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Research paper

Removal of As(III) from acidic waters using schwertmannite: Surface speciation and effect of synthesis pathway

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ABSTRACT

The removal of arsenic(III) from aqueous solution by three different schwertmannite specimens that were synthesized by i) biogenic precipitation (SHM_MS), ii) slow abiotic dialysis (SHM_DS) and iii) fast abiotic oxidation of Fe(II) (SHM_FS) was studied through sorption experiments at pH 3.0. Marked differences in dissolution rates, Fe:S ratios (4.7–6.4) and structural properties were found among the specimens. The sorption mechanisms are governed by multilayer processes as indicated by highly non-linear Freundlich adsorption isotherms. The affinities increased in the sequence SHM_FS ($K_F = 0.02\ L^{0.57}/(mol^{-0.43}\ g)$) < SHM_MS ($K_F = 0.04\ L^{0.64}/(mol^{-0.36}\ g)$) < SHM_DS ($K_F = 0.10\ L^{0.66}/(mol^{-0.34}\ g)$) possibly owing to the corresponding increase in specific surface area (5.3, 14.7, and 210 m^2/g, respectively). XANES results show that no detectable oxidation of As(III) occurred on any of the schwertmannite surfaces within 5 days equilibration time even though oxidation both by O_2 and Fe(III) was favorable thermodynamically. A relationship between As(III) uptake and sulfate release was observed at high initial As(III) concentrations only suggesting that As(III) retention through ligand exchange is of minor relevance under the experimental conditions examined in this study. Higher As(III) loading caused morphological degradation yielding angular particles with porous centers and the extent of degradation varied accordingly with As(III) partitioning. Appearance of new infrared absorption bands after As(III) sorption and shifting in diffractogram peaks with increasing As(III) concentrations suggest the formation of a ferric arsenite surface precipitate.

1. Introduction

Removal of arsenic from contaminated water is a serious concern worldwide. Considering its extent of pollution, providing safe and economically affordable drinking water is a challenging research topic even today. Iron oxides including ferrihydrite, hematite and goethite are predominant constituents in natural systems which have been demonstrated to retain significant quantities of arsenic through surface complexation and/or adsorption processes (Raven et al., 1998; Dixit and Hering, 2003; Ona-Nguema et al., 2005). Schwertmannite, an amorphous Fe-oxyhydroxy sulfate mineral ($Fe_8O_8(OH)_x(SO_4)_y$; $x = 8 - 2y$, $1 < y < 1.75$) commonly reported as a brownish yellow precipitate in acid mine drainage precipitates (Bigham et al., 1990, 1994) and acid sulfate soil environments (Burton et al., 2006, 2007), removes significant amounts of arsenate during its precipitation in acid mine drainage (AMD) areas and the arsenate retention is controlled by ligand exchange with surface adsorbed SO_4^{2-} (Fukushi et al., 2003, 2004; Casiot et al., 2005). After incorporation of As(V) the structure of schwertmannite collapses at a high As/Fe molar ratio (≥0.4) and arsenic becomes coordinated by 4 O_2 to form AsO_4 tetrahedra that connect with two apical O_2 of FeO_6 octahedra (Jiang et al., 2007). Previous studies focused on co-adsorption of As(V) subsequent to its release during leaching from arsenical pyrites or arsenopyrites enriched mine dumps simultaneously with precipitation of schwertmannite in acid mine discharges (Carlson et al., 2002; Fukushi et al., 2003, 2004; Regenspurg and Peiffer, 2005).

Due to the abundance of As(V) species as $H_2AsO_4^-$ in acid mine drainage affected environments and its higher retention capacities at acidic pHs, most of the studies focused on the retention of As(V). However, also As(III) may occur in hundreds of milligrams in AMD (e.g., Carnoulés mine, France, Morin et al., 2003; Egal et al., 2009). Research on evaluating the sorption behavior of As(III) onto schwertmannites is thus potentially important for waste water treatment aspects, the study of which has been given less attention yet. Most recently, Burton et al. (2009) in a comparative study between As(III) and As(V) demonstrated the exchange of structural SO_4^{2-} during the non-oxidative sorption of As(III) onto schwertmannite. Sun and Doner (1998) and Greenleaf et al. (2003) observed that As(III) sorbed onto goethite and hydrous ferric oxides is unstable and oxidized at the surface to As(V). The authors reported that As(III) oxidation to As(V) by O_2 is favoured by high pH values whereas low pH values favour the oxidation of As(III) by goethite. In contrary,

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Manning et al. (1998) did not find spectroscopic evidence of As(III) oxidation on goethite surfaces under similar experimental conditions. Therefore, redox stability of As(III) and As(V) on Fe(III)-oxide surfaces is not clearly resolved and even investigations in the case of schwertmannite are rare (Burton et al., 2009). The authors have pointed out that sorption interactions with schwertmannite may enhance the redox stability of As(III). Structure of sorbed As(III) on schwertmannite is currently not known. However, non-oxidative As(III) sorption onto α-FeOOH was shown to form bidentate binuclear bridging complexes (Manning et al., 1998) and identical bidentate structural complexation was also proposed for sorbed As(V) onto schwertmannite (Waychunas et al., 1995). This present research primarily focuses on the removal potential of As(III) by biotically and abiotically produced schwertmannites at pH 3. Surface speciation, possible retention mechanisms and redox stability in the presence of O_2 are discussed based on adsorption experiments in combination with spectroscopic investigations.

2. Materials and methods

All laboratory glass and plastic wares were conditioned by 10% HNO_3 overnight and rinsed several times by aqua milli-Q water before use. Reagents and chemicals used in the present study were all analytical grade (>99%) and all solutions were prepared fresh when required with aqua milli-Q water.

2.1. Schwertmannite samples

Three different schwertmannite (SHM) specimens produced through chemical and biological processes were used in the current study. SHM_MS was synthesized in a mine water treatment plant (GEOS, Freiberg, Germany) by microbial oxidation of Fe(II) between pH 2.9–3.2 (Glombitza et al., 2007) from SO_4^{2-} rich mine waters. Batch cultivations using acidophilic bacterial species *Acidithiobacilius ferrooxidans* were performed after incubation at 30 °C and 130 rpm in a rotary shaker. The cultures were incubated at room temperature for ~1 month. The experiments were continued until the Fe(II) concentrations remained constant after which the precipitates were separated by centrifugation. The brownish yellow precipitates were air dried at room temperature (20–25 °C) after synthesis. One schwertmannite sample was synthesized by fast synthesis method called 'oxidative synthesis' as described by Regenspurg and Peiffer (2005). 10 g of $FeSO_4.7H_2O$ was dissolved in deionized water and ~5 ml of 32% H_2O_2 was added drop wise to accelerate the oxidation of Fe^{2+} to Fe^{3+}. The reaction was preceded for 24 h and the pH remained stable at 2.4. The precipitated orange coloured solids were filtered and oven dried at 35–40 °C. The samples were used directly for further experimental purposes without any treatment, called here after SHM_FS. Schwertmannite was also synthesized as described by Bigham et al. (1990) through 35 days dialysis techniques. 2 L of deionized water was heated in an oven to 60 °C. After adding 10.8 g of $FeCl_3.6H_2O$ (~ 40 mmol Fe^{3+}) and 1500 mg/L SO_4^{2-} as Na_2SO_4 salt, the solution was kept for further 12 min at 60 °C. The suspension was cooled to room temperature and dialysed for 35 days (Serva dialysis bags, pore radius 24 nm) in ~4.0 L of deionized water which was renewed daily 4 times. After this time the conductivity of the dialysis water was found to be <5 μS for the last 5 days indicating no further ion exchange taking place. After 35 days schwertmannite samples were filtered and oven dried at 60 °C. The specimen is called SHM_DS.

2.2. Sorption experiments

The sorption studies were conducted as batch experiments. The suspension was allowed to equilibrate for 5 days with a sediment load of 0.25 g/25 ml at pH 3.0 and initial As(III) concentrations ranging from 0.13 to 1.33 mmol/L. Preliminary kinetic experiments demonstrated that equilibrium is achieved after this time. The suspension was continuously stirred during the whole reaction time. The pH of the As(III) containing solutions were adjusted to pH 3.0 ± 0.05 before addition of schwertmannite to avoid possible transformation of SHM at changing pH conditions (Jönsson et al., 2005). The ionic strength was maintained at 0.01 mol/L by $NaNO_3$. Experiments were performed in the dark in the presence of oxygen in polypropylene reactor vials that were preconditioned by 10% nitric acid overnight. After the equilibration time samples were filtered through <0.45 μm cellulose filter papers and the aqueous phase was analyzed for pH, Fe(II), Fe(t), SO_4^{2-} and As(t) concentrations. Solid phase was characterized by XRD, FTIR, SEM and XANES techniques. Solid phase arsenic loading was determined by mass balance $c_s = \left(\frac{C_i - C_{eq}}{M/V}\right)$, where C_i and C_{eq} are initial and equilibrium As concentrations (mol/L), M is mass of sorbent (g), L is volume of solution (L). SHM samples were stored in crimp sealed serum vials in O_2 free glove box to eliminate the effect of atmospheric O_2 in As(III) oxidation during storage for As species measurement by XANES.

Two commonly used statistical isotherm models were fitted with experimental data using IsoFit v1.2 (Matott and Rabideau, 2008) to evaluate the sorption behavior. Langmuir model (Eq. (1)) demonstrates a monolayer sorption mechanism with homogeneous sorption energies, while Freundlich model is an empirical model demonstrating multilayer sorption sites and heterogeneous sorption energies (Eq. (2)) (Weber and DiGiano, 1996).

$$c_s = c(s_{tot})\frac{K_{Ads}c_{eq}}{\left(1 + K_{Ads}c_{eq}\right)} \tag{1}$$

$$c_s = K_F \cdot C_{eq}^n \tag{2}$$

c_s	concentration of As(III) adsorbed at the solid phase (mol/g)
c_{eq}	equilibrium concentration of As(III) in the aqueous phase (mol/L)
$c(s_{tot})$	total concentration of surface sites (mol/g)
K_{Ads}	Langmuir sorption coefficient (L/mol)
n	Freundlich exponent (≤1)
K_F	Freundlich adsorption coefficient ($L^n/(mol^{n-1}$ g))

2.3. Analytical methods

The solids were X-rayed (D5000, SIEMENS; Germany) using Co-Kα radiation (20 kV, 5 mA) from 10° to 80° 2θ and the X-ray diffractograms were analyzed from the d-spacings either with the library evaluation programme DiffracAT (v. 3.3) or comparing the d-values with reference spectra from previous studies. Four repeated scans were carried out for each sample and the mean of all intensities were analyzed. Fourier transformed infrared (FTIR) spectra of the specimens were recorded using a Vektor 22 Bruker FTIR spectrometer equipped with a KBr beam splitter, LADTGS detector, KBr window and silicium carbide radiation source. 2 mg of samples were homogeneously mixed with 200 mg KBr and finally pressed to pellets with approximately 8 kbar pressure. The specimens were scanned from 350 to 4000 cm^{-1} with 1 cm^{-1} resolution. 32 scans were collected for each measurement in transmission mode and the background spectra were subtracted automatically by background scans. Scanning Electron Microscopic (SEM) study was carried out by a LEO 1530 equipped with Shotky Cathode and GEMINI column with ZrO_2 radiation source (Zeiss, Germany). The specific surface area (SSA) was determined by a five point N_2 point adsorption isotherm (BET) method (Gemini 2375 v 5.01).

The chemical composition of specimens was determined after dissolution by 1.0 M HCl (0.1 g/10 ml) for ~20 h. Iron concentrations