



Potential mechanisms of cadmium removal from aqueous solution by *Canna indica* derived biochar



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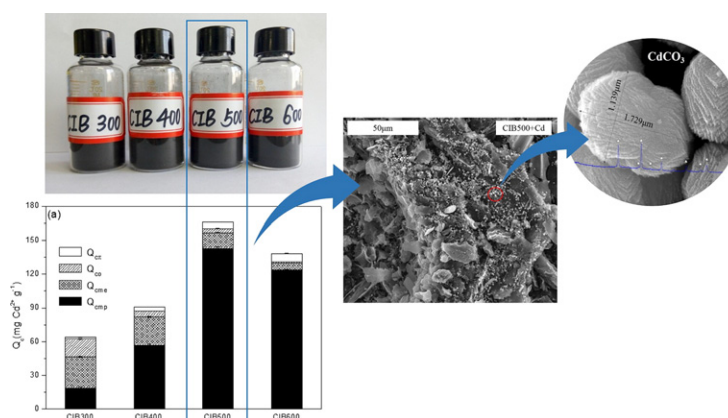
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HIGHLIGHTS

- Sorption capacity of metal on biochars is affected by pyrolysis temperature.
- Biochar derived from *Canna indica* at 500 °C has a high sorption capacity for Cd²⁺.
- Cd²⁺ sorption on the biochars fits a pseudo second order and Langmuir model.
- Precipitation and ion exchange mechanisms dominated Cd²⁺ sorption on the biochars.

GRAPHICAL ABSTRACT



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ABSTRACT

The objective of this study was to investigate the mechanisms of cadmium (Cd) sorption on biochars produced at different temperature (300–600 °C) and their quantitative contribution. The sorption isotherms and kinetics of Cd²⁺ sorption on biochars were determined and fitted to different models. The Cd²⁺ sorption data could be well described by a simple Langmuir model, and the pseudo second order kinetic model best fitted the kinetic data. The maximum sorption capacity (Q_m) obtained from the Langmuir model for CIB500 was 188.8 mg g⁻¹, which was greater than that of biochars produced at other temperature. Precipitation with minerals, ion exchange, complexation with surface oxygen-containing functional groups, and coordination with π electrons were the possible mechanisms of Cd²⁺ sorption on the biochars. The contribution of each mechanism varied with the pyrolysis temperature. With increasing pyrolysis temperature, the contribution of surface complexation and metal ion exchange decreased from 24.5% and 43.3% to 0.7% and 4.7%, while the contribution of precipitation and Cd²⁺- π interaction significantly increased from 29.7% and 2.5% to 89.5% and 5.1%, respectively. Overall, the precipitation with minerals and metal ion exchange dominated Cd²⁺ sorption on the biochars (accounted for 73.0–94.1%), and precipitation with minerals was the primary mechanism of Cd²⁺ sorption on the high-temperature biochars (≥ 500 °C) (accounted for 86.1–89.5%).

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1. Introduction

Cadmium (Cd) is considered one of the most toxic heavy metals due to its high mobility and persistence, which accumulates easily and causes severe damage to human health (Kula et al., 2008; Mohan et al., 2007). Several technologies have been developed to remove heavy metal from water, such as ion exchange, chemical precipitation, membrane separation and adsorption (Dabrowski et al., 2004; Sud et al., 2008; Fang et al., 2008; Ge et al., 2012; Pan et al., 2010). In comparison, sorption is considered a cost-effective approach for remediation of contaminated water because of its low cost, high efficiency and environment-friendly (Chen et al., 2011; Sun et al., 2011). A number of sorbents have been studied to remove Cd from water recently, including activated carbon, organic material, microbial biomass, agricultural waste materials and carbon nanotubes (Kumar et al., 2014; Sud et al., 2008; Ok et al., 2007; Li et al., 2003), but most of the sorbents have limitations of either high cost, low efficiency, or disposal restrictions.

Biochar, a by-product obtained from the thermochemical conversion of biomass in an oxygen-limited environment (IBI, 2012), has been well applied for soil improvement, waste management and climate change mitigation (Bell and Worrall, 2011; Lehmann, 2007; Uchimiya et al., 2011; Woolf et al., 2010). In recent years, biochar has also shown great potential for sorption of contaminants in soil and water (Ahmad et al., 2014; Cao et al., 2009; Cui et al., 2016; Xu et al., 2012), especially for effective removal of Cd from water. Xu et al. (2013) reported that the maximum sorption capacity of Cd by dairy manure biochar was 51.4 mg g^{-1} . Zhang et al. (2015) indicated that *Eichornia crassipes* derived biochar had a greater sorption capacity (70.3 mg g^{-1}) for Cd in aqueous solution. Sun et al. (2014) found that biochars derived from various crop straws showed an even greater sorption capacity for Cd ($57.7\text{--}96.4 \text{ mg g}^{-1}$) in aqueous solution. The possible mechanisms for Cd sorption on biochar included: (i) Cd precipitates with minerals (e.g., PO_4^{3-} , CO_3^{2-}) (Kim et al., 2013; Xu et al., 2013; Zhang et al., 2015); (ii) metal ion exchange with Cd^{2+} (such as K^+ , Ca^{2+} , Na^+ , Mg^{2+} , $-\text{COOM}$, $-\text{R-O-M}$) (Ahmad et al., 2014; Mohan et al., 2007; Lu et al., 2012); (iii) surface complexation between Cd^{2+} and oxygen-containing functional groups (OFGs, e.g., $-\text{OH}$, $-\text{R-OH}$, $-\text{COOH}$) (Sun et al., 2014; Wan et al., 2014); and (iv) coordination of Cd^{2+} with π electrons (e.g., $\text{C}=\text{C}$, $\text{C}\equiv\text{C}$) (Cao et al., 2009; Zhang et al., 2015). The proposed mechanisms may be ascribed to the pyrolysis temperature-dependent properties of biochar, such as pH, ionic strength, and surface characteristics (Uchimiya, 2014). However, these mechanisms have not been confirmed with elaborated experiments (Ahmad et al., 2014; Zhang et al., 2013). In addition, previous studies failed to provide quantitative information regarding the relative contribution of the involved mechanisms to Cd sorption on biochars produced at different pyrolysis temperature.

In this research, biochars were obtained at $300\text{--}600 \text{ }^\circ\text{C}$ through slow pyrolysis of *Canna indica*, and the physicochemical properties of samples were characterized. The objectives were to: (1) determine the sorption capacity of Cd^{2+} on the biochars in aqueous solution; and (2) understand the mechanisms of Cd^{2+} removal from water by the biochars on a qualitative and quantitative basis.

2. Materials and methods

2.1. Biochar preparation

Canna indica (CI) samples were collected from Lin'An constructed wetland, Zhejiang, China. The raw materials were washed with water three times and air-dried for a week, then dried at $80 \text{ }^\circ\text{C}$ for 24 h and sieved to $<2.0 \text{ mm}$ particles using a stainless grinding machine (Retsch MM400, Germany). The powdered biomass was tightly placed in a ceramic pot, and then pyrolyzed in a muffle furnace under N_2 atmosphere, the pyrolysis was programmed to raise the internal biomass chamber temperature to 300, 400, 500 and $600 \text{ }^\circ\text{C}$ at a rate of $5 \text{ }^\circ\text{C}/\text{min}$ and held at the peak temperature for 2 h before cooling to room

temperature. The biochars (i.e. the solid residues from the pyrolysis) were referred to as CIB300, CIB400, CIB500, and CIB600 in accordance with the pyrolysis temperature. All of the biochar samples were ground to pass through a 0.25-mm sieve prior to use. The demineralized biochar samples were obtained by rinsing with 1 M HCl solution, and then washed using distilled water until the pH value of the liquid became constant (Qiu et al., 2008). This acid dipping procedure did not alter the oxygen-containing functional groups on biochar surface (Wang et al., 2015; Zheng et al., 2013). The HCl-treated biochars were identified as CIBA300, CIBA400, CIBA500, and CIBA600, respectively.

2.2. Characterization of biochars

Elemental (C, H, N) analyses were conducted using a CHN Elemental Analyzer (Flash-EA112, Thermo Finnigan). Scanning electron microscope (SEM) imaging analysis was conducted using a scanning microscope (FEI QUANTA FEG 650) to compare the structure and surface characteristics of biochars. Surface element analysis was conducted simultaneously with the SEM at the same surface locations using energy dispersive X-ray spectroscopy (EDS, EDAX Inc. Genesis XM). Fourier transform infrared spectroscopy (FTIR) analysis (Nicolet 6700) was performed in the 400 and 4000 cm^{-1} region with 50 scans being taken at 2 cm^{-1} resolution to identify the surface functional groups. The specific surface area and porosity properties of the biochars were measured by N_2 adsorption isotherms at 77 K with the Brunauer-Emmett-Teller (BET) method using a Quadrasorb Si-MP surface area analyzer. Zeta-potential was determined at different pH values using a potential analyzer (Malvern Nano-ZS90, England). The surface chemical composition was determined by X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) using a D8 Advance Bruker and PHI 5000 Versa Probe spectrometer, respectively. Ash content was measured by heating the biochar samples at $750 \text{ }^\circ\text{C}$ for 5 h. The pH of biochars was measured by adding biochar to deionized water at a mass/water ratio of 1:20 (Inyang et al., 2012).

2.3. Sorption experiments

Cadmium stock solution (1000 mg L^{-1}) was prepared by dissolving cadmium nitrate ($\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, certified A.C.S., Fisher Scientific) in 0.01 mol L^{-1} NaNO_3 solution as background electrolyte. The effect of pH on Cd^{2+} sorption was investigated with an initial pH range between 2.0 and 8.0, and the initial pH of cadmium solutions was adjusted to the required values by using 0.5 M HNO_3 or NaOH solutions. In these experiments, the original biochar samples (0.03 g) were placed into 30 mL solutions containing 200 mg L^{-1} Cd^{2+} with different initial pH values at 180 rpm and room temperature ($25 \text{ }^\circ\text{C}$) for 24 h, and the blank system without Cd^{2+} also was conducted under same condition as control. The final pH and residual Cd of solutions were determined after equilibration. Sorption kinetics was evaluated at room temperature ($25 \text{ }^\circ\text{C}$) and the initial pH for each sorption solution was adjusted to 5.0 ± 0.05 by adding 0.5 M HNO_3 or NaOH solutions. The original biochar (0.03 g) was placed into 30 mL solutions containing 100 mg L^{-1} Cd^{2+} as Cd (NO_3)₂ in vitreous vials, and the subsamples were taken at the interval times after shaken at 180 rpm in a mechanical shaker. Sorption isotherms of Cd^{2+} were determined using batch experiments in vitreous vials under the same conditions as stated above, and the concentration of Cd^{2+} varied from 0 to 200 mg L^{-1} . After shaken for 24 h, and the final suspensions were centrifuged, filtered, and the supernatant solution was separated for analysis of Cd^{2+} using inductively coupled plasma-mass spectrophotometer (ICP-MS) (Agilent 7500a, USA).

In order to determine the contribution of each mechanism to the overall sorption of Cd^{2+} on biochars, the untreated and demineralized biochars were placed into Cd solution (200 mg L^{-1}) and deionized water (control), respectively, under the same conditions above. After pH analysis, the concentrations of anions (PO_4^{3-} , CO_3^{2-} , SO_4^{2-} , NO_3^- , and Cl^-) in the aqueous solutions were determined using ion chromatography (IC) after

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