



Reduction of adsorbed As(V) on nano-TiO₂ by sulfate-reducing bacteria



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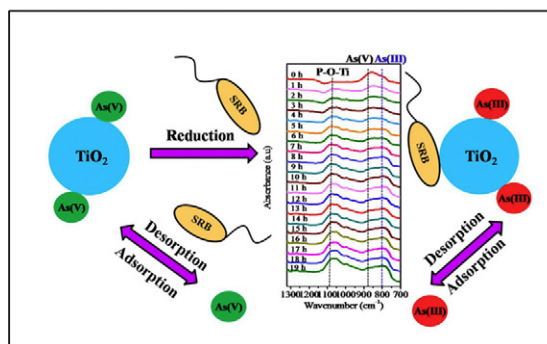
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HIGHLIGHTS

- As(V), either adsorbed or dissolved, was reduced in the presence of SRB.
- Reduction was faster for adsorbed As(V) than for dissolved As(V).
- SRB promoted As(V) desorption from TiO₂ compared with abiotic sulfide.
- As(V) desorption due to competition with phosphate surface complexation

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 16 February 2017

Received in revised form 19 April 2017

Accepted 20 April 2017

Available online 27 April 2017

Editor: F.M. Tack

Keywords:

Surface-bound arsenate

Reducing condition

Arsenate desorption

FTIR

Sulfate-reducing bacteria

ABSTRACT

Reduction of surface-bound arsenate [As(V)] and subsequent release into the aqueous phase contribute to elevated As in groundwater. However, this natural process is not fully understood, especially in the presence of sulfate-reducing bacteria (SRB). Gaining mechanistic insights into solid-As(V)-SRB interactions motivated our molecular level study on the fate of nano-TiO₂ bound As(V) in the presence of *Desulfovibrio vulgaris* DP4, a strain of SRB, using incubation and in situ ATR-FTIR experiments. The incubation results clearly revealed the reduction of As(V), either adsorbed on nano-TiO₂ or dissolved, in the presence of SRB. In contrast, this As(V) reduction was not observed in abiotic control experiments where sulfide was used as the reductant. Moreover, the reduction was faster for surface-bound As(V) than for dissolved As(V), as evidenced by the appearance of As(III) at 45 h and 75 h, respectively. ATR-FTIR results provided direct evidence that the surface-bound As(V) was reduced to As(III) on TiO₂ surfaces in the presence of SRB. In addition, the As(V) desorption from nano-TiO₂ was promoted by SRB relative to abiotic sulfide, due to the competition between As(V) and bacterial phosphate groups for TiO₂ surface sites. This competition was corroborated by the ATR-FTIR analysis, which showed inner-sphere surface complex formation by bacterial phosphate groups on TiO₂ surfaces. The results from this study highlight the importance of indirect bacteria-mediated As(V) reduction and release in geochemical systems.

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1. Introduction

Arsenic (As) is a toxic metalloid naturally occurring as As(V) and As(III). Mounting evidence over the past decade suggests that coupled redox and adsorption/desorption processes regulate the concentration and speciation of As in groundwater (Smedley et al., 2002; Islam et al.,

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2004; Kumar et al., 2016a, 2016b). Nevertheless, a great challenge in the biogeochemical study of As is to decipher the reduction and release process at the molecular level in the complex real environment.

In natural environments, As is primarily bound to soil minerals, especially to iron (hydr)oxides, which are responsible for As release or stability in soils and sediments (Daus et al., 1998). When iron (hydr)oxides dissolve, As is released, which leads to elevated As in groundwater (Islam et al., 2004). Meanwhile, the reduced iron (hydr)oxides may form various secondary iron minerals, which can re-uptake the released As (Tufano and Fendorf, 2008; Muehe et al., 2016; Wang et al., 2014).

Under anoxic conditions, microorganisms such as sulfate-reducing bacteria (SRB) play an important role in the biogeochemical cycling of As (Burton and Kocar, 2014; Kumar et al., 2016a, 2016b; ThomasArrigo et al., 2016). SRB reduce sulfate to sulfide (Oremland et al., 2000; Burton et al., 2011), and the biogenic sulfide is capable of reducing As(V) to As(III) at appreciable concentrations, particularly in sulfidic environments (Xu et al., 2016; Wilkin et al., 2003; Oremland et al., 2005). The detailed knowledge of As reduction and desorption processes on metal oxides in the presence of microbes is the key to understanding As contamination.

Great efforts have made to explore the impact of microbes on As reduction and release from metal oxides (Stuckey et al., 2016; Zobrist et al., 2000; Zhang et al., 2016; Sun et al., 2016). Some studies concluded that As(V) bio-reduction occurred predominantly in solution, rather than on mineral surfaces (Jones et al., 2000; Langer and Inskeep, 2000). For instance, Huang et al. (2011a, 2011b) suggested that dissolved As(V) reduction by *Shewanella putrefaciens* strain CN-32 followed first-order kinetics with a 3 h half-life, and the addition of goethite resulted in a significant decrease in the reduction rate (32 h As(V) half-life). In contrast, some studies hypothesized that adsorbed As(V) was directly reduced on solids by bacteria. For example, Ohtsuka et al. (2013) reported that a dissimilatory arsenate-reducing bacterium (*Geobacter pelophilus*, OR-18) directly reduced As(V) on a paddy soil. Rochette et al. (1998) also found that As(V) was rapidly reduced to As(III) and remained mostly associated in the solid phase.

The complexity of the As redox and release processes has motivated the application of in situ spectroscopic techniques such as in situ ATR-FTIR (Yan et al., 2016a, 2016b). Previous ATR-FTIR studies implied that the functional groups of microbes such as phosphate and phosphodiester may play an important role in the attachment of bacterial cells to iron oxide minerals through the formation of covalent bonds (Omoike et al., 2004; Parikh and Chorover, 2008; Burnett et al., 2006). Then, bacteria may facilitate As desorption by competing with As for coordination at surface sites.

The objective of the present study was to investigate the reduction and desorption of adsorbed As(V) on nano-TiO₂ in the presence of SRB using batch incubation experiments and in situ ATR-FTIR spectroscopy. Nano-TiO₂ is an effective As adsorbent (Luo et al., 2010; Yan et al., 2015; Yan et al., 2016a, 2016b), and its physicochemical stability enables it to be a good template to de-couple the As reduction and release processes. The insights gained from this study shed new light on the risk assessment of As-laden solids in the environment.

2. Materials and methods

2.1. Nano-TiO₂, artificial groundwater and SRB preparation

Nano-TiO₂ used in this study was prepared with titanium sulfate. The basic properties of synthetic nano-TiO₂ can be found in our previous work (Luo et al., 2010). Artificial groundwater was composed of 0.5 mM NaHCO₃, 0.02 mM NH₄Cl, 0.07 mM KCl, 9 mM Na-lactate, 21 mM MgSO₄, and 1.5 mM CaCO₃ (Luo et al., 2013). The electron acceptor was sulfate (MgSO₄), and the electron donor was lactate (Na-lactate). The SRB, named as *Desulfovibrio vulgaris* DP4, was isolated from a soil sample collected at a naturally-occurring As-contaminated site

in China, which was described in detail in our previous study (Luo et al., 2013).

2.2. Batch incubation experiments of adsorbed/dissolved As(V) in the presence of SRB and sulfide

2.2.1. Adsorption experiments

Suspensions containing 50 mL As(V) (3 mg L⁻¹, Na₂HAsO₄·7H₂O) and 1 g L⁻¹ nano-TiO₂ were prepared in 50 mL centrifuge tubes. The background solution was artificial groundwater. The pH of batch experiments was adjusted to 8.0 ± 0.1 using NaOH and H₂SO₄ solutions. Suspensions were mixed on a rotator for 24 h, and then centrifuged. As-laden nano-TiO₂ solids were thus obtained. The supernatant was filtered by a 0.22-μm membrane filter for soluble As(V) analysis. The final adsorption capacity of As(V) on nano-TiO₂ was approximately 3 mg g⁻¹.

Reduction experiments of adsorbed As(V) on nano-TiO₂ were conducted with SRB and an abiotic reducer sulfide (21 mM, Na₂S) in the glovebox. The reduction experiments were conducted in 500 mL serum bottles. After the As-laden nano-TiO₂ solid was obtained, the solid (As adsorption capacity 3 mg g⁻¹, TiO₂ 1 g L⁻¹) was suspended in artificial groundwater, and SRB were added at 1 mL per 100 mL solution (Luo et al., 2013). For comparison with the reduction induced by SRB, the sulfide as an abiotic reducer was added to the suspension. Reduction experiments of dissolved As(V) in the presence of SRB and sulfide were conducted as well in order to compare with adsorbed As(V). As(V) (3 mg L⁻¹) solution was prepared with Na₂HAsO₄·7H₂O and artificial groundwater. As(V) solution was transferred to 500 mL serum bottles, and SRB were added at 1 mL per 100 mL solution. Moreover, the sulfide was added to the As(V) solution to examine As(V) reduction. All of the experimental solutions were adjusted to pH 8.0 ± 0.1 with NaOH and H₂SO₄. Finally, the bottles were sealed and transferred out of the glovebox and incubated at 25 °C for 4 d. During this period, homogenized samples were extracted using a syringe and passed through a 0.22 μm filter at predesigned intervals. Eh and pH were also monitored during the incubation experiments. All batch incubation experiments were performed in triplicate.

2.3. Analysis

The concentrations of soluble As were determined using a furnace atomic absorption spectrometer (Perkin-Elmer AAS-800) with a detection limit of 0.7 μg/L. The As speciation was analyzed with high performance liquid chromatography atomic fluorescence spectrometry (HPLC-AFS, Jitian, China) with a detection limit of 0.6 μg/L. Separation of As was carried out in a Hamilton PRP-X100 anion exchange column, using 10 mM phosphate buffer at pH 5.8 as mobile phase. Sulfate concentrations were determined using a DX-1100 ion chromatograph (Dionex, Sunnyvale, CA) with an AS11-HC Ion Pac column. Sulfide concentrations were measured using the methylene blue method (Luo et al., 2013) immediately following the sample collection.

2.4. In situ ATR-FTIR spectroscopy flow cell experiments

In situ ATR-FTIR experiments were performed for direct monitoring of the reduction of adsorbed As(V) on nano-TiO₂ in the presence of SRB. The ATR-FTIR spectra were recorded on a Perkin-Elmer Spectrum 100 IR spectrometer equipped with a liquid N₂-cooled MCT/A detector and an optics compartment that was continuously purged with high purity nitrogen.

ATR-FTIR experiments were conducted by a flow cell technique. Firstly, a nano-TiO₂ thin layer was prepared on the ZnSe ATR crystal. After 5 g L⁻¹ nano-TiO₂ was added to ultrapure water, the suspension was sonicated for two or three hours. Then about 300 μL of the nano-TiO₂ suspension was dropped onto the ZnSe ATR crystal with a pipette, and the colloidal TiO₂ thin layer was sealed in a flow cell. The flow cell

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