Influence of pyrolysis conditions on the properties of bio-chars produced from aquatic biomass – alga and hornwort

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Hornwort and alga

Hornwort (*Ceratophyllum demersum*)
- fast growing freshwater aquatic biomass
- high ability for nutrient accumulation
- eutrophication of waters

Alga (*Cladophora glomerata*)
- fast growing abilities
- eutrophication of waters
Thermochemical conversion

PROCESS PARAMETERS

• inert atmosphere (20 dm³/h N₂ flow)
• heating rate 10°C/min, residence time 1 hour
• pyrolysis (500-800°C)
Hornwort and alga – chemical composition characterization

- high amounts of ash (~20%) in both hornwort and alga
- significant difference in cellulose and hemicellulose contents
- over 3 fold higher amount of lignin in alga in comparison to hornwort
- higher extractives amount (20%) in hornwort than in alga (13%)

Hornwort and alga – chemical composition characterization

Solid yield after pyrolysis

<table>
<thead>
<tr>
<th>Temperature, °C</th>
<th>Bio-char yield, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>250</td>
<td>73</td>
</tr>
<tr>
<td>300</td>
<td>75</td>
</tr>
<tr>
<td>400</td>
<td>63</td>
</tr>
<tr>
<td>500</td>
<td>50</td>
</tr>
<tr>
<td>600</td>
<td>45</td>
</tr>
<tr>
<td>800</td>
<td>33</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Temperature, °C</th>
<th>Solid yield after pyrolysis, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>250</td>
<td>0</td>
</tr>
<tr>
<td>300</td>
<td>0</td>
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<tr>
<td>400</td>
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<td>500</td>
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<tr>
<td>600</td>
<td>0</td>
</tr>
<tr>
<td>800</td>
<td>0</td>
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</tbody>
</table>

Mercury porosimetry

<table>
<thead>
<tr>
<th>Temperature, °C</th>
<th>Total pore area, m²/g</th>
<th>Intrusion (H)</th>
<th>Intrusion (A)</th>
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<tbody>
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<td>250</td>
<td>18.1</td>
<td>22.0</td>
<td>10.2</td>
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<tr>
<td>500</td>
<td>19.4</td>
<td>19.4</td>
<td>16.0</td>
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<tr>
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<td>20.1</td>
<td>20.1</td>
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<tr>
<td>800</td>
<td>7.9</td>
<td>7.9</td>
<td>4.4</td>
</tr>
</tbody>
</table>
Hornwort and alga characteristics

Proximate analysis

- Ash (dry basis), % vs. Temperature, °C

- pHpzc

- SEM of 800°C bio-chars
### Hornwort and alga characteristics

**FTIR**

**Ultimate analysis**

<table>
<thead>
<tr>
<th>Sample</th>
<th>$C_{daf}$</th>
<th>$H_{daf}$</th>
<th>$O_{diff}$</th>
<th>$N_{daf}$</th>
<th>$S_{d}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>%</td>
<td>%</td>
<td>%</td>
<td>%</td>
<td>%</td>
</tr>
<tr>
<td>Hornwort</td>
<td>45.5</td>
<td>6.1</td>
<td>42.5</td>
<td>5.3</td>
<td>0.64</td>
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<td>3.1</td>
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<tr>
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<td>Alga</td>
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<td>31.9</td>
<td>5.0</td>
<td>2.97</td>
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<td>3.08</td>
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<tr>
<td>A800</td>
<td>73.3</td>
<td>2.2</td>
<td>12.2</td>
<td>4.2</td>
<td>3.49</td>
</tr>
</tbody>
</table>

$d_{daf}$ - dry ash-free basis, $O_{diff}$ – calculated by difference, $d$ – dry basis

**Van Krevelen diagram**

- Hornwort
- Alga
- Lignin
- Cellulose
- Char
- Temperature

Wrocław University of Science and Technology
Single point adsorption of dyes

**Phenol**
- Initial concentration: 100 mg/dm³
- Initial solution pH value: 7.73
- Mass of bio-char: 0.1 g
- Solution volume: 100 cm³
- Sorption time: 24 h

**Methylene blue**
- Initial concentration: 50 mg/dm³
- Initial solution pH value: 7.77
- Mass of bio-char: 0.1 g
- Solution volume: 100 cm³
- Sorption time: 24 h
„Single point” adsorption of herbicides

**Atrazine**

Initial concentration: 10 mg/dm$^3$
Initial solution pH value: 7.70
Mass of bio-char: 0.1 g
Solution volume: 100 cm$^3$
Sorption time: 24 h

**Isoproturon**

Initial concentration: 10 mg/dm$^3$
Initial solution pH value: 7.68
Mass of bio-char: 0.1 g
Solution volume: 100 cm$^3$
Sorption time: 24 h
"Single point" adsorption of heavy metal

- **Initial concentration:** 300 mg/dm³
- **Initial solution pH value:** 4.61
- **Mass of bio-char:** 0.1 g
- **Solution volume:** 100 cm³
- **Sorption time:** 24 h

**Diagram:** Graph showing the percentage removed of Cr³⁺ with different temperatures and organisms (Hornwort, Alga).

**Chemical Reaction:**

- **Cr³⁺**
- **EDTA** 0.095g

**Chemical Structure:**

- **Hornwort**
- **Alga**

**Temperature:**

- 0°C
- 80°C

**Solution pH:**

- 4.0
- 5.0
- 6.0
- 7.0

**Temperature, °C**

- 0
- 1
- 2
- 3
- 4
- 5
- 6
- 7

**% removed**

- 0
- 10
- 20
- 30
- 40
- 50
- 60
- 70
- 80
- 90
- 100

**Solution pH**

- 0
- 1
- 2
- 3
- 4
- 5
- 6
- 7

**Temperature, °C**

- 0
- 1
- 2
- 3
- 4
- 5
- 6
- 7

**% removed**

- 6.9
- 26.2
- 21.5
- 28.8

**Solution pH**

- 6.9
- 6.0
- 4.9

**Temperature, °C**

- 0
- 1
- 2
- 3
- 4
- 5
- 6
- 7

**% removed**

- 6.9
- 26.2
- 21.5
- 28.8

**Solution pH**

- 6.9
- 6.0
- 4.9
Conclusions

• high amounts of ash in bio-chars derived from aquatic biomass (up to 57%), is a result of presence of silica (from diatoms) and alkali metals oxides

• alkali metals oxides presence results in high pHpzc values of obtained bio-chars (up to 13)

• bio-chars were examined in „single point” adsorption of dyes: i) phenol and methylene blue, ii) herbicides: atrazine, isoproturon, iii) heavy metal: Cr$^{3+}$

• significant coefficient between the pHpzc value and sorption capacity was observed
Thank you for your attention!