Treatment of two-phase olive mill wastes and recovery of phenolic compounds

Isolation of phenolic compounds from agroindustrial Byproducts

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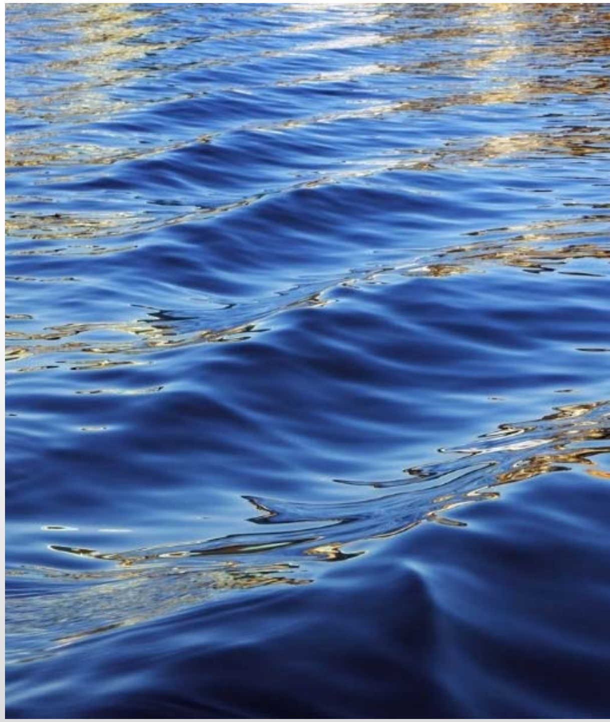


Recovery of phenolic compounds from:
Olive Mill Wastewater + Olive Mill solid wastes- Olive leaves

- Olive oil is a major agro-industrial product for all Mediterranean countries.
- Unfortunately large quantities of olive mill wastewater (OMW) or semi-solid wastes are produced.
- Its treatment is difficult and expensive due to its high organic load and phenolic content.


OMW

Treatment of Wastewaters and Solid Wastes-
Isolation, Recovery and Purification of phenolic compounds from agricultural by–products (wastes)




- Purification of olive mill wastewater phenols
- Purification of olive leaf phenols
- Purification of grape marc phenols
- Purification of olive mill solid waste phenols
- Purification of coffee beans phenols

Scope

- Large amounts of agricultural byproducts are produced every year, some of them rich in phenolic compounds.
- Phenols are antioxidants with high-added value and positive effects to the human health.
- Their separation for the production of cosmetic products, food supplements etc., is of great interest.
- For this purpose, a combination of solid-liquid extraction, membrane filtration and resin adsorption/desorption following by evaporation is proposed, for the production of phenolic concentrates.
- The final products of the proposed process contain a large percentage of the byproducts' phenolic content, in a small fraction of the initial volume.
- This technique, after modification, can be applied to a variety of phenol-rich byproducts, allowing the operation of phenol separation plant adjustable to local agricultural activities.

Physicochemical Separation Techniques

- **Solid-liquid extraction** is the separation of target compounds from a solid matrix through the use of the appropriate solvent.

  Solvents: WATER- ETHANOL (accepted in food Industry)

Important parameters:

- *Physical characteristics of the solid*
- *Solvent*
- *Temperature*
- *Agitation*

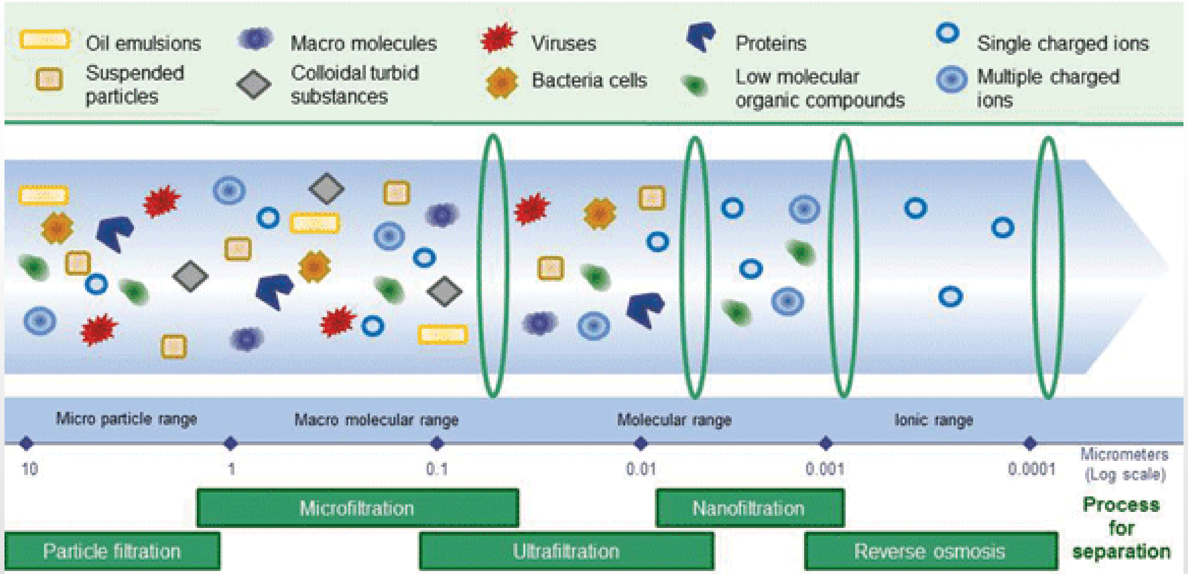
Type of extraction	Solutes	Free solids	Solvent/product
Diffusional extraction	Soluble coffee	Coffee beans	water
	Sugar	Sugar beets	Water, to produce sugar
Washing extraction	Vegetable oils	Oilseeds	Hexane, hydrocarbons
	Flavors/Odors	Flowers	Ethanol
	Sugar	Sugarcane	Water
Leaching	Phosphoric acid	Phosphate rock	Sulfuric acid
	Gold	Gold ore	Sodium cyanide
Chemical reaction	Gelatin	Bones and skins	Aqueous solution (pH 3 to 4)
	Lignins	Wood chips	NaOH solution, sulfide/sulfite

Physicochemical Separation Techniques

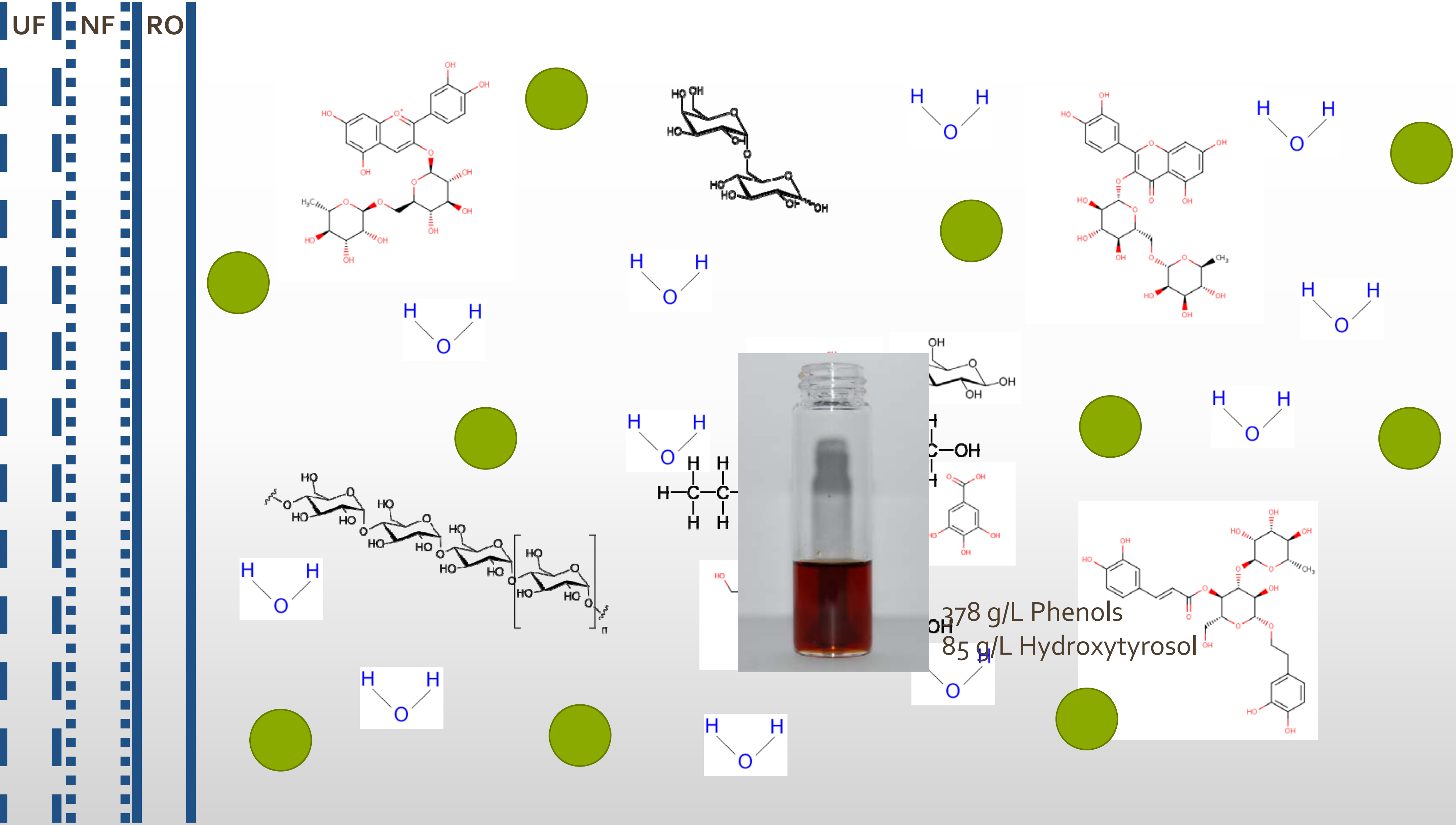
- **Membrane filtration** is a separation technique that has many applications in chemical process industries.

The most important attributes of a membrane material are:

- *Good permeability*
- *High selectivity*
- *Chemical stability*
- *Resistance to fouling*



http://www.watertechonline.com/sustainable-membranes-for-wastewater-applications/

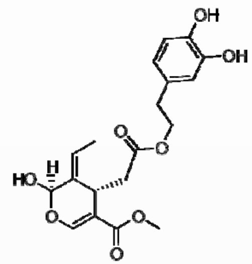

UF
NF
RO
378 g/L Phenols
85 g/L Hydroxytyrosol

Analytical Techniques

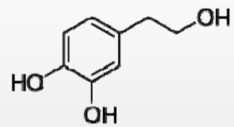
- Total Phenols: Folin-Ciocalteu reagent, gallic acid as standard, 720 nm.
- Total Carbohydrates: L-Tryptophane reagent, glucose as standard, 525 nm.
- COD: 5220 D, Standard Methods.
- TS: 2540 B, Standard Methods.
- TSS: 2540 D, Standard Methods.
- Simple Phenols: HPLC analysis, gradient elution, DAD detector.

Olive Mill Wastewater Phenolic Compounds

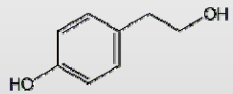
- Olive mill wastewater (OMW) is a byproduct of the THREE-phase extraction systems during the production of olive oil.
- Olive mill semi-solid (alperujo or pomace) is a byproduct of the TWO-phase extraction systems during the production of olive oil.
- Because of their partition coefficient, most phenolic compounds of olive fruits end up in the wastewater produced and not in olive oil.
- Oleuropein is the most common phenolic compound of unripe olive fruits, but during maturity it is hydrolyzed to several simpler phenolic compounds like hydroxytyrosol and tyrosol.



Oleuropein

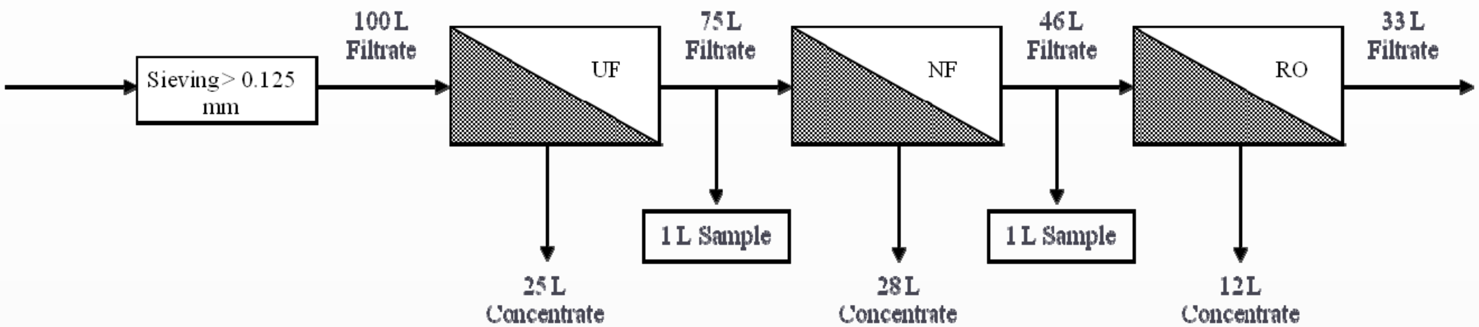


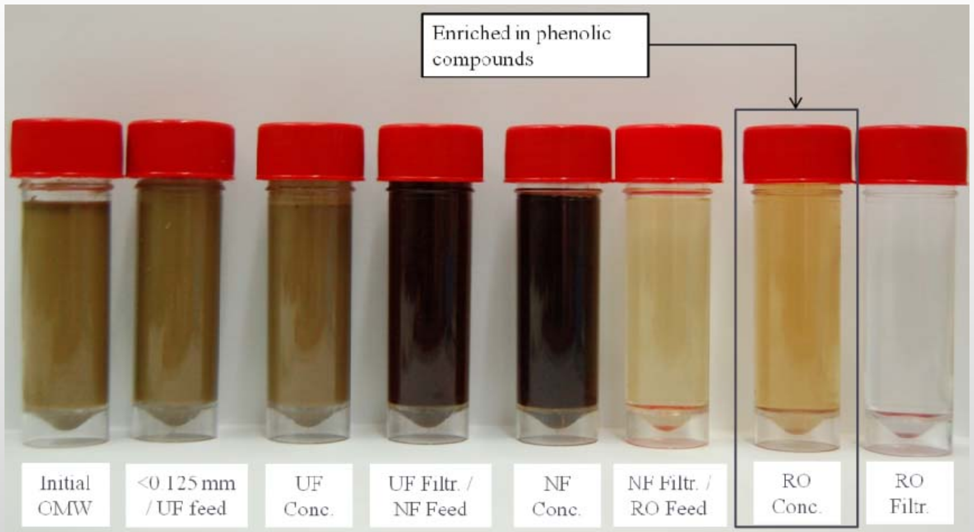
Hydroxytyrosol



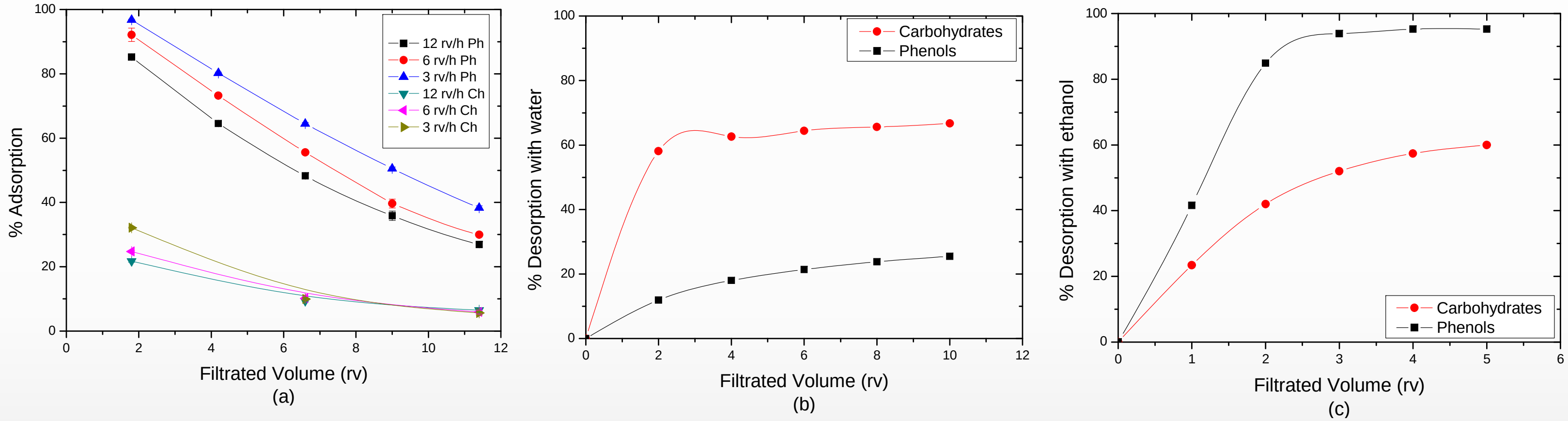
Tyrosol

Membrane Filtration of OMW (three phase decanter)





Resin Adsorption/Desorption of OMW RO_c



- XAD4 and XAD16N yielded the best results. Even though the sample contained more carbohydrates than phenols, resins adsorbed the dissolved phenols at a higher percentage.
- When water was used as a desorption solvent, the small amount of carbohydrates that was adsorbed on the resin was desorbed at a high percentage (60%). Ethanol, on the other hand, almost selectively removed the adsorbed phenols, while acetone removed both, carbohydrates and phenols.
- Kinetic experiments allowed the optimization of flow rates and total volume of treated sample before the resin surface was saturated.

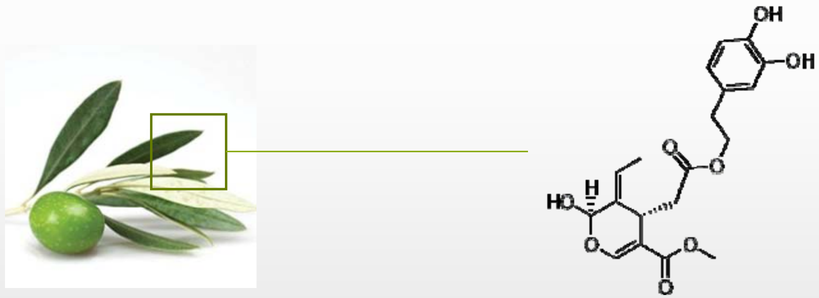
Final Concentrate of OMW Phenolic Compounds

- After carbohydrates removal via the proposed resin process, the **distillation under vacuum** (-0.95 bar, 55 °C) of the resin ethanolic effluent resulted to a final phenol concentration of 378 g/L in gallic acid equivalents in the distillation residue.

	Initial OMW	RO concentrate	Ethanolic resin effluent	Distillation residue
Volume, mL	16700	2000	1500	9
Phenols, g/L	2.64 *±0.04*	2.09 *±0.02*	2.36 *±0.01*	**377.50** *±8.34*
Carbohydrates, g/L	12.34 *±0.49*	14.96 *±0.03*	3.84 *±0.01*	293.92 *±1.28*

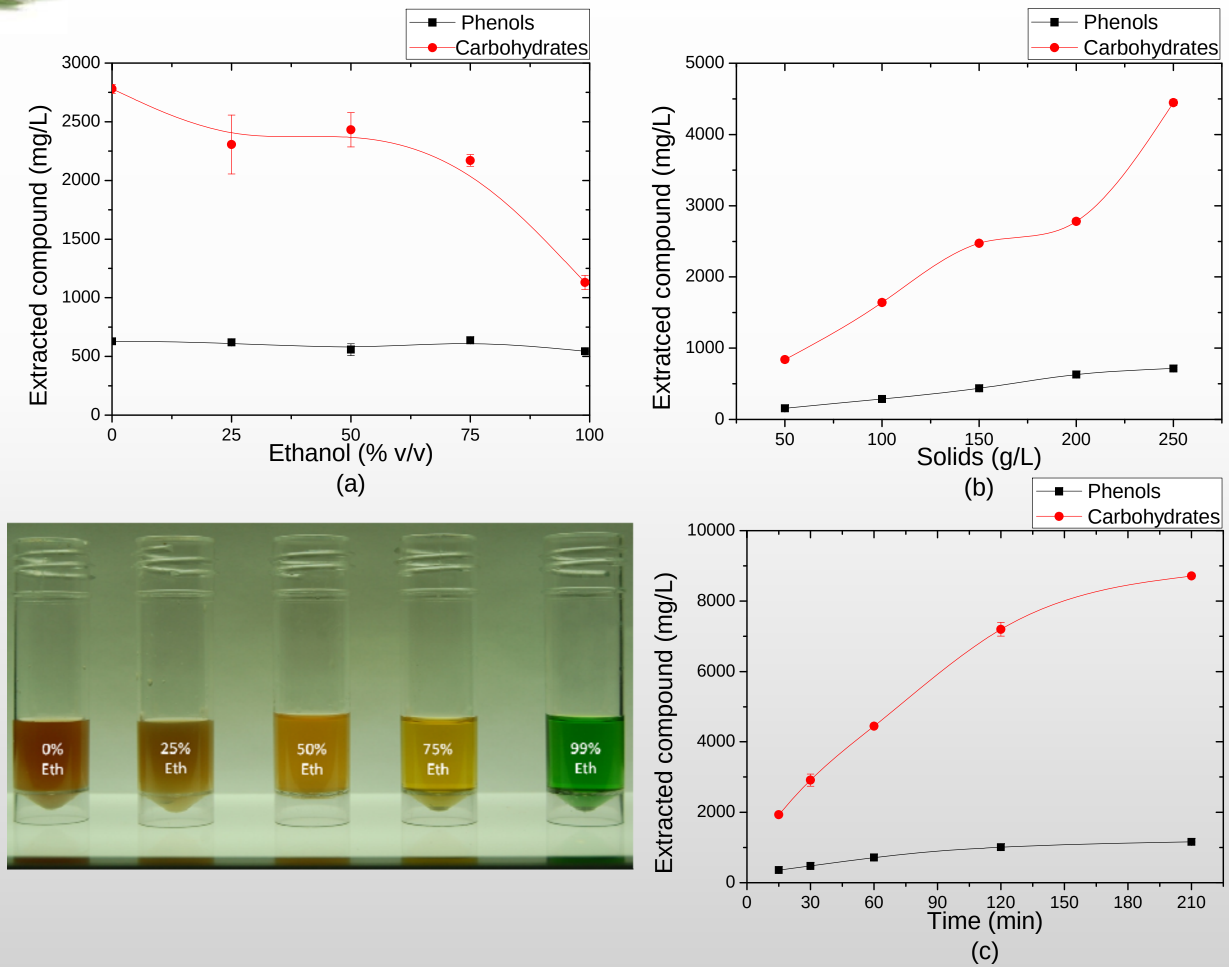
Olive Leaf Phenolic Compounds

- Olive leaves are a byproduct of olive fruit harvesting and initial stages of olive oil extraction, during their separation from olive fruits.
- Olive leaf extracts have been proven to be rich in phenolic compounds, with the most prominent one being **oleuropein**, which, unlike in the olive fruit, it is not hydrolyzed to simpler phenols.
- Oleuropein can be either bound to a sugar molecule (Oleuropein glycoside) or be present in its free form (Oleuropein aglycon).



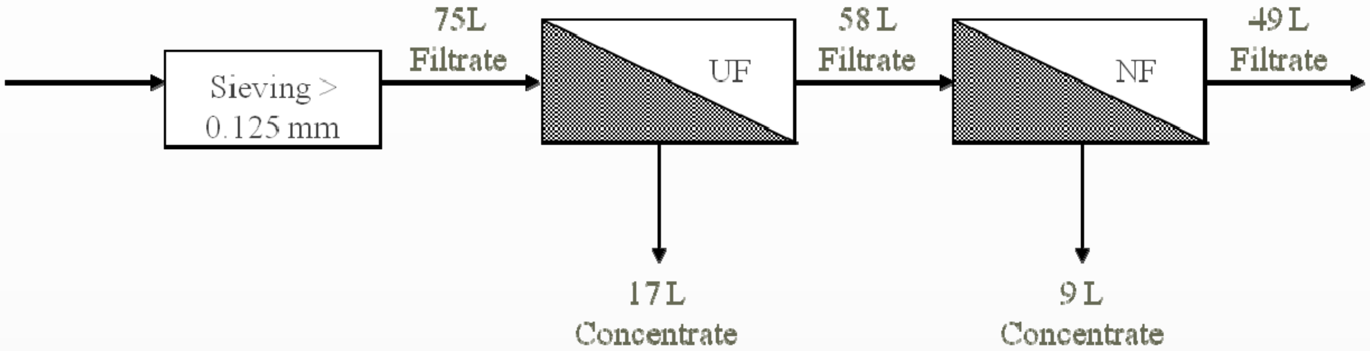
Oleuropein

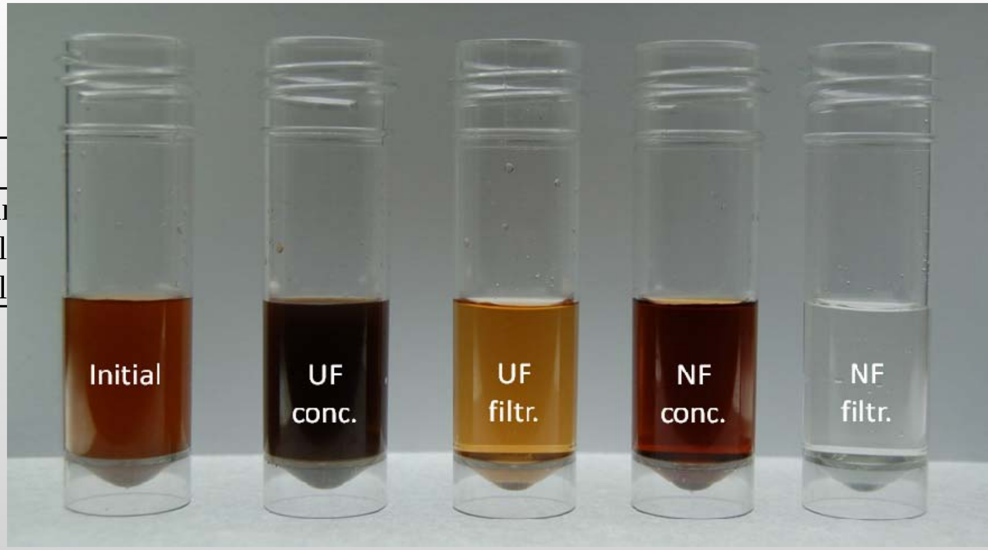
Extraction of Olive Leaf Phenols



Optimum extraction conditions	
Ethanol %	0
Duration	120 min
Solids/Solvent	250 g/L

Membrane Filtration of Olive Leaf Extract





	tr.
Volu	
Total	
Total	±24

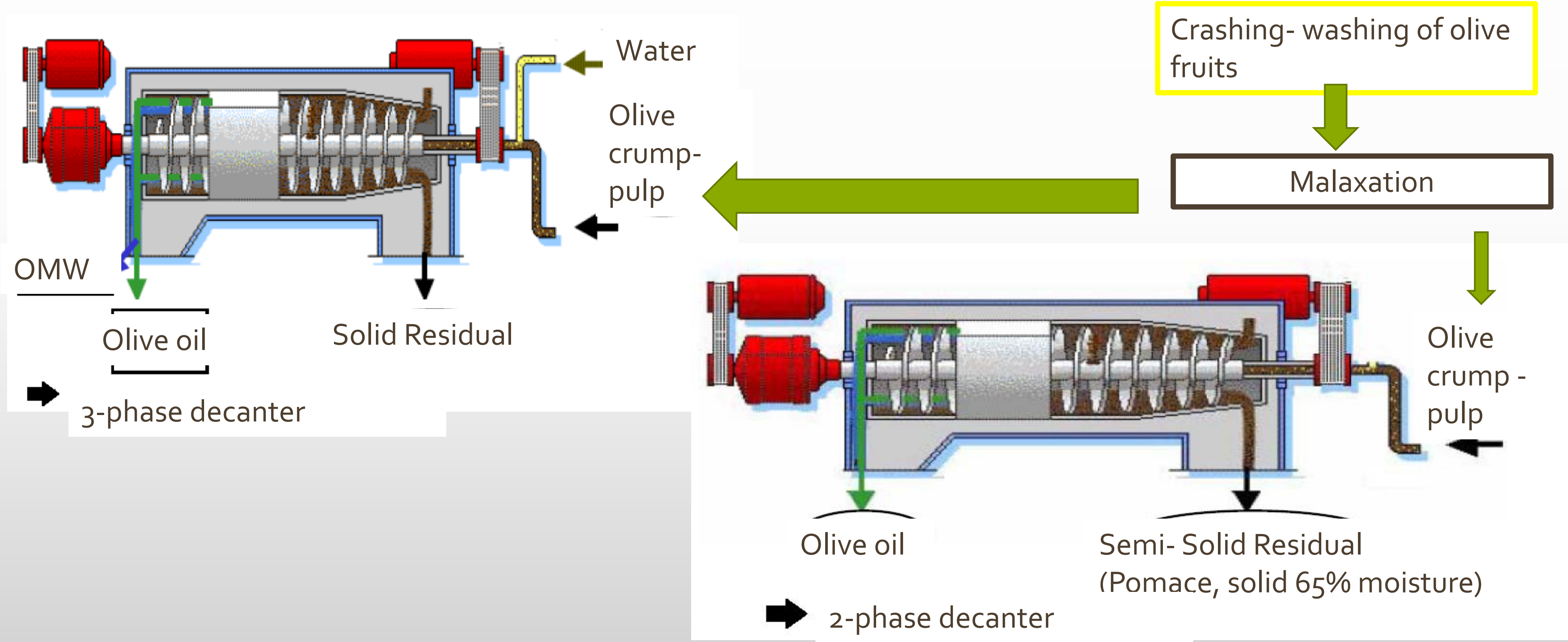
Final Concentration of Olive Leaf Phenols

- 1.44 L of NF concentrate were treated with the proposed resin process, leading to the production of 0.72 L of ethanolic effluent that was evaporated under vacuum (0.05 bar, 50 °C). The final concentrate had a volume of 10 mL .

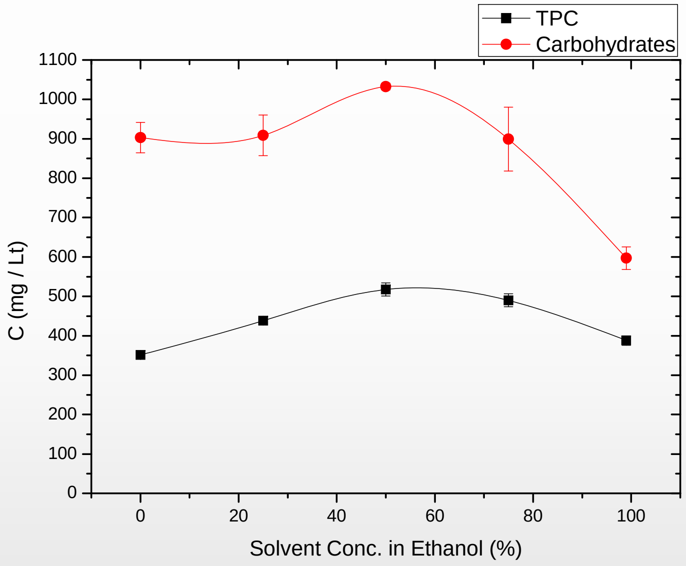
	Volume mL	Total Phenols mg/L	Total Carbohydrates mg/L
NFc	1440	988 ±25	5410 ±37
Desorbed	720	1480 ±1	5260 ±35
Final concentrate	10	**97890 ±1230**	322333 ±3933

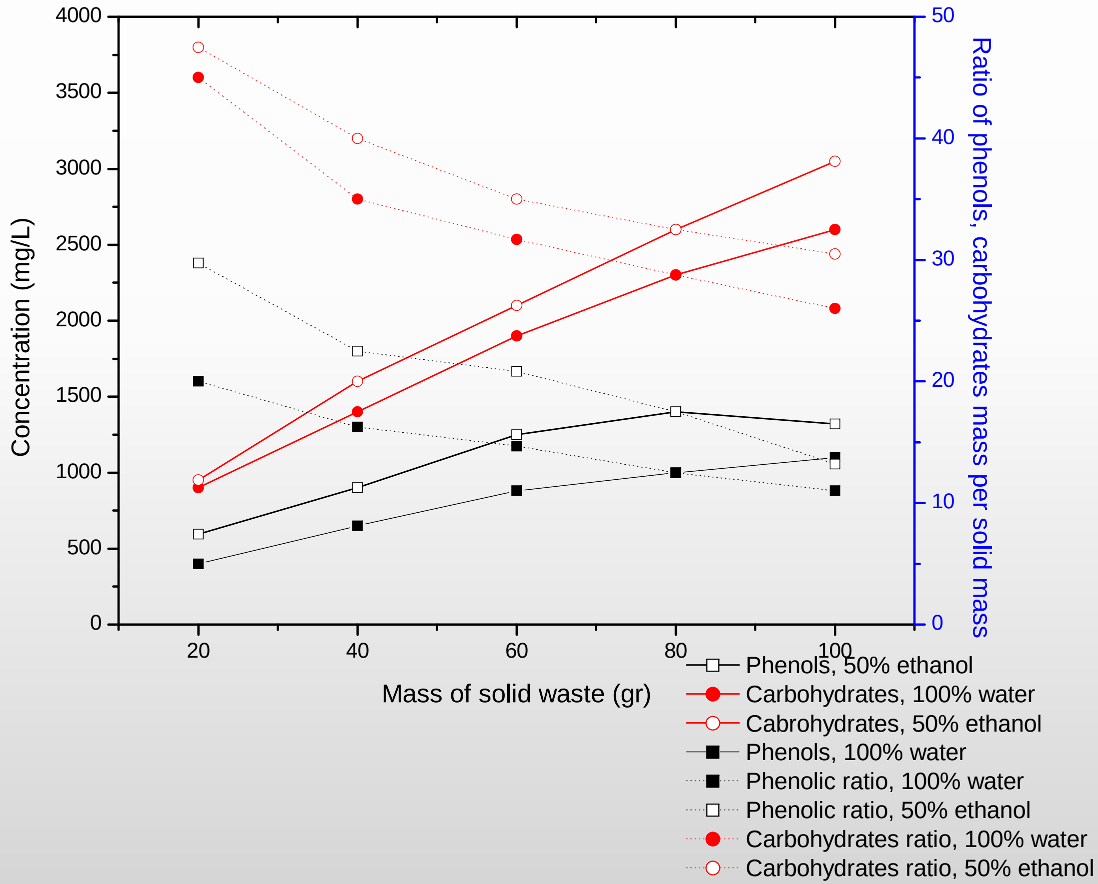
Olive oil semi-solid wastes (pomace or alperujo)

Residual from the 2-phase olive oil extraction process
60-70% moisture



Extraction of phenols from olive oil semi-solid wastes: A parametric study





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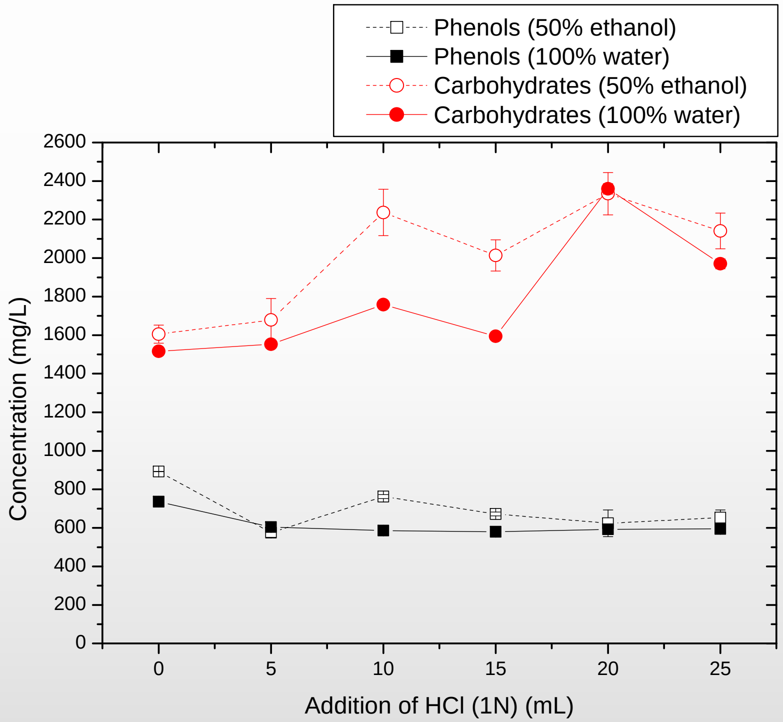

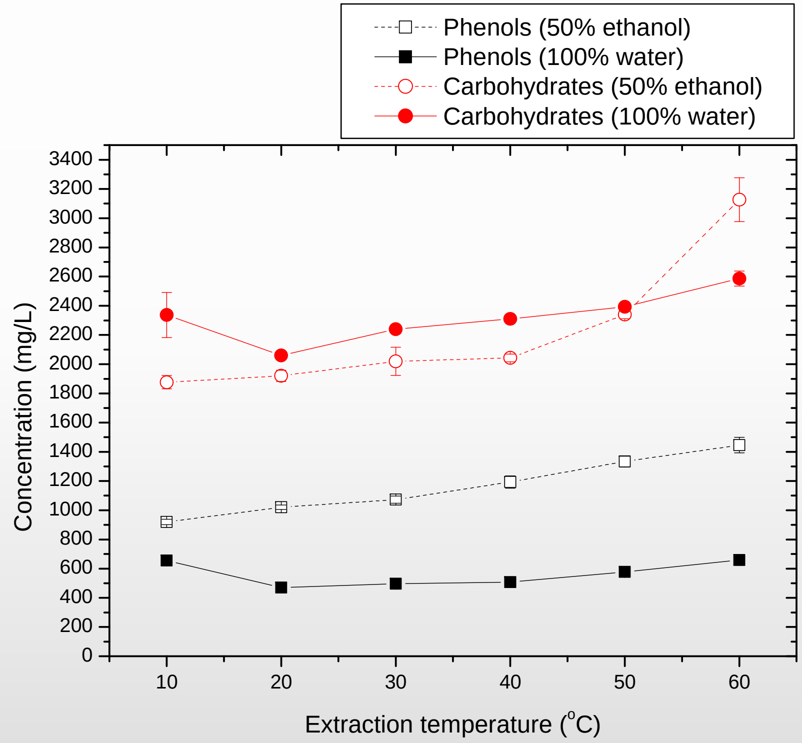

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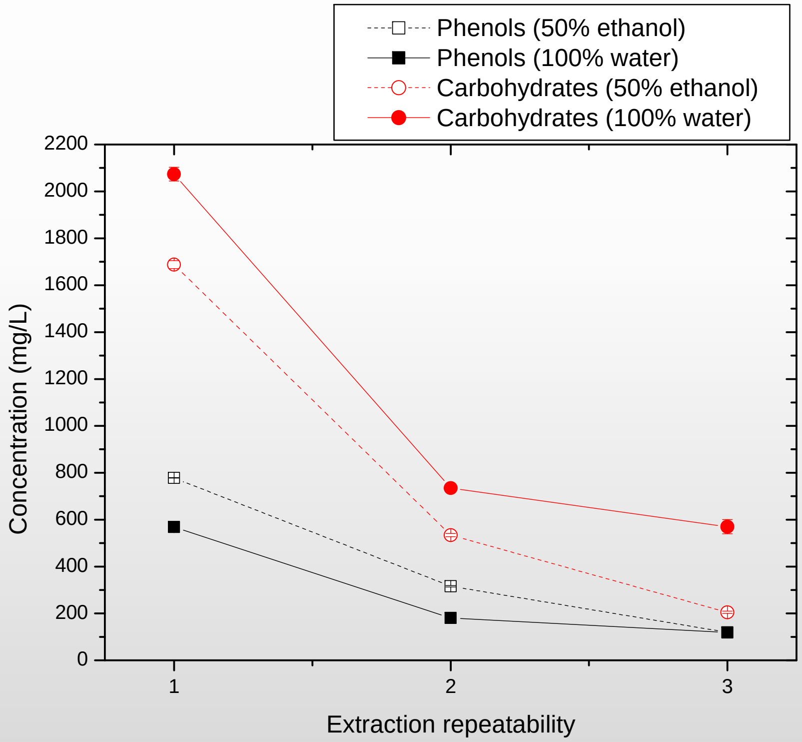

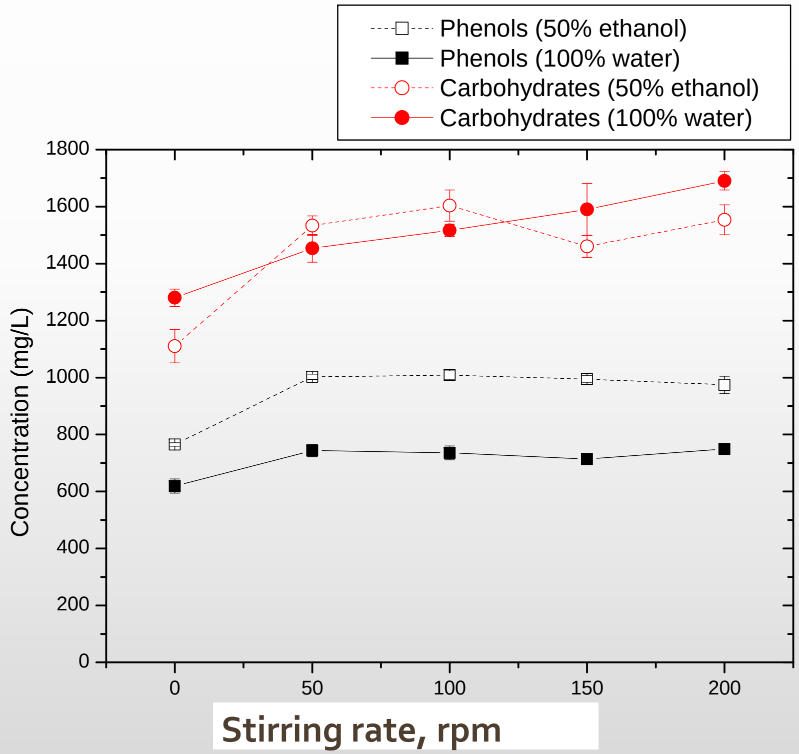

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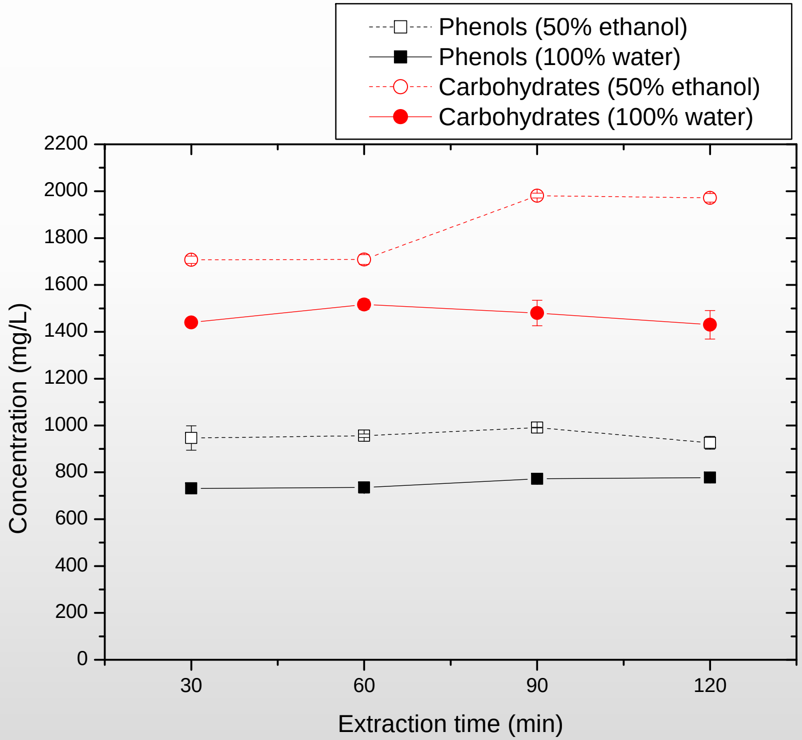
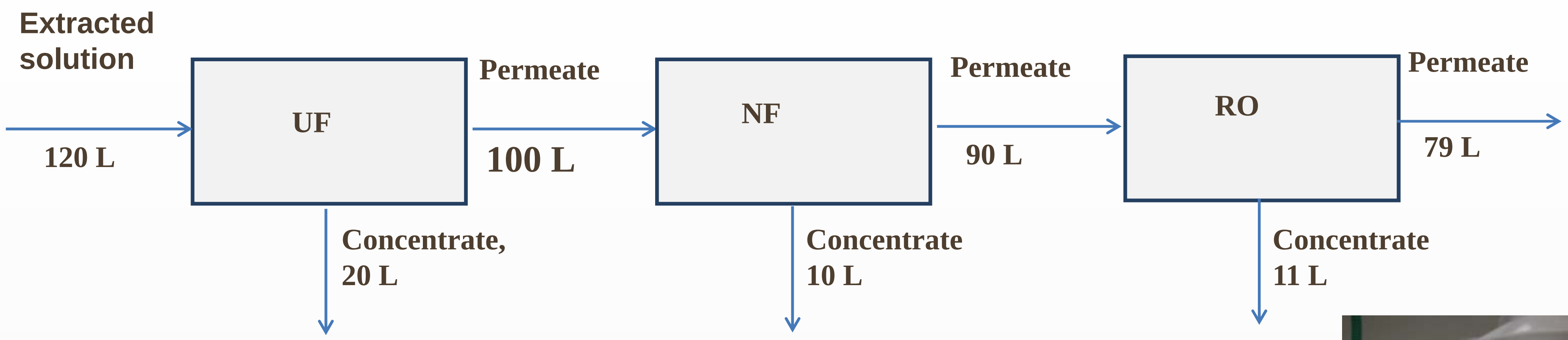


	Maximum TPC concentration (mg/L)		Maximum Carbohydrate concentration (mg/L)	
Solvent Type Conditions	**100% H_2O**	**50 % ethanol (95%), 50 % H_2O**	**100% H_2O**	**50 % ethanol (95%), 50 % H_2O**
Temperature, 20^oC	471.0	1020.3	2060.0	1373.3
Rate, 100 rpm	735.5	1008.3	1516.7	1603.3
Duration, 60 min	735.5	956.3	1516.7	1708.3
HCl, 0 mL	678.0	892.5	1436.0	1605.3
Mean Concentration	**655.0**	**969.3**	**1632.3**	**1572.6**

Extraction of phenols from olive oil semi-solid wastes: A pilot study



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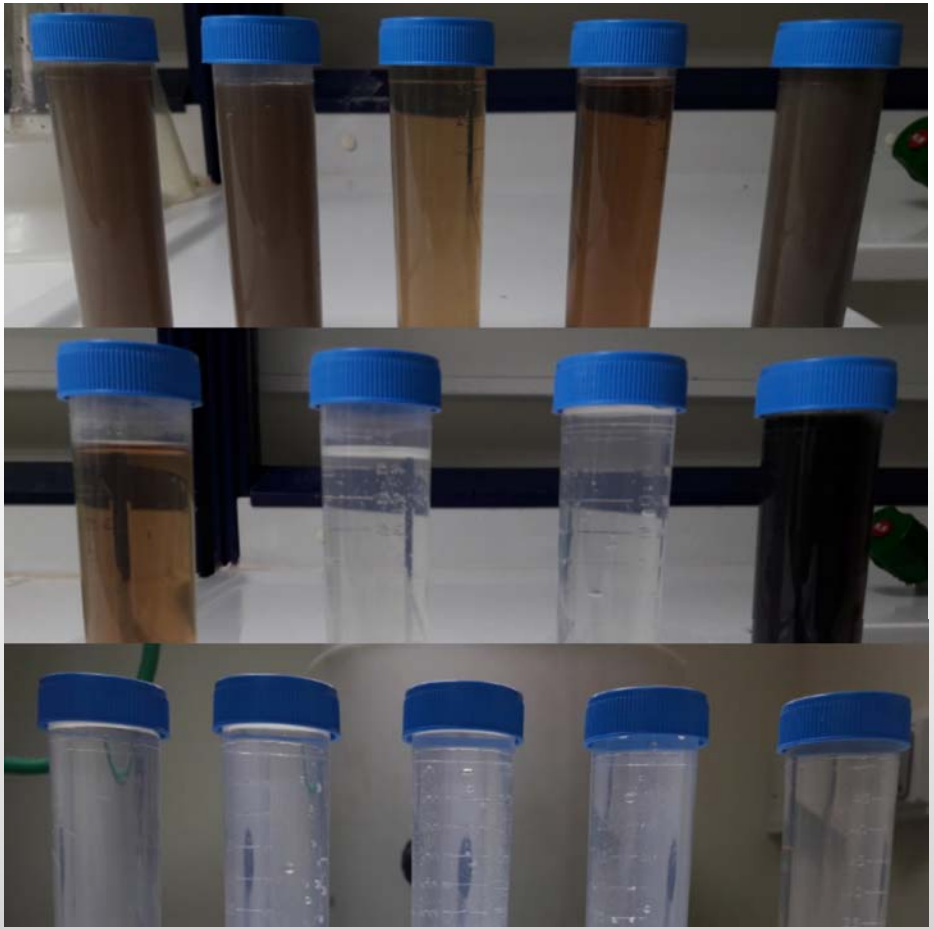
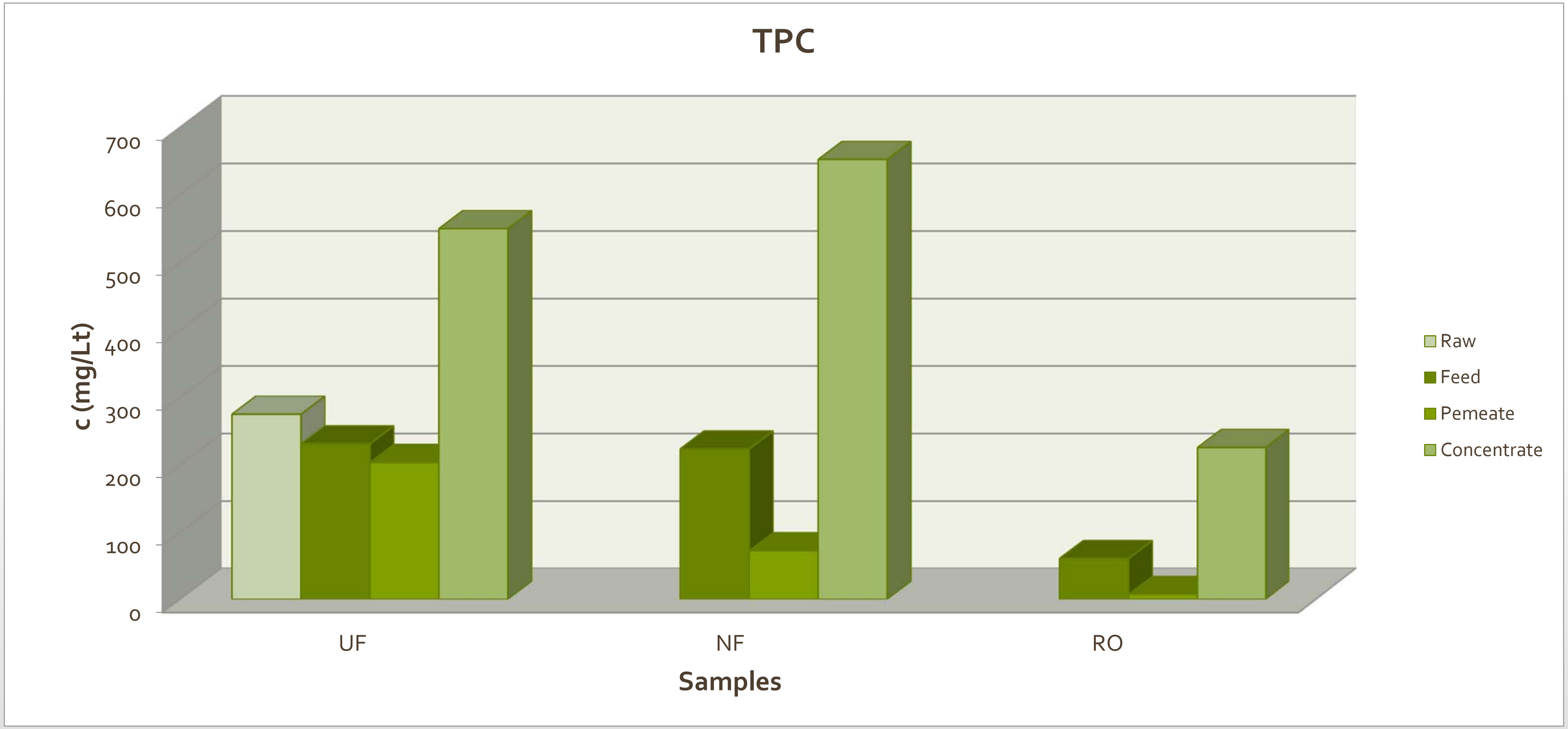


UF- Feed- intermediate permeates- concentrates

NF- Feed- intermediate permeates- concentrates

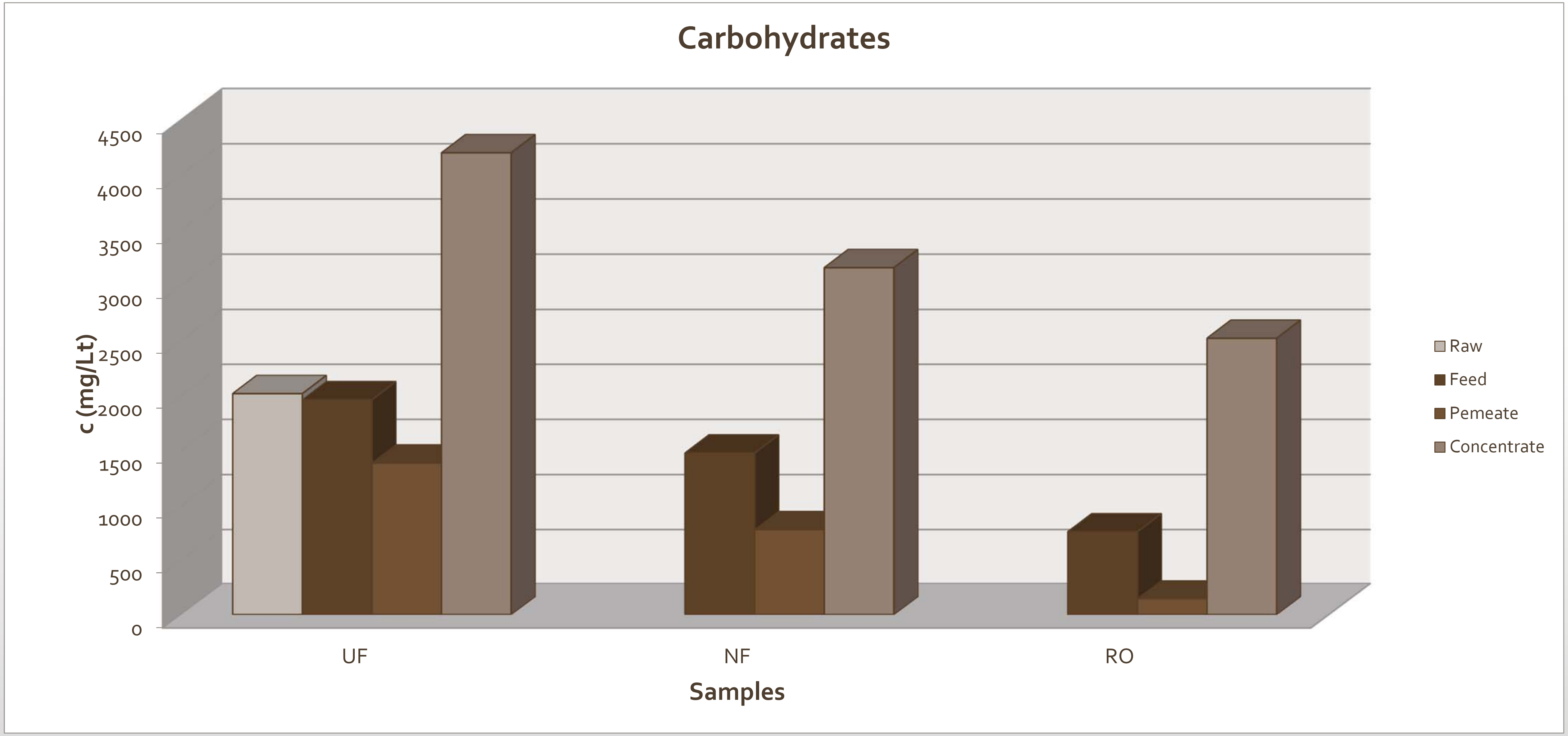
RO Feed- intermediate permeates- concentrates

Extraction of phenols from olive oil semi-solid wastes: A pilot study



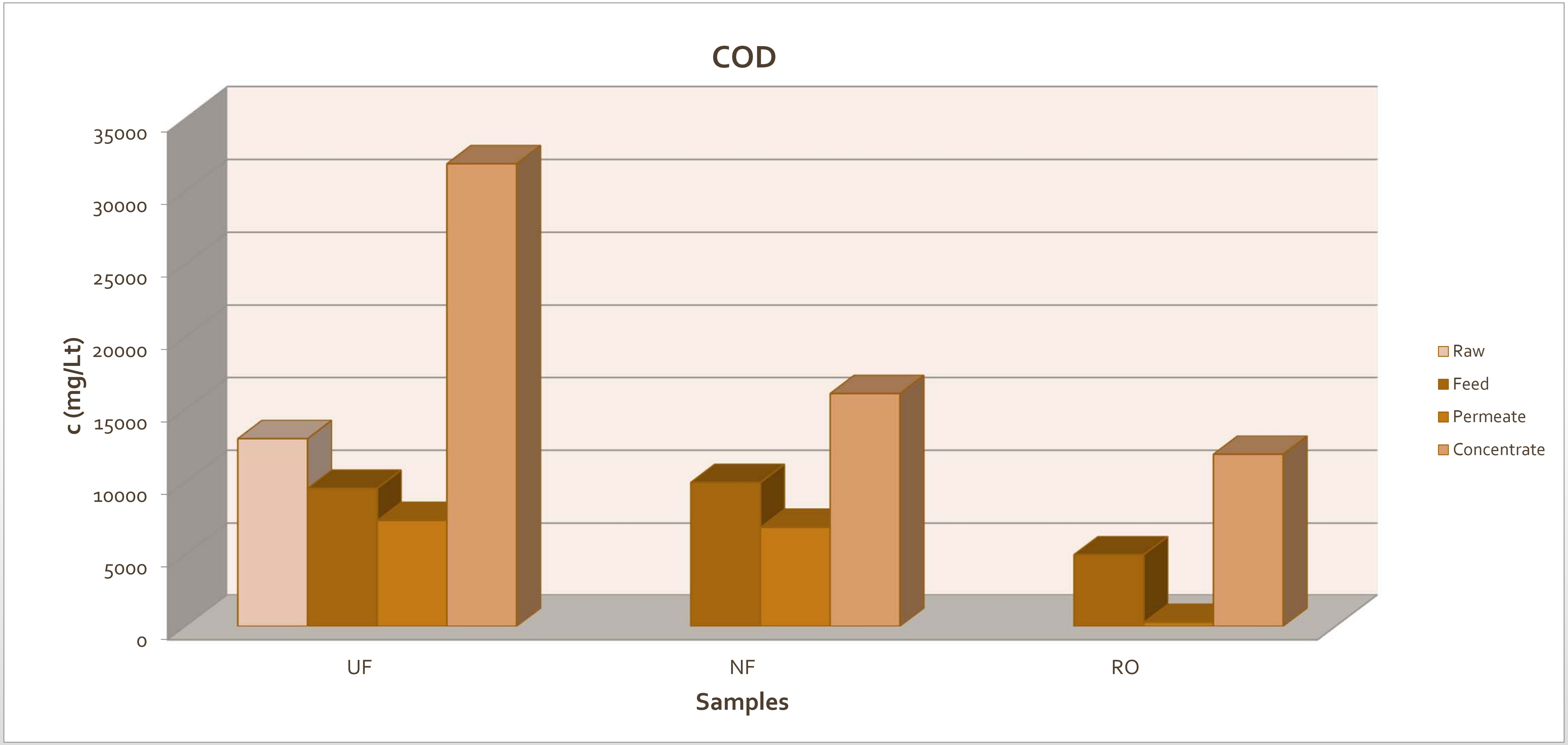
TPC concentration at the raw, feed, permeate and concentrate streams at the UF, NF, RO membranes.

Extraction of phenols from olive oil semi-solid wastes: A pilot study



Carbohydrates concentration at the raw, feed, permeate and concentrate streams at the UF, NF, RO membranes

Extraction of phenols from olive oil semi-solid wastes: A pilot study



COD at the raw, feed, permeate and concentrate streams at the UF, NF, RO membranes.

Conclusions: Extraction of phenols from olive oil semi-solid wastes

Optimal conditions

Solvent: Water 50% - ethanol 50 %

Solid/solvent ratio: 20 gr/100 ml

Temperature: 30- 40 °C

Stirring rate: 100 rpm

Duration: 1 hr

Pilot study

Fat and lipids and polyphenols are concentrated in UF retentate stream

Simple phenolics are included in NF and RO concentrates

Unfortunately carbohydrates are everywhere…

Adsorption/desorption on specific resins / cooling crystallization/ melting crystallization/ freeze drying→ better purification of phenols… current work

Acknowledgements

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Thank you for your attention