Ecotoxicology and Environmental Safety 132 (2016) 224–230

Contents lists available at ScienceDirect

Ecotoxicology and Environmental Safety

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

Remediation of lead contaminated soil by biochar-supported nano-hydroxyapatite

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ARTICLE INFO

Article history:
Received 7 March 2016
Received in revised form
2 June 2016
Accepted 6 June 2016
Available online 20 June 2016

Keywords:
Lead contaminated soil
nHAP@BC
Soil properties
Bioavailability
Accumulation
Translocation

ABSTRACT

In this study, a high efficiency and low cost biochar-supported nano-hydroxyapatite (nHAP@BC) material was used in the remediation of lead (Pb)-contaminated soil. The remediation effect of nHAP@BC on Pb-contaminated soil was evaluated through batch experiments. The stability, bioaccessibility of Pb in the soil and the change in soil characteristics are discussed. Furthermore, the effects of the amendments on the growth of cabbage mustard seedlings and the accumulation of Pb were studied. The results showed that the immobilization rates of Pb in the soil were 71.9% and 56.8%, respectively, after a 28 day remediation using 8% nHAP and nHAP@BC materials, and the unit immobilization amount of nHAP@BC was 5.6 times that of nHAP, indicating that nHAP@BC can greatly reduce the cost of remediation of Pb in soil. After the nHAP@BC remediation, the residual fraction Pb increased by 61.4%, which greatly reduced the bioaccessibility of Pb in the soil. Moreover, nHAP@BC could effectively reduce the accumulation of Pb in plants by 31.4%. Overall, nHAP@BC can effectively remediate Pb-contaminated soil and accelerate the recovery of soil fertility.

1. Introduction

The survey of Chinese soil pollution bulletin in 2014 showed that the overall national soil exceeding rate was 16.1%. The exceeding rate of farmland and the point exceeding rate of lead (Pb) were 19.4% and 1.5%, respectively (Singh et al., 2003; Teng et al., 2014). Pb contamination of soil is very serious. The development of green, efficient and economic soil remediation technologies are urgently needed.

Nano-hydroxyapatite (nHAP) has been widely used in the immobilization of heavy metals for its large specific surface area, high stability under reducing and oxidizing conditions and its high sorption capacity for heavy metals (He et al., 2013; Wang et al., 2014a, 2014b). The main remediation mechanism of Pb in soil by nHAP was dissolution-precipitation. This process causes the formation of pyromorphite, which has a lower solubility, reducing the bioavailability of Pb (Li et al., 2014). However, the application of nHAP has negative effects on the soil environment, such as reducing the organic matter content in soil and causing an imbalance in the nutrient elements. Moreover, nHAP are not mobile in soils, which prevents solid phosphate from being delivered to the Pb affected zone and from the effective remediation of Pb in the deep soil. Biochar (BC) has recently been used as a support to disperse and stabilize nanoparticles, enhancing their environmental application.

Biochar is an organic carbon-rich material produced via pyrolysis of agricultural wastes, in an oxygen-limited environment (Gaunt and Lehmann, 2008). Recent studies have highlighted BC's role in improving the physical and chemical properties of soil and immobilizing heavy metals (Beesley et al., 2011, 2010; Wu et al., 2012), attributed to its large specific surface area and porous structure, generally high pH and active functional groups. On the one hand, it can reduce the agglomeration of nHAP, thus improving its mobility. On the other hand, it can absorb phosphorus, preventing excessive phosphorus leaching into underground water and causing secondary pollution. Typically, the composite material can improve soil fertility and decrease the mobility and bioavailability of heavy metals. Zhou et al. (2014) studied the removal efficiency of BC-supported zero-valent iron for heavy metal ions in aqueous solution. The results showed that BC-modified iron has an excellent ability to remove heavy metals. The removal

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http://dx.doi.org/10.1016/j.ecoenv.2016.06.008
0147-6513/

rate of Pb in aqueous solution was more than 93%. Wang et al. (2015) used BC-modified hematite to remove arsenic (As) from aqueous solution, which not only had more sorption sites but also showed a greater ability to remove As, with a maximal adsorption capacity of 429 mg/kg. At present, BC-modified materials are often used for the removal of heavy metals in aqueous solution, however, it is rarely used for soil remediation.

In this paper, a BC-supported nHAP (nHAP@BC) material was prepared and used for the remediation of Pb-contaminated soil, to avoid the negative effects of hydroxyapatite on soil remediation and improve soil fertility, achieving a green, efficient, economical soil remediation technology. The research contents of this study are, (1) the preparation and characterization of nHAP@BC, (2) remediation of Pb-contaminated soil, (3) remediation mechanisms and (4) toxicity evaluation of plant seedling growth.

2. Materials and methods

2.1. Materials

All chemicals used in this study were analytical grade. The soil sample was collected from the Higher Education Mega Center in Guangzhou, China. The soil was sieved with a 2 mm standard sieve after air-drying and stored in a dryer. The physicochemical characteristics of the soil are shown in Table 1. Cabbage mustard seeds were purchased from the Vegetable Research Institute at the Guangdong Academy of Agriculture Sciences (Guangzhou, China).

2.2. Preparation and characterization of materials

Pb-spiked soil samples were prepared using the following procedure. The raw soil was mixed with a $Pb(NO_3)_2$ solution at a soil-to-solution ratio of 1:5, then stirred for 24 h, which has been proven experimentally to be a sufficient time to reach equilibrium conditions. The soil suspension was centrifuged and the supernatant was decanted. The remaining soil was washed twice with deionized water, to remove any traces of the soluble Pb(II) spike. The decanted supernatant and rinse water were filtered through a 0.22 μm membrane filter, and the concentration of Pb(II) in the filtrate was analyzed. The Pb concentration of remaining soil was tested by acid digestion. The Pb uptake by the soil was calculated by comparing the initial and final concentration of Pb in the aqueous phase. The resultant Pb concentration in the soil was 640.5 mg/kg. The Pb-loaded soil was then air-dried for future use.

BC was produced by pyrolysis of bagasse (Jiang et al., 2012a, 2012b; Ding et al., 2014). The bagasse was oven-dried at 105 °C and used to tightly fill ceramic crucibles. The materials with the ceramic crucibles were then placed in a muffle furnace to pyrolyze under oxygen-limited conditions. The pyrolysis temperature was raised to 600 °C at a rate of approximately 10 °C per min and kept constant for 2 h. The BC was then allowed to cool to room temperature inside the muffle furnace. All BCs were taken out and then ground, to examine their characteristics without further treatment.

The nHAP@BC was prepared as follows. A given quantity of nHAP particles were dispersed in the solution for 30 min, followed by the addition of KCl and bagasse. The mixture was then stirred for 30 min and oven-dried at 80 °C for 8 h after the separation (Wang et al., 2015; Yao et al., 2014). The following steps were in accordance with the preparation method of BC.

Table 1
Physical and chemical properties of the soil sample.

Pb (mg/kg)	pH	Organic matter (g/kg)	A-N[a] (mg/100g ±)	A-P[b] (mg/kg)
19.90 ± 2.14	5.80 ± 0.12	40.77 ± 1.82	13.37 ± 0.84	7.77 ± 0.65

[a] A-N: the available nitrogen content of the soil.
[b] A-P: the available phosphorus content of the soil.

The surface morphology of the materials was observed by scanning electron microscopy (SEM, NoVaTMNano430). The specific surface area was measured by nitrogen adsorption isotherm using a Brunauer-Emmett-Teller surface analyzer (BET, ASAP2020M, Micro-meritics Instrument Corp, USA). A Fourier transform infrared spectrometer was used to analyze the types of surface functional groups of the materials (IRPrestige21). X-ray diffraction (XRD) were performed by using Cu Kα radiation (D8 Advance, Bruker Corporation, German).

2.3. Remediation experiment

For the determination of optimal repair time, the remediation experiments were performed with 2 g of soil at a soil-to-solution ratio of 1:4. The soil samples were amended with 10% (w/w) BC, 8% nHAP and 8% nHAP@BC, and the mixtures were placed in a shaker to react for 1, 3, 7, 14, 28 and 42 days. For the determination of the optimum dosage, the dosages of BC were 1%, 5%, 10% and 20% respectively, and the dosages were 1%, 5%, 8% and 10% for nHAP and nHAP@BC. The soil-to-solution ratio was 1:4. The samples were placed into a shaker to react for an optimal repair time. Pb-spiked soil without amendment treatment was used as the control sample. Three replicates were used. The GBT 23739-2009 method was used to extract the available Pb from the soils. The Pb content of the soils was determined by flame atomic absorption spectrophotometry.

2.4. Chemical stability of Pb in soil after remediation

To estimate the in vitro bioaccessibility of soil-bound Pb for humans, a biochemically-oriented method, PBET (Kelley et al., 2002), was used, which compares the leachability of Pb in the soil before and after the amendment treatment. Moreover, a sequential extraction procedure (SEP) was used to quantify the fraction of the various Pb species (Tessier et al., 1979; Reddy et al., 2001). All of the tests were duplicated to ensure data quality.

2.5. Soil characteristics after remediation

To analyze the effect of amendment on the soil characteristics and to further discuss the repair mechanism, soil pH, organic matter (OM) and available phosphorus content (A-P) were determined. The soil pH was evaluated by potentiometry. The potassium dichromate method was used to analyze the change in the soil organic matter content before and after remediation. The content of A-P in the soil was determined using the sodium bicarbonate extraction Mo-Sb anti-spectrophotometry method.

2.6. Plant growth experiment

According to the research of Wang et al. (2014a, 2014b), uncontaminated soil (S0), Pb-contaminated soil (S1), BC-amended soil (S2), nHAP-amended soil (S3) and nHAP@BC-amended soil (S4) were investigated, to estimate the accumulation of Pb and the effects of the amendments on the growth of cabbage mustard seedlings. The plant growth experiments were conducted in a set of 120 mm culture dishes covered with double-layer filter papers. Each of dishes received 5 g of soil sample and 25 mL deionized water. Then, 15 seeds were placed inside each dish and placed in a growth chamber (GP-01, Huangshi Hengfeng Med-ical Instrument Co., Ltd, China) with day and night temperatures of 25 °C (1700 lx,