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The effect of citrate, oxalate, acetate, silicate and phosphate on stability of synthetic arsenic-loaded ferrihydrite and Al-ferrihydrite

D. Mohapatra, P. Singh*, W. Zhang**, P. Pullammanappallil

Division of Science and Engineering, Murdoch University, Murdoch, Western Australia 6150, Australia

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Abstract

The effect of the organic species oxalate, citrate and acetate and the inorganic species silicate and phosphate on release of As(V) from synthetic arsenic-loaded ferrihydrite and Al-ferrihydrite in the pH range 4–8 was investigated. For ferrihydrite, the organic species increased %As(V) extraction in the order: acetate < oxalate ≪ citrate. In each case, the %As(V) extraction increased when acidity changed to pH's lower than 6, but remained unchanged when the pH increased from 6 to 8. For Al-ferrihydrite, the trend for %As release as a function of pH in the presence of acetate and oxalate was similar to that for ferrihydrite. However, unlike the ferrihydrite case, in the presence of citrate the %As extraction went through a minimum at pH 6. This is postulated to be related to the solubility equilibria of Al-ferrihydrite as a function of pH. The co-presence of silicate or phosphate with each of the organic species enhanced As(V) extraction in the order $SiO_3^{2-} > PO_4^{3-}$. Competitive adsorption of the investigated organic and inorganic species on ferrihydrite and Al-ferrihydrite could explain the enhanced release of As(V) into solution. However, disproportionate adsorption of other species relative to amount of As(V) release occurs, suggesting that mechanisms other than competitive adsorption are also operative. The results could best be explained in terms of combination of competitive adsorption and processes involving pH-dependent dissolution of ferrihydrite/Al-ferrihydrite, formation of various complex ionic species involving Al(III), Fe(III), As(V), SiO_3^{2-}, PO_4^{3-}, OH^-, H^+ and organic species: acetate, oxalate and citrate.

Keywords: Arsenic; Ferrihydrite; Citrate; Oxalate; Acetate

1. Introduction

Arsenic contamination in water is a worldwide problem [1]. This contamination can be classified as primary and secondary. The primary contamination results mainly from rock weathering, biological activity and volcanic emissions followed by transportation through the environment by water [2]. The secondary contamination is related to various human activities such as milling, combustion, wood preservation, and pesticide applications [3,4].

In recent years, several methods for arsenic removal from contaminated water have been developed. These include ion exchange, reverse osmosis, lime softening, bio-conversion to arsine, and co-precipitation/adsorption on iron oxyhydroxides. The co-precipitation and adsorption on iron oxyhydroxides (e.g. ferrihydrite) is the most cost-effective and commonly used method for arsenic removal from contaminated drinking water and metallurgical waste liquors. In our recent studies, we have shown that removal of arsenic by adsorption on Al-ferrihydrite at its optimum Fe/Al ratio of 1:1 is more effective than on ferrihydrite. Residual As(V) concentration of <10 ppb is achieved in the pH range 6–7 [5]. However, this method yields solid residues which are highly concentrated in arsenic (approximately 18 mg/g for ferrihydrite and 23 mg/g for Al-ferrihydrite) and could be classified as hazardous wastes. The safe disposal of these toxic residues is of great concern in relation to their stability under the environmental conditions [6].

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* Corresponding author. Fax: +61 8 936 023 79.
** Corresponding author.
E-mail addresses: p.singh@murdoch.edu.au (P. Singh), wzhang@murdoch.edu.au (W. Zhang).

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The stability of the As-loaded residues when disposed to the environment in the form of landfills or residue ponds may be affected by three major types of actions. The first is related to the gradual transformation of amorphous hydroxides to corresponding well-crystalline minerals as time elapses, e.g. from ferrihydrite to goethite. These transformation processes lead to a decrease in surface area, and subsequent release of arsenic. The second is related to the pH variation and long term exposure of leachates which consist of organic and inorganic species such as acetate, citrate, oxalate, silicate, phosphate, etc. The third is related to the bio-reduction of As(V) to less stable As(III).

The 'hazardous waste' classification is usually determined by the Toxicity Characteristic Leaching Procedure (TCLP) developed by The Environment Protection Agency of the United States (USEPA). However, the TCLP test is not a comprehensive measure of a hazardous waste. It underestimates leachability of arsenic from solid residuals under real site conditions such as landfill and residue pond because it poorly simulates pH, low redox potential, long retention time, bio-reduction, and organic composition of mature landfill [7–9]. The extraction could be 10 times greater by actual landfill leachates than by the TCLP [9]. The arsenic extraction from As-loaded ferrihydrite tends to pass the EPA TCLP test owing partly to the fact that the TCLP extraction fluid consists of only weak acetic acid in pH range 3–5. Other active organic species such as citrate and oxalate, which are also commonly present in landfills and residual pond, are not considered. The effect of these organic species on arsenic extraction and dissolution of iron from the arsenic-rich residue, which is formed during removal of arsenic from contaminated water by adsorption on ferrihydrite and Al-ferrihydrite, has not received much attention and very few data in this area are available in the literature [9–11].

Apart from organic species, inorganic species such as silicate and phosphate are also usually present in contaminated water. For example, the typical Bangladesh tube-well water contains about 1 mg L^{-1} As, together with up to 20 mg L^{-1} Si (as silicate), and 2 mg L^{-1} P (as phosphate). The ability of PO_4^{3-} to compete with arsenate for goethite surface sites is well documented [12,13] since PO_4^{3-}, like arsenate, is sorbed as an inner-sphere complex via a ligand-exchange mechanism. Also, several studies have established that soluble silica exhibits high affinity for surfaces of aluminium and ferric oxides [14,15]. Species which result from Al(III) hydrolysis are also known to form complexes with Fe(III) and soluble Si(IV) [16]. A yellow-brown Fe–Al sol is reported to be formed by reaction of a ferrihydrite with the Al hydrolysis species at pH 4–4.2. This solution has been shown to be stable over long periods [16]. However, not much work has been reported on the effect of co-presence of both organic and inorganic species on the stability or leachability of arsenic from arsenic-loaded ferrihydrite sludges.

In this paper, we report the results of our investigation of the effect of the presence of organic species including citrate, oxalate, and acetate, on leaching of arsenic from synthetic As-loaded ferrihydrite and Al-ferrihydrite in the pH range 4–8. The effect of co-presence of the inorganic species silicate and phosphate on arsenic release was also examined. The objective of this study was to determine how the stabilities and leachabilities of As-loaded ferrihydrite and Al-ferrihydrite were affected as a function of pH in the presence of each of the organic and inorganic species noted above. The investigated pH covers the range that is normally found under landfill conditions [7,9]. The concentration of organic species used in this study was comparable to the TCLP extraction in which 0.1 M acetate is used. The As-loaded ferrihydrite and Al-ferrihydrite were synthesized by using As(V) because it is in this form arsenic is usually removed by adsorption on solid adsorbents. As(III) is generally preoxidised to As(V) in arsenic removal process. [17].

2. Materials and methods

2.1. Synthesis of arsenic-loaded ferrihydrite and Al-ferrihydrite

For As-loaded ferrihydrite, a solution mixture of 0.1 M Fe(III) as $FeCl_3$ and 5 mM As(V) as Na_2HAsO_4 at pH 2 was first prepared. For As-loaded Al-ferrihydrite, the initial solution contained a mixture of 0.05 M Fe(III), 0.05 M Al(III) (Fe:Al = 1:1) and 55 mM As(V) as Na_2HAsO_4. The solution pH was then adjusted to 7 with sodium bicarbonate and maintained at this pH at room temperature for 4 h with constant stirring when the precipitation of arsenic-loaded ferrihydrite occurred. The precipitated material slurry was aged at 70 °C in a temperature-controlled oven for 24 h [18,19]. After filtration, the precipitate was washed thoroughly with deionised water till free of As(V) and Cl^-, and dried at 60 °C for 48 h. The composition of the precipitate was determined by dissolving 1 g of the residue in HCl and analysing for As, Fe and Al in the solution by inductively coupled plasma followed by atomic emission spectroscopy (ICP-AES). XRD spectra of the synthetic materials were obtained by using a Philips PW 2236/20 machine with a Co Kα radiation source.

2.2. Leaching procedure

Stock solutions of silicate and phosphate were prepared from reagent-grade $Na_2SiO_3 \cdot 5H_2O$ and $NaH_2PO_4 \cdot 2H_2O$, respectively. Approximately, 1 mL of chloroform per litre was added to all the solutions to prevent microbial breakdown of the organic acids. For each leaching experiment, 3 g of the prepared As-loaded residue were added to 150 mL of the appropriate extractant solution in a 250 mL glass conical flask. The extractant solution was 0.1 M with respect to the organic salt. Thus, the solid/liquid ratio (w/v) used was 1:50. When needed, the initial concentration of silicate was adjusted to 22.3 mg L^{-1} Si and that of phosphate at 6.8 mg L^{-1} P. The pH adjustment was made with dilute HCl or NaOH as necessary. The mixture in each flask was