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Effect of the operating conditions on a nanofiltration process to separate low-molecular-weight phenolic compounds from the sugars present in olive mill wastewaters

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Abstract

The efficiency of nanofiltration to purify the tyrosol present in the olive mill wastewaters (OMWWs) has been studied. The similar molecular weight of tyrosol and the sucrose existing in this kind of by-products restricts the discrimination between both molecules through a membrane process, but the interest of phenolic compounds to be applied in cosmetics and pharmacology greatly motivates its recovery at the highest purity possible. Thus, two different simulated OMWWs composed of tyrosol and mixtures of tyrosol and sucrose, respectively, were nanofiltered using the NF270 membrane. Three transmembrane pressures (TMPs) and three cross-flow velocities were tested. The optimum results were obtained at 0.5 $m \cdot s^{-1}$ and 15 bar. The rejections of the chemical oxygen demand (COD) were above 78%, whereas phenolic compounds were barely retained. This indicates that the sugar was accurately separated from tyrosol, which was recovered in the permeate stream at a high purity.

Keywords: nanolfiltration; olive mill wastewater; phenolic compounds; sucrose; separation.

Introduction

For some years now, phenolic compounds from the olive fruit have called particular attention. Apart from being responsible for the sensorial characteristics and stability of virgin olive oil, their principal meaning relies on their antioxidant and anti-inflammatory properties, that have been widely related with potential health benefits, including preventing the risk of suffering some heart and neurological diseases and even cancer. As a consequence of these outstanding properties, food, pharmaceutical and cosmetic industries have shown a great interest in these compounds (Casaburi et al., 2013; Ghanbari et al., 2012; López-Miranda et al., 2010; Ray et al., 2019).

Phenolic compounds are present in every product derived from the olive grove, including olive leaves, stems, seeds, fruit skin, fruit pulp and obviously olive oil (Olmo-García et al., 2018). As a result, these molecules can be found in the residues obtained after olive processing too. A considerable percentage of the phenolic compounds of the olive drupe is transferred to the wastewaters obtained in the olive mills (olive mill wastewaters[1], OMWWs) (Di Mauro et al., 2017), and they are also present in the brines derived from the production of table olives, where tyrosol and hydroxytyrosol stand out by their high concentration (Fendri et al., 2013).

However, despite the beneficial effect for human health, the reducing power of phenolic compounds implies a huge environmental impact if these products are directly discharged to the medium. Even at low concentrations, phenolic compounds are able to negatively impact the viability of microorganisms, plants and small vertebrates (Babic et al., 2019; Pinho et al., 2017). For these reasons, the treatment of olive mill wastewaters before their discharge to the environment is mandatory, in order to reduce the high content in organic matter and the presence of phenolic compounds, which could damage the normal plant growth and the aquatic ecosystem (Dermeche et al., 2013).

In consequence, the recovery of phenolic compounds from OMWW results in a reduction of the toxicity of these streams (improving their further applicability as fertilizers, compost etc) as well as a corresponding collection of high-added value products with commercial or pharmaceutical applications. In this context, membrane technology appears as a relevant approach. In the recent years, the application of membrane processes to separate bioactive compounds has emerged as a satisfactory strategy (Castro-Muñoz and Fíla, 2018). The low requirements of energy, the environmental safety, the high selectivity and the easy scale up of the process make

[1] Abbreviations used: COD: chemical oxygen demand, KSM: Kedem-Spiegler model, MWCO: molecular weight cut-off; OMWW: olive mil wastewater, TMP: transmembrane pressure.

membrane technology very appropriate to selectively separate and purify phenolic compounds from the rest of species present in these by-products. To achieve this objective, some aspects regarding the membrane of choice and the sample to be treated should be considered. The efficiency of the process will highly depend on the proper choice of the membrane material, interactions among the solutes present in the feed solution and the applied operational parameters (Díaz-Montes and Castro-Muñoz, 2019).

Also, the combination of different techniques and membrane procedures may be of interest. Some reported approaches to recover and purify phenolic compounds from OMWW are based in sequential membrane processes. For instance, Cassano and co-workers designed a process based on two ultrafiltration procedures followed by a nanofiltration step to fractionate OMWW from the three-phase olive oil production process (Cassano et al., 2013). In other cases, nanofiltration was carried out after one ultrafiltration operation (Alfano et al., 2018), or even after a microfiltration process, obtaining satisfying results in terms of COD rejection and recovery of polyphenols as well (Bazzarelli et al., 2016; Garcia-Castello et al., 2010).

The ultrafiltration of OMWW allows the removal of suspended solids and organic compounds of relatively high molecular weight. The corresponding permeate stream that is obtained is rich in phenolic compounds, as demonstrated by Carbonell-Alcaina et al. when wastewaters from the production of table olives were treated (Carbonell-Alcaina et al., 2018). However, a subsequent nanofiltration step is essential to remove other species of lower molecular weight that remain in the ultrafiltration permeate. Enlarging the purity of the phenolic extract highly benefits its further applicability in the industry, as they may be incorporated in cosmetic preparations, food supplements etc.

In this work, the viability of nanofiltration to recover tyrosol from OMWW has been investigated using as feed a model solution composed of tyrosol and sucrose. The effect of the operating conditions on the recovery has been considered. Tyrosol was selected as it is a major constituent of OMWW and it has been widely accepted as one of the principal representatives of phenolic compounds from olive-derived matrices (Borja et al., 1996; Cassano et al., 2011; Najjar et al., 2007; Richard and Delgado-Nuñez, 2003). Additionally, low molecular weight phenolic compounds have been reported to have greater antioxidant activity than polymeric ones (Syed et al., 2017). Thus, this phenolic compound attracts special interest for the cosmetic and pharmaceutical industries (Miralles et al., 2014), being its recovery a great opportunity to revalue the residues from olive mills. In the case of sucrose, it was chosen as representative of the sugars present in OMWWs.

The molecular weights of tyrosol (138.18 g·mol^{-1}) and sucrose (342.30 g·mol^{-1}) are quite similar, which hinder a proper purification of the phenolic extract. Kontos and co-workers specifically targeted the separation of tyrosol and sucrose from a synthetic solution, but it was not through a membrane process, but a cooling crystallization treatment (Kontos et al., 2018). In fact, there are not many papers addressing the partition of these two compounds and, to our knowledge, their separation by membrane processes has not been tackled in the literature despite its interest.

1. Materials and Methods

1.1. Feed solutions

Simulated feed solutions were prepared trying to obtain a concentration of phenolic compounds and COD similar to the actual content of real olive mill wastewaters. An olive vegetation wastewater whose characterization was previously published (Ochando-Pulido et al., 2012) was simulated. Two synthetic OMWWs were prepared: one of them only contained tyrosol (OMWW I); the second solution reproduced more accurately the actual content of OMWW, containing both tyrosol and sucrose (OMWW II). The sucrose content was the only difference between both solutions. Thus, it was possible to compare the behaviour of tyrosol by itself and that for tyrosol in the presence of the sugar. The influence of sucrose in the results and the study of its separation from the phenolic alcohol were then investigated.

According to the reference sample, the concentration of tyrosol (Maybridge, United Kingdom) was near to 373 mg·L^{-1} for both OMWW I and OMWW II. The COD of the OMWW II was required to be 2.875 g of oxygen·L^{-1}, which corresponded to a concentration of 2.61 g·L^{-1} of sucrose (Panreac, Spain). Chlorhydric acid, supplied by J.T. Baker (The Netherlands) was employed to adjust the pH to 5.3, which is the typical pH of OMWW.

1.2. Nanofiltration plant and experimental procedure

To conduct the nanofiltration tests, a pilot plant was designed. It has been schematized in Figure 1. The utilized feed tank had a capacity of 10 L. A NF270 membrane (Dow Chemical, EEUU), with an active area of 0.00472 m^2, was located in a flat module, which was preceded by a plunger pump. Some specifications about the membrane can be found in Table 1. Considering the molecular weight of the target molecule (tyrosol) and that of sucrose, the MWCO of the membrane was judged adequate to separate it from sucrose. A flowmeter and two manometers were employed. Each manometer was situated at the inlet and outlet side of the membrane module. The permeate stream was collected in a recipient placed onto a balance (PKP Balance,

Kern & Sohn GmbH, Germany) which measured the permeate mass every 5 seconds. The plant was operated in a total recycle mode; therefore, the collected permeate was periodically flowed back to the feed tank and the retentate stream was continuously recycled back to the feed tank. Temperature was controlled by means of an electric resistance, that allowed the heating of the feed solution, and a cooling coil to refrigerate it.

Before the conduction of any experiment, the NF membrane was washed with osmotized water (with a conductivity of 6.5 $\mu S \cdot m^{-1}$) to remove the preservative agent. After that, the membrane was immersed in an osmotized-water bath during 24 h, in order to hydrate it and remove impurities that might reduce its functionality. The compactation of the membrane was addressed afterwards. To this end, osmotized water was nanofiltrated during 4h, at 1 m/s and 18 bar. This pressure was higher than the largest pressure applied during the experiments (15 bar), to ensure that the membrane is adapted and resists this value.

Before the filtration experiments, pure water flux was measured at a crossflow velocity of 1 $m \cdot s^{-1}$ and different transmembrane pressures (5, 10 and 15 bar) with osmotized water in order to determine the hydraulic permeability of the membrane (L_p) ($L \cdot h^{-1} \cdot m^{-2} \cdot \ bar^{-1}$), according to the following equation:

$$L_p = \frac{J_p}{\Delta P} \quad (1)$$

where J_p $(L \cdot h^{-1} \cdot m^{-2})$ is the permeate flux and ΔP (bar) is the transmembrane pressure.

The simulated OMWWs were nanofiltered at different transmembrane pressures (5, 10 and 15 bar) and cross-flow velocities of 0.5, 1 and 1.5 $m \cdot s^{-1}$ until stable permeate flux and retention values were reached (1 hour). Temperature was maintained at 25 °C.

The tested values of cross-flow velocity were decided after performing a nanofiltration experiment with type II simulated OMWW at a wide range of cross-flow velocities (0.25, 0.5, 0.75, 1, 1.25 and 1.5 $m \cdot s^{-1}$) and a TMP of 15 bar, as that is the tested TMP that was expected to cause the greatest membrane fouling. The indicated values of 0.5, 1 and 1.5 $m \cdot s^{-1}$ were selected as appropriate for the subsequent experiments.

The membrane was conveniently cleaned after each run by flushing the pilot plant with different solutions at 1 $m \cdot s^{-1}$. First, tap water was flushed through the system without recirculation for 10 min. Then, P3 Ultrasil 115 (Ecolab, Barcelona, Spain) was used to remove the solutes adsorbed on the membrane surface and embedded inside the membrane pores. Six litres of an aqueous solution of this detergent at pH 11 were recirculated for 1 h. Finally, the membrane was rinsed

with tap water (10 min, without recirculation) and then with osmotized water (5 min, without recirculation and pressure, and then at 1 bar for 30 min). Water permeability was again determined after each cleaning cycle, in order to corroborate that the membrane cleaning was efficient. The cleaning process was repeated if needed until at least a 90% of the initial membrane permeability was recovered.

1.3. Streams characterization

The synthetic solutions were characterized in order to measure the concentration of phenolic compounds and the COD. Moreover, 20 mL aliquots of the permeate streams were taken at time-points of 10, 30 and 55 minutes, in order to characterize them and evaluate the rejection of the solutes and the efficiency of the process to separate them. The Folin-Ciocalteu method was conducted to determine the concentration of total phenolic compounds (Singleton et al., 1999). The COD (mg · L^{-1}) was measured by means of the LCK 014 kits supplied by Hach Lange (Germany). Then, rejection (*R*) of the membrane towards tyrosol or COD was calculated as:

$$R = \left(1 - \frac{C_p}{Cf}\right) \cdot 100 \quad (2)$$

where C_p (mg · L^{-1}) and C_f (mg · L^{-1}) are the solute concentration in the permeate and feed solution, respectively.

In order to estimate the percentage of the COD that corresponded only to the oxidation of tyrosol (COD_{TY}), the following calculation was performed:

$$COD_{TY} = \frac{TPC \cdot COD_{TY}^{+}}{COD} \cdot 100 \quad (3)$$

TPC (mg · L^{-1}) corresponds to the value of total phenolic content. COD_{TY}^{+} (mg oxygen · mg tyrosol^{-1}) is the theoretical consumption of oxygen that is necessary to oxidize one gram of tyrosol, and that is given by the chemical formula of the molecule:

$$C_8H_{10}O_2 + 9.5\ O_2 \rightarrow 8\ CO_2 + \ H_2O$$

Those 9.5 mol of oxygen that are needed to oxidize one mol of tyrosol correspond to 2.20 grams of oxygen per gram of tyrosol, which is the value of COD_{TY}^{+}.

1.4. Kedem-Spiegler Model

In order to theoretically predict the values of permeate flux obtained for the type II model solution, which is more similar to a real OMWW, the KSM was applied (Spiegler and Kedem, 1966):

$$J_w = J_p = L_p \cdot (\Delta P - \sigma \Delta \pi) \quad (4)$$

being $\Delta\pi$ (bar) the osmotic pressure and σ the reflection coefficient, which is the maximal retention that is possible for a given solute (Van der Bruggen, 2018).

The concentration of tyrosol was much lower than that of sucrose. Moreover, as the molecular weight of tyrosol is lower than that of sucrose, it was expected that its rejection was lower too. Therefore, taking into account both aspects, it can be considered that the osmotic pressure gradient is mainly due to sucrose. On the other hand, considering that the MWCO of the membrane is 300 Da (López-Muñoz et al., 2009) and the molecular weight of sucrose, it was supposed that sucrose did not cross the membrane, being the reflection coefficient, σ, equal to 1. As a consequence, according to the KSM, the water flux (J_w) can be defined as follows:

$$J_w = J_p = L_p \cdot (\Delta P - \Delta \pi) \quad (5)$$

The osmotic pressure of a sucrose solution was determined according to the following expression (Nabetani et al., 1992):

$$\Delta\pi = -\frac{R_g \cdot T}{V_w} \cdot \ln\left(\frac{\frac{100 - C_m}{M_w} - \frac{4 \cdot C_m}{M_S}}{\frac{100 - C_m}{M_w} - \frac{3 \cdot C_m}{M_S}}\right) \quad (6)$$

where R_g (J mol^{-1} K^{-1}) is the ideal gas constant, T is the solution temperature (K), V_w is the partial molar volume of water (it was assumed as the partial molar volume for pure water, which is $18.07 \cdot 10^{6}$ m^3·mol^{-1}), C_m (kg·m^{-3}) is the concentration of sucrose on the membrane surface and M_S (kg·mol^{-1}) and M_w (kg·mol^{-1}) are the molecular weight of sucrose and water, respectively.

C_m was calculated according to the film theory, which defines J_w as:

$$J_w = k \cdot ln\left(\frac{C_m - C_p}{C_f - C_p}\right) \quad (7)$$

In this expression, k (m·s^{-1}) is the mass transfer coefficient and C_f and C_p are solute concentrations in the feed and in the permeate, respectively. When considering that sucrose does not cross the membrane, $C_p \approx 0$ and then

$$C_m = C_f \cdot e^{\frac{J_w}{k}} \quad (8)$$

225 *k* was determined by means of semiempirical correlations of dimensionless numbers that were
226 particularized for spacer-filled flat sheet and spiral wound membrane modules at turbulent flow
227 conditions (Schock and Miquel, 1987):

228 $$Sh = 0.065 \cdot Re^{0.875} \cdot Sc^{0.25} \quad (9)$$

229 The Sherwood number (*Sh*) is a function of *k*, the hydraulic diameter of the membrane (d_h) (m)
230 and the diffusion coefficient (D_{AB}) ($m^2 \cdot s^{-1}$):

231 $$Sh = \frac{k \cdot d_h}{D_{AB}} \quad (10)$$

232 The Reynolds number (Re) is defined as function of the density of the solution (ρ) ($kg \cdot m^{-3}$), the
233 cross flow velocity (u) ($m \cdot s^{-1}$), d_h and the viscosity (μ) (Pa·s):

234 $$Re = \frac{\rho \cdot u \cdot d_h}{\mu} \quad (11)$$

235 And finally, the Schmidt number (*Sc*) is defined as function of μ, ρ and D_{AB}:

236 $$Sc = \frac{\mu}{\rho \cdot D_{AB}} \quad (12)$$

237 Grouping the expressions (8, 9 and 10), the following equation is obtained:

238 $$k = 0.065 \cdot \rho^{0.625} \cdot \mu^{-0.625} \cdot D_{AB}^{0.75} \cdot d_h^{-0.125} \cdot \mu^{0.875} \quad (13)$$

239 The parameters ρ, μ and D_{AB} were determined as previously reported (Nabetani et al., 1992),
240 using empirical equations. The equation to determine ρ was the following:

241 $$\rho = \frac{100}{\frac{100 - C_f}{\rho_w} + \overline{v} \cdot C_f} \quad (14)$$

242 where ρ_w is the water density and $\overline{v}$ ($kg \cdot m^{-3}$) is the partial specific volume of sucrose.

243 Viscosity was calculated by the following expression, where μ_w corresponds to water viscosity.

244 $$\mu = \mu_w \cdot e^{\frac{2.61 \cdot C_f}{100 - C_f}} \quad (15)$$

245 Finally, the diffusion coefficient was determined as follows:

246 $$D_{AB,in\ mix} = D_{0,s} \cdot \left(\frac{\mu_w}{\mu}\right)^{0.45} \quad (16)$$

247 being $D_{0,s}$ the diffusion coefficient of a diluted solution of sucrose ($5.24 \cdot 10^{-10}$ $m^2 \cdot s^{-1}$).

Taking into account all these correlations (equations 9 to 16), the simultaneous resolution of equations 5 (KSM) and 8 (film theory) allow the estimation of the concentration on the membrane surface and the permeate flux.

2. Results and Discussion

2.1. Characterization of the feed solutions

The synthetic OMWWs were characterized right before the nanofiltration experiments, in order to know the real concentration of the analytes, COD and pH. The obtained results can be reviewed in Table 2.

2.2. Membrane characterization

The water permeability of the membrane was determined to be 15.73 $L \cdot h^{-1} \cdot m^{-2} \cdot bar^{-1}$. This value was the resulting slope of the linear fitting when permeate flux was expressed as a function of TMP. The value of permeability obtained is similar to those obtained by other authors for this membrane (Avram et al., 2017).

2.3. Variation of permeate flux with cross-flow velocity and transmembrane pressure

In Figure 2, the variation of permeate flux with the cross-flow velocity for the type II model solution at a TMP of 15 bar is presented. A wide range of cross-flow velocities was contemplated. In the figure, the results of permeate flux are presented in different colours and shapes for each of the tested velocities. It can be noted that permeate flux increased with the cross-flow velocity within the considered range. However, the differences observed were not remarkable, thus indicating that concentration polarization and fouling were not severe. From these results, it was decided to continue the following set of experiments at the highest cross-flow velocity tested (1.5 $m \cdot s^{-1}$) and at two cross-flow velocities within the tested range (1 and 0.5 $m \cdot s^{-1}$).

Figure 3 shows the obtained results for the nanofiltration of the two simulated OMWWs at the tested conditions of TMP and cross-flow velocity. Experiments conducted at the same cross-flow velocity have been plotted in the same graphic, in order to facilitate the interpretation and comparison of the results. The three graphics reflect a substantial increment of permeate flux as TMP increases. Moreover, no noticeable decline of permeate flux with time was appreciated and the values of the relative flux (compared to the flux obtained during the nanofiltration of pure water) were always above 77%, even in the case of the lowest cross-flow velocity tested. These aspects indicate that membrane fouling was not significant.

At 5 and 10 bar, the values of the permeate flux were very similar for both types of solutions, I and II, for all the cross-flow velocities tested. Considering the composition of each simulated solution, some differences in the values of the permeate flux could be expected. However, this variation was probably reduced because, at those TMPs, the concentration polarization phenomenon was not relevant. On the contrary, at 15 bar, the simulated solution II showed lower values of permeate flux than those observed for the solution I (only containing tyrosol). The relative flux of OMWW II ranged between 89-98% (depending on the cross-flow velocity applied), whereas OMWW I presented a relative flux of 99-100%. The higher pressure applied in this case contributed to the concentration polarization phenomenon, which was logically more significant for the simulated solution II. Similar conclusions can be reached from Figure 4, which contains the stationary permeate flux observed at every pressure and cross-flow velocity studied. The values of permeability for the three tested feeds (deionized water, OMWW I and OMWW II) were very similar, being that of deionized water greater. However, at 15 bar, the lower permeate flux of OMWW II was more noticeable. It can also be observed that as cossflow velocity increases, the difference between the permeability for OMWW I and OMWW II decreases.

2.4. Rejection of solutes

The just discussed difference in the values of permeate flux observed at 15 bar occurred mainly at the cross-flow velocities of 0.5 and 1 $m \cdot s^{-1}$. However, at 1.5 $m \cdot s^{-1}$ the values of permeate flux for both solutions were much closer. Higher values of cross-flow velocity provided a major turbulence inside the membrane module that contributed to the back diffusion of solute from the membrane surface, thus reducing the concentration polarization phenomenon, featuring higher values of permeate flux when compared with lower velocities. The highest influence of cross-flow velocity on permeate flux was observed at the largest TPM tested (15 bar), as at this TMP the convective transport of solutes towards the membrane is greatest and, therefore, the concentration polarization phenomenon is more significant. Figure 5A shows the rejection of phenolic compounds at different operating conditions. The data presented in the figure corresponds to steady state rejection. As it can be observed, low rejection values of tyrosol were obtained. The NF270 membrane hardly retained the phenolic compound, which facilitated its recovery in the permeate stream. In contrast, Avram and co-workers reported a complete rejection of phenolic compounds from hot water extracts of blueberry pomace, using the same membrane (Avram et al., 2017). This discrepancy is explained by the MWCO of the membrane and the substantial difference between the molecular weight of tyrosol (present in the simulated OMWWs) and the large-size polyphenols from the blueberry pomace (mainly

anthocyanins). Also, some polymerizations may have occurred among the molecules of the extract, thus increasing the rejection. In our case, the molecular weight of tyrosol was considered and the membrane NF270 was carefully chosen in order not to retain the compound of interest, but to separate it from the sugar present in the feed solution. Regarding the potential electrostatic interactions between the membrane and the compound of interest, the isoelectric point of the NF270 membrane has been described to be in the range of 3.3-5.2 (Mänttäri et al., 2006; Nghiem et al., 2005). Being the pH of the OMWWs around 5.3, it is reasonable to assume that the membrane surface may be negatively charged, at least partially. However, this scenario did not conflict with the permeation of tyrosol, because the molecule was neutral at the working pH, since it has been observed by several authors that pH values greater than 9 have to be reached in order to obtain tyrosol in its deprotonated form (Vulcano et al., 2015; Carrasco-Pancorbo et al., 2006). This facilitated the diffusion of tyrosol to the membrane and the subsequent low rejection that was observed.

According to the figure 5A, when the TMP was increased from 5 to 10 bar, rejection raised too, which is in accordance with the KSM for a nanofiltration process. However, when the TMP increased from 10 to 15 bar, phenolic compounds rejection decreased, which may be explained by a fouling phenomenon, prompted by the concentration polarization that was favoured at this pressure level. The effect of cross-flow velocity was barely observed, as the differences in rejection with the variations of the velocity were very small. Nevertheless, rejection did slightly increase with the cross-flow velocity, as expected. As can be seen in the figure, phenolic compounds rejections for the simulated OMWW II were lower than those for the solution I. This effect was not related with a reduction in the permeate flux, as could be expected (Bellona et al., 2004), because, according to Figure 3 and Figure 4, the values of permeate flux were similar for both types of simulated solutions. As explained before, the fouling of the membrane was not harsh, thus, the observed values of permeate flux were very similar for both solutions. Instead, the decrease in the rejection for the simulated solution II may be explained by an increase in the viscosity of OMWW II (prompted by the presence of sucrose). In that case, the mass transfer coefficient of tyrosol, k, would be affected too. This parameter is a diffusion rate constant related to the back diffusion of tyrosol from the membrane surface towards the bulk solution. If k is lower, the concentration of tyrosol on the membrane surface, C_m, is higher, which results in an increase of the concentration in the permeate and the subsequent decrease of the rejection.

Additionally, Figure 6 shows the values of rejection obtained at the different operation times. In general, the rejection values observed for a given pressure and cross-flow velocity scarcely varied with time, which confirms that the occurring fouling of the membrane was low. However,

346 at the highest TMP tested (15 bar), the rejection slightly increased with time, what indicates that
347 fouling is more noticeable at this TMP.

348 COD rejection for both simulated solutions at the different operating conditions that were
349 tested is shown in Figure 5B. The data refer to steady state rejection. The same as it was
350 observed for the rejection of phenolic compounds, the differences of COD rejection observed
351 during the time were very small. The variation of COD rejection with TMP and cross-flow velocity
352 followed the same trend that was already commented for the phenolic compounds.
353 Nevertheless, the simulated OMWW II displayed much higher COD rejections than the simulated
354 OMWW I, what indicates that sucrose rejection was very high, as sucrose is only present in
355 OMWW II and not in OMWW I. As tyrosol rejection was observed to be low and sucrose is the
356 only additional component in OMWW II, it is assumable that sucrose was being rejected in a
357 high percentage. These rejection values were indicative of the selectivity of the process, which
358 leaded to a permeate stream enriched in tyrosol and purified from the rest of components of
359 the feed solution. Indeed, the percentage of COD in the permeate stream that corresponded
360 only to tyrosol (calculated according to equation 3), which is shown in Figure 7, was above 90%
361 for all the operating conditions tested. This indicated that practically the whole organic matter
362 that was present in the permeate was tyrosol itself. The initial objective of the study (based on
363 the separation of tyrosol from the sugars of the OMWW) was then satisfactorily achieved. On
364 the other hand, the assumption of a value of σ equal to 1 for sucrose that was made at the
365 beginning to predict the values of the permeate flux was confirmed to be correct.

366 According to these results, a TMP of 15 bar and a cross-flow velocity of 0.5 $m \cdot s^{-1}$ were selected
367 as optimum for the separation of tyrosol and sucrose. The observed fouling was considered
368 minor, whereas the highest permeate flux (above 225 $L \cdot h^{-1} \cdot m^{-2}$) (Figure 3) and the lowest
369 phenolic compounds rejection were obtained (12.3% ± 0.2%, for OMWW II) (Figure 5). All these
370 parameters should be further studied with real OMWW. Ongoing experiments are being
371 conducted in our lab in this regard. In any case, at these conditions, it is possible to obtain a pure
372 product, perfectly able to be incorporated in other preparations, as cosmetic or nutraceutical
373 formulas. The format of the final product will determine if more treatments are needed, as
374 drying, encapsulation etc. However, as the tyrosol is recovered in an aqueous phase, the solution
375 is biocompatible, safe and easy to handle.

376 **2.5. Predictions of Kedem-Spiegler Model**

377 KSM was initially conceived for reverse osmosis operations; nevertheless, it has been
378 successfully applied to the nanofiltration of uncharged molecules in previous reports (Cuartas-

Uribe et al., 2010, 2007). The values of different parameters estimated by means of the combination of the KSM and the film theory for the solution II are listed in Table 3. This Table also contains the calculated Reynolds numbers, according to equation 11. All values of Re were above 1000. Schock and Miquel demonstrated that Re values above 400 correspond to turbulent flow when working with spacer-filled spiral wound or flat sheet elements (Schock and Miquel, 1987). This conclusion supports the application of equation 9.

To facilitate the comparison with the experimental results, only one value of experimental permeate flux has been given. This is the media of each registered value after 30 minutes of operation, where the steady state was achieved and the flux was constant. The table reflects the phenomenon that has been commented in the previous sections: an increase in the cross-flow velocity is related with an increase in the turbulence inside the membrane module, which contributes to increase the back-diffusion of the solute towards the bulk solution and produces a decline in the osmotic pressure gradient due to the lower concentration of sucrose on the membrane surface. The theoretical values of permeate flux predicted by the model were accurately confirmed by the experimental values. According to Figure 8, good agreement was achieved. The difference between estimated and experimental data was lower than 5% in all cases (Table 3).

The values of J_p experimentally observed were lower than the predicted ones, as a consequence of membrane fouling, which is not contemplated by the KSM and causes the corresponding resistance to the permeation through the membrane (Giacobbo et al., 2018). As the discrepancies between experimental and theoretical flux were very small, membrane fouling can be considered to be small too. Additionally, differences between predicted and experimental values of permeate flux can be also justified by the small fraction of sucrose that was not retained by the membrane. The consideration of σ equal to 1 was indeed reasonable, but, as the sucrose rejection did not achieved the 100%, it could contribute to some discrepancies between the model and the experimental results.

3. Conclusions

An efficient nanofiltration process to purify phenolic compounds from OMWWs has been developed. Special attention has been given to their separation from sugars due to the similar molecular weight. The increase of TMP resulted in higher permeate fluxes. Similarly, higher values of cross-flow velocity contributed to remove the solutes from the membrane surface and reduce the concentration polarization effect.

Tyrosol was observed to be recovered in the permeate stream, as the values of rejection ranged between 12.3% ± 0.2% and 23.9% ± 0.7%. COD rejection ranged between 77.8% and 83.9%. From the low values of COD that were determined in the permeate, more than 90% of the permeate COD can be attributed to tyrosol. Thus, it can be concluded that sucrose was highly retained by the membrane. Rejection to both tyrosol and COD increased with the increment of TMP and cross-flow velocity, but the effect of TMP was more significative.

The obtained values of permeate flux were accurately predicted by the KSM. The error was always under 4.7%, which demonstrates that the KSM was an appropriate model to predict the effect of the operating conditions on the permeate flux.

The results presented here demonstrate the suitability of membrane technology and, specifically, nanofiltration, to recover valued bioactive compounds from olive mill wastes. The retirement of the phenolic compounds from the by-products generated during the olive oil campaign contributes to their decontamination and also constitutes their revalorization, through the future industrialization of the obtained beneficial molecules.

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