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Additional Information

Comparison of different ultrafiltration membranes as first step for the recovery of phenolic compounds from olive-oil washing wastewater

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Abstract

The production of olive oil generates wastewater with a high organic load and toxicity due to the high concentration of phenolic compounds. In recent years, the treatment of these waters has been intensified together with the search for a process to recover these phenolic compounds due to their great antioxidant potential. All this with the aim of implementing the concept of circular economy. In this study, four different organic ultrafiltration membranes were evaluated in order to recover the phenolic compounds present in olive oil washing wastewater (OOWW) from an oil mill in the Valencian Community (Spain). The tested membranes differ in materials and molecular weight cut-off (MWCO): two permanently hydrophilic polyethersulfone (PESH) membranes with MWCO of 4 and 50 kDa, respectively, one polyethersulfone (PES) membrane with a MWCO of 5 kDa and a regenerated cellulose acetate (RCA) membrane with a MWCO of 10 kDa. Transmembrane pressure (TMP) and crossflow velocity (CFV) were varied from 1 to 3 bar and from 1.5 to 3.4 m·s⁻¹, respectively. The effectiveness of the different membranes and operating conditions were evaluated comparing the permeate flux and the rejection of chemical oxygen demand (COD) and total phenolic compounds (TPhs). The membranes with lower MWCO showed stable permeate fluxes without significant changes over time, while the UHO50 membrane showed a gradual decrease, without achieving a stable flux. Low rejection of phenolic compounds was observed in all cases, while the rejection of COD varied between 19.5% to 62.9% depending on the membrane and operating conditions tested. Except for the 50 kDa PESH membrane, initial permeability recovery greater than 95% was achieved with a 35 °C water rinse, indicating that membrane fouling was not severe. Since the aim was to recover the TPhs in the permeate stream and separate them from the organic matter, the 5 kDa PES membrane at 2 bar and 2.5 m·s⁻¹ was noticed to be the best option. At those conditions a stable permeate flux of 40 L·h⁻¹·m⁻² was obtained, while the lowest TPhs rejection was observed (8.01%) with a high COD rejection (61.18%).

Keywords: Ultrafiltration; Olive Oil washing wastewater; Phenolic compounds; Separation

1. Introduction

The worldwide concern for the recovery of effluents from industrial processes is becoming increasingly powerful due to the shortage of freshwater sources and the environmental protection initiatives. The large volumes of wastewater generated, together with their inadequate disposal, lead to the contamination of water sources from the sea to rivers (Lee et al., 2019). In this context, the recovery of waste and water from the food and agriculture industry is presented as a challenge and, at the same time, is the key factor in the development of new strategies to achieve a circular economy (El-Abbassi et al., 2014; Volpe et al., 2018).

In the Mediterranean countries, the production of olive oil is one of the most important industrial sectors, generating, in the last years, an estimated amount of 30 million m³ per year of an acidic and dark liquid, called olive mill wastewater (OMWW) (Ioannou-Ttofa et al., 2017). This wastewater is a mixture of different effluents generated in the production process of olive oil. Its composition depends on the olive oil extraction method (conventional press process, three-phase centrifugal continuous process or two-phase centrifugal continuous process). Most of the countries where olive oil is produced use the three-phase centrifugal process, although the more recent two-phase centrifugal process shows greater efficiency and produces lower amount of wastes. However, in Spain about 90% of the olive oil is produced by the two-phase centrifugal process (Borja et al., 2006). Olive mill effluents can include the following streams: olive washing water (OWW), olive vegetation water mixed with the water added in the horizontal centrifugation (OVW), olive oil washing wastewater (OOWW) generated in the vertical centrifugation and water used for process machinery washing (Gebreyohannes et al., 2016). Apart from having high loads of organic matter, these wastewaters are characterized by high levels of phenolic compounds. These phenolic compounds are highly phytotoxic and recalcitrant substances, presenting a great risk to aquatic life, microorganisms and vegetables. That is the reason why biological treatment plants result inadequate, since wastewater toxicity may inhibit the microbial population. Therefore, the efficient treatment of phenolic wastewater before discharge is crucial for sustainable development (Sun et al., 2015). Due to this, OMW has been considered as a problematic wastewater until now. However, the natural antioxidant character of the polyphenols, converts this effluent into a potential low-cost material for food, pharmaceutical and cosmetic industries (Kaleh and Geißen, 2016; Obied et al., 2005b). Several studies point to phenolic compounds as great natural antioxidants, presenting them as beneficial for the prevention of heart, microbial, diabetes and cancer diseases (Abbas et al., 2017).

Approximately, only 2% of the phenolic compounds of the olive fruit are transferred to the oil phase, while the remaining percentage is lost in the wastes, especially in the liquid streams, since most phenols are water soluble (Obied et al., 2005a).

Many physical and chemical methods have been proposed for phenolic compounds recovery and for the treatment of these wastewaters (El-Abbassi et al., 2011), focusing on the main problems, which are high energy consumption, low efficiency and generation of secondary pollution. The treatments should guarantee not only a significant reduction of the organic matter, but also the possibility of the phenolic compounds recovery. In addition, it is necessary to meet a series of requirements, related to the composition, purity and quality of the recovered compounds (El-Abbassi et al., 2014).

Research studies have shown that the actual management of OMW cannot be achieved without the combination of different technologies (Yangui et al., 2017). In this regard, several published articles suggest the combination of membrane processes (e.g. microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), reverse osmosis (RO)), as a good option. This is also an environmentally friendly alternative due to the no need for chemicals addition. (Bazzarelli et al., 2016; Nazir et al., 2019; Ochando-Pulido et al., 2013; Stoller and Ochando-Pulido, 2012; Zagklis et al., 2015).

Although the reported works have shown good results in eliminating the organic load and concentrating the phenolic compounds, the process bottleneck is the fouling of the membranes. Several studies have focused on preventing fouling of UF membranes. A statistical review carried out by Al Aani et al. (Al Aani et al., 2020) reported that 27% of all publications on ultrafiltration membranes applied for wastewater and water processing focused on this topic (fouling). Among the possible strategies to control the fouling of the membranes, pretreatment is presented as a fundamental step. These pretreatments must be adapted to the specific feed and the type of membrane (Ochando-Pulido et al., 2018). It should be noted that the characteristics of the wastewater from olive oil production are affected both by the variety of the olives and the production process used.

In the present work, different ultrafiltration membranes have been evaluated as a possible pretreatment in view of a further recovery of the phenolic compounds from the two-phase OOWW by nanofiltration. Membranes with different molecular weight cut-offs (MWCO) and made of different materials were tested in order to achieve the highest permeate flux and organic matter rejection and the lowest rejection of phenolic compounds. All the membranes were evaluated under the same parameters (temperature, cross flow velocity (CFV) and transmembrane pressure (TMP)). Previous to ultrafiltration, a pretreatment was also carried out, consisting of flotation, sedimentation and filtration. Since most of the countries that

produce olive oil use the three-phase centrifugal process, there are very few studies on the treatment of this wastewater (olive oil washing water from the two-phase process). Based on its higher efficiency, it is expected that most of the olive oil producers will adopt the two-phase process in the next future.

2. Material and Methods

2.1 Feed samples

The samples were provided by an olive oil milling plant located in the Valencian Community (Spain), where the two-phase continuous centrifugal process is used. The collection was carried out in November 2018. The samples correspond to the olive oil washing water (OOWW) obtained during the olive oil production, at the exit of the vertical centrifuge after the olive oil washing. Samples were immediately stored at -20 °C, to prevent degradation.

2.2 Pretreatment

Before starting the ultrafiltration process, a pretreatment was carried out to avoid the rapid fouling of the membrane due to the large particles present in the wastewater and for the care of the ultrafiltration plant. A three-stage pretreatment was planned. The first stage consisted of natural flotation. The flotation process was carried out in 8-liter vessels, leaving the samples between 2 and 3 hours without any stirring. The duration was determined from previous tests (data not shown). Then, the supernatant, which mainly contained oils and fats, was withdrawn using a graduated pipet. Afterwards, a sedimentation process was performed in the same vessels to remove suspended solids (settling time = 24 h). The settled solids were removed through a small valve located at the bottom of the vessel. Finally, in the third stage, the sample was filtered through a 60 µm pore size polyester cartridge (CA-0202-00, model GT, HidroWater, Spain). As in the case of the raw sample, the pretreated wastewater was stored at -20 °C, to avoid degradation.

2.3 Adsorption tests

To evaluate the interaction between the membranes and phenolic compounds, adsorption tests were performed. The tests consisted of immersing membrane pieces 24 hours in a stirred water solution that contained phenolic compounds following the procedure as previously described (Sotto et al., 2013). The solution contained 1 g·L⁻¹ of two phenolic compounds of different molecular weight, 0.98 g·L⁻¹ of tyrosol (138.164 g·mol⁻¹) and 0.02 g·L⁻¹ of catechin (290.26 g·mol⁻¹). The amount of phenolic compounds adsorbed (mg·m⁻²) was calculated as the concentration difference of the total phenolic compounds in the solution before (C_{Before}) and after adsorption (C_{After}) (Ji et al., 2019), as Eq. 1 shows.

$$M_p = (C_{before} - C_{after}) * \frac{V}{A} \quad (1)$$

where M_p is the mass (g) of the phenolic compound adsorbed on the membrane, V corresponds to the volume of the solution (500 mL) and A to the effective membrane area (10 cm²).

2.4 Ultrafiltration experiments

Ultrafiltration experiments were carried out in a laboratory-scale membrane plant. The feed stream was pumped from the feed vessel (8 L) to a Rayflow membrane module (Orelis, France), which contained two flat sheet membranes (0.025 m² of total active surface). The permeate and concentrate streams were returned to the feed container. From the permeate stream, samples of 50 mL were collected every 30 minutes for further analysis. A precision balance (Kern, Germany) was used to monitor the permeate flux and the collected data were recorded by a data acquisition system. A schematic flow diagram of the ultrafiltration system used is shown in Fig. 1.

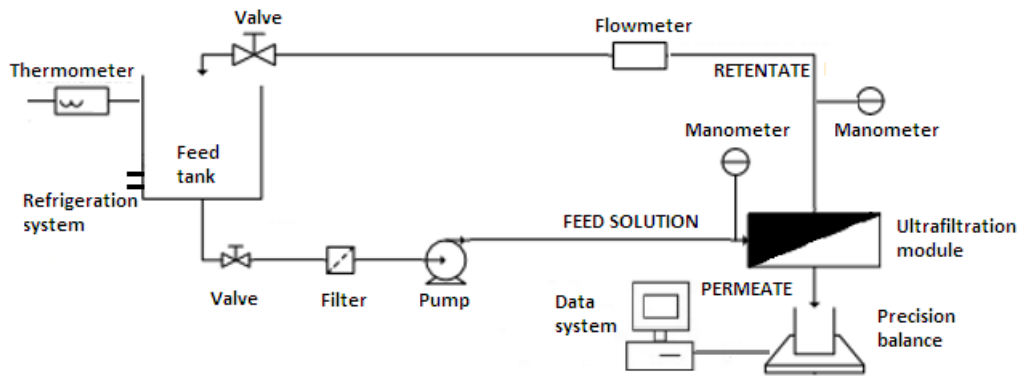


Fig. 1 Schematic diagram of the ultrafiltration plant.

The feed tank was provided with a cooling system to keep the temperature at 25°C. The working conditions used were five different CFVs between 1.5 and 3.4 m·s⁻¹, four TMPs between 1 and 3 bar and a duration of 3 hours, which was enough time to reach the steady state permeate flux. The performance of the membrane was evaluated by calculating the rejection of chemical oxygen demand (COD) and phenolic compounds (Eq. 2).

$$R_j(\%) = \left(1 - \frac{C_{Pj}}{C_{Fj}}\right) \times 100 \quad (2)$$

Where R_j is the rejection of parameter j (COD or phenolic compounds) in %, C_{Pj} is the concentration of parameter j in the permeate stream and C_{Fj} is the concentration of parameter j in the feed solution. The characteristic of the selected membranes according to manufacturers as well as the permeability experimentally determined in this work are presented in Table 1.

Table 1. Characteristic of the UF membranes used in this work (data obtained from the manufacturer and experimentally)

Membrane	UH004	UP005	RC70PP	UH050
Manufacturer	Microdyn Nadir	Microdyn Nadir	Alfa Laval	Microdyn Nadir
Material	PESH ^b	PES ^c	RCA ^d	PESH ^b
MWCO ^a (kDa)	4	5	10	50
T max (°C)	95	95	60	95
pH operating range	0 - 14	0 - 14	0 - 10	0 - 14
Permeability* (L·h ⁻¹ ·m ⁻² ·bar ⁻¹)	>27 ^e 32.67 ^f	>30 ^e 44.07 ^f	>40 ^e 78.50 ^f	>200 ^e 191.75 ^f

^aMWCO: molecular weight cut-off

^bPESH: Permanently hydrophilic polyethersulfone

^cPES: Polyethersulfone

^dRCA: Regenerated cellulose acetate

* water, at 25°C

^e: Manufacturer data ^f: Experimentally determined in this work

All membranes were initially compacted for 3 hours at a transmembrane pressure of 3 bar. Then, the hydraulic permeability (K) of all the membranes was determined from experiments performed with osmotized water (conductivity <40 $\mu\text{S}/\text{cm}$) and it was calculated as the slope of the straight line obtained by plotting the water flux values measured at 25 °C, versus the applied TMP, following the Darcy's equation (Eq. 3):

$$J = K \cdot \Delta P = \frac{\Delta P}{\mu \cdot R_m} \quad (3)$$

Where J represents the water permeate flux at a specific TMP (ΔP), μ the viscosity of the permeate and R_m the intrinsic membrane resistance.

2.5 Cleaning protocol

The membranes were cleaned after each ultrafiltration experiment. Four cleaning protocols were proposed. Cleaning procedure one (C1) consisted of rinsing the membranes with osmotized water at 25°C for 40 min. Cleaning procedure two (C2) was performed under the same conditions as C1 except for the temperature (35°C). Cleaning procedure three (C3) included chemical cleaning with P3 Ultrasil 115 (1% v/v) (Ecolab, España) at 25°C for 30 min. Finally, cleaning procedure four (C4) was identical to C3 but varying the temperature (35°C). All of the cleaning methods were carried out at 2.2 m·s⁻¹, with a TMP of 0.25 bar. The efficiency of the cleaning protocol was obtained by comparing the hydraulic permeability of the membrane before and after each experiment. The membrane was considered to be clean if the method led to recover more than 95% of the initial water permeability (P_0).

2.6 Analytical methods

The raw wastewater and the feed and permeate samples from the UF process were characterized, each parameter was measured in triplicate and the average value was

calculated. Electrical conductivity (EC) and pH were determined by digital calibrated conductivity meter (EC-Meter GLP 31+) and pH-meter (GLP 21+), respectively, both from Crison, Spain. A D-112 turbidimeter (DINKO, Spain) was used to measure the turbidity following the UNE-EN ISO 7027 standard method. For colour determination (FZ, Farb-Zahl in German), the procedure proposed by Döepkens et al. (Döepkens et al., 2001) was followed. A DR600 spectrophotometer (Hach Lange, Germany) was utilized for the measurement of the absorbances at different wavelengths.

$$FZ = \frac{A_{436}^2 + A_{525}^2 + A_{620}^2}{A_{436} + A_{525} + A_{620}} \quad (4)$$

The FZ was calculated according to Eq. 4, where A_{436} , A_{525} and A_{620} are the absorbance values measured at 436, 525 and 620 nm, respectively.

Sugar concentration was determined by the Anthrone colorimetric method (Frolund, B et al., 1996), where glucose (Panreac, Spain) was used as standard. The sugars present in the sample react with anthrone (Panreac, Spain) under acidic conditions, presenting a greenish blue colour. The total concentration of phenolic compounds was determined by means of the Folin-Ciocalteu method (Singleton et al., 1999). Tyrosol (VWR Chemicals, USA) was used as standard and the results were expressed as milligrams of tyrosol equivalents per liter (mg ty eq·L⁻¹).

Oils and fats were measured using a modified Soxhlet protocol. The extraction process consisted of shaking 500 mL of sample with 250 mL of hexane (25°C) and letting it rest in a separating funnel for 30 min. The supernatant (which contains solvent + oils and fats) was extracted with the help of a pipette, then 250 mL of hexane were added to the rest, repeating the extraction process. This step was repeated 3 times. All supernatants (extracts) were filtered with a cellulose filter (45 µm pore diameter). They were then weighed before and after evaporation of the solvent (at 50 °C using a rotary evaporator). The difference in mass corresponded to the amount of oils and fats and the result was expressed in mg·L⁻¹.

The measurement of total suspended solids (TSS) was performed following the UNE 77034 standard method. The amount of TSS corresponded to the difference between the initial weight of a glass microfiber filter (1.2 µm pore size) and its weight after the filtration of 25 mL of sample and subsequent drying in an oven at 105°C for 2 hours. The COD was measured using commercial kits supplied by Merck (Germany).

3 Results and discussion

3.1 Characterization of the feed samples

OOWW sample presented a dark green-brown colour due to the natural pigments of the olives. Two layers with different density were visibly distinguished. A large amount of fats and oils were clearly observed in the surface layer. The main physicochemical characteristics of the OOWW before (raw OOWW) and after (PR-OOWW) the pretreatment are presented in Table 2.

Table 2. Characteristics of the raw and pretreated (PR) olive oil washing wastewater (OOWW).

Parameter	Raw OOWW	PR-OOWW	Reduction %
pH	5.09 ± 0.01	4.82 ± 0.01	5.3
Conductivity (mS·cm ⁻¹)	3.77 ± 0.25	3.44 ± 0.03	8.7
FZ ^a (colour index)	4.30 ± 0.11	2.58 ± 0.01	40.0
Turbidity (NTU ^b)	364.2 ± 7.90	211.6 ± 1.25	41.9
TSS ^c (mg·L ⁻¹)	986.67 ± 15.92	397.20 ± 9.09	40.3
Sugars (mg glucose ·L ⁻¹)	1645.32 ± 17.24	1334.75 ± 8.14	18.9
Oils and fats (mg·L ⁻¹)	308.15 ± 3.08	33.55 ± 0.81	89.1
COD ^d (mgO ₂ ·L ⁻¹)	23775 ± 238.17	17545 ± 220.61	26.2
TPhs ^e (mg tyrosol eq.·L ⁻¹)	1161.8 ± 13.43	1103.8 ± 9.32	5.0

^a FZ: Farb-Zahl, colour index

^b NTU: Nephelometric Turbidity Units

^c TSS: Total suspended solids.

^d COD: chemical oxygen demand

^e TPhs: Total phenolic compounds

The presence of a large amount of organic matter (COD around 24 gO₂·L⁻¹) as well as an acidic pH value (pH 5.09) in the raw wastewater can be highlighted from the results shown in Table 2. In addition, a high concentration of total phenolic compounds (more than 1 g of tyrosol·eq.·L⁻¹) was found; among them hydroxytyrosol, tyrosol, succinic acid, oleuropein derivatives and other phenolic compounds (Jiménez-Herrera, Silvia; Ochando-Pulido, J.M.; Martínez-Ferez, 2017). A similar acidic profile was reported by Ochando-Pulido et al. (Ochando-Pulido et al., 2020), who characterized the OOWW from a two-phase centrifugal process. However, these authors reported lower values of COD (around 14 gO₂·L⁻¹) and total phenolic compounds (758.6 mg·L⁻¹). This variation may be attributed to the different olive cultivars, since the composition qualitatively and quantitatively varies with the olive variety and with all the factors that affect olive growth and olive oil production (climate conditions, soil composition, cultivation practices, olives storage time and the extraction process (Justino et al., 2012)).

The presence of a high sugar content (around 1.6 g glucose·L⁻¹) was expected, since, apart from phenolic compounds and organic acids, one of the main components of these wastewaters are sugars (Dermeche et al., 2013). The oil and fat content is within the range observed in other raw OMWs (200- 10000 mg·L⁻¹) (Lee et al., 2019).

The samples also showed a high concentration of TSS (986.67 mg·L⁻¹) and turbidity (364.2 NTU). These two parameters together with the colour (FZ), presented a decrease of around 40% after the pretreatment process. The reduction in the content of fats and oils was large, reaching an efficiency of 89.1%. This is important for the care of the membranes, as reported by Bolto, et al. (Bolto et al., 2020). These authors indicated that organic membranes, although they have advantages in oily wastewater treatment, such as low manufacturing cost, ease of processing and low energy requirements, show a relatively high tendency to fouling compared to inorganic membranes. This is due to the oil droplets, which adhere to the surface of the membrane. It leads to flux decay, due to heavy fouling, which implies a diminution of the membrane lifetime. According to organic matter values, the pretreatment managed to reduce the COD by 26% without affecting the total concentration of phenolic compounds (only 5% reduction).

An important point to note is that blockage of the filter was observed after filtering 50 litres of sample. However, the particles attached to the filter were easily removed with water. In industrial-scale applications, it is important to consider the life of the filter and also to choose the specific pore size after determining the particle size distribution of the solids in the sample (Akdemir and Ozer, 2009).

3.2 Adsorption of phenolic compounds on the membranes

Since polyphenols can interact with the membranes (Li et al., 2019), an adsorption test was made to find out whether the phenolic compounds were adsorbed on the different membranes considered in this work. Table 3 shows the amount of phenolic compounds adsorbed on each membrane.

Table 3. Adsorption of phenolic compounds on the surface of each membrane

Membrane	UH004	UP005	RC70PP	UH050
Amount adsorbed (mg·m ⁻²)	0.331 ± 0.045	0.349 ± 0.014	0.195 ± 0.019	0.465 ± 0.037

Adsorption experiments demonstrated a higher affinity of phenolic compounds for the PES membranes compared to the RCA membrane. The measured values were of the same order of magnitude, although slightly lower, as those observed by Ulbricht et al. (Ulbricht et al., 2009). These authors reported a higher adsorption of wine polyphenols (tannic acid) on PES MF membranes (~0.7 mg·m⁻²) compared to polypropylene (PP) membranes (< 0.1 mg·m⁻²). According to Cassano et al. (Cassano et al., 2011), the polar character of the PESH membranes would result in strong adsorption of polyphenols on the membrane, probably due to specific interactions between these compounds and the membrane itself (electron donor-receptor interactions, hydrogen bonds).

Although it was expected that the RCA membrane (RC70PP) had the highest adsorption due to its higher hydrophilicity (contact angle between 8°- 20° (Abd-Razak et al., 2019; Damar et al., 2020)), the lowest phenols adsorption was measured for this membrane. This may be due to specific characteristics of the membrane surface. Damar et al (Damar et al., 2020), observed that the hydraulic permeability values of the RC70PP membrane did not correlate with its hydrophilicity in comparison with the other membranes tested (ETNA10PP and GR73PP). These authors reported that this membrane yielded the lowest hydraulic permeability and, at the same time, the highest hydrophilicity. They concluded that this might be due to a reorientation of the active groups of the membrane upon contact with water or due to the effect of other surface characteristics such as pore size distribution, porosity, morphology, thickness and roughness. In this case, a rearrangement in the membrane matrix might generate a lower affinity of the membrane towards phenolic compounds. These authors also pointed out that the spongy pore morphology presented by the active layer of the RC70PP membrane caused greater resistance to water permeation. It should also be noted that these authors remarked that this membrane had a high resistance to fouling. As adsorption is one of the causes of membrane fouling, it agrees with the low adsorption data observed.

The UH050 membrane presented the highest adsorption of phenolic compounds, 2.39 times the value of the membrane that produced the lowest adsorption (RC70PP). This was expected, as it is the most hydrophilic membrane (35 ° contact angle) compared to the other PES tested membranes. This can be explained due to the pore size, as the larger the pore size the more water is absorbed, which is reasonable, as there is more pore volume available to be filled with water. Furthermore, compared to membranes made of the same polymeric material (UH004), but with a smaller pore size, it retains more water than membranes with a smaller pore size due to capillarity (Proner et al., 2020).

UH004 and UP005 membranes presented similar phenolic compounds adsorption (0.327 and 0.365 mg·m²). Although the UH004 membrane has been modified to improve its hydrophilicity, the manufacturer reports both membranes as hydrophilic. This is confirmed by their contact angle values, which are practically the same (53° and 54° for the UH004 and UP005 membranes, respectively, according to (Luján-Facundo et al., 2015; Penha et al., 2015a)).

Li et al (Li et al., 2019), analysed the effects of phenolic moieties present in dissolved organic matter (DOM) solutions on membrane fouling. These authors observed that the greater the presence of species with aromatic structures, the greater the adsorption on the surface of the membrane. This would explain the adsorption values of phenolic compounds observed for the membranes. The simulated water prepared for the adsorption tests had a similar concentration of phenolic compounds (1 g·L⁻¹ phenolic compounds) to that of the OOWW (1.1 gTyeq ·L⁻¹).

According to the results obtained, it was expected that the UH050 membrane presented greater fouling than the other membranes.

3.3 Hydraulic permeability of the membranes

The permeate fluxes obtained at different transmembrane pressures for all the tested membranes in the water permeability tests are shown in figure 2.

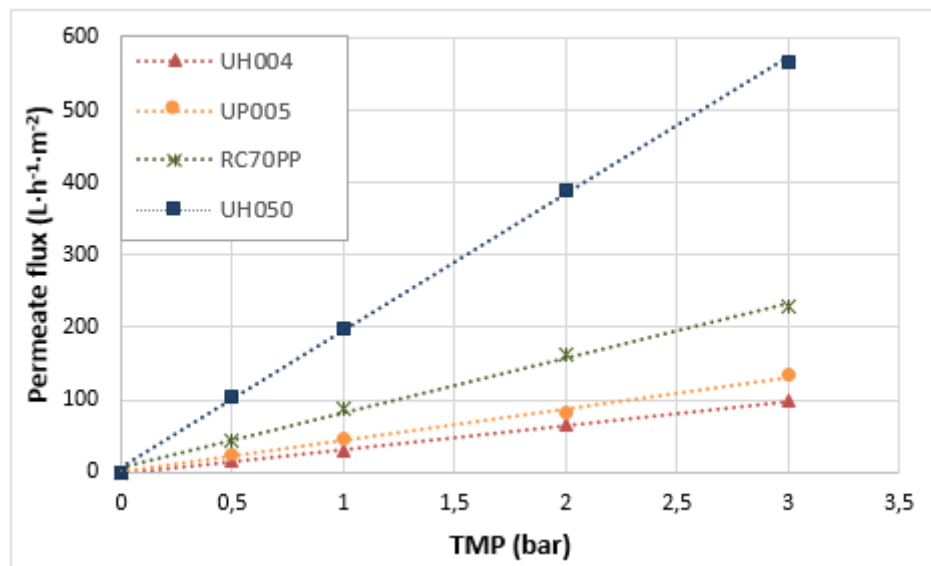


Fig. 2 Variation of permeate flux with transmembrane pressure (TMP) in the permeability tests for the different ultrafiltration membranes (osmotic water, 25°C)

With the Darcy equation (Equation 3), it was possible to estimate the hydraulic permeability for the UH004, UP005, RC70PP and UH050 membranes, which was 32.67, 44.07, 78.49 and 191.75 L·h⁻¹·m⁻²·bar⁻¹, respectively (with a regression coefficient (R^2) between 0.990 and 0.999). It was observed that the permeability value was directly related to the pore size, as expected. When water permeabilities were compared with those specified by the manufacturers (table 1), it was observed that all the experimental values were within the ranges provided (except for the UH050 membrane, whose measured permeability was slightly lower). The variability observed for the hydraulic permeability, which has been reported by different authors (Penha et al., 2015b; Sun et al., 2013), may be due to several factors, such as the total number of TMP values considered for the permeability calculation, the compaction time, the different TMP values used in the experiments, the size of the membrane pieces used for the test and the configuration of the membrane module used.

3.4 Permeate fluxes in the ultrafiltration of pretreated OOWW

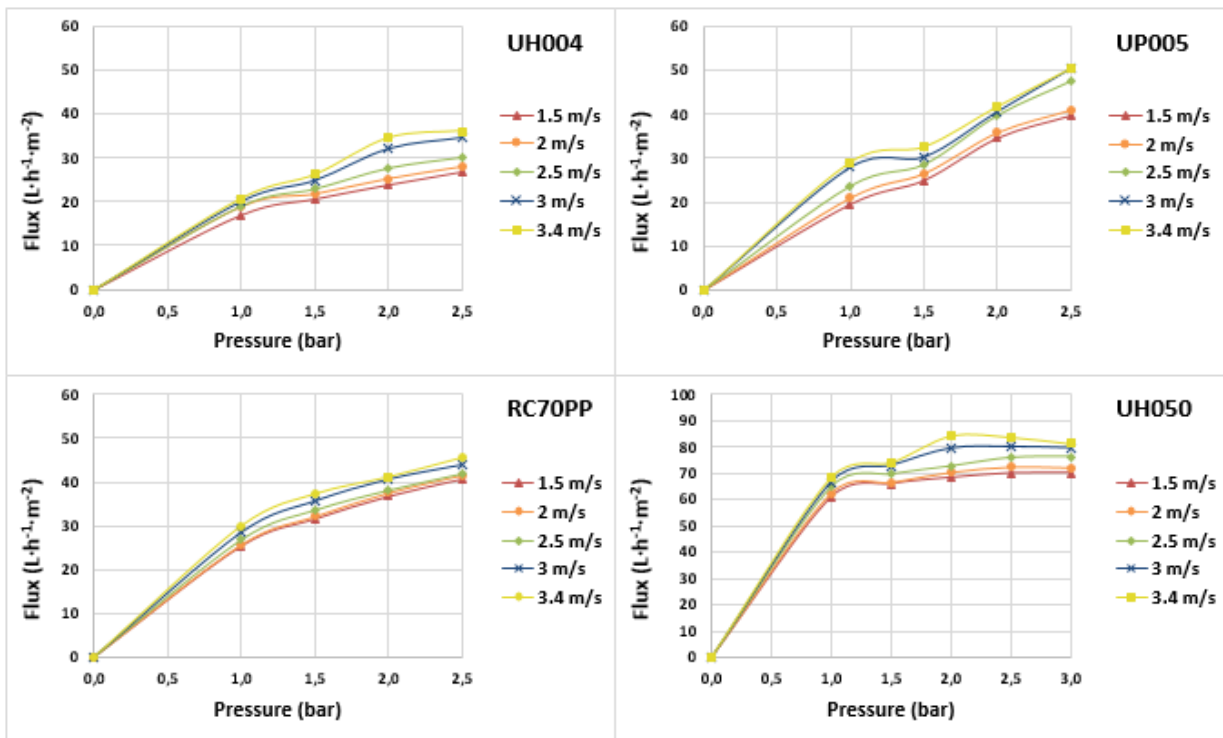


Fig. 3 Steady state permeate fluxes for the membranes tested when the pretreated wastewater was ultrafiltered at different operating conditions

Fig. 3 shows the permeate flux obtained at different operating conditions when OOWW was ultrafiltered. As it can be observed, the UH004, UP005 and RC70PP membranes exhibited a similar variation of flux with TMP, since the increase in TMP produced an increment in the permeate flux within the range considered. The UP005 membrane exhibited the most remarkable growth of flux with TMP for all the CFVs tested. Thus, at the highest TMP tested (2.5 bar) this membrane showed higher values of permeate flux than the other two, despite of having smaller pore size than the RC70PP membrane.

On the other hand, for this three membranes, permeate flux was observed to increase with CFV too. For the UH004 and UP005 membranes the increment in flux with CFV was less noticeable when the values of CFV were high (variation from 3 to 3.4 m·s⁻¹). The RC70PP membrane showed a small influence of CFV on permeate flux. Similar results were reported in a study performed by Sun, X. et al. (Sun et al., 2013). These authors tested different membranes to ultrafilter a microalgae medium, observing that when CFV increased from 3.86 m·s⁻¹ to 7.72 m·s⁻¹ under a constant TMP of 2.3 bar, the RC70PP membrane showed a less pronounced increment in flux than the other membranes tested (polysulfone membrane GR40PP and fluoro polymer membrane FS40PP, both with a MWCO of 100 kDa). These authors attributed this observation to a relatively weaker binding of the cake layer to the membrane surface and a high intrinsic resistance of the membrane ($R_m > 6 \cdot 10^{12} \text{ m}^{-1}$).

For the UH050 membrane a different performance was observed, as the variation of flux with TMP was much smaller. This may be explained by the fact that the critical transmembrane pressure was reached and therefore the linear relationship between TMP and flux was lost (Cassano et al., 2018). At TMPs higher than 2 bar a stable flux was achieved at the lowest CFVs tested, while for the 2 highest CFVs, a slight decrease in flux was observed with increasing TMP. Thus, the limiting flux was reached. Therefore, it can be considered that a gel layer was formed on the surface of the membrane. Once a gel layer is formed, an increase in the TMP does not lead to an increase in the flux, but it increases the gel layer thickness. The reduction in permeate flux when TMP increases was also observed by other authors that ultrafiltered different feed streams (Minhalma & De Pinho, 2001). The reduction in permeate flux with TMP can be due to the compaction of the gel layer. Moreover, this membrane presented the highest adsorption of phenolic compounds, as commented in section 2.2. This adsorption results in the formation of a monolayer of solutes on the surface of the membrane, representing an additional resistance for permeation (Bacchin et al., 2006). For this membrane, the increase in flux with CFV was observed too.

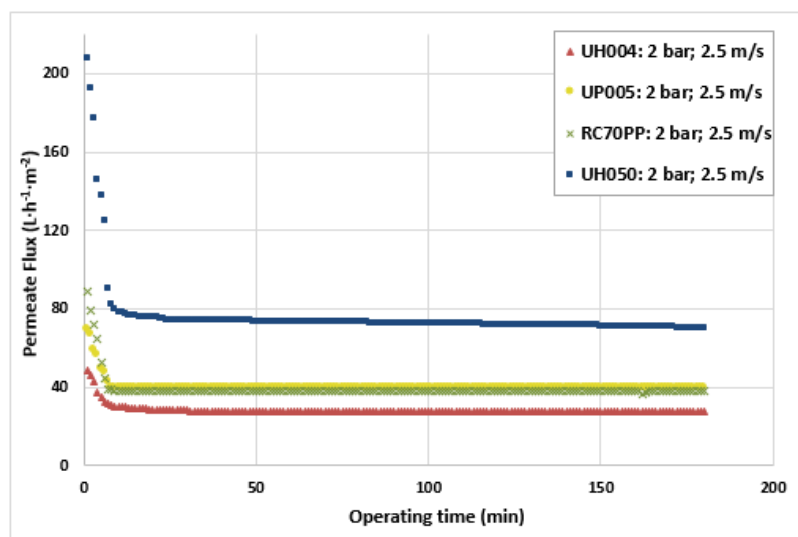


Fig. 4 Evolution of permeate flux with time for the different ultrafiltration membranes at a cross flow velocity of $2.5 \text{ m}\cdot\text{s}^{-1}$ and a transmembrane pressure of 2 bar (25°C)

The evolution of permeate flux with time at 2 bar and $2.5 \text{ m}\cdot\text{s}^{-1}$ is presented in Fig. 4. All the membranes exhibited a fast drop in the permeate flux at the beginning of the run, reaching stable values after the first minutes. The same trend was observed in all the tests carried out at the other operating conditions. The values of all of the stationary permeate fluxes were far from the permeate fluxes obtained with osmotized water (Fig. 2), indicating severe fouling. This variation of permeate flux with time, which is typical of UF processes, is due to two important effects: concentration polarization and membrane fouling. In the first minutes, a high amount of rejected particles is deposited on the membrane surface in a short time, which

results in a rapid accumulation and compaction of foulants at the membrane surface. This accumulation of particles form a mass transfer boundary layer on the surface of the membrane, increasing the filtration resistance (Ochando-Pulido, 2016). This is a particular problem in UF process, due to the presence of low and high molecular-weight solutes in the feed stream (Shi et al., 2014), appearing both of them in the OOWW too.

As expected, the UH050 membrane yielded the highest permeate flux at the beginning of the run ($208.07 \text{ L}\cdot\text{h}^{-1}\cdot\text{m}^{-2}$), followed by the RC70PP membrane ($82.59 \text{ L}\cdot\text{h}^{-1}\cdot\text{m}^{-2}$), which agreed with the corresponding molecular weight cut offs of the membranes. However, the UH050 membrane showed the greatest decrease in the permeate flux compared to the initial flux (60% - 65% reduction), presenting a slow and continuous flux decline as the operating time increased. Penha et al. (Penha et al., 2015b) observed similar results when they tested five Microdyn-Nadir membranes (including UH004, UP005 and UH050) to pretreat mixtures of macauba oil and n-hexane before solvent separation. The UH050 membrane showed the greatest decrease in flux over time (50% - 70%). This indicates that the membrane presented severe fouling. As mentioned above, this can be attributed to the larger pore size of the membrane, which favours the passage of the solutes through the pores, blocking them partially. Moreover, this membrane showed the greater affinity for the phenolic compounds according to the adsorption tests performed. It is important to note that this behaviour was observed in all the tests performed at different operating conditions and it was more noticeable at the highest TMPs. As TMP increases, the convective transport of solute molecules towards the membrane surface is greater due to the increase in the driven force. Therefore, the amount of solute molecules that reach the membrane surface is higher and membrane fouling increases, observing a greater decrease in the permeate flux. The UH004 membrane showed the smallest decrease in permeate flux during the test (42.1%), but the steady permeate flux was the lowest ($27.96 \text{ L}\cdot\text{h}^{-1}\cdot\text{m}^{-2}$).

The RCA membrane presented lower fouling than the UH050 membrane, but higher than that observed for the UP005 and UH004 membranes. Although the RCA membrane initially showed higher flux than the UP005 membrane ($82.59 \text{ L}\cdot\text{h}^{-1}\cdot\text{m}^{-2}$ vs $69.59 \text{ L}\cdot\text{h}^{-1}\cdot\text{m}^{-2}$), the steady flux was slightly higher for the UP005 ($39.65 \text{ L}\cdot\text{h}^{-1}\cdot\text{m}^{-2}$ vs $38.16 \text{ L}\cdot\text{h}^{-1}\cdot\text{m}^{-2}$), which indicates that fouling was less severe for the UP005 membrane. This could be explained by the larger pore size of the RC70PP membrane in comparison with the UP005 membrane. More particle paths are observed in membranes with higher MWCO, favouring pore blocking, which generates greater resistance to the passage of fluid. Another aspect to take into account is the hydrophilicity of this membrane, which is the highest among the tested membranes. as it shows the lowest contact angle, as commented in section 2.2. As it was also indicated in that section, several authors concluded that the affinity of phenolic compounds for membrane

materials increases when the hydrophilicity is greater (Cassano et al., 2011; Ulbricht et al., 2009). Therefore, a higher irreversible fouling could be expected for this membrane compared to the UP005 and UH004 membranes.

For all the tested membranes, the highest permeate fluxes were observed at the highest TMP and CFV tested. For the selection of the best working conditions, not only a high permeate flux should be considered, but also if this increase is significant enough to make up for the increment of the energy costs caused by increasing TMP and/or CFV. All this, together with the rejection of both COD and phenolic compounds, will provide the best operating conditions for the process.

3.5 COD and Phenolic compound rejection

First of all, it is important to mention that, in all the performed UF tests, suspended solids were completely removed for all the tested membranes, as expected. Concerning permeate colour, UF permeates presented a slight yellowish pigmentation, despite having reduced the colour between 60% and 80%, depending on the membrane and operating conditions. Fig. 5 shows the rejection of soluble COD and total phenolic compounds at the different operating conditions.

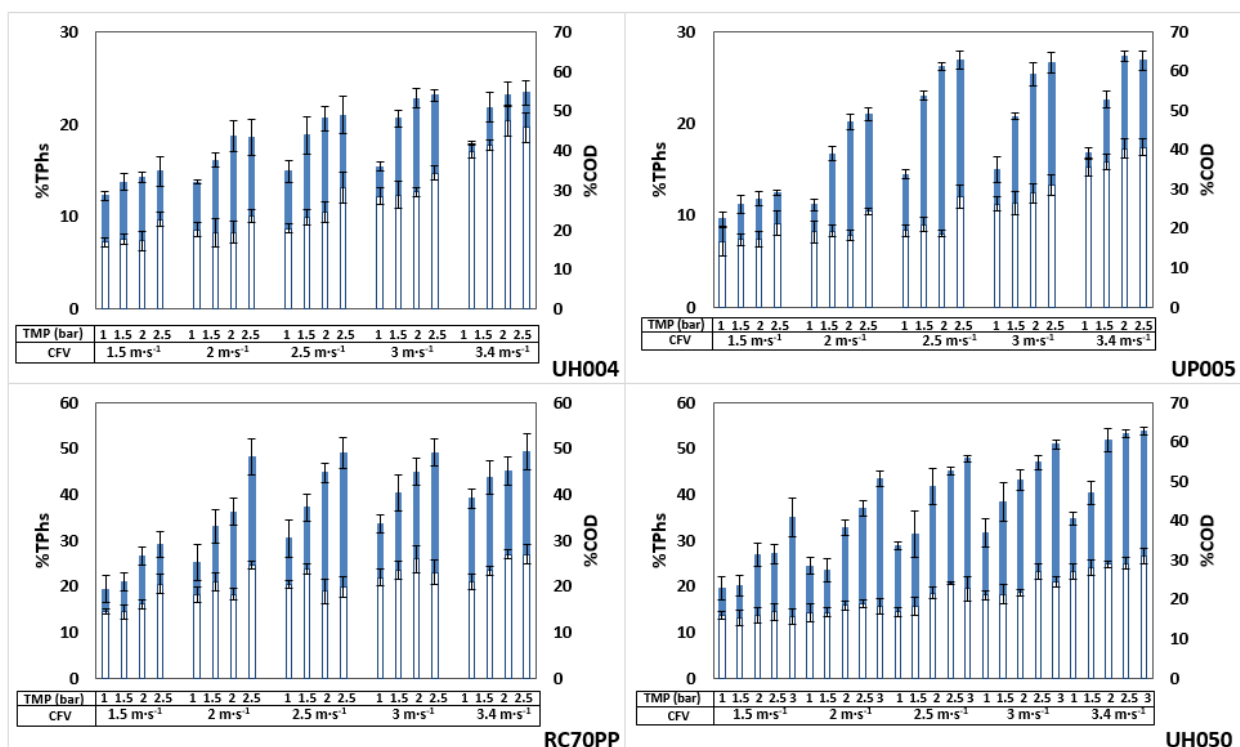


Fig 5. Steady state rejection of total phenolic compounds (white) and COD (blue), for all the ultrafiltration membranes tested at different operating conditions

In general terms, at low values of TMP and CFV, the greatest rejection of COD was observed for the UP005 and UH004 membranes, which was expected, as these membranes are the ones with the lowest MWCO. However, as TMP increased, the differences in COD removal efficiencies decreased, presenting all the membranes high percentages of COD rejection (greater than 50% in some cases). The behaviour of the UH004 and UP005 membranes was very similar, increasing COD rejection when TMP increased. Nevertheless, the influence of TMP on COD rejection became almost negligible at the highest values of CFV and TMP. In this case, the values of COD rejection at 2 and 2.5 bar were similar. The UH050 membrane presented the highest COD rejection ($62.87\% \pm 1.68$; at $3.4 \text{ m}\cdot\text{s}^{-1}$ and 3 bar), which was very similar to the highest rejection yielded by the UP005 membrane ($62.83\% \pm 1.20$; at $3.4 \text{ m}\cdot\text{s}^{-1}$ and 2 bar). The high rejection of the membrane with the highest molecular weight cut-off (UH050) is again attributed to the severe membrane fouling observed for this membrane. The high concentration of solutes in the wastewater promoted the formation of a gel layer. This layer generated an extra resistance to the passage of solutes, thus increasing the rejection of COD. The increase in COD rejection with TMP can be attributed to the increase in solvent flux with TMP, but also to the increase in membrane fouling with this parameter, as the fouling layer creates an additional filtration layer.

COD rejection was observed to increase when CFV was raised. This can be attributed to the reduction in solute concentration on the membrane surface when CFV is raised, thus increasing the observed rejection. For all the membranes, the greatest influence of CFV on COD rejection was observed when this parameter increased from 1.5 to $2 \text{ m}\cdot\text{s}^{-1}$.

Regarding the rejection of phenolic compounds, for the UH004 and UP005 membranes, it increased significantly at CFVs higher than $2.5 \text{ m}\cdot\text{s}^{-1}$. The greatest change in phenolic compounds rejection was observed by increasing the CFV from 3 to $3.4 \text{ m}\cdot\text{s}^{-1}$ for the UH004 membrane (12.69% vs 20.44% at a fixed 2 bar) and from 2.5 to $3 \text{ m}\cdot\text{s}^{-1}$ for the UP005 membrane (8.01% vs 12.46% at a fixed 2 bar). For these two membranes, the increase in TMP generated as well an increase in the rejection of phenolic compounds, as expected due to the increment in the permeate flux. The greatest increase in phenolic compounds rejection was observed when TMP was raised from 2 to 2.5 bar (8.01% vs 12.05% for the UP005 membrane and 10.54% vs 13.20% for the UH004 membrane, at a CFV of $2.5 \text{ m}\cdot\text{s}^{-1}$). However, for the RC70PP membrane, the effect of TMP and CFV on the rejection of phenolic compounds did not follow a regular trend. In addition, the influence of TMP on phenolic compounds rejection was not significant for the UH050 membrane, which is due to the fact that water permeate flux did not change with the TMP as explained in section 3.4.

Giacobbo, et al. (Giacobbo et al., 2017), also observed an increase in polyphenols rejection with increasing TMP using wine lees from the second racking as feed solution. They explained that this behaviour is attributed to the fact that the higher the TMP, the more severe the phenomena of concentration polarization and fouling is, giving rise to an additional formation of selective layers on the surface of the membrane, thus increasing the rejection coefficients. Other authors (Sanches et al., 2017) also reported increases in the retention of phenolic compounds from oil mill wastewater with the increase in TMP. In this work, despite the variations with TMP and CFV, phenolic compounds were poorly retained by the tested membranes, which indicates that most of these compounds have molecular weights lower than the MWCO of the membranes. However, the increase in TMP led to a much less marked increase in the rejection of phenolic compounds compared to the increase in CFV.

The lowest rejections of phenolic compounds occurred at the lowest values of TMP and CFV ($1.5 \text{ m}\cdot\text{s}^{-1}$ and 1 bar), being 7.11%, 7.27%, 13.83% and 14.47%, for the UP005, UH004, UH050 and RC70PP membranes, respectively. Phenolic compounds rejection for the first three membranes is in agreement with the adsorption values commented in section 3.2. The UP005 and UH004 membranes showed similar and small adsorption of phenolic compounds on the membrane surface, while it was greater for the UH050 membrane. The adsorption of phenolic compounds on the membrane could affect the values of rejection measured for these membranes. However, the RC70PP membrane presented the lowest adsorption of phenolic compounds and their rejection was the largest.

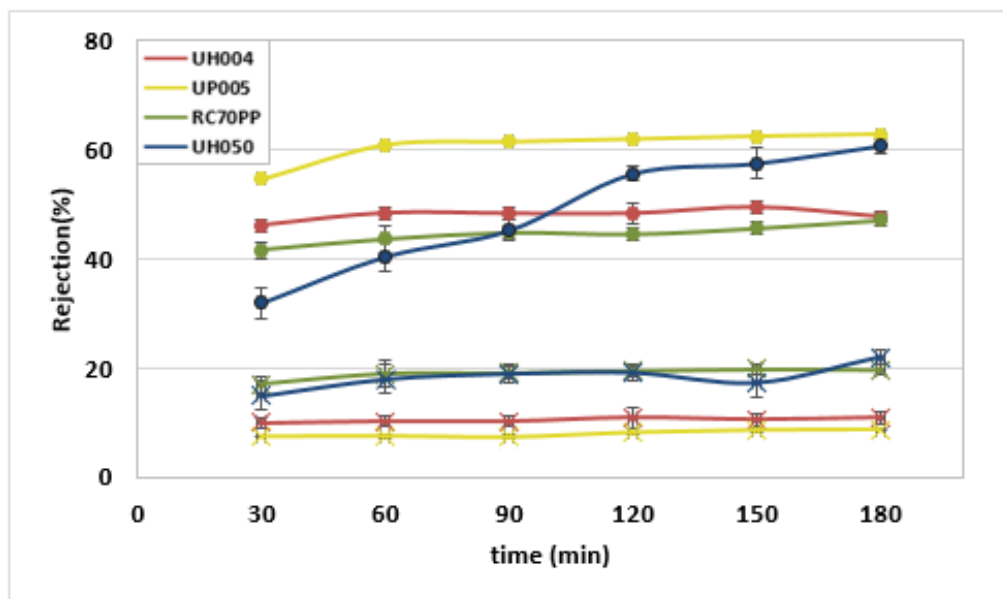


Fig. 6. Evolution of COD (•) and Total phenolic compounds (x) rejection with time for all the

membranes tested at a cross flow velocity of $2.5 \text{ m}\cdot\text{s}^{-1}$ and transmembrane pressure of 2 bar (25°C)

It is important to note that the values shown in fig. 5 are average values. The evolution of the rejection of both COD and phenolic compounds over time was also studied. Fig. 6 shows the evolution of COD and phenolic compounds rejection during the operating time for all the tested membranes at the same operating conditions ($2.5 \text{ m}\cdot\text{s}^{-1}$, 2 bar and 25°C). It can be seen that the UH004 and RC70PP membranes showed a quite stable rejection of COD over time, with a mean value of 48.05% and 44.63%, respectively. In the case of the rejection of phenolic compounds, the UH004 membrane presented a similar stable rejection with an average value of 10.50%. However, the RC70PP membrane presented a slight rejection increase of 9% in the first minutes, stabilizing after the first half hour of work with an average of value 19.01%. This could be attributed to the adsorption of phenolic compounds on this membrane as it is the more hydrophilic one (Cassano et al., 2011; Ulbricht et al., 2009). In general, this behaviour was observed at all the operating conditions tested for these membranes. For the UP005 membrane, at high TMP and CFV values, rejection increased in the first minutes and then reached a stable value. The increase in rejection can be attributed to a rapid fouling of the membrane in the first minutes of work. For the operating conditions considered in Fig. 6, the membrane showed an increase in COD rejection from 54.6% to 60.9% in the first hour, and then it stabilized at 62%. The rejection of phenolic compounds was more stable and varied between 7.4 to 8.7% throughout the test.

However, in the case of the membrane with the largest MWCO (UH050), both rejections increased during the experiment and reached the highest value at the end (rejection of 60.8% and 22.1% for COD and phenolic compounds, respectively). The increase in rejection was much greater for COD, which increased by 28.8% in 150 minutes, while the rejection of phenolic compounds increased by 7.1% in the same time period. This can be attributed to a severe fouling of the UH050 membrane. From figure 3, the formation of a gel layer on the UH050 can be assumed, as previously commented. Moreover, as this membrane has large pores, pore blocking at the beginning of the UF process could also occur. Pore blocking could be due to compounds with adequate molar mass (size similar to that of the membrane pores) or to compounds with high affinity for the membrane, as this membrane showed the greatest adsorption of phenolic compounds in the adsorption tests. As a consequence, the size of the pores could be reduced, increasing the retention. After solute adsorption, the formation of a gel layer would occur, which would further increase rejection, thereby generating an upward curve of rejection versus time. This is supported by the evolution of permeate flux versus time, which steadily decreased. As it will be commented in section 3.6, intensive cleaning protocols

were necessary to recover the initial permeability of this membrane, which also indicates severe fouling.

The best operating conditions for each membrane were selected taking into account high permeate flux, high COD rejection and low rejection of phenolic compounds. These conditions are shown in table 4.

Table 4. Best operating conditions for each membrane to obtain high permeate flux, high chemical oxygen demand rejection and low phenolic compounds rejection

Parameter	UH004	UP005	RC70PP	UH050
CFV ^a (m·s ⁻¹)	3.0	2.5	2.5	2.0
TMP ^b (bar)	2.0	2.0	2.5	3.0
Permeate Flux (L·h ⁻¹ ·m ⁻²)	32.11	39.70	42.02	72.14
%COD ^c rejection	53.28 ± 2.50	61.18 ± 0.92	49.02 ± 3.98	50.58 ± 1.98
%TPhs ^d rejection	12.69 ± 0.50	8.01 ± 0.36	19.82 ± 0.90	15.59 ± 1.68

^a CFV: cross flow velocity

^b TMP: transmembrane pressure

^c COD: chemical oxygen demand

^d TPhs: Total phenolic compounds

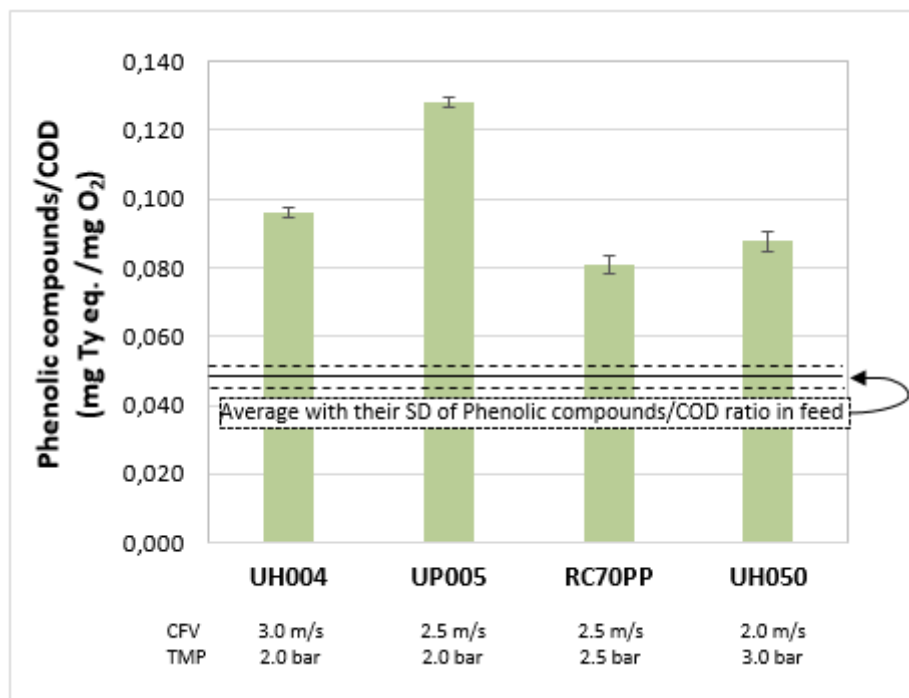


Fig 7. Phenolic compounds/chemical oxygen demand (COD) ratio in the permeate streams at the best operating conditions for each membrane

All the membranes showed good results in terms of low phenolic compounds retention with a significant decrease in the amount of organic matter in the permeate in comparison with the feed stream. Figure 7 shows the phenolic compounds/COD ratio in the permeate streams at the best operating conditions for each membrane. In all the cases the ratio was greater than

that in the feed, which indicates that the permeate was enriched in phenolic compounds. The UP005 membrane presented much higher permeate ratio (0.128 mgTyeq/mgO₂) than the rest of the membranes. In previous works (Carbonell-Alcaina et al., 2018) the UP005 membrane was compared to the UH030 membrane (Mycrodin nadir, Germany) to recover phenolic compounds from a residual brine from table olive production. The authors also obtained the best results with the UP005 membrane, but the ratio phenolic compounds/COD in permeate was lower (0.105 mgTyeq/mgO₂). The difference may be due to the different wastewater used. The phenolic compounds/COD ratios reached in the permeate are also higher than those reported by Casano et al. (Cassano et al., 2011). In their study, they tested four different membranes (two from PESH and two from RC) in the treatment of OMW. They observed that the RC, C010F membrane (Microdyn-Nadir, Germany) presented the greatest increase (approximately 1.2 times) in the ratio compared to the feed (permeate ratio 0.142 vs feed ratio 0.118, approximate data). In our case, all the membranes achieved greater increases in the phenolic compounds/COD ratio, achieving 2.14 times the feed ratio with the best membrane (UP005). It is important to highlight that the results obtained with the UP005 membrane are very good and promising in view of the recovery of the phenolic compounds, since a great separation of them with respect to other organic compounds present in the wastewater was achieved, making the permeate highly enriched in phenolic compounds with small rejection of these compounds.

3.6 Cleaning results

After each test, the membranes were cleaned following the procedures previously described in section 2.4. Fig. 8 shows the average recovery of the hydraulic permeability of the membranes with regard to the permeability measured for the pristine membrane.

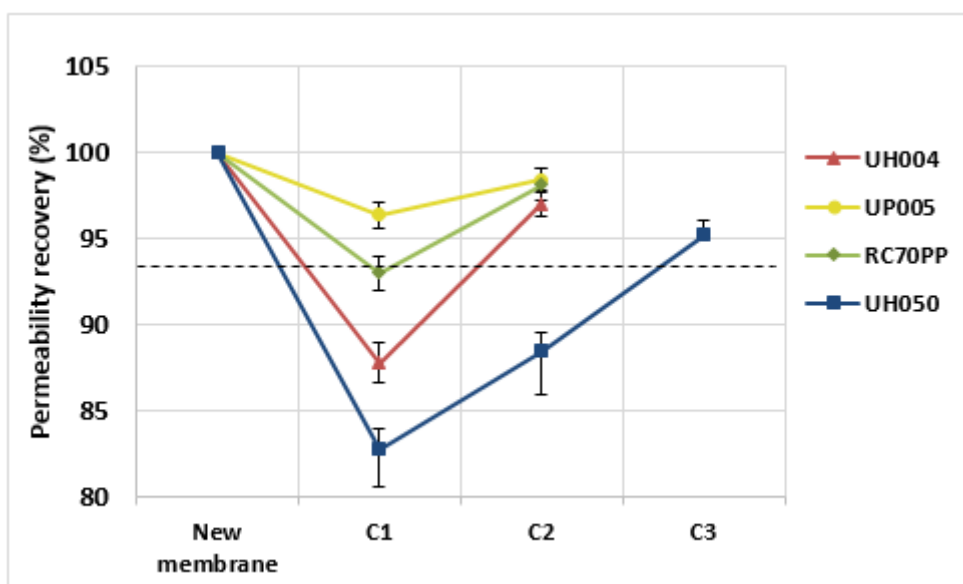


Fig 8. Average recovery of initial pure water permeability after the different cleaning protocols for the different tested membranes. C1: water at 25°C, C2: water at 35°C and C3: chemical cleaning with P3 Ultrasil 115 (1%) at 25°C

Except for the UH050, all the membranes were cleaned efficiently by means of a simple water rinsing, recovering at least 95% of the initial permeability (minimum value assigned to consider a membrane to be clean). The UP005 membrane only needed the first cleaning method (water rinsing at room temperature) to achieve a permeability recovery of $96 \pm 0.85\%$ for all the ultrafiltration tests performed at the different operating conditions tested. The cleaning protocol C2 was also tested to evaluate if greater recovery was achieved, reaching a $98.4 \pm 0.64\%$ average permeability recovery. These results confirmed the low fouling observed for this membrane, since a linear increase in flux with increasing PTM was observed for all the CFVs tested (Fig. 3). It also presented a stable permeate flux over time without a great difference compared to the initial flux (Fig. 4).

The RC70PP and UH004 membranes achieved a permeability recovery greater than 95% when they were cleaned with water at 35°C. This indicates that fouling was not severe. However, the UH050 membrane required the third cleaning method (C3), which involves chemical cleaning, to recover the permeability. The result was expected as this membrane presented the greatest adsorption towards phenolic compounds, the greatest decline in permeate flux with time (Fig. 4) and a progressive increase in rejection with time (Fig. 6). All this implies a severe fouling of the membrane and a greater difficulty to recover the membrane permeability.

Taking into account all the results commented, it can be established that the UP005 membrane was the one that presented the best results. This membrane exhibited the lowest

rejection towards phenolic compounds (8%), a high rejection of COD (61%), a stable value of permeate flux ($40 \text{ L}\cdot\text{h}^{-1}\cdot\text{m}^{-2}$) and it was easily cleaned.

4. Conclusions

In the present work, four UF membranes (UH004, UP005, RC70PP and UH050) were compared to ultrafilter pre-treated wastewater from olive oil production with the aim of obtaining a permeate enriched in phenolic compounds. Permeate flux decreased rapidly over time during the first few minutes of operation for all the membranes and operating conditions tested, which is indicative of membrane fouling. The UH050 membrane showed the greatest decrease in flux with time (60% -65%) due to the larger pore size and also to the highest adsorption of phenolic compounds observed onto the membrane material ($0.463 \pm 0.004 \text{ mg}\cdot\text{m}^{-2}$). The lowest flux decline (42%) was observed for the UH004 membrane. This membrane also presented the lowest value of steady-state permeate flux ($27.96 \text{ L}\cdot\text{h}^{-1}\cdot\text{m}^{-2}$), as it has the lowest pore size.

The UH004, UP005 and RC70PP membranes exhibited a similar influence of TMP on the flux, presenting a linear increase in the permeate flux with increasing TMP. The UP005 membrane exhibited the most remarkable flux growth with TMP for all CFVs tested. The permeate flux for the UH050 membrane was more influenced by CFV than by TMP, since the limiting flux was reached at 2 bar.

All the membranes were able to effectively remove suspended solids, colour, and COD, while the rejection of phenolic compounds was low. The highest rejection of COD ($62.87\% \pm 1.09$) was obtained with the UH050 membrane at a CFV of $3.4 \text{ m}\cdot\text{s}^{-1}$ and 3 bar of TMP, and the lowest rejection of phenolic compounds ($7.1\% \pm 1.55$) was obtained with the UP005 membrane at a TMP of 1 bar and a CFV of $1.5 \text{ m}\cdot\text{s}^{-1}$. This last membrane presented the best performance, with a COD rejection of 61.18% and a phenolic compounds rejection of 8.01% ($2.5 \text{ m}\cdot\text{s}^{-1}$ CFV and TMP of 2 bar). It should be noted that all the membranes were able to enrich the permeate in phenolic compounds; obtaining ratios of phenolic compounds/COD between 1.5 to 2.1 times greater than the ratio in the feed.

The greater fouling of the UH050 membrane was confirmed by the cleaning protocol, since this membrane required a chemical cleaning with P3 Ultrasil 115 (1% v/v) to restore the initial water permeability, while the rest of the membranes were cleaned with a simple water rinsing. The UP005 membrane managed to recover its permeability by more than 95% just by cleaning with water at 25°C , confirming that this membrane suffered the least severe fouling, which can be related to the lowest hydrophilicity of the membrane material.

As the objective of this work was to select the membrane that presented the highest removal of organic matter without affecting the concentration of phenolic compounds (minimum rejection of phenolic compounds) with a high value of permeate flux and easy to clean, the UP005 membrane was observed to be the best option as a pretreatment for the recovery of phenolic compounds from this type of wastewater.

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