Assessment Of Microfiltration And Ultrafiltration Membranes For Olive Mill Wastewater Fractionation

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Abstract

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 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. The recovery of these compounds by different physicochemical methodologies represents an important objective for this 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 olive mill wastewater 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.

Keywords: olive mill wastewater, circular economy, membranes, polyphenols.

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.

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).

A plethora of reclamation practices as well as combined treatments for OMWW have already been proposed and developed but not led to completely satisfactory results, such as lagooning or natural evaporation and thermal concentration (Annesini and Gironi, 1991; 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 majority of the processes proposed until today for the treatment of OMWW are rather cost-ineffective, and olive oil industry in its current 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 and represents an environmental problem of this agro-industrial process. It is extremely difficult 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 (Niaounakis and Halvadakis, 2006; Obied *et al*., 2005). 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.

Conventional solvent extraction has been the most used chemical method for the recovery of phenolic compounds from OMWW due to its simplicity and convenience (Obied *et al*., 2005). Many different solvents, including water, have been checked for the extraction of phenolic compounds from OMWW. Nevertheless, hydro-alcoholic mixtures in different proportions have been the most popular solutions (Obied *et al*., 2005)

However, membrane technologies, comprising microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO), can offer a series of advantages in contrast with other separation processes, making them very promising and environmentally friendly for the purpose of the recovery of polyphenolic compounds and remediation of OMW: no need to use chemical reagents - such as solvents - to achieve separation and concentration; lower capital and operating costs and energy consumption than most conventional separation procedures, but still ensuring high purifying capacity, selectivity and recovery rates; and also easy industrial scaling in virtue of 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 definitely 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). 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. Effluent samples

The raw feedstock was olive mill wastewater samples collected during the winter campaign from 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.

2.2. Physico-chemical analyses

Analyses of the chemical oxygen demand (COD), total suspended solids (TSS), ashes, total phenolic compounds, total iron, electrical conductivity (EC) and pH were performed in both the influent (OMW2TT) and in the permeate of the RO unit, following standard methods (Greenberg *et al*., 2005).

A Helios Gamma UV-visible spectrophotometer (Thermo Fisher Scientific) was used for the analyses of the COD, total phenols and total iron. An ion chromatograph (Dionex DX-120) was used to measure the ionic concentrations. EC and pH were analyzed with a Crison GLP31 conductivity-meter and a Crison GLP21 pH-meter, provided with autocorrection of temperature (25 °C), previously calibrated with buffer standard solutions for EC (1,413 µS/cm and 12.88 mS/cm) and pH (pH 4.01, 7.00 and 9.21) purchased as well from Crison. For the measurement of the total iron concentration, all iron ions were reduced to iron ions (II) in a thioglycolate medium with a derivative of triazine, forming a reddish-purple complex that was determined photometrically at 565 nm (Standard German methods ISO 8466-1 and German DIN 38402 A51) (Greenberg *et al*., 2005). Ionic concentrations were analyzed with a Dionex DX-120 ion chromatograph (Ochando-Pulido *et al*., 2012).

2.3. Membrane plant

The membrane bench-scale plant, from Prozesstechnik GmbH (Fig. 1), was provided with a non-stirred jacketed tank (5 L) where the effluent was contained, and a diaphragm pump (Hydra-Cell) to drive the feed to a plate-and-frame membrane module (3.9 cm width x 33.5 cm length).

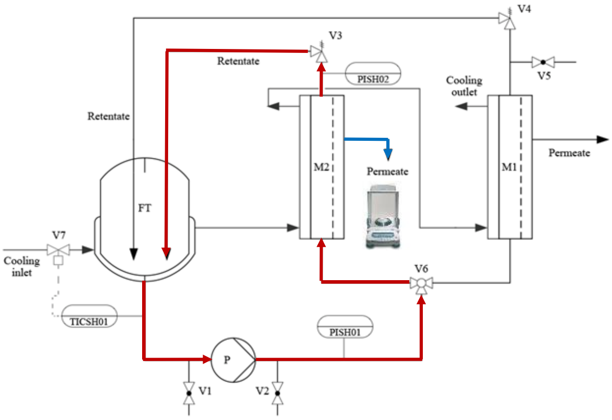

Fig. 1. Flow diagram of the membrane pilot plant. V1, V2: emptying valves; V3, V4: pressure regulating valves for module 2 and 1 respectively; V5: venting valve for module M1; V6: three-way valve to select desired membrane module; V7: magnetic valve for cooling jacket inlet; M1: flat-sheet membrane module; M2: spiral-wounded module; P: feedstock pump; FT: feedstock tank; PISH01, PISH02: pressure gauges; TICSH01: temperature gauge.

The main operating variables were measured and displayed: the pressure, for which a constant pressure strategy (PC) was adopted, adjustable with a spring-loaded pressure-regulating valve on the concentrate outlet (Swagelok) and monitored by a digital pressure gauge (Endress+Hauser). This permitted the independent control of the applied pressure (PTM set point ± 0.01 bar) and the flowrate (0.1 L h^{-1} precision), regulated by a feed flow rate valve to fix the tangential velocity over the membrane; the operating temperature was regulated automatically ($T_{set\ point}$ ± 0.1 °C) via a proportional-integral-derivative (PID) electronic temperature controller (Yokogawa), connected to a chiller (PolyScience).

2.4. Assessment of UF and MF membranes

The procedure performed consisted of filtering 100 mL samples of OMW2 through 0.45 μm nitrate cellulose membrane filters. After this, 15 mL of the filtered samples were poured into Falcon tubes provided with membranes 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. 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.

After 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 (Ochando-Pulido *et al.*, 2015).

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, with a high COD of about 13.9 ± 0.6 g L^{-1}.

Table 1: OMW2 physicochemical characterization.

Parameter	Raw
pH	5.0 ± 0.1
EC, mS cm^{-1}	1.8 ± 0.1
TSS, g L^{-1}	3.6 ± 0.2
COD, g L^{-1}	13.9 ± 0.6
Total phenols, mg L^{-1}	770.0 ± 21.2

* EC: electrical conductivity; TSS: total suspended solids; COD: chemical oxygen demand.

Subsequently, samples of OMW were conducted to the MF-UF screening formerly described (MWCO ranging from 100 down to 3 kDa). In Fig. 2, a photograph of the resulting concentrate and permeate streams after the procedure is reported. As it can be seen, the concentrate 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.

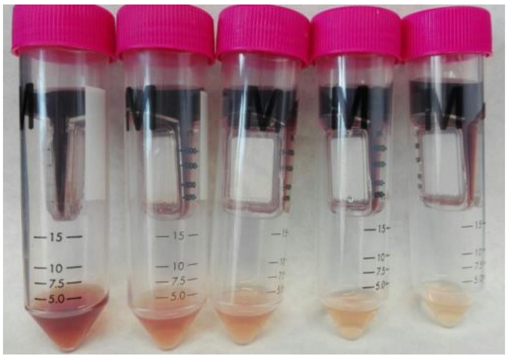

Fig. 2: Concentrate (dark) and permeate fractions of OMW samples conducted to the MF-UF screening formerly described (MWCO ranging from 100 down to 3 kDa).

In Fig. 3, the rejection of the total phenolic compounds as a function of the membrane MWCO (ranging from 100 down to 3 kDa) is shown. As it can be seen, the rejection performance of the tested membranes 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 58.8% for a membrane with a MWCO of 3 kDa (Fig. 3).

On another hand, the quantity of the permeate stream was found to be increased from 5 to approximately 9 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 Fig. 4.

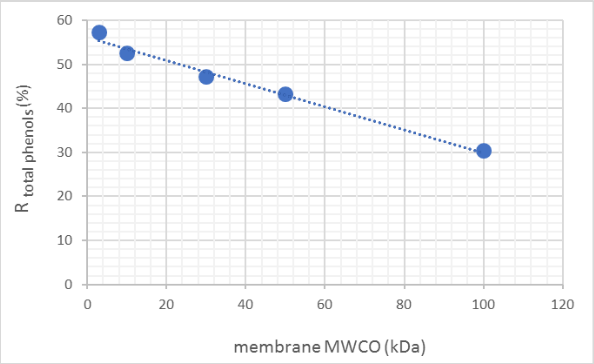

Fig. 3: Rejection of total phenolic compounds as a function of the membrane MWCO (ranging from 100 down to 3 kDa).

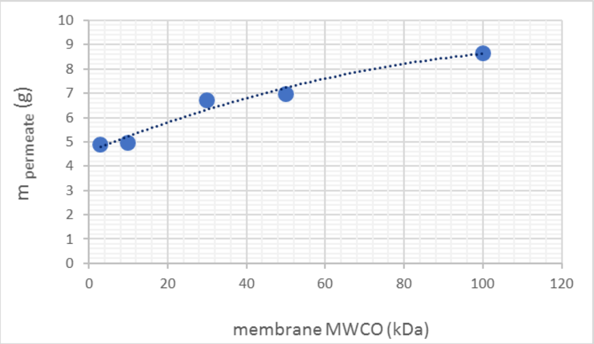

Fig. 4: Permeate quantity (grames) recovered as a function of the membrane MWCO (ranging from 100 down to 3 kDa).

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 polyphenolic fraction present in olive mill wastewater (OMW) was achieved.

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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