Implementation of different physicochemical techniques for the more efficient management of olive mill wastewater streams

S.S. Kontos, P. G. Koutsoukos, C.A. Paraskeva

Department of Chemical Engineering, University of Patras
Institute of Chemical Engineering Sciences, Foundation for Research and Technology, Hellas (FORTH/ICE-HT)
Outline

- Size of the problem
- Current available treatment methods
- Removal and Recovery of phenolic compounds
- Melt Layer Crystallization
  - Theoretical computation of mass thickness
  - Theoretical and experimental mass thickness of Tyrosol
  - Effect of carbohydrate fraction on the total phenolic recovery
- Proposed method for the more efficient treatment of OMW
- Application of the proposed method in raw OMW
- Conclusions
Olive tree agriculture and the process of olive oil production are of vital importance for the Mediterranean countries.

Mediterranean countries produce 95% of the total world production of olive oil which is estimated to reach 2.4 million metric tons per year.

Olive mill wastewater production is approximately 15 million tons/year and includes a high pollution load.
Size of the problem

- Olive mill wastewater (OMW)
  - hardly degradable waste
  - The high organic load and
  - The content of very high concentrations of phenolic compounds.

- Disposal of untreated OMW
  - Water contamination
  - Eutrophication
  - Bad odor
  - Aesthetic deterioration of the ecosystems
Current available treatment methods

- **Disposal practices**
  - Disposal of OMW to lagoons, the surface waters or the sea
  - Controlled disposal of OMW to cultivated or uncultivated fields

- **Biological Methods**
  - Aerobic digestion
  - Anaerobic digestion
  - Bio-composting

- **Physicochemical methods**
  - Flocculation-Coagulation
  - Lime treatment
  - Oxidation (ozonation, Fenton oxidation, photo Fenton oxidation)
  - Membrane filtration
  - Melt crystallization
Removal and Recovery of phenolic compounds

Isolation of Organic Compounds with High Added Value

**Scope and objectives**

To develop a method for the maximum, cost-effective exploitation of agro-industrial wastewaters, using a combined process of membrane filtration and other physicochemical processes. The final solution of the proposed process contains a sufficient amount of the high added value phenolic content in a small fraction of the initial volume.

→ Profit from the exploitation of compounds with high added values
→ Effective treatment of wastewaters

Isolation of phenols:

- **Hydroxytyrosol**
- **p-Tyrosol**
- **p-Coumaric acid**
- **Caffeic acid**

- Exploitation of other organics for pharmaceuticals, food industry, animal food, co-composting, etc

Melt Layer Crystallization

• The crystallized solid is recovered on the cooled surface due to the imposed supercooling ($\Delta T = T_{\text{melt}} - T_{\text{cold}}$) which is the driving force for the crystallization of phenolic compounds.

• During this process, it is possible to separate the various components according to their freezing points.

✓ Chianese, Santilli (1998): pure $\epsilon$-caprolactam, mixtures of $\epsilon$-caprolactam and water, pure naphthalene

✓ Choi, Kim (2012): acetic acid from water

✓ Ulrich, Ozoguz (1990): binary mixture of dodecanole with 3.3 % w/w decanole

✓ Hengstermann et al. (2009): acrylic acid

✓ Jones, Mullin (1974): seeded potassium sulphate solutions
Theoretical computation of mass thickness

Energy balance of the solid:
\[ \frac{\partial T_s}{\partial t} = \alpha \frac{\partial}{\partial r} \left( r \frac{\partial T_s}{\partial r} \right) \]

Boundary condition for the cooled surface: \( T_s(r = r_o, t) = T_{cold} \)

Boundary condition for the solid-melt interface:
\[ T_s(r = r_o + s(t), t) = T_m \]
\[ k_s \frac{dT_s}{dr} \bigg|_{r_o+s(t)} = \rho \lambda \frac{ds(t)}{dt} + h(T_b - T_m) \]

Temperature profile:
\[ T_s(r, t) = a + b(r - r_o) + c(r - r_o)^2 \]

Theoretical and experimental mass thickness of Tyrosol

Operating conditions
• $T_{hot}=97^\circ C$
• $T_{cold}=70^\circ C$
• $T_{melt}=91^\circ C$

Solid layer growth of tyrosol deposited on the cooled surface as a function of time
Effect of carbohydrate fraction on the total phenolic recovery

Experimental Conditions
• $T_{\text{hot}} = 97^\circ\text{C}$
• $T_{\text{cold}} = 70^\circ\text{C}$
• Initial mass of tyrosol 70g
• Initial mass of glucose 0, 5, 10, 15 g

Recovery of tyrosol and glucose deposited on the cooled surface for different initial mass of glucose
Proposed method for the more efficient treatment of OMW

Synthetic OMW

NF

Retentate: Enriched in sugars (sucrose)

RO

Retentate: Enriched in phenolics (tyrosol)

Permeate: Water

Vacuum Evaporation + freeze drying

Kontos S., Iakovides I., Koutsoukos P., Paraskeva C., 2016, Isolation of purified high added value products from olive mill wastewater streams through the implementation of membrane technology and cooling crystallization process, Chemical Engineering Transactions, 47, 337-342
Proposed method for the more efficient treatment of OMW

Membrane Filtration

<table>
<thead>
<tr>
<th>Filtration step</th>
<th>Sugars [g]</th>
<th>Phenolics [g]</th>
</tr>
</thead>
<tbody>
<tr>
<td>initial solution</td>
<td>100</td>
<td>43</td>
</tr>
<tr>
<td>final retentate NF</td>
<td>94,63</td>
<td>16,99</td>
</tr>
<tr>
<td>final tank permeate NF</td>
<td>4,86</td>
<td>24,68</td>
</tr>
<tr>
<td>(initial RO)</td>
<td>99,49</td>
<td>41,68</td>
</tr>
<tr>
<td>final retentate RO</td>
<td>4,24</td>
<td>19,20</td>
</tr>
<tr>
<td>final tank permeate RO</td>
<td>0,04</td>
<td>1,73</td>
</tr>
<tr>
<td></td>
<td>4,28</td>
<td>20,93</td>
</tr>
</tbody>
</table>

Ratio of phenolics to sugars in NF ret is equal to 0.18

Ratio of phenolics to sugars in RO ret is equal to 4.5
Proposed method for the more efficient treatment of OMW

Vacuum Evaporation + Freeze Drying

- Permeate and Retentate of NF step (sucrose + tyrosol)
- Sucrose crystals of NF retentate after the implementation of evaporation
- Precipitated tyrosol of RO retentate past the evaporation step
- Recovered solid of RO retentate after removal of solvent through freeze drying application
Proposed method for the more efficient treatment of OMW

Melt crystallization

<table>
<thead>
<tr>
<th></th>
<th>Sugars [g]</th>
<th>Phenolics [g]</th>
</tr>
</thead>
<tbody>
<tr>
<td>initial solution</td>
<td>100</td>
<td>43</td>
</tr>
<tr>
<td>final retentate NF</td>
<td>94,63</td>
<td>16,99</td>
</tr>
<tr>
<td>final retentate RO</td>
<td>4,24</td>
<td>19,20</td>
</tr>
<tr>
<td>Recovered solid after melt crystallization</td>
<td>1,8</td>
<td>10,8</td>
</tr>
</tbody>
</table>

Ratio of phenolics to sugars after melt crystallization is equal to 6
Application of the proposed method in raw OMW
Application of the proposed method in raw OMW

Final retentate of OMW Phenolic Compounds

- The total recovered solid past the implementation of membrane technology, rotary evaporation and freeze drying process was estimated **3.5g**. The total phenolics and carbohydrates were measured around **0.6g** and **0.75g** respectively.

- The melt crystallization process was not applied to the final residue because of its low mass recovery. However for the application of the proposed method, a higher initial feed stream is required.
Conclusions

• The main objective of the present work was the investigation of the possibility of recovering phenolic compounds from OMW.
• Membrane technology is proposed as a first treatment step for the fractionation and separation of low molecular weight compounds. Most of the simple phenolic compounds and mono-carbohydrates concentrate in the retentate of the RO step.
• Further separation of phenolic compounds from carbohydrates can be achieved through the implementation of vacuum evaporation, freeze drying and melt crystallization process.
• Model experiments, involving tyrosol and sucrose showed that this separation is possible.
• The results of the present work contribute to the development of a novel method for the exploitation of OMW.
Acknowledgments

The current study was funded by the State Scholarship Foundation/IKY through the operational program ‘RESEARCH PROJECTS FOR EXCELLENCE IKY/SIEMENS’.

Contact information:
Petros Koutsoukos, Professor
pgk@chemeng.upatras.gr
Christakis Paraskeva, Associate Professor
takisp@chemeng.upatras.gr
Spyros Kontos, Ph. D student
spyretos@chemeng.upatras.gr
Department of Chemical Engineering, University of Patras, GR 26504, Rion, Patras, Greece, tel: +30 2610 997252
Crystallization of tyrosol and monohydrate glucose

Effect of supersaturation on cooling crystallization

Solubility diagram of tyrosol and monohydrate glucose in water

Solubility of glucose monohydrate and tyrosol in water as a function of temperature; (■) Glucose monohydrate, (●) Tyrosol
Effect of carbohydrate concentration on the total phenolic recovery

Experimental Conditions

• $T_{hot}=70$ °C
• $T_{cold}=5$ °C
• Active volume in the reactor 250 mL
• Initial concentration of tyrosol 65 g/L (16.25 g in 250 mL water)
• Initial concentration of glucose 0, 65, 600 g/L (0, 16.25, 150 g in 250 mL water respectively)

Recovery of tyrosol and glucose deposited on the cooled surface for different concentration values of glucose