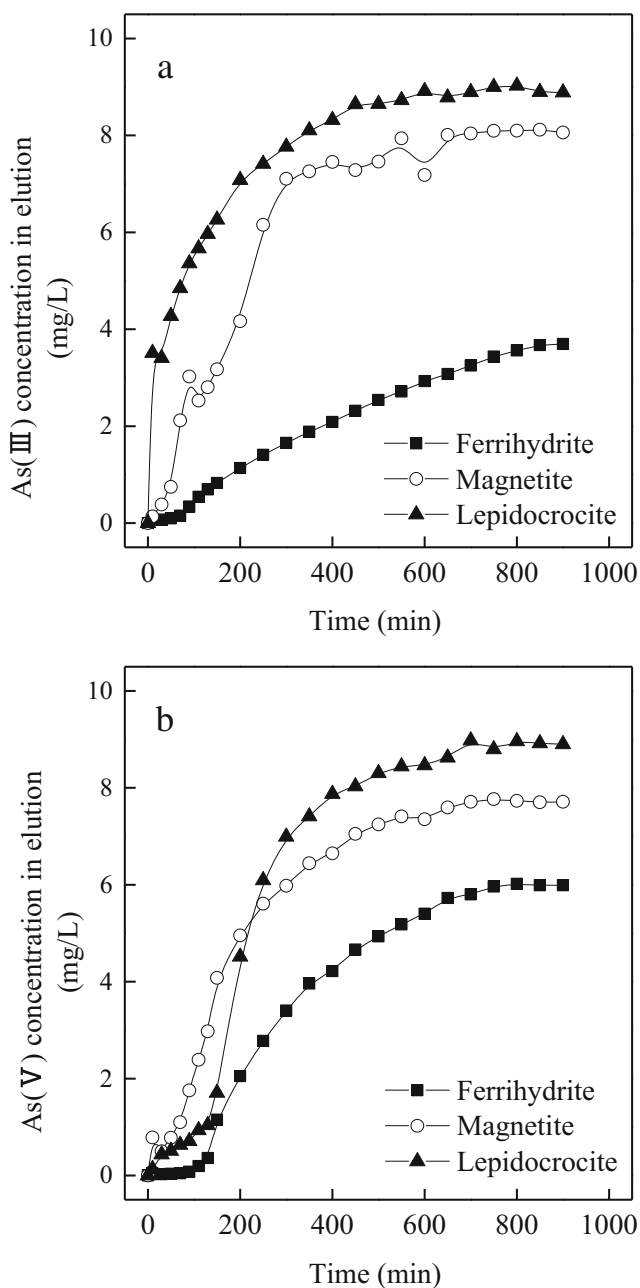
check lepidocrocite, ferrihydrite, and magnetite before and after leaching. A 2.6×20 cm glass column and an automatic sampling instrument were used for leaching experiments (Shanghai Huxi Analysis Instrument Factory Co., Ltd). SEM conditions were voltage 7–15 kV; working distance 8–12 mm. Samples were scanned from 20° to 80° ( $2\theta$ ) with a 1° ( $2\theta$ ) step-size and a 1-min count time. Results were interpreted with the support of the JADE 6.5 software package.

## 3 Results and discussion

### 3.1 As(III) and As(V) leaching from iron (hydr) oxide-coated sand column

As(III) (a) and As(V) (b) leaching from columns loaded with ferrihydrite-, magnetite-, or lepidocrocite-coated quartz sand column are plotted and showed in Fig. 1. Results indicate that the concentrations of As(III) and As(V) in the eluents are changing before 800 min of leaching time. The retention performances of As(III) and As(V) depend on the type of iron (hydr) oxides: ferrihydrite>magnetite>lepidocrocite, and this order is consistent with a previous report (Raven et al. 1998), suggesting that the strongest retention performance of As(III) and As(V) is found in the ferrihydrite-coated quartz sand column. Throughout the experiment, the As(III) and As(V) concentrations in the eluents are within 0–3.5 mg/l (As(III)) and 0–6.0 mg/l (As(V)). Obviously, retention capacity of As(III) by ferrihydrite is stronger than the As(V). On the adsorption curve of magnetite, the arsenic concentrations within 0–200 min change rapidly first and then slowly and increase from 0.135 mg/l at the beginning to 8.06 mg/l at the end. The adsorption ability of lepidocrocite is relatively weaker than versus ferrihydrite and magnetite. After 400 and 700 min, the As(III) and As(V) concentrations in the elution solutions are balanced, respectively. In the As(III) leached by the lepidocrocite-coated sand column, the initial level (3.51 mg/l) and balanced level (8.93 mg/l) are larger versus the other two iron oxides. The retention abilities of As(III) and As(V) by ferrihydrite versus the magnetite and lepidocrocite are 3.25, 5.63(As(III)) and 1.75, 3.65(As(V)) times higher.

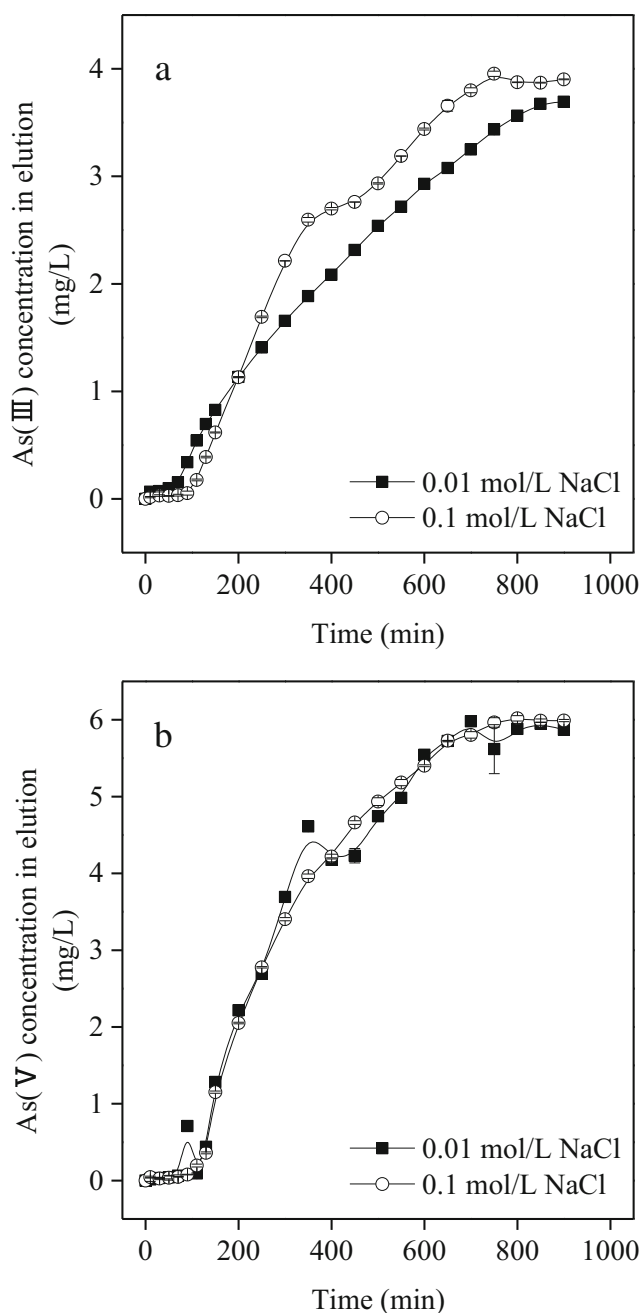
Ferrihydrite is an amorphous iron oxide possessing an extremely large specific surface area (SSA) and high reaction activity. The core of its structure is dominated by octahedrons, and its surface is occupied by abundant tetrahedral units. The surface unsaturation together with weak crystallinity and large SSA endows ferrihydrite with stronger retention ability compared with the other two iron oxides. Thus, ferrihydrite was selected and used to investigate the leaching and retention ability of As(III) and As(V).



**Fig. 1** As(III) (a) and As(V) (b) leaching from columns loaded with ferrihydrite-, magnetite-, or lepidocrocite-coated quartz sand column; 10 g/kg of iron (hydr)oxides added at quartz sand column; initial concentration of As(III) or As(V)=10 mg/l; flow rate at 1 ml/min; pH 7.0 in the eluent

### 3.2 Effects of ionic strength on As(III) and As(V) leaching

Ionic strength can affect the macroscopic adsorptive performances, which provide valuable information on the formation of surface complexes (Kim et al. 1988). In order to make identification effects of ionic strength on As(III) and As(V) leaching, we test the leaching and retention dynamics of As(III) and As(V) by a 1 % ferrihydrite-coated sand column (Fig. 2 a, b) with 0.1 or 0.01 mol/l NaCl as the supporting



**Fig. 2** Effect of ionic strength on As(III) (a) and As(V) (b) elution from ferrihydrite-sand column. 10 g/kg of ferrihydrite added at sand column; initial concentration of As(III) or As(V)=10 mg/l; flow rate=1 ml/min; pH 7.0 in the eluent

electrolyte. Results showed that the As(III) and As(V) concentrations in the two groups of solutions all increase with reaction time. The As(III) concentrations in the solutions increased slowly from 0 to 0.5 mg/l within 0–100 min then increased rapidly within 100–800 min but are gradually balanced after 800 min. Similarly, the As(V) concentrations in the eluents continue to increase before 800 min leaching time and increase from 0.01 mg/l at the beginning to 5.99 mg/l at the end. In different ionic strength solutions, the adsorption

capacity of As(III) by ferrihydrite is stronger than the As(V). AVONA via least significant difference (LSD) was conducted on SPASS 19.0. The significance level is  $p > 0.05$ , so the adsorptions of arsenic by ferrihydrite are not significantly different among different ionic strengths in the leaching solutions. In other words, ionic strength is not a main influence factor on the leaching of As(III) or As(V) by the ferrihydrite-coated sand column.

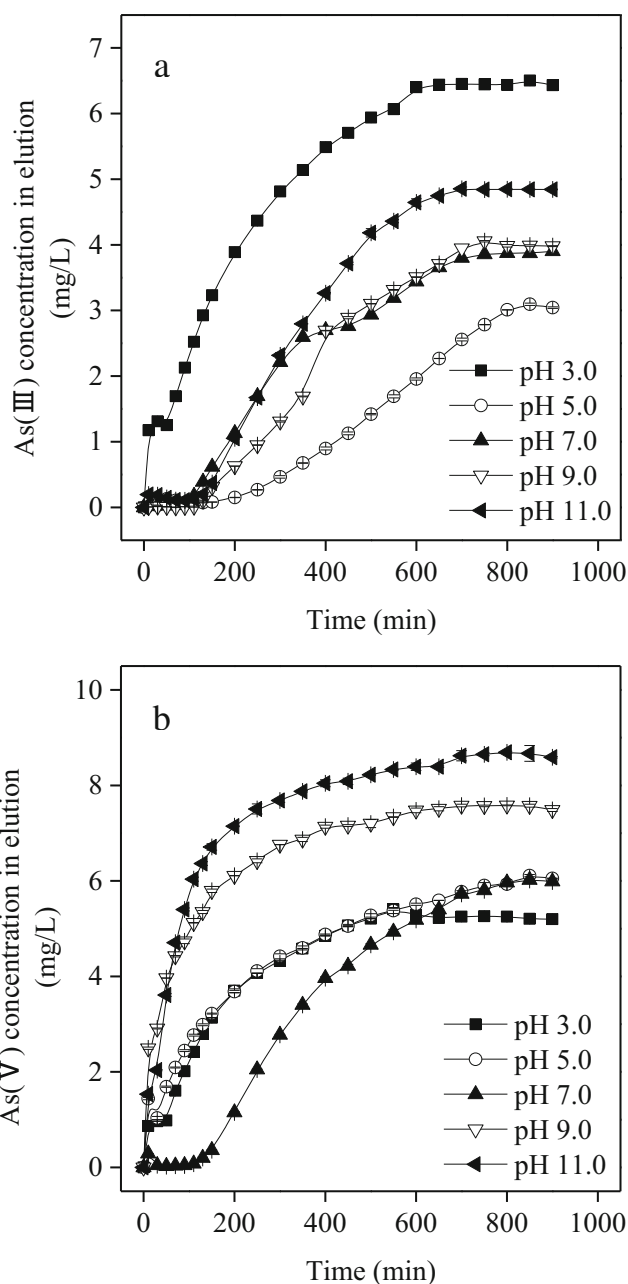
The formation of outer sphere complexes was relative in that the adsorptive capacity decreases with the elevation of ionic strength. On the contrary, when ionic strength has little effect or favorable effect on the adsorption capacity, the formation of inner sphere complexes may be inferred (He et al. 2015). These As(III) and As(V) leaching results indicate that the inner sphere complexes might dominate in the leaching and retention of As(III) and As(V) onto the ferrihydrite accordingly (Manning et al. 1998).

### 3.3 Effects of eluent pH on As(III) and As(V) leaching

The leaching and retention kinetics of As(III) and As(V) over a wide pH range from 3.0 to 11.0 is illustrated in Fig. 3a, b. The As(III) and As(V) concentrations in the eluents gradually increase with the prolonging of reaction time and are balanced after 800 min leaching time. The retention ability of As(III) or As(V) by the ferrihydrite-coated quartz sand column varies with different pH values of solution. Quantitatively, the retained concentrations of As(III) increase from 3.57 at pH 3.0 to 6.96 mg/l at pH 5.0 and decrease from 6.42 at pH 9.0 to 5.16 mg/l at pH 11.0. When the solution pH value is 7.0, the retained concentration of As(III) is 6.10 mg/l after reaching equilibrium. The pH significantly impacts the adsorption capacity of As(III) by ferrihydrite. The adsorption ability changed as follows:  $\text{pH } 5.0 > \text{pH } 7.0 > \text{pH } 9.0 > \text{pH } 11.0 > \text{pH } 3.0$ , and the maximum adsorption quantity (at pH 5.0) is 1.95 times larger than the minimum one (at pH 3.0). Results show that both weak acid or weak alkali environments are favorable for the adsorption of As(III) by ferrihydrite. The leaching adsorption ability of As(III) by ferrihydrite is minimized at pH 3.0. The reason is that pH 3.0 is a strongly acidic environment relative to other pH levels, leading to the partial dissolution and severe reduction of the amount of iron mineral and resulting in the reduction of adsorption ability.

Similarly, the solution pH significantly impacts the leaching and retention of As(V) by the ferrihydrite-coated sand column. After leaching, solution concentration is stabilized, the concentration of As(V) in the leaching solution increases from 5.20 at pH 3.0 to 8.59 mg/l at pH 11.0. However, the concentration of As(III) leached by the ferrihydrite-coated sand column changes in the first trend and then increased trend with the pH increase.

As pH increases, the decreasing concentration of aqueous protons drives more protons from the surfaces of iron



**Fig. 3** Effect of eluent pH on As(III) (a) and As(V) (b) leaching from a ferrihydrite-sand column; 10 g/kg of ferrihydrite added alt sand column; initial concentration of As(III) or As(V)=10 mg/l; flow rate=1 mL/min; pH value in the eluent was adjusted by 0.1 mol/l HCl and NaOH

(hydr)oxides, thus making it more negatively charged (Ghosh et al. 2006b). The point of zero charge (PZC) of ferrihydrite is about pH 7.0 to 8.5 (Raven et al. 1998; Qi and Pichler 2014). Thus, the range of pH investigated brackets the PZC of the media and consequently brackets the largest change in surface charge per unit change in pH occurs.  $pK_a$  values of arsenious acid ( $\text{H}_3\text{AsO}_3$ ) and arsenic acid ( $\text{H}_3\text{AsO}_4$ ) are as follows:  $pK_1=9.22$ ,  $pK_2=12.13$ , and  $pK_3=13.4$ ;  $pK_1=2.20$ ,  $pK_2=6.97$ , and  $pK_3=11.53$ , respectively. Inflections or maxima in the retention envelopes of anions at pH values close to their

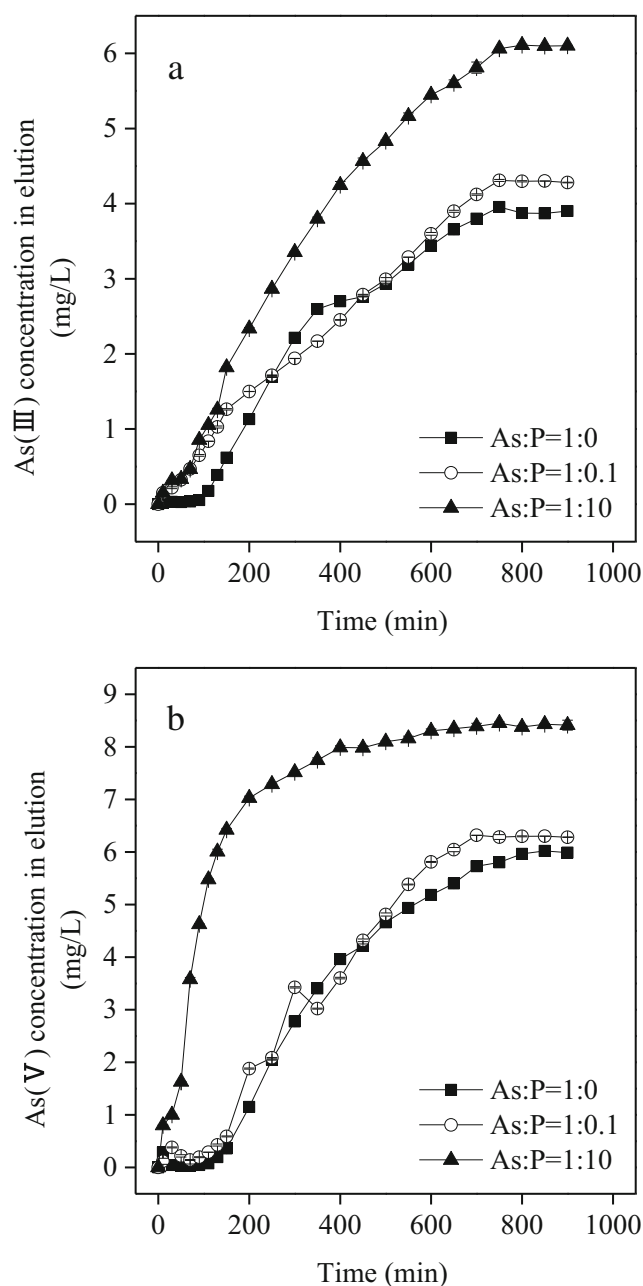
$pK_a$  are a well-documented phenomenon (Raven et al. 1998). Arsenite retention ability is not reduced significantly until pH values were greater than 9.0. The higher fraction of aqueous arsenic in the adsorption experiments than in the desorption experiments might be due to the presence of an energy barrier, which must be overcome to mobilize absorbed arsenic and thus slow down the release (for desorption) compared to the uptake (for adsorption). This indicates the surface sites, on which arsenate is irreversibly bound in the operating conditions employed and is consistent with a shift from monodentate to bidentate surface bonding after retention.

To sum up, the wide pH range from 3.0 to 11.0 has a significant effect on the surface charge distribution of iron (hydr)oxides and ionization of As (III) and As (V), thus affecting the leaching and retention ability of As (III) and As (V) from iron (hydr)oxide-coated sand columns.

### 3.4 Effects of phosphate on As(III) and As(V) leaching

In this section, in order to investigate the effects of phosphate on As(III) and As(V) leaching, we test the leaching dynamics of As(III) and As(V) by the 1 % ferrihydrite-coated sand column (Fig. 4a, b) with a molar ratio of As to  $\text{HPO}_4^{2-}$  as 1:0.1 or 1:10 in the stock solution. As shown in Fig. 4a, at the molar ratio of As to  $\text{HPO}_4^{2-}$  of 1:0 or 1:0.1 in the stock solution, the retention concentration of As(III) by the ferrihydrite-coated sand column after balance dropped by 4.83 % from 6.01 to 5.72 mg/l. At the ratio of As to  $\text{HPO}_4^{2-}$  of 1:10, the retention concentration of As(III) by ferrihydrite after equilibrium is only 3.99 mg/l, 66.39 % of the baseline (no addition of  $\text{HPO}_4^{2-}$ ). As illustrated in Fig. 4b, at the molar ratio of As to  $\text{HPO}_4^{2-}$  of 1:0 or 1:0.1, the concentration of As(V) by the ferrihydrite-coated sand column in the eluent after equilibrium rises by 5.01 % from 5.98 to 6.28 mg/l. At the molar ratio of As to  $\text{HPO}_4^{2-}$  of 1:10 in the stock solution, the adsorption concentration of As(V) by ferrihydrite after adsorption equilibrium is 1.59 mg/l, only 39.55 % of the baseline.

It is known that the sorption process of arsenate onto the iron (hydr)oxide is strongly disturbed by phosphate (Dixit and Hering 2003; Zhang et al. 2007b). Water contaminants are usually not as single ions in the water. In the previous chapter, the sorption of several iron-bearing mineral species was investigated at a constant ionic strength (added salt: NaCl) and a selected pH value, but without addition of any ion that is known to compete for the sorption sites. In this section, the influence of phosphate is investigated because of its competitive effect on the sorption of arsenate (Kolbe, et al. 2011). The addition of  $\text{HPO}_4^{2-}$  severely inhibits the adsorption of As(III) and As(V) by ferrihydrite, and a higher  $\text{HPO}_4^{2-}$  concentration is obvious more inhibitory. Since the elements of P and As are in the same main group of chemical periodic table, they have

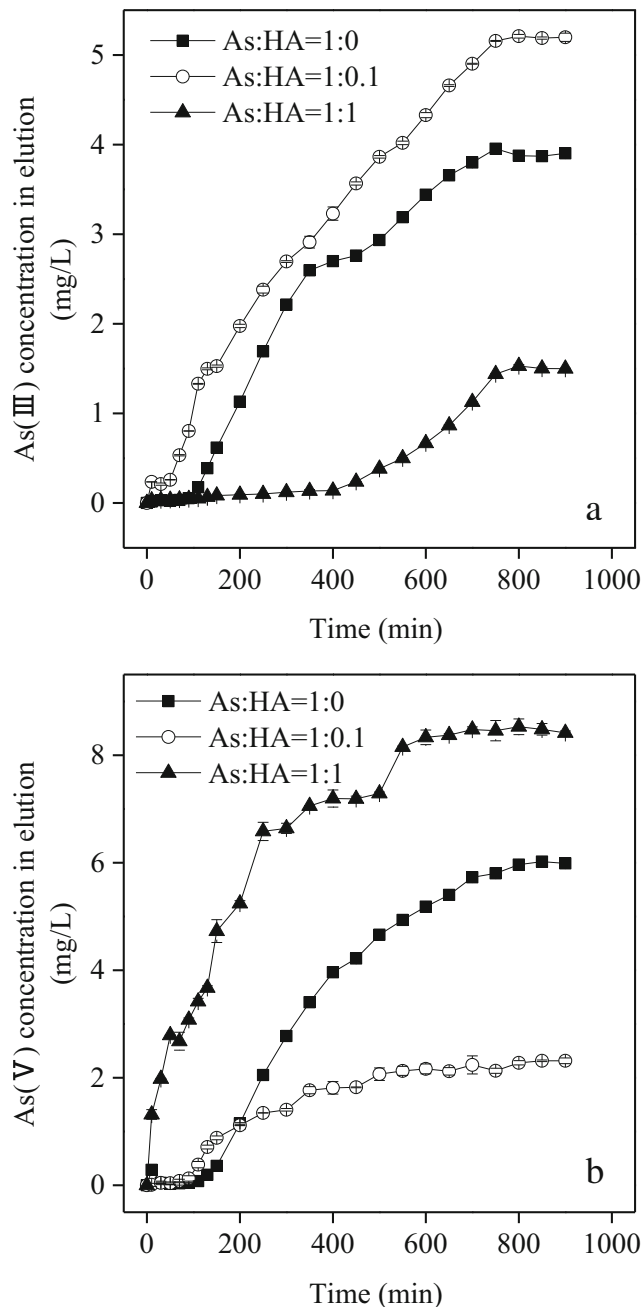


**Fig. 4** Effect of phosphate content on As(III) (a) and As(V) (b) elution from ferrihydrite-sand column; 10 g/kg of ferrihydrite added at sand column; initial concentration of As(III) or As(V)=10 mg/l; flow rate=1 ml/min; pH 7.0 in the eluent; the molar ratio of As to  $\text{HPO}_4^{2-}$  at 1:0 was set up as the blank control

similar properties.  $\text{HPO}_4^{2-}$  can compete with  $\text{AsO}_2^-$  and  $\text{AsO}_3^-$  for absorption, which reduces the amount of adsorption sites on surface of ferrihydrite as well as the adsorption ability of ferrihydrite. Ghosh's study suggests a number of sites where arsenite or arsenate ions can be exchanged by phosphate, but the arsenite or arsenate adsorption to phosphate addition is indifferent at higher phosphate loadings, suggesting that not all arsenic or arsenate sites are exchangeable (Ghosh et al. 2006a).

### 3.5 Effects of HA on As(III) and As(V) leaching

The leaching dynamics of As(III) and As(V) by the 1 % ferrihydrite-coated sand column are showed in Fig. 5a, b with the As to HA concentration ratio 1:0.1 or 1:1. HA also shows a greater difference in the leaching stock solutions between the lowest and highest concentrations. When the HA concentration is 1 mg/l, the residual concentration of As(III) after balance



**Fig. 5** Effect of HA content on As(III) (a) and As(V) (b) elution from ferrihydrite-sand column; 10 g/kg of ferrihydrite added at sand column; initial concentration of As(III) or As(V)=10 mg/l; flow rate=1 ml/min; pH 7.0 in the eluent; the concentration ratio of As to HA at 1:0 was set up as the blank control

decreases from 3.90 mg/l (without addition of HA, baseline) to 1.49 mg/l, about 61.8 % reduction. In the same conditions, the concentration of As(V) in the leaching solution after balance decreases from 5.99 mg/l (baseline) to 2.32 mg/l, about 61.3 % reduction (38.7 % of 5.99 mg/l). These results indicate that the addition of HA significantly improves the adsorption of As(III) and As(V) by ferrihydrite. However, with addition of 10 mg/l HA, the residual concentration of As(III) after balance increases from 3.90 mg/l (baseline) to 5.20 mg/l, about 1.33 times larger than baseline and 3.49 times larger than with addition of 1 mg/l HA. The residual concentration of As(V) after balance increases from 5.99 mg/l (baseline) to 8.41 mg/l, about 1.40 times larger than baseline and 3.63 times larger than with addition of 1 mg/l HA. These data indicate that addition of HA has a similar effect on As(III) and As(V) leaching from the ferrihydrite-coated sand column. In conclusion, the retention of As(III) and As(V) by ferrihydrite is significantly enhanced by the addition of low-dose HA, but is inhibited by the addition of excessive HA.

HA contains 50 % of NOM and is a unique anionic poly-electrolyte at all pH values (Warwick et al. 2005). It readily forms both aqueous and surface inner-surface complexes with cationic metals and metal oxides (Murphy et al. 1994). Arsenic uptake is suppressed by HA, and with the level of suppression increasing with HA concentration, the added HA hardly affects the adsorption of As (Warwick et al. 2005; Fakour and Lin 2014; Kong et al. 2014; Fakour and PanYF 2015). The suppression is attributed to the partial coverage of the adsorption sites, as confirmed by elemental analysis. HA may affect the retention ability of As(III) and As(V) from ferrihydrite through various mechanisms by (1) direct competition with the arsenic for surface sites (Parks, 1990), (2) absorption to the surface to create additional surface attraction and enhanced sorption at low HA concentration (Schwarzenbach et al. 1993), (3) acting as a soluble partitioning agent to bind the ions and keep them in solution (Stumm and Morgan 1996), (4) direct reaction with the sorbent surface to enhance dissolution of the surface and loss of sorption sites (Schwarzenbach et al. 1993), or (5) deposition of HA onto the solid surface to shield active sites (Ghosh et al. 2006b). The effects of HA on the retention of As(III) and As(V) from the ferrihydrite-coated sand column might be attributed to several mechanisms together, rather than a single mechanism.

### 3.6 Retention mechanisms of As(III) and As(V) on iron (hydr)oxides

In the leaching process, the retention capacity of As(III) and As(V) from iron (hydr)oxide-coated sand columns depends on the adsorption capacity of As(III) and As(V) by different iron (hydr)oxides. Numerous studies show that iron (hydr)oxides can adsorb of As(III) and As(V) effectively. Moreover, the adsorption performances of As(III) and As(V) depend on the type of iron oxides: ferrihydrite>magnetite>lepidocrocite,

and this order is consistent with retention performance in the leaching process.

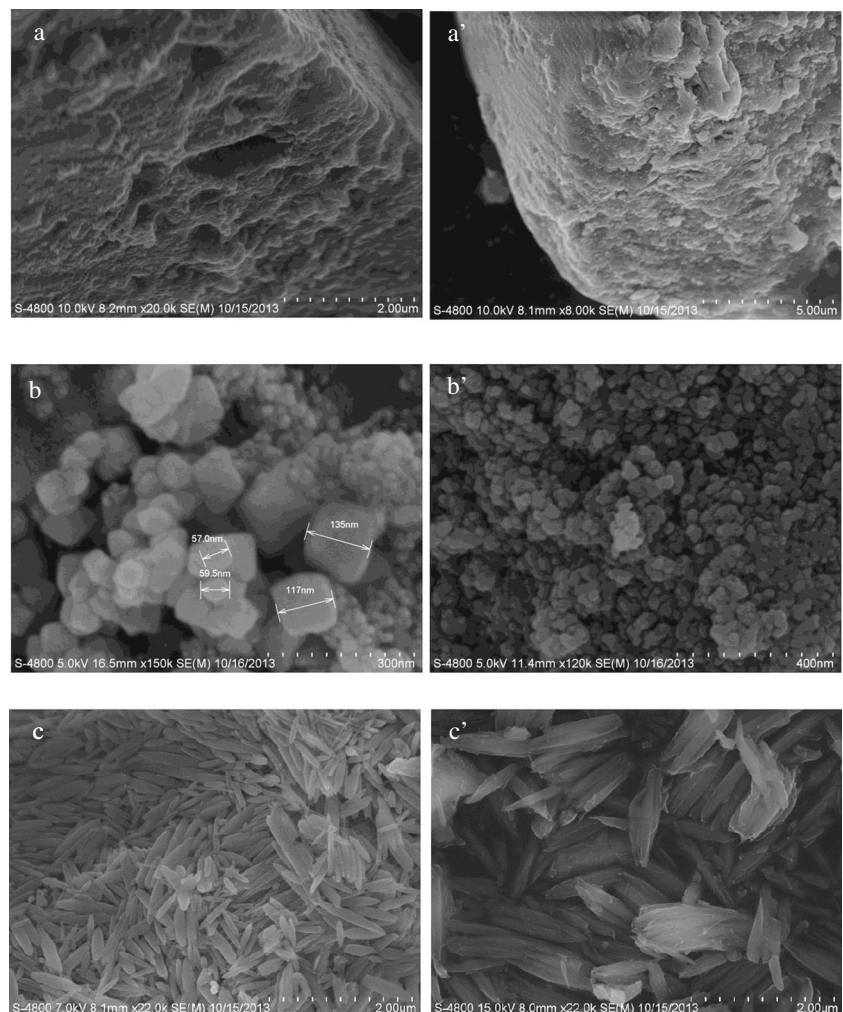
In order to better understand the mobilization and repartition of arsenic during the dissolution and coprecipitation process, we identify morphological changes of ferrihydrite, lepidocrocite, magnetite, and speciation of secondary minerals by technology of SEM (Fig. 6) and XRD (Fig. 7).

Clearly, in the leaching reaction, all three iron-bearing minerals underwent obvious geometric and morphologic changes, such as agglomeration, rounding, and smoothing, indicating the presence of interparticle magnetic force, surface tension, and oxidoreduction on the surface of iron (hydr)oxides. Before leaching reaction, lepidocrocite was shaped as rod-like spindles each 1  $\mu\text{m}$  long and 300 nm wide; the whole size was 2–7  $\mu\text{m}$ , which was similar to a previous report. After As(III) or As(V) leached, lepidocrocite was nest-shaped under the interparticle surface tension, and the complexation via adsorption and coprecipitation with arsenic. The diameter of a unit increased from 2–7  $\mu\text{m}$  to about tens of  $\mu\text{m}$ . The unreacted ferrihydrite was obviously gully on the surface

and sponge-like inside. The surface of reacted ferrihydrite was smoother without clear gully, while the sponges inside were more filled-up. Because of small grain-size and weak crystallization, the ferrihydrite did not show obvious peaks on SEM. The magnetite was like sharp-crystal cubes, in diameter of 50–100 nm, indicating a typical micro-nanostructure. After As(III) or As(V) leached, the sharp-crystal cubes gradually smoothed to irregular spheres.

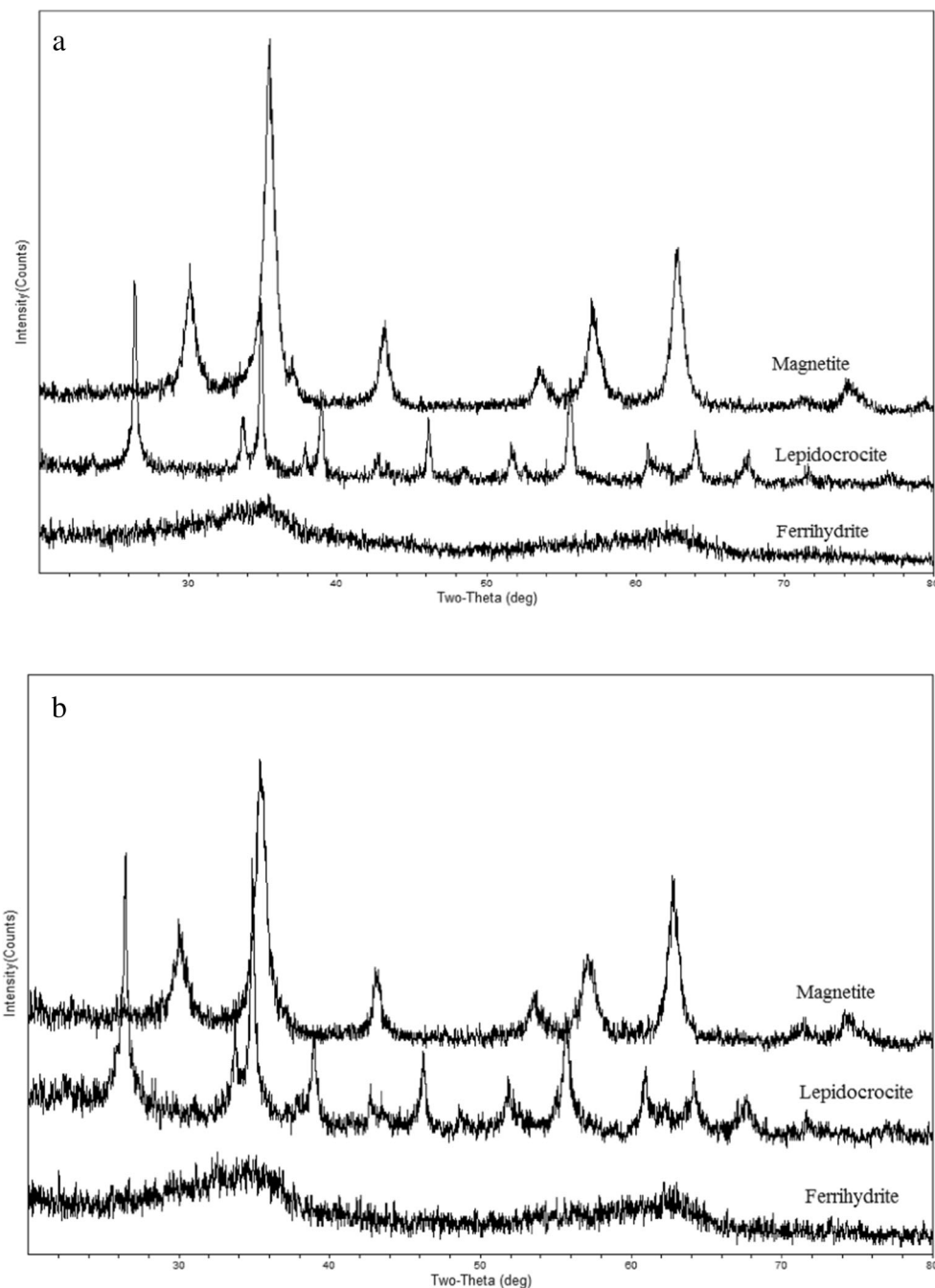
Before As(III) and As(V) leached, lepidocrocite and magnetite show clear characteristic peaks (Fig. 7), which are consistent with a previous report that ferrihydrite is featured by wide distribution, small grain-size, and weak crystallization. Ferrihydrite shows two unclear characteristic peaks, which are consistent with the prepared two-line ferrihydrite. With the prolonging of reaction time, the As(III) or As(V) contents in the three iron-bearing minerals all increase, and the mineralogy also changes, indicating that the iron ions in the iron-bearing minerals are gradually released to flocculate and coprecipitate with arsenic ions in the solutions to form new minerals. Moreover, Pedersen's research suggested that

**Fig. 6** SEM images of ferrihydrite, magnetite, and lepidocrocite before (a, b, c) and after (a', b', c') arsenic leaching from sand column



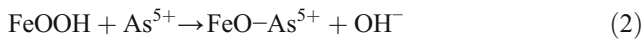
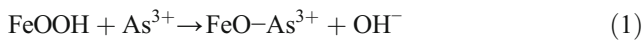


**Fig. 7** XRD patterns of ferrihydrite, magnetite, and lepidocrocite before (a) and after (b) arsenic leaching from sand column. Samples were scanned from 20° to 80° (2θ) with 1° (2θ) step-size and 1-min count time



ferrihydrite could be transformed into lepidocrocite and goethite at low  $\text{Fe}^{2+}$  concentrations and into goethite and magnetite at high  $\text{Fe}^{2+}$  concentrations (Pedersen, et al. 2006). Huang's research indicated that magnetite and goethite could be formed at suitable pH value and initiated by adsorption of  $\text{Fe}^{2+}$  onto the ferrihydrite surface (Huang, et al. 2015). Iron (hydr)oxides have highly reactive surface areas than other iron oxides due to bidentate and bimolecular surface complexes between arsenic species and  $=\text{FeOOH}$  (Sakthivel et al., 2011; Maji et al., 2012; Rahman et al., 2013). Thus, under aqueous

environment, the iron (hydr)oxides could effectively bind arsenic species by ligand exchanges on the iron (hydr)oxides containing adsorbent's internal and external surfaces (Eqs. 1 and 2) and form the new minerals (Shams et al., 2014). In our study, the newly formed substances were identified via library searching to be  $\text{Fe}_4\text{O}_3(\text{AsO}_4)_2$  (Angelelite, PDF 13–0121),  $\text{FeAs}_2$  (Loellingite, PDF 53–1197),  $\text{FeFe}_3(\text{As}_5\text{O}_{13})$  (Scheiderhoehnite, PDF 35–0462), and  $\text{FeAsO}_4(\text{H}_2\text{O})_2$  (Scorodite, PDF 37–0468). These second minerals were obtained from flocculation and coprecipitation between Fe and As.



## 4 Conclusions

In this study, the retention performance of As(III) and As(V) from a sand column coated with ferrihydrite is greater than that coated with magnetite or lepidocrocite, and the influence factors such as pH, phosphate, and humic acid (HA) affect the leaching and retention of As(III) and As(V). For solutions with different pH levels, the retention of As(III) by ferrihydrite changes as follows: pH 5.0 > pH 7.0 > pH 9.0 > pH 11.0 > pH 3.0; the adsorption of As(V) by ferrihydrite decreases with the increase of pH in the leaching solution. Weak acid environments are favorable for the adsorption of As(III) by ferrihydrite. The addition of phosphate severely inhibits the leaching adsorption of As(III) and As(V) from the ferrihydrite-coated sand column, and the inhibitory effect is more obvious along with the increase of phosphate concentration. The adsorption of As(III) and As(V) by ferrihydrite is significantly enhanced by the addition of low-dose HA, but is inhibited by the addition of excessive HA. The results will provide the theoretical underline for the application of iron (hydr)oxide in arsenic pollution control.

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