Applied Geochemistry xxx (2017) 1–9

Contents lists available at ScienceDirect

Applied Geochemistry

journal homepage: www.elsevier.com/locate/apgeochem

Impact of competitive adsorption on microbial arsenate reduction at the water-goethite interface

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ARTICLE INFO

Article history:
Received 16 January 2017
Accepted 27 March 2017
Available online xxx

ABSTRACT

Competitive adsorption between arsenate, extracellular polymeric substances (EPS), phosphate and sulphate and resulting impacts on microbial arsenate reduction was investigated at the water-goethite interface at 10 μM arsenate with *Shewanella putrefaciens* strain CN-32 at pH 7. Addition of phosphate and *S. putrefaciens* EPS to 2 g L^{-1} goethite suspensions increased dissolved arsenate concentrations and enhanced arsenate reduction rates. The half-life of first order kinetics was 343 h without competitive species, whereas adding 50–500 μM phosphate and 0.28 g L^{-1} EPS decreased half-lives to 141–177 and 223 h, respectively. Phosphate and EPS addition did not increase arsenate reduction rates at 10 and 0.4 L^{-1} goethite, reflecting stronger effect of arsenate mobilisation induced by microbe-mineral interaction than competitive adsorption, respectively. Addition of 100 μM sulphate did not accelerate arsenate reduction, reflecting its weak competitive adsorption. Moreover, phosphate may slow down but EPS accelerate arsenate reduction in solution. Addition of 300–700 μM phosphate increased half-life of dissolved arsenate reduction in solution from 21.3 to 29.4–32.2 h but the presence of 1.4 g L^{-1} EPS decreased half-life to 2.2 h. Depending on surface coverage and the nature and concentrations of competitive species, competitive adsorption may enhance arsenate reduction kinetics and cause arsenic mobilisation.

1. Introduction

Over 100 million people worldwide drink and use water with high arsenic (As) concentrations, which substantially affect health (Nordstrom, 2002). As a result, the causes and mechanism of As release from the solid phase into solution has received much attention. Arsenic mobilisation is mostly induced by changes of environmental conditions, such as redox state and pH (Smedley and Kinniburgh, 2002). For example, As was released from arid soils into water at elevated soil pH values, since As adsorption to mineral surfaces is less favourable under basic conditions (Smedley et al., 2002). At mining sites, exposure to oxygen will lead to oxidation of As pyrite, contributing to As dissolution in water (Cheng et al., 2009). Hot water-rock leaching is the major cause of high As concentrations in geothermal fluids (Webster and Nordstrom, 2003).

The establishment of reducing condition has been identified as a major cause of As mobilisation in several regions, e.g. in Bangladesh, West Bengal and South-eastern Asia (Smedley and Kinniburgh, 2002). Field observations (Corsini et al., 2011; Islam et al., 2004) point out the importance of microbially mediated reductive dissolution of Fe (hydr)oxides in inducing reductive As mobilisation. However, several laboratory model experiments showed that formation of secondary Fe(II) Fe(III) (hydr)oxides, e.g. magnetite, vivianite and siderite and nanoparticles formed during microbial reduction may trap released As again (Coker et al., 2006; Islam et al., 2005; Tadanier et al., 2005). In parallel with Fe (hydr) oxide dissolution, As mobilisation under reducing conditions is also enhanced by reduction of arsenate (As(V)) to arsenite (As(III)), while As(III) is more mobile than As(V) at most environmental As concentrations (Dixit and Hering, 2003; Huang and Matzner, 2006; Smedley and Kinniburgh, 2002). Arsenic reduction in the environment is mostly biotic (Meng et al., 2003). Abiotic reduction of As(V) has been shown to be substantially slower and is believed less important than microbially mediated reduction (Ahmann et al., 1997; Jones et al., 2000). Arsenate undergoes microbial reduction primarily in the solution phase of water-solid systems. The rate of As(V) reduction is influenced by the binding modes with which As(V) is associated with the mineral phases and coupled strongly

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http://dx.doi.org/10.1016/j.apgeochem.2017.03.012
0883-2927/

with As(V) adsorption and desorption rates (Huang et al., 2011b; Zobrist et al., 2000). The presence of mineral sorbents has been evidenced to result in pronounced decreases in microbial As(V) reduction rates and the magnitude of such effect increased with increasing sorbent concentration and sorption capacity (goethite < boehmite < ferrihydrite) (Huang et al., 2011b). Microbial As(V) reduction rate was found to decrease in the order: dissolved ≫ As(V) added to ferrihydrite suspensions at the start of the incubation > As(V) reacted with ferrihydrite for 24 h before incubation > As(V) coprecipitated during ferrihydrite synthesis (Zobrist et al., 2000).

Competitive adsorption at the water-mineral interface is another important factor which determines aqueous As concentrations in soils and sediments (Melamed et al., 1995; Peryea, 1991; Peryea and Kammereck, 1997; Reynolds et al., 1999). Phosphate and As(V) appear to compete for similar sorption sites due to their similar chemical structures. Phosphate addition at high rates enhanced As leaching in laboratory column studies, increased extractable fractions of As in batch experiments, and reduced sorption of As(V) and As(III) onto soils (Peryea, 1991; Peryea and Kammereck, 1997; Smith et al., 1998). Other competing anions were less effective in displacing As from the exchange complex, the pattern for As(V) being $H_2PO_4^-$ > $H_2AsO_4^-$ > SO_4^{2-} > CO_3^{2-} and for As(III) being $H_2PO_4^-$ > H_3AsO_3 > F^- > SO_4^{2-} > CO_3^{2-} (Adriano, 2001). Recently, microbial extracellular polymeric substances (EPS) were demonstrated to form inner-sphere complexes with phosphate and carboxyl functional groups onto Fe (hydr)oxide surface and thereby compete As(V) adsorption to Fe (hydr)oxides (Huang et al., 2011a).

Microbial As(V) reduction and competitive adsorption may occur simultaneously in the natural environment, e.g. The release of phosphate adsorbed to Fe (hydr)oxides during microbial reductive dissolution (Huang and Matzner, 2006; Hutchison and Hesterberg, 2004) or microbe-mineral surface interaction (Huang et al., 2011a). Reynolds et al. (1999). showed that phosphate addition enhanced As(V) reduction rates in flooded soils based on X-ray absorption near edge structure speciation of As(III) and As(V) in soil solids (both As and phosphate at sub mM level), but the mechanisms leading to increase As(V) reduction remained unclear. To date, the combined effects of microbial As(V) reduction and competitive adsorption on the mobility of As at the water-mineral interface has not been studied in well controlled laboratory studies. Therefore, the objectives of this research are to (1) study the interaction between competitive adsorption and microbial As(V) reduction, (2) assess the conditions where competitive adsorption to increase microbial As(V) reduction rates (3) and quantify As mobilisation caused by the combined effect of competitive adsorption and As(V) reduction in comparison with those caused individually. This information is essential for accurate assessment of the release of As from soils and sediments following reduction, which is a concern with respect to the fate of As in contaminated soils or sediments under temporarily or permanently flooded conditions. It also allows a more accurate assessment of the risks arising from As contaminated soils and sediments and for the design of appropriate site-remediation measures.

2. Materials and methods

2.1. Goethite

Goethite (α-FeOOH) was synthesised by pouring 180 mL 5.0 M NaOH to 100 mL 1.0 M $FeCl_3$ solution. The suspension was diluted to 2 L with deionised water and hold in a polypropylene flask in a 70 °C oven for 72 h. The suspension was then centrifuged (30 min, 2100 *g*, 20 °C) and washed with deionised water until the conductivity as low as the deionised water. After freeze drying, the product was stored at 4 °C before use. Ferric chloride was used instead of ferric nitrate in order to avoid any use of nitrate as an electron acceptor by bacteria. The N_2-BET (Sorptomatic, Thermo, USA) surface areas of goethite were 18.1 $m^2\ g^{-1}$. Sterilisation of the working assays without and with mineral suspensions was done by autoclaving. X-ray diffraction (Bruker Model AXS D4 Endeavor, Karlsruhe, Germany) analyses of autoclaved goethite indicated no changes in mineral structure resulting from the autoclaving procedure.

2.2. Ternary As-competitive ions batch adsorption experiments

Adsorption isotherms of As(III) and As(V) were determined at 0.2 g L^{-1} goethite in solutions at pH 7 containing 5 mM NaCl, 0.5 mM $CaCl_2$, 0.5 mM $MgCl_2$, 25 μM sodium lactate and 10 mM PIPES (piperazine-*N*,*N*′-bis-(2-ethanesulfonic acid)) buffer. Goethite suspensions (1 L) in PIPES-buffered solutions were first allowed to equilibrate while stirring for 24 h. A 10 mL subsample was removed from the main vessel under vigorous stirring and pipetted into a 10 mL polyethylene vial then spiked with As(V) or As(III) to achieve final concentrations in the range 0.1–50 μM for As (V) and 0.1–25 μM for As(III). The As concentrations were so chosen possibly to represent the environmental approaching conditions. Phosphate was added at concentrations of 0, 1, 5, 10, 50 or 100 μM, standing for different extents of competitive adsorption effects. All As(V)-spiked suspensions were equilibrated on an end-over-end shaker (50 rpm) at room temperature for 24 h. The equilibration time for As(III) was limited to 2 h to minimise oxidation (Goldberg, 2002; Huang et al., 2011b).

Additional batch experiments were carried out to understand the adsorption competition between As(V) and phosphate and sulphate to goethite in the absence of microbial cells, in which apparent competitive adsorption gave significant influences on microbial As(V) reduction. For this purpose, 10 μM As(V) with either 0–100 μM phosphate or 0–10 000 μM sulphate in 2 g L^{-1} goethite suspensions containing 5 mM NaCl, 0.5 mM $CaCl_2$, 0.5 mM $MgCl_2$, 25 μM sodium lactate and 10 mM PIPES (pH 7). Following 24 h equilibration, the solutions were syringe-filtered through 0.2 μm nitrocellulose filter membranes for As analysis. The adsorbed amounts of As were calculated from the difference between the initial and final As concentrations.

2.3. Experiments of microbial As(V) reduction

Shewanella putrefaciens strain CN-32 obtained as ATCC® BAA-1097™ was grown for 24 h to late-exponential phase under aerobic conditions in tryptic soy broth at 30 °C. Cell densities of each culture were estimated from optical density measurements at 600 nm (OD_{600}), which were calibrated against total cell numbers determined by counting of DAPI (4′,6-diamidino-2-phenylindol)-stained cells using an optical microscope (Leica Microsystems, Wetzlar, Germany) (Huang et al., 2011b). Cells were harvested by centrifugation (2100 *g*, 15 min at 4 °C) and washed twice with a solution containing 10 mM PIPES buffer at pH 7.0 and neutral salts (5 mM NaCl; 0.5 mM $CaCl_2$; 0.5 mM $MgCl_2$). The cells were re-suspended with 2 mL wash solution and ready for microbial reduction experiments.

Batch experiments were performed to study microbial reduction of As(V) in solutions with and without mineral suspensions. The experiments were carried out in 50 mL serum bottles capped with butyl rubber septa, crimp-sealing, evacuation and $N_{2(g)}$ purging in turns for 10 min before beginning the experiments. All microbial As(V) reduction experiments with *S. putrefaciens* contained the final concentrations of 10 mM PIPES buffer (pH 7.0), 25 μM sodium lactate, neutral salts (5.0 mM NaCl; 0.5 mM $CaCl_2$;

Please cite this article in press as: Huang, J.-H., Impact of competitive adsorption on microbial arsenate reduction at the water-goethite interface, Applied Geochemistry (2017), http://dx.doi.org/10.1016/j.apgeochem.2017.03.012