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Removal of lead, copper, cadmium, zinc, and nickel from aqueous solutions by alkali-modified biochar: Batch and column tests

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ABSTRACT

Engineered biochar was obtained through slow pyrolysis of hickory wood and then further modified with NaOH. After modification, biochar's surface area, cation-exchange capacity, and thermal stability were significantly improved. The modified biochar exhibited much larger (2.6–5.8 times) metal adsorption capacities than the pristine biochar. Competitive batch adsorption of mixed metal ions (Pb^{2+}, Cd^{2+}, Cu^{2+}, Zn^{2+}, and Ni^{2+}) showed preferential adsorption of Pb^{2+} and Cu^{2+} onto the modified biochar. The alkali-modified biochar in a fixed-bed column also showed strong ability to filter heavy metals from aqueous solutions. The alkali-modified biochar thus can serve as alternative absorbent for heavy metals.

Introduction

Biochar, a pyrogenic carbon material, recently has been regarded as a novel, low-cost alternative adsorbent for environmental remediation [1,2]. The existing literature covers a wide range of studies on adsorption of different heavy metals onto biochars derived from various feedstocks including agricultural and forest residuals [3–7]. Most of these studies only employed batch experiments to examine of the sorption behaviors and mechanisms of aqueous heavy metals onto the biochars under optimal conditions. Relatively few studies were carried out with fixed-bed columns to determine the kinetic removal of aqueous heavy metals by biochar-based filters [8,9].

Various modification methods have been developed in recent years to further enhance the sorption ability of biochars (i.e., engineered biochars). For example, magnetic biochars have been synthesized for the removal of aqueous arsenic, cadmium, lead [10–12]. Zhang and Gao [13] found that the presence of AlOOH nanoparticles on biochar surfaces can greatly its sorption of arsenic, methylene blue, and phosphate. Song et al. [14] and Wang et al. [15] found that MnO_x-loaded biochars have enhanced sorption ability to aqueous copper and arsenic. Oxidation chemical agents such as hydrogen peroxide were also used to modify biochars to enhance their sorption ability to heavy metals in aqueous solutions [8,16]. All these modifications dramatically alter the surface properties of the biochars and greatly enhance their sorptive ability to heavy metals in aqueous solutions. This makes the engineered biochars more attractive for many environmental applications, particularly with respect to heavy metal remediation.

Alkali modification is another commonly used engineering method to improve the sorption ability of carbonaceous materials for their applications in wastewater treatment [17,18]. In comparison to other engineering methods such as acid and organic solvent modifications, alkali modification may be more effective in generating high BET surface area and altering surface functional groups [17]. Although this method should have great potential for biochar engineering, its effects on biochar's surface properties and sorption ability are still not well understood. This work used alkali (NaOH) to modify biochar derived from hickory wood chips to improve its heavy metal sorption ability. The pristine and modified biochar samples were examined using thermogravimetric analyzer (TGA) and X-ray photoelectron spectroscopy (XPS). Other basic physicochemical properties of the biochars, such as elemental composition, surface area (SA), and cation exchange capacity (CEC), were also determined. In addition, both batch isotherm sorption and column filtration experiments were conducted to determine

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the sorptive ability of the biochars to heavy metals (i.e., Pb^{2+}, Cd^{2+}, Zn^{2+}, Cu^{2+}, and Ni^{2+}) in single and mixed metal systems. The regeneration of the spent biochar column was also investigated. The specific objectives of this work were to: (1) determine the effects of alkali modification on biochar's physiochemical properties; (2) measure the batch sorption isotherms of heavy metals onto the biochars in single and mixed metal systems; and (3) evaluate the performances of the modified biochar as filter media in fix-bed column to filtrate aqueous heavy metals.

Materials and methods

Chemical reagents

Chemical reagents of analytic grade including NaOH, HNO_3, HCl, $Pb(NO_3)_2$, $Cu(NO_3)_2$, $Ni(NO_3)_2$, $CuCl_2$, and $ZnCl_2$ were purchased from Fisher Scientific. All solutions were prepared using deionized (DI) water (18 MΩ cm).

Biochar preparation and modification

Hickory is one of the most common deciduous trees and distributed widely throughout the world. Hickory chips have been used as representative woody feedstock for biochar preparation in previous studies [19,20]. In this study, dried hickory chips were ground in a knife mill (Model No. 4, Arthur H. Thomas Company, Philadelphia, PA) to achieve 0.5–1 mm hickory powders. The powders were placed inside tubular quartz reactors (50 g in 6 cm diameter × 28 cm cylinders) inside a bench-top furnace (Barnstead 1500 M/Olympic 1823 HE) purged with N_2 gas (10 psi). The pyrolysis temperature of the furnace was ramped to 600 °C at a rate of 20 °C/min and then held at this temperature for 2 h. The produced biochar samples were washed with tap water and DI water several times, oven dried at 80 °C, and placed in a sealed container prior to use. The pristine biochar was notated as HB.

Alkali modification was carried out in a 100 mL Teflon bottle containing 10 g HB and 20 mL of 5 M NaOH solution at 70 °C for 4 h. The resulting composite was dried at 110 °C and then heated to 600 °C inside a bench-top furnace (Barnstead 1500 M/Olympic 1823 HE) purged with N_2 gas (10 psi) for 2 h. After cooled to room temperature, the resulting biochar was washed with tap water and 0.1 M HCl repeatedly until neutral pH, then rinsed with DI water for several times, and finally dried at 110 °C for 24 h. The modified biochar was notated as HMB.

Biochar characterization

Contents of C, H and N in the biochar samples were determined using a CHN Elemental Analyzer (Carlo–Erba NA–1500). Mineral elements were determined using inductively coupled plasma optical emission spectroscopy (ICP–OES, Perkin Elmer Optima 2100 DV, USA) after ashing at 550 °C and acid dissolution. Surface areas were measured with a Quantachrome Autosorb-1 surface area analyzer using N_2 (BET) sorption methods. Cation exchange capacity was analyzed using the US EPA SW-846 method 9081. The thermogravimetry (TG/DTG) curves were carried out using a Mettler TGA/DSC thermogravimetric analyzer (TGA/DSC 1, STARe System, METTLER TOLEDO, USA) at a heating rate of 10 °C/min from 50 °C to 800 °C under an atmosphere of oxygen (50 mL/min). Surface elemental composition and elemental species were analyzed using XPS with a PHI 5100 series ESCA spectrometer (Perkin Elmer).

Batch sorption

Sorption isotherm experiments were carried out at room temperature (20 ± 2 °C) by adding 0.1 g biochars to 100 mL polyethylene centrifuge tubes containing 50 mL either single metal (Pb^{2+}) or mixed metal (Pb^{2+}, Cu^{2+}, Zn^{2+}, Ni^{2+}, and Cd^{2+}) solutions. The metal concentrations ranged from 2.0 to 250 mg/L for Pb^{2+} and from 2.0 to 100 mg/L for others (Cd^{2+}, Cu^{2+}, Zn^{2+} and Ni^{2+}). Initial pH of the metal solutions was adjusted to about 5.0 using 0.01 M HCl and 0.01 M NaOH. At this pH, the metal ions in the solution are stable without precipitation. The mixture was shaken for 24 h in a rotary shaker to ensure a sorption/desorption equilibrium was reached (predetermined), and then centrifuged at 4000 rpm for 10 min. Concentrations of Pb^{2+}, Cu^{2+}, Zn^{2+}, Ni^{2+}, and Cd^{2+} in the supernatant were determined using ICP–OES (Optima 2300, Perkin–Elmer SCIEX, USA). In all cases, sorbed metal ions were calculated as the difference between the amount of each sorbate in the initial and final solutions.

Column filtration and regeneration

About 1.0 g of HMB was wet-packed as an interlayer in an acrylic column of 5 mm in diameter. Acid-cleaned quartz sand (0.5–0.6 mm average size) was used at each end of the column to help distribute the flow. The final height of the biochar layer in the column was about 1.55 cm. The column was initially flushed with DI water for about 2 h. A peristaltic pump (Masterflex L/S, Cole Parmer Instrument, Vernon Hills, IL) was used at the inlet (bottom) of the column to maintain an upward flow rate of 2 mL/min. The filtration experiment was initiated by switching the influent to a mixed metal solution of Pb^{2+}, Cd^{2+}, Cu^{2+}, Zn^{2+} and Ni^{2+} (100 mg/L for each at pH = 5.0 ± 0.2) for 140 min. The column was then flushed with DI water for another 120 min.

After the column was flushed with DI water, the regeneration experiment was initiated by switching to 0.2 M HCl solution at the same flow rate for 120 min. The filtration ability of the regenerated column was then evaluated by switching influent to single metal solution (Pb^{2+}, 150 mg/L) for 80 min. The column was flushed with DI water for 70 min and then regenerated for the second time by flushing with acid solution again for 80 min.

Effluent samples were collected every 2 min with a fraction collector (IS-95 Interval Sampler, Spectrum Chromatography, Houston, TX) and analyzed for metal concentrations by the ICP–OES.

Results and discussion

Influences of alkali modification on biochar surface properties

Alkali modification only had slight effects on the mineral element contents of the biochar (Table 1). The Ca and Mg contents were reduced, but the Al and K contents were increased, after the

Table 1
Elemental content, surface area (SA) and cation-exchange capacity (CEC) of the pristine and modified biochars.

	Elemental contents (%)								SA (m^2/g)	CEC (cmol/kg)
	C	N	H	O[*]	Ca	Mg	Al	K		
HB	84.7	0.30	1.83	11.3	1.17	0.29	0.04	0.28	256	45.7
HMB	82.1	0.25	2.25	13.2	0.63	0.20	0.66	0.65	873	124.5

[*] Contents of O were obtained by the subtraction method.