Bioresource Technology 133 (2013) 537–545

Contents lists available at SciVerse ScienceDirect

Bioresource Technology

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

Application of crop straw derived biochars to Cu(II) contaminated Ultisol: Evaluating role of alkali and organic functional groups in Cu(II) immobilization

Jun Jiang, Ren-kou Xu *

State Key Laboratory of Soil and Sustainable Agriculture, Institute of Soil Science, Chinese Academy of Sciences, Nanjing 210008, China

HIGHLIGHTS

- Oxygen-containing functional groups and alkali contributed to Cu immobilization.
- Oxygen-containing functional groups played a greater role than alkali.
- Biochars were relatively stable in its ability to immobilize Cu.

ARTICLE INFO

Article history:
Received 21 November 2012
Received in revised form 23 January 2013
Accepted 29 January 2013
Available online 6 February 2013

Keywords:
Straw-derived biochar
Cu(II) immobilization
Heavy metal polluted Ultisol
BCR sequential extraction

ABSTRACT

When Cu(II) contaminated Ultisol was mixed with biochar derived from straw and incubated for 120 d, acid-soluble Cu(II) decreased by 0.08–0.33 mmol/kg due to the liming effect of biochar; 1.00–1.93 mmol/kg due to organic functional groups of biochar when it was added to the soil at 30 g/kg, and by 1.40–2.43 mmol/kg at 50 g/kg. The total functional groups and volatile matter (VM) were significantly related to Cu(II) immobilization ($P < 0.01$), suggesting that it is functional groups in VM that are essential to Cu(II) immobilization in soil. The percentage of acid soluble Cu(II) decreased from 43.07% for the control, to 18.83–27.45% and 11.03–20.97% for the treatments with 30 and 50 g/kg of crop straw biochars added, respectively. The immobilized Cu(II) was primarily transformed to reducible and oxidizable forms. Biochar could retain Cu(II) for at least 120 d, indicating the long-term stability of biochar in Cu(II) immobilization.

1. Introduction

Heavy metals are persistent and difficult to remove once introduced into soil ecosystems. Many techniques have been developed to reduce the activity and toxicity of heavy metals in soils, including physical means (Di et al., 2002; Lee et al., 2008), chemical remediation (Dermont et al., 2008), biological remediation (Ma et al., 2001; Whicker et al., 2004) and a combination of remediation technologies (Maini et al., 2000; Aresta et al., 2008). Soil amendments rapidly change the properties of soils and, in turn, the chemical behavior of heavy metals, the usual result being a decrease in their mobility and bio-availability. Inorganic minerals have been studied extensively along with organic materials for that purpose (Lothenbach et al., 1999; Cordova et al., 2011). In the past few years, biochar derived from crop residues has been used to adsorb heavy metals from aqueous solutions and to enhance adsorption of heavy metals by soil particles. The results obtained indicated that heavy metals are adsorbed by biochar through different mechanisms: to form surface precipitates of the metals on biochar; to be adsorbed through electrostatic interaction between metal cations and negatively charged surface of biochar; to be adsorbed specifically through formation of surface complexes between metal cations and organic functional groups of biochar (Cao et al., 2009; Uchimiya et al., 2010; Beesley and Marmiroli, 2011a). Biochar can also enhance adsorption of heavy metals by acidic variable charge soils from tropical and subtropical regions through the similar mechanisms (Uchimiya et al., 2011a; Jiang et al., 2012a), because these soils have relatively low pH and cation exchange capacity (CEC), and thus low adsorption capacity for heavy metals.

Biochar contains some alkaline substances and normally has high pH (Yuan et al., 2011). Therefore, incorporation of biochar increased pH of acid soils (Yuan et al., 2011) and thus should accelerate the formation of heavy metal precipitates in the soils. Oxygen-containing functional groups on biochar can form complexes with heavy metal cations, leading to the increase of the adsorption of heavy metals by such soils (Uchimiya et al.,

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* Corresponding author. Tel.: +86 25 8688 1183.
E-mail address: rkxu@issas.ac.cn (R.-k. Xu).

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http://dx.doi.org/10.1016/j.biortech.2013.01.161

2012; Beesley et al., 2011b; Cao et al., 2011). Both mechanisms increased immobilization of heavy metals in acid soils, and thus decreased the activity and bio-availability of heavy metals in the soils following incorporation of biochar (Jiang et al., 2012b). Therefore, the immobilization of heavy metals in acid soils by biochar was generally attributed to precipitation and adsorption (including electrostatic and specific adsorption) (Cao et al., 2011; Uchimiya et al., 2011b). Many analytical techniques in molecular level, such as X-ray Diffraction (XRD), Fourier Transformed Infra-Red Spectroscopy (FTIR), and Nuclear Magnetic Resonance (NMR) have greatly increased our understanding of these mechanisms in recent years (Chun et al., 2004; Cao et al., 2009; Uchimiya et al., 2011b). However, the relative contributions of alkali and functional groups of biochars on heavy metal immobilization need to be distinguished more clearly.

In general, chemical composition and properties of biochar derived from different materials are determined not only by feedstock but also by pyrolysis temperatures. Specifically, biochar alkalinity increases significantly and directly with the rising pyrolysis temperature (Mukherjee et al., 2011; Yuan et al., 2011), whereas the content of oxygen-containing functional groups changes inversely with pyrolysis temperature (Yuan et al., 2011). Consequently, the immobilizing effect of biochar, in terms of alkali and organic functional groups may vary depending on the temperature at which the biochar was produced.

Life cycle of biochar has been assessed primarily for its rate of decomposition and also in the context of greenhouse gas emissions (Bolan et al., 2012; Roberts et al., 2010). It is reported that biochar has a high content of stable carbon, resists decay and remains in soils for long periods of time. However, the duration of heavy metals immobilized by biochar in acid soils is not clearly known and must be investigated to ensure that using biochar to manage environmental pollution is ecologically sustainable as well (Beesley et al., 2011b).

The immobilization of Cu(II), Pb(II) and Cd(II) in a simulated polluted Ultisol by the addition of rice straw biochar has been investigated in the previous report (Jiang et al., 2012b). In present study, an actual Cu(II) contaminated Ultisol was collected near a copper smelting plant to set its objectives, namely (1) to examine Cu(II) immobilization in the actually polluted soil due to incorporation of biochars and assess the relative contributions of the different mechanisms in Cu(II) immobilization, i.e. precipitation due to the increase of soil pH induced by alkaline substances from biochars and surface complexation between Cu(II) and organic functional groups on biochars; (2) to compare the retention effect of biochar derived from different sources of straw and produced at different temperatures, and (3) to estimate the duration over which biochar derived from different sources of straw remains effective as an amendment for soils polluted with Cu(II).

2. Method

2.1. Soil and varieties of biochar

Sample of surface soil (0–20 cm), which was an Ultisol, was collected from a site polluted with multiple pollutants in Guixi in China's Jiangxi province (28°20.31′N, 117°14.13′E). The excessive concentration of heavy metals in the soil was probably due to illegal discharge of sewage and exhaust gas from an adjacent copper smeltery. The soil samples were air-dried and ground to pass through a 60-mesh sieve. Samples in duplicate (0.1 g each) were digested in a mixture of HNO_3, HF, and $HClO_4$ and the extracts were used for determining the initial level of the metals. These heavy metals, namely Cu, Zn, Cr, Ti, Ni, Pb, Co, Sb, and Mo, were measured by ICP–OES (Optima 8000, PerkinElmer, USA). Some properties of the soil are given in Table 1. The concentration of Cu was the highest among all trace metals, and this paper is mainly concerned with the activity and bio-availability of Cu with and without biochar amendment.

Straw from four crops, namely peanut (*Arachis hypogaea* L.), soybean (*Glycine max* L.), canola (*Brassica campestris* L.), and rice (*Oryza sativa* L.), was collected from a suburb of Nanjing, China. The straw was air-dried at room temperature and ground to pass through a 10-mesh sieve. Samples of the ground straw were then placed in ceramic crucibles, each covered with a close-fitting lid, and pyrolyzed under limited supply of oxygen in a muffle furnace (Shanghai Xinmiao Electricity Furnace Inc, China). The pyrolysis temperature was raised to 300, 400, or 500 °C at about 20 °C per min and held constant for 4 h (Chun et al., 2004; Yuan et al., 2011). The biochar was allowed to cool down to room temperature and ground to pass through a 60-mesh sieve. In addition to pyrolysis temperature, pyrolysis time is an important factor influencing biochar chemistry and morphology (Mukherjee et al., 2011). When biochar was used as amendment to immobilize heavy metals in soils, the pyrolysis time was normally 3–4 h (Cao et al., 2011; Mukherjee et al., 2011; Uchimiya et al., 2011b). Similarly, the pyrolysis time of 4 h was used in present study.

Commercial activated carbon (AC) obtained from Shanghai Tongshi Chemical Engineering Company, China, was used for comparison.

2.2. Properties of biochar

The distribution of acid functional groups on the surface of the biochar was determined using the Boehm titration method (Boehm, 1994; Mukherjee et al., 2011): the pH of a suspension of biochar in water (1.0 g of biochar in 40 g of water) was adjusted to 5.0. The suspension was left undisturbed for 7 days, dried at 60 °C, and homogenized. Samples of the homogenized biochar (0.100 g each) were added to 10 mL of each of the three bases: $NaHCO_3$, Na_2CO_3, and NaOH (all at 0.05 M). The mixtures, along with a control solution without any biochar, were shaken for 24 h, centrifuged at 4500 rpm for 5 min, and then filtered through a 0.45 μm Millipore filter. Aliquots of the filtrates (5 mL each) were pre-neutralized with 10 mL of 0.05 M HCl and titrated to pH 7.0 by adding 0.05 M NaOH solution at 0.5 ml/min, the process being controlled by a TIM 854 automatic titration system (Radiometer, France). Purified N_2 was introduced into the whole titration process to expel CO_2. Surface acidity was calculated on the assumption that $NaHCO_3$ neutralizes only the carboxyl groups (the strong acid fraction); Na_2CO_3 neutralizes the acidic groups including carboxyl, lactones, lactols, and low p*K*a phenols (the strong and moderate acid fractions); and NaOH neutralizes total acidity (carboxyl, lactones, phenols, carbonyls, and any other acidic components) (Boehm, 1994; Chun et al., 2004).

Alkalinity of biochar was measured based on the acid–base titrations. Biochar samples (0.100 g) were placed in 50 mL plastic bottles, 15 mL of deionized water was added to each bottle, along with a control solution without any biochar, and each bottle was stirred on a magnetic stirrer for 2 h at 25 °C. The samples were then titrated with 0.05 M HCl at 25 °C to the end point (pH 2.0) using an automatic titration instrument (TIM 854, Radiometer, France) with magnetic stirring. Purified N_2 was injected in the whole titration process to expel CO_2. The titration rate was kept at 1.0 ml/min, with data collected every 6 s. Alkalinity of biochar was calculated as the difference in the quantity of HCl required to attain the end point with and without biochar.

Volatile matter (VM) was determined using, with slight modification, the method (D–1762–84) suggested by the American Society for Testing and Materials (ASTM, 1990). Samples of biochar (approximately 0.2 g each) from different sources were dried in a drying oven for at least 2 h at 100 °C, allowed to cool in a desiccator,