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

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- Current available treatment methods
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  - Effect of carbohydrate fraction on the total phenolic recovery
- Proposed method for the more efficient treatment of OMW
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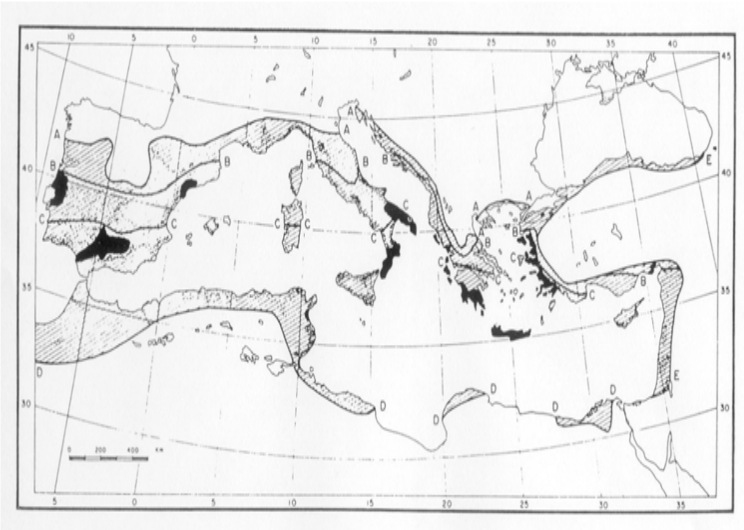
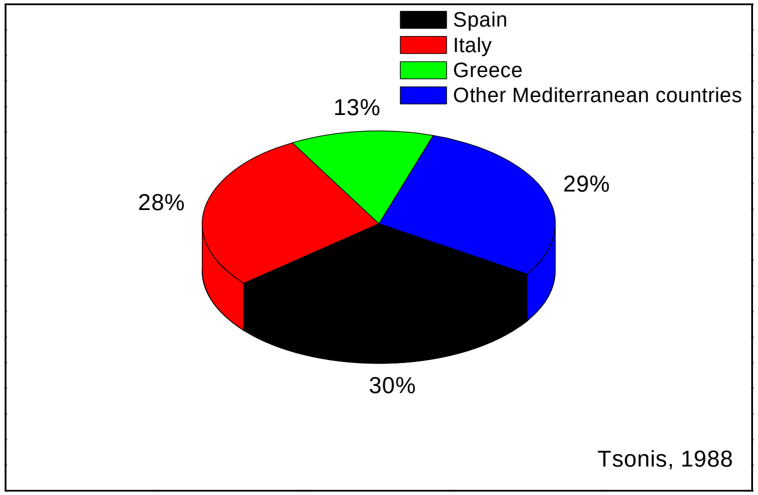
Size of the problem



Areas of olive tree cultivation in the Mediterranean area



Olive oil production percentages in the area of Mediterranean sea countries

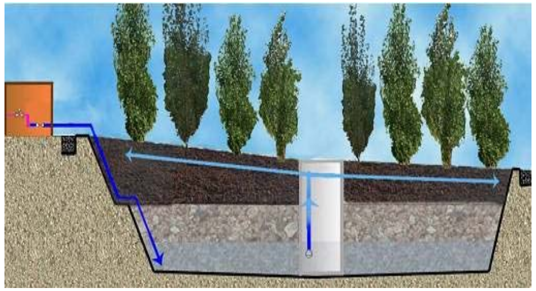
- Olive tree agriculture and the process of olive oil production are of vital importance for the Mediterranean countries.
- Mediterranean countries produce 95% of the total world production of olive oil which is estimated to reach 2.4 million metric tons per year.
- Olive mill wastewater production is 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 for 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 contain 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

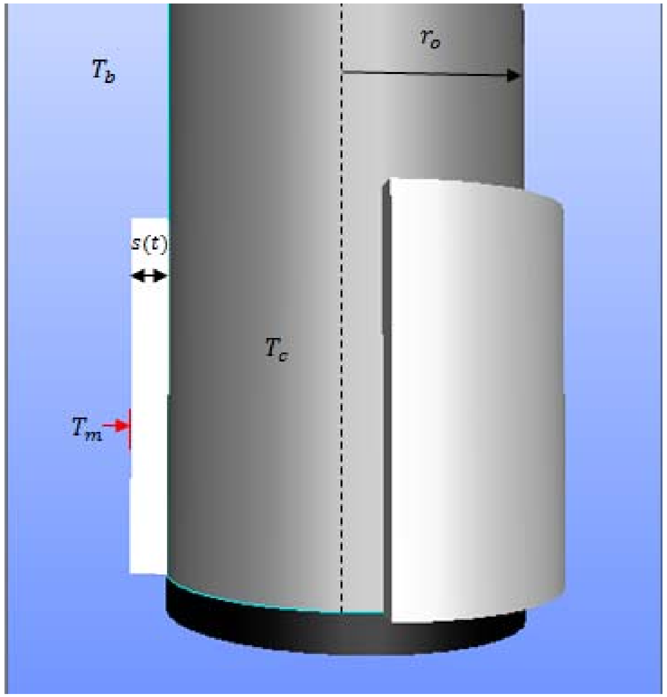
S. S. Kontos et al. 2014. Removal and Recovering of Phenolic Compounds from Olive Mill Wastewater by Cooling Crystallization. Chemical Engineering Journal, vol. 251, no. 179, pp.319-328.

Melt Layer Crystallization

- The crystallized solid is recovered on the cooled surface due to the imposed supercooling (ΔT=Tmelt-Tcold) 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 ε-caprolactam, mixtures of ε-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



Crystallization of tyrosol on a cooled surface

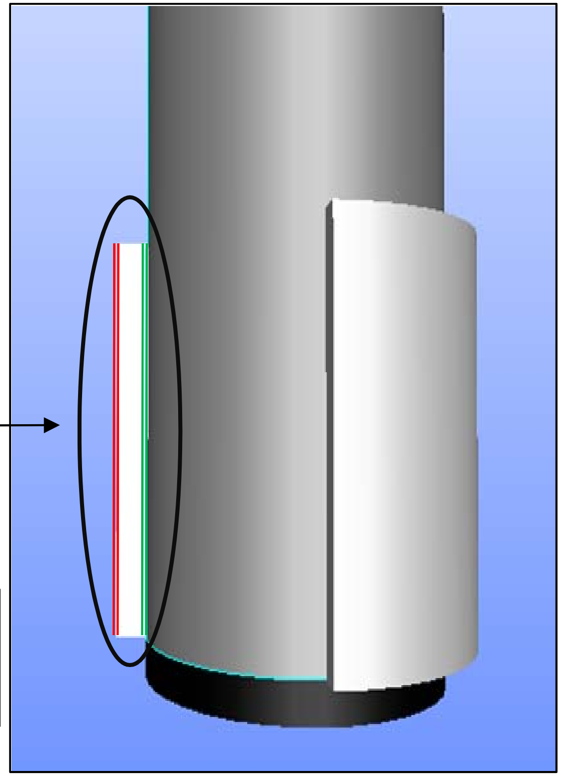
Theoretical computation of mass thickness

Energy balance of the solid: $\frac{\partial T_s}{\partial t} = \frac{a}{r}\frac{\partial}{\partial r}\left(r\frac{\partial T_s}{\partial r}\right)$

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

Boundary condition for the solid-melt interface:

$$\left.\begin{aligned} & T_s\left(r = r_o + s_{(t)}, t\right) = T_m \\ & k_s \left.\frac{dT_s}{dr}\right|_{r_o + s_{(t)}} = \rho\lambda' \frac{ds_{(t)}}{dt} + h\left(T_b - T_m\right) \end{aligned}\right\}$$



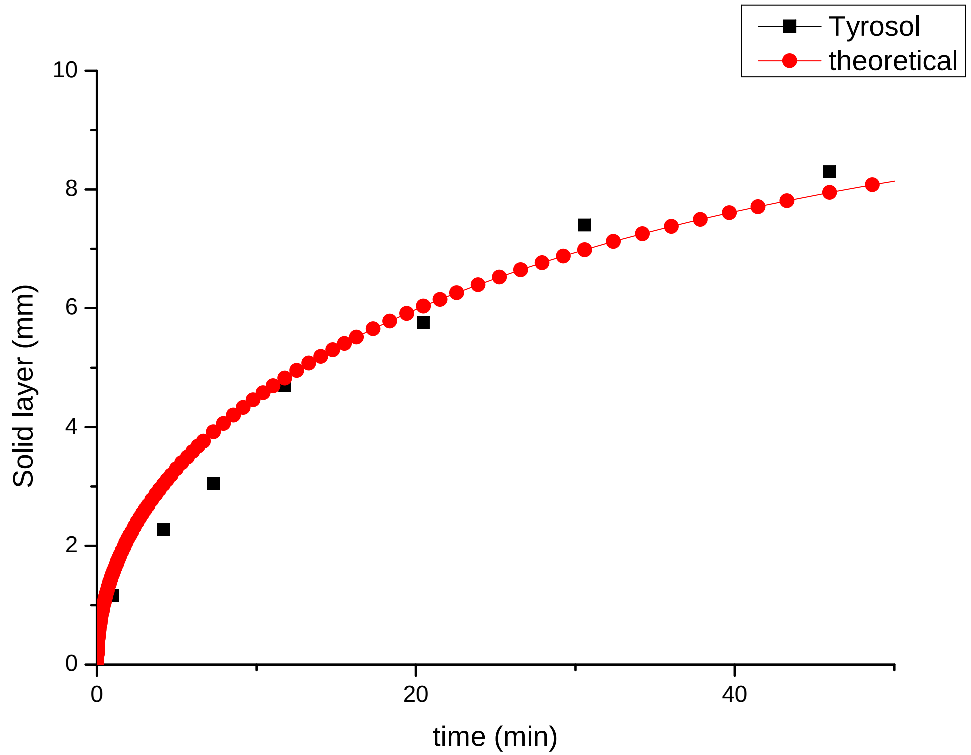
$$\boxed{\frac{ds_{(t)}}{dt} = -\frac{h}{\rho\lambda'}\left(T_b - T_m\right) + \frac{r_o k_s}{\rho\lambda'\left(r_o + s_{(t)}\right)}\left.\frac{dT_s}{dr}\right|_{r_o} + \frac{k_s}{\rho\lambda' a\left(r_o + s_{(t)}\right)}\frac{d}{dt}\left(\int_{r_o}^{r_o + s_{(t)}}\left(T_s - T_m\right) r\,dr\right)}$$

Temperature profile: $T_s\left(r, t\right) = a + b(r - r_o) + c(r - r_o)^2$

A. Chianese, N. Santilli, Modelling of the solid layer growth from melt crystallization—the integral formulation approach, Chem. Eng. Sci. 53 (1998) 107–111.

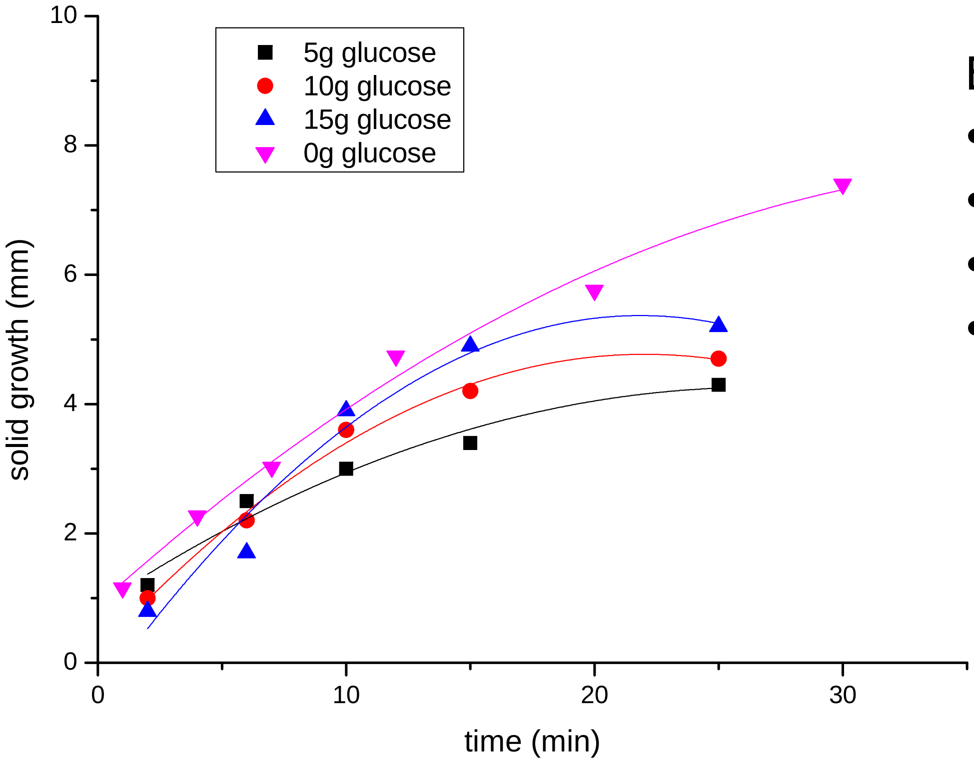
Theoretical and experimental mass thickness of Tyrosol

Operating conditions
- Thot=97°C
- Tcold=70°C
- Tmelt=91°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

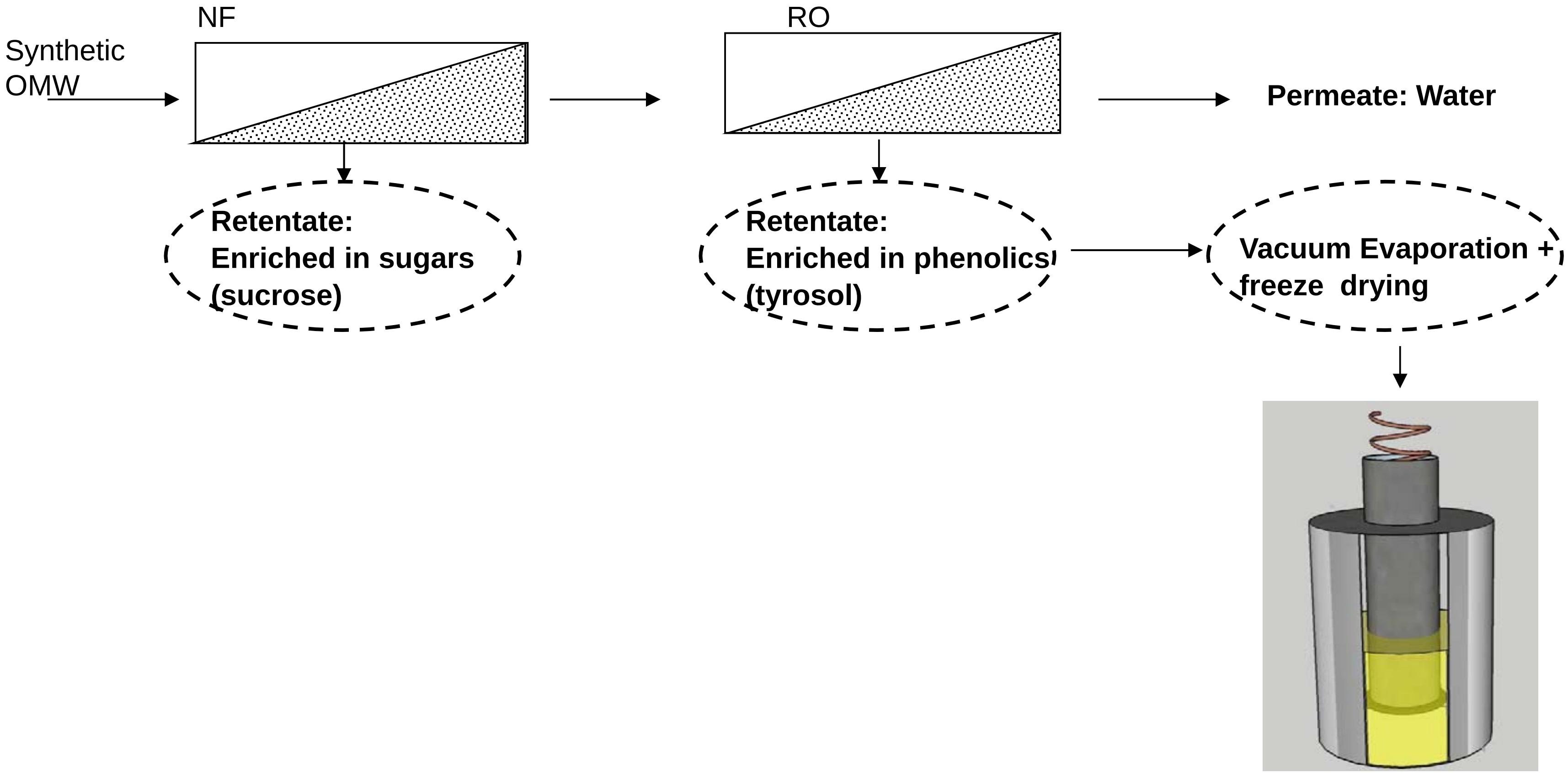


Recovery of tyrosol and glucose deposited on the cooled surface for different initial mass of glucose

Experimental Conditions

- T_{hot}=97°C
- T_{cold}=70°C
- Initial mass of tyrosol 70g
- Initial mass of glucose 0, 5, 10, 15 g

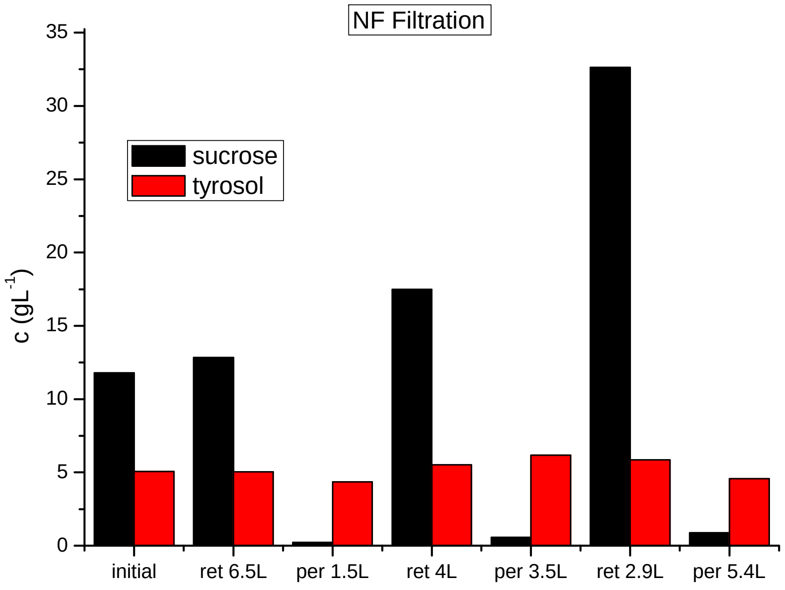
Proposed method for the more efficient treatment of OMW

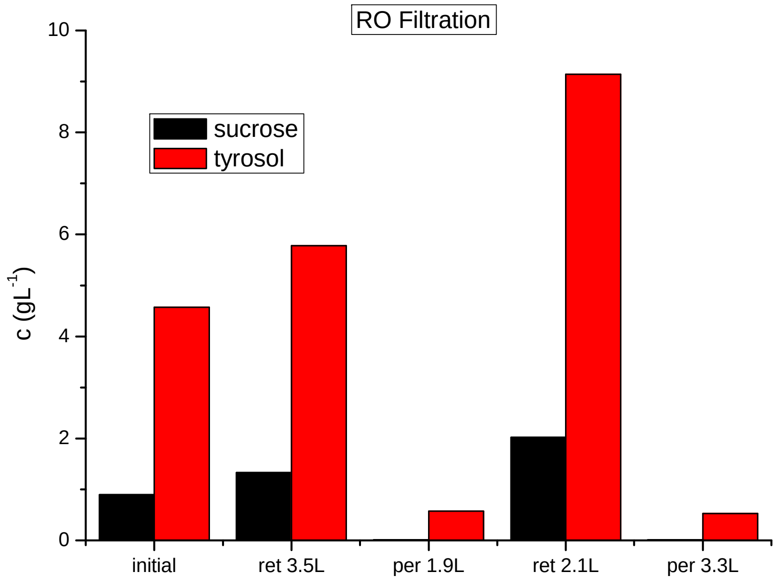


Kontos S., Iakovides I., Koutsoukos P., Paraskeva C., 2016, Isolation of purified high added value products from olive mill wastewater streams through the implementation of membrane technology and cooling crystallization process, Chemical Engineering Transactions, 47, 337-342

Proposed method for the more efficient treatment of OMW

Membrane Filtration





Filtration step	Sugars [g]	Phenolics [g]
initial solution	**100**	**43**
final retentate NF	94,63	16,99
final tank permeate NF (initial RO)	**4,86**	24,68
	= 99,49	**= 41,68**
final retentate RO	4,24	19,20
final tank permeate RO	0,04	1,73
	=4,28	**=20,93**

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

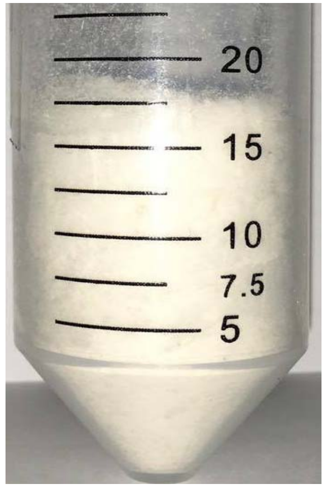
Proposed method for the more efficient treatment of OMW

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

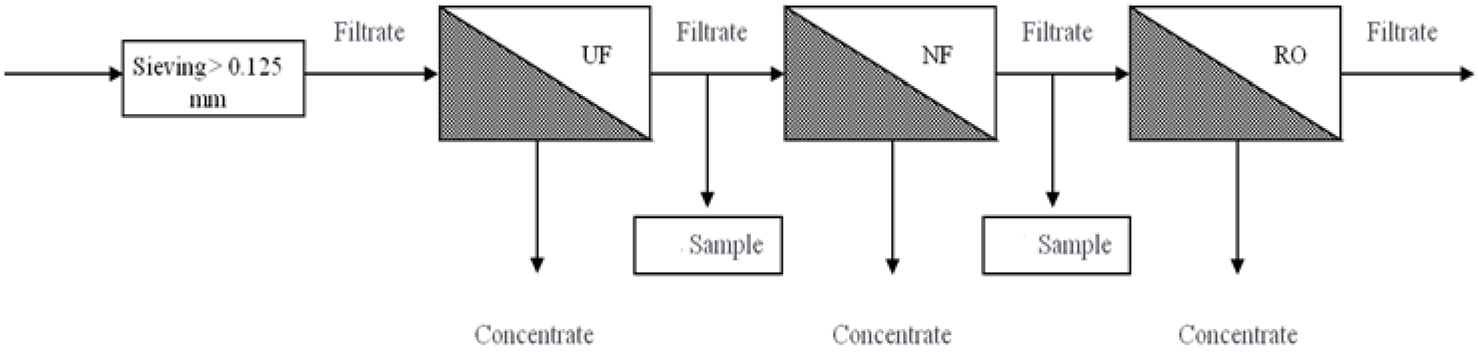
Proposed method for the more efficient treatment of OMW

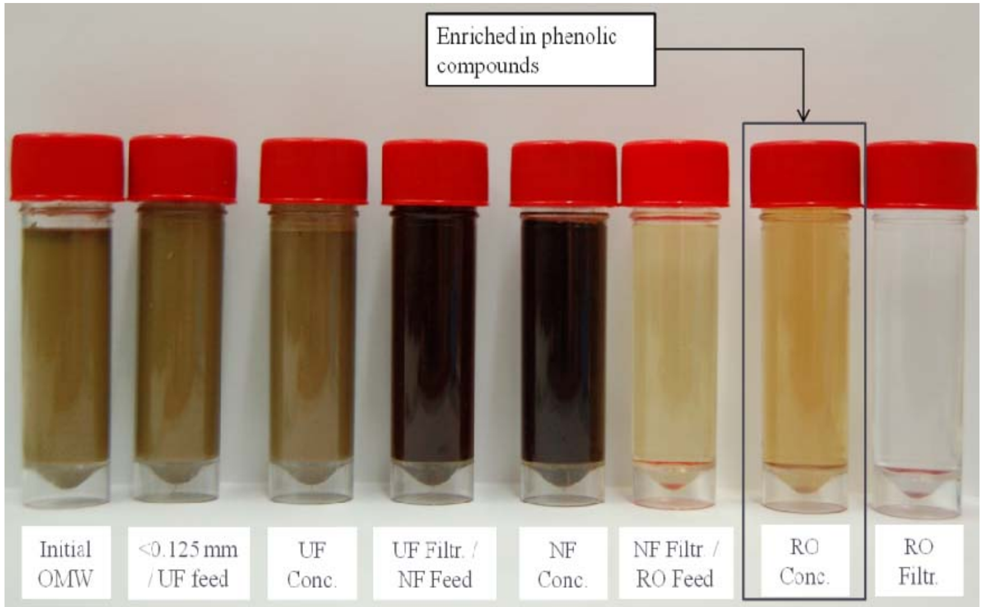
Melt crystallization

	Sugars [g]	Phenolics [g]
initial solution	**100**	**43**
final retentate NF	94,63	16,99
final retentate RO	4,24	19,20
Recovered solid after melt crystallization	1,8	10,8

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.

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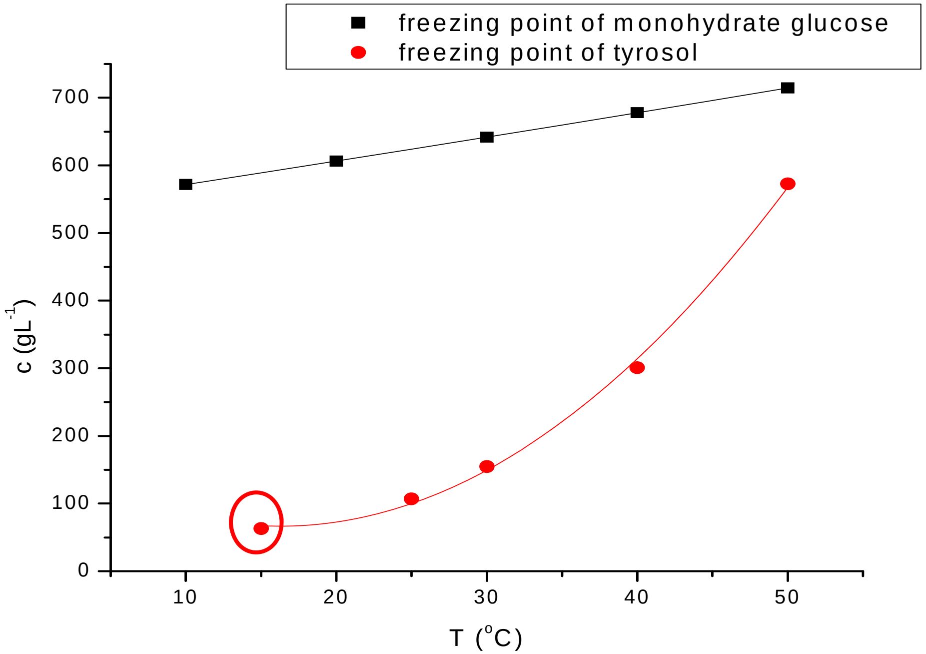
Crystallization of tyrosol and monohydrate glucose

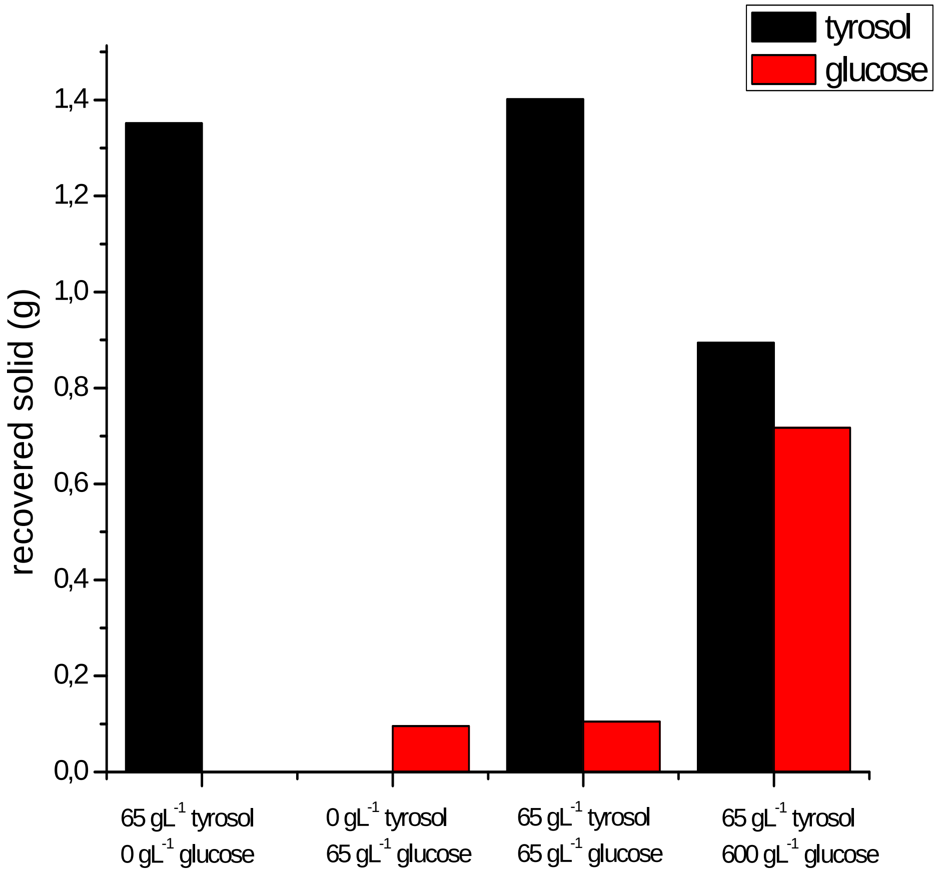
Effect of supersaturation on cooling crystallization

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



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

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)