



Formation of iron (hydr)oxides during the abiotic oxidation of Fe(II) in the presence of arsenate



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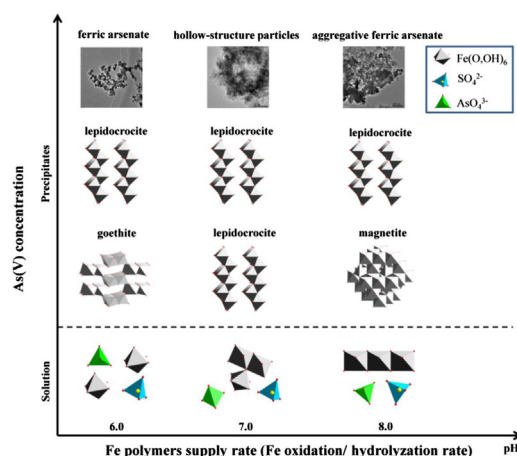
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HIGHLIGHTS

- Ferric arsenate is more favorable to precipitate compared with other Fe (hydr)oxides in the presence of arsenate.
- Arsenate causes the formation of special hollow-structured particles at pH 7.0.
- Trace amount of arsenate significantly inhibits the formation of magnetite.
- The oxidation rate of Fe(II) and the subsequent hydrolyzation of Fe(III) are mainly driven by pH in the presence of arsenate.

GRAPHICAL ABSTRACT



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ABSTRACT

Abiotic oxidation of Fe(II) is a common pathway in the formation of Fe (hydr)oxides under natural conditions, however, little is known regarding the presence of arsenate on this process. In hence, the effect of arsenate on the precipitation of Fe (hydr)oxides during the oxidation of Fe(II) is investigated. Formation of arsenic-containing Fe (hydr)oxides is constrained by pH and molar ratios of As:Fe during the oxidation Fe(II). At pH 6.0, arsenate inhibits the formation of lepidocrocite and goethite, while favors the formation of ferric arsenate with the increasing As:Fe ratio. At pH 7.0, arsenate promotes the formation of hollow-structured Fe (hydr)oxides containing arsenate, as the As:Fe ratio reaches 0.07. Arsenate effectively inhibits the formation of magnetite at pH 8.0 even at As:Fe ratio of 0.01, while favors the formation of lepidocrocite and green rust, which can be latterly degenerated and replaced by ferric arsenate with the increasing As:Fe ratio. This study indicates that arsenate and low pH value favor the slow growth of dense-structured Fe (hydr)oxides like spherical ferric arsenate. With the rapid oxidation rate of Fe(II) at high pH, ferric (hydr)oxides prefer to precipitate in the formation of loose-structured Fe (hydr)oxides like lepidocrocite and green rust.

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1. Introduction

Arsenic is a toxic contaminant in aqueous environment and commonly originates from the weathering of arsenic-bearing sulfide minerals exposed to the atmosphere naturally or by anthropogenic activities [1,2]. In neutral aqueous environments, arsenate [As(V)] primarily exists as H_2AsO_4^- and HAsO_4^{2-} as pK_a values of the arsenate are $\text{pK}_{a1} = 2.1$, $\text{pK}_{a2} = 6.7$ and $\text{pK}_{a3} = 11.2$, while arsenite [As(III)] mainly exists as H_3AsO_3 with $\text{pK}_{a1} = 9.1$, $\text{pK}_{a2} = 12.1$ and $\text{pK}_{a3} = 13.4$ [3]. Both As(V) and As(III) show strong affinities to Fe (hydr)oxides such as goethite ($\alpha\text{-FeOOH}$), ferrihydrite ($\text{Fe}_5\text{HO}_8 \cdot 4\text{H}_2\text{O}$), lepidocrocite ($\gamma\text{-FeOOH}$) and schwertmannite ($\text{Fe}_8\text{O}_8(\text{OH})_{8-2x}(\text{SO}_4)_x$, $1.0 \leq x \leq 1.85$) [4–9]. Apart from adsorption, co-precipitation of As(V) and Fe(III) with the formation of scorodite ($\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$) or ferric arsenate ($\text{FeAsO}_4 \cdot n\text{H}_2\text{O}$) also contributes to arsenate immobilization in aqueous environments [10–12].

As(V) and Fe(II) may co-exist in acid-mine drainage (AMD) or anoxic groundwater. The highly As(V)-contaminated groundwater typically contains Fe(II) with concentrations ranging from 0.05 to 44.3 mg L^{-1} [13–16]. In areas with serious arsenic contamination, the molar ratio of As:Fe can reach 0.03 [17]. When groundwater reaches the surface, Fe(II) is rapidly oxidized to Fe(III) (hydr)oxides.

The formation of different species of Fe(III) (hydr)oxides depends on pH value. The oxidative hydrolysis of Fe(II) is ready to form schwertmannite at pH 2.5–4.0 with the combination of a small amount of goethite, while ferrihydrite and goethite are the dominant species in the pH range of 4.4–8.4 [18]. Under anaerobic conditions, the hydrolysis of the mixed Fe(II) and Fe(III) solution results in the formation of schwertmannite at pH 2.8–4.5, following by the formation of goethite at pH > 5.0, while green rust at pH > 7.0 [19].

Concomitant anions also play important roles in the speciation of Fe (hydr)oxides. Weak binding between Fe(III) and NO_3^- results in the development of ferrihydrite, whereas strong binding anions like SO_4^{2-} favor the formation of schwertmannite under similar conditions [20]. Lepidocrocite forms during the abiotic oxidation of Fe(II) at pH-neutral conditions in the absence of phosphate, while amorphous $\text{Fe}(\text{OH})_3$ or phosphate-rich hydrous ferric oxides become the dominant species when phosphate is present [21,22]. To the best of our knowledge, little attention has been paid to the presence of arsenate on the formation of Fe (hydr)oxides during the abiotic oxidation of Fe(II) under pH-neutral conditions. Due to the strong affinity between arsenic and $\text{Fe}(\text{O}, \text{OH})_6$ unit, the normal linkage of $\text{Fe}-\text{O}-\text{Fe}$ during the growth of Fe (hydr)oxides may be destructed by the interference of arsenic, and thus producing different species of Fe (hydr)oxides. Our recent study suggested that the presence of As(V) can significantly inhibit the formation of schwertmannite in $\text{Fe}(\text{III})-\text{SO}_4^{2-}-\text{As}(\text{V})$ system, while favors the formation of amorphous FeAsO_4 under acidic conditions [23]. As(III) also causes the formation of a nano $\text{Fe}-\text{As}-\text{O}$ complex (structure is not known) and reduces the amount of lepidocrocite and goethite under pH-neutral conditions during the abiotic oxidation of Fe(II); while both As(V) and As(III) can accelerate the formation of ferrihydrite during Fe(III) hydrolysis under similar pH conditions [24,25]. Although both As(III) and As(V) may co-exist with Fe in natural aqueous environment, As(V) is chosen in this study because it has stronger affinity with Fe than As(III) does [26,27].

The objectives of this study are exploration of (i) the effects of arsenate and pH on the precipitation of Fe (hydr)oxides, and the mechanism of arsenate upon the formation of Fe (hydr)oxides and, (ii) the structure, morphology and speciation of Fe (hydr)oxides in these processes. For these purposes, oxidation of Fe(II) under different molar ratios of As(V):Fe(II) was carried out at pH 6.0, 7.0

and 8.0, and FTIR, XRD as well as TEM were used to characterize the formed Fe (hydr)oxides.

2. Materials and methods

2.1. Chemicals

All reagents were analytical grade unless otherwise stated and all solution was prepared with distilled deionized water.

2.2. Abiotic oxidation of Fe(II) in the presence of As(V)

Abiotic oxidation of Fe(II) was carried out in 0.1 M NaCl solution with the addition of a measured amount of 3-morpholinopropanesulfonic acid (MOPS) as buffer to provide a stable background of ionic strength and pH, similar to natural waters [28,29]. A series concentrations of As(V) were prepared by dissolving Na_2HAsO_4 in 400 mL water with the addition of 10 mM MOPS with initial pH of 6.0, 7.0 or 8.0 by the addition of 6 M NaOH. The solution was equilibrated in the atmosphere with dissolved oxygen ranging from 7.52 to 7.59 mg L^{-1} , measured by a dissolved oxygen meter (HQ30d, HACH). To avoid Fe(II) oxidation before contacting As(V), $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ solid was added into the As(V)-containing solution with vigorous stirring to reach molar ratios of As(V):Fe(III) from 0 to 0.11 [5 mM Fe(II)]. The experimental conditions for Fe(II) oxidation in the presence of As(V) are summarized in Supplementary data Table A.1. The stirrer was removed immediately after the complete dissolution of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, and then the solution was exposed to the air. Solution pH was only maintained by 6 M NaOH if pH change was larger than 0.2. During the experiments, 1.2 mL sample was taken out regularly and centrifuged at 5500 $\times g$ for 5 min. The supernatant was used for the determination of Fe(II), total Fe [including Fe(II) and Fe(III)] and As(V). After 10 h, Fe precipitates were centrifuged, washed three times and freeze-dried for characterization.

2.3. Analysis of Fe and As concentrations

The supernatant after centrifugation was immediately acidified by adding 0.1 mL of 0.5 M HCl to prevent further oxidation of the dissolved Fe(II). Concentrations of As(V) and Fe(II) were determined by a modified colorimetric method [30] and a modified ferrozine method [23], respectively. In the measurement of total Fe, samples were diluted and acidified with 1 wt% HNO_3 before ICP-AES (Varian-715S, Varian) analysis at $\lambda = 238.2 \text{ nm}$.

2.4. Transmission electron microscopy (TEM)

The samples were imaged on a JEM-2100F JEOL transmission electron microscopy using a voltage of 200 kV under 10^{-5} Pa vacuum. EDX spectrum and EDX mapping (DPP-FR2 with Genesis v6.04, EDAX) were used to analyze the elemental compositions and distribution in Fe (hydr)oxides. Fast Fourier transformed images were calculated based on TEM images (iTEM, Olympus) and were used for the determination of the crystalline structure of Fe (hydr)oxides.

2.5. X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR)

For XRD analysis, the freeze-dried samples were pressed on glass slides. XRD patterns were recorded from 10° to 90° 2θ with a step-size of 0.0334° and a scanning speed of $5^\circ/\text{min}$ using $\text{Co K}\alpha$ radiation (X' Pert Pro, PANalytical). XRD data were analyzed with the two-phase Rietveld quantitative analysis using the program

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