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Research article

Comparison of characteristics of twenty-one types of biochar and their ability to remove multi-heavy metals and methylene blue in solution

Yan Wang, Ronghou Liu *

Biomass Energy Engineering Research Centre, School of Agriculture and Biology, Shanghai Jiao Tong University, 800 Dongchuan Road, Shanghai 200240, People's Republic of China
Key Laboratory of Urban Agriculture (South), Ministry of Agriculture, 800 Dongchuan Road, Shanghai 200240, People's Republic of China

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ABSTRACT

The characteristics of twenty-one types of biochars as well as their capacities to remove multi-heavy metals (Cu^{2+}, Pb^{2+}, Cd^{2+}, and Zn^{2+}) and methylene blue were compared in order to screen biochars applied for pollutants removal. The adsorption mechanisms of heavy metals and methylene blue by biochars were analyzed. Results showed that the oxygen and hydrogen contents, molar O/C and H/C ratios of biochars decreased while the carbon and ash contents, the pH value increased with pyrolysis temperature increased from 350 °C to 550 °C. The removal efficiency of Pb^{2+} (1.90–30.42%) was higher than Cu^{2+} (0.34–12.83%) and other metals in 100 mg L^{-1} multi-heavy metals solutions. Cotton straw biochar from slow pyrolysis showed the highest removal capacity for Pb^{2+} and Cu^{2+} in multi-heavy metals solutions, while wheat straw biochar from gasification showed the highest removal efficiency of methylene blue (96.28%). Dissolved phosphorus and magnesium participated in the precipitate forming with heavy metals and K played an important role in ion exchange with heavy metals.

1. Introduction

Nowadays, environment pollution, especially for soil and water pollution by heavy metals is becoming severe problem. In addition, soil acidification is also a major problem in soils of intensive Chinese agricultural systems [1]. Biochar which is pyrogenic black carbon derived from thermal degradation of carbon-rich biomass in an oxygen-limited environment [2] has increasing attention due to its important role in carbon sequestration, organic and inorganic pollutants removal and soil fertility enhancement [3,4]. However, the sorption of heavy metals onto biochar is related to the biochar characteristics due to the feedstock type and pyrolysis condition such as reactor type and pyrolysis temperature [5–9]. Previous studies reported that as pyrolysis temperature increased, the pH value, ash and carbon contents, surface areas, and total pore volumes of biochars increased, while the biochar yields, the H/C and O/C ratios, cation exchange capacity (CEC), average pore widths decreased [10–12]. Cluster analysis suggested that biochars derived from similar feedstock types belonged to the same category [10]. Kloss et al. [12] reported straw-derived biochars contained higher salt (4.92 mS cm^{-1}) and ash (12.7%) contents than wood-derived biochars. Manure-derived biochars contained more nutrients than plant-derived biochars.

The removal capacity for inorganic and organic pollutants of biochar is closely related to the biochar characteristics (such as surface area, functional groups, negative charge and cation exchange capability) [2]. Several mechanisms for heavy metals removal by biochars have been proposed. (1) Precipitation and co- precipitation [13,14]:PO_3^{2-} and CO_3^{2-} play an important role in the formation of precipitation [15]. In addition, the high pH value of biochar also promotes the precipitation production as hydroxides. (2) Cation exchange [16]: Biochar has high CEC, and it could adsorb heavy metal ions by releasing other cations like Ca^{2+}, Mg^{2+}, K^{+} or Na^{+}. (3) Electrostatic interaction [17,18]: Amount of negative charges exited on the biochar surface, which could adsorb heavy metal ions with positive charge by electrostatic interactions. (4) physical sorption [19]: Physical adsorption often happens when the biochar has a large surface area with appropriate pore structures. (5) Complexation [20]: The oxygen functional groups (phenol-OH, C═O and C═C) on the biochar surface can generate complex with heavy metals.

At present, most studies are about the characteristics and pollutant removal mechanism of one or few types of biochars or the adsorption kinetics and isothermal curve. Few studies focus on comparing the characteristics of biochars produced from most common agriculture residue by different pyrolysis condition as well as their potential to remove pollutants, especially for biochars produced by fast pyrolysis and gasification. The mechanism of heavy metals removal for biochars was also discussed. Cu^{2+}, Pb^{2+}, Cd^{2+}, and Zn^{2+} were chosen to represent multi-heavy metals because the four types of heavy metals are common in industrial wastewater and soil. The aim of this study is to give a

* Corresponding author at: Biomass Energy Engineering Research Centre, School of Agriculture and Biology, Shanghai Jiao Tong University, 800 Dongchuan Road, Shanghai 200240, People's Republic of China.
E-mail address: liurhou@sjtu.edu.cn (R. Liu).

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reference to the choice of feedstock type and pyrolysis method for multi-heavy metals and organic dye removal.

2. Materials and methods

2.1. Raw materials

Cotton stem, wheat straw (without leaves), rice husk, corn stem (without leaves), peach branch, walnut shell, yak manure, eucalyptus sawdust and wood sawdust were collected in Chinese rural area. Raw materials were air dried and then ground to particles <2 mm.

2.2. Biochars preparation

The slow pyrolysis of the air-dried feedstock was carried out in a tubular furnace with a nitrogen purge gas at a flow of 900 mL min^{-1}, following two temperature settings (350 and 550 °C) with 5 °C min^{-1} of heating rate for 2 h. Table 1 lists the biochar types, feedstocks and pyrolysis conditions. The biochars produced from cotton stem, wheat straw, rice husk, corn stem, peach branch, walnut shell, yak manure and eucalyptus sawdust by slow pyrolysis at 350 or 550 °C were labeled as SP350/550-CTB, SP350/550-WHB, SP350/550-RHB and SP350/550-CNB, SP550-PEB, SP350/550-WNB, SP350/550-YMB and SP350/550-EUB, respectively (SP means slow pyrolysis; 350/550 means that the pyrolysis temperature was 350 °C and 550 °C, respectively; the first two letters means the feedstock type and B mean biochar). The fast pyrolysis of rice husk, wood sawdust and peach branch was carried out using a fluidized bed reactor at about 550 °C and the obtained biochars were labeled as FP-RHB, FP-WSB and FP-PEB, respectively (FP means fast pyrolysis). The gasification of wheat straw, polar wood and olive residue was carried out in a fixed bed reactor at 1200 °C, and the obtained biochars were labeled as GF-WHB, GF-POB and GF-OLB, respectively (GF means gasification).

All biochars were ground and sieved (~0.18 mm) for subsequent applications. Slow pyrolysis biochar yield was calculated by the following equation:

$$\text{Yield}\ (\%) = \frac{M_b}{M_f} \times 100\% \quad (1)$$

where, M_b is the mass of biochar after pyrolysis, and M_f is the mass of oven-dried feedstock.

Table 1
Biochar types, feedstocks and pyrolysis conditions.

Biochar type	Feedstock	Pyrolysis type	Temperature (°C)
SP350-RHB	Rice husk	Slow pyrolysis	350
SP350-CTB	Cotton stem	Slow pyrolysis	350
SP350-WNB	Walnut shell	Slow pyrolysis	350
SP350-WHB	Wheat straw	Slow pyrolysis	350
SP350-YMB	Yak manure	Slow pyrolysis	350
SP350-EUB	Eucalyptus sawdust	Slow pyrolysis	350
SP350-CNB	Corn stem	Slow pyrolysis	350
SP550-RHB	Rice husk	Slow pyrolysis	550
SP550-CTB	Cotton stem	Slow pyrolysis	550
SP550-WNB	Walnut shell	Slow pyrolysis	550
SP550-WHB	Wheat straw	Slow pyrolysis	550
SP550-YMB	Yak manure	Slow pyrolysis	550
SP550-EUB	Eucalyptus sawdust	Slow pyrolysis	550
SP550-CNB	Corn stem	Slow pyrolysis	550
SP550-PEB	Peach branch	Slow pyrolysis	550
FP-RHB	Rice husk	Fast pyrolysis	550
FP-PEB	Peach branch	Fast pyrolysis	550
FP-WSB	Mixed wood sawdust	Fast pyrolysis	550
GF-WHB	Wheat straw	Gasification	1200
GF-POB	Poplar wood	Gasification	1200

2.3. Analysis of biochar characteristics

Ash contents of the biochars were determined according to ASTM D 1782-84. The C, H and N contents of the biochars were determined according to ASTM D 3176 using an elemental analyzer (Vario EL Cube, Elementar). The oxygen values of biochars were calculated by difference. The pH of the biochar was measured (1:10 ratio of biochar solutions in de-ionized water) by a pH meter (FE-20K, Mettler Toledo). Scanning Electron Microscopes (SEM) of biomass and biochar samples were taken by using Extreme-resolution Analytical Field Emission SEM (JEOL JSM-7800F Prime, Japan). Fourier-transformed infrared (FTIR) spectra were used to identify functional groups on the biochar surfaces. FTIR spectra were obtained at 4 cm^{-1} resolution from 4000 to 400 cm^{-1} using Fourier transform infrared spectrometer (Nicolet 6700, Thermo Fisher). Prior to FTIR analyses, all biochar samples were oven-dried overnight at 80 °C. Brunauer-Emmett Teller (BET) surface area (S_{BET}) was measured by nitrogen gas sorption analysis at 77 K (ASAP 2460, Micromeritics Instrument Corp.). Before analysis, samples were vacuum degassed at 200 °C or 300 °C (biochar from gasification) for 12–24 h based on the biochar type.

2.4. Adsorption test

Pb^{2+}, Cu^{2+}, Cd^{2+} and Zn^{2+} stock solutions (1000 mg L^{-1}) were prepared by dissolving $Pb(NO_3)_2$, $Cu(NO_3)_2 \cdot 3H_2O$, $Cd(NO_3)_2 \cdot 4H_2O$ and $Zn(NO_3)_2 \cdot 6H_2O$ in deionized water, respectively. Working solution (100 mg L^{-1}) was prepared by diluting the stock solutions. The sorption equilibrium was attained by shaking 20 mg of biochar in 200 mL of working solution at 180 rpm in an shaker at 23 ± 1 °C for 48 h. Initial pH was adjusted to pH 5.5 ± 0.1 by 0.1 M NaOH or HNO_3 solution. After the adsorption, the solution was filtered through a 0.45-μm syringe filter, and diluted with 1% HNO_3. Concentrations of Pb^{2+}, Cu^{2+}, Cd^{2+} and Zn^{2+} were analyzed using inductively coupled plasma optical emission spectrometry (iCAP6300, Thermo).

Methylene blue (MB) stock solutions (1000 mg L^{-1}) were prepared by dissolving 1000 mg methylene blue in 1000 mL of deionized water. Working solution was prepared by diluting the stock solutions. 20 mg of biochar was added into flask containing 50 mL of 100 mg L^{-1} of MB solution. After shaken 24 h at 25 ± 1 °C to establish the adsorption-desorption equilibrium, the solution was centrifuged at 37,000 rpm, and the supernatant was transferred to test tube and diluted. The concentration of MB was determined by a UV spectrophotometer (UV-1800, Shimadzu) at an absorbance wavelength of 664 nm. The adsorption test was repeated twice and the standard error was used to express the error bar.

The removal efficiency of pollutant was calculated as follows:

$$R = \frac{C_0 - C_e}{C_0} \times 100\% \quad (2)$$

where, R is the removal efficiency of pollutants (%); C_0 and C_e are the initial and equilibrium concentrations of pollutant (mg L^{-1}).

2.5. Acid washing

To analyze the effect of soluble components on pollution removal capacity, five types of biochars were selected for their strong adsorption capacity. The biochars were treated with 0.1 M HCl (1 biochar:50 solution, w/v) three times and separated by vacuum filtration to remove the supernatants. Then, the residues were rinsed with distilled water until the pH value of the biochar became nearly neutral. The resulting biochars were oven-dried at 105 °C and then milled <0.18 mm. The treated biochar was labeled A–M (A stands for acid washing and M stands for biochar type). The adsorption experiment was carried out as previous described.