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Ultrafiltration of residual fermentation brines from the production of table olives at different operating conditions

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Abstract

The membrane process of ultrafiltration (UF) has been investigated as a pretreatment previous to the further recovery and concentration of phenolic compounds from residual table olives fermentation brines. Two UF membranes were tested: a permanently hydrophilic polyethersulfone (PES) membrane with a molecular weight cut-off (MWCO) of 30 kDa and a PES membrane with a MWCO of 5 kDa. Transmembrane pressure and

crossflow velocity were varied from 1 to 3 bar and from 2.2 to 3.7 $m \cdot s^{-1}$, respectively. The best membrane in terms of permeate flux and selectivity was that with MWCO of 5 kDa and the best operating conditions were transmembrane pressure of 3 bar and crossflow velocity of 2.2 $m \cdot s^{-1}$. In these conditions permeate flux was 21.6 $L \cdot h^{-1} \cdot m^{-2}$, while the rejection of COD and phenolic compounds were 50.0% and 21.9%, respectively and the removal of color and turbidity was almost complete. In addition, an alkaline cleaning protocol was proposed, which was effective to restore the initial permeability of the selected membrane.

Keywords: Ultrafiltration; polyethersulfone membranes; table olive fermentation brine wastewater; phenolic compounds.

1. Introduction

In the last years, there has been a growing interest in obtaining high added value compounds from renewable raw materials and wastes. Some of these compounds have a potential use in food, cosmetic and pharmaceutical industries. Among these compounds, those with antioxidant properties have generated great interest. These compounds, which are abundant in the Mediterranean diet in the form of vitamins C and E, carotenoids and phenolic compounds, have beneficial effects on human health (Sánchez-Moreno et al., 2006) (Zulueta et al., 2007) (Guedes et al., 2011).

Phenolic compounds are present especially in fruits and vegetables. Olive fruit, which is one of the bases of the Mediterranean diet, contains a great quantity of these compounds. The production of olive fruits amounted to 5,700 tonnes in the 2014/2015

crop season (International Olive Council, 2015). Olive fruits can be processed to obtain olive oil or treated to be consumed directly as table olives. The number of olive fruits dedicated to the production of olive oil has always been higher than those used to prepare table olives. However, in recent years, such numbers are tending to equalize. The total world production of table olives in 2014 was close to 2,600 tonnes. Approximately, 85% of the production takes place in the Mediterranean area, being Spain in 2014 the major producer (around 22.1% of the world production), followed by Turkey and Egypt (around 16.6% and 15.4% of the world production, respectively) (International Olive Council, 2015). According to the Spanish Ministry of Environment, it is estimated that 1.5 kilograms of wastewater are generated per each kilogram of table olives produced in Spain.

To be consumed as table olives, the olive fruits must be processed to reduce their bitterness. Three types of wastewater streams are mainly generated from this process, which consists of three steps: lye treatment with NaOH, lye washing and olive fermentation in brine (Sánchez Gómez et al., 2006). Each of these three steps approximately generates the same volume of wastewater. According to the Spanish Ministry of Environment, in Spain, per each kilogram of table olive produced, 0.5 kg of fermentation brine wastewater is obtained. This is the wastewater that has been considered to carry out this work. During the fermentation in brine, the lactic fermentation of the olives occurs, thus reducing the basic pH of the solution to a pH of about 4. The fermentation of sugars is almost complete. In this process, part of the phenolic compounds from the olive fruits (mainly oleuropein) solubilises into the acid solution (Soler-Rivas et al., 2000). In this solution, most of the phenolic compounds disappeared, while the concentration of hydroxytyrosol and tyrosol increased (Brenes et

al., 1995). This is due to the hydrolysis of the phenolic compounds like oleuropein, as an example, that hydrolyzed into hydroxytyrosol (Brenes et al., 1995).

Apart from the acid pH, the fermentation brine wastewater is also characterized by a high salt concentration (conductivity from 80 to 95 $mS \cdot cm^{-1}$) and high soluble chemical oxygen demand (COD), of 15000 to 30000 $mgO_2 \cdot L^{-1}$. Part of this organic matter corresponds to the phenolic compounds (these concentration varying from 1000 to 2000 mg of tyrosol equivalents$\cdot L^{-1}$) (García-García et al., 2011) (Ferrer-Polonio et al., 2014). The main phenolic compounds present in olive brine are hydroxytyrosol (HTY) and tyrosol (TY) and they show an outstanding antioxidant activity (Brenes et al., 1995) (Fendri et al., 2013). Nevertheless, the presence of these compounds in the wastewater represents one of the major problems for its treatment, primarily because they are hardly biodegradable and secondly because of their significant antimicrobial activity, which reduces the efficiency of the biological processes in wastewater treatment plants (WWTP) (Parinos et al., 2007). Besides, the high salt concentration can also have a negatively impact on the WWTP process as it causes activated sludge deflocculation (Woolard and Irvine, 1994) (Kargì and Dinçer, 1999) (Reid et al., 2006) (Lefebvre and Moletta, 2006). On the other hand, if the organic matter and phenolic compounds are removed, the brine can be reused in the table olive fermentation process. In this perspective, the recovered phenolic compounds, due to their potential antioxidant properties, are an attractive ingredient for the food, cosmetic and pharmaceutical industries (Tripoli et al., 2005).

It is therefore of a great interest the recovery of these valuable compounds from the waste streams from fruits and vegetables processing. Historically, the treatment of the olive brine waste water has been based on the reduction or elimination of the organic

matter with the aim of its reuse in later stages of the processing, as in the packaging stage. To this end, the treatments that have been considered were ultrafiltration (UF) (Brenes et al., 1990), UF and active carbon (Garrido et al., 1992), biological treatment (Brenes et al., 2000) (Ferrer-Polonio et al., 2015), advanced oxidation (Rivas et al., 2003) and electro-coagulation (García-García et al., 2011).

Nevertheless, in the literature, there are some works dealing with the recovery of phenolic compounds from olive mill wastewater (OMW), generated during olive oil production. In some of these studies, membrane process have been proposed by several authors (Garcia-Castello et al., 2010) (Cassano et al., 2013) (Zirehpour et al., 2015). These works have shown that the combined utilization of ultrafiltration and nanofiltration (NF) processes for treating OMW is more effective than performing the separation in one single step (Paraskeva et al., 2007) (Garcia-Castello et al., 2010) (Cassano et al., 2013). In these combined processes, UF was applied as pretreatment for COD removal, as this membrane process is not able to separate low-molecular-weight compounds. Then, the UF permeate was treated by NF in order to obtain a permeate rich in phenolic compounds (Cassano et al., 2013). Also, reverse osmosis, osmotic distillation and vacuum membrane distillation were used to concentrate the phenolic compounds from the NF permeate (Paraskeva et al., 2007) (Coskun et al., 2010) (Zagklis et al., 2015) (Garcia-Castello et al., 2010). In these works, it was observed that the ultrafiltration membranes suffered severe fouling, whereas the fouling of the NF membranes was largely reduced when UF was used as pretreatment.

In spite of the number of works aimed to the recovery of the phenolic compounds from OMW, up to now there are very few studies in the literature where the phenolic

compounds are recovered from wastewaters resulting from table olive production. El-Abbassi et al., 2014, used UF as a pretreatment for a subsequent extraction process of phenolic compounds from table olive production wastewaters (El-Abbassi et al., 2014). They used a magnetically stirred unit and compared the results obtained at different pH values. The best results in terms of decolorization and COD removal were obtained at acidic pH values. Kiai et al., 2014, considered membrane distillation technology in the treatment of table olive wastewaters for the concentration of phenolic compounds and to obtain high quality water (Kiai et al., 2014).

In this work, membrane processes were used to recover phenolic compounds from the fermentation brine wastewater generated during Spanish-style green table olive processing. For this purpose, an integrated process that combines UF and NF was proposed. This work investigates the UF step as a pretreatment prior to the NF step. Two flat sheet UF membranes and different operating conditions were compared with the objective of reducing the presence of a great amount of total suspended solids (TSS) and soluble COD. Then, the UF permeate would be processed by NF in order to obtain a permeate stream enriched in phenolic compounds, with a low content of soluble COD. Therefore, the UF membrane should show a low rejection of phenolic compounds. In this work, the capability of the UF process to remove TSS and soluble COD with less phenolic compounds rejection from table olive wastewaters has been investigated in order to improve the performance of the subsequent NF process. Therefore, according to this objective, the operating conditions that maximize the phenolic compounds/COD ratio have been sought.

2. Material and methods

151

152 *2.1. Feed samples*

153

154 In the present work, different real samples of residual table olive fermentation brine
155 were supplied by a table olive packing plant in Valencia region (Spain). Due to the high
156 content of suspended solids observed in the residual wastewater, a previous filtration
157 step with a polyester cartridge filter of 60 μm pore size (CA-0202-00, model GT,
158 HydroWater, Spain) was performed. The samples were stored at 5 °C.

159

160 *2.2. Analytical methods*

161

162 Regarding the analytical methods considered, each parameter was measured in triplicate
163 and the average value was calculated.

164

165 The conductivity and the pH were measured with an EC-Meter GLP 31+ conductimeter
166 and a GLP 21+ pH-meter (Crison, Spain), respectively, at room temperature (25 ºC).
167 Turbidity was measured with a turbidimeter (D-112, DINKO, Spain) following the
168 UNE-EN ISO 7027 standard method. The color of the samples was determined from
169 absorbance readings at 440 and 700 nm using a DR600 spectrophotometer (Hach
170 Lange, Germany). The color value was calculated as the difference between the two
171 absorbance readings in 1 cm pathlength cells as described by (De Castro and Brenes,
172 2001).

173

174 The amount of TSS was determined from 25 mL samples by means of glass microfiber
175 filters (1.2 μm pore size), according to UNE 77034 standard method. After the filtration

of the samples, the microfiber filters were dried at 105 ºC for 2 h. The amount of TSS corresponded to the difference between the initial weight of the filter and its weight after being dried.

The concentration of chloride ions was determined with LCK311 kits, (Hach Lange, Germany) and soluble COD with LCK014, LCK114 and LCK614 kits (Hach Lange, Germany). The DR600 spectrophotometer (Hach Lange) was used. In order to determine the COD, the samples were diluted to avoid the interferences caused by the high chloride concentration. The concentration of sodium ions was determined with Sodium Cell Test in nutrient solutions for fertilization photometric method (Merck Millipore, Germany). A NOVA 30 Spectroquant photometer (Merck Millipore, Germany) was used for the measurements.

In order to determine total concentration of phenolic compounds, the samples were previously acidified to pH 2 with HCl, washed with hexane and submitted to a liquid–liquid extraction with ethyl acetate (El-Abbassi et al., 2011). The ethyl acetate extract was evaporated to dryness using an R-114 Rotavapor (BüchiLabortechnik AG, Switzerland) at 40 ºC. Then, the residue was dissolved in methanol. Total phenolic compounds concentration was determined by means of the Folin-Ciocalteu method following the procedure described by (Singleton et al., 1999). A solution of sodium carbonate (Panreac, Spain) in water (20% w/v) and the Folin and Ciocalteu's reagent (Sigma Aldrich, USA) were used. At the end of the procedure, the absorbance at 765 nm (Abs_{765}) was measured with the DR600 spectrophotometer. The results were expressed as milligrams of tyrosol equivalents per liter (mg tyrosol eq·L^{-1}). The relation obtained was mg tyrosol eq·L^{-1} = 558.96 · Abs_{765}, with R^2 = 0.996.

High performance liquid chromatography (HPLC) was used to determine the phenolic profile, and the concentration of tyrosol and hydroxytyrosol. The device was equipped with a PU-2089 Plus quaternary gradient pump (Jasco, Japan) and a MD2018 Plus Photodiode Array detector (Jasco, Japan). A Kinetex 5u C18 100A column (4.6×250mm, 5μm) (Phenomenex, USA) was used for the separation of the compounds. The operating conditions were the following: flow rate 1.5 $mL \cdot min^{-1}$, injected volume 10.0 μL and wavelength UV detection 275 nm. The mobile phase was water/methanol (HPLC grade, VWR Chemicals, USA) with 1% v/v of glacial acetic acid (HPLC grade, Fisher Chemical, USA) in 30 min gradient. The gradient curve was 5% v/v of methanol for 1 minute, followed by a linear increase to 80% v/v over 25 min and return to 5% v/v of methanol over 2 min. An isocratic mobile phase of 5% v/v of methanol was passed through the column for 10 min before the next sample injection. The samples injected were prepared by the method developed by El-Abbassi et al. 2011. These samples were prepared so that they have a final concentration of 7 $mg \cdot mL^{-1}$ in methanol. Calibration curves of TY (Sigma Aldrich, USA) and HTY (Sigma Aldrich, USA) were prepared at different concentrations (C_{TY} and C_{HTY}, respectively). Hydroquinone (Sigma Aldrich, USA) at 0.5 $mg \cdot mL^{-1}$ concentration (C_{HQ}) was used as internal standard. The calibration curves obtained were the following: $A_{TY}/A_{HQ} = 1.0117 \cdot C_{TY}/C_{HQ}$ ($R^2 = 0.9999$) and $A_{HTY}/A_{HQ} = 1.0117 \cdot C_{HTY}/C_{HQ}$ ($R^2 = 0.9967$). Where A_{TY} is de peak area corresponding to tyrosol, A_{HTY} is de peak area corresponding to hydroxytyrosol and A_{HQ} is de peak area for hydroquinone.

2.3. Ultrafiltration

Fig. 1 shows the diagram of the ultrafiltration plant. This plant was automated, being the cross flow velocity (CFV), the transmembrane pressure (TMP) and the temperature automatically regulated. The plant was equipped with an UF module for a single flat sheet membrane (Rayflow, Orelis, France) with a total active surface of 0.0125 m^2. Two ultrafiltration polyethersulfone membranes from Microdyn Nadir (Germany) were tested: the permanently hydrophilic UH030 membrane and the UP005 membrane, with a molecular weight cut-off (MWCO) of 30 and 5 kDa, respectively.

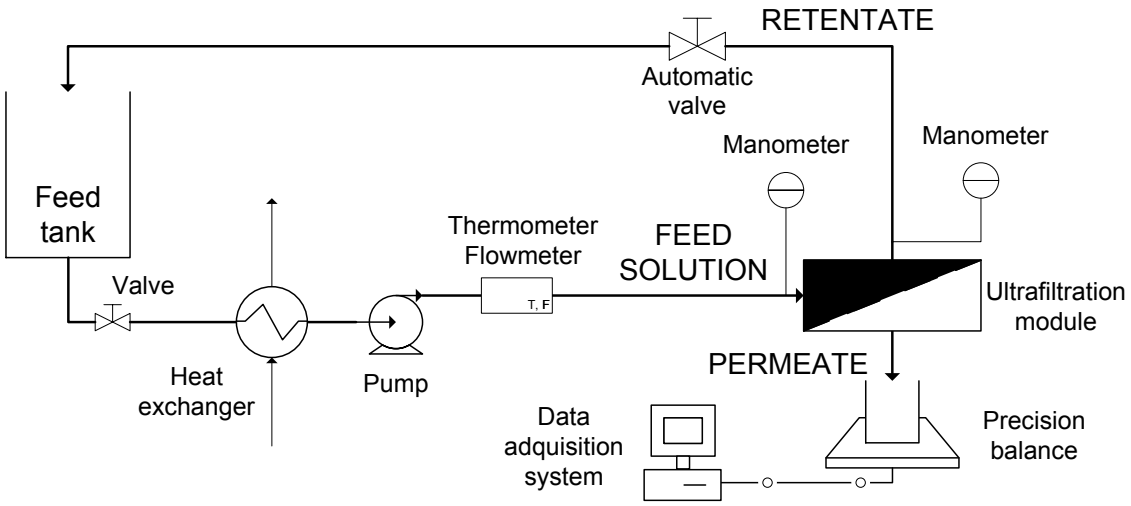


Fig. 1. Schematic diagram of the ultrafiltration plant.

The CFV was varied from 2.2 to 3.7 $m \cdot s^{-1}$ and the TMP from 1 to 3 bar. The ultrafiltration tests lasted 2.5 h, time enough to reach steady state permeate flux. Temperature was kept constant at 25 ºC by a heat exchanger connected to tap water. The runs were performed according to a design of experiments with two factors (CFV and TMP) for each membrane. The objective of these tests was to study the evolution of the permeate flux with time, the stationary permeate fluxes achieved and the rejection of COD and phenolic compounds by the membranes. Permeate flux was gravimetrically measured with a Kern PKP precision balance (Kern, Germany) and the collected data

were recorded with a data acquisition system. During each test, retentate and permeate were recycled back to the feed tank in order to keep constant feed concentration.

The membranes separation efficiency was evaluated by calculating the removal of color, turbidity and conductivity by means of equation (Eq. 1) and the rejection of COD and phenolic compounds according to equation (Eq. 2).

$$E_i(\%) = \left(1 - \frac{V_{Pi}}{V_{Fi}}\right) \cdot 100 \qquad \text{(Eq. 1)}$$

$$R_j(\%) = \left(1 - \frac{C_{Pj}}{C_{Fj}}\right) \cdot 100 \qquad \text{(Eq. 2)}$$

where E_i is the elimination efficiency of parameter i (color, turbidity or conductivity), V_{Pi} is the value of parameter i in the permeate, V_{Fi} is the value of parameter i in the feed solution, R_j is the rejection of parameter j (COD or phenolic compounds), C_{Pj} is the concentration of parameter j in the permeate and C_{Fj} is the concentration of parameter j in the feed solution.

At the end of each ultrafiltration run, the membranes were cleaned. The cleaning protocol proposed was the following (C1): rinsing the membranes with osmotic water for 9 min, chemical cleaning with a concentrated basic solution of NaOH (pH 11) (Panreac, Spain) for 5 min with recirculation of the solution, rinsing with osmotic water for 9 min, chemical cleaning with a solution of citric acid (1% w/v) (Panreac, Spain) for 5 min with recirculation of the solution and a final rinsing with osmotic water for 9 min. All of the cleaning steps were carried at a CFV of 2.2 $m \cdot s^{-1}$ and room temperature. In

these conditions TMP was set to 0.6 bar. The membrane was considered to be cleaned if the hydraulic permeability after the cleaning step reached more than 95% of the initial one. If membrane hydraulic permeability was not recovered with this cleaning method, the temperature of chemical solutions and cleaning times were increased as follows: i) cleaning temperature was set at 35 ºC for 15 min (C2), and ii) if membrane permeability remained unrecovered, temperature was set at 40 ºC for 30 min (C3). The efficiency of the cleaning protocols was determined by comparing the hydraulic permeability of the new membrane with that of the cleaned membrane. After being cleaned, the membrane module was filled with osmotic water. The hydraulic permeability of the membrane was checked again before starting a new run.

3. Results

3.1. Characterization of the feed samples

The main physicochemical characteristics of the residual olive fermentation brine wastewater are shown in Table 1. This wastewater is characterized by an acid pH (4.3), a high salt concentration and a high concentration of phenolic compounds (~ 1 g Tyrosol eq·L^{-1}). This wastewater showed a high conductivity due to the presence of NaCl added in the fermentation step (73.8 ± 13.1 mS·cm^{-1}). The residual water was yellow coloured due to the natural pigments contained in the olives. As it was explained, during lactic fermentation, the brine was enriched in phenolic compounds. As shown in Table 1, about half of the concentration of phenolic compounds corresponded to HYT and TY. The samples also showed a high concentration of TSS (759.7 ± 642.5 mg·L^{-1}) and a high value of soluble COD (13.3 ± 4.6 g·L^{-1}) and turbidity

(378.5 ± 136.0 NTU). Such data exhibited quite a large standard deviation (SD) (see Table 1) owing to several factors, such as the different variety of olive fruits processed, harvest-time and fermentation time (Pereira et al., 2006).

Table 1.
The main physicochemical characteristics of real samples from residual olive fermentation brine, supplied by a table olive packing plant in Valencia region.

Parameter	Mean value	SD[a]
pH	4.3	± 0.3
Conductivity ($mS \cdot cm^{-1}$)	73.8	± 13.1
Color	0.564	± 0.111
Turbidity (NTU)	378.5	± 136.0
TSS[b] ($mg \cdot L^{-1}$)	759.7	± 642.5
Soluble COD[c] ($mgO_2 \cdot L^{-1}$)	13295	± 4616
Cl^- ($mg \cdot L^{-1}$)	39302	± 6689
Na^+ ($mg \cdot L^{-1}$)	55667	± 22485
Total phenolic compounds (mg Tyrosol $eq \cdot L^{-1}$)	998.8	± 474.7
Hydroxytyrosol ($mg \cdot L^{-1}$)	473.4	± 306.6
Tyrosol ($mg \cdot L^{-1}$)	71.7	± 41.1

[a]SD: Standard deviation; [b]TSS: Total suspended solids; [c]COD: chemical oxygen demand

The preliminary filtration by means of the polyester cartridge filter reduced the amount of organic matter and the turbidity without modifying the concentration of salts, phenolic compounds and soluble COD. Due to the great variability in the content of TSS (759.7 ± 642.5 $mg \cdot L^{-1}$), the samples that had the largest concentration of TSS showed a greater percentage of elimination. Those samples with TSS greater than 1500 $mg \cdot L^{-1}$ exhibited a reduction around 70 to 74%, while those with lowest TSS (between 550 and 350 $mg \cdot L^{-1}$) exhibited a reduction between 14 and 21%. Also, the reduction in turbidity ranged between 8 and 39% depending on its initial value. The values of TSS and turbidity in filtered samples were 530.1 ± 267.7 $mg \cdot L^{-1}$ and 231.1 ± 61.5 NTU, respectively. This preliminary filtration conducted to more homogeneous samples with less SD.

Fig. 2 shows the phenolic compounds profile of one of the samples of the residual olive fermentation brine after being filtered. It can be observed that HTY and TY were the main phenolic compounds. They were present in all the analysed samples, while other phenolic compounds were not present in all of them. The results were similar to those obtained by other authors (Brenes et al., 1995) (Fendri et al., 2013) (Ferrer-Polonio et al., 2015), who reported that, for Spanish-style green olives, these compounds are those mainly present in residual wastewaters. However, other phenolic compounds showed lower concentrations as they gradually disappear during the fermentation stage. The concentrations of HTY and TY obtained by HPLC at the above described conditions were 473.36 ± 306.61 $mg \cdot L^{-1}$ and 71.70 ± 41.14 $mg \cdot L^{-1}$, respectively, reported in Table 1. The concentration of these compounds in the different samples was quite variable, depending on the olive fruit variety (Kiai and Hafidi, 2014) and the duration of the fermentation process (Ryan et al., 1999).

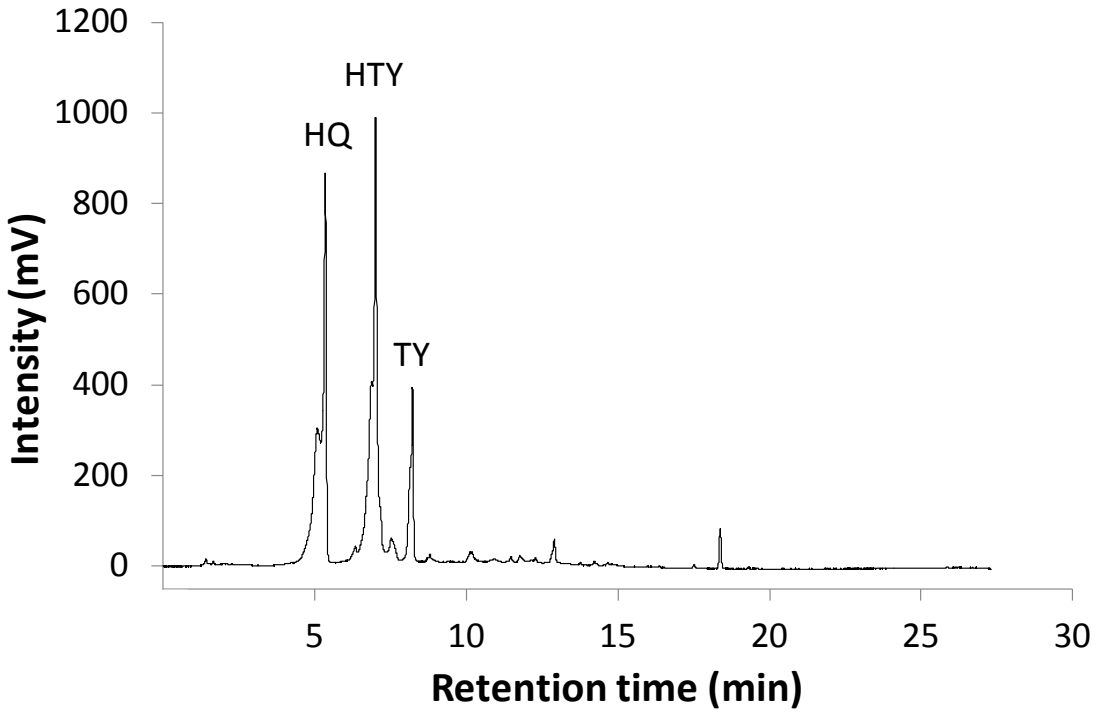


Fig. 2. HPLC phenolic compounds profile for a sample of the residual olive fermentation brine after being filtered.

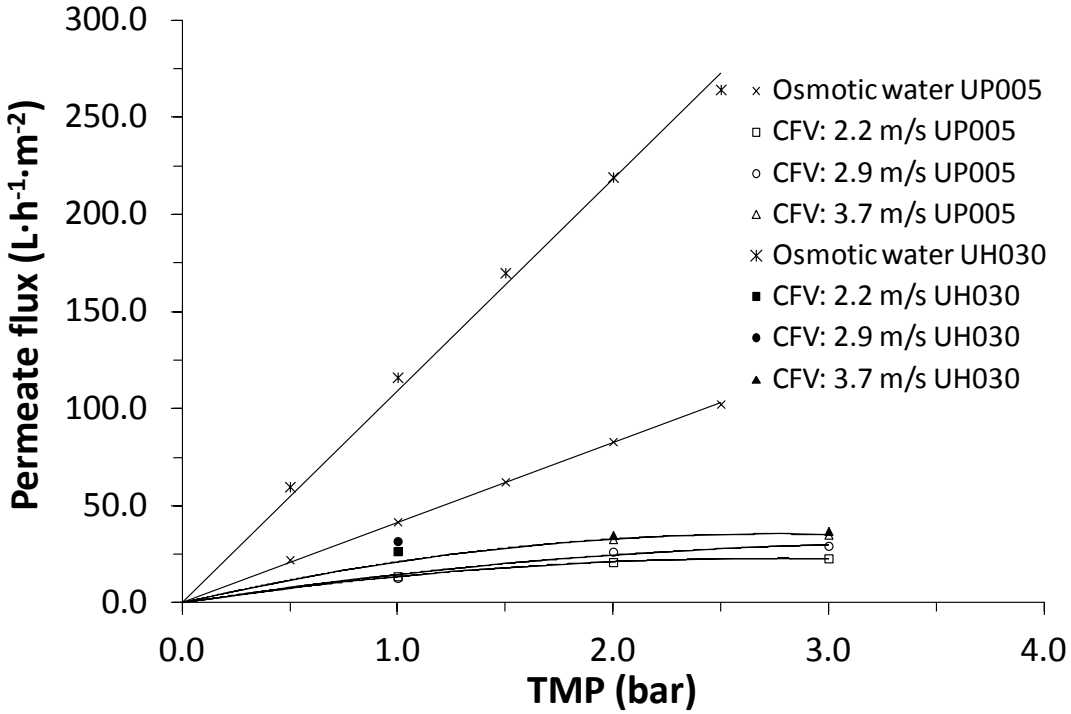
3.2. Ultrafiltration step

Fig. 3 shows the values of permeate flux obtained when osmotic water was ultrafiltered with both membranes, respectively, at different TMPs. From the observed linear relationship between osmotic water permeate flux (J) and TMP (ΔP), the hydraulic permeability (K) of both membranes can be calculated by means of the Darcy's equation (Eq. 3):

$$J = K \cdot \Delta P = \frac{\Delta P}{\mu \cdot R_m} \qquad \text{(Eq. 3)}$$

In this equation μ and R_m, respectively, represent the viscosity of the permeate and the intrinsic membrane resistance. By fitting osmotic water permeate flux at 25 ºC against

344 the TMP, it was possible to estimate the following hydraulic permeability for the UP005
345 and UH030 membranes tested: 45.48 ± 4.01 and 95.84 ± 10.87 $L \cdot h^{-1} \cdot m^{-2} \cdot bar^{-1}$,
346 respectively (R^2 higher than 0.999 for the UP005 membrane and higher than 0.993 for
347 the UH030 membrane).
348



349
350 **Fig. 3.** Permeate flux in the ultrafiltration of osmotic water and residual brine at
351 different operating conditions for both UP005 and UH030 membranes.
352

353 Fig. 3 also shows the steady state permeate flux when the residual brine was
354 ultrafiltered with both membranes. Permeate flux was found to tend to an asymptotic
355 value, quite lower than the osmotic water permeate flux whatever the operating
356 conditions tested and for the both membranes used. This trend is indicative of severe
357 membrane fouling (Field and Pearce, 2011). Also, indicates that all the operating
358 conditions considered in this study were in the critical flux area (Bacchin et al., 2006).
359

When the steady state permeate flux for both membranes is compared, it can be observed that at 1 bar the value reached was higher for the UH030 membrane (26.6 $L \cdot h^{-1} \cdot m^{-2}$ versus 13.7 $L \cdot h^{-1} \cdot m^{-2}$ at 2.2 $m \cdot s^{-1}$). At low pressure, the convective transport of solute molecules towards the membrane surface is less intense. Thus, concentration polarization and fouling are lower and the highest permeate flux is obtained with the membrane with higher MWCO. However, by increasing TMP to 2 and 3 bars the steady state permeate flux was similar for both membranes. This indicates that, at those TMPs, the fouling was greater for the UH030 membrane. Also, it can be observed that for the UP005 membrane the steady state permeate flux achieved at 1 bar was lower than the ones obtained at 2 and 3 bars, as it was expected. However, the differences between the permeate fluxes obtained at 2 and 3 bar for the same CFVs were lower. This fact indicates that these operating conditions are close to the limiting flux area (Bacchin et al., 2006) (Field and Pearce, 2011). On the other hand, for the UH030 membrane, it can be appreciated that the stationary permeate flux was similar for the three TMPs tested, clear indication that these operating conditions are in limiting flux area. In addition it was observed that, at the TMPs considered in this work, the CFV had a more significant influence on the stationary permeate flux than the TMP. The Reynolds numbers (*Re*) for the CFVs considered, 2.2, 2.9 and 3.7 $m \cdot s^{-1}$, are 4990, 6578 and 8392, respectively, which correspond to turbulent flow regime ($Re \geq 4000$) (Cheryan, 1998). The highest steady state permeate fluxes reached were 37.1 ± 0.2 $L \cdot h^{-1} \cdot m^{-2}$ for the UH030 membrane at 3 bar and 3.7 $m \cdot s^{-1}$ and 35.2 ± 0.1 $L \cdot h^{-1} \cdot m^{-2}$ for the UP005 membrane at the same conditions.

Fig. 4 displays the time course of permeate flux for both membranes under the operating conditions tested. In all the cases the evolution of permeate flux was similar, with a

385 severe decrease in the first minutes followed by a smooth gradual decline until a quasi-
386 steady state permeate flux was reached (permeate flux decline was higher than 65% for
387 both membranes). This evolution of permeate flux is typical in UF processes. According
388 to several authors (Field et al., 1995) (Ho and Zydney, 2000), the great flux decline
389 during the first minutes is due to a pore blocking phenomenon and the subsequent
390 gradual slow flux decline is caused by the accumulation of foulant molecules on the
391 membrane surface, forming a cake layer or a gel layer on it. Obviously, the initial
392 permeate flux for the UH030 membrane was higher than that for the UP005 membrane
393 at all the operating conditions tested. The greatest flux decrease for both membranes
394 was observed at 3 bar, especially for the UH030 membrane (permeate flux decline close
395 to 89%). At TMP equal to 2 and 3 bar, the permeate flux was similar for both
396 membranes after an ultrafiltration time of 40 min. At TMP equal to 1 bar the permeate
397 flux decreased rapidly too, but at that TMP the permeate flux was higher for the UH030
398 membrane, as already noted in Fig. 3. The fast decline in the permeate flux in the first
399 ultrafiltration times may be attributed to severe fouling caused by pore blocking
400 (Carbonell-Alcaina et al., 2016). Also, the UH030 membrane suffered more severe
401 fouling caused by pore blocking than the UP005 membrane during the first minutes of
402 operation. The greatest fouling observed in the UH030 membrane may be due to the
403 larger pore size. Also, Cassano et al. 2011, observed a strong adsorption of polyphenols
404 on permanently hydrophilic PES membranes during the UF of OMW, that was probably
405 due to polar interactions (electron donor-acceptor interactions, hydrogen bonds)
406 between polyphenols and the membrane (Cassano et al., 2011). This degree of affinity
407 between the phenolic compounds and PES membranes is enhanced the more
408 hydrophilic the membrane is (Ulbricht et al., 2009).
409

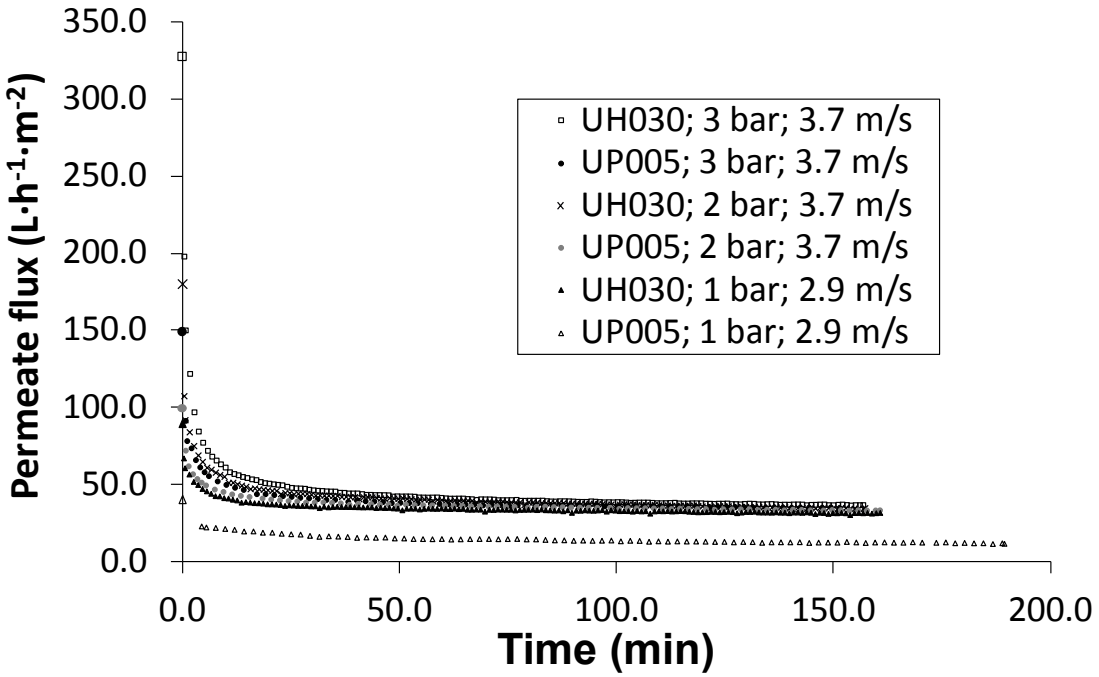


Fig. 4. Evolution of permeate flux with time for UP005 and UH030 membranes at 25ºC and for certain transmembrane pressures and cross flow velocities.

In a previous work (Carbonell-Alcaina et al., 2016), it was demonstrated that, when residual brines from table olive packing plants were ultrafiltered, at the beginning of the run the adsorption and concentration polarization resistance dominated, while at the steady state the cake layer resistance was greater. Also, a rapid increase of the adsorption and concentration polarization resistance (R_a) was observed at the beginning of the test. However, the increase of the cake layer resistance (R_{cf}) with time was more gradual, but it overcame the value of R_a before the steady state permeate flux was reached.

Fig. 5a and 5b show the evolution of permeate flux with time under constant TMP (3 bar) at different CFVs and under constant CFV (2.9 $m \cdot s^{-1}$) at different TMPs, respectively, for the UP005 membrane. The evolution of permeate flux was similar for all the operating conditions, as it was previously commented. From Fig. 5a, at TMP equal to 3 bar, by increasing CFV it was possible to increase the permeate flux. This

trend was also observed at TMP equal to 2 bar. However, at TMP equal to 1 bar the effect of CFV on flux was lower, probably due to the lower concentration polarization at that TMP. At a fixed CFV of 2.9 $m \cdot s^{-1}$ (Fig. 5b), it can be appreciated that an increase in the TMP from 1 to 2 bar caused an increment in the permeate flux. However, the permeate flux was practically the same at 2 and 3 bar. At the highest TMP values tested (2 and 3 bars), the limiting flux was reached (Fig. 3). Therefore, at those pressures, it was not observed a significant dependence of permeate flux on TMP. This trend was also noticed for the rest of the CFVs tested and for the UH030 membrane.

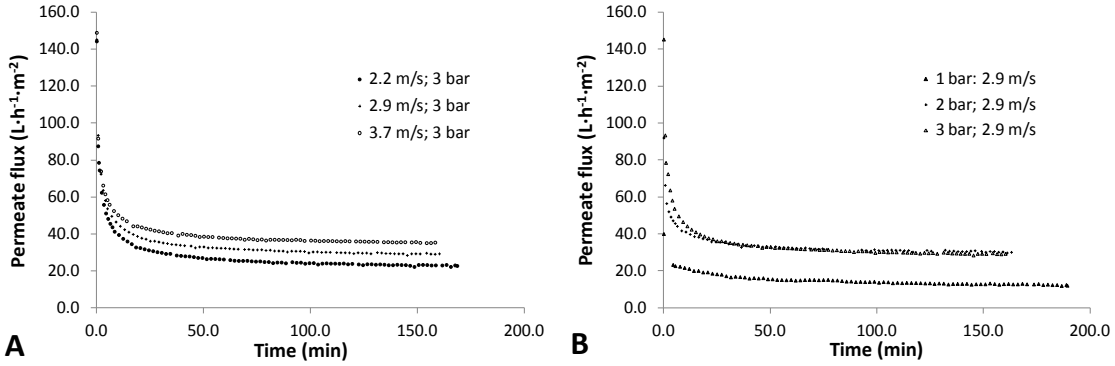


Fig. 5. Comparison of permeate flux evolution with time at 25ºC for the UP005 membrane at a fixed TMP and different CFVs (A) and at a fixed CFV and different TMPs (B).

The residual fermentation brines from the production of table olives are complex mixtures of various solutes, apart from tyrosol and hydroxytyrosol, with unknown transport properties such as diffusivity. Among the solutes, polysaccharides and pectin can be found, which are usually related to the formation of a gel layer on the membrane surface (Mondal et al., 2012). This mixture of compounds also contains a high amount of total suspended solids. Mondal et al., 2012 proposed, for complex mixtures, a method to determine the mass transfer coefficient (k) and quantify the concentration polarization factor (CP). In this work the film theory and a correlation of the type $Sh=Sh(Re,Sc)$ are

used to determine the effective diffusivity (D) and the gel layer concentration (C_g) of a mixture of various solutes from previously centrifuged Stevia plant extracts.

In the present work, in the area where the permeate fluxes have reached the limiting flux it has been considered that the gel layer was developed. If it is considered that solutes form a gel layer on the membrane surface and the permeate concentration is low, the classical film theory can be expressed as the following equation, where C_b is the bulk concentration:

$$J = k \cdot ln\left(\frac{C_g}{C_b}\right) \qquad (Eq.4)$$

According to Cheryan, 1998, for flat ultrafiltration membranes and turbulent flow (Re ≥ 4000), the Sherwood number can be calculated by the following correlation:

$$Sh = \frac{k \cdot r}{D} = 0.023 \cdot Re^{0.8} \cdot Sc^{0.33} \qquad (Eq.5)$$

Combining equations (Eq. 4) and (Eq. 5) the following expression is obtained:

$$J = \frac{D}{r} \cdot 0.023 \cdot Re^{0.8} \cdot Sc^{0.33} \cdot ln\left(\frac{C_g}{C_b}\right) \qquad (Eq.6)$$

Where the ratio C_g/C_b, is equivalent to a concentration polarization factor (CP). In this expression the diffusivity and C_g have been considered to be constant and independent on the operating conditions (i.e. transmembrane pressure, crossflow velocity and feed concentration), while the mass transfer coefficient depends on the Re number. In order

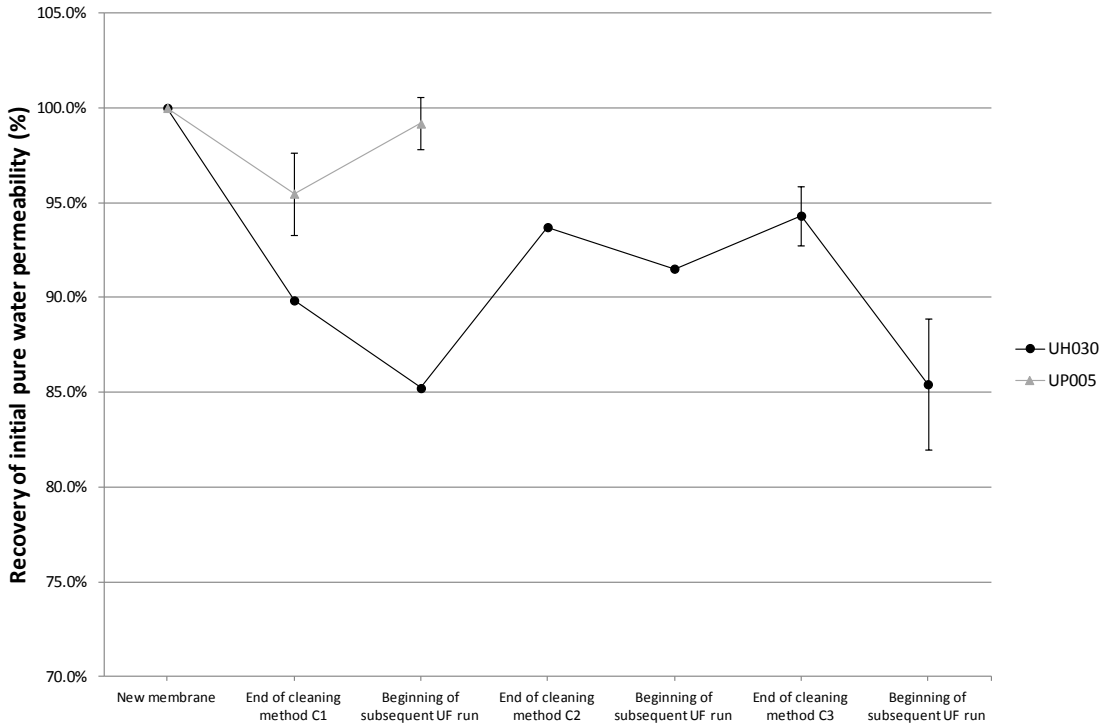
to determine *D* and *CP*, an optimization method was employed. The method consisted in an initial guess for the values of these parameters in order to minimise the error between the experimental permeate flux and the theoretical permeate flux:

$$S = \frac{\sum_{i=1}^{N_{exp}} \left(\left[\frac{J_{i,theorical} - J_{i,exp}}{J_{i,exp}} \right]^2 \right)^{0.5}}{N_{exp}} \qquad (Eq. 7)$$

The mass transfer coefficients estimated were (1.99 ± 0.02) $\cdot 10^{-6}$ m$\cdot$s^{-1}, (2.40 ± 0.13) $\cdot 10^{-6}$ m$\cdot$s^{-1} and (2.82 ± 0.16) $\cdot 10^{-6}$ m$\cdot$s^{-1} for 2.2, 2.9 and 3.7 m$\cdot$s^{-1}, respectively. The effective diffusivity estimated was $9 \cdot 10^{-13}$ m$^2\cdot$s^{-1}, and *CP* varied from 19.0 to 40.0 depending on feed concentration ($S < 0.046$).

After each run, the membranes were cleaned following the procedures previously described. Fig. 6 displays the average recovery of pure water permeability for the two membranes tested after the cleaning process. As regarding the UP005 membrane, the cleaning method C1 resulted to be sufficient to achieve a permeability recovery greater than 95% for all the ultrafiltration tests performed at the different operating conditions tested. The hydraulic permeability of the UP005 membrane was newly checked before to start a new run. After a certain time period membrane submersion in osmotic water the hydraulic permeability increased, this resulting in an average permeability recovery greater than 99% for all the runs. However, the cleaning method C1 was not so efficient to recover the initial hydraulic permeability of the UH030 membrane. Thus, methods C2 and C3 were in sequence applied. As it is shown in Fig. 6, even after applying the C3 cleaning procedure, the initial hydraulic permeability of the UH030 membrane was not recovered. As it already noted, the fouling of this membrane was quite severe and its

494 fouling layer appeared to be more difficult to remove. Probably this membrane suffered
495 a greater irreversible fouling (Field and Pearce, 2011). Also, the roughness of such
496 membrane was greater than that of the UP005 membrane (Luján-Facundo et al., 2015).
497 The greater the membrane roughness the more severe fouling is and the fouling layer
498 can be more difficultly removed from the membrane surface (Vatanpour et al., 2014).
499 Despite the fact that the UH030 membrane is more hydrophilic than the UP005 one, its
500 fouling resulted to be more severe and the cleaning protocol used less effective. The
501 greater pore size of this membrane should have favoured fouling due to internal pore
502 blocking. This type of fouling was not only difficultly removed by means of the
503 cleaning protocols used, but also the membrane hydraulic permeability tending to
504 decrease became more persistent after membrane submersion in osmotic water. As it
505 can be observed in Fig. 6, for the UH030 membrane, the hydraulic permeability
506 recovery decreased after a certain time period submerged in osmotic water.
507



508
509 **Fig. 6.** Average recovery of initial pure water permeability for both membranes after the
510 different cleaning processes. The average permeability recovery shown was calculated

as the mean of recovery for all the runs performed at different operating conditions with each membrane, respectively.

Table 2 shows the removal of salts, turbidity and colour, and the rejection of soluble COD and phenolic compounds, by both membranes, as estimated by equations 1 and 2. As it can be observed, the elimination of turbidity was greater than 99% for all the operating conditions tested and both membranes. In all the runs, the permeate turbidity was lower than 1.4 NTU.

Table 2.
Removal of salts, colour and turbidity, and rejection of soluble COD and phenolic compounds, for the different operating conditions and for both ultrafiltration membranes.

Operating conditions		UP005 membrane					UH030 membrane				
TMP[a] (bar)	CFV[b] ($m \cdot s^{-1}$)	Removal of salts (%)	Removal of colour (%)	Removal of turbidity (%)	Rejection of soluble COD[c] (%)	Rejection of phenolic compounds (%)	Removal of salts (%)	Removal of colour (%)	Removal of turbidity (%)	Rejection of soluble COD[c] (%)	Rejection of phenolic compounds (%)
1	2.2	7.0	66.4	99.7	9.4	11.7	0	79.1	99.8	3.2	0.2
	2.9	3.1	67.1	99.9	16.0	2.8	0	78.9	99.8	0.7	0.0
2	2.2	6.6	66.1	99.7	11.8	-0.8	-				
	2.9	5.6	78.7	100.0	18.9	-1.7	-				
	3.7	11.5	76.8	99.6	34.0	17.9	3.2	81.5	99.6	6.6	1.8
3	2.2	8.1	82.8	99.4	50.0	21.9	-				
	2.9	17.3	77.0	99.3	31.6	44.0	-				
	3.7	33.7	78.8	99.3	13.5	34.5	0	81.9	99.7	21.5	24.5

[a]TMP: transmembrane pressure; [b]CFV: crossflow velocity; [c]COD: chemical oxygen demand

It can also be observed that the reduction of colour was slightly greater for the UH030 membrane. For this membrane, the removal of colour was similar for the different operating conditions tested and it was around 80%. This membrane shows a greater pore size, however, as it has been already commented, it exhibited greater fouling. Thus, the fouling layer might contribute to increase the rejection of coloured compounds. In the case of the UP005 membrane, colour rejection increased as TMP raised. The greater rejection was observed for the operating conditions at which the limiting flux was reached (2 and 3 bar). At those conditions colour rejection was similar to that observed for the UH030 membrane.

Both membranes showed low salts removal, which is in agreement with the low molecular weight of NaCl. For the UH030 membrane it tended to zero at all the operating conditions tested, because of its greater pore size. For the UP005 membrane salts removal increased with TMP due to the greater fouling of the membrane as well as increased with CFV due to the reduction of the concentration at the membrane surface. The highest rejection of salts was 33.7% and it was achieved at 3 bar and 3.7 $m \cdot s^{-1}$. As show in Table 2, the rejection of COD was greater for the UP005 membrane, because of its smaller pore size. The rejection of COD depended as well on TMP and CFV. For the UP005 membrane, the removal of COD increased with CFV at 1 and 2 bar, as expected. However, at 3 bar, when the limiting flux was reached, the rejection of COD decreased with CFV. At this TMP, membrane fouling was severe, as already commented. Thus, the fouling layer could represent an additional resistance for the permeation of the solutes. At TMP equal to 3 bar and low CFVs the hydraulic resistance of the fouling layer was greater, as demonstrated by (Carbonell-Alcaina et al., 2016). This fact can be also observed from Fig. 5a, as permeate flux was observed to be lower at low CFV. The severe fouling observed at 3 bar and 2.2 $m \cdot s^{-1}$ could be the reason for the higher rejection of COD (50%) observed in such conditions. By increasing CFV, the fouling layer might have been partially removed, thus reducing the COD rejection up to 13.5% at 3.7 $m \cdot s^{-1}$. For each CFV, the rejection of COD increased with TMP, except at 3.7 $m \cdot s^{-1}$. The increase in rejection with TMP can be attributed to the compaction of the fouling layer as TMP rises. As regarding the UH030 membrane, COD removal at TMP equal to 1 or 2 bar was very low. The greatest COD removal for this membrane occurred in the limiting flux area due to severe fouling.

556 The rejection of phenolic compounds, was low for both membranes, due to the low
557 molecular weight (MW) of the main phenolic compounds (MW_{HTY} = 154,16 g·mol^{-1};
558 MW_{TY} = 138,16 g·mol^{-1}) present in the feed. The rejection of these compounds was
559 slightly higher for the UP005 membrane due to the lower MWCO. The greatest
560 rejection was observed at TMP equal to 3 bar for both membranes, due to greater
561 fouling, while the lowest rejection was obtained at lower TMP and CFV values.
562
563 The different rejection for COD and phenolic compounds causes that the phenolic
564 compounds/COD ratio in the permeate stream varies (Fig. 7a and 7b). As it can be
565 observed in Fig. 7a, for the UP005 membrane the phenolic compounds/COD ratio
566 increased in comparison with the feed solution, except at 3 bar and the highest cross
567 flow velocities, due to the low COD rejection observed at those conditions. The greatest
568 phenolic compounds/COD ratio in the permeate stream was achieved at 3 bar and 2.2
569 m·s^{-1}. Thus, at these conditions the permeate stream showed the highest enrichment in
570 phenolic compounds. However, for the UH030 membrane the phenolic
571 compounds/COD ratio in the permeate practically did not vary in comparison with the
572 feed (Fig. 7b). The same trend was observed by Cassano et al., 2011, when OMW were
573 ultrafiltered by means of permanently hydrophilic membranes (Cassano et al., 2011).
574
575 The objective of this work was to obtain a permeate stream enriched in phenolic
576 compounds, with low values of turbidity, colour and soluble COD. Permeate flux was
577 similar for both membranes. On the other hand, the UH030 membrane suffered greater
578 fouling and the fouling layer was not completely removed after the cleaning process.
579 Therefore, from this point of view, the UP005 membrane showed better results. This
580 membrane also presented the largest rejection of DQO, being the rejection of phenolic

compounds low. Thus, UP005 membrane was chosen. The operating conditions selected were a TMP of 3 bar and a CFV of 2.2 $m \cdot s^{-1}$. At those conditions the rejection of colour and COD were the highest, while the rejection of phenolic compounds was low.

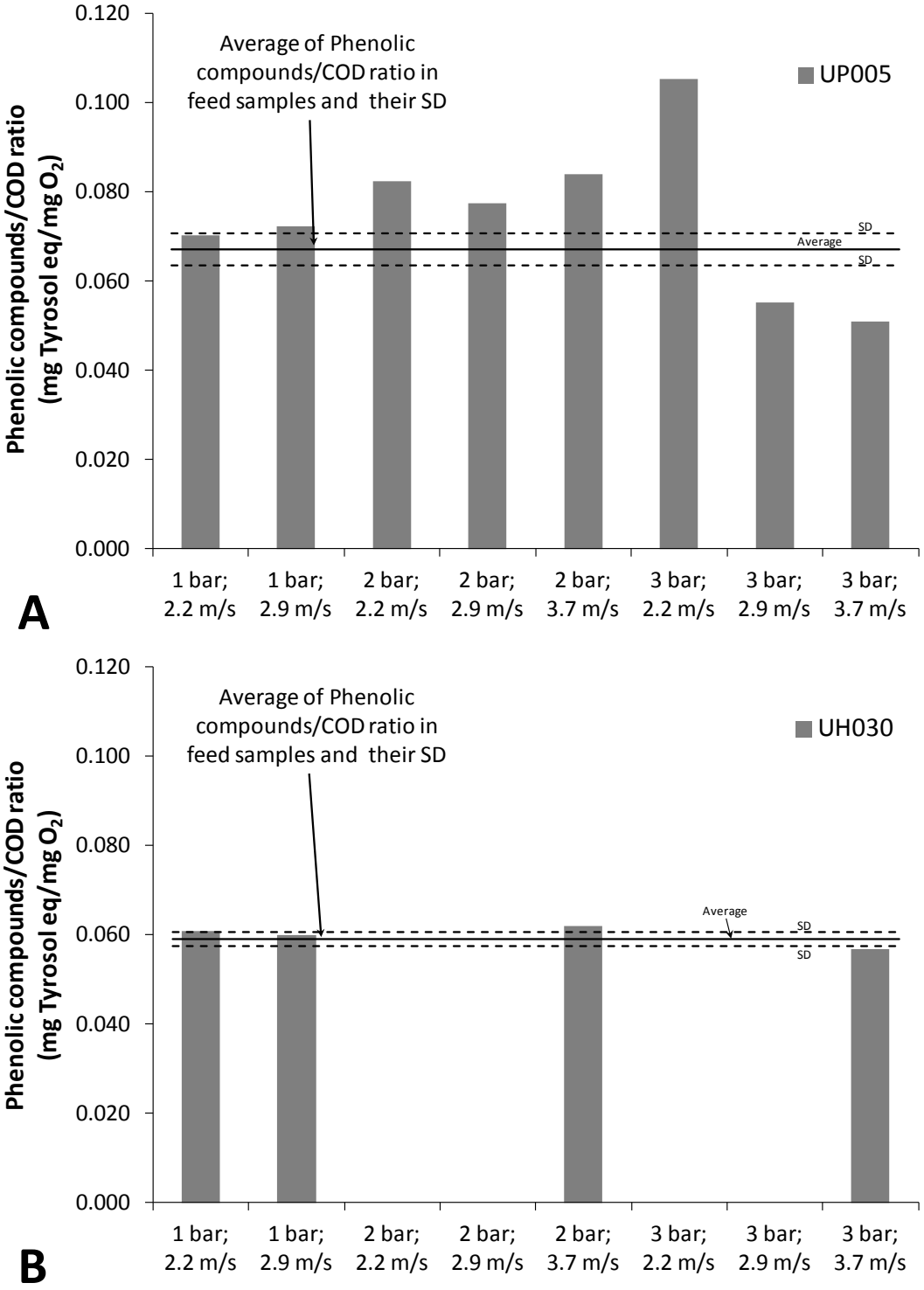


Fig. 7. Phenolic compounds/COD ratio in the permeate stream at different operating conditions and for UP005 (A) and UH030 (B) membranes. SD: standard deviation.

589

590 Table 3 shows the characterization of the permeate stream obtained when the residual
591 brine was ultrafiltered with the UP005 membrane at the selected operating conditions.
592 The permeate conductivity was slightly lower than that of the feed. The colour, turbidity
593 and TSS of the samples were mostly removed. As it was previously commented, the
594 value of COD in permeate was approximately 50% of that of the feed stream. At these
595 conditions, the losses of phenolic compounds were around 21.9% with a final
596 concentration of 744.9 ± 17.9 $mg \cdot L^{-1}$ Tyrosol eq. The rejection of HTY and TY was
597 20.0% and 19.3%, respectively.

598

599 **Table 3.**
600 Characterization of ultrafiltration permeate obtained with the UP005 membrane at
601 3 bar, 2.2 $m \cdot s^{-1}$ and 25ºC.

Parameter	Mean value	SD[a]
pH	4.1	± 0.1
Conductivity ($mS \cdot cm^{-1}$)	67.5	± 0.3
Color	0.098	± 0.004
Turbidity (NTU)	1.081	± 0.035
TSS[b] ($mg \cdot L^{-1}$)	0.0	± 0.0
Soluble COD[c] ($mg \cdot L^{-1}$)	7071.6	± 59.9
Total phenolic compounds ($mg \cdot L^{-1}$ Tyrosol eq.)	744.9	± 17.9
Hydroxytyrosol ($mg \cdot L^{-1}$)	442.2	± 6.1
Tyrosol ($mg \cdot L^{-1}$)	66.3	± 1.0

602 [a]SD: Standard deviation; [b]TSS: Total suspended solids; [c]COD: chemical oxygen demand
603

604 ## 4. Conclusions

605

606 Permeate flux decreased fast with time during the first minutes of operation for both
607 membranes at all the operating conditions tested. Therefore membrane fouling was
608 severe. Although both membranes have different MWCO, the steady state permeate flux
609 was similar and ranged between 20 and 40 $L \cdot h^{-1} \cdot m^{-2}$ except for the UP005 membrane at
610 1 bar. In this case permeate flux was much lower. At 2 and 3 bar the values of permeate
611 flux were analogous, but they increased with CFV.

612

613 The alkaline cleaning protocol proposed was effective to restore the initial permeability
614 of the UP005 membrane. However, it was not effective for the UP030 as it suffered
615 more severe fouling.

616

617 At all the operating conditions examined both membranes were able to remove most of
618 the colour and turbidity of the feed samples. Nevertheless, the rejection of COD and
619 phenolic compounds varied with TMP and CFV. The greatest phenolic compounds/COD
620 ratio (0.105 mg Tyrosol eq/mg O_2) in permeate stream was obtained at 3 bar and 2.2
621 $m \cdot s^{-1}$ for the UP005 membrane. At these conditions COD and phenolic compounds
622 rejection were 50.0% and 21.9%, respectively. As it is commented in the introduction
623 section, a further treatment step, such as nanofiltration, is required for phenolic
624 reclamation. The objectives of the UF step were to remove TSS and soluble COD with
625 less phenolic compounds rejection in order to improve the performance of the
626 subsequent NF process.

627

628 According to the results obtained, the ultrafiltration process carried out with the UP005
629 membrane at the selected conditions can be considered as an efficient pretreatment for the
630 subsequent recovery of polyphenols from table olive fermentation brine wastewaters.

631

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633

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637

638 **Nomenclature**

639

640 *List of symbols*

641	A_{HQ}	peak area corresponding to hydroquinone
642	A_{HTY}	peak area corresponding to hydroxytyrosol
643	A_{TY}	peak area corresponding to tyrosol
644	Abs_{765}	Absorbance at 765 nm
645	C_b	bulk concentration
646	C_{Fj}	Concentration of parameter *j* in the feed solution
647	C_g	gel layer concentration
648	C_{HQ}	hydroquinone concentration
649	C_{HTY}	hydroxytyrosol concentration
650	C_{Pj}	Concentration of parameter *j* in the permeate solution
651	CP	concentration polarization factor
652	C_{TY}	tyrosol concentration
653	D	effective diffusivity
654	E_i	Elimination rate of parameter *i*
655	J	Permeate flux
656	k	mass transfer coefficient
657	K	Hydraulic permeability
658	R_a	Resistance due to adsorption on membrane surface and inside its pores and
659		concentration polarization
660	R_{cf}	Cake layer resistance
661	Re	Reynolds number

662	R_j	Rejection rate of parameter *j*
663	R_m	Intrinsic hydraulic resistance of the new membrane
664	*Sc*	Schmidt number
665	*Sh*	Sherwood number
666	V_{Fi}	Value of parameter *i* in the feed solution
667	V_{Pi}	Value of parameter *i* in the permeate solution
668	ΔP	Transmembrane pressure
669	μ	Viscosity of feed solution
670		
671	*Abbreviations*	
672		
673	CFV	Crossflow velocity
674	COD	Chemical oxygen demand
675	C1	Cleaning protocol 1
676	C2	Cleaning protocol 2
677	C3	Cleaning protocol 3
678	HPLC	High performance liquid chromatography
679	HTY	Hydroxytyrosol
680	MW	Molecular weight
681	MWCO	Molecular weight cut-off
682	NF	Nanofiltration
683	NTU	Nephelometric turbidity unit
684	OMW	Olive mill wastewater
685	PES	Polyethersulfone
686	TMP	Transmembrane pressure

687 TSS Total suspended solids

688 TY Tyrosol

689 UF Ultrafiltration

690 WWTP Wastewater treatment plants

691

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