Concentration of phenolic compounds from olive washing wastewater by forward osmosis using table olive fermentation brine as draw solution

Magdalena Cifuentes-Cabezas [a,*], Alessio Pavani [a], María Cinta Vincent-Vela [a,b], José Antonio Mendoza-Roca [a,b], Silvia Álvarez-Blanco [a,b]

[a] Research Institute for Industrial, Radiophysical and Environmental Safety (ISIRYM), Universitat Politècnica de València, C/Camino de Vera s/n, 46022, Valencia, Spain
[b] Department of Chemical and Nuclear Engineering, Universitat Politècnica de València, C/Camino de Vera s/n, 46022, Valencia, Spain

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ABSTRACT

The olive industry has a considerable amount of process water consumption. As a result of the process, a large volume of oil mill wastewater (OMW) and table olive wastewater (TOW), both of them with high concentrations of organic matter, phenolic compounds and conductivity, are released. The appropriate management of these wastewaters is of paramount importance due to their toxic impacts on the environment. In this work, forward osmosis (FO) process is presented as an option to concentrate phenolic compounds for their further recovery. Two membranes, OsmoF2O^{TM} (FTS, USA) and HFFO.6 (Aquaporin, Denmark) were evaluated with NaCl as draw solution (DS) and olive oil washing wastewater (OOWW) filtered at 5 μm (5F) as feed solution (FS). Both membranes were able to concentrate the phenolic compounds with acceptable volume reduction (VR) values. The HFFO.6 membrane, which presented the lowest passage of phenolic compounds (TPhC) to the DS, was tested with fermentation brine from table olive processing (FTOP) as DS. As FS the same 5F-OOWW as well as an OOWW ultrafiltration permeate (UF-OOWW) were considered. Interestingly, greater percentages of TPhC concentration were observed compared to the tests with NaCl as DS (74.13–76.93% versus 62.6%, respectively). Although the tests with UF-OOWW presented greater flux, the recovery percentages of TPhC were similar, even slightly lower than those obtained with 5F-OOWW. Therefore, FO appears as a promising option to concentrate TPhC from OOWW and as well as to dilute FTOP. Thus both wastewaters from the olive industry could be treated at the same time.

1. Introduction

Due to the great industrial development that exists today, millions of litres of industrial wastewater are generated every year, becoming an environmental pressure. Most of the industrial effluents are collected by a municipal sewage system after their conditioning at the industries, treated in an urban wastewater treatment plant and finally discharged into the environment. However, there are cases in which these wastewaters are discharged into a water body either directly or

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after an insufficient treatment in the industrial facility. Therefore, wastewater treatment is a key element for the care and control of the environment (European Environment Agency, 2018). Wastewaters generated in industrial plants are characterized by containing substances that, due to their nature or concentration (toxicity or long-term biological effects), cannot always be eliminated by conventional urban wastewater treatments (Ochando-Pulido et al., 2020). In processes related to olives, such as the production of olive oil and table olives, a large amount of wastewater containing high levels of organic matter and phenolic compounds is generated. Due to their phytotoxic nature, phenolic compounds pose an environmental threat. Therefore, any discharge of phenolic effluents into the environment should be prohibited or at least controlled and reduced (El Moussaoui, 2022; Hodaifa et al., 2019; Torrecilla et al., 2007). On the other hand, from some time ago, phenolic compounds have been targets for the food and pharmaceutical industries (Obied et al., 2005). Several phenolic compounds such as tyrosol, hydroxytyrosol, oleuropein and catechin, among others, are being studied for the treatment of various diseases, including prevention of neurodegenerative diseases and cancer (Rodríguez-Morató et al., 2015), improvement of type 2 diabetes (Lee et al., 2016) and for prevention of heart diseases (Owen et al., 2000). Therefore, oil mill wastewater (OMW) and table olive process wastewater (TOPW) are potential sources of phenolic compounds whose concentration and isolation could have two great benefits: obtaining valuable substances and solving eventual environmental problems, avoiding damaging soil and watercourses.

Different treatment processes have been proposed for the recovery of phenolic compounds from OMW (Goula and Lazarides, 2015). Among them, pressure-driven membrane technologies provide some environmentally friendly advantages, such as no need for chemical reagents such as solvents, simplicity of industrial scaling given its modular configuration, and easy operation (Gómez-Caravaca et al., 2017). Nevertheless, fouling is the bottleneck that affects pressure-driven membrane processes, restricting the scaling of conventional membrane technologies. Severe fouling directly affects the investment costs as a result of the reduction of the membrane useful life and the increase in chemical costs, necessary to clean the membranes (Gebreyohannes et al., 2015). Due to this, it has been necessary to incorporate different techniques (hybrid processes) to care for the membranes and reduce fouling. The combination of different membrane processes is a solution too. In this field Cassano et al. (2018) proposed a process for the recovery of phenolic compounds from OMW, which includes a combination of micro/ultrafiltration (UF), followed by tight UF or nanofiltration (NF), and finally a reverse osmosis (RO). It has to be pointed out that a pretreatment with more open membranes is very often necessary to provide an adequate solution to the fouling problems of NF or RO membranes used for the recovery of phenolic compounds from OMW. However, adding more steps to the treatment process implies higher investment and maintenance costs. Forward osmosis (FO) is resurfacing as a membrane operation that requires little energy for the concentration of aqueous solutions, with a membrane fouling that is mainly reversible due to the low compaction of the fouling layer as a result of the insignificant hydraulic pressure. This technique is based on the phenomenon of osmosis, where the driving force for water transport across a semi-permeable membrane is the osmotic pressure difference between both sides of the membrane (Lutchmiah et al., 2014). FO requires two solutions that, due to their different chemical potential, promote solvent flow through the membrane. These two solutions are a feed solution (FS), generally the solution to be concentrated, with low chemical potential, and an extraction/draw solution (DS) that, due to its high chemical potential, promotes the passage of water through the membrane, diluting itself at the same time as the FS is concentrated. Among the available commercial FO membranes, cellulose triacetate (CTA) and thin-film composite (TFC) ones stand out in two configurations, flat sheet and hollow fibre (Blandin et al., 2020). Other types of membranes with new materials are also being currently developed (Azadi et al., 2021b).

To date, only two studies have been published on the application of FO to the treatment of OMW. One of them is the work carried out by Gebreyohannes et al. (2015), who investigated cellulose acetate FO membranes for the treatment of OMW from a three-phase centrifuge located in Italy. These authors studied two options. The first one consisted of a FO step with 3.7 M $MgCl_2$ as DS and a crossflow velocity of $6 \ cm \cdot s^{-1}$, achieving a volume reduction of 71% with a rejection greater than 98% of the OMW components, including biophenols and ions. The second option included a membrane bioreactor (MBR) prior to the FO step, achieving a permeate flux improvement of 30%. These authors observed a strong decrease in permeate flow (23%) one hour after the start of the operation, followed by a continuous decrease until matching the values obtained in the tests without MBR. It was attributed to a reduction in the osmotic driving force, due to an increase in the osmotic pressure of the feed solution. This was due to the hydrolysis of pectins by enzymes immobilized on the membrane surface, generating an MBR permeate rich in galacturonic acid (low molecular weight). Another study was carried out by Sponza and Biyink (2020), who reported an increase in the concentration of phenolic compounds of 74% from raw OMW from an olive mill in Turkey with FO. These authors proposed a hybrid FO–CMD (contact membrane distillation) process, successfully achieving a high removal of COD and TSS and total phenols removal yield of 99.98%. However, before the FO process, a pretreatment with Polyethylene (PE) hollow fibre membranes was performed, where 24% of the phenolic compounds present in the raw OMW were lost. Both studies mentioned above were carried out with wastewater extracted from olive oil production processes by three-phase centrifugation. Currently Spain, the country that leads the production of olive oil, uses the two-phase centrifugation process for its production. This process uses less water than pressing or three-phase centrifugation (Cifuentes-Cabezas et al., 2022b). Therefore, it is expected that more countries will opt for it in the future. To date there are no FO treatment studies carried out with residual water from oil mills that operate with this two-phase centrifugation process.

Unlike for OMW, many studies have been carried out with urban wastewater, highlighting the FO process as a promising process for the removal of emerging pollutants. These works report high volume reduction factors and rejection

Table 1
Feed solutions (FS) and draw solutions (DS) used for each test performed.

Test	Membrane tested	FS	DS
E1[a]	FTSH20 and HFFO.6	Synthetic (tyrosol 1 g · L^{-1})	Synthetic (30 g · L^{-1} NaCl)
E2[a]	FTSH20 and HFFO.6	5F-OOWW	Synthetic (30 g · L^{-1} NaCl)
E3[a]	HFFO.6	5F-OOWW	60F-FTOP
E4[a]	HFFO.6	UF-OOWW	60F-FTOP

OOWW: olive oil washing wastewater; FTOP: table olive fermentation brine wastewater; 5F-OOWW: 5 μm filtered OOWW; UF-OOWW: UF permeate from OOWW; 60F-FTOP: 60 μm filtered FTOP.
[a]Each test was performed in duplicate.

of specific compounds, being the process economically and technically feasible (Ansari et al., 2017; Kim et al., 2019). The large number of studies carried out with municipal wastewaters has allowed to test different membranes and operating conditions, being a key point the DS used. Salamanca et al. (2022) pointed out that, with a hollow fibre aquaporin membrane, NaCl solution seemed to be the most appropriate DS because it led to higher permeate flux and lower reverse salt flux. Other studies carried out by Valladares Linares et al. (2013) presented the use of sea water as DS to integrate the purification of municipal wastewater and the desalination of seawater for the production of drinking water. With nutrients retention (N and P) between 56% and 99%, and almost complete retention of trace metals, the study provides a possible energy-saving strategy to combine municipal wastewater treatment and seawater desalination, promoting sustainable urban water management and water reuse in coastal cities. Summarizing, both salt solutions and residual brines could be used as DS. Alternatively, the use of DS from natural compounds may be a suitable option, since it would not be necessary to regenerate them and their dilution is a crucial step for their subsequent use, discharge, or treatment (Bagheri et al., 2021). Other alternative DS that are of great interest are those based on magnetic nanoparticles due to the simplicity of their regeneration (Azadi et al., 2021a; Shoorangiz et al., 2022)

In the table olive production process, different wastewaters are generated depending on the process step. The first step is debittering with sodium hydroxide solution (1%–2% w/v), followed by rinsing cycles to remove excess alkali. It ends with the fermentation of the olives in a brine (4%–8% w/v) of sodium chloride for several months, generating the residual fermentation brine from the processing of table olives (FTOP). Although it represents only 20% of the total volume of TOPW (3.9 to 7.5 m^3/t of green olives), it contributes to 80%–85% of the global wastewater pollution generated in these types of agro-food industries (Ferrer-Polonio et al., 2015).

In this work, the main objective is to use the characteristics of the FO process to treat simultaneously two wastewaters of the olive industry: olive oil washing wastewater (OOWW) and table olive fermentation brine wastewater (FTOP). The large difference in chemical potential (due to the difference in salt content) between the feed solution (OOWW) and the extraction solution (FTOP), will not only allow the concentration of phenolic compounds, but will also dilute the fermentation brine, whose treatment is extremely difficult due to its hypersalinity. For this, two different membranes were tested to analyse their performance in terms of concentration of phenolic compounds and transmembrane flux.

Thus, this work is presented as a novelty in two different areas. It is presented as the first work using the FO process to treat OOWW; as well as the first study carried out with the objective of simultaneously treating two different wastewaters from the olive production processes, both with a high polluting load.

2. Materials and methods

2.1. Feed solution, draw solution and performed tests

Both synthetic and actual wastewaters have been used as FS and DS in the experiments. The synthetic wastewater used as FS was prepared with 1 g · L^{-1} of tyrosol (Ty) (Maybridge, United Kingdom). This concentration was selected due to the total phenolic compound concentration measured in the characterization of an OOWW sample (1115.72 mgTy eq · L^{-1}). For the synthetic DS, a solution of 30 g · L^{-1} of sodium chloride (NaCl) provided by VWR chemicals (Belgium) was used, since this value was close to the concentration of NaCl registered in the characterization of the FTOP.

OOWW samples were provided by a cooperative located in the Valencian Community (Spain), meanwhile FTOP samples were taken from a table olive packaging industry located in the same area. The performed experiments are summarized in Table 1.

This table shows the FS and DS considered for each experiment and the membrane used. The wastewater samples were filtered through cartridges (CA-0202- 00, model GT, HydroWater, Spain), one of 5 μm and another of 60 μm for OOWW and FTOP, respectively. Regarding the UF permeate, this was obtained with the UP005 membrane (Microdyn Nadir, Germany), under the operating conditions of 2.5 m s^{-1} CFV and 2 bar TMP. The operating conditions were selected from the results obtained in a previous work (Cifuentes-Cabezas et al., 2021).
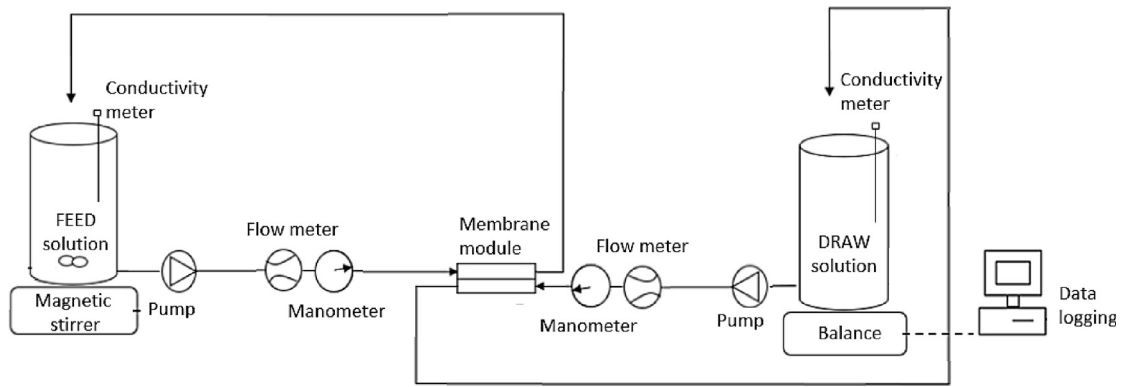
Fig. 1. Scheme diagram of the forward osmosis pilot plant.

Table 2

Characteristics of the studied forward osmosis membranes (based on literature (Khanafer et al., 2021; Sanahuja-Embuena et al., 2019; Xie et al., 2018)).

Parameter	FTSH2O™	HFFO.6
Membrane material	Cellulose triacetate (CTA)	Thin film composite (TFC) polyamide with integrated aquaporin proteins
Configuration	Flat sheet	Hollow fibre
Area (m^2)	0.0042	0.6
A ($L \cdot m^{-2} \cdot h^{-1} \cdot bar^{-1}$)	0.69	2.09
B ($L \cdot m^{-2} \cdot h^{-1}$)	0.34	0.07
S (μm)	707	301–150
Contact angle active layer (°)	68.1	68.2
Zeta potential (mV)	-12.8 ± 1.18	-17 ± 2

2.2. Plant setup

The experiments were carried out in two plants, which were very similar, changing the type of the module and the volume of the tanks for the FS and DS, since the membranes used had different configuration and active surface. The configuration of the plants is shown in Fig. 1.

As mentioned above, due to the differences in membrane area, different tanks were used. Plastic tanks, with a volume of 5 L (for flat sheet membrane) and 50 L (for hollow fibre membrane), were used as containers for draw and feed solutions. 5 L DS tank was mounted on a digital balance (PKP 4200-2, Kern, Germany) which was used for continuous measuring of its mass. The data from scale were transferred to data logging software on personal computer. For the membrane with the largest area, the flux measurement was measured as a volume difference due to the water volume transferred from the FS tank to the DS tank. FS tanks of both membranes were placed on magnetic stirrers (SBS, Spain) to prevent particle deposition. The tanks were connected to rubber tubes, through which the solutions were fed to the FO module, where the streams interacted through the membrane. Between the tanks and module, each circuit had a manometer (Nuova Fima, Italy), flowmeter (Psm-21, Tecfluid, Spain) and peristaltic pump (Pumpdrive 5106, Heidolph, Germany). The plant was also equipped with two electrical conductivity meters (CDH-SD1, Omega Engineering), one for each solution. The CFO42 module manufactured by Sterlitech Corporation (USA) was used to house the FTSH2O™ (Fluid Technology Solutions, USA) flat sheet membrane. The other membrane studied was a hollow fibre membrane (HFFO.6, Aquaporin Inside, Denmark), which was provided with its own module. The characteristics of the membranes are presented in Table 2.

It was decided to work in counter-current mode since it has been reported that, when working with FS with a high amount of solutes, the osmotic pressure can rise to a large extent. Thus, the counter-current operation increases the driving force compared to co-current operation (Sanahuja-Embuena et al., 2019). The membrane position was FS facing the active layer for all the experiments. For membrane characterization, different concentrations of DS were prepared, using NaCl of 25, 50, 75, 100, 125, 150 and 200 g $\cdot$ L^{-1} (0.43, 0.85, 1.3, 1.7, 2.1, 2.6, 3.5 M, respectively). The operating conditions of the characterization tests were flow rates of 25 L $\cdot$ h^{-1} for FS and of 15 L $\cdot$ h^{-1} for DS. For the experiments with wastewater, in the case of the FTSH2O membrane, both FS and DS pumps were adjusted to a flow rate of 30 L $\cdot$ h^{-1}, whereas for the HFFO.6 the experiments were performed at 60 L $\cdot$ h^{-1} for the FS and 25 L $\cdot$ h^{-1} for the DS. The membrane performance was evaluated by the ability to increase the phenolic compounds concentration in the feed solution [% TPhC] through Eq. (1):

$$[\%TPhC] = \left(\frac{C_f}{C_i} - 1 \right) \cdot 100 \tag{1}$$

where C_f (ppm) and C_i (ppm) are the total phenolic compounds concentration in the feed solution at the end of the experiment and at the beginning, respectively. In order to characterize the membranes, water and reverse salt fluxes were measured. Water flux (Jw, $L \cdot m^{-2} \cdot h^{-1}$) was measured by the variation in weight of the DS as described in Eq. (2).

$$Jw = \frac{\Delta_m}{A_m \cdot \Delta t} \tag{2}$$

where Δ_m correspond to the mass change of the draw solution (g), A_m (m^2) is the membrane active surface and Δ_t (h) is the time between mass measures.

The reverse salt flux (Js, $g \cdot m^{-2} \cdot h^{-1}$) represents the salt passing through the membrane from the DS to the FS and it is experimentally valued considering the mass salt variation in the FS, through the following expression:

$$Js = \frac{V_t \cdot C_t - V_{t-1} \cdot C_{t-1}}{A_m \cdot \Delta_t} \tag{3}$$

where C_t (ppm) and V_t (L) are the salt concentration and the volume of the feed solution, respectively, at time t. The volume reduction (VR) of the FS was also evaluated for each experiment and it was determined based on the volume of permeate (volume transferred to the draw in relation to the initial volume of the feed (Singh et al., 2019)) (Eq. (4)):

$$\%VR = (\frac{V_p}{V_i}) \cdot 100 \tag{4}$$

Where V_p (L) and V_i (L) are the volume of the permeate and the initial feed solution, respectively. The tests carried out with the flat sheet membrane were performed with 4.5 L of initial FS and 2.5 L of initial DS, while 25 L of FS and 15 L of DS were used for the tests with the hollow fibre membrane. Due to the volume involved in each test, the tests performed with the FTSHO2, with the smallest surface area, lasted 4300 min (71.6 h), while the test with the HFFO.6 lasted about 120 min (2 h). After each experiment, the membranes were flushed for 30 min with tap water and then 10 min with osmotized water through both the feed and draw solution sides. The tests were carried out at 20 °C at flow rates of 40 $L \cdot h^{-1}$ and 20 $L \cdot h^{-1}$ for FS and DS sides, respectively. If the membrane does not recover its permeability (over 90%), cleaning with water was repeated. Cleaning with P3 Ultrasil (Ecolab, Spain) 1% v/v under the same conditions was carried out only if two cleaning cycles with water do not achieve the recovery of the initial permeability of the membranes. Before (with the pristine membrane) and after cleaning, a single pass test (without recirculation) was carried out to verify the membrane permeability recovery. For it, a 0.5 M NaCl solution was used as DS and osmotized water as FS. The flow rates were 25 $L \cdot h^{-1}$ and 15 $L \cdot h^{-1}$ for FS and DS, respectively. Jw and Js average values were measured and used for comparison. The represented values of Js and Jw have been calculated according to Eqs. (2) and (3) considering Δt of 10 min (duration of the rinsing with osmotized water).

2.3. Analytical methods

The characterization of the draw and feed solutions consisted of determining the concentration of total phenolic compounds (TPhC), chemical oxygen demand (COD), chloride ions (Cl^-), pH and conductivity. COD and Cl^- concentration were measured with Merck kits (Germany) and a photometer (Nova 30, Merck, Germany). For the phenolic compounds content determination, the Folin–Ciocalteu (F–C) spectrophotometric method (Singleton et al., 1999), with tyrosol as a standard, was used. F–C reagent was acquired from Panreac (Spain) and absorbance (765 nm) of samples was measured with a UV VIS spectrophotometer DR 6000 provided by Hach Lange (USA). pH and conductivity were determined with the pH-Meter GLP 21+ and the conductivity meter EC-Meter GLP 31+, respectively, both supplied by Crison (Spain). High performance liquid chromatography (HPLC) was performed to identify low molecular weight phenolic compounds, such as tyrosol, and high molecular weight phenolic compounds, such as catechin, in the DS samples. For this, 5 mL of sample were mixed with 10 mL of ethyl acetate for 4 min in a vortex (Heidolph, Germany). Then it was centrifuged for 5 min at 3000 g (model Thermo Heraeus Megafuge 16 R model, Thermo Scientific, USA), then the supernatant was separated with a micropipette. The extraction was repeated 3 times. Then, with a rotary evaporator (R-114, BUCHI, USA) at 30 °C, the ethyl acetate was separated from the extract. The extract was mixed with 5 mL of NaOH/water (50:50) in a vortex, then filtered at 0.22 µm. Finally, 20 µL of the filtered extracts were injected into the HPLC device (model AS-4150, Jasco, USA). The HPLC system was equipped with a MD-2018 Photodiode Array detector and a Phenomenex Kinetex 5u Biphenyl 100 A column (4.6 × 250 mm, 5 µm). The flow rate was 1 $mL \cdot min^{-1}$ with an injection volume of 10 µL and the solvent system was phase A (0.5% acetic acid in water) and phase B (acetonitrile). The applied mobile phase gradient was based on a previous work (Sánchez-Arévalo et al., 2022). Tyrosol and catechin (Sigma Aldrich, Germany) were used as standards.

3. Results and discussion

3.1. Membrane water flux and reverse salt flux

The relationship between permeate flux and reverse solute flux with the DS concentration for both membranes is presented in Fig. 2. The experiment was carried out in a recirculation mode with osmotized water as FS. The results
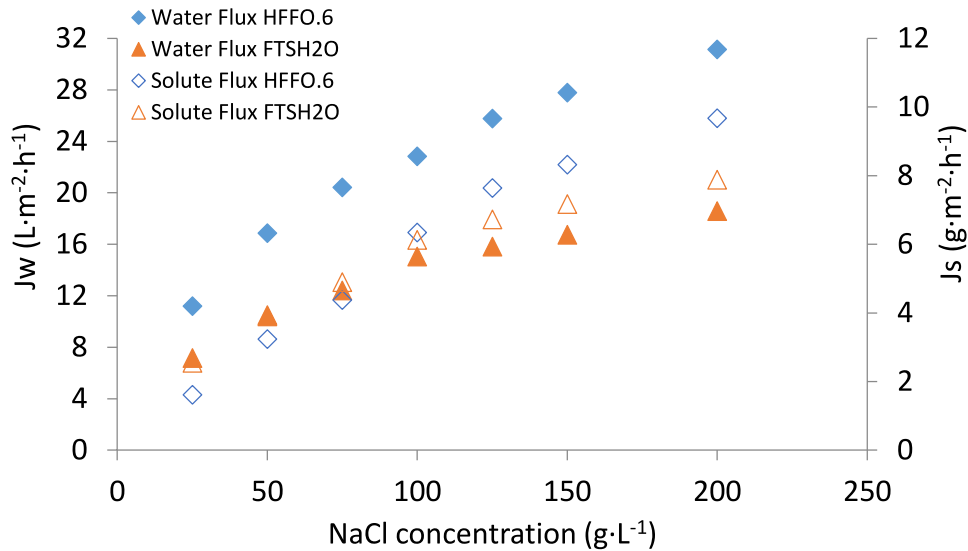
Fig. 2. Permeate flux and reverse solute flux for both membranes as a function of NaCl concentration in the draw solution (DS) when the feed solution (FS) was osmotized water: flow rates of 25 L · h^{-1} (FS) and 15 L · h^{-1} (DS).

showed that, for both membranes, water flux increased gradually as the concentration of salt in the DS increased. In the concentration range of 100 g · L^{-1}–150 g · L^{-1}, it was observed that, for the FTSHO2 membrane, the increment in water flux was lower than that observed from 50 g · L^{-1} to 100 g · L^{-1}, reaching a more or less stationary state. On the other hand, the HFFO.6 membrane presented an ascendingly tendency. The increase in salt concentration from 150 g · L^{-1} to 200 g · L^{-1} generated an increase in flux similar to that initially observed. Water flux increased from 7.16 L · m^{-2} · h^{-1} to 18.59 L · m^{-2} · h^{-1}, with an increase in reverse salt flux from 2.55 g · m^{-2} · h^{-1} to 7.73 g · m^{-2} · h^{-1}, for HFFO.6 membrane. A linear behaviour was expected since an increase in osmotic pressure produces an increase in Jw and an increase in the concentration gradient between the DS and the FS increases diffusive salt transport, Js (Salamanca et al., 2021). On the other hand, the existence of the plateau at high concentrations is due to the fact that the greater the applied osmotic force, the greater the influence of the dilutive external concentration polarization on the permeate side of the membrane, which significantly reduces the osmotic driving force. As a consequence, for high salt concentrations, the permeate flux does not increase proportionally with the applied osmotic pressure difference (Camilleri-Rumbau et al., 2019).

The specific reverse salt flux (Js/Jw) has been used as a measure to determine membrane selectivity, with a lower Js/Jw indicating less solute loss per unit of water permeated (Ren and McCutcheon, 2018). The HFFO.6 membrane presented lower Js/Jw than the FTSHO2, with both values corresponding to those given by the manufacturer and the literature (Nikbakht Fini et al., 2020; Salamanca et al., 2021). For the HFFO.6 membrane, it was measured a specific reverse salt flux of 0.145 g · L^{-1} and a water flux of 11.2 L · m^{-2} · h^{-1}, meanwhile for the FTSHO2 the specific reverse salt flux was 0.41 g · L^{-1} and water flux was 6.16 L · m^{-2} · h^{-1} (measured under flow rates of FS and DS of 25 L · h^{-1} and 15 L · h^{-1} respectively, using a 0.5M NaCl solution as DS).

The higher value of Js/Jw presented by FTSH2O is mainly due to the fact that the FTSH2O membrane has a higher coefficient of salt permeation (see value of B in Table 2).

The higher water permeability of the HFFO.6 membrane compared to the FTSHO2 may be due to the material of the membranes. On the one hand, the active layer made of polyamide is more hydrophilic, while the support layer is thinner, more porous and less tortuous. These parameters are directly related to the intrinsic characteristics of the membrane, influencing the solute transport through the support layer, which would decrease with greater porosity and less tortuosity, which in turn reduces the effect of the internal concentration polarization (Volpin et al., 2018). On the other hand, this is also explained by the presence of aquaporin proteins in its selective layer, which can transport 5 to 1000 times more water than other membranes (Aende et al., 2022). The higher fluxes shown by the polyamide TFC membrane compared to the CTA one when pure water was used as FS, are consistent with those available in the literature (Ortega-Bravo et al., 2016).

3.2. Experiments with NaCl solution as DS (E1 and E2)

Permeate flux values obtained in the four tests corresponding to E1 and E2 (Table 1) can be seen in Fig. 3. It is observed for E1 how Jw for the FTSHO2 membrane was 6.20 L · m^{-2} · h^{-1} at the beginning of the test, reaching 3.98 L · m^{-2} · h^{-1} in 4300 min, when a more or less stationary flux was reached. On the other hand, the HFFO.6 membrane presented a more pronounced decrease in Jw, decreasing from 8.81 L · m^{-2} · h^{-1} to 4.42 L · m^{-2} · h^{-1}, in 120 min. When the FS was
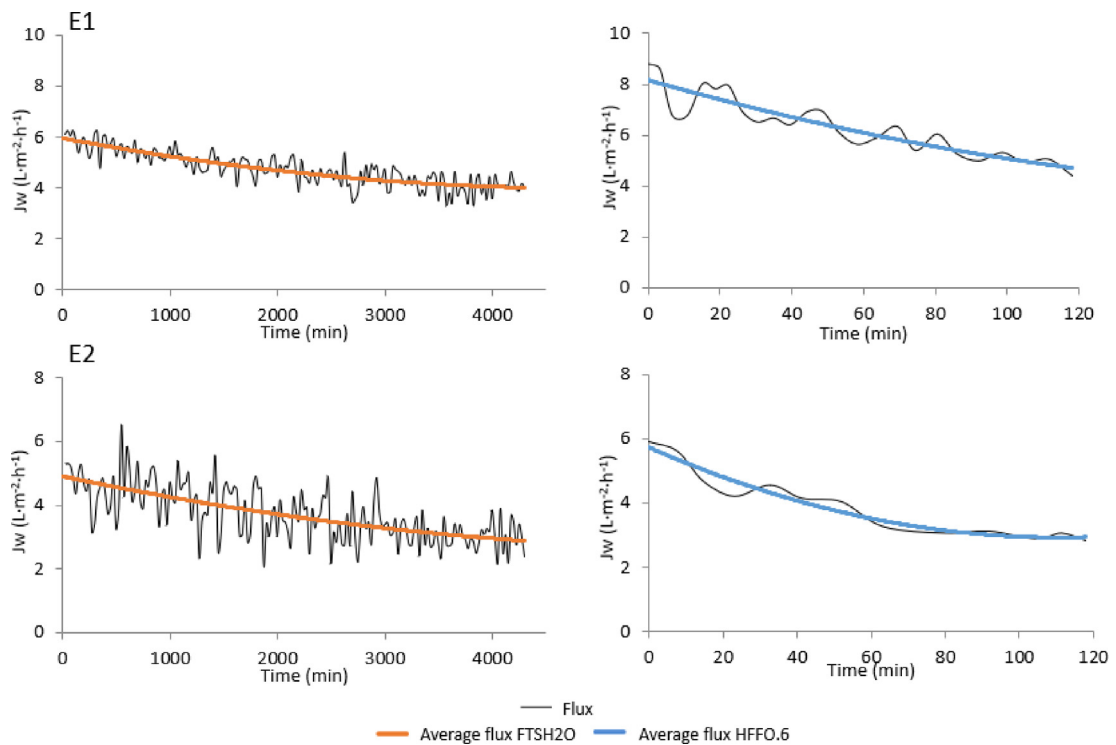
Fig. 3. Permeate water flux for the FTSH2O (left) and HFFO.6 (right) membranes for test E1 (1 g · L^{-1} tyrosol as FS and 30 g · L^{-1} NaCl as DS) and E2 (Pre-treated OOWW as FS and 30 g · L^{-1} NaCl as DS). FS: feed solution; DS: draw solution; OOWW: olive oil washing wastewater.

changed, feeding 5F-OOWW, a decrease in the initial Jw was observed for both membranes, being more pronounced for the HFFO.6 membrane. However, this membrane reached a stationary value of flux in E2, while the FTSHO2 membrane presented a continuous flux decline in E2.

The decrease in flux in E2 when compared to E1 could indicate that fouling has occurred. Moreover, concentration polarization is the limiting factor in the FO process (Loeb et al., 1997), affecting it externally (ECP) at the boundary of FS-membrane and DS-membrane, as well as internally (ICP) inside the substructure of porous support layer (Achilli et al., 2010). In E1, working only with model solutions, there is little influence of fouling by solute deposition on the membrane surface, so the decrease in Jw is mainly due to the decrease in osmotic pressure over time due to the passage of water from the FS to the DS, forming the dilutive ICP (characteristic of asymmetric FO membranes) (Singh et al., 2021). Therefore, this behaviour could be due to the combined effects of the loss of driving force over time, because of the progressive change in the volumes of FS and DS, and the dilutive ICP, discarding while membrane fouling was expected to be negligible (Tang et al., 2010).

The greater decline in Jw during the E2 test (55 and 52% for the FTSH2O and HFFO.6 membranes, respectively, when initial and final flux are compared), may be due to two factors, both influenced by the formation of a fouling layer, in addition to dilutive ICP As can be seen in Table 3 (FSF values), in the E2 tests a more noticeable diffusion of salts was observed from the DS to the FS. This greater salt accumulation near the active surface of the membrane, together with the other solutes already present in the FS, generates a greater osmotic resistance (cake-enhanced osmotic pressure, CEOP). CEOP is one of the main contributors to the general decrease in permeate flux (Boo et al., 2012). On the other hand, the cake also influences the capillary force resistance (CFR), which manifests itself as a pressure loss. This pressure loss of the feed solution at the membrane interface results in a decrease in the flow of water from the feed solution to the membrane surface. Therefore, the inflow of water from the FS to the membrane surface is reduced by the CFR, while the outflow of water through the membrane is reduced due to the CEOP effect (Takahashi et al., 2016). It has been reported that phenolic compounds contributed to gel layer fouling formed on the FO membrane surface (Singh et al., 2019). Regarding the continuous flow decrease in test E2 with FTSHO2 membrane (without reaching a stationary state), previous studies indicate that it may be due to the thicker CTA support layer of the FTSH2O membrane in comparison with the HFFO.6 membrane. This would lead to intense ICP, reducing its permeation flux compared to HFFO. 6 (50% thinner support layer) (Khanafer et al., 2021).

Also, it can be seen in Table 3 that both membranes managed to concentrate TPhC in the FS stream. However, the FTSH2O membrane allowed a fairly low increment in the concentration of tyrosol in the FS (around 15%), compared to the VR reached (43% regarding the initial volume). This may be due to the observed passage of tyrosol from FS to DS.

Table 3

Characteristics of the feed and draw solutions at the beginning and end of the tests carried out with NaCl solution as draw solution (E1 and E2), for both membranes tested.

Test	Parameter	HFFO.6 membrane				FTSH2O membrane			
		FSI[a]	DSI[c]	FSF[b]	DSF[d]	FSI[a]	DSI[c]	FSF[b]	DSF[d]
E1	[e]EC (mS · cm⁻¹)	0.08 ± 0.01	45.50 ± 2.00	0.77 ± 0.15	20.10 ± 2.00	0.07 ± 0.01	39.70 ± 5	0.92 ± 0.05	25.50 ± 2.50
	Cl⁻ (g · L⁻¹)	0.00	24.90 ± 4.00	0.014 ± 0.01	10.97 ± 1.83	0.00	26.5 ± 5.5	0.70 ± 0.01	14.10 ± 3.00
	[f] TPhC (gTyeq · L⁻¹)	1.00 ± 0.02	0.00	1.92 ± 0.10	0.03 ± 0.01	1.00 ± 0.01	0.00	1.17 ± 0.50	0.15 ± 0.09
	TPhC increase (%)			91.44 ± 9.39				15.02 ± 3.82	
	[g]VR (%)			66 ± 3.4				43 ± 2.1	
E2	EC (mS · cm⁻¹)	3.83 ± 0.20	44.30 ± 1.50	4.48 ± 0.57	24.00 ± 1.00	3.96 ± 0.15	41.50 ± 1.00	*	31.9 ± 0.50
	Cl⁻ (g · L⁻¹)	0.05 ± 0.002	27.90 ± 0.40	0.11 ± 0.03	14.40 ± 1.00	0.06 ± 0.01	27.60 ± 2.00	1.05 ± 0.10	15.0 ± 6.74
	TPhC (gTyeq · L⁻¹)	1.02 ± 0.03	0.00	1.81 ± 0.10	0.02 ± 0.01	1.03 ± 0.02	0	1.17 ± 0.01	0.10 ± 8.18
	TPhC increase (%)			62.60 ± 4.25				12.72 ± 1.57	
	VR (%)			53 ± 2.7				39 ± 0.9	

[a]FSI: initial feed solution.
[b]FSF: final feed solution.
[c]DSI: initial draw solution.
[d]DSF: final draw solution.
[e]EC: electrical conductivity.
[f]TPhC: total phenolic compounds.
[g]VR: volume reduction.
*not presented, measurement error.

This membrane was also the one that presented the greatest reverse passage of salts. On the other hand, the HFFO.6 membrane achieved an increment of 91% in the concentration of TPhC with a VR of 66%. Although tyrosol was observed in the final DS, its concentration was low compared to that measured for the other membrane and low salt concentration was also observed in the FSF. In the second test (E2), both the concentration of TPhC in the final DS and the achieved VR were lower, affecting the HFFO.6 membrane at higher extent. This can be explained due to the presence of organic matter (COD of 15.13 ± 2.86 g · L⁻¹), which caused membrane fouling, affecting the pass of water through the membrane. In fact, the water flux was also reduced compared to the results of the previous tests (Fig. 3). Also, the passage of phenolic compounds was lower than that observed in E1; therefore fouling could also interfere. The influence was greater for the FTSH2O membrane, since the final concentrations in the DS were 150.9 mgTyeq · L⁻¹ for E1 and 102.7 mgTyeq · L⁻¹ for E2.

Other authors, working with a combination of water produced in a gas field extracted from an offshore reservoir and process water from onshore operations as FS and brine from a desalination plant as DS, reported that hollow fibre membranes had better flux and greater rejection compared to the FTSHO2 membrane with the same effective membrane area (Minier-Matar et al., 2016). It is known that both the configuration of the membrane and its material affect the fouling propensity of the membrane and therefore the permeate flux. Other authors have also emphasized the different Jw of the polyamide TFC membrane membranes and the CTA membrane, the flux of the latter being lower (Chung et al., 2012). As commented before, this can be attributed to the hydrophilicity of the polyamide TFC membrane, with a thinner support layer (Table 2). The operating conditions of the HFFO.6 membrane is also a point to take into account. Studies have indicated the importance of improving hydrodynamics to minimize membrane fouling (Shaffer et al., 2015). Therefore, the hollow fibre configuration of the membrane favours hydrodynamics, since higher cross-flow velocities are generated within the fibres, generating higher shear forces that minimize the boundary layer. It is also important to note that membranes operate at different flow rates. While the FTSH2O membrane works with the same DS and FS flow rates (30 L · h⁻¹), the HFFO.6 membrane works with a higher FS flow rate (60 L · h⁻¹) and a lower DS flow rate (25 L · h⁻¹). This is also important, since operating at higher flow rates can also minimize fouling (Minier-Matar et al., 2022).

On the other hand, it has also been reported that TFC membranes generally have higher Jw and phenolic compound rejection than CTA membranes under the same operating conditions (Chia et al., 2021; Zhang et al., 2017). The lower rejection of phenolic compounds observed for the CTA membrane could be due to the passage of these compounds through the membrane due to a solution-diffusion mechanism, being adsorbed on the active layer of the FS side of the membrane, diffusing through the membrane and being desorbed to the DS. Studies indicate that it is due to the strong solute-membrane affinity as a consequence of the attraction of hydrogen bonds between phenols and the hydroxyl functions of CTA membranes, generating a greater adsorption capacity and, therefore, a much lower rejection than that of TFC membranes (Xiao et al., 2017).

The DS used may also play an important role, as studies observed that when NaCl is used as DS, sodium and chloride ions flowing from the DS side into the FO membrane of CTA can suppress the pore hydration shell. This results in an increase in the average pore size of the membrane, thus allowing small molecules to easily pass through the membrane (Lee et al., 2019). Finally, lower TPhC rejection could be also due to the fouling layer. It has been reported that in CTA membranes, fouling facilitated the transport of hydrophobic and hydrophilic organic contaminants across the membranes, resulting in high concentrations of target solutes in the permeate (Xu et al., 2006).

Table 4
Characterization of the feed and draw solutions used in the tests performed with residual table olive fermentation brine as draw solution.

Parameter	Feed Solutions		Draw Solution
	5F-OOWW[a]	UF-OOWW[b]	60F-FTOP[c]
pH	5.03 ± 0.04	5.19 ± 0.02	4.70 ± 0.05
[d]EC (mS · cm^{-1})	4.27 ± 0.11	5.15 ± 0.01	55.20 ± 14.1
Turbidity (NTU)	200.8 ± 2.2	0.04 ± 0.00	376.4 ± 25.4
[e]SS (ppm)	287.17 ± 36	< 5	762 ± 107
Colour	1.80 ± 0.14	1.19 ± 0.02	0.41 ± 0.11
[f]COD (gO$_2$ · L^{-1})	15.13 ± 2.86	10.14 ± 0.01	10.80 ± 4.21
Cl$^-$ (g · L^{-1})	0.03 ± 0.01	0.01 ± 0.01	33.42 ± 1.25
Ca$^+$ (g · L^{-1})	0.12 ± 0.02	0.10 ± 0.02	0.69 ± 0.07
Mg$^+$ (g · L^{-1})	0.19 ± 0.03	0.11 ± 0.01	0.25 ± 0.04
[g]TPhC (mgTy eq · L^{-1})	1182.78 ± 284.65	1074.12 ± 114.70	835.19 ± 167.59

[a]5F-OOWW: 5 μm filtered olive oil washing wastewater.
[b]UF-OOWW: ultrafiltrated olive oil washing wastewater.
[c]60F-FTOP: 60 μm filtered table olive fermentation brine wastewater.
[d]EC: electrical conductivity.
[e]SS: suspended solids.
[f]COD: chemical oxygen demand.
[g]TPhC: total phenolic compounds.

The VR and TPhC increase values were checked by mass balance to analyse the possible adsorption of compounds. Chloride concentrations at the beginning and at the end of the experiment also accomplish the chloride balance calculation.

Regarding the permeability recovery of the membrane after cleaning, the HFFO.6 membrane presented better permeability recovery and only one rinsing with osmotized water was necessary. However, the FTSHO2 membrane had to be cleaned with chemicals for the permeability recovery. Other authors working with the same membrane but in a hollow fibre configuration also observed irreversible fouling (Yee et al., 2019). They attributed this to pore clogging by humic acid due to the similar size (hydration radius between 2.3 nm and 7.7 nm (Kawahigashi et al., 2005)) when compared to the support layer pore sizes, which resulted in enhanced ICP and thus increased membrane resistance. In this case, the compounds present in the OOWW could also favour the fouling of the membrane. On the other hand, the easy cleaning of the HFFO.6 membrane compared to the FTSHO2 could also be due to its advantages of high packing density, self-supporting structure and uniform flow distribution, which not only facilitates membrane cleaning, but also mass transfer (Sanahuja-Embuena et al., 2019). It is important to note that although the area of each membrane has been taken into account in order to establish the operating conditions appropriate for the comparison, the different membrane area can imply different behaviours in terms of fouling. As Engelhardt points out (Engelhardt et al., 2019), aside from the material difference, both the differences in membrane size and architecture do not allow for a fair comparison due to variations in many experimental parameters (eg, water recovery, fluid flow rates, draw and feed volumes). For higher membrane area, contaminants will be more dispersed and cake layer will be less likely to form.

Due to the high passage of phenolic compounds to the DS with the FTSHO2 membrane, it was decided to analyse the DS at the end of E2. The idea was to identify which compounds crossed the membrane (low or high molecular weight phenolic compounds). For this purpose, the final DS was analysed by HPLC. Two standard solutions, one of tyrosol (MW: 138.164 g · mol^{-1}) representing the low molecular weight phenolic compounds and other of catechin (MW: 290.271 g · mol^{-1}), representing the high molecular weight ones were used. Tyrosol was quantified in the DS (Fig. S1), while catechin was not, so it can be induced that the passage is mainly due to the phenolic compounds with the lowest molecular weights. In previous studies, more than 20 phenolic compounds have been identified in olive oil washing wastewater from two-phase olive oil mills, 12 of them with a molecular weight lower than catechin (Cifuentes-Cabezas et al., 2022a). Therefore, working with this membrane would imply a considerable loss of phenolic compounds from the sample. For these reasons, it was decided to continue the experiments only with the HFFO.6 membrane.

3.3. Experiments with FTOP as DS (E3 and E4)

The characteristics of the feed and draw solutions used in E3 and E4 tests are shown in Table 4. The OOWW is characterized by an intense brown colour and a slightly acid pH. This acid profile is also a characteristic of the FTOP, but as difference, this wastewater has a yellow colour. As shown in Table 4, OOWW and FTOP have high levels of suspended solids, being 2.7 times higher the amount in the 60F-FTOP compared to the 5F-OOWW. Accordingly, turbidity, which is related to suspended solids concentration, is also higher in the 60F-FTOP and 5F-OOWW samples (376.4 NTU and 200.8 NTU, respectively, vs 0.04 NTU). The concentrations of calcium and magnesium ions are also represented. It is observed that the FTOP presents higher values than OOWW of both ions. On the other hand, though the UF does not manage to eliminate these ions, a certain decrease in their concentrations was observed. The organic matter present
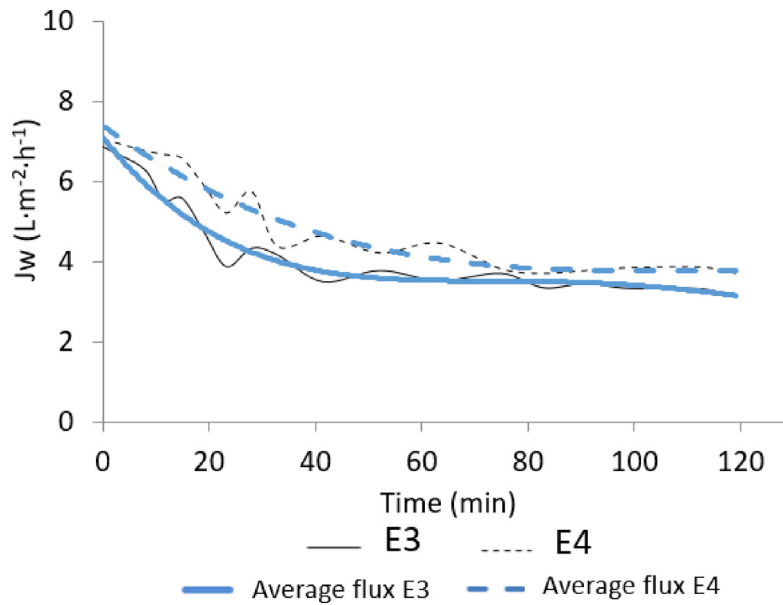
Fig. 4. Permeate water flux for the HFFO.6 membrane from tests E3 (pre-treated olive oil washing wastewater (OOWW) as feed solution (FS) and residual table olive fermentation brine (FTOP) as draw solution (DS)) and E4 (Ultrafiltration permeate from OOWW as FS and FTOP as DS).

in the samples were in the range of 10000 mg $\cdot$ L^{-1}–15000 mg $\cdot$ L^{-1}, being the content of COD in 5F-OOWW 40% higher compared with the 60F-FTOP sample. In all the samples, there was an important presence of phenolic compounds (between 800 mg Ty eq $\cdot$ L^{-1} and 1200 mg Ty eq $\cdot$ L^{-1}), with the lowest concentration value present in 60F-FTOP. Similar acidic profile and phenolic compounds concentrations were reported by Ferrer-Polonio et al. (2017), where four samples of FTOP were analysed, presenting a pH between 4 and 4.5 and an average of total phenolic content of 1114.25 $\pm$ 396.25 mgTy eq. $\cdot$ L^{-1}. Regarding the UF-OOWW sample, the absence of SS and turbidity was due to the UF process, as expected. On the other hand, COD also showed a decrease from 13.13 to 10.14 gO$_2$ $\cdot$ L^{-1}, while TPhC were not affected (9% decrease). The results obtained in this work are within the ranges observed in other studies (Cifuentes-Cabezas et al., 2021).

Fig. 4 shows the permeate values obtained in E3 and E4 experiments with the HFFO.6 membrane. It can be seen a more pronounced decrease with respect to E1 and E2 tests, i.e. with the tests using NaCl solution as DS. However, the average flux values were higher than those observed in E2, with flux values from E3 and E4 being 1.2 and 1.3 times higher, respectively. This was due to the higher osmotic pressure difference caused by FTOP (higher salt concentration than in the NaCl solution used in the previous tests). It can also be observed that, when working with the UF-OOWW (E4), permeate flux was higher, more stable and showed a lower drop in the first few minutes. This was due to the higher fouling that occurs when working with the 5F-OOWW compared to the UF-OOWW, since, as mentioned above, this fouling would increase the ICP, reduce the pore size and hinder back diffusion of dissolved substances. However, a greater difference between the Jw of E3 and E4 was expected. Similar water fluxes between E3 and E4 means that filtration of OOWW at 5 µm could be enough for maintaining the membrane without severe fouling during the process. Studies carried out by Volpin et al. (2018), pointed out the importance of pre-treating a wastewater with a high organic load before a FO treatment. They observed a large decrease in Jw when working with samples with a high organic matter content (primary effluent), compared to secondary effluents, with less organic matter content. It should not be forgotten that the FTOP used as DS, apart from a large amount of salts, also contained a high concentration of both total suspended solids and phenolic compounds, which can adhere to the membrane surface that faces the DS (support layer), causing fouling and concentration polarization (ECP and ICP), and therefore resistance to the passage of water (Mayko et al., 2018). Therefore, the reverse solute flux, concentration polarization and fouling on the surface of both sides of the membrane could affect water flux.

In Table 5, the characterizations of FS and DS after and before tests E3 and E4 are presented. Interestingly, it was observed that the tests carried out with FTOP as DS presented greater percentages of TPhC concentration and higher VR than the tests performed with NaCl solution as DS (E2). This was attributed to the high conductivity (and consequently high osmotic pressure) presented by the FTOP, which has been also used as DS in other studies, obtaining good results in terms of the generation of the osmotic pressure difference necessary between both sides of the membrane for the permeation of treated water towards the DS side (Luján-Facundo et al., 2020). Salih and Dastgheib (2017) observed a similar trend when working with a hypersaline brine extracted from a potential CO$_2$ sequestration site such as DS, obtaining a higher flux than with MgSO$_4$ (20%) as draw solution.

Table 5

Characteristics of the feed and draw solutions at the beginning and end of the E3 (pre-treated olive oil washing wastewater (OOWW) as feed solution (FS) and residual table olive fermentation brine (FTOP) as draw solution (DS)) and E4 (Ultrafiltration permeate from OOWW as FS and FTOP as DS) tests performed with the HFFO.6 membrane.

Test	Parameter	HFFO.6 membrane				Mass balance (g)		
		FSI[a]	DSI[c]	FSF[b]	DSF[d]			
						Initial	Final	|△|
E3	[e]EC (mS · cm^{-1})	2.86 ± 0.05	56.20 ± 2.00	4.88 ± 0.15	40.10 ± 1.00	663.1	655.1	7.9
	Cl$^-$ (g · L^{-1})	0.03 ± 0.001	40.10 ± 0.80	0.05 ± 0.003	23.44 ± 2.27	38.8	38.5	0.3
	[f]TPhC (gTyeq · L^{-1})	1.00 ± 0.01	0.83 ± 0.00	1.78 ± 0.00	0.59 ± 0.01	14.1	14.0	0.1
	Ca$^+$ (g · L^{-1})	0.11	0.68	0.17	0.41	8.9	8.8	0.1
	Mg$^+$ (g · L^{-1})	0.19	0.25	0.28	0.18			
	%[f]TPhC			77.43 ± 0.89				
	%[g]VR			53.0 ± 2.1				
E4	[e]EC (mS · cm^{-1})	2.38 ± 0.49	54.10 ± 1.50	5.21 ± 0.20	42.67 ± 2.14	634.2	615.9	18.3
	Cl$^-$ (g · L^{-1})	0.02 ± 0.002	39.10 ± 0.70	0.07 ± 0.005	18.40 ± 2.00	36.2	35.6	0.6
	[f]TPhC (gTyeq · L^{-1})	1.00 ± 0.03	0.80 ± 0.05	1.63 ± 0.10	0.57 ± 0.01	11.5	12.9	1.4
	Ca$^+$ (g · L^{-1})	0.09	0.59	0.14	0.41	6.4	6.2	0.2
	Mg$^+$ (g · L^{-1})	0.11	0.25	0.20	0.14			
	%[f]TPhC			74.13 ± 0.46				
	%[g]VR			49 ± 1.01				

[a]FSI: initial feed solution.
[b]FSF: final feed solution.
[c]DSI: initial draw solution.
[d]DSF: final draw solution.
[e]EC: electrical conductivity.
[f]TPhC: total phenolic compounds.
[g]VR: volume reduction.

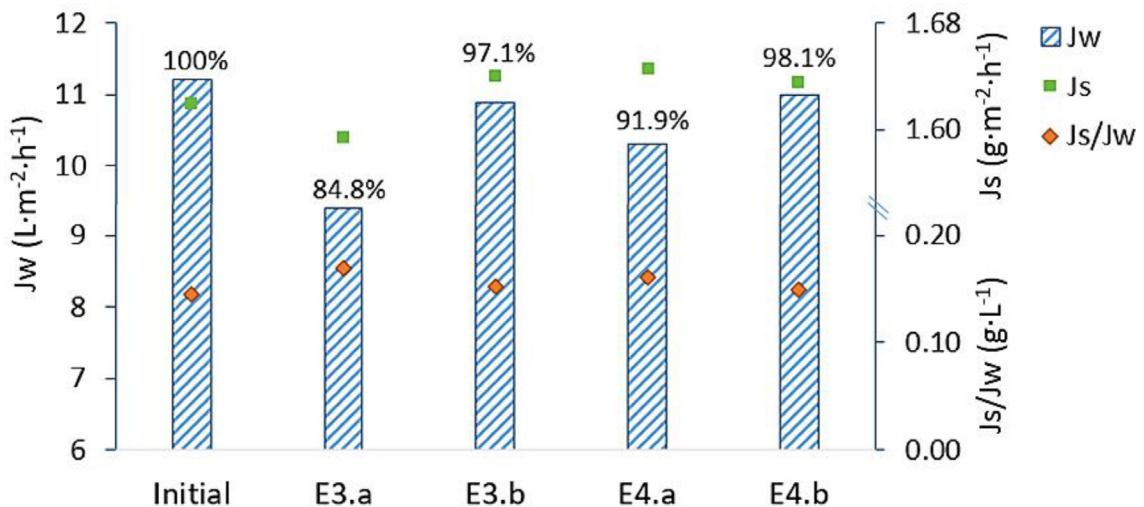**Fig. 5.** Recovery of the permeability, reverse salt flux (Js) and Js/Jw ratio after cleaning the membrane HFFO.6 after the experiments E3 (5F- OOWW as FS and 60F-FTOP as DS) and E4 (UF-OOWW as FS and 60F-FTOP as DS). The parameters were calculated at flow rates of 25 L · h^{-1} for FS and 15 L · h^{-1} for DS, using a 0.5 M NaCl solution as DS and osmotized water as FS. Cleaning was performed with water (20 °C) in two steps (a) and (b).

In addition to the higher osmotic pressure difference, the higher concentration of TPhC when FTOP was used as DS was due to the lower difference between TPhC concentration in FS and DS (compared to E2, in which NaCl solution was used). It is important to point out that the mass balance showed that there was no adsorption of TPhC on the membrane, since the concentrations measured at the beginning of the tests were very similar to those measured at the end of the process (SD 4.7%). These results are important when considering using the FTOP as DS, since, apart from delivering the osmotic force necessary for the concentration of TPhC in the FS, it generates an environment that reduced the passage of TPhC from the FS to the DS. In addition, it was checked that there was no adsorption of phenolic compounds, since calculated mass balance showed no loss of these compounds (Table 5).

Fig. 5 shows the Jw, Js and Js/Jw values of the HFFO.6 membrane after two cleaning steps. The results were obtained under the same conditions of the initial permeability (pristine membrane, initial value in Fig. 5) presented in Section 3.1. It

can be seen that after a cleaning cycle (E3.a and E4.a) the HFFO.6 operated with UF-OOWW as FS achieved a permeability recovery of 91.9%, while 84.8% was obtained when working with 5F-OOWW. However, in the next cycle (E3.b and E4.b) the global recovery percentages were more or less equal, achieving 98.1% and 97.1%, respectively. This may be due to the fact that the fouling is generated mainly due to cake layer formation, being mainly reversible (Boo et al., 2012; Singh et al., 2019; Zhang et al., 2014). This cake layer formation could also be responsible for the value of Js observed in E3a, being lower than the initial one (1.58 vs 1.63 $g \cdot m^{-2} \cdot h^{-1}$), indicating a lower reverse salt passage. As the calculated Js was after a cleaning cycle, it can be inferred that Js during the test was lower than that measured after E3a (verified by calculating Js with final values of Cl^- in FS and DS, value Js = 1.53 $g \cdot m^{-2} \cdot h^{-1}$). This may be due to the fact that when working with wastewater on both sides of the membrane, fouling occurs on both sides of the membrane. Although fouling decreases Jw (observed in E3 and E4), it also causes a decrease in Js. This was not observed after E4a (Js of 1.65 $g \cdot m^{-2} \cdot h^{-1}$) because the first rinsing recovered more than 90% of the initial permeability, which means that cake layer has been mostly removed, and because the FS came from a previous ultrafiltration step, and therefore contained smaller particles. This agrees with the higher concentration of chlorides observed in the final FS from E3 (Table 5). This lower passage of salts in E3 was also verified by mass balance, with the measured value of the concentration of Cl^- in the final FS being slightly higher than that obtained from the theoretical balance. This could explain the slightly higher percentage of TPhC concentration in the final FS and the higher VR. Fouling could enhance the rejection of TPhC. Something similar was observed by Valladares Linares et al. (2011), who observed an increase in the rejection of micropollutants in the presence of the fouling layer. They attributed this to a higher hydrophilicity of the fouled than of the clean FO membranes, reduced mass transport capacity, membrane swelling, and higher negative charge of the membrane surface (related to natural organic matter (NOM) acids and polysaccharides).

Although fouling implies a drop in Jw and Js, the relationship between the parameters (specific reverse salt flux) was practically constant, with Js/Jw values of 0.17 and 0.16 $mg \cdot L^{-1}$ for E3a and E4a, respectively, and 0.15 $mg \cdot L^{-1}$ for E3b and E4b (pristine membrane value of 0.15 $mg \cdot L^{-1}$).

It is important to point out that in all the tests carried out with the HFFO.6 membrane (i.e. independently of the DS), high permeability recovery values were achieved after two cleaning cycles. However, in E2 (NaCl solution as DS) a Jw recovery higher than 96% was achieved after only one rinsing cycle. This was a result of the higher fouling caused by the FTOP, due to the organic matter and divalent salts present. It has been reported that water containing calcium ions would be associated with increased membrane fouling due to the chemical interactions with the organic matter present, forming bridges between other molecules, which gives rise to a cross-linked gel layer that increases adherence to the membrane surface (Mi and Elimelech, 2008; She et al., 2012). This was justified by analysing the Ca^+ and Mg^+ ions present in the samples both in the FS and in the DS (see Tables 4 and 5). In tests E3 and E4, it can be observed high concentration of the divalent ions both in FS and DS. Studies have also indicated that the carboxyl groups on the polyamide TFC membrane surface are susceptible to organic fouling in the presence of divalent ions such as Ca^{2+}. Ca^{2+} ions bind to carboxyl groups on the membrane surface and to those of organic contaminants to form membrane-Ca^{2+}-organic bridges (Hao et al., 2019). On the other hand, it is observed that the concentration of the divalent ions is higher in the FS of E3 than in the FS of E4. Therefore, this greater fouling observed in test E3 could also be related to the lower passage of salts and TPhC to the DS observed in the test.

Finally, it has to be commented that though working with UF-OOWW generated lower flux decay, it did not present a greater concentration of phenolic compounds or volume reduction compared to 5F-OOWW. Thus, including the UF step would only generate an increase in process costs.

Through this study, it was shown that FO is a promising technology to concentrate phenolic compounds from oil mill wastewater without large associated costs because its less energy consumption compared to other membrane processes, as well as because of the reduced use of chemical reagents.

On the other hand, taking into account the circular economy, it was shown that the FTOP, effluent from the processing of table olives, is a DS suitable for the process with high osmotic pressure. This is a favourable point, both from an economic point of view (because there is no need either to buy reagents for a synthetic DS or to regenerate it), and from an environmental one (due to the use of wastewater). Finally, using FO with the HFFO.6 membrane, it was possible to obtain simultaneously a concentrate rich in phenolic compounds as well as to dilute a residual brine (FTOP).

4. Conclusions

The concentration of olive oil washing wastewater (OOWW), effluent rich in phenolic compounds, was studied by forward osmosis. Two membranes, FTSH2O and HFFO.6, were evaluated for this process in terms of Jw, Js/Jw, TPhC concentration and VR. The HFFO.6 membrane presented higher flux and lower Js/Jw, which was attributed to its material. When working with NaCl as DS, both membranes tested were able to concentrate phenolic compounds without presenting a high decrease in Jw. However, the reverse passage of salts and the passage of phenolic compounds from the FS to the DS was higher using the FTSH2O membrane.

Then, with HFFO.6, for the first time the concentration of OOWW was studied using FTOP as draw solution in a FO process. FTOP results as a suitable wastewater to be used as DS for the proposed FO process. Its two main advantages are the high osmotic pressure and the concentration of TPhC, which implies that the loss of these compounds by passage through the membrane from the FS to the DS is lower, achieving a concentrated OOWW with higher concentration of

these compounds in comparison by using NaCl as draw solution. In addition, unlike a NaCl solution, this is not a DS that has to be regenerated, since the diluted FTOP can be managed and fresh FTOP can be used in the process.

The use of UF-OOWW permeate as FS in comparison to 5F-OOWW, generated a lower decrease in flux. However, it did not present a greater concentration of phenolic compounds. The fouling observed was mainly reversible, being mitigated with two cleaning cycles with water. In this way, the process can be performed with 5F-OOWW, since severe fouling was not observed, being not needed an ultrafiltration step.

Summarizing, it was shown that FO is a promising process for both the concentration of phenolic compounds from OOWW and the dilution of FTOP. In addition, the proximity of table olive processing plants with olive oil mills (both near olive tree cultivars) make the process feasible since the cost of the brine transport will be very low. More studies at higher scale need to be done to evaluate long-term fouling and the economic viability of the process.

CRediT authorship contribution statement

Magdalena Cifuentes-Cabezas: Conceptualization, Methodology, Validation, Formal analysis, Investigation, Writing – original draft, Writing – review & editing, Visualization, Supervision. **Alessio Pavani:** Conceptualization, Methodology, Investigation. **María Cinta Vincent-Vela:** Conceptualization, Methodology, Writing – review & editing, Project adminis-tration, Funding acquisition. **José Antonio Mendoza-Roca:** Conceptualization, Methodology, Writing – review & editing, Visualization, Supervision, Project administration. **Silvia Álvarez-Blanco:** Conceptualization, Methodology, 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.

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