Extraction of Humic substances from residual mixed Municipal Solid Waste

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Background

Humic substances are present in all organic ecosystems, i.e. oceans, rivers, lakes and top soils due to biodegradation of dead organic matter.

Humic Acids (HA) are a mixture of weak aliphatic and aromatic organic acids characterized by large amounts of carboxylic and phenolic groups.

These compounds can act as:
- Chelating agents
- Ion-exchangers
- Surfactants
Based on the **Circular economy** concept, several works performed so far demonstrated the possibility of using **Humic Substances extracted from organic waste** (as the **compost**) for various purposes:

- formulation of detergents
- textile dyeing baths
- soil fertilizers and plant bio-stimulants for agriculture
- dispersants and binding agents for ceramics manufacture
- auxiliaries for soil/water remediation and enhanced oil recovery
- nanostructured materials for chemical and biochemical catalysis

**Background**

Others waste materials, as the residual mixed wastes from Mechanical-Biological Treatment (**MBT waste**), could be adopted for the extraction of these substances.
**Background**

**Aim**
- Evaluation of the viability of extracting humic substances from MBT wastes
- Assessment of the operating parameters that allow to enhance the performance of the process

**Experimental activities**
- Material: Residual mixed wastes from Mechanical-Biological Treatment collected in a plant near Rome
- Extraction of humic substances from MBT wastes by **changing the operating parameters**
  - Waste particle dimension
  - S/L ratio
  - Extract concentration
  - Extraction time
- Extraction of humic substances from MBT wastes that underwent a further **maturation phase**
Methods: Humic substances Extraction

Mechanical-Biological Treated Waste (solid)

**ALKALINE EXTRACTION**
(NaOH, 65°C)

CENTRIFUGATION

HU
- Humin (solid residue)

SBO
- Soluble Bio-Organic substances (liquid extracted)

**Acidification**
(pH < 2)

FA
- Fulvic Acid (soluble at any pH)

HA
- Humic Acid (insoluble at pH < 2)
Methods: Humic substances Extraction

Operating Conditions

Test **T1**: Standard procedure commonly used for extracting organic matter from soil:
- 500 ml of NaOH (0.1 M)
- 50g of MBT Waste
- \(T = 65^\circ\)
- Time = 4h

Effect of the variation of the operating conditions (tests **T2**, **T3**, **T4** and **T5**)

<table>
<thead>
<tr>
<th>Pre-Treatment</th>
<th>T1</th>
<th>T2</th>
<th>T3</th>
<th>T4</th>
<th>T5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grinding</td>
<td>No</td>
<td>Yes</td>
<td>No</td>
<td>No</td>
<td>No</td>
</tr>
<tr>
<td>S/L Ratio [mg/l]</td>
<td>1:10</td>
<td>1:10</td>
<td>1:5</td>
<td>1:10</td>
<td>1:10</td>
</tr>
<tr>
<td>NaOH Molarity [M]</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
<td>0.25</td>
<td>0.1</td>
</tr>
<tr>
<td>Extraction time [h]</td>
<td>4</td>
<td>4</td>
<td>4</td>
<td>4</td>
<td>24</td>
</tr>
</tbody>
</table>

Material

All the extraction (**T1**, **T2**, **T3**, **T4** and **T5**) were performed using 3 MBT samples:
- After treatment (no maturation)
- 90 days of maturation
- 180 days of maturation

![Graph showing biological stability degree](image.png)
**Analysis**

- **Amounts of extracted HA**

- **Functional groups quantification** by HCl titration (HA)

- **Optical Properties** by Spectrophotometric analyses
  - Most interesting wavelength:
    - $\lambda = 280\text{nm}$
    - $\lambda = 465\text{nm}$
    - $\lambda = 665\text{nm}$

- **Humic substances polymerization** by Elemental analyses (MBT waste, HA and FA)
  - Total Organic Carbon (TOC)
  - CHNS-O analysis
  - Aromaticity, Molecular Weight
  - $E_4/E_6$
  - $\Delta \log K$
Results: Amounts of Extracted Humic Acids

- 0.4 – 25 g/kg of HA extracted from the MBT waste before the maturation phase
- 21 – 60 g/kg of HA extracted from the MBT waste that underwent at least 90 days of further maturation
- In tests T4 and T5 higher amount of HA were extracted
Results: Functional groups quantification

- The amounts of functional groups generally decreased with the maturation
- The distribution of the functional groups in the extracted HA proved to be similar to the one of commercial HA (30% Phenolic and 70% Carboxylic groups)
- Functional groups resulted slightly less than the one extracted from commercial HA (red column)
- Slightly higher amounts of functional groups for tests T4 and T5

<table>
<thead>
<tr>
<th>T1</th>
<th>T2</th>
<th>T3</th>
<th>T4</th>
<th>T5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reference</td>
<td>Ground</td>
<td>S/L Ratio</td>
<td>NaOH molarity</td>
<td>Time</td>
</tr>
</tbody>
</table>
Results: Spectrophotometric analyses

- Peak of absorbance near $\lambda=280$nm
- Lower absorbance than the commercial HA
- Higher absorbances for increasing maturation times
**Results: Aromatic content**

Correlation was observed between the molar absorptivity at 280 nm of the Humic Substances (Chin et al. ‘94, Peuravuori et al. ‘97) and their aromaticity/molecular weight.

\[ \varepsilon = \frac{A}{(C \cdot b)} \]

- **Aromaticity [%]**:
  - \(0.050\varepsilon + 6.740\) (Chin et al. ‘94)
  - \(3.990\varepsilon + 490\) (Chin et al. ‘94)

**Molecular Weight [g/mol]**: 490 (Chin et al. ‘94)

- Aromaticity increased with the maturation
- After 180 days of maturation the aromatic content resulted comparable with commercial HA
- **Molecular Weight** from 900÷1200 [g/mol] to 1200÷1600 [g/mol] after maturation
Results: Elemental Analysis of Humic Acids

<table>
<thead>
<tr>
<th></th>
<th>C</th>
<th>H</th>
<th>N</th>
<th>O</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>[%]</td>
<td>[%]</td>
<td>[%]</td>
<td>[%]</td>
</tr>
<tr>
<td>T1 0</td>
<td>43.80</td>
<td>6.11</td>
<td>4.12</td>
<td>6.13</td>
</tr>
<tr>
<td>T1 90</td>
<td>36.44</td>
<td>4.38</td>
<td>5.87</td>
<td>8.54</td>
</tr>
<tr>
<td>T1 180</td>
<td>38.18</td>
<td>4.54</td>
<td>6.25</td>
<td>8.40</td>
</tr>
<tr>
<td>T2 0</td>
<td>48.02</td>
<td>5.95</td>
<td>6.42</td>
<td>8.78</td>
</tr>
<tr>
<td>T2 90</td>
<td>41.17</td>
<td>4.91</td>
<td>6.88</td>
<td>9.39</td>
</tr>
<tr>
<td>T2 180</td>
<td>41.31</td>
<td>5.05</td>
<td>6.82</td>
<td>8.82</td>
</tr>
<tr>
<td>T3 0</td>
<td>44.18</td>
<td>5.67</td>
<td>5.15</td>
<td>6.84</td>
</tr>
<tr>
<td>T3 90</td>
<td>32.93</td>
<td>4.08</td>
<td>5.62</td>
<td>8.28</td>
</tr>
<tr>
<td>T3 180</td>
<td>38.19</td>
<td>4.77</td>
<td>6.70</td>
<td>9.04</td>
</tr>
<tr>
<td>T4 0</td>
<td>47.89</td>
<td>5.99</td>
<td>6.21</td>
<td>7.50</td>
</tr>
<tr>
<td>T4 90</td>
<td>38.66</td>
<td>4.67</td>
<td>6.11</td>
<td>8.11</td>
</tr>
<tr>
<td>T4 180</td>
<td>38.15</td>
<td>4.63</td>
<td>6.23</td>
<td>8.29</td>
</tr>
<tr>
<td>T5 0</td>
<td>45.40</td>
<td>5.62</td>
<td>6.25</td>
<td>8.71</td>
</tr>
<tr>
<td>T5 90</td>
<td>39.46</td>
<td>4.77</td>
<td>6.41</td>
<td>9.48</td>
</tr>
<tr>
<td>T5 180</td>
<td>39.53</td>
<td>4.72</td>
<td>6.55</td>
<td>8.70</td>
</tr>
</tbody>
</table>

The C/N atomic ratio decreased for increasing maturation times.

Based on the elemental composition of the extracted Humic Acids, the following parameters were estimated:

- **H/C atomic ratio**
  \[
  \frac{H}{C} = \frac{[\text{atomic}]}{[\text{atomic}]} 
  \]
  (Niemiałkowska-butrym et al., 2012)

- **Humification Index**
  \[
  \text{HI (\%)} = \frac{C_{HA}}{C_{organic}} 
  \]
  (Bustamante et al., 2012)

- **Polimerization Rate**
  \[
  \frac{C_{HA}}{C_{FA}} 
  \]

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H/C atomic ratio is inversely proportional to the aromaticity of compounds:

- **H/C of 1.5 to 1.7** correspond to alicyclic hydrocarbons
- **H/C of 0.7-1.5** correspond to aromatic systems related with aliphatic chains composed of up to 10 carbon atoms
Results: Elemental Analysis of Humic Acids

Humification Index

\[ \text{HI} (%) = \frac{C_{\text{HA}}}{C_{\text{organic}}} \times 100 \]

- HI increased for increasing maturation times
- Higher HI values for tests T4 and T5

Polimerization Rate

\[ \frac{C_{\text{HA}}}{C_{\text{FA}}} \]

- **Polymerization rate** grew with the maturation (humic structure more branched)
- Higher Polymerization rate for tests T4 and T5

<table>
<thead>
<tr>
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<tr>
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<td>Ground</td>
<td>S/L Ratio</td>
<td>NaOH molarity</td>
<td>Time</td>
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</tbody>
</table>
Conclusions

- The viability of extracting Humic substances from MBT Waste was assessed evaluating the effects of the applied operating conditions and of the material maturation.

- An increase in the concentration of NaOH and in the extraction time proved to be beneficial for:
  - Growing the amounts of both extracted Humic Acids and Fulvic Acids
  - Slightly increasing the amounts of functional groups
  - Enhancing the Humification Index and Polymerization Rate of the humic acids

- The application of a further maturation phase (at least 90 days) to the MBT waste proved to enhance the chemical properties and the amount of extracted humic substances.

- In view of the reuse of the extracted substances their environmental behaviour needs to be investigated.
Thanks for your attention!

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