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Enhanced adsorption of Cu(II) and Cd(II) by phosphoric acid-modified biochars☆

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ABSTRACT

In this research, adsorption of Cu(II) and Cd(II) by biochars was investigated. To enhance the adsorption of these two metal ions, a simple modification of biochars by phosphoric acid (H_3PO_4) was carried out. The surface area was larger and the contents of oxygen-containing functional groups of modified biochars were more than pristine biochars. In comparison with pristine biochar, modified biochars sorbed Cu(II) and Cd(II) much more strongly. Surface area had significant effects on the sorption of Cu(II) and Cd(II) by modified biochars, it also resulted in the higher sorption for the pristine biochar at high pyrolysis temperature. X-ray photoelectron spectroscopy analyses indicated that the quantities of carboxyl (-COOH) and hydroxyl (-OH) functional groups of modified biochars were larger than those of pristine biochar at the same pyrolysis temperature. Compared with that of pristine biochars, the strong ability of -COOH and -OH of modified biochars to form complexes with Cu(II)/Cd(II) ions resulted in higher adsorption of these two metal ions. The phosphorus-containing groups of modified biochars, such as P=O and P=OOH from the result of Fourier transform infrared spectroscopy, interacted and also formed complexes with metal ions, possibly resulting in the enhanced adsorption of Cu(II) and Cd(II). Thus, sorption of metal ions by modified biochars was controlled by the mechanism of surface complexation between oxygen containing functional groups and metals. In general, the H_3PO_4 modification was an effective method to prepare biochars with a high affinity for the sorption of heavy metals.

1. Introduction

Heavy metals are significant contaminants because they threaten human beings along food chains (Wang and Chen, 2009; Wang et al., 2012). Heavy metals are discharged into the industrial and agricultural environments (Kılıç et al., 2013). Copper is an ubiquitous heavy metal and is categorized as a priority pollutant by the US EPA (Yang and Jiang, 2014). Another toxic heavy metal, cadmium, attracts significant concern due to its mobility and biological accumulation. Cd can cause the damages to bone and kidney with long time exposure (Belhalfaoui et al., 2009). Adsorption and precipitation are usually used to remove these heavy metals from the environment (Eloussaief and Benzina, 2010). Adsorption is considered as the good choice because of its low-cost and straightforward design (Kılıç et al., 2013). It is important to choose an effective adsorbent with high sorption capacity for heavy metals.

Biochar is an emerging carbonaceous solid residue which can be prepared by agricultural and industrial biomass under lower temperature in oxygen limited conditions (Kookana, 2010; Woolf et al., 2010). Removal of metal ions such as Cd^{2+}, Pb^{2+} or Cu^{2+} by biochars at different temperatures has been widely investigated in recent years (Doumer et al., 2016). Thus, many studies focus on the application of biochars in carbon sequestration, contaminant reduction and soil amendment (Kookana, 2010). However, the adsorption capacity of the biochars was limited, and it was hard to selectively adsorb pollutants due to the biochar physicochemical properties (for example, the surface area of some biochars was lower than10 m^2/g). To further improve the metal sorption efficiency of biochars, modification of biochars after pyrolyzation is needed.

As detailed discussed by other authors, the methods of modifying biochars are: (i) magnetization by natural hematite (Wang

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et al., 2015a); (ii) physical activation by nitrogen flow or steam (Lima et al., 2010); and (iii) chemical modification using hydroxides or acid (Regmi et al., 2012; Yang and Jiang, 2014). An effective modification method for improving the adsorption capacity of metals is urgently needed among these methods. The properties of biochars hardly improve using the physically activated and magnetized methods. In particular, the surface area of biochars altered by the magnetization method usually decreases (Mohan et al., 2014; Wang et al., 2015a). Surface areas of biochars are increased by using chemical methods to modify the biochars (Yang and Jiang, 2014). Among the modifying chemical agents, potassium hydroxide (KOH), zinc chloride (ZnCl) and phosphoric acid (H_3PO_4) are widely reported. Compared with other agents, H_3PO_4 is nonpolluting and is easily washed away by water (Reddy et al., 2012). Thus, the present work used H_3PO_4 as the modification agent. This study focuses on exploring a simple and effective method to chemically modify biochars to have a strong capacity for adsorption of heavy metals.

Adsorption of heavy metals from aqueous solutions by biochars was controlled by many mechanisms, such as surface precipitation, metal complexation by functional groups, each using physical sorption and/or electrostatic interactions (chemisorption) (Lu et al., 2012; Tan et al., 2015). Because of the surface heterogeneity and well-distributed pores, the sorption affinity of heavy metals by biochars was high (Kasozi et al., 2010). In addition, the large specific surface areas and pore volumes of biochars could result in a high sorption affinity for metals. Metal ions can be physically adsorbed on the surface of biochars or retained within their pores (Kumar et al., 2011). Fang et al. indicated that biochars contain many functional groups like -COOH, C-O and -OH. Various metals can interact with these functional groups to form complexes (Fang et al., 2014). Positively charged metal ions can also sorb on biochars with negatively charged surfaces through electrostatic attractions (Dong et al., 2011). Compared with pristine biochars, the properties of the modified biochars may change significantly. The mechanisms of heavy metal sorption by modified biochars may differ from those of pristine biochars. To the best of our knowledge, few researches investigate the properties of H_3PO_4-modified biochars, as well as their adsorption mechanisms for heavy metals.

Thus, a low cost and effective modification method which can be used to prepare biochars with high affinity for the sorption of heavy metals was investigated in this work. There may be great changes for properties of the modified biochars, such as increases of specific surface area and the formation or transformation of surface functional groups which can interact with heavy metals. In addition, we aim to investigate the properties of modified biochars, to explore their sorption behaviors for heavy metals and to determine the interaction mechanisms of metals on pristine/modified biochars.

2. Experimental section

2.1. Preparation and modification of biochars

Preparation of biochars: Pine sawdust was collected in Kunming, China as the biomass for biochar production. The pine sawdust was air-dried and ground to pass through a 0.83 mm sieve. A muffle furnace was used to pyrolyze ground pine sawdust under nitrogen-rich environment. The pyrolysis temperatures were 200, 350, 500 and 650 °C and the biomass was pyrolyzed at these temperatures for 4 h. The obtained biochars were washed several times by deionized water until pH values was about 6.0. These biochar samples were dried at 60 °C, ground (0.2 mm sieve) and then denoted P200, P350, P500 and P650, following the increased pyrolysis temperatures.

Modification of biochars: Different pyrolyzed biochars were impregnated in 47.5% (wt.) H_3PO_4 solutions at room temperature for 24 h. The impregnation weight ratio (acid solution:biochar) was 1:1. The ratio 1:1 was determined to be economically and environmentally advantageous from other studies (Budinova et al., 2006). The impregnated biochar samples were dried at 60 °C, pyrolyzed in atmosphere of nitrogen to the heat treatment temperature (200, 350, 500 and 650 °C) and then kept at these temperatures for 2 h. After being cooled, all modified biochars were washed by deionized water to remove the excessive H_3PO_4, and the pH of biochars was at the range of 5.5–6.0. The washed samples were dried, ground to powder (0.2 mm sieve), and denoted PM200, PM350, PM500 and PM650.

2.2. Characterization of biochars

Total elemental composition such as C, O, N, H and S of biochars were measured by elemental analyzer (Vario EL, Elementar). Brunauer-Emmett-Teller (BET) (Autosorb-1C, Quantachrome) was used for the detection of specific surface area of biochars. Heated the biochar samples at 750 °C using muffle furnace for 4 h and were calculated by comparing the weights of the original biochars and the residue particles to obtain the ash contents. The zeta potentials of all biochars were measured using a Zeta Potential Analyzer. Fourier transform infrared (FTIR) spectra of biochars were conducted by an FTIR instrument (Varian 640-IR, Varian Australia pty ltd, Mulgrave, Australia). Biochars were ground with dried KBr, the ratio of KBr to biochar particles was 800:1. In addition, the resulting mixture was pressed into pellets to detect, and the infrared spectra were collected at 4400-400 cm^{-1}.

2.3. X-ray photoelectron spectroscopy (XPS)

The surface elemental content analysis (C, O, N, P and Si) of all biochars was determined using X-ray photoelectron spectroscopy (XPS). The XPS peaks were deconvoluted for both beam intensity and charging (referencing the binding energy at 285 eV of the C 1s peak) after a linear background subtraction (Akhavan, 2015). Quantitative analyses were conducted according to the sensitivity factor of each element and the peak area ratio from XPS results. This XPS analysis was conducted by XPSPEAK41, and the surface elemental compositions were calculated by MultiPak.

2.4. Adsorption experiments

Batch sorption experiments of Cu(II) and Cd(II) on biochars were conducted. Dissolution of $Cu(NO_3)_2 \cdot 3H_2O$ and $Cd(NO_3)_2 \cdot 4H_2O$ (analytical grade) in a background electrolyte of 0.01 M $NaNO_3$ for 10 mg/L Cu(II) and Cd(II) solutions, respectively. The prepared Cu(II)/Cd(II) solutions was diluted to nine different concentrations (1–10 mg/L) using background solution. In preliminary experiments, pH of pristine biochar solution was adjusted to 4.0 ± 0.1, and pH was adjusted to 5.0 ± 0.1 for modified biochar solution. 8 mg of pristine biochar and 2 mg of modified biochar were added into 8 mL of the metal-containing solutions. Equilibrium sorption experiments of Cu(II) and Cd(II) were proceeded in 8-mL vials, these vials were shaken (the speed was100 rpm) for 5 d at room temperature. Five days were sufficient for the samples to reach apparent sorption equilibria, and the pH value of the solutions was 4.5 ± 0.1. After equilibrium, the mixtures were separated at 3000 rpm for 15 min using a centrifugation, 0.45 μm Millipore filters were used for the suspensions filtered. The residual aqueous concentrations of Cu(II) and Cd(II) were measured using an atomic absorbance spectrometer (Z-2000, Hitachi) by the flame method.