Factors affecting sorption of halogenated phenols to polymer/biomass-derived biochar: Effect of pH, hydrophobicity, and deprotonation

Seok-Young Oh* and Yong-Deuk Seo
Department of Civil and Environmental Engineering
University of Ulsan, South Korea
Biochar production in South Korea

• Since 2013, approximately 15% of biosolids (~1,000 ton/d) from WWTFs have been disposed via pyrolysis/carbonization.

• Biosolid biochar is being used for supplementary fuels for local power plants.
• One commercial biochar is available from Kyungdong Agro. Co.
Polymer wastes: plastics

- Used in everyday life
- Global plastic production: 264 million tons (2010)
- In South Korea,
  - Plastic/polymer wastes generation: 6000 tons/day (2014)
  - About 60% recycling
- Resistant to biodegradation
- Final disposal: incineration and landfilling
- Pyrolysis of plastic wastes: pyrolysis oil and gas
Co-pyrolysis of polymer and biomass wastes

• Significantly improves the quality of bio-oil due to the synergistic effect of the high content of carbon and hydrogen in the polymers.
• Increases yield of bio-oil and higher heating values.
• Reduces acidity, density, and oxygen content.
• Studies on char produced from co-pyrolysis of biomass and polymers were limited.
Chars co-pyrolyzed with biomass and polymer wastes

(Oh and Seo, 2016, BT; Oh et al., 2018, JEQ)
Co-pyrolysis of polymer and biomass wastes

• Co-pyrolysis of polymer and biomass wastes improved the properties of biochar.

• Increasing carbon content and the development of surface functional groups significantly enhanced the sorption capacity of NACs and Pb on polymer/rice straw (RS)-derived biochar.

Can ionizable aromatic compounds be sorbed to polymer/RS-derived biochars more effectively?
Hypothesis

• Polymer/RS-derived biochar may promote the sorption capacity of halogenated phenols through various sorption mechanisms and that some factors may significantly affect the sorption of halogenated phenols onto polymer/RS-derived biochar.
Objectives

• To synthesize polymer/RS-derived biochar.

• To investigate the sorption of halogenated phenols onto polymer/RS-derived biochar.

• To examine affecting factors such as pyrolysis temperature, number of chlorinated functional groups, equilibrium pH, competition among halogenated phenols, and dissolved metals.
Biochar production

- Biomass: rice straw (RS)
- Polymers: polypropylene (PP), polyethylene (PE), polystyrene (PS)
- Mixing ratio of polymer:RS = 40:60 v/v

Rice straw

Co-pyrolysis
(550-900 °C, 4 h, under N₂ at 1000 cc/min)

Biochar
Batch experiments

- At 25 °C
- 180 rpm shaking
- Duplicate sampling
- Equilibrium time: 24 h
- Filtration: 0.025-µm cellulose membrane filter
- Chemical analysis: HPLC (Ultimate® 3000, Dionex)

- Screw cap
- 40-mL vial

20 mL of solution including,
1) Halogenated phenols: TCP/DCP/DFP,DBP/4CP/2CP/phenol
2) Initial conc.: 25-800 mg/L
3) pH 7.4/4.7 (HEPES/acetate)

Duplicates
Control without sorbents

Polymer/RS-derived biochar (0.1-5.0 g)
Properties of polymer/RS-derived biochar

<table>
<thead>
<tr>
<th>Polymer Type</th>
<th>Polymer Content Before Pyrolysis (v.%)</th>
<th>Pyrolysis Temp. (°C)</th>
<th>pH</th>
<th>BET SA (m²/g)</th>
<th>CEC (cmol/kg)</th>
<th>PZC</th>
<th>Elemental Contents (%)</th>
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</thead>
<tbody>
<tr>
<td>-</td>
<td>0</td>
<td>550</td>
<td>9.12</td>
<td>16.4</td>
<td>77.5</td>
<td>8.4</td>
<td>55.8 2.88 13.1 2.02</td>
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<tr>
<td>PE</td>
<td>40</td>
<td>550</td>
<td>10.4</td>
<td>25.7</td>
<td>260</td>
<td>10.4</td>
<td>57.7 2.13 6.64 0.52</td>
</tr>
<tr>
<td>PS</td>
<td>40</td>
<td>550</td>
<td>10.5</td>
<td>20.0</td>
<td>191</td>
<td>9.8</td>
<td>58.1 1.56 4.71 0.54</td>
</tr>
<tr>
<td>PP</td>
<td>40</td>
<td>550</td>
<td>11.1</td>
<td>27.5</td>
<td>321</td>
<td>9.7</td>
<td>57.9 2.10 7.43 0.54</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>700</td>
<td>11.1</td>
<td>33.6</td>
<td>99.9</td>
<td>9.8</td>
<td>56.8 1.55 6.46 0.40</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>900</td>
<td>11.4</td>
<td>34.8</td>
<td>98.9</td>
<td>10.0</td>
<td>56.6 0.75 5.14 0.37</td>
</tr>
</tbody>
</table>
# Properties of halogenated phenols

<table>
<thead>
<tr>
<th>Name</th>
<th>Chemical Formula</th>
<th>Molecular Weight</th>
<th>logK&lt;sub&gt;ow&lt;/sub&gt;</th>
<th>pKₐ</th>
<th>Water Solubility (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2,4,6-trichlorophenol (TCP)</td>
<td>C₆H₃Cl₃O</td>
<td>197.45</td>
<td>3.69</td>
<td>6.23</td>
<td>800</td>
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<tr>
<td>2,4-dichlorophenol (DCP)</td>
<td>C₆H₄Cl₂O</td>
<td>163.0</td>
<td>3.20</td>
<td>7.90</td>
<td>4500</td>
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<tr>
<td>2-chlorophenol (2CP)</td>
<td>C₆H₅ClO</td>
<td>128.56</td>
<td>2.15</td>
<td>8.48</td>
<td>28500</td>
</tr>
<tr>
<td>4-chlorophenol (4CP)</td>
<td>C₆H₅ClO</td>
<td>128.56</td>
<td>2.39</td>
<td>9.41</td>
<td>24000</td>
</tr>
<tr>
<td>2,4-dibromophenol (DBP)</td>
<td>C₆H₄Br₂O</td>
<td>251.9</td>
<td>3.22</td>
<td>7.79</td>
<td>1900</td>
</tr>
<tr>
<td>2,4-difluorophenol (DFP)</td>
<td>C₆H₄F₂O</td>
<td>130.09</td>
<td>1.91</td>
<td>8.72</td>
<td>8109</td>
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<tr>
<td>Phenol</td>
<td>C₆H₆O</td>
<td>94.11</td>
<td>1.46</td>
<td>9.95</td>
<td>82800</td>
</tr>
</tbody>
</table>
Sorption to polymer/RS-derived biochar:
Types of halogenated functional groups

- Log $K_{ow}$ (pH) of DCP, DBP, and DFP = 2.71, 2.83, and 0.26
- Equilibrium pH of RS- and polymer/RS-derived biochars = 9.1 and 10.1-10.3
- PZC of RS- and polymer/RS-derived biochars = 8.4 and 9.7-10.4
Sorption to polymer/RS-derived biochar:
Numbers of chlorinated functional groups

- Log $K_{ow}$(pH) and $pK_a$ of TCP = 3.67 and 6.23
- Log $K_{ow}$(pH) and $pK_a$ of 4CP = -0.12 and 9.41
- Log $K_{ow}$(pH) and $pK_a$ of 2CP = 0.89 and 8.48
- Log $K_{ow}$(pH) and $pK_a$ of phenol = -1.32 and 9.95
Effect of pyrolysis temperature:
PP/RS-derived biochar

Hydrophobicity vs. aromaticity (EDA interactions)
Effect of pH: PP/RS-derived biochar

- logK_{\text{ow}}(pH) of DCP at pH 10.0, 7.4, and 4.7 = 2.71, 0.33, and 0.30
- logK_{\text{ow}}(pH) of DBP at pH 10.0, 7.4, and 4.7 = 2.83, 0.36, and 0.32
- logK_{\text{ow}}(pH) of DFP at pH 10.0, 7.4, and 4.7 = 0.26, -0.99, and -0.98

& degree of deprotonation
Correlation between the maximum sorption capacity (mg/g) and pH-modified octanol-water partition coefficient ($\log K_{ow}(pH)$) or the degree of deprotonation ($pK_a$-$pH$).
Effect of competition:
PP/RS-derived biochar
Effect of dissolved Zn\textsuperscript{2+} (~50 mg/L)

(a) DCP

(b) DBP

(c) DFP
Schemes on sorption of halogenated phenols to polymer/RS-derived biochar
Conclusions

• Polymer/RS-derived biochar could significantly enhance the sorption of halogenated phenols according to polymer residues, net surface charge, and deprotonation of compounds.

• Increasing the pyrolysis temperature from 550 to 700 and 900°C was not advantageous due to compensation between the removal of polymer residues and surface functional groups and increasing π-π EDA interactions.

• Solution pH was an important factor in controlling the hydrophobicity and deprotonation of compounds.
Conclusions

• Competition with other halogenated phenols and dissolved cations implied that similar sorption mechanisms existed and that surface complexation and EDA interactions were involved in sorption onto polymer/RS-derived biochar.

• Co-disposal of thermoplastic and biomass wastes through pyrolysis may be an effective option to produce high-performance upgraded biochar as a sorbent for various types of contaminants.
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Any questions?

Application of biochar in urban farming [Gwangju (Gyunggi-do), South Korea]