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About the Recovery of the Phenolic Fraction from Olive Mill Wastewater by Micro and Ultracentrifugation Membranes

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The adoption of a new economic model, the circular economy, that promotes closing-the-loop of product lifecycles through greater recycling and re-use, is driving attention to by-products and waste valorisation. Food production chain has been considered one of the main waste producers and therefore several studies have been developed on its by-products and waste valorization, producing a range of secondary raw materials. Membrane technologies can be used for the recovery of valuable compounds such as fibers, pectin, sugars, proteins, and phenolic compounds from agroindustrial wastes.
In this sense, olive mill wastewater (OMW) is one of the main wastes generated during the production of olive oil and represents an environmental problem of this agro-industrial process. It is extremely difficult to treat due to its considerable volume and high organic matter concentration. Its principal components are polysaccharides, sugars, polyphenols, polyalcohols, proteins, organic acids, and oil.
Among them, phenolic compounds represent one of the major factors of the environmental problems caused by OMW. They are present in high concentration and they have different negative effects such as phytotoxicity, toxicity against aquatic organisms, suppression of soil microorganisms and difficulty to decompose. On the other hand, phenolic compounds possess high antioxidant activity that makes them interesting for the food, pharmaceutical and cosmetic industries. Because of that, the recovery of these compounds by different physicochemical methodologies represents an important objective for olive oil industry that will help to obtain interesting extracts and reduce the volume of this industrial by-product.
In this work, the goal was the fractionation of fresh OMW, directly taken from the centrifuges of two-phase olive oil mills. For this goal, and prior to run bench or pilot-scale experiments, a novel screening of microfiltration (MF), ultrafiltration (UF) and loose nanofiltration (NF) membranes was performed. The procedure consisted of filtering the samples of OMW through 0.45 μm membrane filters. After this, the filtered samples were poured into Falcon tubes provided with membranes of different mean pore size (MWCO ranging from 100 down to 3 kDa). Finally, they were subjected to quick centrifugation, after which the total polyphenols concentration, the COD, the electroconductivity and the pH of both the permeate and concentrated fractions of the centrifuged-filtered samples were analyzed in both outlet streams to assess the adequate membrane pore size selection.

1. Introduction

Olive oil production not only represents one of the most important agro-food industries in the Mediterranean area, but has as well made its way in many European countries and also in the USA, Argentina, Australia, the Middle East and China. In fact, a growing demand of olive oil worldwide has been registered in the recent decades in virtue of its nutritional, antioxidant and heart-healthy properties. In order to satisfy this increasing demand, discontinuous olive oil pressure-based extraction processes were not sufficient, and therefore have been rapidly replaced by more efficient two-phase and three-phase continuous centrifugation-based procedures. On one hand these processes guarantee a higher yield in recovering olive oil from the olives, up to 21%, but on the other they lead to an increased production of wastewater streams, commonly known as olive mill wastewater (OMW). OMW derives from olives washing wastewater (OWW) and olive vegetation wastewater (OVW). The latter, a mix of olive-fruit humidity and process-added water, contains organic pollutants at high load and represents an environmental threat.

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Up to 0.8 m^3 and 1.2 m^3 of potable water per ton of processed olives are added in case of two-phase and three-phase extraction processes, respectively. An average-sized olive oil factory processes 10 t/day of olives, leading to the production of 10 m^3/day of OVW in average. Moreover, 1 m^3/day of potable water per ton of processed olives is used for their washing, leading to the by-production of OWW.
The general solution applied in the last decades has been the construction of artificial lagoons to promote natural evaporation. Over the years, this rule has resulted inefficient because of the low evaporation potential of these ponds, which cause this residue to become more and more concentrated in time, incrementing each year its polluting effect. Moreover, due to the limited capacity of these artificial ponds when they become saturated there is a need to construct new ones, leading to problems in this sector in relation to the increase of the occupied terrain, overflows and cessation of the activity, hindrance of the implementation of quality systems, atmospheric contamination, underground leakages causing pollution to the terrain and aquifers, odor release, insects pests, as well as problems in zones with high rainfall (Fragoso and Duarte, 2012; Ochando-Pulido et al., 2012). In this line, the European Union is committed with the regeneration of used resources, and this implies the treatment of wastewaters of diverse sources (Vilardi et al., 2017; Vilardi and Di Palma, 2017).
A plethora of reclamation practices as well as combined treatments for OMW have already been proposed and developed but not led to completely satisfactory results, such as lagooning or natural evaporation and thermal concentration (Paraskeva and Diamadopoulos, 2006) composting (Cegarra et al., 1996; Papadimitriou et al., 2007), treatments with clay (Al-Malah et al., 2000) or with lime (Aktas et al., 2001), physico-chemical procedures such as coagulation-flocculation (Martínez-Nieto et al., 2011; Sarika et al., 2005), electrocoagulation (Inan et al., 2004; Tezcan Ün et al., 2006) and biosorption (Hodaifa et al., 2013a), advanced oxidation processes including ozonation (Cañizares et al., 2009), Fenton´s reaction (Hodaifa et al., 2013b) and photocatalysis (Ruzmanova et al., 2013), electrochemical treatments (Papastefanakis et al., 2010) and hybrid processes (Grafias et al., 2010; Khoufi et al., 2006).
The processes proposed until today for the treatment of OMW are rather cost-ineffective, and olive oil industry in its status, composed of little and dispersed factories, is not willing to bear such high costs.
These effluents represent the principal liquid wastes generated during the production of olive oil, an environmental problem of this agro-industrial process. OMW is extremely difficult to degrade due to its considerable volume and high organic matter concentration. Its principal components are polysaccharides, sugars, polyphenols, polyalcohols, proteins, organic acids, and oil.
Among them, phenolic compounds represent one of the major factors of the environmental problems caused by OMW. They are present in high concentration and have different negative effects such as phytotoxicity, toxicity against aquatic organisms, suppression of soil microorganisms and difficulty to decompose.
On the other hand, phenolic compounds possess high antioxidant activity that makes them interesting for the food, pharmaceutical and cosmetic industries (Niaounakis and Halvadakis, 2006; Obied et al., 2005). Because of that, the recovery of these compounds represents an important objective for olive oil industry that will help to obtain interesting extracts and reduce the volume of this industrial by-product.
Conventional solvent extraction has been the most used method for the recovery of phenolic compounds from OMW due to its simplicity (Obied et al., 2005). Different solvents, including water, ethyl acetate, ethanol and others, have been checked for the extraction of phenolic compounds from OMW. Nevertheless, hydro-alcoholic mixtures in different proportions have been the most popular solutions (Obied et al., 2005).
However, membrane technologies - microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO) - offer a series of advantages in contrast with other separation processes, making them very promising and environmentally friendly for the recovery of added-value compounds and remediation of OMW: no need of chemical reagents - solvents - to achieve separation and concentration; lower capital and operating costs and energy consumption than most conventional separation procedures, still ensuring high purifying capacity, selectivity and recovery rates; and easy industrial scaling per its modular nature, ease of design and operation and low maintenance requirements (El-Abbassi et al., 2014; Garcia-Castello et al., 2010).
On another hand, inhibition and control of fouling is vital to achieve the competitiveness of membrane technology at industrial scale (Field and Pearce, 2011; Stoller and Chianese, 2006a, b and 2007; Stoller, 2009, 2011; Stoller et al., 2013a, b; Stoller et al., 2016, 2017). In this sense, OMW2 contains high concentrations of a wide range of solutes in the form of suspended solids and colloidal particles which are all very prone to cause membrane fouling, such as organic pollutants comprising phenolic compounds, organic acids, tannins and organohalogenated contaminants, as well as inorganic matter.
In this work, the goal was the fractionation of fresh olive mill wastewater, directly obtained from the vertical centrifuges of two-phase olive oil production mills and directly driven to the laboratory. For this objective, and prior to run bench or pilot-scale experiments, a novel screening of microfiltration (MF), ultrafiltration (UF) and loose nanofiltration (NF) membranes was performed.

2. Experimental

2.1. Analytical proceedings

Analytical grade reagents were used for the analytical proceedings, which were triplicated. Chemical oxygen demand (COD), total suspended solids (TSS), total phenols (TPh), electroconductivity (EC) and pH analysis, were performed following standard methods (Greenberg et al., 2005). EC and pH were measured with a Crison GLP31 conductivity-meter and a Crison GLP21 pH-meter. A Helios Gamma UV-visible spectrophotometer (Thermo Fisher Scientific) was used for the COD and TPh measurements (Standard German methods ISO 8466-1 and German DIN 38402 A51). Ionic concentrations were analyzed with a Dionex DX-120 ion chromatograph (Ochando-Pulido et al., 2012).

2.2. OMW effluent samples

The raw feedstock was olive mill wastewater samples collected during the winter campaign from various olive mills operating with the two-phase centrifugation technology (OMW2) in the region of Andalucia (Spain), the major olive oil producer world-wide. The samples of OMW2 were thereafter taken to the laboratory and freshly analyzed.

2.3. Ultracentrifugation membranes

The procedure followed in this research work for the fractionation of the OMW stream consisted, beforehand, in the filtration of 100 mL samples of OMW2 through 0.45 μm nitrate cellulose membrane filters (Sartorius, 111306-047N).

After this step, volumes of 15 mL of the filtered samples were poured into Falcon tubes (Merck Millipore) provided with membranes (regenerated cellulose) of different mean pore diameters (molecular weight cut-off, MWCO ranging from 100 down to 3 kDa). Finally, the Falcon tubes were subsequently centrifuged at 4000 rpm for 3 min. The specifications of the selected membranes are reported in Table 1.

After this procedure, the total polyphenols concentration, as well as the COD, the electroconductivity and the pH of both the permeate and concentrated fractions of the centrifuged-filtered samples was analyzed.

At the end of each run the membrane was fully cleaned in situ with 0.1 - 0.5 % w/v NaOH, sodium dodecyl sulfate (SDS) and citric acid solutions (Panreac S.A.) to recover it for the next experiment, as formerly described by Ochando-Pulido et al. (2015).

Table 1: Specifications of the selected membranes

Membrane type	Characteristics
Membrane type	MF-UF-NF
Provider	Millipore
Model	Amicon Ultra-15
Material	Regenerated cellulose
MWCO, kDa	3 - 10 - 30- 50 - 100

[*] MWCO: molecular weight cut off.

3. Results and discussion

The physicochemical characterization of the raw OMW2 stream is reported in Table 1. As it can be seen, a considerable concentration of phenolic compounds was quantified in the effluent from the vertical centrifuges of the two-phase olive oil production process, in the range of 770.0 mg L^{-1}. On another hand, the pH of the effluent was confirmed to be slightly acid (5.0 ± 0.1), with a high organic matter concentration (COD) of about 13.9 ± 0.6 g L^{-1}, and an EC 1.8 ± 0.1 mS cm^{-1}. Also, a considerable concentration of suspended solids was measured (3.6 ± 0.2 mg L^{-1}).

Subsequently, samples of OMW were conducted to the MF-UF screening formerly described (MWCO ranging from 100 down to 3 kDa). As a consequence of the procedure followed, a visual analysis of both fractions obtained for each MWCO assayed showed that the concentrate fraction was a dark stream, disregarding the MWCO of the membrane selected, whereas the permeate was increasingly clearer as the MWCO of the membrane was narrowed from 100 to 3 kDa.

Table 2: Physicochemical characterization of OMW2[a]

Parameter	OMW2
pH	5.0 ± 0.1
EC (mS cm^{-1})	1.8 ± 0.1
TSS (mg L^{-1})	3.6 ± 0.2
COD (mg L^{-1})	13.9 ± 0.6
Total phenolic compounds (mg L^{-1})	730.0 ± 21.2

[a] OMW2: to-phase olive mill wastewater.

The rejection of the total phenolic compounds as a function of the membrane MWCO (ranging from 100 down to 3 kDa) is reported in Table 3. The rejection performance of the tested membranes towards the concentrations of phenols in the OMW2 stream was found to be linear as a function of the MWCO of the membrane.
This implied that the rejection of the total phenols concentration could be increased from around 30% for a membrane with a MWCO of 100 kDa, up to 57 % for a membrane with a MWCO of 3 kDa (Table 3).
On another hand, the quantity of the permeate stream was found to be increased from 4.9 g to approximately 8.7 g when the membrane MWCO increased from 3 up to 100 kDa. The results of the quantification of the permeate vs. concentrate recovery as a function of the MWCO of the membrane is given in Table 4.
Moreover, the use of a membrane in the range of MF, with a mean pore size of 0.45 nm, permitted the concentration of 19.7% of the phenolic fraction, and a reduction of 3.3% of the COD as well as the rejection of 100% of the suspended solids present in the effluent.

Table 3: Rejection of total phenols as a function of the membrane pore size.

Membrane size	R_{TPh}, %
0.45 µm	-19.7
100 kDa	30.3
50kDa	43.1
30 kDa	47.2
10 kDa	52.5
3 kDa	57.1

[a] OMW2: to-phase olive mill wastewater.

Table 4: Rejection of total phenols as a function of the membrane MWCO.

Membrane MWCO	Permeate weight, g
3 kDa	4.89
10kDa	4.96
30 kDa	6.73
50 kDa	6.98
100 kDa	8.66

[a] OMW2: to-phase olive mill wastewater.

To sum up, this method can be quick and reliable in order to perform a primary assessment of the adequate membrane needed for a particular purification process. This fact is very relevant, given that it can aid in the selection of the adequate membrane pore size by carrying out fast experiments, so as to make a first screening analysis. This contrasts with the long-term, time consuming experiments that have to be carried out with common lab membrane experiments with bench-scale units.

4. Conclusions

In this work, a method quick and reliable for primary assessment and screening of the adequate membrane needed for a specific purification process is given. Particularly, the concentration and fractionation polyphenolic fraction present in olive mill wastewater (OMW) was achieved, with the removal of the suspended solids present in the effluent.

Phenolic compounds represent one of the major factors of the environmental problems caused by OMW. They are present in high concentration and they have different negative effects such as phytotoxicity, toxicity against aquatic organisms, suppression of soil microorganisms and difficulty to decompose, whereas on the other hand, they present high antioxidant activity that makes them interesting for the food, pharmaceutical and cosmetic industries.

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