



Green management of wet olive pomace by means of ultrafiltration of an aqueous extract of phenolic compounds

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ABSTRACT

Wet olive pomace is a major by-product generated by olive mills. To contribute to the circular economy of the olive industry, the recovery of interesting compounds from wet olive pomace was assessed. To that end, a previously optimized solid-liquid extraction, only employing water as the extractant, was first applied to the wet olive pomace. Afterwards, an ultrafiltration process to treat the obtained extract was developed. Several membranes (UP005, UH030, UH050, and UP150, from Microdyn Nadir) were studied, in a wide range of cross-flow velocities (1.5–3.5 m/s) and transmembrane pressures (0.75–5.5 bar). By a thorough characterization of the ultrafiltration streams by LC-ESI-QToF-MS, it was possible to describe the evolution of the rejection of 29 phenolic compounds. Some adsorption processes were also observed in the ultrafiltration process. The UP005 and UH030 membranes displayed satisfactory values of permeate flux and rejection. Both membranes efficiently retained a high fraction of the total solids, chemical oxygen demand, and color. On the contrary, the phenolic compounds were obtained in the ultrafiltration permeate, which constitutes a source of antioxidant molecules with applications in cosmetics, pharmacy, and nutraceuticals.

1. Introduction

The current worldwide situation regarding water shortage along with the vast, daily generation of residues, underlines more than ever the necessity of implementing the principles of circular economy in all industries. In particular, the ecological footprint of the agri-food industry is highly relevant (Cazcarro et al., 2015; Kumar and Chakabarti, 2019), considering the spread of intensive agriculture in order to supply the growing population. One of the most important food industries is related to the production of virgin olive oil. According to the estimations of the International Olive Council, the world production of olive oil surpassed 3 million tons during the crop year 2021/2022 (International Olive Council, 2023).

In the Mediterranean area, the majority of the olive mills apply the two-phase methodology. This is known for lower water consumption and higher extraction efficiency than the alternative method, which is the three-phase method (Sygouni et al., 2019). After the application of the two-phase method, wet olive pomace is produced. It is a semi-solid past containing all the remnants of the olive drupes after the olive oil extraction. This includes the olive pulp, skin, stone, seeds, and vegetation water. As a result, the organic load

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of this by-product is very high. Interestingly, many phenolic compounds from the olive fruit remain in the wet olive pomace (Sciubba et al., 2020). This residue has a dual character. On one side, the phytotoxicity of the biophenols is a threat to the environment if the disposal of wet olive pomace is not taken seriously (Caporaso et al., 2018). On the other side, wet olive pomace can be considered a source of antioxidant molecules with applications in cosmetics, pharmacy, and nutrition (Caporaso et al., 2018; Miralles et al., 2014; Roselló-Soto et al., 2015).

Therefore, the recovery of phenolic compounds from wet olive pomace permits its valorization and contributes to the circular economy of the olive oil sector. This objective can be addressed by membrane technology. Several research groups have demonstrated the feasibility of membrane processes to purify or concentrate phenolic compounds from olive residues (Bottino et al., 2020; Cassano et al., 2013; Cifuentes-Cabezas et al., 2021; Saf et al., 2022). However, the results available in the literature are mainly referred to liquid streams, both from the two-phase and the three-phase methodology. Therefore, the conclusions achieved by these valuable contributions cannot be directly correlated with the treatment of wet olive pomace.

Wet olive pomace is the most challenging olive waste when it comes to the treatment by membrane technology. The two-phase process is the most popular methodology for producing olive oil and its implementation increases every year (Silvestri et al., 2021). However, the research about the most abundant olive mill by-product is by far less common than the studies dealing with the olive mill wastewater obtained in the three-phase process, or with olive oil washing wastewater. To recover the phenolic compounds from wet olive pomace, a solid-liquid extraction has to be performed in advance and, as a result, a liquid extract with dark color and high organic load is obtained. This extraction can be performed using an organic solvent (such as ethanol, and mixtures of ethanol and water) as the extractant agent. In this case, previous studies have demonstrated that a high content of biophenols, surpassing 9 mg/kg of wet olive pomace, can be obtained. Also, the extraction of phenolic compounds can be addressed only with water, reaching around 6 mg/kg (Sánchez-Arévalo et al., 2022; Sygouni et al., 2019). In this case, the recovery can be slightly lower, but important advantages are derived instead. First of all, avoiding the organic solvent means a lower environmental impact. Secondly, the cost of the process is reduced if only water is needed. This premise is especially relevant if an industrial approach is considered, as large volumes of the extractant will be needed. And thirdly, obtaining an aqueous extract may imply a benefit for the subsequent treatment of the stream. In the case of a membrane process, the presence of an organic solvent in the feed solution may represent an additional challenge to consider, due to a possible modification of the membrane structure, affecting its permeation characteristics. Therefore, employing water as the extractant agent during the solid-liquid extraction is an efficient strategy to simplify the process. Furthermore, replacing the organic solvent contributes to reduce the impact of the process and its environmental repercussion. Moreover, being all the streams water-based, conventional materials (not specific for the treatment of organic solvents) can be employed, both for the selected membranes and for the conductions and elements of the processing plant. In consequence, the combination of an aqueous solid-liquid extraction with membrane technology contributes to develop a green process to manage wet olive pomace. Through its application, several of the Sustainable Development Goals (SDGs) adopted by the United Nations Organization can be addressed. These include SDG 9 (Industry, Innovation, Infrastructure), as innovative techniques can be implemented in the olive oil sector, SDG 12 (Responsible Consumption and Production), through the fostering of the circular economy and minimization of the environmental impact of this industry, and SDG 13 (Climate Action), as the utilization of wet olive pomace as a source of valued compounds reduces the volume of final by-products in the olive mill.

The result of the mentioned extraction is a highly foulant stream, containing the polyphenols of interest and many other molecules that are inevitably extracted as well, hindering the purification of the target molecules (Sánchez-Arévalo et al., 2022). In this context, the selection of the most appropriate membrane is not direct, because the severe fouling that may affect the membrane will influence its productivity and the rejection values (Sánchez-Arévalo et al., 2023). The membrane pore size is a key characteristic to consider. Normally, a higher pore size can result in higher values of permeate flux. However, when a complex feed solution is treated (as in the case of a vegetal extract), membranes with a higher pore size may be more susceptible of suffering from pore blocking and inter-pore fouling (Guo et al., 2014; Mah et al., 2012; Tomczak and Gryta, 2023), then resulting in a lower productivity of the process. The operating conditions are also of high relevance. In the case of transmembrane pressure (TMP), higher values will commonly conduct to a higher permeate flux, as it is the driving force of the process. However, the organic load of the feed solution may lead to the contrary effect, as the relationship between TMP and permeate flux is not linear due to concentration polarization (Cifuentes-Cabezas et al., 2021). As the driving force increases, the convective transport of solute molecules towards the membrane surface increases too and, if a certain concentration is reached, a gel layer may be formed on the membrane surface. Once this layer is formed, a further increase in the TMP does not result in an increase in the permeate flux, but it causes a growth of the gel layer thickness (Bacchin et al., 2006). In this context, the fabrication of new membranes less affected by fouling is essential, and the scientific community is becoming more and more aware of the importance of this task (Eryildiz et al., 2023; Wang et al., 2022; Wibisono et al., 2023; You et al., 2023). However, the new membranes that are currently being developed at a laboratory scale are still not available for the industry and cannot be considered yet for their implementation in the circular economy of the olive mills. Thus, it is essential to study the commercial membranes that are right now on the market and investigate their viability to work with a problematic residue such as the wet olive pomace.

In this work, we have focused on the management of a concerning by-product, whose treatment is not abundant in the literature. We have proposed its processing through solid-liquid extraction and ultrafiltration, which is a novel approach. To that end, several commercial ultrafiltration membranes were studied. The productivity and efficiency of the membranes have been assessed, in order to select the most appropriate strategy to purify the phenolic compounds present in aqueous extracts of wet olive pomace. Furthermore, the cleaning of the membranes was studied, to explore their reusability.

2. Materials and methods

2.1. Extract of wet olive pomace

The samples of wet olive pomace were collected from the olive mill San Isidro de Segorbe (Castellón, Spain), which applies the two-phase methodology. Samples were stored at 5°C before their processing. In order to extract the phenolic content from wet olive pomace, an ultrasound-assisted solid-liquid extraction was accomplished for 45 min at 40°C. The sonication was performed at 37 kHz and 220 W. 600 g of wet olive pomace were treated, applying a solid/solvent ratio of 1:10. Only osmotized water was employed as a solvent. Later, the obtained extracts were centrifuged at 17200 RCF for 6 min to remove the olive stone and seed remnants. This procedure was developed in a previous work (Sánchez-Arévalo et al., 2022).

After the ultrasound-assisted solid-liquid extraction, the obtained extracts were characterized in terms of phenolic content (which are the compounds of interest) and amount of organic matter, which should be reduced as much as possible during the following ultrafiltration process. In order to avoid the degradation of the different compounds in the extracts or their biological contamination, the extract (ultrafiltration feed) was periodically renovated. In total, three extractions were performed. The composition of each extract and the corresponding operating conditions of its processing are detailed in Table 1.

As shown in Table 1, the organic load of the extracts of wet olive pomace is high. This supports the application of an ultrafiltration process for retaining a high percentage of the organic matter, while phenolic compounds are aimed to be recovered in the permeate stream.

2.2. Ultrafiltration

The ultrafiltration plant was equipped with a Rayflow membrane module (Orelis Environnement, France), where a flat sheet membrane was placed. The membrane area was 129 cm². Four commercial membranes (Microdyn Nadir, Germany) were tested, at three different cross-flow velocities (1.5, 2.5, and 3.5 m·s⁻¹) and a wide range of transmembrane pressure (0.75 – 5.5 bar). All the employed membranes were purchased from the same manufacturer, and all of them were made of polyethersulfone. However, some of them have undergone a treatment on their surface to make them more hydrophilic. This was the case of the UH030 membrane, with a 30 kDa molecular weight cut-off (MWCO), and the UH050 membrane, with a 50 kDa MWCO. Apart from them, the UP005, with a 5 kDa MWCO, and the UP150 membrane, with a 150 kDa MWCO, were employed. Before the processing of the wet olive pomace extracts, the membranes were immersed in osmotized water overnight, to hydrate them and remove the residual conservatives. Afterwards, they were compacted (at the highest transmembrane pressure of the applied operating conditions) and characterized through the determination of their water permeability (Sánchez-Arévalo et al., 2023).

Six liters of wet olive pomace extract were treated with each membrane. Both the retentate and the permeate streams were

Table 1

Characterization of the organic matter present in the aqueous extracts of wet olive pomace employed as feed for the ultrafiltration process. The operating conditions at which each extract was treated are also detailed.

Parameter	Value	Operating conditions	Employed membranes
Phenolic content (mg/L extract)	523 ± 3	1.5 m·s ⁻¹	UP005, UH030, UH050, UP150
COD ¹ (mg/L)	9200 ± 364	0.75 – 5.5 bar	
Total solids (mg/mL)	7.6 ± 0.5		
Color coefficient	1.7 ± 0.5		
Conductivity (µS/cm)	1675 ± 17		
pH	5.13 ± 0.07		
Phenolic content (mg/L extract)	633 ± 22	2.5 m·s ⁻¹	UP005, UH030
COD ¹ (mg/L)	14,985 ± 2019	0.75 – 4.5 bar	
Total solids (mg/mL)	7.0 ± 1.0		
Color coefficient	2.42 ± 0.02		
Conductivity (µS/cm)	1721 ± 62		
pH	5.04 ± 0.02		
Phenolic content (mg/L extract)	637 ± 24	3.5 m·s ⁻¹	UP005, UH030
COD ¹ (mg/L)	11,688 ± 548	0.75 – 5.5 bar	
Total solids (mg/mL)	7.3 ± 0.3		
Color coefficient	2.484 ± 0.003		
Conductivity (µS/cm)	1699 ± 32		
pH	5.02 ± 0.01		
Parameter	Mean Values		
Phenolic content (mg/L extract)	598 ± 65		
COD (mg/L)	11,957 ± 2902		
Total solids (mg/mL)	7.2 ± 0.5		
Color coefficient	2.2 ± 0.4		
Conductivity (µS/cm)	1698 ± 23		
pH	5.06 ± 0.06		

1 Chemical oxygen demand

recirculated to the feed tank, to keep the concentration in the feed solution constant. Samples of 50 mL were collected from the feed and the permeate streams to be analyzed and determine the rejection of solutes. This rejection (R) was calculated according to the following formula:

$$R = 1 - \frac{C_p}{C_f} \cdot 100 \quad (1)$$

where C_p refers to the concentration in the permeate and C_f refers to the concentration in the feed.

The membranes were cleaned after each experiment, in order to start the next one with a clean membrane. Afterwards, the hydraulic permeability was tested, aiming to recover at least 90% of the initial permeability of the membranes to consider them properly cleaned. To clean the membranes, several chemical cleaning protocols were employed, as reflected in Table 2.

A solution of P3 Ultrasil 115 (Ecolab, USA) at 1% (v/v) was applied for 1 h after a first rinsing (15 min) with tap water, at ambient temperature. Afterwards, a water rinsing was again applied, at ambient temperature, to remove the detergent from the ultrafiltration plant. Finally, the membrane was rinsed with osmotized water. In order to reduce the water consumption during this study, the water employed for the second membrane rinsing was kept and employed during the following cleaning cycle in the plant, as the water for the first rinsing. During the application of Ultrasil, the temperature had to be raised in some cases, in order to increase the cleaning efficiency. The membranes were considered to be clean when a water permeability recovery higher than 90% was obtained. In the case of the UP150 membrane, the water permeability was not recovered with the detergent solution, at any of the tested temperatures. Other alternatives were tested, such as a solution of P3 Ultrasil 110 (Ecolab, USA) at 1% (v/v) and a solution of sodium hypochlorite at 200 mg·L⁻¹. However, the UP150 membrane could not be reused.

2.3. Analytical methods

2.3.1. Analysis of the olive minor fraction

The analytes corresponding to the olive minor fraction were determined by liquid chromatography coupled to mass spectrometry (LC-MS), employing an Agilent 1290 Infinity II liquid chromatograph (Agilent Technologies, USA). The mass spectrometer was equipped with electrospray ionization (ESI) and a 6546 quadrupole-time-of-flight (QToF) mass analyzer (Agilent Technologies, USA). The injection volume was 4 µL. To separate the compounds, a Zorbax Extend C18 column (4.6 × 100 mm, 1.8 µm) (Agilent Technologies, USA) was used, working at 40 °C and a flow rate of 0.9 mL·min⁻¹. Ultrapure water and acetonitrile (Honeywell, USA) were the mobile phases, both acidified with 0.5% of acetic acid (v/v). The LC gradient and MS conditions (with a negative ionization) were adapted from a previous work (Sánchez-Arévalo et al., 2022).

2.3.2. Analysis of organic matter

Chemical oxygen demand (COD) of the samples was assessed through commercial kits (Merck, Germany). The analysis of total solids was performed by evaporating a determined volume of the samples and calculating the difference in the weight of the container before and after the evaporation. Finally, to determine the color, the absorbance of the samples at different wavelengths was measured with a UV-VIS DR 6000 spectrophotometer (Hach Lange, Germany). The color coefficient was given by the following formula (UNE-EN ISO, 2012 Method B):

$$\text{Colour coefficient} = \frac{(A_{436}^2 + A_{525}^2 + A_{620}^2)}{(A_{436} + A_{525} + A_{620})} \quad (2)$$

Where A_{436} is the absorbance of the sample at 436 nm, A_{525} is the absorbance at 525 nm and A_{620} is the absorbance at 620 nm.

Table 2
Cleaning protocol applied to each membrane employed in this work.

Membrane	Cleaning protocol	
	Cleaning agent	Temperature
UP005 (after working at 0.75, 1.5 and 2.5 bar)	P3 Ultrasil 115 at 1% (v/v)	25 °C
UP005 (after working at 3.5, 4.5 and 5.5 bar)	P3 Ultrasil 115 at 1% (v/v)	35 °C
UH030	P3 Ultrasil 115 at 1% (v/v)	40 °C
UH050	P3 Ultrasil 115 at 1% (v/v)	35 °C
UP150	P3 Ultrasil 115 at 1% (v/v)	40 °C
	P3 Ultrasil 110 at 1% (v/v)	40 °C
	NaClO at 200 mg·L ⁻¹ (v/v)	40 °C

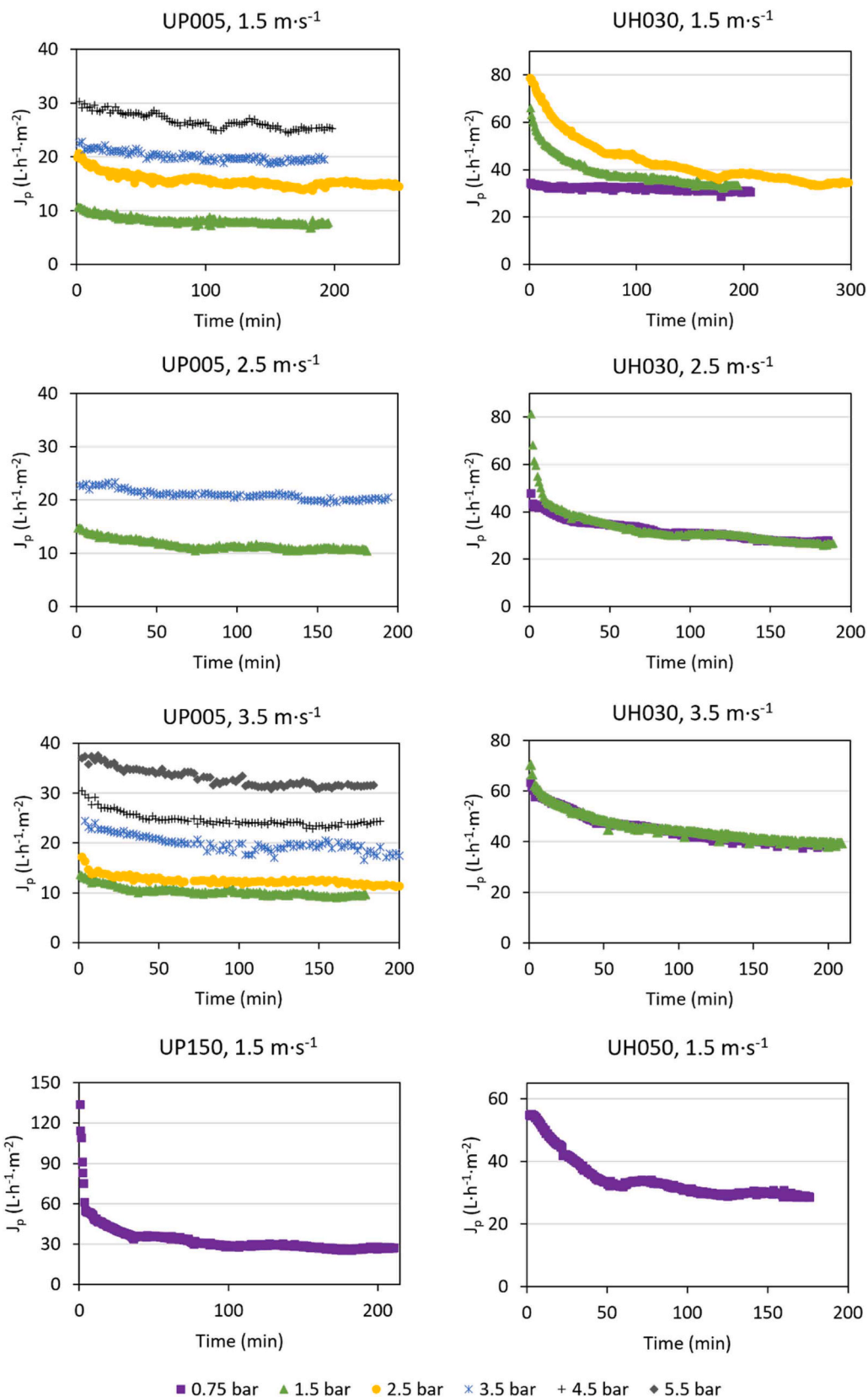


Fig. 1. Evolution of permeate flux with time, at the different operating conditions, for the UP005, UH030, UH050, and UP150 membranes.

3. Results and discussion

3.1. Permeate flux

Once the membranes were compacted, their water permeability was calculated, obtaining $13 \pm 2 \text{ L}\cdot\text{h}^{-1}\cdot\text{m}^{-2}\cdot\text{bar}^{-1}$, $168 \pm 12 \text{ L}\cdot\text{h}^{-1}\cdot\text{m}^{-2}\cdot\text{bar}^{-1}$, $213 \pm 18 \text{ L}\cdot\text{h}^{-1}\cdot\text{m}^{-2}\cdot\text{bar}^{-1}$ and $228 \pm 14 \text{ L}\cdot\text{h}^{-1}\cdot\text{m}^{-2}\cdot\text{bar}^{-1}$ for the UP005, UH030, UH050, and UP150 membranes, respectively. This data was consistent with the MCWO of the membranes, as the permeability increased with higher values of MCWO. Also, the obtained permeabilities were in line with the manufacturers' specifications and previous works dealing with some of these membranes (Cifuentes-Cabezas et al., 2021; Sánchez-Arévalo et al., 2023).

Afterwards, the aqueous extract of wet olive pomace was treated in the ultrafiltration plant. The results regarding the permeate flux obtained at the different operating conditions are shown in Fig. 1.

When comparing the tests performed at the same pressure, it can be observed that the membranes with larger pore size (UH030, UH050, and UP150) presented greater permeate flux at the beginning of the process. However, these membranes displayed a more drastic drop of the permeate flux with time. After a certain time period, the permeate flux decreased slowly until a steady state was reached. The difference in flux drop is especially notable if the flux of the UH030 and UP005 membranes is compared at 1.5 and 2.5 bar (Fig. 1). This trend in the evolution of permeate flux with time is normally found in ultrafiltration processes (Luján-Facundo et al., 2013) and can be attributed to cake layer formation and pore blocking. As reflected in Table 1, the aqueous extract of wet olive pomace contains a high COD and a high concentration of total solids, which supports the formation of the cake layer and the membrane fouling phenomenon. As the UP005 membrane is tight, the initial permeate flux is low and the convective transport of solutes towards the membrane surface is smaller than for the rest of the membranes. Therefore, it was less affected by concentration polarization and fouling. In consequence, permeate flux decline was less pronounced. Furthermore, its lower pore size can prevent the inter-pore fouling, prompted by the organic molecules from the extract of wet olive pomace, more efficiently (Mah et al., 2012). Another reason that prevented the fouling of the UP005 membrane is the polarity of the active layer. It has been demonstrated that membranes with lower hydrophilicity are less fouled when feeds containing polyphenols are treated (Cai et al., 2018; Sánchez-Arévalo et al., 2023). Then, the UP005 membrane combined a small pore size and a less hydrophilic active layer, reducing the fouling of this membrane. Fig. 1 suggests that fouling was more severe for the membranes with larger MWCO and it was more relevant at higher pressures, because a faster drop of the flux was displayed. This was prompted by the higher concentration of solutes at the membrane surface occurring at higher pressures. Considering the pore size of the UH050 and UP150 membranes and the permeate flux that was observed at the steady state, a severe fouling can be inferred for these membranes. Corbatón-Báguena et al. and Qu et al. found that membranes with large pore diameter, and close to that of the solutes present in the feed solution, suffered a more severe fouling and poor recyclability due to pore constriction, as a result of the solutes penetrating the membrane pores and blocking them (Corbatón-Báguena et al., 2014; Qu et al., 2014). Therefore, no further transmembrane pressures were tested for the UH050 and UP150 membranes, as the fouling was expected to increase at higher pressures. In the particular case of the UH050 membrane, the rejection values that were obtained for this membrane also discouraged its utilization, as will be commented in Section 3.2.

When the flux at the steady state was plotted against the transmembrane pressure (Fig. 2), the low fouling of the UP005 membrane was confirmed. When the transmembrane pressure was increased, the permeate flux exhibited by this membrane increased linearly too, even at 3.5, 4.5, and 5.5 bar, which can be considered high pressures for an ultrafiltration process. However, the opposite was found for the UH030 membrane. When the pressure was increased from 0.75 to 1.5 bar, the flux at the steady state remained constant, suggesting the formation of a gel layer on the surface of the UH030 membrane. For this membrane, the limiting pressure was 0.75 bar (Aimar and Field, 1992; Field and Aimar, 1993) and, beyond that value, the applied TMP did not influence the permeate flux.

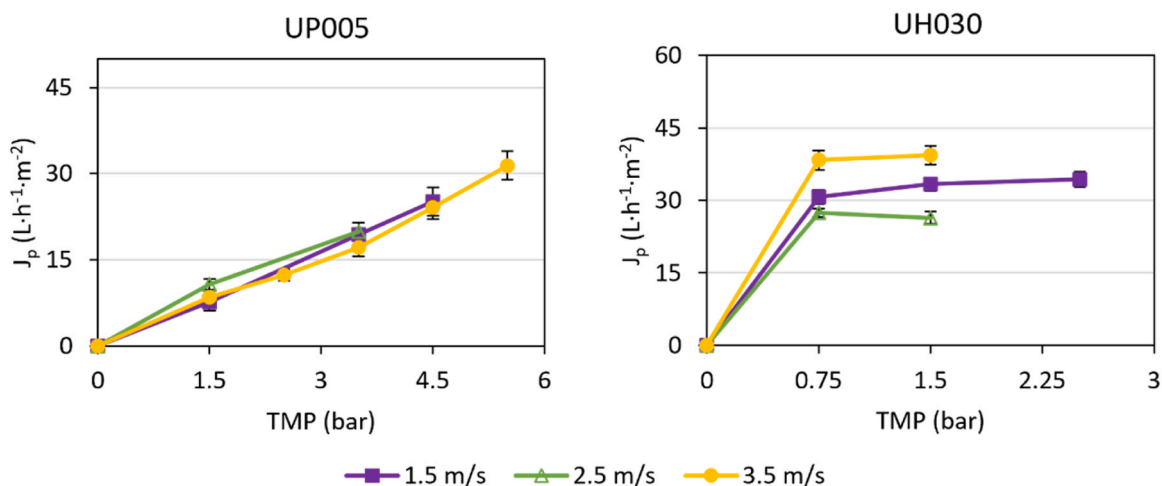


Fig. 2. Permeate flux at the steady state for the UP005 and UH030 membranes, at the different operating conditions.

The effect of the cross-flow velocity was also evaluated. However, the influence of this parameter on the permeate flux was much less important than the transmembrane pressure. Regarding the UP005 membrane, the modification of the cross-flow velocity did not derive in an increase of the permeate flux. This can be attributed to the low fouling that was suffered by this membrane. In that situation, the softer turbulence achieved by the lowest cross-flow velocity ($1.5 \text{ m}\cdot\text{s}^{-1}$) was already sufficient and the increment of the tangential velocity did not lead to any benefit in the productivity of the process. In fact, at $2.5 \text{ m}\cdot\text{s}^{-1}$, pressures higher than 2.5 bar were not tested, because the obtained permeate flux was very similar to the permeate flux obtained at $1.5 \text{ m}\cdot\text{s}^{-1}$ and the increase in energy investment was not considered to be necessary. In the case of the UH030 membrane, the fouling was more relevant. As expected, the greatest permeate flux was achieved at the highest cross-flow velocity ($3.5 \text{ m}\cdot\text{s}^{-1}$). At this high velocity, the diffusive

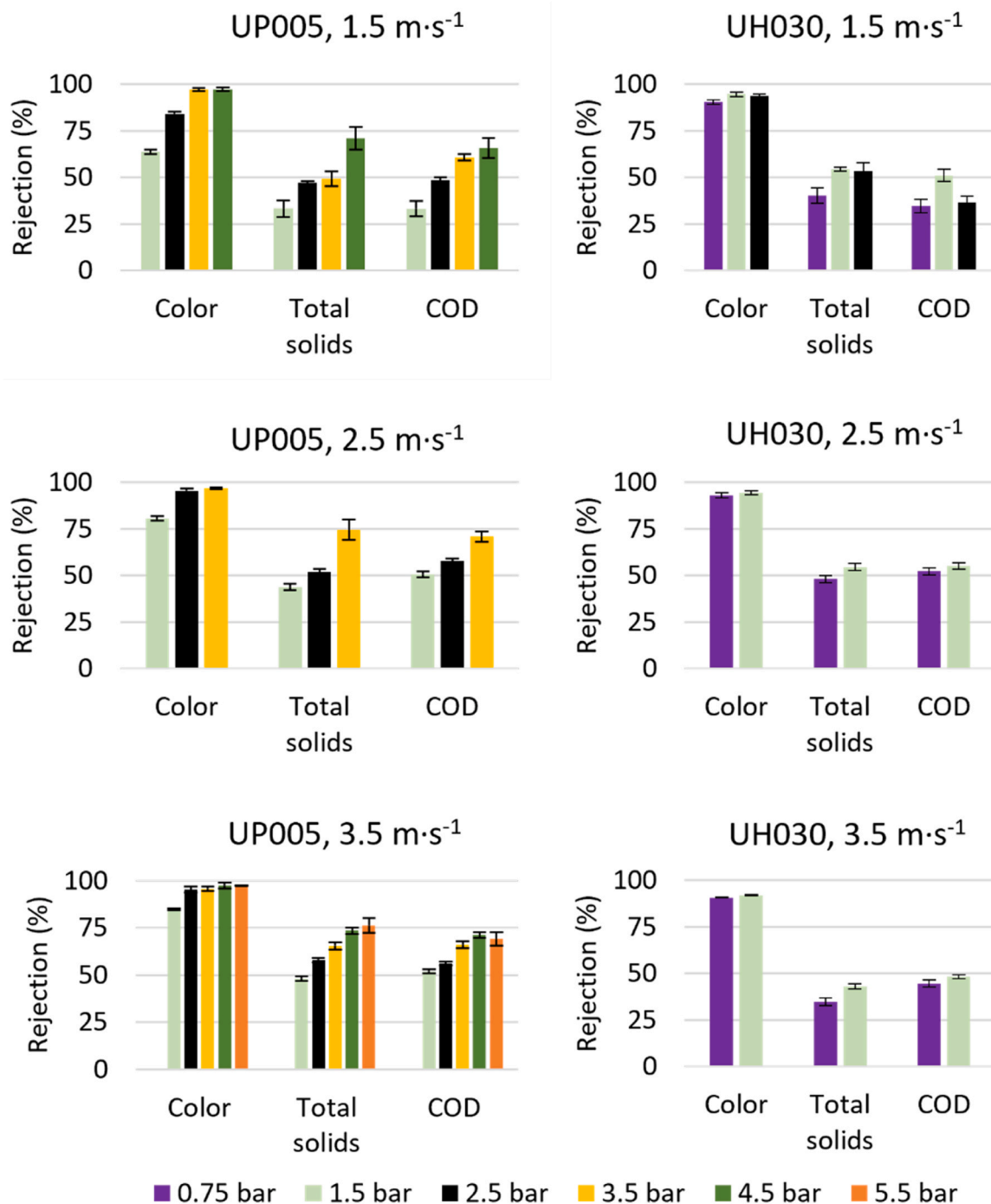


Fig. 3. Rejection of color, total solids and COD achieved with the UP005 and UH030 membranes at all tested operating conditions.

transport from the cake layer back to the bulk solution is enhanced, leading to a higher permeate flux (Vincent-Vela et al., 2009). However, at $2.5 \text{ m}\cdot\text{s}^{-1}$, the permeate flux displayed by the UH030 membrane was lower than that observed at $1.5 \text{ m}\cdot\text{s}^{-1}$, despite the increase in the turbulence in the module. The reason for this lower permeate flux is the higher value of COD in the extract of wet olive pomace that was treated at $2.5 \text{ m}\cdot\text{s}^{-1}$ (see Table 1). In consequence, a greater fouling was expected for the experiments carried out at this velocity and, therefore, a lower flux was obtained. In any case, an increment in the cross-flow velocity did have a beneficial effect on the permeate flux for the UH030 membrane.

3.2. Rejection values

3.2.1. Rejection of the organic matter

Fig. 3 and Fig. 4 show the rejection of the organic matter (except phenolic compounds) achieved with each tested membrane. As can be observed, the rejection values regarding the UP005 membrane increased with the pressure, at all cross-flow velocities, which is in line with a higher water flux. At the highest pressures, interesting rejection values (greater than 50%) were obtained with the UP005 membrane, because a high withdrawal of the organic matter was pursued, in order to recover the polyphenols from the wet olive pomace at higher purity in the permeate. In the case of the UH030 membrane, the gel layer formation (Fig. 2) determined that the permeate flux did not increase with transmembrane pressure. In consequence, the rejection was only slightly increased by increasing the pressure.

In the case of the UH050 (Fig. 4), the higher MWCO of the membrane determined lower rejection values for color, total solids, and COD. This was not interesting, considering the aim of the work. As the purification of polyphenols was not favored by the UH050 membrane and the obtained permeate flux (Fig. 1) was not higher than the permeate flux obtained with other membranes more effective in terms of rejections, the UH050 membrane was not tested at any further conditions of transmembrane pressure or cross-flow velocity. On the contrary, the high rejection values (for all three parameters of color, total solids, and COD) obtained with the UP150 membrane were not expected, considering the MWCO of the membrane. Interestingly, the rejections achieved with the UP150 membrane were higher than the rejection values obtained with the UP005 membrane at $1.5 \text{ m}\cdot\text{s}^{-1}$ and 0.75 bar, even when the UP150 membrane has a pore size 30 times larger than that of the UP005 membrane. The flux drop observed for the UP150 was sharper than the flux decline obtained for the rest of the membranes. This suggested that the UP150 suffered from the thickest cake layer, in comparison with the UP005, UH030, and UH050 membranes. In fact, the UP150 membrane was the only one whose hydraulic permeability could not be recovered after the applied cleaning protocols (Table 2), which also supported the formation of a thick layer on its surface. According to previous studies (Chang et al., 2001; Ersahin et al., 2016), a strong cake layer (as in the case of the UP150, which reflected the strongest cake layer in this study) can act as a secondary membrane, increasing the rejection values for the UP150 membrane. Furthermore, the sharp flux decline observed and the high difficulty to clean this membrane suggested the occurrence of internal pore fouling, which is the most difficult to reverse with the cleaning treatment. This type of fouling can be expected for this membrane, as the pore size is higher. In this case, the internal pore fouling reduces the effective diameter, then increasing the rejection (Mah et al., 2012; Meireles et al., 1991).

3.2.2. Rejection of the phenolic compounds

The rejection of phenolic compounds and its variation with the transmembrane pressure are shown in Fig. 5 and Fig. 6. In order to

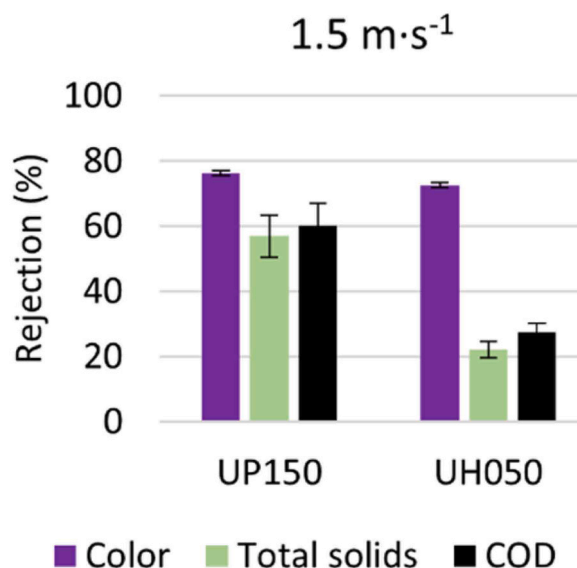


Fig. 4. Rejection of color, total solids and COD achieved with the UP150 and UH050 membranes at $1.5 \text{ m}\cdot\text{s}^{-1}$ and 0.75 bar.

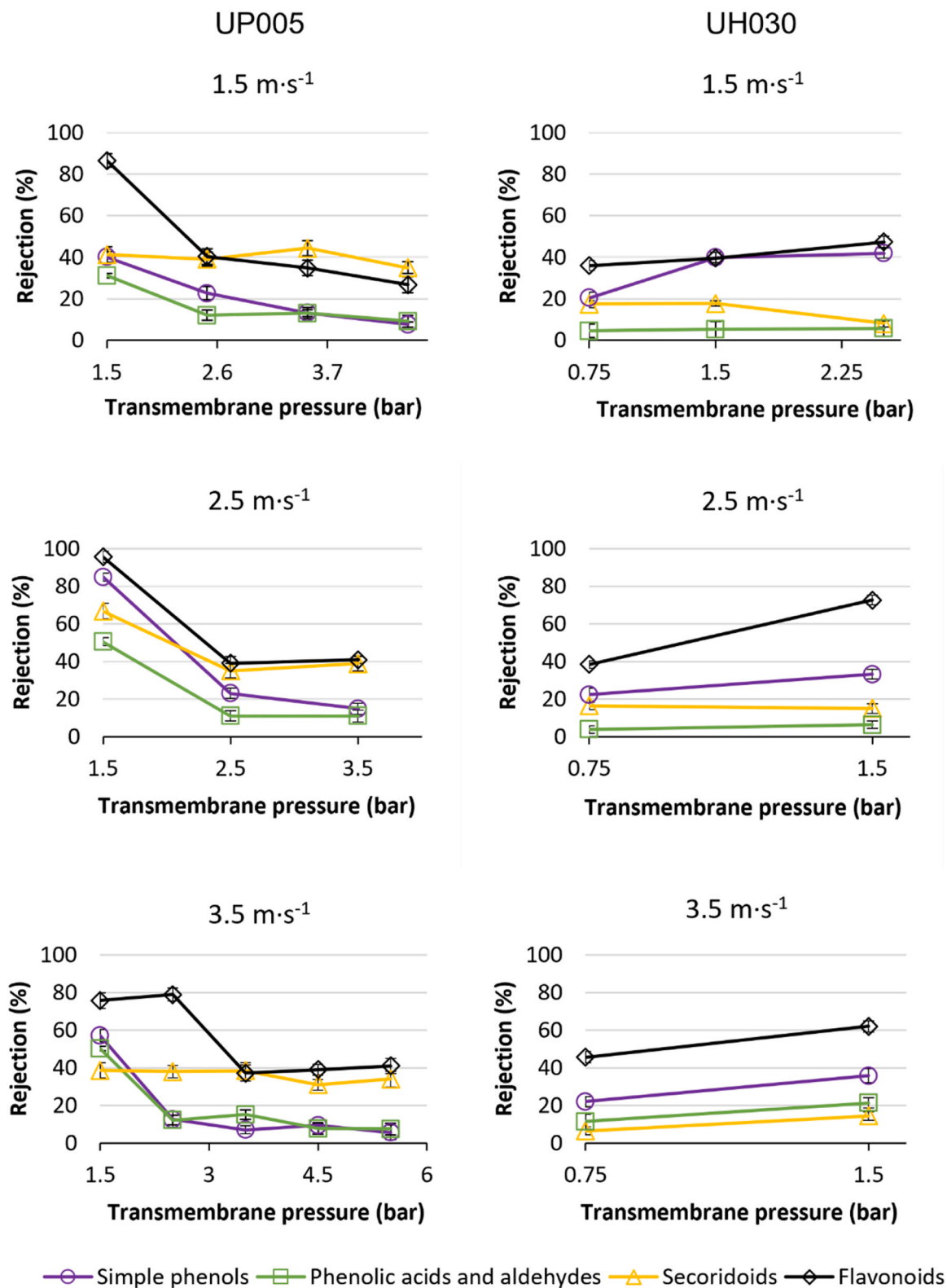


Fig. 5. Rejection of phenolic compounds achieved with the UP005 and UH030 membranes at all the tested operating conditions.

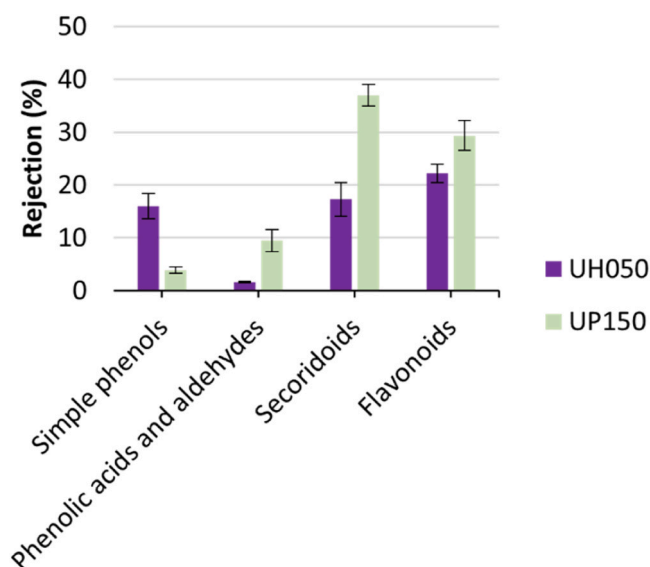


Fig. 6. Rejection of the phenolic compounds achieved with the UH050 and UP150 membranes at $1.5 \text{ m}\cdot\text{s}^{-1}$ and 0.75 bar.

determine the individual rejection of each chemical family of polyphenols, the permeate and feed streams were analyzed by LC-ESI-QToF-MS. Then, each compound was quantified and assigned to a chemical class, according to their structure. This analytical strategy allowed a deep understanding of the transport of the target compounds throughout the membranes. All the compounds identified in the aqueous extracts of wet olive pomace and the permeates of the employed membranes are listed in Table 3. The samples were analyzed by means of a non-targeted methodology, which allowed the determination of all the phenolic compounds present in a sample within the same run. This powerful strategy allowed the identification and individual quantification of 29 phenolic compounds, belonging to four different chemical families, namely simple phenols, phenolic acids, secoiridoids, and flavonoids. The great majority

Table 3

Compounds determined by LC-ESI-QToF in the aqueous extracts of wet olive pomace and derived ultrafiltration streams, listed according to their retention time in the chromatographic column. The m/z and chemical family of each analyte have been provided.

Compound Identity	m/z	Concentration in the extract of wet olive pomace (mg/kg) ^a	Chemical family
Vanillic acid	167.0352	94 ± 2	Phenolic acids and aldehydes
Hydroxytyrosol	153.0551	18.07 ± 0.14	Simple phenols
Hydroxytyrosol glucoside	315.1081	27.14 ± 0.21	Simple phenols
Acyclodihydroelenolic acid hexoside	407.1560	161 ± 1	Secoiridoids
Hydroxy-decarboxymethyl elenolic acid	199.0607	1630 ± 20	Secoiridoids
Vanillin	151.0396	41.62 ± 0.51	Phenolic acids and aldehydes
Caffeic acid	179.0347	42 ± 1	Phenolic acids and aldehydes
Gallocatechin	305.0702	104 ± 5	Flavonoids
Tyrosol	137.0608	20.45 ± 0.40	Simple phenols
Hydroxyelenolic acid	257.0669	405.80 ± 29.96	Secoiridoids
Decarboxymethyl elenolic acid	183.0658	970 ± 10	Secoiridoids
Elenolic acid glucoside	403.1246	166 ± 6	Secoiridoids
<i>p</i> -Coumaric acid	163.0397	54 ± 2	Phenolic acids and aldehydes
Aldehydic form of Decarboxymethyl Elenolic acid	215.0925	313 ± 21	Secoiridoids
Phenylethyl primeveroside	415.1612	53.97 ± 0.76	Secoiridoids
Hydroxyoleuropein	555.1717	37.8 ± 0.9	Secoiridoids
Luteolin 7-O-glucoside	447.0933	38 ± 1	Flavonoids
Dehydro-oleuropein aglycone	375.1087	18.7 ± 0.1	Secoiridoids
Elenolic acid	241.0720	657 ± 28	Secoiridoids
Hydroxytyrosol acyclodihydroelenolate	381.1560	21.0 ± 0.4	Secoiridoids
Ferulic acid	193.0503	36.11 ± 0.01	Phenolic acids and aldehydes
Luteolin rutinoside	593.1516	17.94 ± 0.03	Flavonoids
Oleuropein	539.1769	19.65 ± 0.19	Secoiridoids
Luteolin	285.0405	21 ± 2	Flavonoids
Decarboxymethyl oleuropein aglycone	319.1187	0.050 ± 0.007	Secoiridoids
Ligstroside	523.1820	19.52 ± 0.56	Secoiridoids
Diosmetin	299.0558	17.39 ± 0.17	Flavonoids
Oleuropein aglycone	377.1242	22 ± 2	Secoiridoids

^a Calculated as the mean values of the three aqueous extracts employed in this study.

of them have demonstrated antioxidant activities or have been related with interesting bioactivities (Kunhachan et al., 2012; Obied et al., 2007; Tsimidou and Papoti, 2010), including antimicrobial effects (Thielmann et al., 2017) and the prevention of some degenerative diseases (Mohammad-Beigi et al., 2019). Only in the case of three secoiridoids derivatives (dehydro oleuropein aglycone, elenolic acid glucoside, and hydroxy-decarboxymethyl elenolic acid), specific studies about their bioactivity could not be found in the literature. Therefore, the aqueous extract of wet olive pomace can be considered a proper source of bioactive molecules. This bioactive content was extremely interesting, considering the aim of valorizing the wet olive pomace and its derived extracts.

As shown in Fig. 5, the UP005 membrane allowed the passage of a large proportion of simple phenols and phenolic acids, because these two chemical families were poorly rejected. Both chemical classes include the smallest molecules present in the feed stream, as reflected in Table 3. This was an essential outcome, because greatly valuable molecules, such as ferulic acid, *p*-coumaric acid, tyrosol, and hydroxytyrosol (Fernández-Prior et al., 2020; Ou and Kwok, 2004; Robles-Almazan et al., 2018) were recovered in the permeate at a higher purity. The greater rejection values for this membrane corresponded to larger molecules, such as flavonoids and secoiridoids, which, at the highest pressures (2.5 – 5.5 bar) were rejected at 40% approximately. At all cross-flow velocities, the rejection of biophenols decreased when the transmembrane pressure was increased for the UP005 membrane. According to the results presented in Fig. 1 and Fig. 2, the UP005 membrane did not suffer an intense fouling. Therefore, it is reasonable to conclude that this phenomenon did not largely influence the observed tendency regarding the rejection values. On the contrary, this effect can be attributed to a slight enlargement of the membrane pores at high pressures, enabling a higher flux of solutes and the consecutive lowering of the rejection. This phenomenon was also described by Arkhangelsky and Gitis during the ultrafiltration of viruses. These authors found a relevant increment in the presence of viruses in the permeate of a polyethersulfone membrane (which is the same material as that of the membranes tested in this work) as a result of pressure increase. When they measured the rejection of PEG and PEO in the range 0.3–600 kDa, the MWCO varied from 28 kDa to 35 kDa as a result of a pressure increment from 1 bar to 5 bar. Therefore, these authors attributed the lowering of the rejection of viruses to the enlargement of the membrane pores (Arkhangelsky and Gitis, 2008). In this work, the pore enlargement benefited the recovery of phenolic compounds, decreasing their rejection, because the molecular size of these compounds is similar to the pore size. However, the macromolecules (proteins, polysaccharides, etc.) and organic matter with large molecular weight were effectively rejected (as shown in Fig. 3), as their size was much higher than the size of the membrane pores and they were not affected by the pore enlargement.

In the case of the UH030, the rejection of phenolic compounds was also low, achieving the recovery of these valuable compounds in the permeate stream as well. Due to the gel layer formation (as commented in Section 3.1), the transmembrane pressure was not increased beyond 1.5 bar. Again, the flavonoids were the most rejected molecules, whereas phenolic acids and aldehydes, secoiridoids, and simple phenols were successfully obtained in the permeate. Interestingly, the simple phenols, which include small compounds such as tyrosol (138 g/mol) and hydroxytyrosol (154 g/mol), were rejected at higher percentages than larger compounds, such as oleuropein (540 g/mol) or ligstroside (524 g/mol), belonging to the family of secoiridoids. This was more notable at the lowest cross-flow velocity ($1.5 \text{ m}\cdot\text{s}^{-1}$), and can be explained by an adsorption process, favored by the hydrophilic character of the UH030 membrane, in comparison with the UP005 membrane. In fact, the adsorption of phenolic compounds on the UH030 membrane has been previously reported (Sánchez-Arévalo et al., 2023). Virtanen et al., analyzed, by computational molecular dynamics simulation, the possible interactions between the UH004 membrane (which is a hydrophilic PES membrane, the same as the UH030, and is provided by the same manufacturer) and vanillin, which is a phenolic aldehyde. They described hydrophobic interactions as the main mechanism of the interaction and, additionally, they reported a significant number of hydrogen bonds occurring between the hydroxyl group of the vanillin molecules and the PES membrane, both at the ether group and the sulfur oxygen group of the PES polymer (Virtanen et al., 2018). The molecule of vanillin only contains one hydroxyl group available for a hydrogen bond. However, the simple phenols present in the extract of wet olive pomace (tyrosol, hydroxytyrosol, and hydroxytyrosol derivatives) have several hydroxyl groups in their chemical structure. This suggests a high relevance of the hydrogen bonding between the simple phenols and the membrane surface, which supports the adsorption of this chemical family and, therefore, the observed rejection.

Regarding the UH050 and UP150 membranes, which had the highest MWCO, the rejection of phenolic compounds was higher for those chemical families involving molecules of larger size. Therefore, phenolic acids and aldehydes were poorly rejected, and the rejection value increased for secoiridoids and flavonoids. Still, no rejection surpassed 25% for the UH050 membrane. For the UP150 membrane, secoiridoids and flavonoids were rejected in a higher percentage. Even though the MWCO of this membrane is high, the severe fouling hindered the passage of larger compounds. Nevertheless, the purification of phenolic compounds achieved by the UP150 membrane was much more relevant than in the case of the UH050. This is because, even though both membranes displayed low rejections of the interesting biophenols, the UH050 membrane also displayed low rejections of the COD, as shown previously in Fig. 4. Therefore, no separation was provided by this membrane. Furthermore, the rejection of simple phenols achieved by the UH050 was expected to be lower, considering its MWCO. As occurred with the UH030 membrane, which was made of the same material as the UH050 membrane, an adsorption process is a plausible explanation for the increment in the rejection of simple phenols. Cifuentes-Cabezas et al. demonstrated the significant adsorption of tyrosol (one of the main simple phenols) and catechin (a flavonoid) onto the surface of the UH050 membrane (Cifuentes-Cabezas et al., 2021).

4. Conclusions

The phenolic content of the wet olive pomace was recovered by means of a simple, aqueous extraction, followed by a purification through an ultrafiltration process. According to our results, the UP005 and UH030 membranes displayed the best performance. Both membranes allowed the recovery of phenolic compounds in the permeate, and rejected unwanted species, as reflected by the high rejections of color, total solids, and COD. The selection between these two membranes is dependent on the final application. If the

productivity of the process is to be pursued, the UH030 membrane displayed higher values of permeate flux (at low transmembrane pressures, when the gel layer was not so significant). On the contrary, if a finer purification of phenolic compounds is aimed, the UP005 membrane displayed higher rejections of the concomitant organic matter. In both cases, the ultrafiltration of the aqueous extracts of wet olive pomace has demonstrated to greatly contribute to the reutilization of a concerning by-product, obtaining high added-value compounds in the process.

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CRedit authorship contribution statement

Carmen M. Sánchez Arévalo: Conceptualization, Methodology, Validation, Formal analysis, Investigation, Writing – original draft, Visualization. **María Cinta Vincent-Vela:** Conceptualization, Resources, Writing – review & editing, Visualization, Supervision, Project administration, Funding acquisition. **Silvia Álvarez-Blanco:** Conceptualization, Resources, Writing – review & editing, Visualization, Supervision, Project administration, Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data Availability

Data will be made available on request.

References

- Aimar, P., Field, R., 1992. Limiting flux in membrane separations: a model based on the viscosity dependency of the mass transfer coefficient. *Chem. Eng. Sci.* 47, 579–586. [https://doi.org/10.1016/0009-2509\(92\)80008-Z](https://doi.org/10.1016/0009-2509(92)80008-Z).
- Arkhangelsky, E., Gitis, V., 2008. Effect of transmembrane pressure on rejection of viruses by ultrafiltration membranes. *Sep. Purif. Technol.* 62, 619–628. <https://doi.org/10.1016/j.seppur.2008.03.013>.
- Bacchin, P., Aimar, P., Field, R.W., 2006. Critical and sustainable fluxes: theory, experiments and applications. *J. Memb. Sci.* 281, 42–69. <https://doi.org/10.1016/j.memsci.2006.04.014>.
- Bottino, A., Capannelli, G., Comite, A., Jezowska, A., Pagliero, M., Costa, C., Firpo, R., 2020. Treatment of olive mill wastewater through integrated pressure-driven membrane processes. *Membranes* 10, 334 10, 334. <https://doi.org/10.3390/MEMBRANES10110334>.
- Cai, M., Lv, Y., Luo, S., Liu, Y., Sun, P., 2018. Fouling behavior of polyphenols during model juice ultrafiltration: effect of membrane properties. *Food Bioprocess Technol.* 11, 1787–1793. <https://doi.org/10.1007/s11947-018-2110-9>.
- Caporaso, N., Formisano, D., Genovese, A., 2018. Use of phenolic compounds from olive mill wastewater as valuable ingredients for functional foods. *Crit. Rev. Food Sci. Nutr.* 58, 2829–2841. <https://doi.org/10.1080/10408398.2017.1343797>.
- Cassano, A., Conidi, C., Giorno, L., Drioli, E., 2013. Fractionation of olive mill wastewaters by membrane separation techniques. *J. Hazard. Mater.* 248–249, 185–193. <https://doi.org/10.1016/j.jhazmat.2013.01.006>.
- Cazcarro, I., Duarte, R., Sánchez-Chóliz, J., Sarasa, C., Serrano, A., 2015. Environmental footprints and scenario analysis for assessing the impacts of the agri-food industry on a regional economy: a case study in Spain. *J. Ind. Ecol.* 19, 618–627. <https://doi.org/10.1111/JIEC.12209>.
- Chang, I.S., Bag, S.O., Lee, C.H., 2001. Effects of membrane fouling on solute rejection during membrane filtration of activated sludge. *Process Biochem* 36, 855–860. [https://doi.org/10.1016/S0032-9592\(00\)00284-3](https://doi.org/10.1016/S0032-9592(00)00284-3).
- Cifuentes-Cabezas, M., Carbonell-Alcaina, C., Vincent-Vela, M.C., Mendoza-Roca, J.A., Álvarez-Blanco, S., 2021. Comparison of different ultrafiltration membranes as first step for the recovery of phenolic compounds from olive-oil washing wastewater. *Process Saf. Environ. Prot.* 149, 724–734. <https://doi.org/10.1016/j.psep.2021.03.035>.
- Corbatón-Báguena, M.J., Álvarez-Blanco, S., Vincent-Vela, M.C., 2014. Cleaning of ultrafiltration membranes fouled with BSA by means of saline solutions. *Sep. Purif. Technol.* 125, 1–10. <https://doi.org/10.1016/j.seppur.2014.01.035>.
- Ersahin, M.E., Tao, Y., Ozgun, H., Spanjers, H., van Lier, J.B., 2016. Characteristics and role of dynamic membrane layer in anaerobic membrane bioreactors. *Biotechnol. Bioeng.* 113, 761–771. <https://doi.org/10.1002/bit.25841>.
- Eryildiz, B., Keskin, B., Pasaoglu, M.E., Turken, T., Vatanpour, V., Koyuncu, I., 2023. Preparation and characterization of polyvinyl chloride membranes and their fouling behavior in water purification. *J. Appl. Polym. Sci.* 140, e53496 <https://doi.org/10.1002/APP.53496>.
- Fernández-Prior, M.Á., Fatuarte, J.C.P., Oria, A.B., Viera-Alcaide, I., Fernández-Bolaños, J., Rodríguez-Gutiérrez, G., 2020. New liquid source of antioxidant phenolic compounds in the olive oil industry: alperujo water. *Foods* 9. <https://doi.org/10.3390/foods9070962>.
- Field, R.W., Aimar, P., 1993. Ideal limiting fluxes in ultrafiltration: comparison of various theoretical relationships. *J. Memb. Sci.* 80, 107–115. [https://doi.org/10.1016/0376-7388\(93\)85136-K](https://doi.org/10.1016/0376-7388(93)85136-K).
- Guo, J., Hong, L., Jianhong, L., Liying, W., 2014. Ultrafiltration performance of EFOM and NOM under different MWCO membranes. *Comp. Fluoresc. Spectrosc. gel Filtr. Chromatogr.* <https://doi.org/10.1016/j.desal.2014.03.006>.
- International Olive Council, 2023. Designations and Definitions of Olive Oils [WWW Document]. URL <https://www.internationaloliveoil.org/>.
- Kumar, S.N., Chakabarti, B., 2019. Energy and carbon footprint of food industry. In: *Environmental Footprints and Eco-Design of Products and Processes*. Springer, pp. 19–44. https://doi.org/10.1007/978-981-13-2956-2_2.
- Kunhachan, P., Banchonglikitkul, C., Kajsongkram, T., Khayungarnawee, A., Leelamanit, W., 2012. G. Duke of Tuscany 2012. <https://doi.org/10.1155/2012/471312>.
- Luján-Facundo, M.J., Mendoza-Roca, J.A., Cuartas-Urbe, B., Álvarez-Blanco, S., 2013. Ultrasonic cleaning of ultrafiltration membranes fouled with BSA solution. *Sep. Purif. Technol.* 120, 275–281. <https://doi.org/10.1016/j.seppur.2013.10.018>.

- Mah, S.K., Leo, C.P., Wu, T.Y., Chai, S.P., 2012. A feasibility investigation on ultrafiltration of palm oil and oleic acid removal from glycerin solutions: flux decline, fouling pattern, rejection and membrane characterizations. *J. Memb. Sci.* 389, 245–256. <https://doi.org/10.1016/J.MEMSCI.2011.10.037>.
- Meireles, M., Aimar, P., Sanchez, V., 1991. Effects of protein fouling on the apparent pore size distribution of sieving membranes. *J. Memb. Sci.* 56, 13–28. [https://doi.org/10.1016/0376-7388\(91\)85013-U](https://doi.org/10.1016/0376-7388(91)85013-U).
- Miralles, P., Chisvert, A., Salvador, A., 2014. Determination of hydroxytyrosol and tyrosol by liquid chromatography for the quality control of cosmetic products based on olive extracts. *J. Pharm. Biomed. Anal.* 102, 157–161. <https://doi.org/10.1016/j.jpba.2014.09.016>.
- Mohammad-Beigi, H., Aliakbari, F., Sahin, C., Lomax, C., Tawfike, A., Schafer, N.P., Amiri-Nowdijeh, A., Eskandari, H., Møller, I.M., Hosseini-Mazinani, M., Christiansen, G., Ward, J.L., Morshedi, D., Otzen, D.E., 2019. Oleuropein derivatives from olive fruit extracts reduce α -synuclein fibrillation and oligomer toxicity. *J. Biol. Chem.* 294, 4215–4232. <https://doi.org/10.1074/jbc.RA118.005723>.
- Obied, H.K., Karuso, P., Prenzler, P.D., Robards, K., Graham, E.H., 2007. Novel Secoiridoids with Antioxidant Activity from Australian Olive Mill Waste. <https://doi.org/10.1021/jf063300u>.
- Ou, S., Kwok, K.C., 2004. Ferulic acid: pharmaceutical functions, preparation and applications in foods. *J. Sci. Food Agric.* 84, 1261–1269. <https://doi.org/10.1002/jsfa.1873>.
- Qu, F., Liang, H., Zhou, J., Nan, J., Shao, S., Zhang, J., Li, G., 2014. Ultrafiltration membrane fouling caused by extracellular organic matter (EOM) from *Microcystis aeruginosa*: effects of membrane pore size and surface hydrophobicity. *J. Memb. Sci.* 449, 58–66. <https://doi.org/10.1016/J.MEMSCI.2013.07.070>.
- Robles-Almazan, M., Pulido-Moran, M., Moreno-Fernandez, J., Ramirez-Tortosa, C., Rodriguez-García, C., Quiles, J.L., Ramirez-Tortosa, M., 2018. Hydroxytyrosol: bioavailability, toxicity, and clinical applications. *Food Res. Int.* <https://doi.org/10.1016/j.foodres.2017.11.053>.
- Roselló-Soto, E., Koubaa, M., Moubarik, A., Lopes, R.P., Saraiva, J.A., Boussetta, N., Grimi, N., Barba, F.J., 2015. Emerging opportunities for the effective valorization of wastes and by-products generated during olive oil production process: non-conventional methods for the recovery of high-added value compounds. *Trends Food Sci. Technol.* 45, 296–310. <https://doi.org/10.1016/j.tifs.2015.07.003>.
- Saf, C., Villain-Gambier, M., Belaqqiz, M., Ziegler-Devin, I., Trebouet, D., Ouazzani, N., 2022. Fouling control investigation by pH optimization during olive mill wastewater ultrafiltration. *Process Saf. Environ. Prot.* 164, 119–128. <https://doi.org/10.1016/J.PSEP.2022.06.010>.
- Sánchez-Arévalo, C.M., Iborra-Clar, A., Vincent-Vela, M.C., Álvarez-Blanco, S., 2022. Exploring the extraction of the bioactive content from the two-phase olive mill waste and further purification by ultrafiltration. *LWT - Food Sci. Technol.* 165, 113742. <https://doi.org/10.1016/j.lwt.2022.113742>.
- Sánchez-Arévalo, C.M., Pérez García-Serrano, A., Vincent-Vela, M.C., Álvarez-Blanco, S., 2023. Combining ultrafiltration and nanofiltration to obtain a concentrated extract of purified polyphenols from wet olive pomace. *Membr. (Basel)* 13, 119. <https://doi.org/10.3390/membranes13020119>.
- Sciubba, F., Chronopoulou, L., Pizzichini, D., Lionetti, V., Fontana, C., Aromolo, R., Socciairelli, S., Gambelli, L., Bartolacci, B., Finotti, E., Benedetti, A., Miccheli, A., Neri, U., Palocci, C., Bellincampi, D., 2020. Olive mill wastes: a source of bioactive molecules for plant growth and protection against pathogens. *Biol* 2020 9, 450. <https://doi.org/10.3390/BIOLOGY9120450>.
- Silvestri, L., Forcina, A., Di Bona, G., Silvestri, C., 2021. Circular economy strategy of reusing olive mill wastewater in the ceramic industry: how the plant location can benefit environmental and economic performance. *J. Clean. Prod.* 326, 129388. <https://doi.org/10.1016/J.JCLEPRO.2021.129388>.
- Sygouni, V., Pantziaras, A.G., Iakovides, I.C., Sfetsa, E., Bogdou, P.I., Christoforou, E.A., Paraskeva, C.A., 2019. Treatment of two-phase olive mill wastewater and recovery of phenolic compounds using membrane technology. *Membr. (Basel)* 9, 27. <https://doi.org/10.3390/membranes9020027>.
- Thielmann, J., Kohnen, S., Hauser, C., 2017. Antimicrobial activity of *Olea europaea* Linné extracts and their applicability as natural food preservative agents. <https://doi.org/10.1016/j.ijfoodmicro.2017.03.019>.
- Tomczak, W., Gryta, M., 2023. The application of polyethersulfone ultrafiltration membranes for separation of car wash wastewaters: experiments and modelling. *Membr. (Basel)* 13. <https://doi.org/10.3390/membranes13030321>.
- Tsimidou, M.Z., Papatii, V.T., 2010. Bioactive ingredients in olive leaves. *Olives Olive Oil Heal. Dis. Prev.* 349–356. <https://doi.org/10.1016/B978-0-12-374420-3.00039-5>.
- UNE-EN ISO 7887:2012 Method B, 2012. Water Quality. Examination and Determination of Colour.
- Vincent-Vela, M.C., Álvarez-Blanco, S., Lora-García, J., Bergantiños-Rodríguez, E., 2009. Estimation of the gel layer concentration in ultrafiltration: comparison of different methods. *Desalin. Water Treat.* 3, 157–161. <https://doi.org/10.5004/dwt.2009.454>.
- Virtanen, T., Parkkila, P., Koivuniemi, A., Lahti, J., Viitala, T., Kallioinen, M., Mänttari, M., Bunker, A., 2018. Characterization of membrane-foulant interactions with novel combination of Raman spectroscopy, surface plasmon resonance and molecular dynamics simulation. *Sep. Purif. Technol.* 205, 263–272. <https://doi.org/10.1016/j.seppur.2018.05.050>.
- Wang, C., Park, M.J., Yu, H., Matsuyama, H., Drioli, E., Shon, H.K., 2022. Recent advances of nanocomposite membranes using layer-by-layer assembly. *J. Memb. Sci.* 661, 120926. <https://doi.org/10.1016/J.MEMSCI.2022.120926>.
- Wibisono, Y., Alvianto, D., Argo, B.D., Hermanto, M.B., Witoyo, J.E., Bilad, M.R., 2023. Low-fouling plate-and-frame ultrafiltration for juice clarification: part 1-membrane preparation and characterization. *Sustain* 15. <https://doi.org/10.3390/su15010806>.
- You, X., Wang, M., Jiang, G., Zhao, X., Wang, Z., Liu, F., Zhao, C., Qiu, Z., Zhao, R., 2023. Multifunctional porous nanofibrous membranes with superior antifouling properties for oil-water separation and photocatalytic degradation. *J. Memb. Sci.* 668, 121245. <https://doi.org/10.1016/J.MEMSCI.2022.121245>.