Biochar production from olive mill solid wastes for heavy metal removal

Hassan Azaizeh\textsuperscript{a,b}; Samya O. Abdelhadi\textsuperscript{a,c} and Carlos G. Dosoretz\textsuperscript{c}

\textsuperscript{a}Institute of Applied Research, The Galilee Society P.O.Box 437, Shefa-Amr 20200, Israel.
\textsuperscript{b}Tel Hai College, Upper Galilee 12208, Israel.
\textsuperscript{c}Division of Environmental, Water & Agriculture Engineering, Technion Institute, Haifa 32000, Israel.

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Heavy Metals (HM)

- HMs are produced from different sources including mining, industry and even from fertilizers…
- HMs contaminate the Human food chain and the ground water and cause toxic effects.
Physical and Chemical processes have been used for removing HM

- Ion exchange
- Precipitation
- Reduction
- Evaporation
- Membrane filtration

$\text{EPA}$
- **Activated Carbon (AC)** - the most commonly used and the most effective adsorbent

- AC – high cost

- **Alternative:** Low cost, biodegradable, economical solution

- *What about Olive Mill Solid Waste (OMSW)??*

  - palms tree
Olive mill products:

1. Three-phase process

(Three Phase - Centrifugal olive oil mills)

- Olive fruits
- Leaf removal
- Washing
- Crushing - milling
- Paste malaxation
- Addition of warm water

Decanter Process

- Jift
- (Olive oil + water)
- (Aqueous phase + oil)

Centrifugation

- Olive oil
- Wastewater

Olive oil

wastewater
2. Two-phase process

- Olives
  - Cleaning and washing
    - Milling
      - Paste
        - Mixing
          - Water
            - Centrifugation
              - Virgin Olive Oil
                - Two-phase pomace, "alperujo"
Three-phase system

Olives (1000 kg)

↓

Washing (Cold)

↓

Milling and beating

↓

Centrifugation (three-phase decanter)

介

Hot water (0.6-1.3 m³)

Washing water

Oil washing/ recovery of the oil in the liquid fraction

OMW (≈1-1.6 m³)

Oil cake (≈550 kg)

Olive oil (≈210 kg)

Two-phase system

Olives (1000 kg)

↓

Washing (Cold)

Milling and beating

Centrifugation (two-phase decanter)

Olive wet cake (≈800 kg)

Oil washing

Waste water (≈0.2 m³)

Olive oil (≈200 kg)

(Alburquerque et al., 2004).
OMSW biomass

- What it contains?
- agriculture waste with very low economical value and it is an environmental pollutant.
- **Uses:** compost, producing animal feed and as energy source to heat houses (burning).
Lignocellulosic Biomass
Aims:

- Producing biochar from OMSW using pyrolysis process at 350 & 450°C (5 hours).
- Testing the biochar as Absorbent (biofilter) to HM using Batch experiments.
- Looking for functional groups in the Biochar for HM uptake using FTIR.
Bach experiment
Incubation time: 0,5,15,30 and 60 min.

OMSW → Pyrolysis Process → By-Products

Biochar separation: Whole; Cellulose and Kernel

Heavy Metals Solution (polluted waste water)

Cd\(^{+2}\), Cu\(^{+2}\), Ni\(^{+2}\), Pb\(^{+2}\), Se\(^{+2}\) and Zn\(^{+2}\)
**Results:**

Yield of biochar at different temperatures.

Table 1: Mean yield (%) of biochar of the different OMSW types at 350°C and 450°C.

Data is mean of 3 replicates ± SD.

<table>
<thead>
<tr>
<th></th>
<th>Picual</th>
<th></th>
<th>Souri</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Temperature</strong></td>
<td>350°C</td>
<td>450°C</td>
<td>350°C</td>
<td>450°C</td>
</tr>
<tr>
<td><strong>Yield %</strong></td>
<td>35.37 ± 0.45</td>
<td>25.7 ± 0.63</td>
<td>31.477 ± 0.25</td>
<td>23.96 ± 1.1</td>
</tr>
</tbody>
</table>
### Surface area: Langmuir model and BET method

Table 2: The mean surface area of biochar produced at 450°C of the different OMSW types using Langmuir (MB) and BET method. Data is mean of 3 replicates ± SD.

<table>
<thead>
<tr>
<th>Type @450°C</th>
<th>$SA_{MB}$ (m²/g)</th>
<th>$SA_{BET}$ (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Picual Two-phase</td>
<td>1.65 ± 0.14</td>
<td>1.0 ± 0.005</td>
</tr>
<tr>
<td>Picual Three-phase</td>
<td>8.12 ± 0.85</td>
<td>3.5 ± 0.0175</td>
</tr>
<tr>
<td>Souri Two-phase</td>
<td>3.48 ± 0.01</td>
<td>1.2 ± 0.006</td>
</tr>
<tr>
<td>Souri Three-phase</td>
<td>4.30 ± 1.22</td>
<td>5.3 ± 0.0265</td>
</tr>
<tr>
<td>Activated Carbon</td>
<td>-</td>
<td>1100 ± 5.5</td>
</tr>
</tbody>
</table>
Figure 1 A: The removal (%) values of the six heavy metals using the Picual two-phase (a) Whole @350°C, (b) Whole @450°C, (c) Cellulose @350°C, and (d) Cellulose @450°C biochar after incubation for 0, 5, 15, 30, 60 min. Data is mean of 3 replicates ± SD.
Figure 1B: The removal (%) values of the six heavy metals using the Picual two-phase - Whole @350°C, Whole @450°C, Cellulose @350°C, and Cellulose @450°C biochar after incubation for 0, 5, 15, 30, 60 min. Data is mean of 3 replicates ± SD of the 6 HMs.
Figure 2: The cumulative removal (%) values of the six heavy metals using the Picual three-phase biochar after incubation for 0, 5, 15, 30, 60 min. Each bar is mean of 3 replicates ± SD.
Figure 3: The cumulative removal (%) values of the six heavy metals using the Souri two-phase biochar after incubation for 0, 5, 15, 30, 60 min. Each bar is mean of 3 replicates ± SD.
Figure 4: The cumulative removal (%) values of the six heavy metals using the Souri three-phase biochar after incubation for 0, 5, 15, 30, 60 min. Each bar is mean of 3 replicates ± SD.
Figure 5: The cumulative removal (%) values of the six heavy metals using the commercial activated carbon (CAC) after incubation for 0, 5, 15, 30, 60 min. Each bar is mean of 3 replicates $\pm$ SD.
Figure 6: Summary of the FTIR analysis for functional groups associated with the different wavelength ranges between 800-1800 cm$^{-1}$ obtained for the different biochar samples produced at 350°C (left) or at 450 °C (right).
Table 3: Summary of the functional groups of the different OMSW types associated with the different wavelength ranges between 800-1800 cm\(^{-1}\) based on FTIR analysis

<table>
<thead>
<tr>
<th>#</th>
<th>Wavenumber (cm(^{-1}))</th>
<th>Assignment (Functional groups)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>~1740</td>
<td>Unconjugated C = O in hemicellulose</td>
<td>(Pandey and Pitman, 2003; Naumann et al., 2007)</td>
</tr>
<tr>
<td>2</td>
<td>~1670</td>
<td>Conjugated C = O</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>~1580</td>
<td>Aromatic skeletal vibration in lignin</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>~1440</td>
<td>C-H deformation in lignin and carbohydrates</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>~1370</td>
<td>C-H deformation in cellulose and hemicellulose</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>~1250</td>
<td>Syringyl/guaiacyl ring breathing and C-O stretch in lignin and xylan</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>~1170</td>
<td>C-O-C vibration in cellulose and hemicellulose</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>~1120</td>
<td>Aromatic skeletal and C-O stretch</td>
<td>(Pandey and Pitman, 2003)</td>
</tr>
<tr>
<td>9</td>
<td>~1040</td>
<td>C-O stretch in cellulose and hemicellulose</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>~890</td>
<td>C-H deformation in cellulose</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>~830, ~760</td>
<td>Aryl C-H and/or aryl C-O groups</td>
<td>(Baldock and Smernik, 2002)</td>
</tr>
</tbody>
</table>
Conclusions

- The yield of the produced biochar was dependent on pyrolysis temperature.
- The removal capacity for heavy metals dependent on the cultivar and processing type.
- The best heavy metal removal was by using Picual-cellulose of the two-phase obtained at 350°C.
- There was no correlation between surface area and the removal capacity of the different biochar types.
- The FTIR analysis indicated that more significant absorption bands for the two-phase samples, that are considerably smaller in the three-phase. Peaks 5 (C–H) and 9 (C–O).
- The main functional groups in metals removal are related to remains of cellulose in the produced biochar.
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Thank you for your attention