Effect of Biomass charcoal on sorption and toxicity of PCP in sediment

Lou Liping
Zhejiang Univ.
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**Introduction**

**Definition:** Black carbon (BC) is widely defined for carbonaceous particles such as soot or elemental carbon condensed from organic carbon vapor and partially altered residues (char or charcoal) produced during combustion processes.

- BC is a major organic component in aquatic sediments and generally comprises about 9% of the TOC of sediments (median value among 300 sediments) (*Koelmans et al.*, 2006).

- Biochar is an important kind of BC. Approximately 730 million gram of biomass are burnt in Asia annually, of which 250 million gram come from agricultural burning (*Streets et al.*, 2003). Partial combustion produces ash that contains various amounts of BC (*Sheng et al.*, 2005; *Yang and Sheng*, 2003; *Yu et al.*, 2010).
There is accumulating evidence suggests that BC possess high sorptivity for hydrophobic organic compounds (HOCs) (Burgess et al., 2006; Kwon and Pignatello, 2005; Sun and Zhou, 2008). So perhaps it is feasible of applying BC to control the contaminant of HOCs pollutants, especially biochar, which has little ecological risk than other BCs.

To investigate the feasibility of using BC to control organic pollutants in sediments, in this study, the treated rice straw ash and fly ash were chosen to be representative BC, and renamed as RAC and FC, respectively. We investigated the influence of RAC and FC on the sorption of HOC in sediment, and toxicity by using the seed germination method.
Pentachlorophenol (PCP), an industrial antiseptic and biocide used since the 1960s and designated as a “priority toxic pollutant” by the United States EPA, was selected as the model compound.

The wheat seed germination, root elongation and early seedling growth were adopted as toxicity test.
(1) Preparation of BC

Rice straw ash
(burning air-dried rice straw)

Fly ash
(thermoelectric plant)

10g ash
200 mL solution

Treated in 2 M HCl for 24 h at 25 °C, repeated 5 times

Treated in 1M:1M HCl-HF for 24 h at 25 °C, repeated 5 times

Washed with distilled water 5 times and then oven-dried at 105 °C

RAC and FC
## Experimental Section

### (2) Characteristics of BC

<table>
<thead>
<tr>
<th>Testing items</th>
<th>Instrument</th>
</tr>
</thead>
<tbody>
<tr>
<td>Structure and morphology</td>
<td>Scanning electron microscopy (SEM, JSM-5610LV, Jeol, Japan)</td>
</tr>
<tr>
<td>Elemental composition</td>
<td>Element Analyzer (EA 1110, USA)</td>
</tr>
<tr>
<td>Surface area and pore volume</td>
<td>100CX surface area analyzer (Coulter Omnisorp, USA)</td>
</tr>
<tr>
<td>Surface acidity and basicity</td>
<td>Boehm’s titration method</td>
</tr>
</tbody>
</table>
(3) Sorption of PCP to BC

Sorption dynamics:
Conducted at 298K for 5, 15, 30, 60, 120, 240, 480, 960, 440 and 2880 min

Sorption thermodynamics:
Conducted at 298K and 308K for 24h

Sorption isotherm:
Using sediment amended with different content of BC (0%, 0.5%, 1%, 2%, 5% and 10%) as sorbents
Experimental Section

(4) Influence of BC on toxicity of PCP

**Toxicity of PCP**

PCP was spiked in the sediment to a series of concentration ranged from 0 (control) to 100 mg PCP/kg sediment.

**Influence of BC on toxicity and extractability of PCP**

The sediments amended with FC and SC (the content ranged from 0% to 10%) were spiked with 50 mg PCP/kg.

**Toxicity of BC**

The sediments amended with FC and SC (the content ranged from 0% to 10%) without PCP.
Fig. 1 Scanning electron microscopy images of black carbons with a magnification of $\times 3000$: (a) RAC; (b) FC;
## Results and discussion

### 1. Characterization of BC

**Table 1** Elemental compositions, atomic ratios, surface area, and pore volume

<table>
<thead>
<tr>
<th></th>
<th>Elemental composition (%)</th>
<th>Atomic ratio</th>
<th>Surface area (m²/g)</th>
<th>Porosity (mL/g)</th>
<th>Average pore size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C</td>
<td>H</td>
<td>N</td>
<td>H/C</td>
<td>N/C</td>
</tr>
<tr>
<td>BC</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>RAC</td>
<td>18.5</td>
<td>0.71</td>
<td>0.69</td>
<td>0.038</td>
<td>0.037</td>
</tr>
<tr>
<td>FC</td>
<td>29.68</td>
<td>0.26</td>
<td>0.00</td>
<td>0.009</td>
<td>0.000</td>
</tr>
</tbody>
</table>

**Table 2** Boehm titration results and density of surface functional groups (mmol/g).

<table>
<thead>
<tr>
<th></th>
<th>Boehm titration (mmol/g)</th>
<th>Density of groups (group/nm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Carboxyl</td>
<td>Lactone</td>
</tr>
<tr>
<td>BC</td>
<td></td>
<td></td>
</tr>
<tr>
<td>RAC</td>
<td>1.907</td>
<td>1.615</td>
</tr>
<tr>
<td>FC</td>
<td>0.494</td>
<td>0.000</td>
</tr>
</tbody>
</table>
Results and discussion

2. Sorption of PCP to BC

(1) Dynamics and thermodynamics

Fig. 2 Adsorption dynamic curves (a) and thermomechanical curves (b) of PCP by RAC and FC.
## Results and Discussion

### 2. Sorption of PCP to BC

Table 3: Thermodynamic parameters of RAC and FC at different temperature

<table>
<thead>
<tr>
<th>T(K)</th>
<th>△G</th>
<th>△H</th>
<th>△S</th>
<th>△G</th>
<th>△H</th>
<th>△S</th>
</tr>
</thead>
<tbody>
<tr>
<td>298</td>
<td>-25229.9</td>
<td>-40322.9</td>
<td>-52.5</td>
<td>-18702.9</td>
<td>-47930.2</td>
<td>-100.2</td>
</tr>
<tr>
<td>308</td>
<td>-23571.6</td>
<td>-40322.9</td>
<td>-52.5</td>
<td>-16378.0</td>
<td>-47930.2</td>
<td>-100.2</td>
</tr>
</tbody>
</table>

Units of △G, △H, and △S are J·K⁻¹·mol⁻¹.

The results of Fig.2 (a) showed that sorption of PCP to BC leveled off at 24 h. It is observed from Table 3 that △G, △H, and △S of RAC and FC were less than zero, therefore, it can be determined that sorption of PCP to each BC was spontaneous, and more over, the sorption was also exothermic reaction.
Results and discussion

2. Sorption of PCP to BC

(2) Sorption of PCP to pure BC

Fig. 3 Sorption isotherm of PCP to pure BCs.

Table 4 Parameters fitted by Freundlich equation.

<table>
<thead>
<tr>
<th></th>
<th>K_f</th>
<th>N</th>
<th>R^2</th>
</tr>
</thead>
<tbody>
<tr>
<td>RAC</td>
<td>26915.2</td>
<td>0.22</td>
<td>0.975</td>
</tr>
<tr>
<td>FC</td>
<td>1185.0</td>
<td>0.37</td>
<td>0.984</td>
</tr>
</tbody>
</table>

The results of Fig. 3 and Table 4 revealed that sorption isotherm of PCP to each BC was **nonlinear**, and sorption capacity of RAC was about **22 times** higher than FC when Ce=6 mg/l. It was proposed by Pignatello and Xing that **pore-filling** was the main reason for nonlinear sorption.
Results and discussion

2. Sorption of PCP to BC

(3) Sorption of PCP to sediment amended with BC

Fig. 4 Sorption isotherm of PCP by sediment associated with RAC (a) and FC (b).
## Results and discussion

### 2. Sorption of PCP to BC

<table>
<thead>
<tr>
<th>BC</th>
<th>RAC</th>
<th></th>
<th>FC</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$K_f$</td>
<td>$N$</td>
<td>$R^2$</td>
<td>$K_f$</td>
</tr>
<tr>
<td>0.0%</td>
<td>7.02</td>
<td>0.60</td>
<td>0.995</td>
<td>4.02</td>
</tr>
<tr>
<td>0.5%</td>
<td>30.82</td>
<td>0.52</td>
<td>0.953</td>
<td>5.63</td>
</tr>
<tr>
<td>1.0%</td>
<td>77.74</td>
<td>0.44</td>
<td>0.981</td>
<td>6.98</td>
</tr>
<tr>
<td>2.0%</td>
<td>203.60</td>
<td>0.33</td>
<td>0.955</td>
<td>14.85</td>
</tr>
<tr>
<td>5.0%</td>
<td>471.72</td>
<td>0.40</td>
<td>0.948</td>
<td>30.87</td>
</tr>
<tr>
<td>10.0%</td>
<td>951.69</td>
<td>0.39</td>
<td>0.959</td>
<td>56.63</td>
</tr>
</tbody>
</table>

The sorption capacity increased with the content of each BC.

The influence of RAC on sorption capacity and nonlinearity was more obvious.
Results and discussion

3. Effect of BC on toxicity of PCP

(1) Toxicity of PCP

The results demonstrated that a dose-dependent behavior was observed for PCP exposure of wheat seed; In addition, the LC$_{50}$ (lethal concentration of 50%) of PCP in the sediment was 46.42 mg/kg calculated by the linear equation between PCP concentrations and the inhibition rates of germination.

Fig. 5 Inhibiting effects of PCP concentrations on the germination, shoot and root length of wheat seeds; Error bars represent standard deviations (n=3).
Results and discussion

3. Effect of BC on toxicity of PCP

(2) Influence of BC on toxicity of PCP

Fig. 6 Effects of 50 mg PCP/kg and added BCs (RAC and FC) on the germination rate (a), shoot length (b) and root length (c) of the wheat seeds. Error bars represent standard deviations (n=3); compared with the control, ** represent a significant difference for p<0.01 and * represent a significant difference for p<0.05.
It was demonstrated that toxicity of PCP decreased with increasing content of BC in the sediment and was extremely significantly (P<0.01) influenced by the higher BC content (RAC at the content ranged from 1.0% to 10%, while FC at the rate of 5% and 10%). Besides, the influence of RAC on toxicity of PCP was found to be more pronounced than FC.
The result showed that extractable rates of PCP by aqueous solution extraction decreased with the content of BC increasing and decreased to almost 0% as the addition of BC up to 10%.
Results and discussion

3. Effect of BC on toxicity of PCP

(4) Toxicity of BC

Fig. 8 Effects of RAC and FC on the root length (a) and shoot length (b) were determined in samples including sediment associated with BC only.

Error bars represent standard deviations (n=3); compared with the control, ** represent a significant difference for p<0.01 and * represent a significant difference for p<0.05.
Results and discussion

3. Effect of BC on toxicity of PCP

- The results were that the germination rate was almost 100% in all sediment amendments.
- There was no toxic but stimulative effect of BC on growth of wheat seeds within the test ranges.
- Meanwhile, the stimulative effect was more obvious in RAC-amendment groups than in FC-amendments groups. The results may be connected to two aspects, one is the sediment itself can hold contaminants (heavy metal, PAHs, PCBs, and other HOCs), and the sorptivity of RAC was better than FC; the other is after repeated washing, there were still some residual salts like Hematite, Mullite and Quartz in FC.
Results and discussion

3. Effect of BC on toxicity of PCP

Fig. 9 XRD patterns of FC
BC(RAC and FC), especially RAC prepared from rice-straw, could significantly lower the PCP concentration in the liquid extracted from sediment by adsorption and thus reduce PCP’s toxicity to wheat seed growth.

In the tested concentration range, RAC and FC had no obvious toxicity, and it even increased the root length.

The current study could provide the theory basis for applying the straw ash and fly ash waste to reduce the toxicity of HOCs pollutant in a reasonable and effective way.
Thanks for your attention!