Biochar from Chinese herb residues as adsorbent for toxic metals removal

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Abstract. Two biochars were prepared from Chinese herb residues by slow pyrolysis at 300 °C and 600 °C (CHR300 and CHR600) for removing two toxic metal ions (Pb²⁺ and Cd²⁺) from aqueous phase. In this study, both Pb²⁺ and Cd²⁺ were effectively immobilized by CHR300 and CHR600 from water. For an initial concentration of Pb²⁺ and Cd²⁺ (C₀ = 10 mg/L), the removal rate by CHR300 and CHR600 were all greater than 90.0% at a solid:liquid ratio of 50 mg biochar in 10 mL solution. For C₀ of the two toxic metals was 100 mg/L, the Pb²⁺ removal by CHR600 was significantly stronger than that of CHR300, but there was no significant difference of the removal rate of Cd²⁺ between CHR300 and CHR600. Moreover, the removal rate of Pb²⁺ by CHR300 and CHR600 was both markedly greater than that of Cd²⁺, indicating that the biochars had stronger adsorption favorite for Pb²⁺ than Cd²⁺. The SEM-EDX data of the biochars after the toxic metals sorption drew strong evidences on the Pb²⁺ and Cd²⁺ immobilization by CHR300 and CHR600. The existing of phosphorus (P) and sulphur (S) in CHR300 and CHR600 implied that the heavy metals might be removed by forming Pb/Cd-P and Pb/Cd-S precipitates. These results suggested that the biochars from Chinese herb residues would be likely to be good adsorbents for Pb²⁺ and Cd²⁺ removal in water.

1. Introduction

Biochar, as an environmental-friendly and economic material, is developed for reducing or immobilizing contaminants, such as PAHs (e.g., phenanthrene) [1], herbicides and pesticides (e.g., diuron, atrazine, chlorpyrifos and carbofuran) [2], antibiotics (e.g., sulfamethoxazole) [3], and heavy metals (e.g., Pb, Cd, Cu and Zn) [4] in waters or soils. It is well known that the surface oxygen-containing functional groups (e.g., -OH, -COOH and -R-OH), ash components and π electrons (C=C) of carbon fraction of biochar are responsible for the sorption of toxic metals via ion exchange and/or complexation, precipitating action and cation-π interaction. Hence, the biochar production will have a potential market as an engineered sorbent or ameliorant to remove or immobilize some given contaminants in the polluted waters and soils.

In China, the production of Chinese herb residues originated from pharmacy industry is more than 12 million tons every year [5]. The careless disposal or stacking of Chinese herb residues with high moisture content can lead to serious water and soil pollution because that their leachates into environment by runoff and percolating remained a mass of active pharmaceutical ingredients. To minimize the environmental impacts, the production of biochars from this low-value material may be turned into a clean and efficient product for utilizing and reducing environmental and health impacts.
In addition, the biochars prepared from Chinese herb residues have relatively better cost advantage than other biomass (e.g., agricultural straws and woods) due to the easier-collecting and lower-value.

Overall, the slow pyrolysis technology was used to prepare biochars with Chinese herb residues as biomass feedstock to investigate their removal ability of the given heavy metals (Pb\(^{2+}\) and Cd\(^{2+}\)) from waters. Scanning electron microscopy (SEM) equipped with an electron dispersive X-ray analysis (EDX) was employed to observe surface structure of the biochar particles and qualitatively examine the elemental composition of biochar samples before and after Pb\(^{2+}\) and Cd\(^{2+}\) sorption. This work will provide a high-efficiency biochar adsorbent for Pb\(^{2+}\) and Cd\(^{2+}\) removal.

2. Materials and methods

2.1 Materials

Chinese herb residues (CHR), the mixture of angelica sinensis, gastrodia elata and other herbs after boiling with drinking water and pouring extract liquid, were collected from some dispensaries of traditional chinese medicine in Qingdao, Shandong province, China. CHR were dried at 105 °C for 48 h at least, and then smashed into powders (passing through 0.25 mm sieve). 50-g CHR powders were weighed into a quartz ark and pyrolyzed at 300 °C and 600 °C in a N\(_2\) environment for 3 h into biochars [6]. The biochar samples from CHR were several grinded and passed through 0.125 mm sieve and stored in a vacuum dryer before the following adsorption experiments, and are hereafter named as CHR300 and CHR600, respectively.

2.2 Sorption experiment

Pb\(^{2+}\) and Cd\(^{2+}\) stock solution (1 g/L) were prepared using guaranteed reagent Pb(NO\(_3\))\(_2\) and Cd(NO\(_3\))\(_2\), and were diluted to 10 and 100 mg/L, respectively. The toxic metal solutions contained 0.01 M NaNO\(_3\) for maintaining ionic strength, and the solution pHs were adjusted to 5.0 ± 0.05 by adding 0.1 M HNO\(_3\) solution for preventing the formation of precipitation. 50-mg CHR300 or CHR600 were added into 10 mL of the desired concentration of Pb\(^{2+}\) and Cd\(^{2+}\) solutions in 15-mL vials. All the vials were shaken at 150 rpm at 25 °C for over 48 h to reach sorption equilibrium [7], and centrifugated at 3800 rpm for 15 min and filtered through a 0.22 μm filter. The Pb\(^{2+}\) and Cd\(^{2+}\) concentration in the filtrates were analyzed by a flame atomic absorption spectrometer (FAAS, M6, Termo Elemental, USA) at 283.3 nm and 228.8 nm, respectively. All samples were run along with the blanks without the biochars or toxic metal ions by triplication. The removal rate of the toxic metals can be calculated using an equation of \((C_0-C_e)/C_0\times100\%\), where \(C_0\) and \(C_e\) is the initial and equilibrium aqueous concentration of Pb\(^{2+}\) or Cd\(^{2+}\), respectively.

The biochars after Pb\(^{2+}\) or Cd\(^{2+}\) removal (\(C_0 = 100\) mg/L) were collected and washed by excess deionized water, and then dried at 80 °C for 48 h. The surface structure of Pb\(^{2+}\) or Cd\(^{2+}\)-loaded biochars was observed by scanning electron microscopy (SEM, S4800, Hitachi, Japan), and the equipped electron dispersive X-ray analysis (EDX, 7593-H, Horiba, Japan) was employed to determine the sorbed Pb\(^{2+}\) or Cd\(^{2+}\) onto the biochars and other elemental composition.

2.3 Data analysis

Microsoft office excel (2013) was used for data analysis. Significant difference was tested by Statistical Product and Service Solutions (SPSS 20.0, LSD, \(P < 0.05\)).

3. Results and discussion

3.1 Pb\(^{2+}\) and Cd\(^{2+}\) removal by biochars

The removal rate of Pb\(^{2+}\) and Cd\(^{2+}\) by CHR300 and CHR600 is presented in Fig. 1. For \(C_0\) of Pb\(^{2+}\) and Cd\(^{2+}\) is 10 mg/L, the removal rate by the two biochars was greater than 90.0%, suggesting that CHR300 and CHR600 could effectively remove the heavy metals from water. The removal rate of Pb\(^{2+}\) by CHR600 was 97.5% at \(C_0\) of 100 mg/L, significantly greater than that by CHR300 (88.6%), implying that the higher sorption affinity of Pb\(^{2+}\) onto the biochar produced at high temperature. It
should be noted that the adsorption of Pb$^{2+}$ onto the two biochars was both stronger than that of Cd$^{2+}$ at $C_0$ of 100 mg/L of the metal ions, which can well agree with the first stability constant of their associated metal hydroxide (log $K_1 = 7.82$ for Pb(OH)$^+$ and 4.17 for Cd(OH)$^+$) and metal acetate (log $K_1 = 2.52$ for Pb(Ac)$^+$ and 1.5 for Cd(Ac)$^+$). The same affinity order of Pb$^{2+}$ and Cd$^{2+}$ was detected for the oxidized-CNTs [8] and graphene oxide (GO) [9]. The surface oxygen-containing functional groups in these carbonaceous material plays a significant role in the adsorption process of the metal ions by an electrostatic attraction or complexation. In addition, the difference of sorption affinity of CHR300 and CHR600 for Pb$^{2+}$ and Cd$^{2+}$ may be related with the solubility product ($K_{sp}$) of formed precipitation in the sorption of the toxic metals, such as some associated metal chloride, carbonate and phosphate, which was identified as a dominant mechanism for removing the metal ions from solution [10].

![Graph](image1)

Fig. 1. The removal rate of (a) Pb$^{2+}$ and (b) Cd$^{2+}$ by the biochars in aqueous solution ($C_0 = 10$ or 100 mg/L, pH = 5.0, T = 25 °C, t = 48 h). CHR300 and CHR600 are the biochars from Chinese herb residues at 300 °C and 600 °C, respectively. For a given initial concentration of the toxic metal ions, significant difference about the removal rate between CHR300 and CHR600 was marked with **“*” (P < 0.05, n = 3).**

### 3.2 SEM-EDX of biochars after Pb$^{2+}$ and Cd$^{2+}$ sorption

The SEM images of CHR300 and CHR600 after the adsorption of Pb$^{2+}$ and Cd$^{2+}$ ($C_0 = 100$ mg/L, pH = 5.0) are shown in Fig. 2a-d. As reported similarly in numerous previous studies [2, 4], CHR600, as a high-temperature biochar, has abundant pore structures, but little pore was formed during the charring process of CHRs into biochar at 300 °C.

![Graph](image2)

Fig. 2. SEM images for the biochars after the toxic metal ions adsorption: (a) Pb$^{2+}$ on CHR300; (b) Pb$^{2+}$ on CHR600; (c) Cd$^{2+}$ on CHR300; and (d) Cd$^{2+}$ on CHR600. (e-h) EDX spectra was collected from the labeled regions in the panels (a-d), respectively.
The EDX data of the Pb\(^{2+}\)- and Cd\(^{2+}\)-loaded biochars confirmed that both Pb\(^{2+}\) and Cd\(^{2+}\) could be removed by CHR300 and CHR600 from aqueous environment. But, the quantitative information about the removal of Pb\(^{2+}\) and Cd\(^{2+}\) by the biochars can not be accurately provided due to the outofflatness and unevenness of the surface of biochars, which have great influence on the EDX analysis. Moreover, the tested biochar particle for EDX analysis was randomly selected. The EDX analysis found that CHR300 and CHR600 contained the element of phosphorus (P) and sulfur (S), suggesting that the precipitation reaction between PO\(_4^{3-}\) and SO\(_4^{2-}\) released from the P- and S-minerals and the toxic metals may be an important mechanism of Pb\(^{2+}\) and Cd\(^{2+}\) removal by the biochars.

4. Conclusions
Both Pb\(^{2+}\) and Cd\(^{2+}\) can be effectively removed by CHR300 and CHR600 from water. For Pb\(^{2+}\), CHR600 showed greater adsorption capacity than CHR300, but the Cd\(^{2+}\) removal of CHR300 and CHR600 did not have significant difference. The higher removal of Pb\(^{2+}\) by CHR300 and CHR600 than Cd\(^{2+}\) suggested that the stronger sorption favorite for Pb\(^{2+}\) than Cd\(^{2+}\) onto the CHRs-derived biochars. The SEM-EDX data confirmed the sorption of two testing toxic metals onto CHR300 and CHR600, and the P- and S-contained minerals might release some anions (i.e., PO\(_4^{3-}\) and SO\(_4^{2-}\)), and thus result in the metals removal by the biochars through forming Pb/Cd-P and Pb/Cd-S precipitates.

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