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Immobilizing of heavy metals in sediments contaminated by nonferrous metals smelting plant sewage with sulfate reducing bacteria and micro zero valent iron

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HIGHLIGHTS

- mFe^0 + SRB system was effective for practical dredging sediment remediation.
- mFe^0 + SRB system formed more stable mineral phases than contrast tests.
- More than 90% of soluble Cu, Cd, Zn and Pb were removed in mFe^0 + SRB system.

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ABSTRACT

Biological treatment method using sulfate reducing bacteria (SRB) is considered as the most promising alternative for heavy metals stabilization and immobilization due to its low cost and high efficiency. In this study, a series of immobilization experiments were conducted with heavy metals contaminated aquifer sediment under three conditions: combined micro zero valent iron with sulfate reduction bacteria (mFe^0 + SRB), individual sulfate reduction bacteria (SRB) and micro zero valent iron (mFe^0) only. The aim of this study was to investigate the immobilization efficiency of Cu, Cd, Zn and Pb under these three conditions (mFe^0 + SRB, SRB, mFe^0). The results presented that the leaching test performance of mFe^0 + SRB was much better than the contrast tests, the removal efficiencies of Cu, Cd, Zn and Pb (mFe^0 + SRB) were 100%, 98.5%, 90.69%, 100%, respectively. The heavy metal stability of the treated sample was also evaluated with sequential metal extractions experiments, Cu, Cd, Zn and Pb were found to form more stable mineral phases (for example, residual fraction and oxidizable fraction) in mFe^0 + SRB conditions. X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) were used to characterize the mineral phases of treated sediment. According to XRD and XPS characterization, heavy metal may existed in the form of FeO, FeOOH, PbCd, PbZn, ZnS, Zn, CdO, CuZn, and CuS. This study demonstrates that mFe^0 + SRB could be considered as an efficient way for immobilization of multi heavy metals polluted sediment dredged from Xiawangang River.

1. Introduction

Xiawangang River region is one of the most seriously heavy metals polluted areas in China because of long-term inputs of nonferrous metal industrial wastewaters and municipal sewage. Min Jiang and his co-worker reported that this area was severely polluted by Cu, Cd, Zn and Pb, and the total concentrations of these metals all highly exceeded the Chinese environmental quality standard, especially for Cd [1]. Recently, local government has carried out a series of environmental dredging projects to get rid of the heavy metals pollution and protect the water quality of Xiangjiang River. However, how to safely and economically dispose the huge number of dredging sediment became another environmental issue [2].

Various techniques have been developed for the remediation of heavy metals in sediments, including soil washing, thermal extraction, ion exchange, electrokinetic treatment, reverse osmosis, membrane technology, evaporation recovery, solidification, plasma vitrification and bioremediation [3]. Comparing with other techniques, bioremediation technology is more economically feasible, easier to apply to contaminated sites and causes less secondary pollution [4]. And it is able to applied both ex-situ and in-situ to

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the design of economical bioremediation process, because microorganisms have a generic character for survival strategies in heavy metal polluted habitats, their specific microbial detoxifying mechanisms such as bioaugmentation, biotransformation, biomineralization or biosorption [5–7]. Nowadays many studies have demonstrated the feasibility and efficiency of heavy metal remediation by microorganism [8–10]. However, biological process can also mobilize metal by increasing its solubility. A newly research found that the microbial sulfate reduction played a key role in the mobilization of As from Fe-rich aquifer sediment under anoxic conditions, because most of As initially present in the sediment had been leached out in the form of mobile thio-As species [11,12]. To prevent leaching of metals from sediments into the water phase by microorganism, metals should be immobilized by biosorption, forming of metal-binding molecules, reductive precipitation, sulfide precipitation or phosphate precipitation [13]. Sulfate-reducing bacteria (SRB) are the most commonly microorganisms that have been used for bioremediation [14–16]. There are more than 30 genera of SRB having been reported, including gram-negative mesophilic bacteria, gram-positive mesophilic bacteria, and members of other thermophilic groups [17]. SRB are widely distributed in the environment, including paddy soils, sea water, thermal springs, oil field water and sediments. Biological treatment with SRB has been considered as the most promising alternative for heavy metals remediation due to its low cost and high efficiency [18]. The mechanisms of heavy metals remediation by SRB include precipitation of metal with H_2S produced by SRB and biosorption of metal onto SRB culture surface by cell wall and extracellular polysaccharides (EPS) [19]. SRB are chemoautotrophic bacteria, they use sulfate as the terminal electron acceptor and consequently convert sulfate to sulfide [20]. Although, SRB have been testified efficiently for heavy metal remediation in laboratory [8], there were still little cases of successful field trials [21]. An important reason of this is that microbial processes generally require optimal environmental parameters (pH, redox potential, sulfate, temperature, suitable electron donor) for sustainable growth, which often do not meet at natural conditions. In that case, additional reactive materials need to be provided to maintain a suitable growth environment for the bacteria [22,23]. Using Fe^0 for dissolved water contaminant remediation has been demonstrated in both laboratory and field tests [24–26]. The preliminary idea of using metallic iron for the oxidative contaminants was based on the contaminant reduction through electron transfer between Fe^0 with oxidation [27]. Toxic metal should be remedied by Fe^0 through a combination of surface adsorption, precipitation and co-precipitation with iron oxides [28]. In addition to direct contaminant reduction at the surface, Fe^0 particles may also be able to stimulate SRB by depleting O_2, lowering the redox potential, and producing water derived H_2 via corrosion reactions which can also be used as an electron donor for SRB [23,29–31]. Formation of stable metal-sulfide precipitates through sulfate reduction has been well documented [32–34]. Hence, an integrated Fe^0 + SRB process could be of greater interest in heavy metal remediation field. The particle size and dosing of Fe^0 are highly important for optimizing the remediation process. Kumar and his co-worker reported that, micro sized Fe^0 particles (mFe^0, with an average particle size of 20–40 μm) in combination with glycerol were found to enhance microbial sulfate reduction more than granular sized Fe^0 particles (gFe^0, with an average particle size of 0.25–2 mm) and nano sized Fe^0 particles (nFe^0, with an average particle size of 70–100 nm) [22]. Based on the research results, this study was to explore the feasibility and efficiency of combining SRB with micro zero valent iron for immobilizing of multi-heavy metals in sediments contaminated by nonferrous metals smelting plant sewage. The objective of this research was to discover an economical and effectively immobilizing technique for actual heavy metals polluted sediment. The results of this study may provide a new way for dealing with Xiangjiang River sediments contaminated by multi-heavy metals.

2. Materials and methods

2.1. Fluvial sediment

The sediment samples used in this study were collected from wastewater drainage outlet at Xiawangang Port, Xiangjiang River, Hunan Province, China. This area is one of the most serious heavy metals polluted areas in China. Sediment samples were acquired using a shovel and transported to the laboratory in four sealed polyethylene bags. In laboratory, the sediments were air dried naturally for four months, then grinded and sieved through a 100 mesh sieve before it stored for subsequent experiments. The total concentration of heavy metals was analyzed with Aqua-regia method. Firstly, 0.1 g lyophilized sample sieved through a 100 mesh nylon screen was put in a 50 mL PTFE centrifugal tube. Then 4 mL aqua regia was added and put it at fume hood soak overnight. Secondly, the obtained material was dissolved in the electric heat dispelling furnace under different conditions, 80–90 °C or 30 min, 100–110 °C for 30 min, 120–130 °C for 1 h, and then cooled at a ventilated place. Lastly, 1 mL $HClO_4$ was added into the samples and dissolved under various conditions, 100–110 °C for 30 min, 120–130 °C for 1 h, and then transferred to 20 mL volumetric flask after cooled and shook well for the determination of total heavy metals.

2.2. Microbiological cultivation and identification

The activated SRB was collected at the landfill leachate of sewage treatment plant in Zhuzhou city, Hunan Province. The bacteria were cultivated in closed infusion bottles using standard procedures reported in the literature (Table 1) at 37 °C [35]. The pH value of medium was adjusted to approximately 6.2 with NaOH (1 mol/L). 90 mL of medium was added into a 100 mL anaerobic bottle, which was then purged with high purity N_2 for 10–15 min to reduce the dissolved oxygen. Then 10 mL of landfill leachate was put into the medium in the anaerobic bottle, which was purged again for 10–15 min with N_2 [36]. The existence of SRB was determined by the direct observation of the formation of black precipitate (ferrous sulfide). After 3 days, it was time for the bacterium to be inoculated to another new prepared medium with the ratio 1:10 (v/v), the enriched SRB culture was obtained by repeating the process. SRB identification was also discussed in this paper. The DNA extraction process and the operation process of PCR-DGGE were the same as literature [37]. The product was sent to Jinsite Biotechnology Company (Beijing, China) to be sequenced.

2.3. Micro sized zero valent iron particles

Micro sized zero valent iron particles, with the purity of 99.9%, containing approximately 0.002%Al, 0.001%Ca, 0.002%Mg, 0.001% Cu, 0.001%Mn, 0.002%Na, 0.001%Co, 0.001%Ni, 0.002%Si, 0.001%

Table 1
Chemical composition of medium for SRB enrichment.

Composition	Concentration (g/L)	Composition	Concentration (g/L)
KH_2PO_4	0.5	Sodium lactate (70%)	3.5
NH_4Cl	1.0	Yeast extract	1.0
$CaCl_2·6H_2O$	0.1	$FeSO_4·7H_2O$	0.01
Na_2SO_4	0.5	Vitamin C	0.5
$MgSO_4·7H_2$	2.0		