



# Lead and cadmium remediation using magnetized and nonmagnetized biochar from Douglas fir



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## ABSTRACT

Magnetic biochar (MBC) was produced by magnetite (Fe<sub>3</sub>O<sub>4</sub>) precipitation onto Douglas fir biochar (NBC) that had been generated by wet fast pyrolysis. Treating an aqueous Fe<sup>3+</sup>/Fe<sup>2+</sup> solution with NaOH induced Fe<sub>3</sub>O<sub>4</sub> to nucleate and deposit on NBC. The NBC and the resulting MBC were used to remove Pb<sup>2+</sup> and Cd<sup>2+</sup> from water. Both biochars were characterized by SEM, EDX, TEM, PZC, XRD, elemental analysis, and surface area measurements. Batch sorption studies were carried out from pH 2–7 with adsorbate concentrations from 10 to 250 mg/L at 25, 35 and 45 °C. MBC and NBC suspensions in the contaminated solutions were vortexed for two min. Then MBC was magnetically removed, while NBC required filtration. Remediated solutions were then analyzed using AAS. The amounts of lead and cadmium adsorbed onto both NBC and MBC were lower at low pH values and increased with increasing pH. The Langmuir and Freundlich adsorption isotherm models were applied to describe equilibrium data. The maximum Langmuir adsorption capacities at pH 5 and 45 °C for Pb<sup>2+</sup> and Cd<sup>2+</sup> uptake were ~40 and ~16 mg/g for NBC and ~27 and ~11 mg/g for MBC, respectively. NBC and MBC recycling was carried out after metal ion extraction with 0.1 M HCl and water. Adsorption kinetics of NBC and MBC were compared with four other biochars (mixed feed, magnetized mixed feed, pinewood and magnetized switchgrass). Adsorption equilibria of Pb<sup>2+</sup> and Cd<sup>2+</sup> onto both NBC and MBC were reached within 2 min while the other biochars required from 2 to 20 h. NBC and MBC have potential as low cost, green adsorbents for rapid lead and cadmium remediation as replacements for more expensive commercial activated carbon.

## 1. Introduction

Heavy metal waste water pollution is a risk to the environment and human health. Lead and cadmium get into water systems from multiple pathways [1–4]. Unfortunately, these metals can bioaccumulate in the environment with detrimental effects to wildlife and humans at low concentrations. The US Environmental Protection Agency (EPA) has set the lead and cadmium standards to less than 0.015 mg/L and 0.005 mg/L, respectively, for drinking water [5].

Lead is released to the environment through fossil fuel combustion, battery manufacturing, acid mine drainage, smelting of sulfide ores, corrosion of household plumbing systems and erosion of natural deposits [1,6,7]. Lead poisoning can lead to kidney problems, abortion and high blood pressure in adults [2,5]. In children and infants, lead can cause delays in mental or physical development and deficits in attention span and learning ability [5,8,9]. Cadmium is emitted into the environment from waste batteries, paints, discharge from metal refineries,

corrosion of galvanized pipes and through other industrial processes [2,10,11]. Exposure to this metal can result in kidney damage [5].

Methods currently used to remove heavy metals include ion exchange [12], ultrafiltration [13], membrane separation [14], chemical precipitation [15], adsorption [16], electrochemical [17], coagulation [18], and flocculation [19,20]. Adsorption is a cost effective technique. Biosorbents [21] and activated carbon [22,23] are common adsorbents used for heavy metal removal but are currently considered to be relatively expensive. Thus, considerable interest exists in the development of low-cost adsorbents to remove heavy metals.

Biochar is an adsorbent often formed as a bio-fuel industry by-product and is less expensive and more environmentally friendly than activated carbon. Extensive research now confirms that biochar can be used for energy conversion, carbon sequestration, improving soil fertility, and enhancing water quality via adsorption [24,25]. The ability of many biochars to adsorb metals has been extensively studied [26–30]. Magnetic biochar can be easily separated using a magnet after

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removing contaminants from water [31]. Magnetic separation avoids more time-consuming steps like centrifugation and filtration. The availability of magnetic biochar allows the novel use of batch, stirred-tank processes where spent adsorbent can be recovered with a magnet. As adsorbent particle size decreases, filtration or flow through columns becomes very slow. Thus, magnetic separation could allow practical use of small particle size adsorbents with high surface areas and faster adsorption kinetics but which retard flow rates through columns or filters.

Pharmaceuticals and metals are separate pollutant classes to consider when cleaning waste water [26,27,32–35]. The biochar adsorbents presented here for  $Pb^{2+}$  and  $Cd^{2+}$  adsorption have previously been used for the removal of pharmaceuticals from water (Karunanayake et al. [36,37]). We now report the ability of these magnetic and nonmagnetic Douglas fir biochars to remove lead and cadmium from aqueous solutions. The adsorption behavior of  $Pb^{2+}$  and  $Cd^{2+}$  at different concentrations, temperatures and pH values are reported and compared with previous studies.

## 2. Reagents and equipment

All chemicals were either AR or GR-grades purchased from Sigma-Aldrich unless otherwise specified. Stock solutions were made by dissolving  $Pb(NO_3)_2$  and  $Cd(NO_3)_2 \cdot 4H_2O$  (each metal concentration was 250 mg/L), in de-ionized water prepared in a Millipore-Q water system. The pH was adjusted using either 0.1 M  $HNO_3$  or 0.1 M NaOH using a pH meter (HANNA instrument HI 2211 pH/ORP meter).  $Pb^{2+}$  and  $Cd^{2+}$  concentrations were determined using an atomic adsorption spectrophotometer (Shimadzu AA-7000). Adsorption studies were carried out inside a static water bath (BUCHI 461). A vortex mixer (Scientific Industries, T3-1280) was used to stir the samples.

### 2.1. Scanning electron microscopy (SEM) and energy dispersive X-ray analysis (EDX)

Surface morphologies of MBC and NBC were observed using a JEOL JSM-6500F FE-SEM at 5 kV. The sample was coated on a carbon stub attached to carbon tape and then was mounted into a sample holder for SEM/EDX analysis. EDX was carried out using a Zeiss, EVO 40 scanning electron microscope containing a Bruker EDX system.

### 2.2. Transmission electron microscopy (TEM) and energy-dispersive X-ray spectroscopy (EDS)

MBC and NBC were examined with a JEOL model 2100 TEM operated at 200 kV. TEM samples were prepared by mixing ~10 mg of char with ~0.5 mL ethanol followed by 2 min of sonication. A drop of this suspension was then deposited onto a carbon film on a 300 mesh copper grid and allowed to stand overnight prior to TEM/EDS analysis. EDS was carried out using an Oxford X-max-80 detector.

### 2.3. Surface area measurements

The surface areas of all six adsorbents were examined using a  $N_2$  BET, Micromeritics Tristar II Plus surface area analyzer. The adsorption data was used to determine  $N_2$  adsorption isotherms (273 K), which were analyzed by applying the Dubinin-Astakhov equation [38] for pore volume.

### 2.4. X-ray powder diffraction (XRD)

X-ray diffraction (XRD) patterns for MBC were obtained from Rigaku Ultima III (Jade 2010 software with PDF 2 database) using Cu-K  $\alpha$  ( $\lambda = 1.54 \text{ \AA}$ ) radiation at 45 kV and 40 mA. The samples were scanned from 5 to 90° with the scan speed of  $1^\circ \text{ min}^{-1}$ .

## 2.5. Proximate analysis

Ash analysis was done by weighing the mass of ash produced from incinerating 1 g of the biochar sample in a muffle furnace in air at a 650 °C for 15 h. The percent iron in each biochar sample was determined by atomic absorption spectroscopy (Shimadzu AA-7000) using an iron standard solution (Sigma-Aldrich). An acid digestion was performed on 0.1 g of biochar using 50.0 mL of 1:1 95%  $H_2SO_4$ /70%  $HNO_3$ . Iron was dissolved from the biochar into the acid for 24 h with stirring and then diluted 5-fold with deionized water prior to atomic absorption spectroscopy analysis.

## 2.6. Point of zero charge (PZC) measurements

The points of zero charge (PZC) of MBC and NBC were determined using a 0.01 M NaCl aqueous solution with pH values ranging from 2 to 7 at pH intervals of 1. These pH values were fixed using either 0.1 M NaOH or 0.1 M HCl solutions. These solutions (25 mL) were brought into contact with 0.05 g of adsorbent and each system was vortexed for 2 min. After removal of biochar using a magnet (MBC) or filtration (NBC), the pH of the supernatant was measured using an ORION model 210 pH meter. The PZC was obtained from a plot of initial solution pH against pH of the supernatant.

## 3. Experimental

### 3.1. Pyrolysis of Douglas fir biochar

Douglas fir biochar (NBC) was produced as a by-product from the gasification of timber industry waste wood. Auger-fed, chipped (approximately 3 in.) wet green wood was introduced into the air-fed updraft gasifier at 900–1000 °C with a residence time of about 1–10 s. Large biochar particles (~2 cm) were collected and washed several times with water to remove fine particulates, impurities and water soluble organic residuals, before drying at room temperature. The biochar was ground, sieved to a particle size of 0.1–0.6 mm and stored in closed vessels until needed [36].

### 3.2. Preparation of magnetic Douglas fir biochar

Magnetic biochar from Douglas fir (MBC) was prepared from NBC according to the method described by Mohan et al. [39] and Karunanayake et al. [36,37]. Briefly, Douglas fir biochar (50 g) was suspended in distilled water (500 mL). Solutions of  $FeCl_3$  (18 g, 1300 mL) and  $FeSO_4 \cdot 7H_2O$  (36.6 g, 150 mL) were each prepared then mixed and vigorously stirred (200 rpm) at 60–70 °C for 5 min. This combined  $Fe^{2+}/Fe^{3+}$  solution (1450 mL) was then slowly poured into the aqueous (500 mL) biochar (Douglas fir) suspension at room temperature and slowly stirred (50 rpm) for 30 min. Then, 10 M NaOH solution was added dropwise (~1 h) until a pH of ~10–11 was achieved. Predominantly  $Fe_3O_4$  iron oxides nucleated on biochar and also precipitated as tiny particles, adhering to the biochar surfaces. The resulting  $Fe_3O_4$ -magnetized Douglas fir biochar (MBC) was filtered, repeatedly washed with distilled water, and given three ethanol washes. This was followed by vacuum filtration and overnight oven drying at 50 °C at 1 atm.

NBC and MBC's adsorption kinetics were compared with two commercially available biochars (designated as C1 and MC2 herein), and two in-house prepared biochars (pinewood, PW and magnetic switchgrass, MSG) (Table 1). The pinewood biochar was made according to the method described by Essandoh et al. [40], and the switchgrass biochar was made according to Pittman et al. [41].

### 3.3. Sorption studies

Batch sorption studies for NBC and MBC were performed by varying

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