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Efficient removal of lead from solution by celery-derived biochars rich in alkaline minerals

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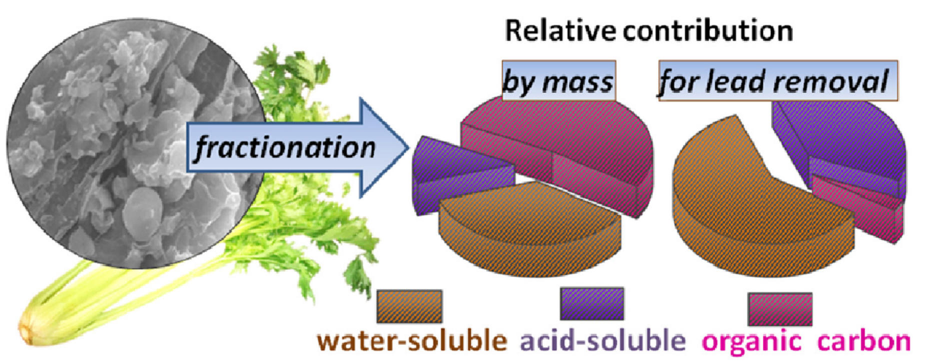
HIGHLIGHTS

- Biochars rich in alkaline minerals were produced from celery biomass.
- The celery biochars showed a Pb^{2+} sorption capacity as high as 300 mg/g.
- The alkaline minerals played a dominant role in the Pb^{2+} sorption.
- Contribution to Pb^{2+} removal by the insoluble organic carbon was less than 4%.

GRAPHICAL ABSTRACT



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ABSTRACT

Biochars were produced from celery biomass by slow pyrolysis at 350 and 500 °C, and featured by high content of alkaline minerals namely salts of alkali and alkaline earth metals. The biochars' efficiency on removing Pb^{2+} from solution was investigated, and two biochars derived from celery stalk (StC350 and StC500) showed higher Pb^{2+} sorption capacity (288 and 304 mg/g) than most biochars reported previously. The sorption mechanisms involving precipitation, cation exchange and surface complexation are related to three biochar fractions namely water-soluble matter, acid-soluble substances and insoluble organic carbon. The relative contributions of water-soluble matter and acid-soluble substances to the total Pb^{2+} removal were 59.8% and 36.6% for the StC350 biochar, and 62.8% and 34.9% for the StC500 biochar, respectively. The results indicate that biochars derived from vegetable wastes are potential candidates for efficient sorption of heavy metals.

1. Introduction

Biochars, a kind of carbonaceous materials obtained by pyrolysis of biomass wastes at oxygen-limited condition, have exhibited good potentials in carbon sequestration, soil improvement, pollution control and waste management (Dai et al., 2013; Ennis et al., 2012; Mohan et al., 2014b; Zhang et al., 2013). Due to their porous structure and abundant surface functional groups, biochars have been applied for sorption of both heavy metals and organic pollutants from water. For example, biochars are good sorbents for aromatics (Chen and Yuan, 2011; Chen et al., 2008), pesticides (Yang et al., 2010; Yu et al., 2009) and antibiotics (Liu et al., 2012; Zheng et al., 2013), and also performed well for removal of dissolved heavy metals like Pb^{2+} and Cd^{2+} (Cao et al., 2009; Inyang et al., 2016; Mohan et al., 2007; Uchimiya et al., 2010) from

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solution. For enhancing the removal efficiency of heavy metals, the composites composed of biochars and inorganic minerals such as clay and oxides, have been developed (Boonamnuayvitaya et al., 2004; Mohan et al., 2014a; Trakal et al., 2015; Wang et al., 2015b; Yao et al., 2014). In addition, some biochars rich in inherent inorganic minerals have shown excellent removal capacity for heavy metal cations, and their sorption capacity to Pb^{2+} and Cd^{2+} were even higher than activated carbons generally recognized to be good sorbents for pollutants, because these mineral-rich biochars removed Pb^{2+} and Cd^{2+} cations through a complex mechanism involving surface adsorption, precipitation and ion exchange (Chen et al., 2015; Cui et al., 2016; Ding et al., 2016; Kim et al., 2013; Lu et al., 2012; Wang et al., 2015c; Xu et al., 2013). Namely, the mineral-rich biochars could be a type of multi-functional materials for removal of heavy metals from solution, and would be more cost-efficient than other mono-functional sorbents like activated carbons (Cao et al., 2009; Chen et al., 2014).

The mineral-rich biochars could be produced from a wealth of biomass wastes including grasses, animal manures and crop straws (Baig et al., 2014; Xu et al., 2013; Xu and Chen, 2015). The salts of alkali and alkali-earth metals in these biomass feedstocks were converted into carbonates during pyrolysis, and gave good alkalinity to the biochars (Yuan et al., 2011), so the mineral-rich biochar could facilitate the precipitation of heavy metal cations like Pb^{2+} from solution. Xu et al. (2014) have exhibited that the inorganic minerals played dominant role on Pb^{2+} removal by biochars prepared from rice straw and diary manure, while the contribution of organic fractions was less than 1.0%. Xu and Chen (2015) evaluated the contribution of various parts of inorganic minerals to Cd^{2+} removal by a rice-bran biochar, and found that the water-soluble matter made great contribution to Cd^{2+} sorption while the role of insoluble silicon could be ignored. In this context, the biomass feedstock rich in alkaline minerals but poor in silicon should be a good candidate for preparing biochars with high removal efficiency of heavy metal cations from solution. If this hypothesis could be verified, the seeking for suitable biochars for more efficient removal of heavy metals will be facilitated. And biochars derived from mineral-rich biomass other than cereal crops are worth trying, because most important cereal crops (e.g. rice and wheat) are good silicon accumulators (Guntzer et al., 2012). In comparison with other non-crop plants, vegetables should be given priority as feedstocks for preparing biochars with high removal efficiency of heavy metals, due to their abundance as food waste and richness in minerals. However, till now, few studies have been performed to evaluate the efficiency of vegetable-derived biochars on removing heavy metals, except Sewu et al. (2017) recently reported that a cabbage-derived biochar was a good sorbent to cationic dyes.

Celery is a common vegetable planted widely around the world, and the celery biomass waste is readily available for producing biochars that could be applied locally in places suffering from heavy metal contamination. In addition, the celery biomass has exhibited good Pb^{2+} sorption in a previous investigation (Li et al., 2017), and high content of inorganic minerals rich in alkali and alkaline earth metals (Na, K, Ca and Mg) but no silicon was found in this feedstock. Therefore, celery biomass is a good model feedstock to verify above-mentioned hypothesis about the biochars for efficient removal of heavy metals. In this work, the celery-derived biochars were prepared by pyrolysis of celery biomass at 350 or 500 °C in N_2 atmosphere, and the specific objectives were to: (1) evaluate the lead removal efficiency by the celery-derived biochars; (2) understand the mechanisms of lead removal by these biochars; and (3) learn about the relative contribution of various fractions of celery-derived biochars to the total lead removal.

2. Material and methods

2.1. Material

The celery (*Apium graveolens*) biomass as a kind of vegetable waste was collected locally in Shaoxing, China. The stalk and leaves were separated before use, then the biomass was rinsed with water and dried in open air. The stalk was cut into pieces of roughly 0.5 cm in length, and both stalk and leaves were dried in an oven at 100 °C to a constant weight, and then pulverized to a size of less than 0.15 mm. $Pb(NO_3)_2$ of analytical grade was used to prepare synthetic Pb^{2+} solution.

2.2. Preparation and characterization of biochars

The celery-derived biochars were prepared by pyrolysis in a quartz tube furnace (ϕ80 mm × 4 mm and 100 cm in length) filled with N_2 gas at an atmospheric pressure that was maintained via a continuous N_2 flow at a rate of 250 mL/min. The pyrolysis temperature was set to 350 or 500 °C, and the heating rate was set to 8 °C/min. After a holding time of 3 h, the furnace was cooled naturally, and the solid residue was collected and ground to less than 0.15 mm in size. The biochar products from various feedstocks and treated at different temperatures are referred hereafter as StC350, StC500 and LeC350 biochars, respectively, where the prefix "StC" refers to the stalk-derived char, the prefix "LeC" denotes the leave-derived char, while the suffix indicates the pyrolysis temperature in degrees Celsius. The yields of biochars were 33.6%, 28.4% and 31.1%, for StC350, StC500 and LeC350 biochar, respectively. For comparison studies, a wood biochar (WoC350) was prepared by pyrolysis of *Pinus radiata* wood (softwood) shavings at 350 °C in the same furnace and N_2 atmosphere, and the average yield was 29.3%.

Bulk compositions (C, H, N and S elements) of the celery biomass and biochars were determined in an EA3000 elemental analyser (Euro Vector) with an average of triplicate experiments, and O element was directly measured with the oxygen analysis model in the same analyser (Li et al., 2015). The ash content of biochars was determined by heating the samples at 750 °C for 5 h. Surface compositions of celery biomass and biochars were estimated with a JSM-6360LV scanning electron microscope (SEM) (JEOL) equipped with an X-act energy dispersive X-ray spectrometer (EDX) (Oxford). Infrared spectra (IR) were recorded in the 4000–400 cm^{-1} region on a Nexus FT-IR spectrophotometer (Nicolet) using a KBr pellet. The crystalline species in celery biomass and biochars were identified by X-ray diffraction (XRD) using D/MAX 3A (Rigaku) equipment with CuKα radiation and a goniometer rate of 4 °/min. The pH of biochar samples was measured after hydration of 1 g sample in 100 mL of de-ionized pure water for 24 h.

2.3. Sorption experiments

The Pb^{2+} sorption isotherms to celery biomass and biochar samples were determined by batch equilibration of solid sorbent in 50 mL of aqueous Pb^{2+} solutions with initial concentrations (C_0, mg/L) ranged from 60 to 400 mg/L (equivalent to 0.30–1.95 mmol (Pb)/L). Background solution contained 10 mmol/L of $NaNO_3$ was used, except for preparation of Pb^{2+}-laden biochar samples for IR, SEM-EDX and XRD analyses. The dose of solid sorbent used in the experiments was 25 mg for celery-derived biochars, 50 mg for celery stalk and leaves, and 300 mg for the wood biochar. The slurry was adjusted to an initial pH of 5.0 by dilute HNO_3 or NaOH solution, and the sorption experiment was carried out in a thermostatic shaker bath at 25 ± 0.2 °C for 24 h when the sorption equilibrium has reached according to previous kinetic studies (Wang