Change of arsenite adsorption mechanism during aging of 2-line ferrihydrite in the absence of oxygen

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ABSTRACT

Arsenite was effectively immobilized by 2-line ferrihydrite at different pH values (4.0, 5.5 and 7.4) and adsorbent dosages (0.4, 1, and 2 g/L) in the absence of oxygen, showing an initial surface diffusion-controlled period (Stage I, <2 h) and a second mixed intra-particle and surface diffusion-controlled period (Stage II, >2 h). Dissolved δ^{56}Fe increased during Stage I and decreased during Stage II, resulting from aging of ferrihydrite and equilibrium isotopic exchange, respectively. The ferrihydrite aging was hampered by both high As concentrations and high pH values close to the pH_{zpc}, due to inhibition of mineral dissolution as a prerequisite for mineral transformation. During Stage I, As was adsorbed by both bidentate binuclear corner-sharing (^2C) and monodentate mononuclear corner-sharing complexes (^1V), while ^2C dominated during Stage II. At stage I, As stability was mainly controlled by As-complexation, by both mineral transformation and As complexation at stage II. It is suggested that adsorbed-As stability can be optimized by regulating As complexation and mineral phases, which are of great significance for remediation of As-contaminated groundwater.

1. Introduction

Arsenic (As), a ubiquitous environmental toxin and carcinogen, endangers hundreds of millions of people worldwide via consumption of As-contaminated groundwater (Zhu et al., 2014). Groundwater with As concentrations exceeding the current WHO limit (10 μg/L) has been found in many countries, including Bangladesh, India, United States, Japan, Argentina, Vietnam and China (Guo et al., 2014; Karn, 2015). Long-term digestion of As-contaminated groundwater causes skin diseases, lung cancer, kidney cancer, and many other diseases (Naujokas et al., 2013; Zhu et al., 2014). The prevalent As forms in aquatic systems are the inorganic oxyanion species arsenate [As(V)] and arsenite [As(III)]. Arsenite predominating in anoxic groundwater is more toxic, soluble, and mobile than arsenate, which predominates in oxic groundwater (Jain and Ali, 2000; Wu et al., 2015). The former remains protonated as arsenious acid ($H_3AsO_3^0$) at ambient pH < 9

(Oremland and Stolz, 2003; Smedley and Kinniburgh, 2002), which is less strongly adsorbed and co-precipitated relative to arsenate (Dixit and Hering, 2003; Guo et al., 2011).

Several methods for As(III) removal from As-contaminated groundwater have been suggested including co-precipitation with Fe(III) hydroxides upon oxidation of the anoxic groundwater (Ciardelli et al., 2008). Ferrihydrite ($Fe_{10}O_{14}(OH)_2$) is one of the most ubiquitous amorphous iron oxyhydroxides in natural low-temperature geochemical environments (Michel et al., 2007). Due to its high specific surface area (>200 m^2 g^{-1}), freshly formed ferrihydrite is the most efficient adsorbent known for As sequestration (Jang et al., 2006; Michel et al., 2007). However, As adsorption on ferrihydrite is highly dependent on redox conditions, pH values, and the dosage of adsorbents (Fuller et al., 1993; Dixit and Hering, 2003; Impellitteri and Scheckel, 2006; Frau et al., 2009; Handley et al., 2013; Qi and Pichler, 2016). Arsenic(III) is rapidly oxidized to As(V) during adsorption on ferrihydrite under oxic conditions (Kim et al., 2014). However, there is a lack of comprehensive data on the stability and mechanisms of As(III) adsorption on ferrihydrite under suboxic conditions. Variations in binding modes within such highly reactive biogeochemical milieu can induce differences in the stability of adsorbed As. Mineral transformation from nano-

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crystalline ferrihydrite to more crystalline phases (e.g., goethite) is conducive to stabilization of the adsorbed As (Saalfield and Bostick, 2009). However, potential change of As binding modes during the mineral transformation, and roles of the interaction between As binding modes and host mineral transformation in the stability of the adsorbed As, are still poorly understood.

Therefore, the main objectives of the present study are to (i) investigate the phase transformation of 2-line ferrihydrite during aging in the absence of oxygen; (ii) evaluate As(III) adsorption kinetics and stability during ferrihydrite aging as functions of contact time, pH, and adsorbent dosage, and (iii) to elucidate As(III) adsorption mechanism and stability changes during aging of the adsorbent phase by using a unique combination of time-lapsed dissolved stable Fe isotope analysis and X-ray adsorption spectroscopy.

2. Materials and methods

2.1. Synthesis and characterization of the 2-line ferrihydrite

Ferrihydrite was synthesized according to the method of Cornell and Schwertmann (2003). Briefly, 1 M KOH solution (Sigma-Aldrich) was added dropwise to 500 mL of 0.2 M $Fe(NO_3)_3 \cdot 9H_2O$ (Alfa Aesar) solution with vigorous stirring until the pH remained constant at 7.4 ± 0.1. Ferrihydrite precipitate was washed with deionized water, freeze-dried, disaggregated in a pestle-and-mortar (<200 mesh), and stored at 4 °C in polyethylene vials under N_2. The morphology of ferrihydrite was characterized using scanning electron microscopy (SEM) and the purity of ferrihydrite was determined by Fourier Transform Infrared Spectroscopy (FTIR) and X-ray diffraction (XRD) spectra.

2.2. Batch experiments

Stock As(III) solution (1000 mg/L) was prepared from sodium arsenite ($NaAsO_2$, Fluka Chemical). Solution pH was adjusted using HCl (0.05 M) and NaOH (0.01 M). All reagents used in this study were of analytical grade, and all solutions were prepared in Milli-Q water. All glassware and sample bottles were soaked with deionized water three times, rinsed with 10% HNO_3 for at least 24 h, and finally rinsed with deionized water three times. Experiments were carried out in a glovebox (Coy Laboratory Products, USA) under a N_2/H_2 (92.5/7.5, v/v) atmosphere. The presence of H_2 in the glovebox did not cause significant Fe(III) reduction as demonstrated by Fe(II) measurements. Batch tests were performed in 100 mL serum glass bottles pre-loaded with a certain dosage of dry ferrihydrite. The unsealed serum bottles were put into the glovebox at least 48 h before filling with As(III) solution to remove any oxygen adsorbed on the mineral surface. After mixture of adsorbent and As(III) solution, the serum bottles were sealed with blue butyl rubber stoppers and covered with a layer of aluminum foil to maintain darkness. All batch equilibrations were conducted in a shaking water bath (150 rpm) at 25 °C.

The adsorption kinetics were examined with initial As(III) concentration of 100 mg/L at three different adsorbent dosages (0.4, 1, and 2 g/L) to obtain different molar ratios of the initial As/Fe (0.27, 0.11 and 0.055 respectively). Solution pH was adjusted to values of 4.0, 5.5, and 7.4 in the glove box, under which similar As(III) loadings could be obtained but different ferrihydrite dissolution conditions (Liang et al., 2000; Kim et al., 2014). An aliquot of the suspensions was sampled at 0.17, 0.42, 1.00, 2.00, 8.00, 24.00, 48, 96, 192, 312 and 408 h of reaction. The suspension subsamples were immediately membrane-filtered (0.22 μm nominal pore size) in the glove box for analysis of total dissolved Fe, Fe(II), Fe isotopes, total As, and As(III). The ferrihydrite solids retained on the membrane

filters (without drying) were eluted with 10 mM HCl for 30 min with a solid-liquid ratio of 6 g/L to presumably dissolve the easily extractable Fe fraction (Wu et al., 2011). All experiments were conducted in duplicate and results were reported using averages. Adsorption kinetic data were evaluated using different models, including pseudo-second-order, pseudo-first-order, power function, Elovich, Avrami, parabolic diffusion, and intra-particle diffusion kinetic models (Ho and McKay, 1999; Jang et al., 2015; Kim et al., 2014; Wu et al., 2009).

2.3. Chemical and spectroscopic analyses

Total dissolved As and Fe concentrations were determined by ICP-OES (iCAP 6300, Thermo). Concentrations of As species were measured using high performance liquid chromatography-hydride generation-atomic fluorescence spectrophotometry (HPLC-HG-AFS, Jitian Corp., Beijing) with a detection limit of 1.0 μg/L for both As(III) and As(V). Concentrations of Fe(II) species were spectrophotometrically determined using the common ferrozine assay with a detection limit of 25 μg/L. Solution subsamples were pretreated for stable Fe isotopes analysis at the isotope laboratories of the U.S. Geological Survey (USGS Denver) as reported by Borrok et al. (2007). Details can be found in the Supplementary Materials. Stable Fe isotope distributions were then determined at the National Institute of Metrology (China) using a MC-ICP-MS instrument (VG IsoProbe) according to the procedure described by Guo et al. (2013a). Each sample was bracketed by concentration-matched IRMM-14 Fe isotopic standard solution, and the results for the samples are expressed relative to the average of the bracketing standards (IRMM-14) in standard delta notation (‰):

$$\delta^{56}Fe = [((^{56}Fe/^{54}Fe)_{sample}/(^{56}Fe/^{54}Fe)_{IRMM14}) - 1] \times 1000 \qquad (1)$$

The validity of the standard-sample bracketing approach was confirmed through mass bias tests. Replicate mass spectrometric analyses were made at different measurement sessions (days). The average standard deviation (2σ) calculated from replicate measurements of unknowns over multiple measurements was 0.06‰. More details on the QA/QC for the isotopic analyses are provided in Supplementary Materials.

Solid samples were freeze-dried and examined by SEM (Zeiss Supra 35VP) to obtain information on adsorbent morphology. Fourier Transform Infrared Spectroscopy (FTIR) spectra of the samples were obtained on a Bruker TENSOR 27 FTIR. The second derivative absorption spectra (SDS) evaluation approach was used for a better resolution of the individual bands in the FTIR spectra (Zhao et al., 2015). X-ray diffraction (XRD) analysis was performed to detect any mineralogical changes due to aging effects of the adsorbent solids before and after As adsorption (Guo et al., 2013b). The X-ray absorption spectroscopy data (both XANES and EXAFS) were recorded at room temperature at Beamlines BL14W1 and BL15U1 of the Shanghai Synchrotron Radiation Facility (SSRF). Data collection and analysis were the same as previously described (Guo et al., 2013b), and details can be found in Supplementary Materials.

3. Results and discussions

3.1. Adsorbent mineral transformation during As adsorption

SEM results showed that ferrihydrite was a very poorly crystallized material, with single particles of less than 200 nm and aggregate particles mostly 0.35–0.40 μm in size. Goethite in the form of needle-like crystals, with a length of 200–800 nm and a width of 5–25 nm, was found together with ferrihydrite nanoparticles at the end of all experiments (Fig. 1a and b). FTIR