Removal of arsenate with hydrous ferric oxide coprecipitation: Effect of humic acid

Jingjing Du[1], Chuanyong Jing[1,*], Jinming Duan[2], Yongli Zhang[3,*], Shan Hu[1]

1. State Key Laboratory of Environmental Chemistry and Ecotoxicology, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China. E-mail: jjdu@rcees.ac.cn
2. School of Environmental and Municipal Engineering, Xi'an University of Architecture and Technology, Xi'an 710055, China
3. College of Architecture and Environment, Sichuan University, Chengdu 610065, China

ABSTRACT

Insights from the adverse effect of humic acid (HA) on arsenate removal with hydrous ferric oxide (HFO) coprecipitation can further our understanding of the fate of As(V) in water treatment process. The motivation of our study is to explore the competitive adsorption mechanisms of humic acid and As(V) on HFO on the molecular scale. Multiple complementary techniques were used including macroscopic adsorption experiments, surface enhanced Raman scattering (SERS), extended X-ray absorption fine structure (EXAFS) spectroscopy, flow-cell attenuated total reflectance Fourier transform infrared (ATR-FTIR) measurement, and charge distribution multisite complexation (CD-MUSIC) modeling. The As(V) removal efficiency was reduced from over 95% to about 10% with the increasing HA concentration to 25 times of As(V) mass concentration. The SERS analysis excluded the HA-As(V) complex formation. The EXAFS results indicate that As(V) formed bidentate binuclear surface complexes in the presence of HA as evidenced by an As-Fe distance of 3.26–3.31 Å. The *in situ* ATR-FTIR measurements show that As(V) replaces surface hydroxyl groups and forms inner-sphere complex. High concentrations of HA may physically block the surface sites and inhibit the As(V) access. The adsorption of As(V) and HA decreased the point of zero charge of HFO from 7.8 to 5.8 and 6.3, respectively. The CD-MUSIC model described the zeta potential curves and adsorption edges of As(V) and HA reasonably well.

Introduction

Arsenic removal using coagulation/filtration process has been demonstrated as the best available technology for large water treatment systems (US EPA, 2000). Because arsenite (As(III)) is more toxic and mobile than arsenate (As(V)), pre-oxidation of As(III) to As(V) is a conventional practice in water treatment facilities (US EPA, 2000). Ferric chloride is an effective and commonly used coagulant to remove arsenic from water, resulting in the formation of amorphous hydrous ferric oxide (HFO) containing coprecipitated arsenic (Mercer and Tobiason, 2008).

Dissolved organic matter (DOM) is ubiquitous in surface and groundwater and its concentration ranges from 1–60 mg C/L in most fresh waters (McDonald et al., 2004). Humic substances usually comprise 50%–75% of DOM in aquatic system (McDonald et al., 2004), which may influence arsenic adsorption on metal oxide surfaces by several mechanisms (Grafe et al., 2001; Wang and Mulligan, 2009). Research has demonstrated that humic acid (HA) and As(V) would compete for available adsorption sites because they are both anions (Grafe et al., 2001). Predominate As(V) species, $H_2AsO_4^-$ and $HAsO_4^{2-}$, as well

* Corresponding author. E-mail: cyjing@rcees.ac.cn (Chuanyong Jing); zxm581212@163.com (Yongli Zhang)

as HA, are negatively charged in the pH range 3–11. As(V) adsorbs on iron oxides mainly through the formation of inner-sphere surface complexes with a predominantly bidentate configuration, along with a minor monodentate contribution, by ligand exchange with hydroxyl groups at oxide surfaces (Sherman and Randall, 2003). Ligand exchange between hydroxyl groups of DOM and iron oxide surfaces is also the predominant DOM adsorption mechanism at acidic conditions (Gu et al., 1994). However, limited knowledge is available about As(V) surface complex structure on the molecular scale in the presence of HA during HFO coprecipitation at environment relevant concentrations. Insights from molecular-level mechanisms of HA-As(V)-HFO interactions can further our understanding of the fate of As(V) in water treatment process and in the environment.

Previous studies suggest that As(V) could be bound to HA through a ternary metal complexation mechanism: As(V)-metal cation-HA (Redman et al., 2002; Lin et al., 2004), and such complexes could be within colloidal size (Ritter et al., 2006). Recently, similar with As(III)-HA complex (Liu and Cai, 2012), direct association of aqueous As(V) and HA has been reported through covalent binding mechanisms (Warwick et al., 2005; Buschmann et al., 2006). Warwick et al. (2005) concluded the formation of HA-As(V) complexes is favorable in the pH range 8–10 with 1500 mg/L Aldrich HA and 7.5 mg/L As(V). Using an equilibrium dialysis method, Buschmann et al. (2006) suggest that about 10% of As(V) may bound to HA through phenolate functional groups in HA. However, the findings of Lin et al. (2004) show that no As(V)-DOM complexes is formed in extract of compost free of metals, whereas 30%–50% As(V) is associated with DOM in the presence of metals.

The objective of this study was to investigate the effect of HA on As(V) removal with HFO coprecipitation. Surface enhanced Raman scattering (SERS) was used to study aqueous As speciation in the presence of HA. The local coordination environment of As obtained with extended X-ray absorption fine structure (EXAFS) spectroscopy and Fourier transform infrared (FT-IR) spectroscopy was employed as a molecular-level constraint in the charge distribution multisite complexation (CD-MUSIC) model. The model was used to predict As(V) adsorption behaviors including adsorption edge and zeta potential under the HA competition.

1 Materials and methods

1.1 Materials

A 1000 mg/L As(V) stock solution was prepared by dissolving 0.4165 g of $Na_2HAsO_4 \cdot 7H_2O$ (Alfa Aesar, USA) in 100 mL ultrapure deionized (DI) water (18.2 MΩ, Milli-

Q). Fe(III) stock solution containing 1000 mg/L Fe and 0.1% $HClO_4$ was prepared using $FeCl_3$ (Aldrich, USA) and trace metal grade $HClO_4$ (Fisher, USA). HA was purchased from Aldrich in sodium form. The treatment of HA is essentially the same as described by Buschmann et al. (2006). In brief, 100 mg of HA was dissolved in 1 L DI water. The pH was adjusted to 10 with NaOH and the solution was then filtered through a 0.45 μm cellulose nitrate filter. The DOC concentration was determined using a Phoenix 8000 total organic carbon (TOC) analyzer (Tekmar-Dohrmann, USA). Stock solutions were stored in the refrigerator at 4°C. A background electrolyte of 0.04 mol/L $NaClO_4$ prepared by dissolving HPLC grade $NaClO_4$ (Fisher, USA) in DI water, was used in the experiments.

1.2 Batch adsorption experiments

Suspension samples containing 100 μg/L As(V), 1.0 mg/L Fe, 0–5 mg/L HA, and 0.04 mol/L $NaClO_4$ were prepared in 100 mL polypropylene bottles. Three contact orders were used in the ternary adsorption system (Ko et al., 2007): (1) pre-equilibration As(V)-HA for 24 hr before the addition of Fe; (2) pre-equilibration HA-Fe for 24 hr before the addition of As(V); and (3) pre-equilibration As(V)-Fe for 24 hr before the addition of HA. Then, the ternary suspension was mixed for 24 hr at pH 7.0 ± 0.1, and filtered through a 0.4 μm membrane. The soluble As concentration in the filtrate was determined with an atomic fluorescence spectrometer (AFS, Ruiguang, China) with a detection limit of 0.6 μg/L (Cui et al., 2013). Triplicate adsorption experiments were performed and averaged values were reported.

Experiments were carried out to determine the As(V) adsorption edge, which is the percentage of As(V) adsorbed as a function of equilibrium pH, in the presence and absence of HA. Suspensions containing 0.04 mol/L $NaClO_4$, 1.0 mg/L Fe, 100 μg/L As(V), and/or 1.5 mg/L HA were prepared in a 1 L beaker. Then, 50 mL aliquots of the uniform suspensions were transferred into centrifuge tubes. The suspension pH was adjusted to desired levels in the range from 4 to 12. After 24 hr mixing, the equilibrium pH was measured and the suspension was filtered through a 0.45 μm membrane filter for As analysis. The HA adsorption edge was determined following the same procedure with 5 mg/L HA and 5 mg/L Fe suspension samples.

1.3 Electrophoretic mobility measurements

Electrophoretic mobility (EM) was determined using a ZetaSizer Nano ZS (Malvern Instrument, UK). All EM experiments were performed under N_2 atmosphere to eliminate CO_2 from the system. The pH of the suspension containing 10 mg/L Fe, 2 mg/L As(V), and/or 2 mg/L HA in 0.04 mol/L $NaClO_4$ was adjusted to between 3 and 11 using NaOH and $HClO_4$ solutions. Suspension samples were placed on a rotating shaker for 24 hr and the final