Ecological Engineering 93 (2016) 1–8

Contents lists available at ScienceDirect

Ecological Engineering

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

Continuous immobilization of cadmium and lead in biochar amended contaminated paddy soil: A five-year field experiment

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ARTICLE INFO

Article history:
Received 17 March 2015
Received in revised form 1 March 2016
Accepted 1 May 2016
Available online 12 May 2016

Keywords:
Biochar
Cadmium
Lead
Contaminated
Paddy soil
Fourier transform infrared

ABSTRACT

Analyzing the fractionation of cadmium (Cd) and lead (Pb) could provide key information to identify how wheat straw biochar (WBC) affects the bioavailability of Cd and Pb in contaminated soils. The fractionations of Cd and Pb were extracted from amended paddy soil according to the approach by European Community Bureau of Reference (BCR). Total Cd and Pb concentrations in contaminated paddy soil were decreased by 7.5–23.3% and 3.7–19.8% with WBC application during five years, respectively. The Cd was distributed primarily in the exchangeable (~50%) and carbonate (>30%) fractions, and Pb was the mainly carbonate-bound fraction (~70%). The exchangeable fractions concentration of Cd and Pb were significantly decreased by 8.0–44.6% and 14.2–50.3% during five years. The residual fractions were increased by 4.0–32.4% (Cd) and 14.9–39.6% (Pb). The percentage of exchangeable Cd fractions decreased by 1.2–6.9%, but the incensements of 1.7–7.2% and 1.3–2.2% were observed in carbonate and residual fractions for Cd. Similarly, the percentage of exchangeable Pb fractions decreased by 0.3–1.6%, though the carbonate and residual fraction were increased by 1.2–2.9% and 1.4–12.2%. The changes of Cd and Pb fractions were mainly due to the abundant functional groups and complex structures in WBC, which could improve soil microstructure and increase soil pH and soil organic matter.

1. Introduction

Heavy metals, especially cadmium (Cd) and lead (Pb), are excessively introduced to agricultural soils mainly from metal smelting industry through gaseous emissions, waste water and solid wastes (Dudka and Adriano, 1997; Bhuiyan et al., 2010). Accumulation of Cd and Pb in crops grain from agricultural soils is the main concern due to their high mobility and toxicity (Zhu et al., 2014). Moreover, high concentrations of Cd (~22 mg kg^{-1}) and Pb (~650 mg kg^{-1}) in soils cause long-term risks to ecosystems and humans (Rignell-Hydbom et al., 2009). Heavy metals are persistent and difficult to remove or degrade once introduced into soils. So it is imperative to amend the heavy metals pollution by feasible measures (Gomes et al., 2014).

Various techniques have been developed and proposed to amend heavy metals polluted soils, which rapidly change the properties of heavy metals in soil and decrease the mobility and bioavailability of metals (Jiang and Xu, 2013). Biochar is considered to be an effective adsorbent for heavy metals and organic pollutants (Tang et al., 2013; Xu et al., 2013). Biochar is predominantly stable and recalcitrant organic carbon compound, which is produced from biomass wastes (wheat straw, rice straw, sewage sludge etc.) at moderate temperature (450 °C) under limited oxygen concentrations (Pöykiö et al., 2006; Verheijen et al., 2010). It has a relatively structured carbon matrix with the high degree of porosity and extensive surface area and increasingly recognized as a multifunctional material for the management of agricultural soils in the world (Lehmann et al., 2011; Chen et al., 2011). Sludge biochar significantly reduced the bioavailability and leaching potential of heavy

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http://dx.doi.org/10.1016/j.ecoleng.2016.05.007
0925-8574/

Table 1
Basic properties of the paddy soil (0–15 cm depth) and WBC.

	pH (H_2O)	Organic Matter (g kg^{-1})	Total N (g kg^{-1})	Total P (g kg^{-1})	Total K (g kg^{-1})	CEC (cmol kg^{-1})	Total Cd (mg kg^{-1})	Total Pb (mg kg^{-1})
Soil	6.07	20.71	3.19	0.82	11.4	18.05	22.65	621.31
WBC	10.35	467.2	5.90	14.43	11.5	21.70	0.03	12.91

metals through immobilization in polluted soil (Devi and Saroha, 2014). In the previous field studies, biochar also efficiently immobilized Cd and decreased its bioavailability by 15–27% in paddy soil (Cui et al., 2013). A pot experiment showed that 10% biochar application significantly decreased Cd and Pb (extracted by 0.01 mol L^{-1} $CaCl_2$) by 71% and 92%, respectively (Houben et al., 2013). In the field experiment, Bian et al. (2014) found biochar addition considerably reduced the bioavailability of Cd and Pb ($CaCl_2$ extracted) by 58.7% and 59.1% respectively. The concentration of Cu and Pb in the *Sedum plumbizincicola* shoots was decreased by 46% and 71% with rice straw biochar while bamboo biochar applied at a level of 5% reduced Cd contents in the shoot by 49% (Lu et al., 2014). Moreover, biochars induced significant improvement of the soil pH, electric conductivity (EC), cation exchange capacity (CEC) and then changed the bioavailability of the metals (Fellet et al., 2014).

Heavy metals contaminated soil often contain high concentrations of potentially toxic metals whose mobility may pose an environmental hazard for local ecosystems. The chemical process of heavy metals extraction can be related to the chemical processes within the soil and the vulnerability of metals to release from the soil matrix. The use of reducing or oxidizing agents can relate directly to the release of metals under different redox conditions (Bacon et al., 2005). Various extraction schemes for heavy metals have been proposed there by making the comparison of data simple; however, the BCR scheme used in the current study is a comparatively simple, developed and standardized procedure. Biochar has been shown the potential for the stabilization of heavy metals in soil and reduced bioavailability and uptake of heavy metal to the plants. However, a very little information is available on the changes in different fractions of Cd and Pb (proposed by BCR scheme) with biochar application in paddy soil over several years. So we hypothesized that the fractions change of Cd and Pb attribute to the biochar application in the polluted soil. The objective of the current study was to evaluate the mobility and retention behavior of Cd and Pb in particular physical-chemical and mineral phases in contaminated paddy soils by applying a sequential extraction procedure.

2. Materials and methods

2.1. Site description

The experiment was conducted in a paddy field (31°24.434′N and 119°41.605′E) where atmospheric fallouts and effluent discharges of a smelter had contaminated the soils since the 1970s. Cd and Pb were the primary pollutants in this area. The paddy soil was characterized as Ferric-accumulic Stagnic Anthrosols. The summer rice (*Oryza sativa* L.) and winter wheat (*Triticumaestivum*) rotation have been practiced at this location for a long time, and the pollutants were well acclimated in the soils. The Cd and Pb concentration in plant tissues and crop grains were significantly reduced with biochar application in previous studies (Cui et al., 2011, 2012).

2.2. Experimental design

The treatments included four biochar levels: 0(C0), 10 (C1), 20 (C2) and 40 (C3) t ha^{-1}. The experiment was laid out in a randomized complete block design with three replicates per treatment. Each plot was with an area of 4 m × 5 m. Biochar used was in black powder produced from wheat straw by pyrolysis at ~450 °C at the Sanli New Energy Company, Henan Province, China. Wheat straw biochar (WBC) was then ground to pass through a 2-mm sieve by the machine and mixed thoroughly with the soils by plowing after wheat harvest in 2009. Basic properties of WBC and soil properties are listed in Table 1 and were determined using methods as described by Lu (2000). Basal fertilizer was broadcasted before sowing. For each treatment, calcium biphosphate, KCl, and urea were applied as basal fertilizers at a rate of 125 kg P_2O_5 ha^{-1},125 kg K_2O ha^{-1} and 120 kg N ha^{-1}, respectively.

2.3. Soil sampling and analysis

Soil samples were collected at 0–15 cm depth prior to initiation of the experiment in 2009. Three undisturbed cores were obtained from each plot. Each soil sample was cleared of plant debris, air dried at room temperature, and ground to pass through a 2-mm sieve. A subsample of the soil was ground to pass through a 0.15-mm sieve for Cd, Pb, and soil organic matter (SOM) analyses following the protocols described by Lu (2000). Functional groups on the biochar and soil surface were examined using Fourier transform infra spectroscopy (FTIR, Nexus-670, USA). Examination of the biochar amended soil was carried out using a scanning electron microscope (SEM, Quanta 200, USA) with energy dispersive X-ray spectroscopy (EDS, Vantage Dsi, USA).

Sequential extraction was performed using the modified four-stage procedure recommended by the European Community Bureau of Reference (BCR) as follows (Pöykiö et al., 2006; Nemati et al., 2011):

Step 1 (Exchangeable fraction): 40 mL of 0.11 M acetic acid was added to 1 g of soil sample in a centrifuge tube and shook for 16 h at room temperature. The extract was then separated from the solid residue by centrifugation using a centrifuge instrument (Eppendorf 5417R, Germany). The operating parameters for working elements were set as recommended by the manufacturer.

Step 2 (Carbonate fraction): 40 mL of a freshly prepared hydroxylammonium chloride was added to the residue from step 1 in the centrifuge tube, and re-suspended by mechanical shaking for 16 h at room temperature. The separation of the extract, collection of the supernatant, and rinsing of residues were the same as described in Step 1.

Step 3 (Organic fraction): the residue in Step 2 was treated twice with 10 mL of 8.8 M hydrogen peroxide. First, 10 mL of hydrogen peroxide was added to the residue from Step 2 in the centrifuge tube. The digestion was allowed to proceed at room temperature for 1 h with occasional manual shaking, followed by digestion at 85 ± 2 °C for another 1 h in a water bath. During the digestion, the centrifuge tube was loosely covered to prevent substantial loss of hydrogen peroxide. Afterwards, the centrifuge tube was uncovered and heating continued until the volume reduced to about 2–3 mL. An additional 10 mL of hydrogen peroxide was added to the tube, covered, and digested with cover at 85 ± 2 °C for another 1 h. Heating was continued, as before, until the volume reduced to 2–3 mL. Finally, 50 mL of 1.0 M ammonium acetate was added to the cold mixture and shaken for 16 h at room temperature. The separation of the extract, collection of the supernatant, and rinsing of residues were the same as described in Step 1.

Step 4 (Residual fraction): the residue from Step 3 was digested using a mixture of aqua regia and HF (Nemati et al., 2011).