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Nano-hydroxyapatite immobilized lead and enhanced plant growth of ryegrass in a contaminated soil

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ABSTRACT

Lead (Pb) is one of the ubiquitous soil contaminants. The strategy to increase Pb phytoremediation is of highly critical considering the difficulty in phytoextraction of Pb due to its low solubility and high retention on soil particles. The effects of application nano hydroxyapatite (NHAP) on Pb phytoextraction by ryegrass (*Lolium Perenne* L.) were evaluated. Ninety pots of Pb-contaminated soil with different Pb concentrations (0–800 mg/kg) were seeded with ryegrass. The effects of NHAP on biomass and Pb uptake were examined. The results indicated that the application of 5 g/kg NHAP to Pb-contaminated soils significantly increased the ryegrass biomass. The removal rates of Pb from the soil by ryegrass were enhanced obviously after NHAP addition. These results suggested that NHAP was suitable for application to in-situ Pb-contaminated soils for remediation. The observation in this study provides useful information about the effects of NHAP on lead removal, which plays an important role in the phytoremediation.

1. Introduction

The presence of heavy metals in an ecosystem can result in the accumulation of heavy metals in the food chain and negatively effect human health. Heavy metals such as lead (Pb), cadmium (Cd), arsenic (As) and mercury (Hg) are potentially toxic elements that can trigger dangerous diseases and chronic poisoning. Compared with organic pollutants, heavy metals cannot be decomposed by microbes. They can only be transferred in the environment. Even relatively low levels of heavy metal emissions will cause pollution because of accumulation, which can poison and destroy soil-plant systems and seriously affect food production and the safety of agricultural products (Raymond and Felix, 2011). Although heavy metals cannot be degraded, phytoremediation can be used to stabilize or extract heavy metals in harvestable plant parts. Thus, phytoremediation, which is the use of plants to extract, adsorb, or detoxify pollutants, has been intensively studied due to its effectiveness, non-intrusive methodology and low cost as an environmentally harmonious and socially accepted method for remediating polluted soils (Alkorta and Garbisu, 2001; Garbisu et al., 2002; Alkorta et al., 2004; Nunez-Lopez et al., 2008).

Nano-materials with large surface areas have been used to improve the environment. Hydroxyapatite is a naturally mineralized calcium apatite and can be applied to soils to reduce heavy metal pollution because it is biocompatible with the soil, readily available and inexpensive (Jiang et al., 2012). Nano-hydroxyapatite (NHAP) can adsorb Pb and reduce its mobility in soils. Over the years, many researchers have explored the use of new synthetic methods for preparing and modifying hydroxyapatite for wide use in pollution treatment (He et al., 2013; Ramesh et al., 2013).

Lead is one of the most biological toxic heavy metals in the environment, and its compounds are classified as priority pollutants by the United States Environmental Protection Agency (EPA, 2000). With the development of industry, agriculture, mining, and transportation sectors, soil Pb pollution has become increasingly important due to atmospheric deposition, precipitation and other means of soil contamination (Perry et al., 2012). To reduce the undesirable effects of Pb pollution, the enhancement of the Pb phytoremediation efficiency is of great significance considering the difficulty in phytoextraction of Pb due to its low solubility and high retention on soil particles. In this study, NHAP were used to fix Pb in contaminated soils. Ryegrass (*Lolium perenne* L.) was used as a model system because of its rapid growth, tolerance to

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Table 1
Some physical and chemical properties of the studied soil.

pH	OM (g/kg)	CEC (cmol/kg)	TN (mg/kg)	TP (mg/kg)	Pb content (mg/kg)	Particle size (%)		
						Sand	Silt	Clay
8.62	25.41	157.98	134	9.62	37.1	15.9	68.8	15.3

various environments, soil types and its common use in phytoremediation studies (Arienzo et al., 2004; Vandenhove et al., 2001; Duo et al., 2005). This study aimed to assess the effects of NHAP in enhancing the phytoextraction of Pb by ryegrass in contaminated soils. The remediation effects of using NHAP with ryegrass in Pb-contaminated soils were assessed by determining the bioaccumulation factors and Pb concentrations in different plant parts. In addition, dynamic changes in the Pb contents of the rhizosphere soil were determined.

2. Materials and method

2.1. Preparation of plants and soil medium

Ryegrass cultivation was conducted in a greenhouse in Hebei University, China. The tested soils were obtained from the surfaces of cultivated farmland soils on the outskirts of Baoding. It belongs to the typical cinnamon soil in North China. The soil was air-dried for 2 weeks and crushed before passing through a 2 mm diameter sieve.

Basic physical and chemical properties, including organic matter (OM), cation exchange capacity (CEC), total nitrogen (TN) and total phosphorus (TP), were determined using regular soil analysis methods. The distribution of soil particle size using the U.S. Department agriculture (USDA) classification scheme was determined by a rapid method proposed by Kettler et al. (2001). The initial concentration of Pb in the tested soil was analyzed. The results of the basic physical and chemical properties of the soil were listed in Table 1. This alkalescent soil presents a sandy-silty-clayey texture. The chemical analysis for the studied soil shows a higher organic matter content of 25.41 g/kg.

In the Pb treatment, the soil samples were contaminated with 0, 100, 350, 500 and 800 mg/kg of Pb in the form of lead nitrate ($Pb(NO_3)_2$) salt. The soil samples were thoroughly mixed and were allowed to stabilize under natural conditions for four weeks before using as a growth medium. Next, 5 g/kg of NHAP (Nanjing Emperor, China) was added to the soil for each metal treatment.

Plastic pots (12-cm diameter, 14-cm height) were filled with a mixture of 1500 g soil and 7.5 g NHAP. Each treatment was performed in three replicates, and each pot was planted with approximately 150 seeds. Seedlings were grown in an environmental chamber at 15–20 °C under natural daylight through a window and supplemented by cool-white fluorescent light for 16 h each day. With daily sprinkler watering, the soil moisture content was maintained at field capacity (approximately 60%) during the stages of plant growth. The ryegrass was harvested respectively at 2, 4 and 6 weeks.

2.2. Preparation and analyses of plant and soil samples for Pb

After harvesting, the plants were removed from the pots and cut into roots and shoots by ceramic scissors. The root biomass were too less to further determination of Pb. The determination of Pb in shoots was carried out. The plant samples were separately washed three times with ultra-pure water before wrapping and storing for 30 min at 105 °C, then kept a 70 °C until constant weight. The plant samples were digested in a nitric acid-hydrogen peroxide-perchloric acid system after shattering. A graphite furnace atomic absorption spectrophotometer (Model TAS-990, Purkinje) was used to determine the Pb concentrations in the plant samples. The soil samples were taken from the pots after harvesting the plants and were air-dried at room temperature before passing through a 2 mm sieve. To determine the total Pb-contents, the nitric acid-hydrogen peroxide-hydrofluoric acid system was used. The Pb concentrations in the soil samples were determined using a flame atomic absorption spectrophotometer (Model AA-6800, shimadzu). A five-point calibration was performed with standard solutions. Each sample was measured in three replications.

The accumulation of heavy metals in a plant can be quantified by the bioconcentration factor (BCF). The BCF is calculated as the ratio of the trace element concentration in plant tissues at harvest to the concentration in the external environment, such as the soil (Zayed et al., 1998). It reflects the ease of migration of an element in a soil-plant system and can be used to evaluate the ability of a plant to absorb heavy metals (Roongtanakiat, 2009). The BCF value is important for estimating the potential of a plant for phytoremediation. When the BCF is >1, the absorption of the heavy metal by the plant is greater than the content in the soil. Thus, most of the heavy metals can be removed by harvesting the plant materials after metal absorption.

The BCF is calculated as shown in Eq. (1):

$$BCF = \frac{C_{plant}}{C_{soil}} \quad (1)$$

where C_{plant} is the concentration of Pb in the above-ground plant parts (stem and leaf) and C_{soil} is the concentration of total Pb in the soil.

2.3. Quality control and statistical analysis

In all measurements, blanks, triplicate measurements of metals in extracts were routinely included for quality control. Maximum allowable relative standard deviation between replicates was set to 5% for soil and 8% for plant analyses. The recoveries were in the range of 97.6–102.6% and 96.3–101.85 for soil and plant samples respectively. Analysis of variance (ANOVA) was used to compare the means of the treatments at a level of significance of $p < 0.05$ using the SPSS 18 package.

3. Results and discussion

3.1. Biomass of ryegrass

In this study, Pb did not inhibit germination and growth of ryegrass seeding growth, and no visual symptoms of Pb toxicity were observed in the plants at the initial stages of the phytoremediation experiment. In fact, the growth of the plants exposed to a Pb concentration of 100 mg/kg soil was greater than the growth of the plants in the blank. This result potentially occurred because the availability of nitrate from $Pb(NO_3)_2$ increased (Selamat et al., 2014). Over time, the biomass of the ryegrass significantly decreased following metal application at 500 mg/kg and 800 mg/kg. In a previous study, when low metal concentrations were added, plant growth was promoted, and when high metal concentrations were added, plant growth was stunted (Sheng et al., 2008).