OLIVE MILL WASTEWATER VALORISATION THROUGH POLYPHENOL ADSORPTION

Aurora Esther Molina Bacca
Chemical Engineering Second Year PhD student
University of Bologna

Dept. of Civil, Chemical, Environmental and Materials Engineering
(DICAM)
INTRODUCTION

OLIVE MILL WASTE WATERS (OMW)

ENVIRONMENTAL IMPACT

ECOSYSTEMS EUTROPHICATION AND CHANGES IN MICROBIAL ACTIVITY

PHYTOTOXICITY

POLYPHENOLS

HIGH ADDED VALUE

HEALTH PROPERTIES

ANTIOXIDANT

ANTIAGING

ANTICARCINOGENIC

ANTIBACTERIAL
OBJECTIVES

Development of a reliable and cost-effective process for polyphenol extraction from OMWs, characterized by the possibility of recycling both the adsorbing phase and the extraction solvent.

The research is in the framework of the UE FP7 research project “Integrating biotreated wastewater reuse and valorization with enhanced water use efficiency to support the Green Economy in EU and India” (Water4Crops).
## OLIVE MILL WASTEWATERS (OMW)

<table>
<thead>
<tr>
<th>OMW</th>
<th>IMPERIA 2012</th>
<th>GALLIPOLI 2012</th>
<th>IMPERIA 2013</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total polyphenols content $(g/L)$</td>
<td>1.6</td>
<td>2.9</td>
<td>0.51</td>
</tr>
<tr>
<td>Total solids $(g/L)$</td>
<td>34</td>
<td>77</td>
<td>13</td>
</tr>
<tr>
<td>Suspended solids $(g/L)$</td>
<td>0.7</td>
<td>40.2</td>
<td>4.5</td>
</tr>
<tr>
<td>Dissolved solids $(g/L)$</td>
<td>33</td>
<td>37</td>
<td>8</td>
</tr>
<tr>
<td>COD $(g/L)$</td>
<td>32</td>
<td>69</td>
<td>21</td>
</tr>
<tr>
<td>Total carbohydrates $(g/L)$</td>
<td>5.4</td>
<td>16.8</td>
<td>3.8</td>
</tr>
<tr>
<td>Density $(g/mL)$</td>
<td>1.01</td>
<td>1.02</td>
<td>1.00</td>
</tr>
<tr>
<td>pH</td>
<td>4.60</td>
<td>4.62</td>
<td>4.59</td>
</tr>
</tbody>
</table>
The resin used in this study was chosen on the basis of previous works that compared the ability of different resins with respect to polyphenol adsorption (Bertin et al. 2011, Ferri et al. 2011, Scoma et al. 2012).

It is a divinylbenzene-styrene crosslinked hydrophobic polymeric adsorbent.

<table>
<thead>
<tr>
<th>PROPERTIES</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Matrix</td>
<td>Macroreticular aliphatic crosslinked polymer</td>
</tr>
<tr>
<td>Physical form</td>
<td>White translucent beads</td>
</tr>
<tr>
<td>Shipping weight</td>
<td>720 mg/L</td>
</tr>
<tr>
<td>Specific gravity</td>
<td>1.0515 g/mL to 1.025 mg/L</td>
</tr>
<tr>
<td>Adsorption saturation capacity (medium molecular weight compounds)</td>
<td>0.37 g of substance /g of dry resin</td>
</tr>
<tr>
<td>Particle Size</td>
<td></td>
</tr>
<tr>
<td>Harmonic mean size</td>
<td>0.56 mm to 0.71 mm</td>
</tr>
<tr>
<td>Uniformity coefficient</td>
<td>2.0</td>
</tr>
<tr>
<td>Fines content (Contractual value)</td>
<td>&lt;0.350 mm: 2.0% max</td>
</tr>
<tr>
<td>Coarse beads</td>
<td>&gt;1.18 mm: 2.0% max</td>
</tr>
<tr>
<td>Maximum reversible swelling</td>
<td>25% (on p-xylene via methanol)</td>
</tr>
<tr>
<td>Surface area (values based on statistical quality control (SQC))</td>
<td>800 m2/g</td>
</tr>
<tr>
<td>Porosity (values based on statistical quality control (SQC)-dry resin)</td>
<td>0.55 mL/mL</td>
</tr>
</tbody>
</table>
OVERVIEW OF THE RESEARCH ACTIVITIES

1. Equilibrium data obtaining (Isotherm)

2. Fluid dynamic characterization

3. Optimization of the Breakthrough tests at different column length

4. Breakthrough repeatability tests

5. Breakthrough tests at different liquid linear velocities

6. Fluid dynamic behavior and adsorption phenomenon modeling by COMSOL 3.5a simulation

7. Desorption curves obtaining

8. Antioxidant Capacity test

1. Analytical methods for OMW analysis

1) HPLC METHOD FOR TOTAL PHENOLS CONTENT MEASUREMENT

![Typical HPLC Chromatogram](image)

2) CHEMICAL OXYGEN DEMAND (COD) ANALYSIS

\[ C_nH_{a}O_{b}N_{c} + \left( n + \frac{a}{4} - \frac{b}{2} - \frac{3}{4}c \right) O_2 \rightarrow nCO_2 + \left( \frac{a}{2} - \frac{3}{2}c \right) H_2O + cNH_3 \]
The isotherm last two points (higher total phenols concentrations) were obtained by OMW evaporation at 55°C.

\[ C_S^{eq} = K_{eq} \times C_L^{eq} \]

\[ K_{eq} = 0.0563 \frac{L_{OMW}}{g_{wet \cdot resin}} \]
Column ID: 24.4 mm
Module Length: 0.524 m
Total Length: 2.096 m
FLUID DYNAMIC CHARACTERIZATION

Step Disturbance (or Frontal Analysis)

Tracer: NaCl 0.04 M
Superficial velocity (range): 2.5 cm/min – 5.0 cm/min

\[ \alpha_L = 0.0223 \pm 0.0006 \]

\[ s = 0.861 \pm 0.001 \]
With 0.52m of column length, until the 20% of breakthrough it was used nearly the 16% of the bed length, while with 2.01m the percentage increased until the 50%.
The polyphenols adsorption efficiency after four cycles has decrease of less than 5%.
BREAKTHROUGH CURVES- FLUID LINEAR VELOCITY EFFECT

Breakthrough Dimensional Curves

- Time (h)
- Dimensionless Conc. (\(-\))

Values range from 0 to 12 on both axes.
BREAKTHROUGH CURVES - FLUID LINEAR VELOCITY EFFECT

Breakthrough Dimensionless Curves

Dimensionless Concentration (--) vs. Dimensionless Time (--)
COD reaches saturation while polyphenols breakthrough is about the 20%.
BREAKTHROUGH CURVES MODELING: NON EQUILIBRIUM ADSORPTION

THE MODEL: Plug flow with axial dispersion + mass transfer

\[ \frac{\partial c_L}{\partial t} = -\delta \frac{\partial c_L}{\partial x} + D_L \frac{\partial^2 c_L}{\partial x^2} - K_{La} (c_L - \bar{c}_L) \]

\[ D_L = D_{iff} + \alpha_L \times \delta \]

\[ c_s^{eq} = k_{eq} \times c_L^{eq} \rightarrow \text{linear isotherm} \]

\[ c_s^{eq} = \frac{(c_L - c_L^{eq}) \times Vol_L}{W_{resin}} \]

\[ K_{eq} = 0.0587 \frac{L_{OMW}}{g_{wet \ res} \ res} \]

\[ K_{La} = 0.0030 \frac{1}{s} \]
The adsorption equilibrium model does not fit the experimental data.
The extraction solvent is acidified ethanol 0.5% (HCl 0.1N). The polyphenols recovered are nearly the 67% of those adsorbed.
ANTIOXIDANT CAPACITY

Antioxidant Activity for red wine and green tea measured with ABTS method.

Results reported in Trolox equivalent antioxidant capacity (TEAC) and ascorbic acid equivalent antioxidant capacity (AEAC). Gil M.I. et al. 2000. J. Agric. Food. Chem.

The polyphenols mix obtained after desorption has a very high antioxidant capacity.
Stationary Phase:
Kinetex 2.6 um PFP column

Mobile Phases:
Phase A: 5mM ammonium acetate in water / 0.5% acetic acid
Phase B: 5mM ammonium acetate in ACN / 0.5% acetic acid
Phase C: 5mM ammonium acetate in methanol / 0.5% acetic acid

Wavelength: 254 nm, 280 nm, 310 nm

Column Temperature: 40 °C

Gradient:

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>Phase A (%)</th>
<th>Phase B (%)</th>
<th>Phase C (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>96</td>
<td>3</td>
<td>1</td>
</tr>
<tr>
<td>4</td>
<td>85</td>
<td>10</td>
<td>5</td>
</tr>
<tr>
<td>6</td>
<td>82.5</td>
<td>11.5</td>
<td>6</td>
</tr>
<tr>
<td>8</td>
<td>80</td>
<td>12</td>
<td>8</td>
</tr>
<tr>
<td>15</td>
<td>65</td>
<td>24</td>
<td>11</td>
</tr>
<tr>
<td>21</td>
<td>0</td>
<td>85</td>
<td>15</td>
</tr>
<tr>
<td>26</td>
<td>0</td>
<td>85</td>
<td>15</td>
</tr>
<tr>
<td>30</td>
<td>96</td>
<td>3</td>
<td>1</td>
</tr>
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<td>35</td>
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<td>3</td>
<td>1</td>
</tr>
</tbody>
</table>
SINGULAR POLYPHENOLS HPLC METHOD

Polyphenols Syntetic mix Chromatogram

Gallic Acid
Dihydroxybenzoic acid
Hydroxytyrosol
Hydroxybenzoic acid
Tyrosol
Hydroxyphenilacetic acid
Vanillic acid
Syringic acid
Coumaric acid
Trans-cinnamic acid
Oleuropein

Dimetoxybenzoic acid
Trimetoxybenzoic acid
SINGULAR POLYPHENOLS HPLC METHOD

OMW Imperia 2013 and OMW Deph. Chromatograms
SINGULAR POLYPHENOLS HPLC METHOD

Desorption Product Chromatogram

Hydroxytyrosol
Tyrosol
CONCLUSIONS

- A longer adsorption column enhances its operational capacity which means an increase in the quantity of recovered polyphenols.
- After some adsorption/desorption cycles the column shows a good performance, which is an important feature from the industrial point of view.
- The proposed model fits the experimental data very well.
- The polyphenols mix obtained after the desorption step has a very high antioxidant capacity, which increases the value of the obtained product.
- The HPLC method for singular polyphenols separates properly the 14 tested polyphenolics.
FUTURE DEVELOPMENTS

- Desorption step enhancement.
- Improvements in the simulation model.
- HPLC mass spectrometry analysis to identify unknown peaks obtained with the new HPLC method.
- Adsorption/desorption tests in the current column with new OMW Imperia 2014 in order to test the column performance after several operational cycles with different OMWs.
REFERENCES

Thank You