Environmental Pollution xxx (2016) 1–10

Contents lists available at ScienceDirect

Environmental Pollution

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

Effects of biochars on the availability of heavy metals to ryegrass in an alkaline contaminated soil☆

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ARTICLE INFO

Article history:
Received 17 May 2016
Received in revised form
8 July 2016
Accepted 12 July 2016
Available online xxx

Keywords:
Soil contamination
Biochar
Heavy metal
Phytoavailability
Remediation
Alkaline soil

ABSTRACT

A pot experiment was conducted to investigate the effects of biochars on the availability of heavy metals (Cd, Cu, Mn, Ni, Pb, and Zn) to ryegrass in an alkaline contaminated soil. Biochars only slightly decreased or even increased the availability of heavy metals assesses by chemical extractant (a mixture of 0.05 mol L^{-1} ethylenediaminetetraacetic acid disodium, 0.01 mol L^{-1} $CaCl_2$, and 0.1 mol L^{-1} triethanolamine). The significantly positive correlation between most chemical-extractable heavy metals and the ash content in biochars indicated the positive role of ash in this extraction. Biochars significantly reduced the plant uptake of heavy metals, excluding Mn. The absence of a positive correlation between the chemical-extractable heavy metals and the plant uptake counterparts (except for Mn) indicates that chemical extractability is probably not a reliable indicator to predict the phytoavailability of most heavy metals in alkaline soils treated with biochars. The obviously negative correlation between the plant uptake of heavy metals (except for Mn) and the (O + N)/C and H/C indicates that biochars with more polar groups, which were produced at lower temperatures, had higher efficiency for reducing the phytoavailability of heavy metals. The significantly negative correlations between the plant uptake of Mn and ryegrass biomass indicated the "dilution effect" caused by the improvement of biomass. These observations will be helpful for designing biochars as soil amendments to reduce the availability of heavy metals to plants in soils, especially in alkaline soils.

1. Introduction

The excessive presence of heavy metals in soil caused by anthropogenic activities (e.g., mining, smelting, electroplating, coking, and other industrial processes) poses risks to human health and ecological systems because of the heavy metals' toxic and non-biodegradable nature (Chen et al., 2015; Karami et al., 2011; Mohamed et al., 2015). To reduce these risks, modern remediation approaches have increasingly focused on *in situ* environmentally friendly and cost-effective techniques, such as the application of soil ameliorant (i.e., biosolid, manure, compost, and sewage sludge) to bind such contaminants (Beesley et al., 2011). Among the numerous ameliorants, biochar from the thermochemical processing (slow/fast pyrolysis and gasification) of biomass has received considerable interest as a waste-derived soil and sediment amendment because of its ability to *in situ* stabilize contaminants and because of its other environmental benefits, such as carbon sequestration, greenhouse gas mitigation, and promotion of soil fertility and crop yield (Chen et al., 2016; Lu et al., 2014; Song et al., 2014; Uchimiya et al., 2011).

Recently, the effect of biochar on the mobility and bioavailability of heavy metals has been increasingly investigated in field and laboratory conditions. Most studies demonstrated that the addition of biochar to acidic contaminated soil significantly reduced the mobility and phytoavailability of heavy metals, such as Cu, Cd, Pb, Zn, and Ni (Al-Wabel et al., 2015; Karami et al., 2011; Lu et al., 2014; Mohamed et al., 2015; Puga et al., 2015). Changes in the soil properties, especially the increase of pH, can affect their

☆ This paper has been recommended for acceptance by B. Nowack.

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http://dx.doi.org/10.1016/j.envpol.2016.07.031
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precipitation and are mainly responsible for the immobilization of heavy metals in these biochar-treated soils, thereby reducing their availability to plants. Meanwhile, the metal immobilization mechanisms, including adsorption, ion exchange, and surface complexation, can occur because of the highly porous micro-structure, cation exchange capacity, and active surface functional groups of biochar (Beesley et al., 2011; Li et al., 2016; Shen et al., 2016; Uchimiya et al., 2011). Nevertheless, the effect of biochar application on the availability of heavy metal to plants depends on various factors, such as biochar feedstock, pyrolysis conditions, metal type, and amount of biochar applied to the soil. For example, corn-straw-derived biochar exhibited higher efficiency in reducing the availability of Cd and Cu to plants than hardwood-derived biochar because more oxygen-containing groups were introduced on its surface during the aging processes (Li et al., 2016). For the pyrolysis temperature, a previous study found that biochars produced at high temperatures (i.e., 700 °C) decreased Pb bioavailability and leachability much more than biochars produced at low temperatures (i.e., 300 °C) (Ahmad et al., 2016). However, Song et al. (2014) found that the addition of sewage-sludge-derived biochar produced at 450 °C more effectively reduced the plant uptake of heavy metals, especially Zn, as compared with biochar produced at lower (400 °C) and higher (500 °C and 550 °C) temperatures. Depending on the biochar and heavy metal type, the increased amount of biochar application either significantly reduced the availability of heavy metal to plant or made no difference (Al-Wabel et al., 2015; Li et al., 2016; Lu et al., 2014; Puga et al., 2015). Therefore, the efficiency of the biochar for the immobilization of heavy metals in contaminated soil to reduce their phytoavailability should be carefully evaluated for each specific site prior to large-scale application, which is crucial for verifying the feasibility of biochar application in practical remediation projects.

Compared with acidic contaminated soil, little attention has been given to the effectiveness of biochar on the mobility and phytoavailability of heavy metals in alkaline contaminated soil. To our knowledge, only two studies reported that application of biochars into alkaline contaminated soils (pH = 7.96–8.04) decreased the availability of heavy metals (i.e., Cd, Cu, Ni, Pb, and Zn) to the plants, such as maize and ryegrass (Al-Wabel et al., 2015; Rees et al., 2016). Although the ecological toxicity of heavy metals was lower in the alkaline soil compared with their similar levels in the acidic soil, their heavy contamination (i.e., in the alkaline soil in North China) can also threaten human and ecosystem health (Tang et al., 2015). In China and most representatives in Shanxi Province located in North China, numerous coking contaminated sites, especially indigenous coking contaminated sites, are abandoned because of the elimination of old, inefficient, and polluting indigenous ovens and small machinery site during last decade when China's coke industry was experienced an unprecedented technological shift (Hou et al., 2012). The concentrations of heavy metals at coking contaminated sites even exceed the Chinese Standard of Soil Quality Assessment for Exhibition Sites (Wang et al., 2011). Even more serious, plants in some indigenous coking contaminated sites are nonviable because of high concentrations of toxic contaminants, including heavy metals. The soil remediation from these hazardous contaminants is urgently needed to rehabilitate such contaminated soils for human and ecosystem health. However, little attention has been given to the problem of heavy metals in the coking contaminated sites to date. In particular, numerous contaminated sites of indigenous coking are even unheeded.

The main objectives of the present study were to investigate (1) the efficiency of biochar application into alkaline contaminated soil from an indigenous coking site for reducing the availability of heavy metals to ryegrass; and (2) the effect of feedstocks, pyrolysis temperatures, heavy metal types, and biochar properties on the availability of heavy metals to ryegrass in the biochar-amended soil. The results of this study will help the design of biochar as soil amendment to immobilize heavy metal in soil, especially in alkaline soil, and to reduce their toxicity to plants.

2. Materials and methods

2.1. Soil collection and physico-chemical analysis

The surface soil (0–20 cm depth) for the present study was collected from a former indigenous coking area where is not favorable for the growth of some plants (in a hilly region in Lin Xian county, Lvliang City, Shanxi Province, China; 37°43′33″N, 110°56′27″E). Soil samples were air dried, homogenized, and sieved (<2 mm). Particle size analysis was performed by a particle size analyzer (clay: 0%, silt: 5.49%, sand: 94.51%, belong to loamy sandy soil). The soil pH and electric conductivity (EC) were determined in a suspension of soil in water (soil:water = 1:2.5, w/v) with a pH/EC meter (pH = 8.23, EC = 0.12 ds m^{-1}). Soil organic carbon (SOC) was determined by a total organic carbon analyzer (Analysis Jena N/C 2100) after soil was treated with 2 mol L^{-1} HCl and dried in a drum wind-drying oven at 105 °C for 2 h. The SOC content was 23.82 g kg^{-1}. The heavy metals in the soil were determined by inductively coupled plasma-atomic emission spectrometry as described in Section 2.4. The total concentrations of target heavy metals, namely, Cd, Cu, Mn, Ni, Pb, and Zn, were 0.28, 44.30, 832.49, 44.63, 19.30, and 109.32 mg kg^{-1}, respectively. Among these heavy metals, the concentrations of Cd, Cu, Ni, and Zn were higher than average concentrations of counterparts in most soil samples collected from various land types, including the cultivated land, woodland, grassland, construction land, and unused land, across China and even higher than maximum concentration of counterparts in the soils collected from these land types in Shanxi Province (Chen et al., 2015).

2.2. Biochar preparation and characterization

The feedstocks for the production of biochar in this study were crop residues, including walnut shells (WS), corn cobs (CC), corn straws (CS), and rice straw (RS). The largest output of crop residues in China is corn residue, followed by rice residue (Yang et al., 2014). These residues represent the lignocellulose feedstocks. Walnut shell is a ligneous feedstock. The reason for the selection of walnut shell is due to that walnut is one of the largest output among the nuts in China, and that Shanxi Province had the second largest walnut production in China (Qi, 2009). Thus the selected feedstocks were representative. Each feedstock was washed and dried in an oven at 80 °C. For biochar production, the materials were placed in a muffle and pyrolyzed under oxygen-limited conditions at different temperatures (15 °C min^{-1} to 250, 400, and 600 °C) for 4 h. The biochar was cooled to room temperature inside the furnace. The biochars were milled to pass a 0.15 mm sieve before further use. The prepared biochars were referred to as WS2, WS4, WS6, CC2, CC4, CC6, RS2, RS4, RS6, CS2, CS4, and CS6.

The pH and EC of biochar were measured in a suspension of soil in water 1:10 (biochar:water = 1:10, w/v) with a pH/EC meter (Puga et al., 2015). The element composition (C, H, and N) was determined with an elemental analyzer (Flash EA 1112). Ash content was measured by heating the biochars in a muffle at 750 °C for 4 h. The oxygen content was calculated from the mass difference. The N_2-BET surface areas (SA) were determined by an ASAP-2020 surface area analyzer (Micromeritics Instrument Corporation, US). The surface chemistry of the biochar was provided by a Nicolet iS10 FT-IR spectrometer (Thermo Nicolet Corporation, US), which recorded the spectra from 4000 cm^{-1} to 400 cm^{-1} with a resolution of