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Sorption and desorption of Pb(II) to biochar as affected by oxidation and pH

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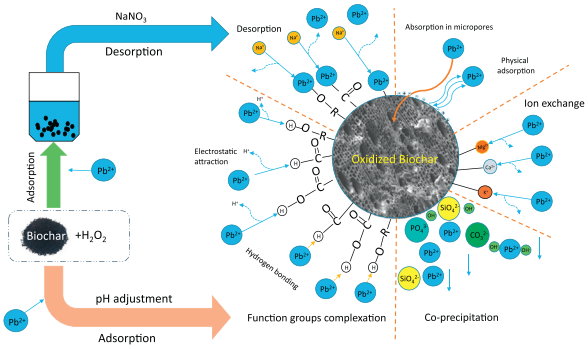
HIGHLIGHTS

- Adsorption is largely affected by oxygen-containing surface functional groups and pH.
- Oxidation increases the affinity of Pb(II) to biochar and decreases the desorption in water.
- Pb(II) adsorption is not fully reversible using $NaNO_3$ irrespective of oxidation.
- Oxidized biochar has the potential for Pb(II) immobilization.

GRAPHICAL ABSTRACT



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ABSTRACT

The use of biochar for the removal of heavy metals from water has environmental benefits. In order to elucidate the potential application of highly functionalized biochar for the removal of Pb(II) in aqueous solution, maple wood biochar was oxidized using hydrogen peroxide. The pH values of oxidized biochar ranged from 8.1 to 3.7, with one set being adjusted to a pH of 7 as a comparison. It was found that oxidizing the biochars increased their Pb(II) adsorption capacity if the pH remained below 6 (strong oxidation), but decreased their Pb(II) adsorption ability above pH 6 (weak oxidation). After adjusting the pH of oxidized biochar to pH 7, the Pb(II) adsorption capacity further increased two to sixfold for oxidized biochars originally at pH 3.7–6. The adsorption characteristics of Pb(II) were well described by the Langmuir equation. Adsorption of Pb(II) was not fully reversible in water. Less than 6% of Pb(II) desorbed in water in two consecutive steps than was previously adsorbed, for biochars with a pH below 7, irrespective of oxidation. Recovery using an extraction with 0.1 M $NaNO_3$ increased from 0.7% to 32.7% of Pb(II) undesorbed by both preceding water extractions with increasing oxidation, for biochars with a pH below 7. Unextractable Pb(II) was lower at low oxidation but increased to 99.0% of initially adsorbed amounts at low pH, which indicated that the adsorption of Pb(II) on oxidized biochar is pH independent.

1. Introduction

Water pollution caused by heavy metals poses a major threat worldwide with a cumulative, chronic and harmful effect on the environment

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and human health (Fu and Wang, 2011). Toxic elements such as lead, cadmium, chromium, and nickel are classified as heavy metals and are associated with water pollution. Among these heavy metals, Pb(II) is considered to be one of the most toxic elements to humans and can be found at high concentrations in liquid industrial waste (Abdel-Halim et al., 2003). Lead enters the human body through the water and food chains, causing respiratory, digestive, nervous, blood, urinary and immune system symptoms of acute or chronic poisoning, and even death (Järup, 2003). Different processing techniques have been adopted to treat heavy metals pollution, such as precipitation, flotation, ion exchange, solvent extraction, cementation onto iron, membrane filtration, chemical oxidation, coagulation, flocculation and electrochemical treatment (Fu and Wang, 2011; Hua et al., 2012). Compared with other techniques, adsorption of heavy metal ions onto solid materials has been found to be advantageous in treating wastewater due to its simplicity, making it often the most economical solution (Bailey et al., 1999; Cao et al., 2011).

Biochar refers to a carbonaceous organic matter prepared by pyrolysis of biomass in a closed system under oxygen-limited conditions (Laird, 2008; Lehmann and Joseph, 2009). Because of its negative surface charge, charge density, high degree of porosity, and extensive surface area, biochar has been considered as a low-cost material with sufficient suitability and selectivity for removal of toxic heavy metal ions in various aqueous environments (Saeed et al., 2005; Liu and Zhang, 2009; Chen et al., 2011; Venkata Ramana et al., 2012; Hina, 2013; Tan et al., 2015). Biochar application to water has been shown to increase heavy metal immobilization through electrostatic and non-electrostatic forces (Xu and Zhao, 2013; Kim et al., 2015). However, untreated biochars usually have a relatively low ability to adsorb cations compared to activated carbon or engineered biochar (Takaya, 2016). Therefore, biochar modification may become more common in the future (Ahmed et al., 2016; Rajapaksha et al., 2016; Wang et al., 2017).

Currently, different biochar modification/activation technologies have been developed to improve its adsorption capacity (Shen et al., 2015; Rajapaksha et al., 2016; Trakal et al., 2016). These methods include chemical, physical and magnetic modification methods (Ahmed et al., 2016; Rajapaksha et al., 2016). Different modification methods have different advantages and disadvantages depending on the purpose of application. Chemical modification can alter the surface chemistry of biochar, thereby leading to enhanced sorption capacity compared with pristine biochar. Hydrogen peroxide (H_2O_2), as a strong and clean oxidant, has been shown to increase oxygen-containing functional groups on the surface of biochar and enhance its ability to remove heavy metals from wastewater (Xue et al., 2012; Huff and Lee, 2016). Previous studies have examined adsorption kinetics on H_2O_2-modified biochar (Xue et al., 2012; Fang et al., 2014; Huff and Lee, 2016). However, few data are available on pH effects and recovery of heavy metal adsorption of oxidized biochars.

Oxidation is an important process controlling the quality of biochars in the environment (Cheng et al., 2008; Qian and Chen, 2014). Oxidation introduces carboxylic and other oxygen-containing functional groups to biochar surfaces that may serve as binding sites for heavy metals. There are several ways that heavy metals interact with biochars including ion exchange, covalent bonding, surface complexation, and precipitation (Tan et al., 2015; Trakal et al., 2016). All these processes could change with pH which plays an important role in elemental solubility in soils/water (Beesley and Marmiroli, 2011). Therefore, it is unclear how the change of pH due to oxidation affects the Pb(II) adsorption capacity of oxidized biochar.

Results from our previous study show that oxidized biochar has significantly greater adsorption and retention of ammonium after neutralization, indicating that pH plays a key role in this process (Wang et al., 2015). Based on this consideration, we investigate if such a pH effect also exists in heavy metal adsorption so as to provide guidance for biochar technology used in sewage treatment. Heavy metals adsorbed by negatively charged organic functional groups on biochar surfaces should be fully desorbable (Rauret, 1998). Results of desorption of heavy metals from peanut biochar showed almost complete desorbability with HCl (Saeed et al., 2005). However, it is not clear whether oxidation of biochar surfaces would change this high desorbability, which would implicate other processes in addition to electrostatic adsorption in the retention mechanism.

The objectives of this study were (i) to quantify the extent to which biochars should be oxidized to increase their Pb(II) retention; (ii) assess the affinity of Pb(II) to oxidized biochar surfaces with increasing oxidation; and (iii) investigate whether Pb(II) adsorption to oxidized surfaces is fully reversible. We hypothesized that (i) oxidation using strong oxidants increases the affinity of Pb(II) to biochar and decreases desorption in water, and (ii) Pb(II) adsorption is not fully reversible using $NaNO_3$ irrespective of oxidation.

2. Experimental methods and materials

2.1. Preparation of biochar

The collection, handling, and pyrolysis conditions of the studied biochars are described in detail by (Wang et al., 2015). Briefly, maple wood biochars (20% sugar maple, 80% red maple) which were pyrolyzed at 500 °C using a modified muffle furnace (Thermo Scientific, Waltham, MA, USA) under argon atmosphere (sweep of 1 L min^{-1}), were ground and sieved to obtain a uniform particle size between 149 and 850 μm. In order to obtain biochars with different pH values, the biochars were oxidized using different concentrations of H_2O_2 as well as different exposure times at 30 °C, in comparison to deionized water (DIW) for 100 h. All samples were prepared using a solid-to-liquid ratio of 1:10 (w/v). Biochar was exposed to oxidant (at 33–35 °C) for 15 min (30% H_2O_2), 45 min (15% H_2O_2), 6 h (30% H_2O_2), 110 h (30% H_2O_2), 350 h (30% H_2O_2) and 100 h in DIW, respectively. Their physical and chemical properties are described in (Wang et al., 2015).

Surface morphology of biochars after water oxidization and washing with water was examined with a scanning electron microscope (SEM) (JSM-6460 LV Scanning Microscope (JEOL, Tokyo, Japan). Surface morphologies of the untreated and oxidized maple wood biochars are shown in Fig. 1. The surface functional groups of the biochars before and after oxidation were determined using a Nicolet iS50 Fourier transform infrared (FTIR) spectrometer (Thermo Fisher Scientific, USA). Infrared spectra were obtained at room temperature in the spectral range from 400 cm^{-1} to 4000 cm^{-1}.

2.2. Adsorption experiments

Batch adsorption experiments were conducted in 50 mL PE centrifuge tubes at room temperature. Stock solutions (1000 mg L^{-1}) of Pb (II) were prepared by dissolving analytical grade $Pb(NO_3)_2$ in ultrapure water (>18.2 MΩ cm). Adsorption experiments were conducted by mixing 0.1 g of biochar with 20 mL of 50 mg L^{-1} Pb(II). The tubes were then agitated on a reciprocating shaker at room temperature at 120 rpm for 24 h. After 24 h, the solid and liquid phases were separated by centrifugation at 3000 rpm for 15 min, and the supernatant was carefully aspirated using a Pasteur pipette. The supernatant was acidified immediately with 0.2% (v/v) HNO_3 for analysis. To obtain the sorption isotherms, solutions of various Pb(II) concentrations (5, 30, 50, 150, 250, 400, 550 mg L^{-1}) were shaken with the adsorbent for 24 h. At the end of each experiment, the mixtures were immediately acidified and Pb(II) concentrations in the supernatant were determined. The concentrations of initial and final Pb(II) in the adsorption experiments were determined using atomic absorption spectrometry (AAS, Buck Scientific Model 200). All experiments were conducted in triplicate including the blank and calibration control.