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Effects of humic acid on arsenic(V) removal by zero-valent iron from groundwater with special references to corrosion products analyses

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ABSTRACT

The effects of humic acid (HA) on As(V) removal by zero-valent iron (Fe^0) from groundwater, associated with corrosion products analyses, were investigated using batch experiments. It was found that arsenic was rapidly removed from groundwater possibly due to its adsorption and co-precipitation with the corrosion products of Fe^0. The removal rate of arsenic by Fe^0 was inhibited in the presence of HA probably because of the formation of soluble Fe-humate in groundwater which hindered the production of iron precipitates. A longer reaction time was then required for arsenic removal. Such an influence of HA on arsenic removal increased with increasing HA concentration from 5 to 25 mg L^{-1}. The binding capacity of HA for dissolved Fe was estimated to be about 0.75 mg Fe mg^{-1} HA. When the complexation of HA with dissolved Fe was saturated, further corrosion of Fe^0 would produce precipitates, which significantly accelerated the removal of arsenic from groundwater via adsorption and co-precipitation with the corrosion products. Iron (hydr)oxides such as maghemite, lepidocrocite, and magnetite were characterized by XRD analyses as the corrosion products, while As(V) was found on the surface of these corrosion products as detected by fourier transform infrared spectrometry and X-ray photoelectron spectroscopy.

1. Introduction

Groundwater contamination by arsenic has become an issue of worldwide concerns because of its threats to human health (Mohan and Pittman, 2007). It has been recognized that arsenic can cause skin lesions and cancers due to its preferential reaction with sulfhydryl groups in enzymes (Brown and Ross, 2002). Therefore, the US Environment Protection Agency (USEPA) lowered the maximum contaminant level for arsenic in drinking water from 50 to 10 $\mu g\,L^{-1}$ (USEPA, 2002). The new standard increases the technical demands for more effective arsenic removal from groundwater.

Permeable reactive barriers (PRBs) packed with zero-valent iron (Fe^0) have been proven to be an effective technology to remove inorganic and organic contaminants from groundwater, and have received increasing attention due to its simplicity, reliability and low cost (Blowes et al., 1997; Gandhi et al., 2002; Lo et al., 2005; Jeen et al., 2006). Studies on the removal of arsenic by Fe^0 indicated that Fe^0 had high potential to treat arsenic-contaminated groundwater (Kanel et al., 2005; Lo et al., 2006). The principal mechanisms of arsenic removal by Fe^0 apparently involved adsorption, surface precipitation, and co-precipitation with various corrosion products (Lackovic et al., 2000; Su and Puls, 2001a; Manning et al., 2002; Nikolaidis et al., 2003). These removal mechanisms were also found to play an important role in the removal of other inorganic and organic contaminants such as U(VI), dichlorophen, and thiobencarb (Noubactep et al., 2006; Noubactep, 2008; Ghauch, 2008; Ghauch and Tuqan, 2008). However, the geochemical components of groundwater could influence the efficiency of arsenic removal by Fe^0. It has been reported that the inorganic anions including phosphate, chromate, silicate, carbonate, sulfate, and nitrate inhibited the removal of arsenic by Fe^0 due to the competition for adsorption sites of corrosion products with arsenic (Su and Puls, 2001b; Tyrovola et al., 2006). However, the effects of dissolved organic matter (DOM), a prevalent constituent of natural waters and typically represented by humic acid (HA), have not been well addressed. DOM has a high tendency to be adsorbed onto the surface of minerals such as iron and aluminum oxides (Gu et al., 1994; Vermeer et al., 1998; Saito et al., 2004), which could modify the properties of mineral surfaces and block the adsorption sites. It has been reported that DOM inhibited the adsorption of arsenate onto iron oxides mainly because of the competition between DOM and arsenate for surface adsorption sites (Grafe et al., 2001). Giasuddin et al. (2007) indicated that HA could compete for adsorption sites on nanoscale Fe^0 with arsenic and

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consequently reduced the arsenic removal rates by 43% for As(III) and 68% for As(V). However, the possible interactions of dissolved iron and HA in solutions and its corresponding impact on arsenic removal have not been mentioned. HA was observed readily to form aqueous complexes with metallic cations, which could further form a ternary complex with arsenic by metal bridging mechanisms and thus increase the mobility of arsenic (Redman et al., 2002; Dries et al., 2005; Buschmann et al., 2006). Furthermore, Liu et al. (2008) has revealed that HA can form Fe-humate with dissolved Fe when using Fe^0 to remove Cr(VI). Their findings provided an implication that HA could play an important role in influencing arsenic mobility in Fe^0–water systems by not only competing the adsorption sites on iron corrosion products with arsenic, but also suppressing the formation of iron corrosion products. However, until now, the interactions among arsenic, HA, and Fe^0 have not been studied in detail.

To provide a better understanding of applying Fe^0 PRBs in DOM-rich groundwater for As(V) removal, the objectives of this study were, therefore, to investigate the effects of HA on the kinetics of the arsenic removal by Fe^0, the fates of HA and the dissolved iron, and the formation of iron corrosion products in the absence and presence of HA.

2. Material and methods

2.1. Materials and chemicals

Iron filings (ETC-CC-1004) were obtained from Connelly-GPM Inc., and the sieved fractions of 18–35 mesh (0.5–1.0 mm) were used for all experiments without chemical pretreatment. The physical and chemical properties of the iron filings were addressed by Liu et al. (2008). Commercial humic acid was obtained from Aldrich Chemical and was dissolved into ultrapure water (>18.1 MΩ cm) followed by filtering through 0.45-μm acetate cellulose membranes (ADVANTEC) for preparing the HA stock solution. Dissolved organic carbon (DOC) was employed to express the concentration of HA. Chemicals used in this study, including $Na_2HAsO_4 \cdot 7H_2O$, $CaCl_2 \cdot 2H_2O$, Na_2SO_4, $NaHCO_3$ and NaCl, were reagent grade and obtained from Aldrich Chemical or Wako Chemical, Ltd. To simulate the compositions of real groundwater, the recipe solution in $mg\,L^{-1}$ initially containing 230 Na^+, 32 Ca^{2+}, 234.3 Cl^-, 183 HCO_3^-, 96 SO_4^{2-}, 2 As(V), and various concentrations of HA was used as synthetic groundwater in this study. The concentrations of all components in synthetic groundwater are within their typical ranges in groundwater (Snoeyink and Jenkins, 1980; Leeden et al., 1990). Ultrapure water for solution preparation was purged with nitrogen gas for 1 h prior to usage.

2.2. Batch experiments

Batch experiments were conducted using 40-mL glass vials containing 0.1 g of Fe^0 and 38 mL of 2 $mg\,L^{-1}$ arsenic simulated groundwater with or without HA. Various concentrations of HA ranging from 5 to 25 $mg\,L^{-1}$ as DOC were used. Initial pH values of solutions were in the range of 8.2–8.6, depending on whether arsenic and/or HA were added or not. No pH adjustment was made during the process of the experiments. Arsenic solutions were prepared and transferred into vials, which were rapidly sealed using screw caps containing Teflon-lined rubber septa. All vials were shaken in end-over-end manner at 26 rpm and 23 ± 1 °C. The DO contents of the solutions in vials were 3.02–3.11 $mg\,L^{-1}$, a typical range in shallow aquifers (Hervant and Malard, 1999), prior to reaction. After regular reaction time from 5 to 60 min (up to 5 h in the presence of 25 $mg\,L^{-1}$ HA), the caps of vials were opened and the solutions were rapidly filtered through 0.45-μm membranes, followed by immediate measurement of pH and subsequent chemical analysis. Total arsenic and HA concentrations in solutions were determined by hydride generation-inductively coupled plasma atomic emission spectroscopy at a wavelength of 188.979 nm (Perkin Elmer Optima 3000XL) and using a total organic carbon analyzer (Shimadzu 5000A), respectively. As(V) and As(III) in the final solutions were separated with arsenic-speciation cartridges (Metal Soft Center, Highland Park, NJ) according to the method mentioned by Bang et al. (2005). Total concentration of dissolved iron was measured using flame atomic absorption spectrometer (Varian 220FS) at a wavelength of 248.3 nm. Solution pH was measured using a pH meter (Orion Model 420A). All batch experiments were run in duplicate.

2.3. Iron corrosion products analyses

The suspended solids in solutions after 1-h experiment were centrifuged at 10000 rpm for 15 min. Then, supernatant solutions were decanted and wet solids in the centrifuge tubes were collected and freeze-dried for 48 h. Freeze-dried solids were then stored in plastic bottles and purged with nitrogen gas before further analyses. Scanning electron microscopy (SEM, model JSM-6300), X-ray photoelectron spectroscopy (XPS, Perkin Elmer PHI 5600), fourier transform infrared spectrometry with transmission mode (FTIR, Perkin Elmer Spectrum BX), and XRD (PW-1830 Philips) were employed to analyze the surface morphology, elemental components, valence of chemical species, and crystalline structures of such solids that were expected to be the iron corrosion products formed during the experiments.

3. Results and discussion

3.1. Removal of As(V)

Fig. 1a shows the changes of arsenic concentrations versus time in the batch experiments. In the absence of HA, arsenic was removed rapidly. More than 75% of arsenic in solutions was immobilized in the first 15 min and residual arsenic concentration was 0.021 $mg\,L^{-1}$ at the end of 1-h experiment, i.e., 99% of arsenic was removed (Fig. 1a). No As(III) was detected in solutions. A pseudo-first order model was tried to describe the kinetics of arsenic removal by Fe^0. The kinetics of arsenic removal fit pseudo-first order model well with a reaction rate constant (k) of 0.081 min^{-1} and a coefficient of determination (R^2) of 0.968. The obedience of pseudo-first order model is in agreement with previous studies (Su and Puls, 2001b).

3.2. Effects of humic acid

In the presence of HA, however, arsenic removal rate was obviously inhibited. As shown in Fig. 1a and Fig. S1a (in Supplementary Information), the time required for arsenic to be reduced to half of its initial concentration were determined to be around 11, 24, 44 and 125 min for the solutions with 0, 5, 10 and 25 $mg\,L^{-1}$ of HA, respectively. When the concentration of HA was as high as 25 $mg\,L^{-1}$, about 28% of arsenic in solutions was removed at the end of 1-h experiment, which was much lower compared with the cases without HA and with lower HA concentrations. Besides, it was observed that the kinetics of arsenic removal by Fe^0 did not follow the pseudo-first order reaction in the presence of HA. This could result from the effects of HA on the formation of iron corrosion products. The removal mechanisms of arsenic are discussed later in more detail.

In applying Fe^0 for arsenic removal, adsorption, surface precipitation, and/or co-precipitation of arsenic with the corrosion