Journal of Hazardous Materials 359 (2018) 290–299

Contents lists available at ScienceDirect

Journal of Hazardous Materials

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

Nanoremediation of cadmium contaminated river sediments: Microbial response and organic carbon changes

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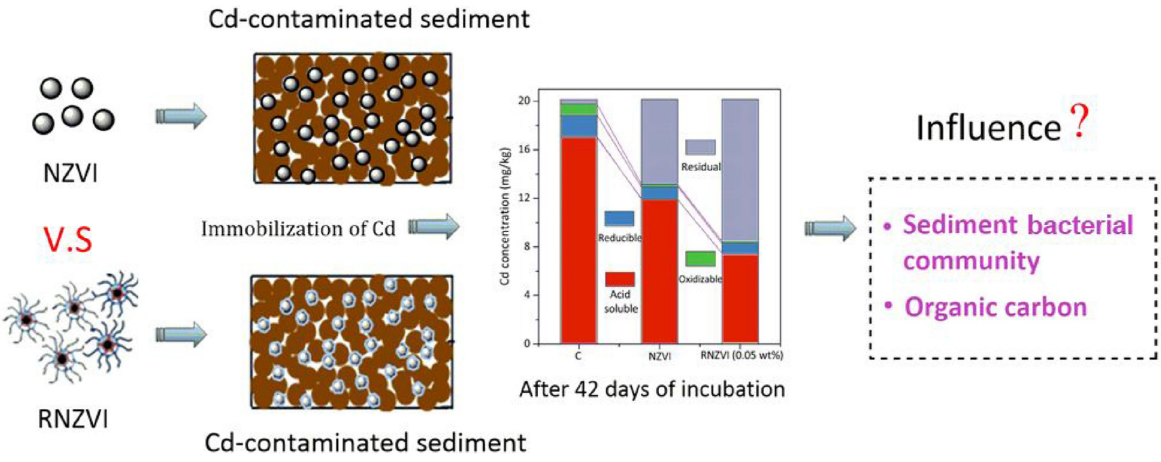
GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:
Nanoscale zero-valent iron
River sediment
Cadmium
Bacterial Community
Organic carbon

ABSTRACT

The application of nanomaterials to contaminated river sediments could induce important changes in the speciation of heavy metals with potential impacts on ecosystem. Here, rhamnolipid (RL)-stabilized nanoscale zero-valent iron (RNZVI) was conducted to test its potential performance in changing the mobility and speciation of cadmium (Cd) in river sediments, with consideration of the influences of microbial community and organic carbon (OC). Compared to NZVI, RNZVI was more effective in transforming labile Cd to stable fraction with a maximum residual concentration increasing by 11.37 mg/kg after 42 days of incubation. Bacterial community structure was tracked using high-throughput sequencing of 16S rRNA genes. Results indicated that the application of RNZVI changed the bacterial community structure and increased the relative abundance of Fe(III)-reducing bacteria, which could redistribute Fe combined Cd into a more stable Fe mineral phase. The contents of OC were gradually decreased and became stable, might resulting from OC

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https://doi.org/10.1016/j.jhazmat.2018.07.062
Received 6 February 2018; Received in revised form 12 July 2018; Accepted 13 July 2018
0304-3894/

bioavailability's being stimulated by RNZVI through changing the bacterial community composition. This study indicates that abiotic process (i.e., from reaction with NZVI) and biotic process fueled by RNZVI lead to the immobilization of Cd in river sediments.

1. Introduction

River sediment contamination caused by heavy metals has become a widespread environmental problem because of their toxicity and persistence [1]. Cadmium (Cd) widely spreads in river sediments and enters into the food chain through incorporation easily, which pose a potential hazard to human health [2,3]. What's more, increasing risk of cancer, such as in breast, bladder and lung is statistically linked with Cd contamination based on newer data on human exposure to Cd in general Cd contamination [4]. Therefore, the development of remediation technology for the effective immobilization of Cd is urgently required.

Nanoscale zero-valent iron (NZVI) has been proven to be engineered nanomaterials which are promising for the removal of various pollutants, such as heavy metals, chlorinated compounds, and others [5]. However, NZVI tends to aggregate rapidly because of its magnetic property and small size effect, which significantly reduces its reactivity towards the contaminant [6]. In order to solve the problems associated with aggregation and reactive particles, NZVI particles are often coated with surface modifiers [7]. Rhamnolipid (RL) is glycolipid anionic biosurfactants and produced by various strains of *Pseudomonas aeruginosa* and related species [8]. Meanwhile, RL has surface/interfacial activities and multifunctional as well as eco-friendly properties with a variety of potential applications [9,10]. In the study of Basnet et al., rhamnolipid was proved to be efficient compared with carboxymethyl cellulose and soy protein stabilized Fe/Pd nanoparticles, which was significantly higher mobility and reactivity [6]. So, the RL may be promising to stabilize NZVI for immobilization of Cd in contaminated sediments.

Considering that the mobility and toxicity of metals strictly rely on their speciation [1,11], it is not completely reliable to determine their mobility and toxicity based on the total concentrations of the metals [12]. Selective extraction method is adopted to measure the mobility of metals by analyzing their different forms [1]. In addition, microbial communities can also directly reflect the toxicity and bioavailability of heavy metals, and better show the heavy metal stabilization effects [13]. However, the impact of nanomaterials on microbial communities is also a controversial topic. Tilston et al. [14] found that NZVI addition could change the composition of soil bacterial community, and decreased the activity of certain microorganisms. The cell membranes of *E. coli* were destroyed when it exposed to NZVI, which may cause the inactivation or enhance the sterilized effects of iron [15]. Conversely, Kirschling et al. [16] demonstrated NZVI had no negative impact on total bacterial abundance in trichloroethylene contaminated aquifer materials, and polyaspartate coated NZVI increased bacterial populations by an order of magnitude compared with controls. Kocur et al. [17] found that microbial community was shifted, with most notable increases in the dechlorinating genera *Dehalococcoides* and *Dehalogenimonas* following carboxymethyl cellulose (CMC) stabilized NZVI injection. However, it is unclear that the change of bacterial community in Cd contaminated sediments due to the addition of iron nanomaterials.

Organic carbon (OC) in buried sediments plays an important role in the global carbon cycle [18,19]. Research shows microbes not only promote the turnover of soil organic carbon, but also are directly involved in the fixation of soil organic carbon [20,21]. The fixation of organic carbon has proved to be significantly affected by the changes of microbial community composition and activity [22]. Previous studies have highlighted that heavy metals affected the growth, shape or metabolism [23], and damaged the integrity of cell membranes. Those physiological changes brought about the reduction of microbial diversity and higher ratios of microbial C to organic C [23,24]. But there are no more details reported on the relationships among metal fractions, microbial community and organic carbon during remediation of Cd contaminated river sediments by nanomaterials up to date.

The aim of this study was to investigate how NZVI and RNZVI (modified with different concentrations of RL) influence Cd mobility in Cd-bearing sediment, based on the changes of bacterial community and organic carbon, for purpose of improving our understanding of the potential impact of nano-treatments on the fate of metals. Therein, high-throughput sequencing was adopted to reveal the change of bacterial community by the gene encoding 16S rRNA.

2. Materials and methods

2.1. Sediment characteristics

Sediment samples (0–20 cm) were collected from the Xiangjiang River (Changsha, Hunan province in China). Such sampling site was selected because this area is rich in nonferrous metals and the wastewater from industrial activities or intensive mining are massively discharged to the river and deposited in sediment, which would require remediation actions [25]. Immediately after collection, some basic physicochemical properties of the sediment samples were determined. Sediment samples were sieved ($< 150\,\mu m$) and stored at 4 °C until the experiments. Water pH of the sediment was 7.71; the content of organic matter was 17.54 g/kg; cation exchange capacity was 12.79 cmol/kg. More sediment characteristics are presented in Table S1. The sediment samples were dispelled according to US EPA standard method (EPA3050B, 1996). Cd concentration was measured by atomic absorption spectrometry after acid digestion of sediment samples.

2.2. Nanomaterials

The RNZVI nanoparticles were synthesized according to liquid-phase methods under the reduction of Fe^{2+} to Fe° by borohydride solution with RL as a stabilizer [26]. Firstly, 0.496 g 25 mL of ferrous sulfate heptahydrate (Sinopharm Chemical Reagent Co., Ltd) solution was mixed with various concentrations of RL (0.01, 0.03, 0.05, 0.1, 0.2 wt%) solutions (Zijin Co. Ltd, Huzhou, Zhejiang, China) and stirred for 30 min in three-necked flasks. Secondly, 0.136 g 25 mL of sodium borohydride solution was added to the mixture drop by drop with constantly stirring for 20 min, while the molar ratio of BH_4^-/Fe^{2+} was 2.0 [27]. The whole preparation process was conducted under the atmosphere of N_2. Under the same conditions, NZVI was synthesized without the addition of RL.

Scanning electron microscopy (SEM) (S4800, Japan), transmission electron microscope (TEM) (FEI Tecnai G2 F20, USA), X-ray diffraction (XRD) patterns and fourier transform infrared (FTIR) (NICOLET, USA) were applied to test the characterization of nanomaterials (Fig. S1). The results showed that RL stabilized NZVI was well dispersed and iron oxides form was not found in RNZVI XRD spectra. Further details on sample characterizations are provided in the Supporting Information.