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

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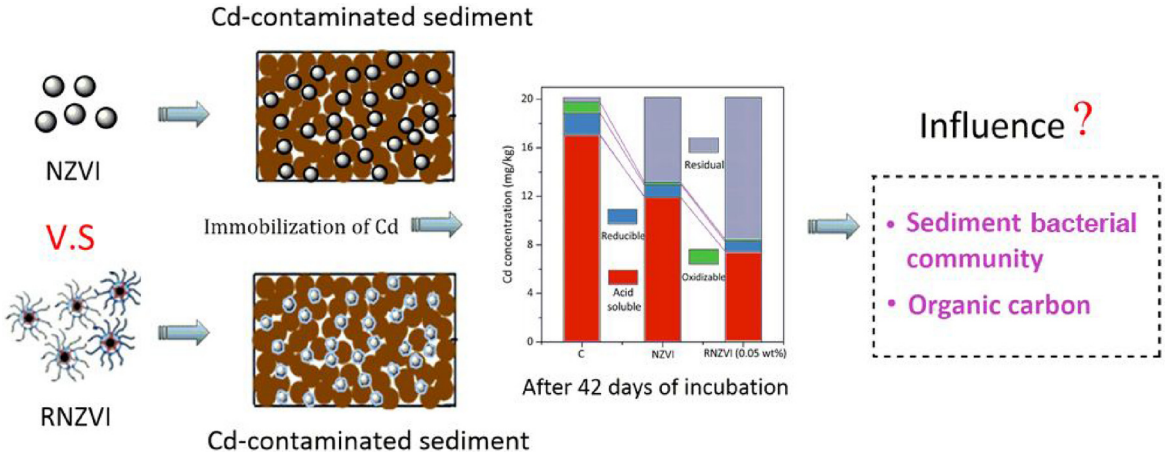
GRAPHICAL ABSTRACT



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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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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 μm) 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.

2.3. Experimental setup

0.5 g of sediment samples were placed into 50 mL centrifuge tubes with screw caps, and adding 2.5 mL of the RNZVI (0, 0.01, 0.03, 0.05, 0.1, 0.2 wt%) suspension. The mixture was performed in triplicate to analyze the fractionation of Cd, bacterial community diversity and organic carbon. The suspension-to-sediment ratio was 5:1 (mL/g). To investigate the possible effects of RL on Cd fraction, RL (0.05 wt%) solution was also added with the same ratio. The iron concentration in NZVI suspension was 0.67 g/L. This experiment was controlled without pH adjustment and stirring. In the control group, NZVI and RNZVI suspension were replaced by ultra-pure water (18.25 MΩ cm, Barnstead D11911) under the same conditions. The sediment samples were treated for day 0, 7, 14, 21, 28, 35, 42 and then centrifuged at 4000 r/min for 20 min, the sediment samples of the supernatant were separated and kept for the further measurement.

2.4. Fractions of Cd in the samples

The speciations of Cd in the samples were measured by the method of European Community Bureau of Reference (BCR) sequential extraction [28]. Four different fractions are considered: i) acid soluble fraction (i.e. exchangeable and carbonate bound fractions), extracted with 0.11 M acetic acid, pH 2; ii) reducible fraction (i.e. iron and manganese oxides fraction), extracted by 0.5 M hydroxylammonium chloride, pH 1.5; iii) oxidizable fraction (i.e. organic and sulfide fraction), extracted with hydrogen peroxide 30% and treated with 1 M ammonium acetate, pH 2, and iv) residual fraction (i.e. the metals in the crystalline lattice of primary and secondary minerals), that remains in the solid, extracted by aqua regia. In above experiments, the extract fluid of each step was decanted and then filtered through a 0.45 μm filter membrane, and the filtrate was measured by atomic absorption spectrometry.

2.5. DNA extraction

DNA analysis was performed with sediment samples from contact time 42 days. Total DNA was extracted from 0.5 g of sediment samples using the FastDNA SPIN Kit for Soil (MP Biomedicals), according to the protocol described by the manufacturer. DNA concentration and quality were determined using spectrophotometry (NanoDrop Inc., USA), which measured the absorbance of the samples at 260 nm.

2.6. 16S rRNA amplification and high-throughput illumina sequencing

The V4 region of bacterial 16S rRNA genes was amplified by using the universal primers 338 F (5′-ACTCCTACGGGAGGCAGCAG-3′) and 518R (5′-ATTACCGCGGC TGCTGG-3′) [29]. DNA sample was amplified in 30 mL reaction mixtures following PCR program: 1 min of initial denaturation at 98 °C; 35 cycles of denaturation at 98 °C for 10 s, annealing at 50 °C for 5 min, extension at 72 °C for 30 s; a final extension at 72 °C for 5 min. Replicate amplicons were pooled for purification with an E.Z.N.A.® Gel Extraction Kit (OMEGA Biotek, USA). A single composite sample was prepared by combining approximately equimolar amounts of purified PCR products from each sample and applied to Illumina MiSeq platform of ORI-GENE (Beijing, China).

2.7. The content of organic carbon

Sample organic carbon was determined according to Nelson et al. [30] and the OC was calculated by the equation presented as follows:

$$OC = \left[\frac{0.5 \times (V_0 - V) \times 0.001 \times 3.0 \times 1.33}{m}\right] \times 1000 \quad (1)$$

Where V_0 is the $FeSO_4$ consumption of the blank, the V is the $FeSO_4$ consumption of the sample, m is the weight of the sediment samples.

2.8. Statistical analysis

The means and standard deviations (SD) were calculated using Microsoft Office Excel 2003. PRIMER 6.0 was used to test the similarity of bacterial community composition by using the cluster analysis (based on BrayeCurtis similarity). Principal component analysis (PCA) was calculated to measure the distributions of bacterial communities and the different RNZVI concentrations using CANOCO software V4.5. Pearson's coefficients were applied to evaluate the correlations of the different fraction of Cd, phylotype abundance data and OC. Only phylotypes that were present in more than 5% of the samples in each species were considered.

3. Results and discussion

3.1. Changes in Cd fractionation during incubation

Generally, metals in residual fraction that combined with the crystalline lattice of primary and secondary minerals, are considered to be stable [31,32]. In contrast, it is more easy for metals in non-residual fractions to be mobilized by biotic and abiotic changes, which has higher bioavailability with potential pernicious influences on ecosystem health [1,33]. The concentration of Cd in the sediment was about 20.14 mg/kg. Changes in Cd fraction were presented in Fig. 1. It was found that Cd mainly existed in the acid soluble fractions, taking up to 84.90% of the total concentration (Fig. 1(a)), indicating its higher mobility and bioavailability [34]. The metal speciation was accordingly changed to different degrees as RNZVI was applied to the sediment samples. The concentrations of acid soluble of Cd decreased from 17.07 mg/kg to 11.92, 8.10, 8.25, 7.43, 8.31 and 8.73 mg/kg with the treatment of RNZVI (NZVI coated with RL of various concentrations from 0, 0.01, 0.03, 0.05, 0.1, 0.2 wt%) after 42 days of incubation. The concentrations of reducible and oxidizable of Cd maximum decreased by 0.89 mg/kg and 0.85 mg/kg, respectively. The shift of Cd from the non-residual fraction towards the residual fraction was also favored by incubation time. The residual fraction of Cd was significantly increased from initial 0.38 mg/kg to 6.99, 10.88, 10.83, 11.74, 10.75 and 10.30 mg/kg in the presence of NZVI, 0.01 wt% RNZVI, 0.03 wt% RNZVI, 0.05 wt% RNZVI, 0.1 wt% RNZVI and 0.2 wt% RNZVI, respectively. From Fig. 1(b) and 1(c), it was demonstrated that RNZVI was very effective in reducing Cd mobility compared with NZVI, and the content of residual Cd in sediment samples treated with NZVI and 0.05 wt% RNZVI was 18.60 and 31.23 times higher than that of the control group, respectively. Corresponding, the decreased times of non-residual of Cd with the treatment of 0.05 wt% RNZVI were also higher than NZVI. We also found that the decreased times of acid soluble and oxidizable fraction of Cd were higher than reducible fraction of Cd (Fig. 1(c)). It was probably because RL had higher complexation efficiency for exchangeable (acid soluble) and organic fraction (oxidizable) of metal [35]. In our study, the RL treated samples without any addition of NZVI showed almost no effects on the percentage of residual fraction in sediment during 42 days (Fig. S2). Moreover, with the increased concentration of RL from 0.05 wt% to 0.2 wt%, the content of residual fraction of Cd did not increase further but instead decrease from 11.74 mg/kg to 10.30 mg/kg. And this was ascribed to the decrease in negative surface charge resulting from an increasing concentration of

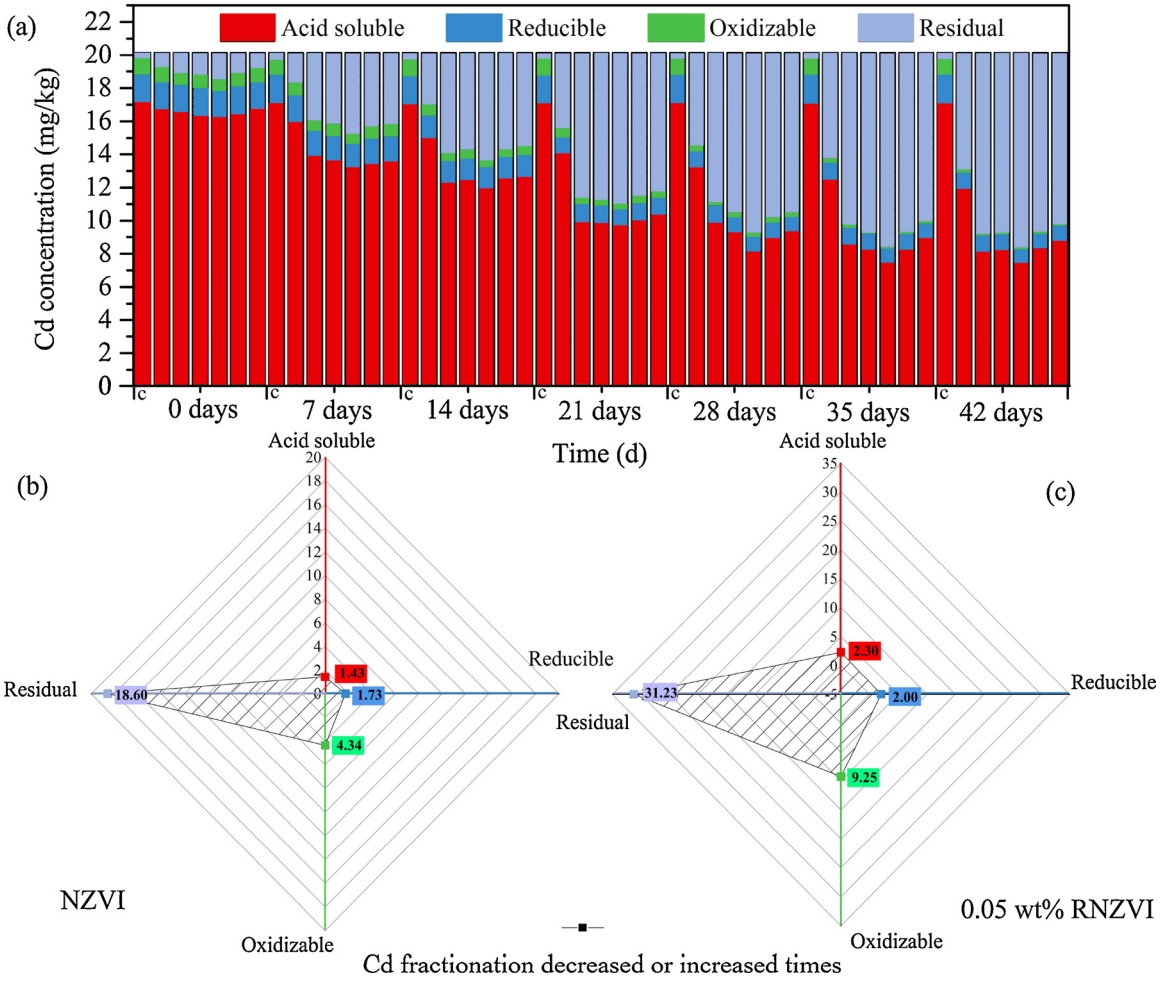

Fig. 1. (a). Fractioning of Cd in sediment with the addition of RNZVI (0, 0.01, 0.03, 0.05, 0.1, 0.2 wt%) and varied as the incubation proceeded. C: control group; (b). Different fraction of Cd decreased or increased times with the treatment of NZVI at 42 days compared to control group; (c). Different fraction of Cd decreased or increased times with the treatment of 0.05 wt% RNZVI at 42 days compared to control group.

RL along with the entanglement or cross-linking of the RL molecules on the surface of RNZVI [36,37]. The change in total Cd did not happen in the course of the experiment. Changes in the fraction of metals indicate that the addition of RNZVI resulted in an alleviating direct toxicity and decreasing the mobility and bioavailability of Cd [64–66].

The mechanisms of Cd immobilization by NZVI are likely adsorption or complexation but not direct reduction due to Cd has a standard potential (E° = -0.40 V) close to that of Fe. During the preparation of NZVI, iron oxidation produces surface hydroxides in proximity to FeOOH [36]. Similar to the metal ion adsorption on Fe (III) (oxyhydro) oxide, which including goethite, ferrihydrite and lepidocrocite, this surface oxide layer provides surface sites for coordination with Cd. Muehe et al. [38] reported that Cd was mainly related to Fe, indicating that Cd was partly adsorption or complexation with Fe(III) minerals. The surface reactions of Cd immobilization by NZVI may be described by the following equations:

$$FeO^{-} + Cd^{2+} \rightarrow FeOCd^{+} \quad (2)$$

$$FeOH + Cd^{2+} + H_2O \rightarrow FeOCdOH + 2H^{+} \quad (3)$$

Moreover, hydroxyl groups and carboxyl group constituted the structure of RL makes it possible to form chelate with Cd [35]. According to previous studies, RNZVI can also be applied to actual polluted waterbody. The shortcoming is that there may be competition for contaminant between the reactive sites on the NZVI and sorption sites on the polymer coating. However, the loss of reactivity is not significant and must be weighed against benefits provided by the polymer coating.

3.2. Shift of bacterial community composition and structure under nanomaterials application

A total of 278,787 valid reads and 253,156 OTUs were obtained from the 7 samples through Illumina MiSeq analysis (Table S2). These OTUs were assigned to 25 different phyla, and the rarefaction curves tended to approach the saturation (Fig. S3). The relative abundances of the bacterial 16S rRNA gene at the phylum and class level were observed to study the affiliated composition of the microbial community (Fig. 2). In the control group, *Proteobacteria, Acidobacteria, Bacteroidetes* and *Gemmatimonadetes* were the most 4 predominant bacterial phyla accounting for 29.25%, 24.04%, 11.61% and 11.09% of total 16S rRNA

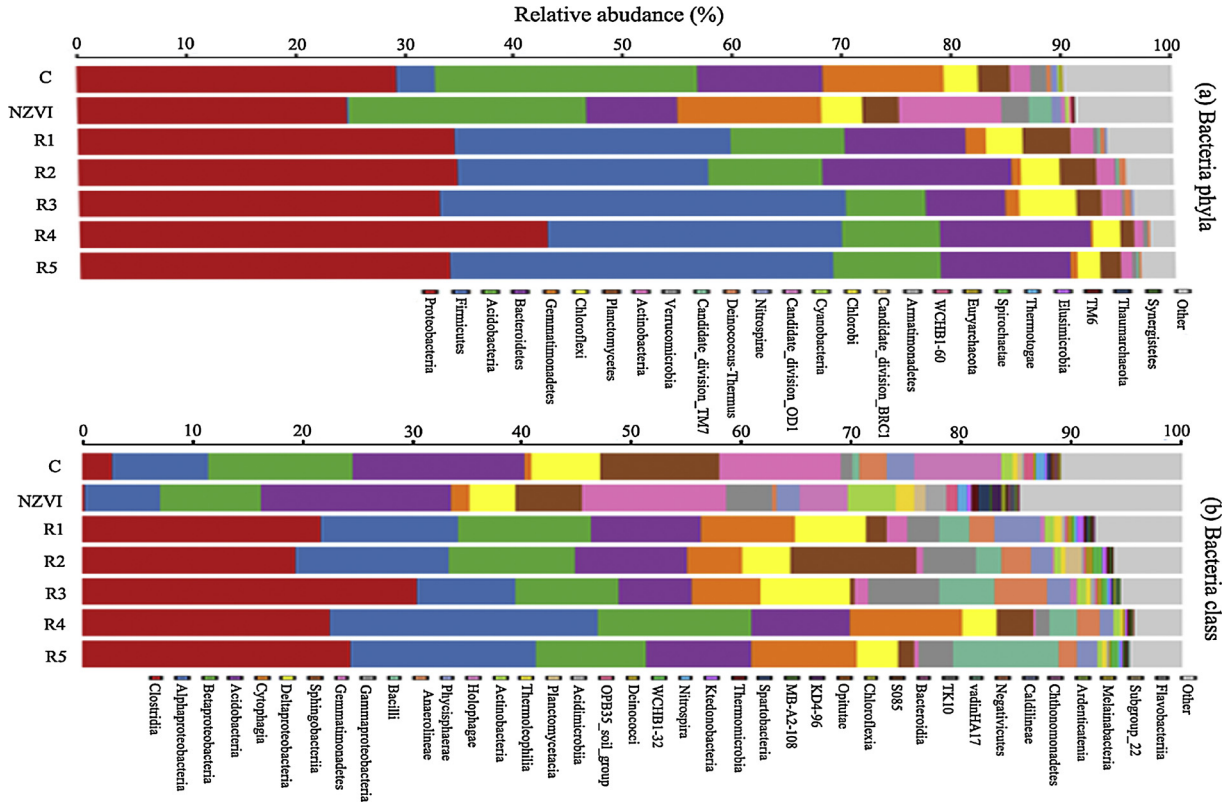

Fig. 2. Relative abundance of bacterial 16S rRNA gene at phylum level (a) and class level (b). C: control group; R1: 0.01 wt% RNZVI; R2: 0.03 wt% RNZVI; R3: 0.05 wt% RNZVI; R4: 0.1 wt% RNZVI; R5: 0.2 wt% RNZVI.

gene sequences, respectively (Fig. 2a). The abundance of the phyla *Firmicutes, Chloroflexi, Planctomycetes, Actinobacteria* and *Verrucomicrobia* composed 12.79% of the community. Following added of NZVI and RNZVI (0.01, 0.03, 0.05, 0.1, 0.2 wt%), the microbial community composition shifted noticeably. Compared to control group, the relative abundance of *Actinobacteria* organisms significantly increased from 2.05% to 9.33% in NZVI community. Studies have shown that *Actinobacteria* has also been found in groundwater samples and has been classified as Fe(III) reducing bacteria (FeBR) [39]. Interestingly, *Proteobacteria* and *Firmicutes* (32.96%–42.76% and 22.91%–37.24%, respectively) became dominant and the relative abundance of *Proteobacteria* and *Firmicutes* were higher than control group and NZVI treatment group after amendment with RNZVI. The relative abundance of *Firmicutes* was significantly increased in RNZVI treatment groups. This is mainly due to the addition of RL. Li et al. [40] reported that bacterial families in the phylum *Firmicutes* were riched relying on the shortchain fatty acid improved. The abundance of the *Acidobacteria* phylum decreased in the RNZVI (0.01, 0.03, 0.05, 0.1, 0.2 wt%) treatment (10.43%, 10.49%, 7.26%, 8.92% and 9.81%, respectively), as compared to the control (24.04%) and NZVI (21.85%). *Acidobacteria* is a cosmopolitan soil or sediment bacterial phylum, that generally consist of oligotrophic organisms [41]. Kielak et al. [42] pointed out that they utilized complex carbon substrates, which were also likely to be present in the native soil organic matter. The decrease of the abundance in *Acidobacteria* decreased was probably due to they may be able to compete with the fast-growing *Proteobacteria* for labile C [42], or they might start with the consumption of lysed cells of opportunistic bacteria under the stimulus of RNZVI (0.01, 0.03, 0.05, 0.1, 0.2 wt%). The abundance of the *Gemmatimonadetes* was also inhibited by RNZVI. Tapia-Torres et al. [43] demonstrated that *Gemmatimonadetes* was more suitable for survival in desert scrub and infertility land. Thus, the abundance of the *Gemmatimonadetes* was decreased by the addition of RNZVI.

In Fig. 2(b), we can see that the relative abundance of *Clostridia* (21.76%, 19.33%, 30.50%, 22.66% and 24.40%) and *Alphaproteobacteria* (12.44%, 14.06%, 9.05%, 24.27% and 16.99%) of class level were significantly increased in the RNZVI treatment compared to control (2.75%) and NZVI (8.74%) group. The relative abundance of *Cytophagia* and *Bacilli* were also stimulated by RNZVI (0.01, 0.03, 0.05, 0.1, 0.2 wt%). *Proteobacteria* affiliated class were mostly *Alphaproteobacteria*, *Betaproteobacteria*, *Deltaproteobacteria* and *Gammaproteobacteria*. *Clostridia*, *Cytophagia* and *Bacilli* were affiliated to *Firmicutes* (Fig. S4). The similarities of microbial community structures in the sediment samples were discussed at class level by hierarchically clustered heatmap analysis (Fig. 3). It was found that the relative abundance of bacteria in NZVI treatment group was higher than other samples, which can be confirmed by chao 1 index (Fig. S5). There is some striking similarity of bacteria species among different RNZVI (0.01, 0.03, 0.05, 0.1, 0.2 wt%), and there is a relatively uniform composition of species in the community. NZVI and control group showed the similar performance.

In particular, the relative abundance of sulfate reducing bacteria assigned to the families *Desulfuromonadaceae* (affiliated to *Proteobacteria*) increased significantly in RNZVI treatment group

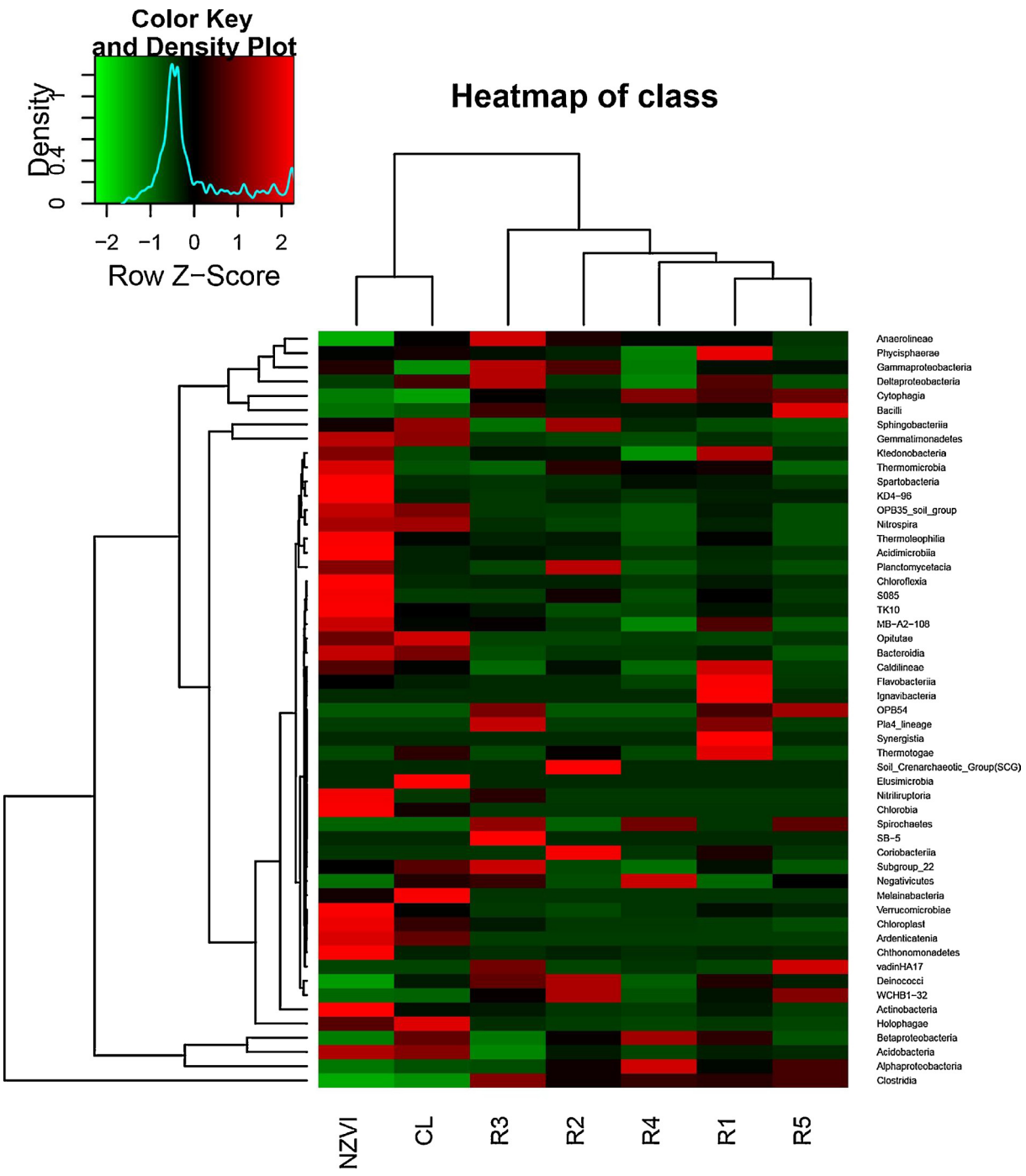

Fig. 3. Hierarchical cluster analysis of microbial communities among the 7 samples. The Y-axis is the clustering of the top 53 abundant class. Different samples were clustered based on complete linkage method. The color intensity of scale indicates relative abundance of each genus.

(accounting for 0.75%, 0.45%, 0.90%, 0.93% and 0.79%, respectively) compared with the control (0.002%) and NZVI (0%). The relative abundance of *Geobacteraceae* (affiliated to *Proteobacteria*) was also significantly increased (accounting for 0.85%, 0.91%, 1.92%, 1.23% and 1.18%, respectively) in RNZVI (0.01, 0.03, 0.05, 0.1, 0.2 wt%) compared to the control (0.03%) and NZVI (0.009%) (Fig. S6). The relative abundance of *Bacillaceae* (affiliated to *Firmicutes*) was also increased in RNZVI treated groups. Corresponding, the changes in bacterial genus abundances included *Desulfuromonas* (0.43%-0.90%), *Geobacter* (0.85%–1.92%) and *Bacillus* (1.29%–8.93%) in which RNZVI had a positive effect on the abundances increase (Table S3). In addition, the discrepancies in the microbial community were investigated by PCA. In

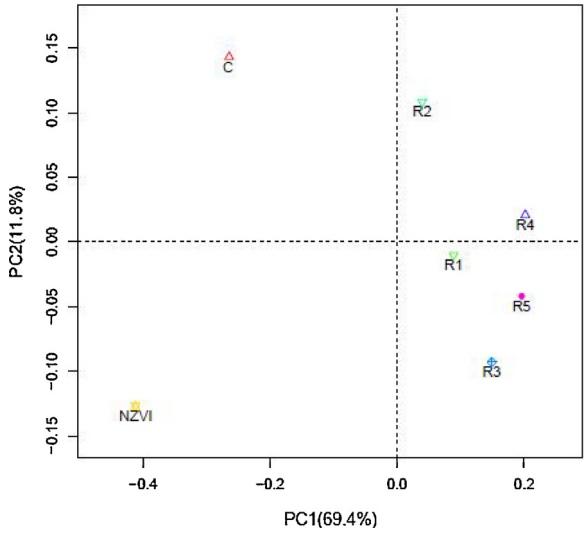

Fig. 4. Output of the Principal Component Analysis (PCA). Score plot of the first and second principal components (PC1, PC2, respectively). C: control group; R1: 0.01 wt% RNZVI; R2: 0.03 wt% RNZVI; R3: 0.05 wt% RNZVI; R4: 0.1 wt% RNZVI; R5: 0.2 wt% RNZVI.

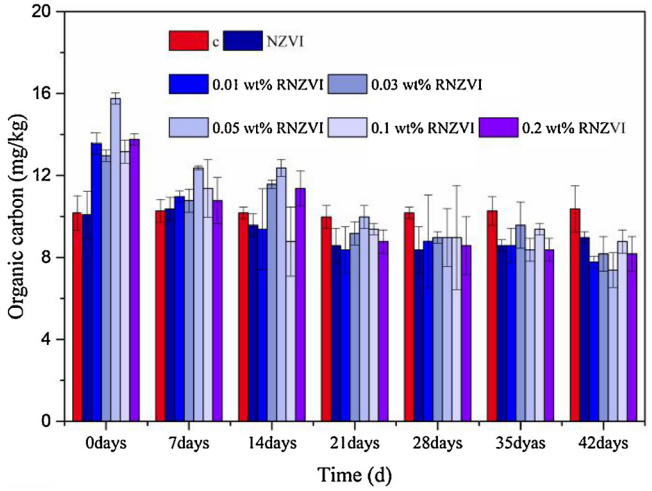

Fig. 5. The changes of organic carbon under different treatments of RNZVI (0, 0.01, 0.03, 0.05, 0.1, 0.2 wt%). Error bars indicate standard deviation (n = 3).

particular, in the score plot reported in Fig. 4, points were split into two groups along the axis of the First Principal Component (explaining 69.4% of the total variance), with microcosms with RL modified NZVI on the right and microcosms containing NZVI and control group on the left. The samples in RNZVI treatment group were clustered more closely, suggesting that the community composition of samples was more similar. The distance between NZVI and control group were relatively far, indicating that the microbial community composition was more different compared to the samples in RNZVI treatment group.

3.3. The changes of organic carbon in sediment samples

OC of the sediment samples, depending on the balance of organic matter accumulation and decomposition processes, represents a significant carbon pool and can act as sink or source of CO_2 [44]. Soil microorganisms are the primary decomposes of organic matter and drivers of soil nutrient cycling in agricultural systems [45]. From Fig. 5, it can be found that OC content was significantly decreased with the growing of incubation time, and gradually became stable at 28 days. This phenomenon can be ascribed to the adsorption or complexation of Cd to RNZVI changed the fraction of Cd into residual forms, and decreased the bioavailability of Cd, then, RNZVI (0, 0.01, 0.03, 0.05, 0.1, 0.2 wt%) could make the certain bacteria to decompose organic matter (both exogenous and indigenous) due to the change of sediment microbial population [46]. As described previously, species belonging to *Proteobacteria* were generally dominant in the consortium for biodegradation of organic compounds [47]. Tan et al. [48] reported that *Bacilli* and *Cytophagia* were dominant microorganisms in degradation of organic pollutants. *Clostridia* was represented as Gram-positive bacteria and responsible for degradation of organic compounds [49]. *Bacilli*, *Cytophagia* and *Clostridia* were all affiliated to *Firmicutes*. Some studies also revealed that the relative abundance of *Acidobacteria* was negatively correlated with soil carbon availability [50,51]. Wang et al. [52] also confirmed that the accelerated decomposition of specific soil C forms was due to elevated C input inducing shifts in soil microbial community composition. Moreover, in the process of microbial decomposition of OC, CO_2 was produced. With the increase of CO_2, HCO_3^- was formed and the pH of sediments was increasing quickly [53]. Due to the increase in pH, the precipitation of carbonate minerals will occur ($Cd(CdCO_3)$) [54]. The changes of organic carbon in sediment samples can be due to several reasons: the reduction of Cd availability decreased sediment toxicity and it could let the development of other bacterias; the increase and change in bacteria population increased the organic carbon availability.

3.4. Relationship among the mobility of Cd, sediment microbial community and organic carbon

According to previous studies, it was demonstrated that the mobility of Cd was affected by microbial Fe(III) reduction [38]. Zhang et al. [55] reported that the shifts in Cd mobility are directly influenced by Fe(III) reduction and the formation of new Fe mineral phases as postulated among others. *Proteobacteria* and *Firmicutes* are typically the dominant groups among the Fe(III)-reducing bacteria (FeRB) communities in paddy soils [56,57]. *Geobacteraceae* (affiliated to *Proteobacteria*) has often been considered to be the most common microorganism in the process of Fe(III) reduction [58]. Lovley et al. [58] reported that *Geobacter* was about 85% of the Fe reducing community in Italian paddy soil. Burkhardt et al. [59] also found the presence of *Geobacter* in anoxic enrichments of Cd-contaminated soil. In addition to the familiar *Geobacter* species, *Firmicutes* has also play a significant role to reduce Fe(III) [60,61]. *Bacillus* (affiliated to *Firmicutes*) have been proven to be capable of promote Fe(III) reduction [62]. *Clostridium* (affiliated to *Firmicutes*) have always been deemed to reduce Fe(III) by fermentation [61]. Moreover, *Acidobacteria* and *Actinobacteria* also have been demonstrated as rare FeRB phyla [63]. Generally, Fe(III) reduction is often followed with the reduction of sulfate by sulfate-reducing bacteria. Muehe et al. [38] reported that in the condition of lactate-/acetate-improved microcosms, decomposition of hydrogen sulfide into HS^-, then reacts with Cd^{2+}, forming CdS. They also demonstrated that Fe

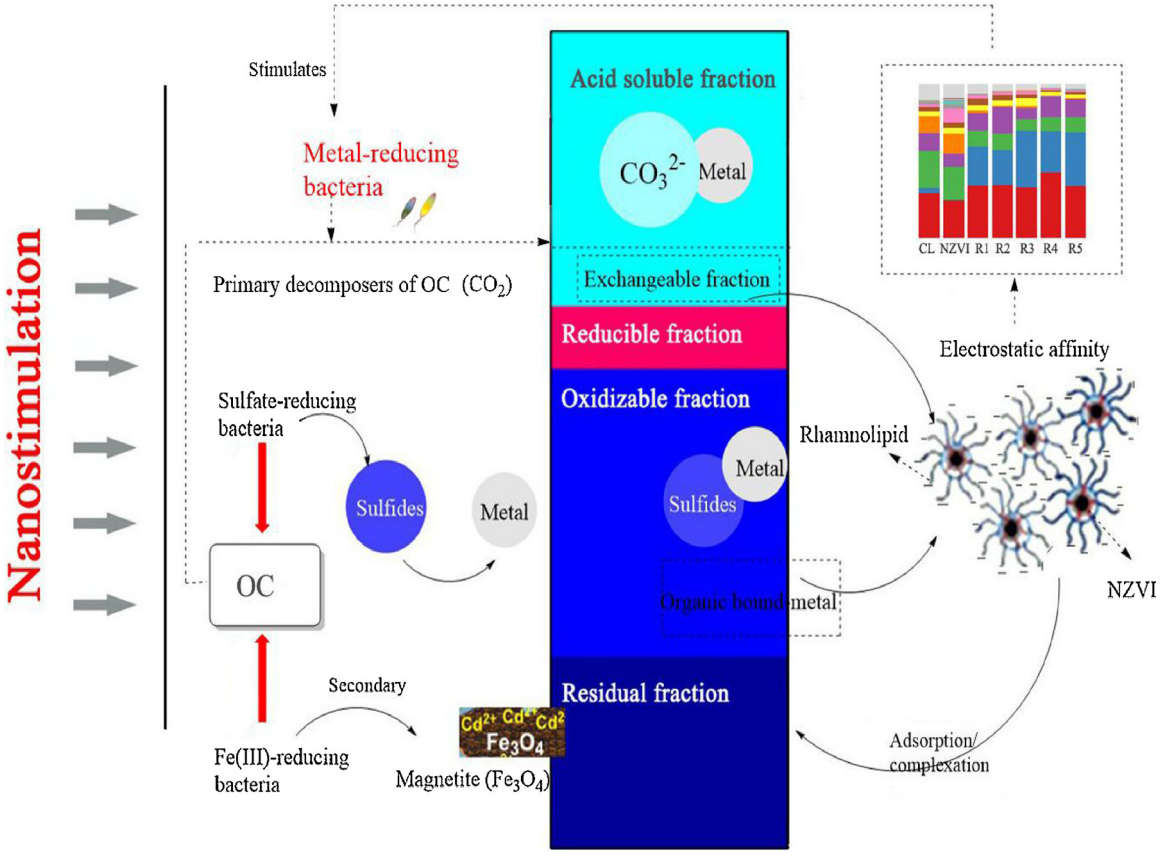

Fig. 6. Conceptual model showing the main abiotic and biotic processes influencing metal fate under nanostimulation.

(III)-reducing bacteria could redistributes Fe and Cd into a more stable Fe mineral phase under the condition of reduction, most likely magnetite, only a small amount of it turns into sulfides and carbonates. And the relative abundance of sulfate reducing bacteria were far lower than those Fe(III)-reducing bacteria in our study. In addition, we have also demonstrated that the content of OC was gradually decreased. Generally, microbial driven metal immobilization process usually depends on energy conservation by utilizing extracellular organic matter for respiration [45]. It was probably RNZVI stimulated some certain bacteria to decomposes organic matter, including Fe(III)-reducing bacteria. According to the above, conceptual model shows the main abiotic and biotic processes influencing metal speciation under nanostimulation (Fig. 6). This simplified model might provides new insights for a better understanding of the potential consequences of nanoremediation strategies on metal fate in contaminated river sediments.

3.5. Pearson's correlations

The pearson correlation analysis of the different fraction of Cd, phylotype abundance data and OC were shown in Table 1. Phylotypes from the *Proteobacteria* and *Firmicutes* phyla could significantly affect the residual fraction of Cd, and the correlation coefficients were 0.547 and 0.796, respectively, indicating that the increase of abundance of *Proteobacteria* and *Firmicutes* could decrease Cd's mobility, and then reduced the bioavailability and toxicity of Cd. And it also can be due to the presence of RNZVI reduced the Cd availability, reducing the sediment toxicity which can favor the development of bacteria species. The residual fraction of Cd was significantly negatively correlated ($P < 0.05$) with OC. OC was significant positive correlated with *Acidobacteria* (correlation coefficients was 0.852). Negative correlation was found among the OC and *Proteobacteria* and *Firmicutes* phyla (correlation coefficients was -0.792, $P < 0.05$).

4. Conclusions

Results of this study suggest that NZVI synthesized in the presence of RL biosurfactants is effective in reducing the bioavailable fraction of Cd. The simultaneous conversion of Cd in high cadmium contaminated sediments was considered to be the result from both abiotic process and biotic process induced by RNZVI, which were important for the speciation and mobilization of Cd. The abiotic process caused by RNZVI induced adsorption and complexation effect. The biotic remediation with RNZVI increased the OC bioavailability through changing the microbial community composition. Particularly, RNZVI application positively increased the abundance of *Proteobacteria* and *Firmicutes*, including the genus *Geobacter* and *Bacillus,* which are responsible for reduction of Fe(III) minerals. It has been demonstrated that secondary Fe-phases formed during microbial reduction of Fe(III) minerals could potentially result in a net immobilization of Cd, shifting Cd from the bioavailable fraction of the soil [58]. More work is required to further assess the impact of nanoparticles and nanotechnology on ecological environment.

Table 1
Pearson's correlation coefficients for relationships among the different fraction of Cd, phylotype abundance and OC.

	Acid soluble	Reducible	Oxidizable	Residual	Proteobacteria	Firmicutes	Acidobacteria	Bacteroidetes	Gemmatimonadetes	Chloroflexi	Planctomycetes	Actinobacteria	OC
Acid soluble	1	0.937**	0.946**	−0.999**	−0.572	−0.817**	0.933**	−0.125	0.833*	−0.183	0.09	0.303	0.930**
Reducible		1	0.996**	−0.953**	−0.376	−0.630	0.770*	−0.001	0.617	−0.185	0.098	−0.014	0.859*
Oxidizable			1	−0.961**	−0.366	−0.629	0.775*	−0.034	0.630	−0.182	0.021	−0.002	0.879**
Residual				1	0.547	0.796*	−0.916**	0.110	−0.808*	0.184	−0.087	−0.259	−0.927**
Proteobacteria					1	0.663	−0.741	0.525	−0.827*	−0.312	−0.495	−0.757*	−0.310
Firmicutes						1	−0.952*	0.088	−0.930**	0.099	−0.378	−0.697	−0.792*
Acidobacteria							1	−0.205	0.961**	−0.121	0.274	0.612	0.852*
Bacteroidetes								1	−0.412	−0.510	−0.027	−0.482	0.111
Gemmatimonadetes									1	0.006	0.293	0.774*	0.716
Chloroflexi										1	0.291	0.208	−0.422
Planctomycetes											1	0.375	−0.102
Actinobacteria												1	0.215
OC													1

* Correlation is significant at the 0.05 level.
** Correlation is significant at the 0.01 level.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at https://doi.org/10.1016/j.jhazmat.2018.07.062.

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