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Immobilization of metals in contaminated soils using natural polymer-based stabilizers☆

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Three low-cost natural polymer materials, namely, lignin (Ln), carboxymethyl cellulose, and sodium alginate, were used for soil amendment to immobilize lead and cadmium in two contaminated soil samples collected from a mining area in Nanjing, China. The remediation effects of the aforementioned natural polymers were evaluated by toxicity characteristic leaching procedure (TCLP) and sequential extractions. The stabilizers could lower the bioavailability of Pb and Cd in the contaminated soils, and the amount of the exchangeable forms of the aforementioned two metals were reduced evidently. TCLP results showed that the leaching concentrations of Pb and Cd were decreased by 5.46%–71.1% and 4.25%–49.6%, respectively, in the treated soils. The contents of the organic forms of the two metals both increased with the increase in stabilizer dose on the basis of the redistribution of metal forms by sequential extractions. These findings were due to the fact that the abundant oxygen-containing groups on the polymeric amendments were effective in chelating and immobilizing Pb and Cd, which have been further confirmed from the metal adsorptions in aqueous solutions. Moreover, Ln achieved the greatest effect among the three polymers under study because of the former's distinct three-dimensional molecular structure, showing the preferential immobilization of Pb over Cd in soils also. Thus, the abovementioned natural polymers hold great application potentials for reducing metal ion entry into the food chain at a field scale.

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1. Introduction

The soil serves as a significant part of the eco-environment and a main resource for human survival. However, an increasing amount of agricultural and urban soils have been polluted with the rapid economic development and industrialization (Cheng, 2003; Shao et al., 2014). Among various kinds of pollutants, metal pollution have received great attention; in these phenomena, metals are released to soils through various kinds of human activities, such as mining, ore refinement, fertilizer industries, tannery, and pesticide use (Bolan et al., 2014; Shao et al., 2014). Unlike organic pollutants, metals are highly dangerous because of their toxicity and non-biodegradability by soil organisms (Cheng, 2003; Wei and Yang, 2010). Such metals could exist in the soil for numerous years, become accumulated through the food chain, and consequently pose considerable threat to human health (Li et al., 2014). Among these metal contaminates, lead and cadmium are two highly popular and toxic examples (Jarup, 2003).

However, metal toxicity in soil depends not only on the total amount but also on the mobility in soil. For a metal to be bioavailable, it must first exist in a form that is mobile and accessible to plants (Bolan et al., 2014). Bioavailability is greatly attached to metal fractionation in soil, which frequently refers to the distribution of various metal forms, including exchangeable carbonate, Fe–Mn oxide, organic, and residual forms (D'Amore et al., 2005; Gleyzes et al., 2002; Tessier et al., 1979). Accordingly, the bioavailability of metal contaminates in each form gradually decreases from the exchangeable form to the residual form. Among the different forms, the exchangeable form is the most dangerous. Greater metal mobility is associated with higher adverse risk. Many techniques have been developed and applied to treat metal-polluted soils, such as the physical isolation method, biological techniques, and stabilization/solidification method (Dermont et al., 2008a, 2008b; Lageman et al., 2005; Liao et al., 2016; Ma et al., 2001; Maini et al., 2000; Rahimi et al., 2013). Among such approaches, in situ solidification/stabilization has attracted great

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attention because of its high efficiency and cost-effectiveness (Bolan et al., 2014; Guo et al., 2006; Kumpiene et al., 2008; Sun et al., 2012; Tica et al., 2011; USEPA, 2007.). The final stabilization performance of the targeted contaminated soils largely depends on the selected immobilization agents. Moreover, many external parameters, such as pH, age of contamination, soil types, cation exchange capacity (CEC), coexisting natural organic matters, and other inorganic contaminants in soils, also affect the remediation efficiency (Bolan et al., 2014; Harter, 1983; Lee et al., 2009). The use of many kinds of soil stabilizers, including lime, phosphate materials, zeolite, bentonite, sepiolite, Fe/Mn oxides, and organic matters, have been attempted (González-Núñez et al., 2011; Guo et al., 2006; Kumpiene et al., 2008; Lee et al., 2009; Mallampati et al., 2012; Mignardi et al., 2012; Querol et al., 2006; Sun et al., 2012).

Organic materials, such as bio-solid composts (Vaca–Paulin et al., 2006) and biochar (Beesley et al., 2011), have constantly attracted researcher attention as potential high-performance immobilization agents for soil remediation (Bolan et al., 2014; Calace et al., 2005; Dahrazma and Mulligan, 2007; Kumpiene et al., 2008; Park et al., 2011). Although these organic materials would decompose after a long period of stabilization and holds certain remobilization risks, they could decrease toxic metal bioavailability and induce metal retention in soils by adsorption and facile formation of stable complexes with metals (Guo et al., 2006). Such effect could also improve soil quality by providing nutrients to plants. Among numerous organic materials, lignin (Ln) is the main byproduct of the paper industry and the precursor of humic substances; Ln contains abundant oxygen-containing groups, including carboxyl, lactonic, and phenolic hydroxyl groups, thereby easily chelating and immobilizing many metals (Jiang, 2009; Zhou and Haynes, 2010). Given its unique chemical composition and richness in nature, Ln holds a significant potential as an effective soil stabilizer (Jiang, 2009; Zhou and Haynes, 2010). However, data related to the stabilizing behaviors of Ln in remediating toxic-metal-polluted soils have not been systematically reported to date, especially its remediation mechanisms (Battaglia et al., 2007; Calace et al., 2005).

In the current study, Ln was employed to treat actual Pb- and Cd-polluted soils collected near the mining areas of Nanjing, China. For comparison, two other organic materials, namely, carboxymethyl cellulose (CMC) and sodium alginate (SA), were adopted. Both materials are polysaccharides containing abundant carboxyl groups. We investigated and compared in detail the remediation performance of the aforementioned three natural polymer stabilizers for metal-contaminated soils. Furthermore, we studied and discussed herein the relevant mechanisms of Ln, CMC, and SA in the immobilization processes by combination of metal adsorption in aqueous solutions, including their competitive immobilizations.

2. Materials and methods

2.1. Materials

2.1.1. Contaminated soils

Two polluted soil samples were collected from the vicinity of Qixiashang lead-zinc mines in Nanjing, China, which is a polymetallic deposit mainly containing lead and zinc associated with sulfur and silver. As for the surrounding rocks of ores, NW plate includes Huanglong formation at the bottom (C_2^1) (coarse grained and dolomitic limestones), Gaolishan group (C_1^2) (siltstone), and Hezhou group (C_1^3) (marlite and calcareous shale); SE plate is weakly mineralized limestone of Huanglong formation (C_2^2). After more than 50 years of mining activities, soils there have been heavily polluted by various kinds of metals. Among them, Pb (80–170 mg/kg) and Cd (7–18 mg/kg) were two mainly ones. Surface soils were obtained at 0–20 cm depth and sieved to <2 mm to remove impurities. Afterward, the samples were fully air dried and finally stored in plastic bags prior to analysis. Meanwhile, the Fourier transform infrared (FTIR) spectra of two different soil samples were obtained using a FTIR spectrometer (Type TENSOR 27; Bruker Co.; Germany; Supplementary Materials Fig. S1(a)). Accordingly, the two soil samples showed fairly similar characteristics. Therefore, a series of techniques were applied to further determine the physicochemical properties of the two soils (Table 1). pH was measured at a soil:water ratio of approximately 1:2.5 (w/w) using a pH meter (Delta320, Mettler–Toledo. Switerland) (Bao, 1981). Organic matter content was determined through the potassium dichromate volumetric method, whereas CEC was analyzed by the ammonium acetate exchange method (Bao, 1981). The soils were digested with a solution of $HCl–HNO_3–HClO_4$ and metal concentrations were determined using a thermo M6 atomic absorption spectrometer.

2.1.2. Natural polymer amendments

Three natural polymers, Ln, CMC, and SA, were selected for soil amendment, all of which were purchased from Nanjing Chemical Reagent Co. Ltd. Ln was pretreated by NaOH to remove impurities (Jiang, 2009). Epoxy chloropropane was employed as crosslinker to increase the stability of CMC (Perkerson et al., 1960). Meanwhile, a certain amount of calcium chloride was used to modify SA into a more stable form (Kuo and Ma, 2001). After slight modifications, the three organic materials were processed into more efficient and stable immobilization agents.

FTIR spectra of Ln, CMC, and SA were obtained (Supplementary Materials Fig. S1(b)) and suggested the possible existence of surface functional groups in their molecular structures. Ln was composed of various oxygen-containing functional groups. CMC and SA both contain abundant carboxymethyl groups. In accordance with the modified Boehm titration method (Boehm, 1994), the detailed amounts of carboxyl, lactonic, and phenolic hydroxyl groups in Ln were determined to be approximately 0.524, 0.053, and 0.628 $mmol \cdot g^{-1}$, respectively. For the other two natural polymers, the total carboxyl groups of CMC and SA were 1.125 and 1.076 $mmol \cdot g^{-1}$, respectively.

2.1.3. Others

HCl, HNO_3, $HClO_4$, NaOH, $CaCl_2$, and other chemical reagents used in this work were all obtained from Nanjing Chemical Reagent Co. Ltd. All the chemicals were of analytical grade, and distilled water was used in all experiments.

2.2. Soil amendment experiments

2.2.1. Incubation experiments

100 g of air-dried soil samples were mixed with different stabilizers thoroughly in polythene cups. The contents of the individual amendments in each soil were maintained at 1, 2, 5, and 10 wt% to determine the optimal dose. A control sample without stabilizer was also included. Four replicates were conducted for each treatment, and each treated soil was incubated with 70% water holding capacity at 25 °C for 30 days. All the soils were

Table 1
The physicochemical properties of two soil samples from the vicinity of abandoned mining areas.

Soil	pH	CEC ($mmol \cdot kg^{-1}$)	Organic matter ($mg \cdot kg^{-1}$)	Total Pb ($mg \cdot kg^{-1}$)	Total Cd ($mg \cdot kg^{-1}$)
Soil1	7.802	21.14	21.57	171.0	17.89
Soil2	7.478	18.27	15.81	80.12	7.490

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