Arsenic transformation mediated by *Pantoea* sp. IMH in spent nZVI waste residue

L. Ye & C.Y. Jing

Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing, China

ABSTRACT: Nanoscale zero-valent iron (nZVI) is an effective arsenic (As) scavenger. However, spent nZVI may pose a higher environmental risk than our initial thought in the presence of As-reducing bacteria. Therefore, our motivation was to explore the As redox transformation and release in spent nZVI waste residue in contact with *Pantoea* sp. IMH, an *arsC* gene container. Our incubation results showed that IMH preferentially reduce soluble As(V), not solid-bound As(V), and was innocent in elevating total dissolved As concentrations. μ -XRF and As μ -XANES spectra clearly revealed the heterogeneity and complexity of the inoculated and control samples. Nevertheless, the surface As local coordination was not affected by the presence of IMH as evidenced by similar As-Fe atomic distance (3.32–3.36 Å) and coordination number (1.9) in control and inoculated samples. The Fe XANES results suggested that magnetite in nZVI residue was partly transformed to ferrihydrite, and IMH slowed down the nZVI aging process. IMH distorted Fe local coordination without change its As adsorption capacity as suggested by Mossbauer spectroscopy. Arsenic retention is not inevitably enhanced by in situ formed secondary Fe minerals, but depends on the relative As affinity between the primary and secondary iron minerals.

1 INTRODUCTION

Nanoscale zero-valent iron (nZVI) has been widely used in arsenic (As) remediation because of its large specific surface area and high surface reactivity. nZVI is readily oxidized and the subsequent iron corrosion products are responsible for As adsorption. This As-laden spent nZVI may oxidize and gradually crystallize over time to more ordered forms such as magnetite and other iron minerals. Because of the natural occurrence of iron and its corrosion products, nZVI is designed for direct use and is disposed of in the environment. However, recent studies suggest that the aging of nZVI may facilitate the heavy metal release and the secondary environmental pollution (Calderon & Fullana 2015), especially when spent nZVI is left unattended at treated sites.

Microorganisms play a prominent role in the redox transformation and mobilization of As through the change in As speciation and Fe(III) oxide dissolution (Tian *et al.*, 2015). Bacteria can reduce As(V) either by an anaerobic respiratory pathway mediated by *arrA* genes or by an aerobic detoxification pathway mediated by *arsC* genes. Recent studies adopted the aeration process in nZVI treatment to enhance As removal due to the formation of Fe (hydr)oxides, therefore, the aerobic As-reducing bacteria with *arsC* genes may play a central role in As bio-mobilization. However, whether *arsC* gene containers can directly reduce adsorbed As(V) remains unclear.

The Fe(III) oxide dissolution leads to As mobilization, but subsequently in situ formed secondary iron

minerals are reported to re-uptake As. Most previous studies found that As retention is actually enhanced during the formation of secondary Fe minerals. However, limited knowledge is available about the iron transformation in spent nZVI in the presence of *arsC* carriers. In addition, the impact of iron transformation in spent nZVI for As retention is unknown. The desire to decipher the coupled biotransformation of As and nZVI by *arsC* carriers motivates our study.

The purpose of this study was to explore As and Fe redox transformation and release in spent nZVI waste residue in the presence of an aerobic As(V)-reducing bacterium, *Pantoea* sp. IMH. Multiple complementary techniques including incubation experiments, X-ray absorption fine structure (XAFS) and Mössbauer spectroscopy were employed to characterize the reaction process. The insights gained from this study shed new light on the risk assessment of nZVI waste residue in the environment.

2 METHODS/EXPERIMENTAL

2.1 Incubation experiments

Spent nZVI waste residue was collected from a rare metal smelting company. IMH was activated first, and then was inoculated into the culture medium containing 5 g L⁻¹ nZVI. The control samples were prepared the same with the incubation samples, except without IMH inoculation. Each incubation and control samples was monitored periodically to determine the number

of living cells and the soluble concentration of As(III), As(V), Fe(II), total Fe, anions and other metals.

2.2 Solid analysis

The solid samples were freeze-dried and deposited onto a strip of Kapton tape for XAFS analysis. Micro X-ray fluorescence (μ -XRF) and μ -X-ray absorption near edge structure (μ -XANES) spectra were collected at beamline 15U, and the As and Fe K-edge XAFS spectra were collected at beamline 14W at Shanghai Synchrotron Radiation Facility (SSRF), China. XANES spectra were analyzed using LCF fitting and EXAFS data were analyzed using standard FEFF shell fitting approach.

Mössbauer spectra were measured at 293 K with an Austin Science S-600 Mössbauer spectrometry using a γ -ray source of 1.11 GBq⁵⁷Co/Rh. Measured spectra were fitted to Lorentzian line shapes using standard line shape fitting routines. The software package WinNoroms-for-Igor was used to analyze measured spectra and the rates of all iron speciation were calculated according to peak area.

3 RESULTS AND DISCUSSION

3.1 Soluble As and Fe speciation

As(V) was almost completely reduced to As(III) by IMH within 30 h, concomitant with the growth of IMH. Almost no difference was observed in total dissolved As in control and inoculated samples, suggesting that IMH had a negligible contribution to the As release from nZVI. The results indicate that IMH plays a decisive role in soluble As speciation, but has no impact on the As release. We therefore speculated that IMH should entirely prefer reduce the dissolved As(V) rather than the solid-bound As(V). No significant difference was observed between inoculated and control samples for both Fe(III) ($p = 0.525$) and Fe(II) ($p = 0.848$), implying that IMH facilitated neither Fe(III) precipitation/dissolution nor its reduction. Interestingly, decrease in dissolved As concentration (9% for the control and 12% for the inoculated sample) was not proportional to that of Fe (61% for the control and 62% for the inoculated sample) (Figure 1b), indicating that the fresh precipitated iron oxides did not uptake As by the same ratio as in the initial nZVI residues.

3.2 Speciation and association of As and Fe

The speciation of the solid As and Fe was characterized using XANES. Incubation with IMH slightly increased the As(III) percentage from 15% in nZVI residue to 19%, probably due to re-adsorption of dissolved As(III). Compared with the 100% As(III) in the soluble phase due to As(V) bio-reduction, in situ As(V) reduction on solid was inhibited, revealing that IMH

prefers to reduce dissolved As(V) rather than adsorbed As(V).

The spatial distribution of As and Fe in solids determined using μ -XRF and the corresponding As μ -XANES spectra at five different spots. The As distribution was linearly correlated with that of Fe in inoculated ($R = 0.97$) and control ($R = 0.95$) samples.

As EXAFS analysis indicated that the As-Fe distance was 3.36 (3.33) Å in the inoculated (control) sample, corresponded to bidentate binuclear corner-sharing As complex on the Fe (hydr)oxides surface.

3.3 Fe speciation in solid

To examine the effect of IMH on Fe speciation in solids, XANES analysis was employed. The Fe K-edge XANES analysis indicates that magnetite would be oxidized and transformed to ferrihydrite during the nZVI aging process. IMH slowed down the nZVI aging process as evidenced by the 34% Fe₃O₄ in the inoculated sample compared with zero Fe₃O₄ in the control. To further explore the Fe phase in the presence of IMH, Mössbauer spectroscopy was used to provide insights into the valence state and coordination of Fe atoms. The analysis shows that although IMH did not change the valence state of Fe, it did cause a more distorted polyhedron coordination of Fe atoms.

4 CONCLUSIONS

As(V)-reducing bacteria with *arsC* genes play an important role in the biotransformation and mobility of As in the aerobic environment. *arsC* containers such as strain IMH can readily reduce dissolved As(V) to more toxic As(III) aerobically. The bacterial activity slow down the nZVI aging process and distort the Fe local coordination which may have an impact on the fate and transport of attached pollutants. Furthermore, the As retention is dependent on the relative As affinity between the primary and secondary iron minerals. Therefore, the consequence of secondary Fe mineral formation to As immobilization should be evaluated on a case-by-case basis.

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