

Arsenic mobilisation induced by bacterial iron reduction and competing phosphorous

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Abstract

Dissimilatory Fe reducing bacteria play a fundamental role in catalysing the redox transformations that ultimately control the mobility of As in aquatic environments. In this study we investigated the stability of As retained by Al and Fe (hydr)oxides (hematite, goethite, 2-line ferrihydrite, three Al-goethites, gibbsite, and a poorly crystalline Al hydroxide) under anoxic conditions in the presence of *S. putrefaciens* cells and phosphate as a competing ion. *S. putrefaciens* cells were able to bind on mineral surfaces and utilise both noncrystalline and crystalline Fe (hydr)oxides as electron acceptor releasing As into solution. Phosphate competed strongly with arsenate and its efficiency seemed to be governed by the nature of the binding mechanism between As and adsorbent surface. High proportion of sorbed As were desorbed by phosphate from gibbsite followed by Al-goethites. Reflecting its low crystallinity, Al hydroxide was the most efficient in retaining arsenate on its surface followed by ferrihydrite, goethite, and hematite.

Key Words

Biological reduction, phosphate, arsenate, Al-goethite, Al and Fe (hydr)oxide.

Introduction

Aluminium and Fe (hydr)oxides are ubiquitous reactive constituents of soils and sediments, and play a fundamental role in the biogeochemical cycle of many elements (e.g. P, S, As, Pb). The environmental distribution of As is controlled by both Al and Fe (hydr)oxides in most oxidised environments, and the main technologies for the removal of As from contaminated waters are based on coagulation/precipitation or adsorption involving Al or ferric compounds.

Although ferric compounds have lower solubility in relation to Al ones and greater binding affinity for As, they are unstable under low Eh conditions. Consequently, the bacterially-induced reductive dissolution of Fe (hydr)oxides may release previously adsorbed As into the environment. (Cummings *et al.* 1999; Zachara *et al.* 2001). The presence of Al substituting Fe in the Fe (hydr)oxides structures depresses the reductive dissolution of Fe (hydr)oxides (Schwertmann 1984; Torrent *et al.* 1987). Bousserhine *et al.* (1999) also demonstrated that biological reduction of Al, Cr, Mn, and Co-goethites was decreased as substitution increased.

Natural attenuation of As by adsorption onto these minerals may be also limited by oxyanions competing for the sorption sites (Hongshao and Stanforth 2001; Sahai *et al.* 2007; Zhang *et al.* 2008). Due to similar acid dissociation constants, phosphate ($pK_{a1} = 2.1$, $pK_{a2} = 7.2$, $pK_{a3} = 12.3$) behaves much like arsenate ($pK_{a1} = 2.2$, $pK_{a2} = 6.9$, $pK_{a3} = 11.4$). Therefore, investigations of the competition between anions can provide insight into the reactions occurring on the mineral surface (Hongshao and Stanforth 2001). The aim of this work was to investigate arsenate release from Al-goethites and other synthetic Al and Fe (hydr)oxides influenced by dissimilatory Fe reduction and competing phosphate.

Materials and Methods

Synthesis of Al and Fe (Hydr)oxides

Hematite (Hm), Goethite (Gt), 2-line Ferrihydrite (Fh), and three Al-goethites (AlGts) with different Al for Fe substitution (13, 20, and 23 cmol Al per mol of Fe) were synthesised according to Schwertmann and Cornell (2000). Gibbsite (Gb) was prepared according to Kyle *et al.* (1975). Similarly, a poorly crystalline Al hydroxide [Al(OH)₃] was also prepared, but with the suppression of the heating step to preserve low crystallinity. These adsorbents were loaded with sufficient As(V) to achieve their maximum adsorption capacity (Silva 2008).

Influence of competing ions

The effect of P on As release under anaerobic conditions were performed taking 0.1000 g of As-loaded adsorbents which were equilibrated with 96 mL of a sterile basal medium, containing 5 mmol/L phosphate (as KH_2PO_4), 20 mmol/L NH_4Cl , 1.34 mmol/L KCl , 10 mmol/L CaCl_2 , 0.34 mmol/L MgCl_2 , 10 mmol/L lactate, and 4.0 mL of *Shewanella putrefaciens* cell suspension in a 125 mL screw cap plastic bottle. The mixture was buffered at pH 7.0 by adding 10 mmol/L 1,4-piperazinediethanesulfonic acid (PIPES). The suspensions were purged with high-purity N_2 and anaerobically incubated in a glovebox for about 500 h. Aliquots were periodically taken, filtered through 0.22 μm membrane filters, acidified using concentrated HNO_3 , and stored for further analyses of Al, As, and Fe by ICP-OES (Perkin Elmer Optima 3300 DV) at The University of Queensland. Typical detection limits (3σ) of 0.42 $\mu\text{mol/L}$ were obtained for As.

Results and Discussions

Influence of phosphate as competing anion

Similar As desorption trends were observed for all materials. The fraction of desorbed As decreased in the following order: $\text{Gb} \geq \text{AlGts} > \text{Hm} > \text{Gt} > \text{Fh} > \text{Al}(\text{OH})_3$. The As release commenced within 4 h after the addition of phosphate, then increased sharply in the next 40 hours, and then gently decreased thereafter (Figure 1). For example, nearly 70 % of the total As in Gt was released within 48 h. Considering that soluble Fe was not detected during the initial stage of the experiment (4 – 48 h), the As displacement may be exclusively attributed to ligand exchange reactions with phosphate. Substantial amounts of As were released from Gb and Al-goethites, typically more than 50 % within the duration of the experiment (450 h). This should be entirely ascribed to exchange by phosphate on the Gb surface, but for AlGts part of the released amount must be attributed to biological iron reduction. Al-goethites followed similar kinetics, and the fraction of mobilised As was higher as the structural Al increased (Figure 1).

Our data is also consistent with the results of Masue *et al.* (2007), who reported increasing As(V) desorption by phosphate from poorly crystalline Al-Fe hydroxides as the Al:Fe ratio increased, reaching almost total arsenate desorption from pure Al hydroxide after 24 h.

The highest P immobilisation (almost 30 % of the added P) was measured in the solutions that had reacted with poorly crystalline (hydr)oxides (Fh and $\text{Al}(\text{OH})_3$) and Al-goethites. Considering that all the solid matrices were subjected to reaction with the same sterile basal medium, P immobilisation due to Ca-P precipitation should have been exactly the same for all the matrices. Therefore, the enhanced P immobilization observed for Fh, $\text{Al}(\text{OH})_3$, and AlGts compared to well crystalline (hydr)oxides can be ascribed to P adsorption onto sites not occupied by As, because P immobilization is not accompanied by release of As. Previous investigations have shown that surface coverage in the competitive adsorption experiments is higher than the adsorption of the individual ions (Hongshao and Stanforth 2001; Zhang and Selim 2008) suggesting that there are some specific sites for each ion as well as other sites that can adsorb both (Manning and Goldberg 1996).

A distinct behaviour was observed for Fh, where the amount of As released reached its maximum 192 h after the beginning of the experiment, and then suddenly decreased to almost zero. This trend coincides with P immobilisation and is possibly due to precipitation of a vivianite-like phase with significant As-P substitution [$\text{Fe}^{(II)}_3[(\text{As}, \text{P})\text{O}_4]_2 \cdot 8\text{H}_2\text{O}$].

Conclusion

This study investigated the mechanisms and extent of As remobilisation from Al-goethites and other synthetic Al and Fe (hydr)oxides under anoxic conditions induced by microbial activity, and competing P. Poorly crystalline Al hydroxide was the most efficient matrix in holding arsenate firmly on its surface, followed by Fh and Gt. Less than 15 % of the As bound to Al hydroxide was desorbed by phosphate, and arsenate adsorption kinetic data for Al hydroxide show that more than 92 % of the arsenate was adsorbed in nearly 6 h (Silva 2008). Although both Al and Fe hydroxides proved to be the most efficient matrices in retaining As, Al hydroxides have an advantage over Fh under reducing conditions.

Fh became more stable than poorly crystalline Al hydroxides only after 240 hours incubation time and in the presence of relatively high levels of P and Fe. Once soluble Fe increased to a certain level, it combined with phosphate to form vivianite [$\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$], as predicted by thermodynamic equilibria. Vivianite can act as a sink for soluble As and thus limit its mobility. This mechanism has significant environmental implications for the fate of As in eutrophic and reducing aquatic systems. In general, however, poorly

crystalline Al hydroxides can be considered the most effective adsorptive matrix for As, because the presence of soluble carbonate is more common than phosphate in most environmental conditions.

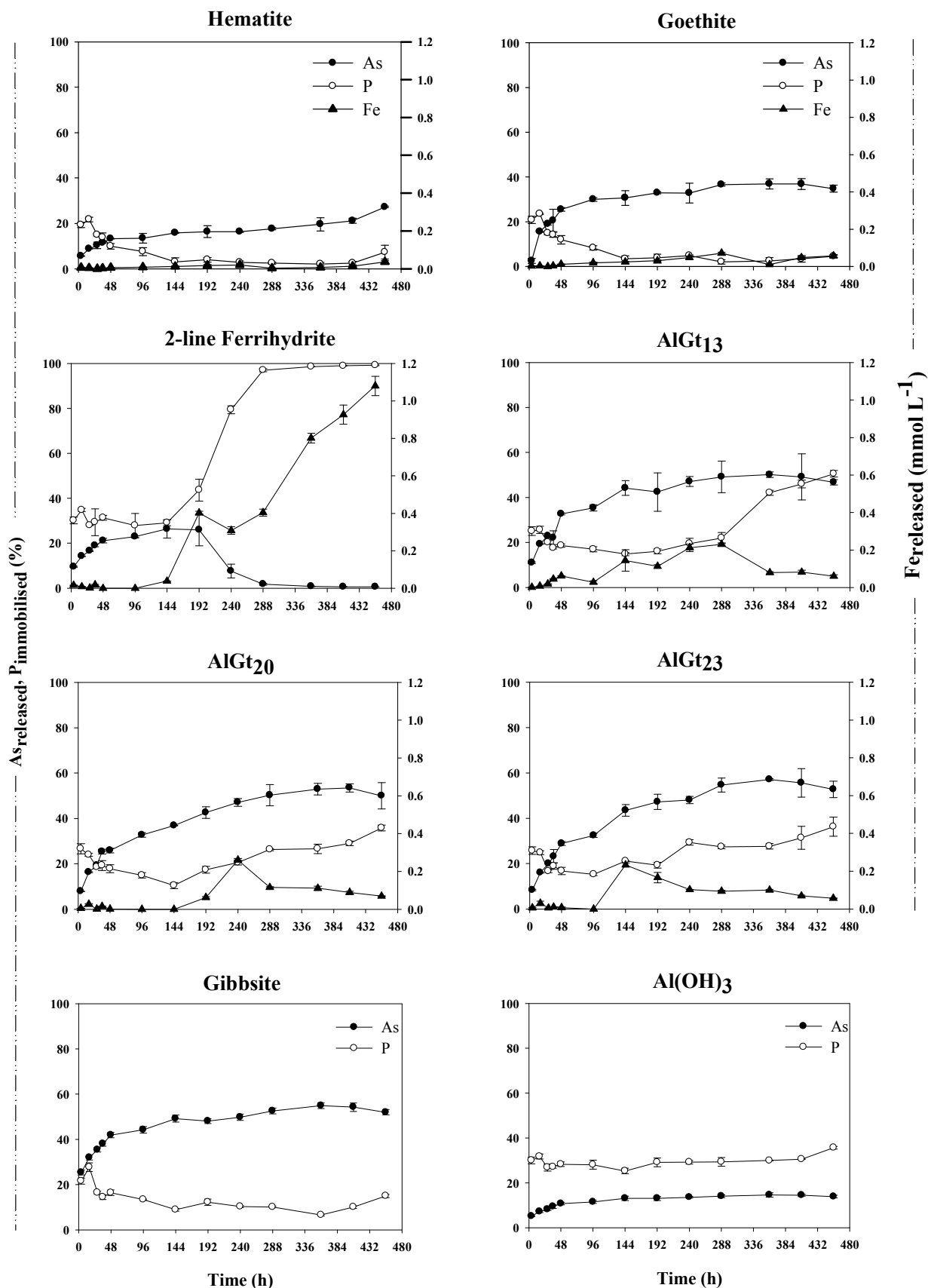


Figure 1. Fe(III) reduction, As release, and P immobilisation from different Al and Fe matrices in the presence of *S. putrefaciens*. Data are represented as means \pm standard error of the mean ($n = 3$); error bars not visible are smaller than the symbol.

Aluminium and Fe (hydr)oxides are ubiquitous in the environment, and goethite is one of the thermodynamically most stable iron oxides (Cornell and Schwertmann 2003). Thus, the presence of goethite with high structural Al may contribute not only to improve the As(V) adsorption capacity of soils and sediments, but also to diminish its mobilisation under reducing conditions. However, the use of phosphate-based fertilisers and microbial metabolism may add further complexity to the mechanisms of As desorption from soils and sediments.

In water treatment, hydrous ferric oxides have been used extensively to remove As from contaminated water. However, the disposal of As-rich residues under reducing conditions, as might occur at mine waste disposal sites (Masue *et al.* 2007), is a very concerning issue, because the redox transformation of Fe(III) to Fe(II) mediated by dissimilatory iron reducing bacteria may lead to As mobilisation. Hence, as Al is not redox sensitive, the use of a poorly crystalline Al(OH)₃ matrix may represent a good alternative for the removal of As from contaminated water. Our experiments showed that indeed both poorly crystalline Al(OH)₃ and Al-goethites, and, under specific environmental conditions, ferrihydrite, can be the most efficient matrix for As retention.

Acknowledgement

The support from Minas Gerais State Foundation- FAPEMIG and Brazilian Research Council is gratefully acknowledged. Part of this study was carried out while the first author was an Academic Visitor at The University of Queensland (UQ), with funding from CNPq (Brazil). Funding was also provided by a UQ grant.

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