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Combination of microbial oxidation and biogenic schwertmannite immobilization: A potential remediation for highly arsenic-contaminated soil

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HIGHLIGHTS

- The strain YZ-1 was able to oxidize As(III) to As(V) efficiently in the soil.
- Biogenic schwertmannite (Bio-SCH) has the advantage of immobilizing As(V).
- Microbial oxidation and Bio-SCH immobilization were combined for As-contaminated soil.
- The combination is superior to individual methods for treating As-contaminated soil.

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ABSTRACT

Here, a novel strategy that combines microbial oxidation by As(III)-oxidizing bacterium and biogenic schwertmannite (Bio-SCH) immobilization was first proposed and applied for treating the highly arsenic-contaminated soil. *Brevibacterium* sp. YZ-1 isolated from a highly As-contaminated soil was used to oxidize As(III) in contaminated soils. Under optimum culture condition for microbial oxidation, 92.3% of water-soluble As(III) and 84.4% of $NaHCO_3$-extractable As(III) in soils were removed. Bio-SCH synthesized through the oxidation of ferrous sulfate by *Acidithiobacillus ferrooxidans* immobilize As(V) in the contaminated soil effectively. Consequently, the combination of microbial oxidation and Bio-SCH immobilization performed better in treating the highly As-contaminated soil with immobilization efficiencies of 99.3% and 82.6% for water-soluble and $NaHCO_3$-extractable total As, respectively. Thus, the combination can be considered as a green remediation strategy for developing a novel and valuable solution for As-contaminated soils.

1. Introduction

Arsenic (As) is a ubiquitous and carcinogenic metalloid element in the environment (Kim et al., 2012; Liang et al., 2016). The widespread contamination of As in soil has become an increasing environmental and toxicological concern (Komárek et al., 2013; Lee et al., 2011b). Mining and smelting operations on As-bearing minerals are among the most serious sources of As contamination where the total As concentration in the soil can be three or four magnitude higher than that in non-contaminated soils (usually below 10 mg kg^{-1}) (Adriano, 2001; Mikutta et al., 2014; Otones et al., 2011; Tang et al., 2016; Yang et al., 2014). Highly As-contaminated soils allow As mobilization and subsequent leaching into ground or surface water, and can pose a sever risk to drinking water and food safety, and eventually human health. Significant health problems caused from As poisoning has arisen in some mine and their vicinity areas (Li and Ben, 2014; Pearce et al.,

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2012). Therefore, active remediation of As-contaminated soil is of great importance.

Among soil remediation techniques, immobilization is a potentially reliable and relatively inexpensive alternative to remediation of the soils that have been highly polluted by metal(loid)s (Mallampati et al., 2012; Sun et al., 2016; Yang et al., 2015). Such technology is typically performed by mixing the contaminated soil with amendments that can immobilize contaminants (e.g., metal(loid)) through adsorption and/or precipitation reactions (Lei et al., 2017; Makris et al., 2009). However, remediation of the As-contaminated soils by immobilization is challenging as As exists mainly in two different oxidation states, arsenate (As(V)) and arsenite (As(III)) (Hyun et al., 2011), and As(III) is more mobile in the environment and more toxic to organisms than As(V) (Bertin and Lett, 2009; Burton et al., 2014). Indeed, due to its higher mobility, As(III) is more bioavailable than As(V) in soils (Bolan et al., 2015).

Since As(V) can be more strongly retained with metal (hydr) oxides (e.g. Fe hydroxide/oxyhydroxide) as compared to As(III) (Yang et al., 2002; Yolcubal and Akyol, 2008; Zhang et al., 2015b), oxidation of As(III) to As(V) is proposed to facilitate As retention by metal (hydr)oxides, and is often used as an approach to remediate the As-contaminated waters and soils (Corsini et al., 2015; Khuntia et al., 2014). For this reason, As-remediation technologies should rely on a two-step approach, involving an initial oxidation of As(III) to As(V) followed by sequestration of As(V) (Bertin and Lett, 2009; Pous et al., 2015). Traditionally, chemical techniques using various chemical oxidants (such as permanganate, chlorine, chloramines and ozone) to oxidize As(III) to As(V) (Dodd and Vu, 2006; Lee et al., 2011a), suffer from high costs and generation of harmful by-products (Bahar et al., 2012). Microbial transformation of As(III) to As(V) could be an eco-friendly and cost-effective alternative to chemical techniques (Bachate et al., 2012; Corsini et al., 2014), and it has been applied in bioremediation of the As-contaminated water (Bachate et al., 2012; Corsini et al., 2015; Ike et al., 2008; Kao et al., 2013; Michel et al., 2007). Many bacteria were reported to oxidize As(III) (Bahar et al., 2012; Ma, 2012; Majumder et al., 2013; Zhang et al., 2015a). However, the bacteria with strong As(III) oxidation ability and high As resistance were rare, and the remediation of the As-contaminated soil, especially for the highly As-contaminated soil by such As(III)-oxidizing bacterium is scanty. After the microbial As(III) oxidation, the subsequent remediation step can be carried out using iron-containing materials for As immobilization in the contaminated soil. Although the combined use of As(III) oxidizing bacteria and iron oxide as adsorbent for removing As from water has been reported (Corsini et al., 2014), no information is available regarding such combination for remediation of the As-contaminated soil.

In the present study, the combination of microbial As(III) oxidation and biogenic schwertmannites (Bio-SCH) immobilization was applied to the highly As-contaminated soils. Bio-SCH was selected for the subsequent As immobilization, considering its high efficiency of As sequestration and slightly effect on soil pH (Liao et al., 2011; Chai et al., 2016). Moreover, Bio-SCH can be naturally formed during Fe(II) oxidation by microorganisms (e.g. *Acidithiobacillus ferrooxidans*), and is widespread in acidic iron and sulfate-rich environments as a common abundant iron mineral (Burton et al., 2007; Guo et al., 2015). Therefore, the application of Bio-SCH might be a promising technique for *in-situ* immobilization of As in soils from some As-contaminated mine areas. This combination could be regarded as "green remediation", because the application of microorganisms and Bio-SCH is eco-friendly and hence is an ideal option to lower the hazardous effects of heavy metals on living beings without destroying soil properties. For microbial As(III) oxidation, we used a novel As(III)-oxidizing bacterial strain *Brevibacterium* sp. YZ-1 (strain YZ-1), which was previously isolated from the highly As-contaminated soil in an abandoned realgar mine area (Yang et al., 2017). The main objectives of this study were to (1) examine the ability of strain YZ-1 to oxidize As(III) in soils; (2) investigate the potential application of combination of microbial oxidation and Bio-SCH immobilization for remediation of As-contaminated soils.

2. Materials and methods

2.1. Soil sampling

The As-contaminated soil samples (Soil A and Soil B) were collected from the surface layer (0–20 cm) of an abandoned realgar mine area located in Shimen County, Hunan Province, central south of China. The sampling locations for Soil A and Soil B belong to mining site and smelting and processing plants, respectively. The soils contained extremely high As concentration, which can reached up to 5240.8 mg kg^{-1}. Both As(III) and As(V) could be detected in the soils. According to FAO/UNESCO soil classification system, the soils were classified as calcaric cambisol. Prior to physicochemical analyses, the soil samples were air-dried at room temperature, ground, and passed through a150-μm nylon sieve (100 mesh). The soil pH, cation exchange capacity and organic matter were analyzed as described previously, and the results were shown in Table S1 in Supplementary Material.

2.2. As(III) oxidizing bacterium

The As(III)-oxidizing bacterium strain YZ-1(CGMCC No.8329) was used in this work. This strain is alkaligenous, and exhibits high resistance to As(III) (1500 mg L^{-1} As(III) in solution) and strong As(III) oxidation ability, which oxidized 74.6% of 100 mg L^{-1} As(III) into As(V) within 72 h (data not shown). Prior to use, the strain cells were grown to early exponential phase in LB medium.

2.3. Microbial As(III) oxidation by stain YZ-1

A batch test was conducted to investigate the capability of As(III) oxidation of strain YZ-1 in the As-contaminated soils. 20 g of Soil A (or Soil B) was placed in a 150-ml conical flask, and mixed with 100 mL nutrient medium containing 5×10^7 cfu mL^{-1} of the stain YZ-1. Then, the mixture was incubated in a shaker at 30 °C. During the incubation, the moisture content of soil was adjusted every 2 d by adding sterile deionized water equivalent to the loss of water. Soil samples were withdrawn at 0, 1, 3, 5, 7 and 10 d, air dried at room temperature, and then passed through a 100-mesh sieve. The sieved soil samples were used for determination of As content. Meanwhile, the control experiment was performed with the same procedure but without addition of strain YZ-1. All the experiments were carried out in triplicate.

Various culture factors affecting As(III) oxidation of strain YZ-1 in contaminated soil were examined. The experiments were performed as described above. The following conditions were evaluated: (i) Carbon source: 5 g L^{-1} of glucose or sucrose, and different concentrations of glucose (3–12 g L^{-1}); (ii) Nitrogen source: 5 g L^{-1} of yeast extract or ammonium nitrate, and different concentrations of yeast extract (0–12 g L^{-1}); (iii) pH: varied from 6 to 10.

2.4. Bio-SCH immobilization

Bio-SCH was synthesized through the oxidation of ferrous sulfate by *Acidithiobacillus ferrooxidans* (CGMCC No.1.6369) and characterized as described by Chai et al. (2016). In the test of As immobilization in contaminated soil by Bio-SCH, 20 g of Soil B was