Biochars derived from various crop straws: Characterization and Cd(II) removal potential

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Five types of biochars prepared from four crop straws and one wood shaving at 600 °C were characterized, and their sorption to Cd(II) were determined to investigate the differences in capacity to function as sorbents to heavy metals. Surface areas and pore volumes of the biochars were inversely correlated to the lignin content of raw biomass. The biochars derived from crop straws displayed more developed pore structure than wood char due to the higher lignin content of wood. Sorption capacity of the biochars to Cd(II) followed the order of corn straw > cotton straw > wheat straw > rice straw > poplar shaving, which was not strictly consistent with the surface area of the chars. The surface characteristics of chars before and after Cd(II) sorption were investigated with scanning electron microscopy equipped with an energy dispersive X-ray spectroscopy and Fourier transform infrared spectroscopy, which suggested that the higher sorption of Cd(II) on corn straw chars was mainly attributed to cation exchange, surface precipitation of carbonate, and surface complexation with oxygen-containing groups. This study indicated that crop straw biochars exhibit distinct sorption capacities to heavy metals due to various surface characteristics, and thus the sorption efficiency should be carefully evaluated specific to target contaminant.

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1. Introduction

Biochar refers to charcoal materials generated from incomplete combustion of carbon-rich biomass with heat treatment and oxygen-limited conditions (Lehmann, 2007; Beesley et al., 2011). Biochar has attracted widespread attention because of its potential use as a soil amendment to improve soil quality (Silber et al., 2012). Therefore, application of biochar in contaminated soil could be a potential management strategy for agricultural sustainability and food security. It is reported that biochar has a strong sorption capacity to many contaminants (including organics and inorganics). For example, the biochar-water partitioning coefficients (K d) of sulfamethazine is 104 times greater than the mean of 12 reported OC-normalized affinity coefficient (K OC) in natural soils (Teixidó et al., 2011); dairy-manure derived biochar exhibited 6 times more effective in Pb sorption than a commercial activated carbon (Cao et al., 2009). Theoretically, biochar could be produced from any carbon-rich biomass (Lehmann and Joseph, 2009). The physicochemical properties of biochar are related to the compositions of the source materials and the heat treatment conditions. Recent studies on biochars derived from wood (lignin-rich) or grass (lignin-poor) demonstrated the existence of various categories of biochars with a unique combination of chemical phases and physical states (McBeath and Smernik, 2009; Keiluweit et al., 2010). The differences in molecular-scale structure cause changes in bulk properties, such as elemental content, surface area and porosity of biochars, although with the similar carbonization conditions. For example, the N2-BET surface area (SBET) of various biochars could vary in a wide range of 12 (corn stovers) (Lee et al., 2010) to 490 m²/g (pine needles) (Chen et al., 2008). Different types of biochars frequently result in large discrepancies in sorption efficiency to contaminants (Ji et al., 2011; Uchimia et al., 2011).

Burning of agricultural crop residues in the field is a common practice of land preparation and disposal of crop waste in China. It releases a large amount of pollutants into the atmosphere and...
causes serious environmental pollution (Zhang et al., 2011). Due to high carbon content and abundant availability, crop residues could be used as a source of biochar to lessen the adverse effects to environment. Several studies have been conducted to investigate the impacts of pyrolysis temperature on structural characteristics of biochars and sorption affinities to heavy metals (Lee et al., 2010; Mukherjee et al., 2011; Uchimiya et al., 2011). However, the knowledge regarding the impacts of original crop residue types on the physicochemical properties of the prepared biochars as well as the associated impacts on sorption efficiency are still limited (Singh et al., 2010; Mukherjee et al., 2011). To successfully predict the sorption potential of various biochars, it is crucial to clarify the relationship between sorption efficiency and the properties of biochars, and determine how these properties vary with feedstock type and pyrolysis conditions.

Consequently, the aims of the present work were (1) to characterize the impacts of starting crop residues on the compositions, structures, and sorption of the obtained biochars; and (2) to address the interaction mechanisms between the chars and a typical contaminant. Five types of biochars derived from four crop residues and one wood shaving were prepared by the same heat treatment (600 °C in N2) and used for comparison. Heavy metals are common pollutants and extensively detected in both aqueous and soils/sediments. Thus, Cadmium (Cd), as a highly mobile contaminant, was selected as a representative contaminant in this study.

2. Materials and methods

2.1. Preparation of biochars

Biochars were produced from four crop straws (i.e., rice, cotton, wheat, and corn) respectively through slow pyrolysis at 600 °C. For comparison, poplar (Populus euramerica cv.) shaving was also included as a typical woody biomass for wood char. All the feedstocks, collected from the outskirts of Tianjin, north part of China, were oven-dried at 80 °C and then ground and sieved through 0.125 mm mesh. The cellulose and lignin contents of the feedstock were determined according to the procedure of Van Soest (1963). Five g of the raw materials was then crushed and sieved through 0.125 mm mesh. The cellulose and lignin contents of the feedstock were determined according to the procedure of Van Soest (1963). Five g of the raw materials was then ground and sieved through 0.125 mm mesh. The cellulose and lignin contents of the feedstock were determined according to the procedure of Van Soest (1963). Five g of the raw materials was then ground and sieved through 0.125 mm mesh.

2.2. Characterization of the biochars

Thermal gravimetric (TG) analysis of raw materials was carried out using a thermogravimetric analyzer (TGA/SOTA 831, Switzerland) with heating rate of 10 °C/min from room temperature to 800 °C in a N2 atmosphere. The biochar yield was calculated by mass balance. Physicochemical properties of the biochars were characterized in detail by complementary analytical technologies. The surface chemical composition was determined using X-ray photoelectron spectroscopy (XPS). XPS measurements were performed on a PHI 5000 VersaProbe spectrometer. Ash contents were measured by heating the samples in a muffle furnace at 800 °C for 4 h. Nitrogen sorption/desorption isotherms were measured at 77 K by an Autosorb-1 gas analyzer (Quantachrome, USA). The surface morphology was examined using scanning electron microscopy (SEM, JEOL Japan), and localized elemental information on the chosen region was viewed with an energy dispersive X-ray spectroscopy (EDS, Phoenix DX 60 s) in conjunction with SEM. Fourier transform infrared spectroscopy (FTIR) spectra were recorded on a Nexus 870 FTIR spectrometer (Nicolet, USA) with 4 cm⁻¹ resolution in the range of 400 and 4000 cm⁻¹. The pH of the biochars was measured by adding 0.4 g to 20 mL of deionized water and stirred overnight. The pH of the suspension was then measured. The point of zero surface charge (pHpzc) (Fig. S1) of the samples was determined using the pH drift method (Valdés et al., 2002).

2.3. Sorption experiments

The sorption experiments were performed in 250 mL Erlenmeyer flasks at 25 °C. The Cd solutions were prepared by dissolving its nitrate salt in 0.01 mol/L NaNO3 as background electrolyte. The initial concentration of Cd(II) in the solution was in the range of 0.05–1.25 mmol/L. 100 mg of biochar and 150 mL of Cd solutions were added to the flasks. The initial pH of the solutions was adjusted to 7.0 ± 0.1 by 0.1 mol/L NaOH and HNO3 solution. All the flasks were sealed with silicon cap and then shaken at 225 rpm in a rotary shaking incubator for 24 h to reach apparent equilibrium based on the preliminary study. Then the solutions were sampled and centrifuged, the concentrations of Cd(II) in the supernatant were determined using atomic absorption spectrophotometer (AA5, Varian AA 140/240, USA). All sorption experiments were conducted in duplicate. Cd(II) nitrate tetra-hydrate was purchased from Sigma-Aldrich (Shanghai, China), and stock solutions were prepared in deionized water.

3. Results and discussion

3.1. Characterization of the biochars

The selected properties of the biochars are presented in Table 1. The surfaces of these chars are dominated by carbon and contain moderate content of O-containing groups. Comparatively, rice straw biochar has the largest content of Si (3.92 percent) and poplar shaving biochar shows the least (0.54 percent), indicating that the elemental compositions of the biochars are greatly dependent on the source materials. Besides, it is found that the crop residue biochars contain substantial amounts of alkaline and alkaline earth metals (including K⁺, Ca²⁺, Mg²⁺, and Na⁺) with K⁺ being the highest (more than 4 percent) in cotton- and corn straw biochars (Table 1). Due to high content of minerals, the biochars derived from crop straws exhibit higher ash content (more significant for rice straw biochar) than the wood char (as low as 2.24 percent). All the tested biochars have high values of pHpzc (more than 9.0, Fig. S1), indicating their relative high

Table 1

<table>
<thead>
<tr>
<th>Sample</th>
<th>Yield (%)</th>
<th>S BET (m²/g)</th>
<th>V p (cm³/g)</th>
<th>Pore width (nm)</th>
<th>Ash content (%)</th>
<th>pHpzc</th>
<th>pHf</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rice straw biochar</td>
<td>34.3</td>
<td>156.2</td>
<td>0.084</td>
<td>21.5</td>
<td>10.65</td>
<td>9.7</td>
<td>7.3</td>
</tr>
<tr>
<td>Cotton straw biochar</td>
<td>30.5</td>
<td>49.4</td>
<td>0.019</td>
<td>15.1</td>
<td>2.90</td>
<td>10.2</td>
<td>8.4</td>
</tr>
<tr>
<td>Wheat straw biochar</td>
<td>33.4</td>
<td>183.3</td>
<td>0.091</td>
<td>19.9</td>
<td>8.11</td>
<td>9.1</td>
<td></td>
</tr>
<tr>
<td>Corn straw biochar</td>
<td>27.6</td>
<td>70.0</td>
<td>0.036</td>
<td>23.7</td>
<td>3.19</td>
<td>10.0</td>
<td>8.5</td>
</tr>
<tr>
<td>Poplar shaving biochar</td>
<td>28.2</td>
<td>37.7</td>
<td>0.012</td>
<td>11.6</td>
<td>2.24</td>
<td>9.2</td>
<td>7.6</td>
</tr>
</tbody>
</table>

Surface elemental composition (%)

<table>
<thead>
<tr>
<th>Sample</th>
<th>C</th>
<th>O</th>
<th>N</th>
<th>Mg</th>
<th>Si</th>
<th>P</th>
<th>Cl</th>
<th>K</th>
<th>Ca</th>
<th>Na</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rice straw biochar</td>
<td>78.5</td>
<td>13.39</td>
<td>0.70</td>
<td>–</td>
<td>3.92</td>
<td>0.23</td>
<td>0.72</td>
<td>1.56</td>
<td>0.49</td>
<td>0.50</td>
</tr>
<tr>
<td>Cotton straw biochar</td>
<td>74.8</td>
<td>17.64</td>
<td>0.69</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>1.12</td>
<td>4.08</td>
<td>1.17</td>
<td>0.53</td>
</tr>
<tr>
<td>Wheat straw biochar</td>
<td>72.9</td>
<td>17.2</td>
<td>0.81</td>
<td>0.42</td>
<td>3.44</td>
<td>–</td>
<td>1.38</td>
<td>1.82</td>
<td>2.08</td>
<td>–</td>
</tr>
<tr>
<td>Corn straw biochar</td>
<td>72.0</td>
<td>18.3</td>
<td>1.09</td>
<td>0.79</td>
<td>1.13</td>
<td>0.26</td>
<td>1.39</td>
<td>4.57</td>
<td>0.52</td>
<td>–</td>
</tr>
<tr>
<td>Poplar shaving biochar</td>
<td>81.1</td>
<td>13.3</td>
<td>0.95</td>
<td>–</td>
<td>0.54</td>
<td>0.35</td>
<td>0.22</td>
<td>2.61</td>
<td>0.98</td>
<td>–</td>
</tr>
</tbody>
</table>

Surface elemental compositions are on a mass basis. V p means total pore volume measured with BET method.
alkalinity and thus strong buffer capacity to acidic soils. This is evidenced by the fact that the equilibrium pH of aqueous solution (its initial pH was 3, 4, and 5, respectively adjusted by 0.1 mol/L HNO₃) increased to 7 or even higher after a certain amount of biochars was added in the solutions (data not shown).

Pyrolysis greatly enhances the surface area and pore volume of the biochars owing to removal of simple molecules (e.g., ethylene, hydrogen and benzene derivatives) from carbon skeleton. $S_{BET}$ varies widely among the biochars, with the highest for biochar (183.3 m²/g) derived from wheat straw followed by rice-, corn-, cotton straw, and poplar shaving char the lowest (37.7 m²/g) (Table 1). The result indicates that high surface area and pore volume could be more easily developed from crop straw than wood shaving at a relatively low pyrolytic temperature (600 °C). Furthermore, the relationship between cellulose and lignin contents of feedstocks and pore structure of biochars was evaluated. To extensively explore the association, other kinds of biomass (i.e., cottonseed hull, peanut shell, corn cob) were also included in this study besides the five tested raw materials. The relationship between $S_{BET}$ of the biochars and the contents of cellulose as well as lignin of the source materials is displayed in Fig. S2. No correlation was observed between the $S_{BET}$ of biochars and the content of cellulose of the source material (Fig. S2a). However, the $S_{BET}$ is inversely correlated with the content of lignin (Fig. S2b). Lignin contains much more aromatic and phenolic carbons relative to cellulose (Wang and Xing, 2007a), leading to its more fraction of condensed domains. Biopolymers with aromatic components could have stiff bonds among cross-links, resulting in reduced molecular flexibility and elevated decomposition temperature during pyrolysis (Young and LeBoeuf, 2000). Therefore, it is speculated that the feedstocks with high content of lignin (e.g., cottonseed hull, cotton straw and poplar shaving) were not easily decomposed as other materials under the pyrolysis condition in this study, and thus leading to incompletely developed pore structures. It was also observed that the poplar shaving biochar exhibits narrower average pore width as compared to the biochars derived from crop straws (Table 1), which is consistent with previous reports that wood char derived from high content of lignin are comparatively microporous under low temperature (>$600$ °C) pyrolysis (James et al., 2005; Zhu et al., 2005). Take a close look, however, the $S_{BET}$ of biochars is not very closely correlated with the lignin content of feedstocks, reflected by the low regression fitting result ($R^2 = 0.21$). This indicates that other factors might be also responsible for the variation in the $S_{BET}$ and pore structure of biochars. It was reported that structural makeup of biopolymers (Wang and Xing, 2007b), mineral oxides (Ji et al., 2011), and inorganic salts (Xu and Sheng, 2012) could affect the surface chemistry and morphology of the biochars. Owing to the complexity of pyrolytic reactions, it is speculated that the biomass pyrolysis is probably a multiple-controlled process mechanism.

Fig. S3(a) depicts the TG curves of the four crop straws (rice, cotton, wheat, and corn) and poplar shaving. It shows that the weight loss of the biomasses can be divided into three zones, where the first zone is from room temperature to ~200 °C, the second one from 200 to ~380 °C, and the third one from 380 to 800 °C. The maximum weight loss (more than 55 percent) is recorded in the second zone, while the first zone corresponds to relatively much smaller weight loss (around 3 percent) mainly due to the removal of moisture. Evidently, the pyrolysis of biopolymers and the pore development of the biochars occur at the temperature of 200 to 400 °C, consistent with previous reports. It is noted that, however, these feedstock exhibits different weight loss of in the third zone, where poplar shaving shows the highest weight loss of 14.9 percent, followed by cotton- (11.7 percent), wheat- (10.9 percent), corn- (9.9 percent) and rice-straw (9.7 percent). This roughly follows the order of their lignin contents (Fig. S2). Meanwhile, it can be seen more clearly from Fig. S3(b) that peaks in the DTC curve are in the order of poplar shaving (344.8 °C), followed by cotton- (329.3 °C), wheat- (327.5 °C), corn- (324.8 °C) and rice-straw (321.8 °C), also consistent with the order of their lignin content. These results suggest that the pyrolysis of lignin component mainly occurred in the third zone (i.e., 380 to 800 °C), and thus the feedstocks (e.g., poplar shaving and cotton straw) with high lignin content would probably exhibit strong thermal stability and relatively higher charring temperature is necessary to develop abundant pore structure.

### 3.2. Characteristics of Cd(II) sorption by the biochars

Sorption isotherms of Cd(II) on the biochars are shown in Fig. 1. The data were fitted with the Freundlich model ($Q = K_{F}C^{n}$), where $Q$ is the amount of Cd(II) on the biochars (mmol/kg), $C_{e}$ is the equilibrium concentration of Cd(II) in the solution (mmol/L), $K_{F}$ is the Freundlich affinity coefficient (mmol⁻¹Lⁿ/kg), and $n$ (unitless) is the Freundlich linearity index. The fitting parameters of Freundlich model are listed in Table 2. The Freundlich model fits the sorption data well, and the strong nonlinearity (departure of $n$ from 1) suggests the favorable sorption of Cd(II) on the biochars.

Distinct sorption affinities of Cd were observed on the biochars. Cd(II) sorption on the biochars significantly increased with the increase of Cd(II) equilibrium concentration in solution. Sorption of Cd(II) on the biochars follows the order of corn straw > cotton straw > wheat straw > rice straw > poplar shaving. The biochars derived from crop straws exhibit much greater sorption capacities than that derived from wood (i.e., poplar shaving), probably due to the limited pore development of the wood char at the low pyrolytic temperature as mentioned above. The data suggest that crop straw biochars, produced at low charring temperature (<600 °C), would be more efficient sorbents for Cd(II) relative to the wood char. The lower surface area and pore volume of poplar shaving char in this work are supported by the observations that high surface area and pore volume of wood chars are developed at
relatively high temperatures (500–900 °C) (Antal and Grønli, 2003). However, it is noted that the sorption affinity of the biochars to Cd correlates poorly with their surface area. For example, although corn straw char has much lower $S_{BET}$ compared with wheat and rice straw chars, sorption of Cd(II) is stronger on the corn straw char than on those derived from wheat and rice straws. The results suggest that other factors might also be responsible for the sorption of Cd(II) on biochars besides surface area.

Surface characteristics of the biochars before and after Cd(II) sorption were examined by SEM-EDS, and the plot of corn straw biochar is shown in Fig. 2. Compared with the original biochars (Fig. 2a and b), some bright zones can be clearly observed on the Cd-loaded chars in the SEM images (Fig. 2c). Elements which have a higher atomic number relative to carbon usually exhibit brighter appearance in SEM. Thus, the brighter zones on the surface of biochar indicate the presence of Mg, Si and Cd according to the EDS (Fig. 2d). However, the contents of Mg (0.26 percent) and Si (0.21 percent) in the square region (Fig. 2c) are much lower than that of Cd (10.17 percent), implying that the brighter zones are probably dominated by element of Cd. The results of SEM-EDS visually demonstrate the strong sorption of Cd(II) on the corn straw biochar. For the other biochars, however, the surface precipitation of Cd(II) is less remarkable compared with the corn straw char illustrated by SEM-EDS. For comparison, the image of rice straw biochar is shown in Fig. S4.

### 3.3. Mechanisms of Cd(II) sorption on the biochars

Based on the results in this work and literatures, several possible mechanisms for the stronger Cd(II) sorption by corn straw char should be considered: (1) cation exchange with K$^+$, Na$^+$, Ca$^{2+}$, and Mg$^{2+}$; (2) surface precipitation of carbonate; and (3) surface complexation with oxygen-containing functional groups. XPS analysis (Table 1) shows that the corn straw char has much higher K$^+$ content (more than 2 times) than the others such as rice- and wheat straw chars. It is noted that the cotton straw char contains similar content of K$^+$ relative to the corn straw char, and consistently it exhibits comparable sorption capacity as the corn straw char. This implies that ion exchange with K$^+$ may partly contribute to the Cd(II) sorption by these chars. Moreover, the corn straw char contains a certain amount of Ca$^{2+}$ (0.52 percent), Mg$^{2+}$ (0.79 percent) and Si$^{2+}$ (1.13 percent) on the surface, and these cations could also involve in ion exchange with Cd(II).

SEM images indicate the formation of precipitation (the brighter spots in the square region of Fig. 2c) on the surface of corn straw char. The surface elemental composition of the observed region is mainly composed of C (81.02 percent), O (8.33 percent), Mg (0.26 percent), Si (0.21 percent) and Cd (10.17 percent) identified by EDS (Fig. 2d). The results suggest that Cd-rich precipitates in the form of carbonates (i.e., CdCO$_3$) could be formed on the surface of corn straw char. Furthermore, we observed that the solution pH at equilibrium was 8.5 for the corn straw char, more than 1 unit higher than those of other chars (Table 1). Thus the formation of Cd(OH)$_2$(s) precipitate may also play an important role in the sorption of Cd(II) by the corn straw char in the relative high pH solution.

Biochars are rich in oxygen-containing groups (e.g., –OH and –COO$^-$) on the surface, and Cd(II) ions could easily outcompete water molecules for these functional groups to form strong surface complexes (Chen et al., 2007). The corn straw char contains more

![Fig. 2. SEM images of corn straw biochars before and after sorption of Cd(II) and corresponding EDS spectra: (a) and (b) photographs of raw corn straw biochar with different magnitude of enlargement, (c) Cd-loaded corn straw biochar, (d) EDS spectra and elemental ratio of the square region inside (c).](image-url)
The physicochemical characteristics of biochars are highly dependent on their source materials. The crop straw biochars exhibit more developed surface area and pore volume compared to poplar shaving char, which could be explained by the observation that pore structure of biochars is inversely correlated with the lignin content of raw biomass under low pyrolysis temperature (600 °C in this study). However, the sorption capacity is not entirely dependent on the surface area and pore volume of chars. Although corn straw char has relatively low $S_{\text{BET}}$, its Cd(II) sorption is the highest among all the biochars. The analysis of SEM-EDS and FTIR indicates that the higher sorption of Cd(II) on corn straw char is mainly attributed to cation exchange, surface precipitation of carbonate, and surface complexation with oxygen-containing groups. The results in this work suggest that the sorption efficiency of crop straw biochars varies greatly with their sources, thus biochars as special sorbents should be carefully selected to improve the sorption efficiency to specific contaminant.

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**Appendix A. Supporting information**

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.ecoenv.2014.04.042.

**References**


