Separation and Purification Technology 360 (2025) 131228

Contents lists available at ScienceDirect

Separation and Purification Technology

journal homepage: www.elsevier.com/locate/seppur

Concentration of phenolic compounds from an orange peel waste extract using a combination of ultrafiltration and forward osmosis☆

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ARTICLE INFO

Handling editor: B. Van der Bruggen

Keywords:
Orange peel waste
Polyphenols recovery
Ultrafiltration
Membrane screening
Forward osmosis

ABSTRACT

Orange juice production industry generates tons of solid waste annually, losing the opportunity of recovering high added value bioactive compounds, such as polyphenols. Solid-liquid extraction was previously studied for extracting the phenolic compounds from the solid waste to a liquid stream. In this work, an integrated membrane process has been investigated for the purification and concentration of phenolic compounds from the orange extract. First, a pretreatment was performed using ultrafiltration membranes to purify the extract and to minimize membrane fouling in the following concentration step, due to the large pectin content of the orange extract. After studying several ultrafiltration membranes, the best results were obtained using the UP010 membrane (10 kDa), separating a significant amount of pectins (50 %). Flavonoids experienced low rejection values, being preferentially recovered in the permeate. The ultrafiltration permeate was then concentrated with forward osmosis using 58 $g{\cdot}L^{-1}$ NaCl as draw solution. Polyphenols were concentrated 2.03 times. Moreover, an insignificant amount of phenolic compounds, sugars and pectins passed through the membrane to the draw solution. Globally, the polyphenols were concentrated achieving a concentration factor of 1.47 in the whole integrated membrane process.

1. Introduction

Global orange juice production for 2023–24 is predicted to reach almost 1.5 million tons [1]. Moreover, 30 % of the total citrus production is mainly used for juice production, while 50 % of the weight of citrus fruits, corresponding to peels, pulp, and seeds, is discarded during processing [2]. Currently, these solid residues, commonly known as orange peel waste (OPW), are used for cattle feeding and composting. However, these uses cannot ensure a total use of OPW, so landfilling is also a common use, being problematic due to the high Chemical Oxygen Demand (COD) of OPW and the phytotoxic character of the phenolic compounds present in the waste. Literature shows in fact that OPW has great potential for utilisation, due to its richness in bioactive compounds, such as polyphenols [3,4]. Furthermore, the recovery of polyphenols from OPW is highly motivated by the circular economy principles which have recently gained importance [5]. The main polyphenols found in OPW include phenolic acids (gallic acid, *p*-coumaric acid, and ferulic acid), and flavonoids (hesperidin and narirutin) [6,7]. The pharmaceutical and cosmetic industries have shown a growing interest in the recovery and purification of phenolic compounds since they have been widely recognised for their antioxidant, anti-inflammatory, and antimicrobial properties [8]. For example, Hesperidin can be used to treat several affections such as hypertension, haemorrhoids, varicose ulcers, varicose veins, and rheumatoid arthritis, and it is capable of reducing pain and cholesterol [9,10]. Moreover, polyphenols have a potential application in animal fodder enrichment, reducing the use of antibiotics due to the antimicrobial properties of phenolic compounds [11].

The recovery of polyphenols from orange juice solid waste can be achieved by a solid–liquid extraction process. Different extraction

Abbreviations: COD, Chemical Oxygen Demand; DS, Draw Solution; FO, Forward Osmosis; FS, Feed Solution; GA, Galacturonic Acid; GAE, Gallic Acid Equivalent; MWCO, Molecular Weight Cut-Off; OPW, Orange Peel Waste; SRSF, Specific Reverse Salt Flux; TPC, Total Phenolic Content; UAE, Ultrasound-Assisted Extraction; UF, Ultrafiltration.

☆ This article is part of a special issue entitled: 'In Honor of Prof De Pinho' published in Separation and Purification Technology.

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https://doi.org/10.1016/j.seppur.2024.131228
Received 19 August 2024; Received in revised form 1 December 2024; Accepted 20 December 2024
Available online 20 December 2024

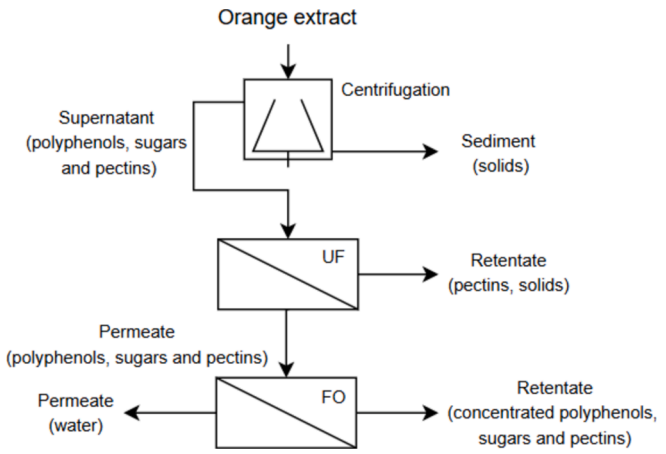

Fig. 1. Proposed flow-sheet for the recovery of phenolic compounds from orange extracts.

Table 1
Ultrafiltration membranes.

MWCO	Model
1 kDa	NP010
4 kDa	UH004
5 kDa	UP005
10 kDa	UP010

technologies have been studied, such as conventional solvent extraction, microwave-assisted extraction, ultrasound-assisted extraction (UAE), and supercritical fluid extraction [12]. The solvent used for polyphenols extraction is an important parameter to optimise. Indeed, solvents such as ethanol, water, or mixtures of both have been studied, which have been mostly accepted as safe for use in the cosmetic and food industries. Other parameters that should be optimised in order to maximize the extraction yield include the solid–liquid ratio, the extraction time and temperature [13,14].

The obtained extract has not only bioactive phenolics but also other components such as pectins and sugars. Therefore, a purification step is crucial. Membrane technology represents an excellent option for the separation and concentration of polyphenols since it allows the possibility of working in mild operating conditions using non-harmful materials, which do not damage phenolic compounds. Membranes require a low energy consumption, they permit working in continuous mode, and the scaling up is easy since they occupy little space due to their modular configuration. The efficiency of membrane technology for the purification of phenolic compounds from agri-food waste has been proved. A sequential process can be designed, combining separation and concentration processes to obtain a concentrated extract of purified polyphenols from agri-food by-products [15,16].

A pretreatment using ultrafiltration (UF) membranes is a good option to minimize membrane fouling in the following concentration step, due to the high total solids and pectin content of the orange extract [15,17]. Total recirculation mode is highly useful for the membrane selection stage, keeping the concentration in the feed tank constant. However, concentration mode, with the selected membrane, during extended periods is necessary for proving the industrial application.

Polyphenol concentration from agri-food waste has been reported using conventional pressure-driven membranes, such as nanofiltration or reverse osmosis [18,19]. However, novel membrane technologies such as forward osmosis (FO) can be an interesting alternative for concentrating polyphenols since they require less energy and membrane fouling is less severe than in pressure-driven membrane processes. In FO, the driving force is generated by a difference in the osmotic pressure between a concentrated draw solution (DS), and a less concentrated feed solution (FS). The presence of a selectively permeable membrane allows the passage of water, from the solution with the lowest osmotic pressure (FS) to the one with the highest (DS). The most widely used DS in FO to concentrate polyphenols from industrial food waste include NaCl, $MgCl_2$ and $CaCl_2$ [20–22]. Moreover, industrial brines, such as the reverse osmosis brine from seawater desalination, can be a promising DS since they possess the osmotic potential to concentrate phenolic compounds in the FS and simultaneously achieve its dilution in the DS, accomplishing the treatment of a problematic industrial wastewater [23]. Nevertheless, in FO, an undesired phenomenon called reverse salt flux usually occurs. The reverse salt flux consists of a passage of solutes from the DS to the FS and it must be controlled. The specific reverse salt flux (SRSF) parameter is used in literature to assess the ratio between the reverse salt flux and the water flux. Low values of SRSF are characteristic of an efficient process, as they represent salt passage to the FS per unit of water permeated [24]. Moreover, the large accumulation of salts near the membrane active layer, together with the solutes already present in the feed, generates a resistance to osmotic pressure known as cake-enhanced osmotic pressure (CEOP), which is one of the main reasons for the decrease in flux [25].

In this work, the main objective is the study of an integrated membrane process for the purification and concentration of phenolic compounds from the OPW aqueous extract. First, centrifugation was used as a pretreatment. Then, different UF membranes were tested for the separation of pectins to reduce membrane fouling in the concentration step. Finally, a forward osmosis process was carried out to concentrate the phenolic compounds. Polyphenol concentration from OPW has been reported using pressure-driven membranes [19,26,27]. Forward osmosis has been narrowly studied for the concentration of phenolic compounds from other agri-food residues [22,28]. The novelty of this work relies on the use of forward osmosis membranes for the concentration of polyphenols from OPW.

2. Materials and methods

2.1. Materials

Samples of Navel variety orange peel waste were kindly provided by Agriconsa S.A. (Algemesí, Valencia, Spain). Solid-liquid extraction was performed with the OPW using water at 80 °C, UAE, for 10 min, and a solid–liquid ratio of 1:10 (on a mass/volume basis) [29].

The reagents used for the sample characterisation were sodium carbonate anhydrous pure (PanReac AppliChem, Barcelona, Spain), sulfuric acid 96 % (PanReac AppliChem, Barcelona, Spain), Folin-Ciocalteu phenol reagent (MP Biomedicals, Irvine, USA), anthrone for analysis ACS (PanReac AppliChem, Barcelona, Spain), and carbazole for synthesis (Sigma-Aldrich, St. Louis, USA). For the DS sodium chloride pure (PanReac AppliChem, Barcelona, Spain) was employed. To prepare mobile phases for liquid chromatography-mass spectrometry (LC-MS), pure acetic acid (VWR, Radnor, USA), LC-MS grade acetonitrile (Honeywell, Charlotte, USA), and MilliQ water were employed. Water was obtained from a Direct-Q ®, 3UV system (Merck Millipore, Rahway, USA). Pure standards of protocatechuic acid, hesperidin, and narirutin were purchased from Sigma-Aldrich (St. Louis, USA) and were employed to quantify phenolic acids, flavonoids and terpenoids.

The proposed flow-sheet for the recovery of phenolic compounds from orange extracts is presented in Fig. 1.

2.2. Ultrafiltration

Previous to the UF process, orange extracts were centrifugated (ThermoFisher, USA) at 17,200 RCF for 6 min. For the UF step, different flat-sheet membranes were tested in total recycle batch configuration (Table 1). Thus, the concentration in the feed was maintained constant, focusing on the transmembrane pressure as the variable of the process. All the tested membranes were made of polyethersulfone and purchased

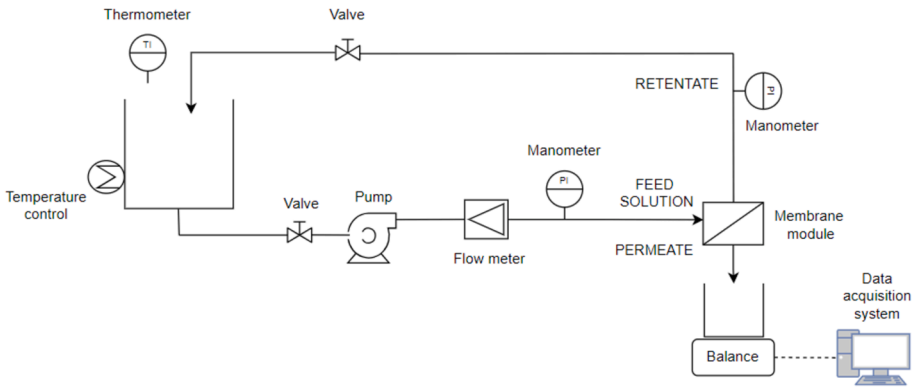

Fig. 2. Diagram of the Ultrafiltration plant.

from Microdyn Nadir (France). In the case of the UH004 membrane, the manufacturer reported a higher hydrophilicity of the active layer. Then, the best membrane was selected to perform a batch concentration test, without recirculating the permeate stream.

Flat-sheet membrane experiments were performed in an UF plant with a tailor-made module of 13 cm^2 and a feed volume capacity of 10 L. In Fig. 2 it is presented the diagram of the UF plant. All the runs were performed in batch operating mode.

Before their utilisation, the flat-sheet membranes were immersed in deionised water for 24 h to condition them. Then, all membranes were compacted at a transmembrane pressure (TMP) of 3 bar with a crossflow velocity of 1 $m{\cdot}s^{-1}$, until the flux was stabilized. Once the compaction finished, the hydraulic permeability (K) of the membrane was measured with osmotized water applying TMPs of 1, 2 and 3 bar, at a crossflow velocity of 1 $m{\cdot}s^{-1}$, using the following Eq. (1):

$$J_p = K{\cdot}\Delta P \tag{1}$$

where J_p is the permeate flux and ΔP is the transmembrane pressure. After assessing the hydraulic permeability, a total recycle batch configuration test was performed with the OPW extract using a TMP of 3 bar, at a crossflow velocity of 1 $m{\cdot}s^{-1}$. The pressure was selected according to previous results of polyphenol separation from mandarin wastewater [18]. Both, the permeate and the retentate were recycled back to the feed tank. Samples of feed and permeate were taken. For each sample, sugars, color and Total Phenolic Content (TPC) were analysed, in order to assess the rejection rate (%R) using the following Eq. (2):

$$R = 1 - \frac{C_p}{C_f}{\cdot}100 \tag{2}$$

where C_p is the concentration in the permeate and C_f is the concentration in the feed.

After the total recycle batch test, each membrane was cleaned by rinsing the plant with water for 30 min, increasing the crossflow velocity to 1.5 $m{\cdot}s^{-1}$ without applying any TMP. In the cases where water rinsing did not recover at least 90 % of the initial permeate flux, a chemical cleaning was performed using Ultrasil 110 at 0.7 % (v/v) for 15 min at room temperature and a crossflow velocity of 1.5 $m{\cdot}s^{-1}$ without applying any TMP. Afterwards, a batch concentration test was performed at a feed crossflow velocity of 1 $m{\cdot}s^{-1}$ and a TMP of 3 bar, with the best membrane selected from the previous tests. A volume reduction factor (VRF) of 2.6 was reached. The initial volume used in the batch concentration test was 8 L. The VRF was calculated using the following Eq. (3):

$$VRF = \frac{V_0}{V_f} \tag{3}$$

where V_0 is the initial volume in the feed tank and V_f is the final volume in the feed tank. Samples of feed and permeate collected during the experiments at different values of VRF were characterised to determine the rejection values of sugars, color and TPC. Also, the global permeate recovered during the entire process was characterized. After the batch concentration test, the membrane fouling was removed by rinsing the plant with water for 30 min, increasing the crossflow velocity to 1.5 $m{\cdot}s^{-1}$ without applying any TMP, first with water at room temperature and then with water at 35 °C. Finally, a chemical cleaning was necessary, using Ultrasil 110 at 0.7 % (v/v) for 15 min at room temperature and a crossflow velocity of 1.5 $m{\cdot}s^{-1}$ without applying any TMP.

2.3. Forward osmosis

The permeate obtained in the UF batch concentration test was used as the feed solution for the concentration process with forward osmosis. This strategy was implemented to concentrate the polyphenols recovered in the UF permeate at a higher purity. The experiments were carried out using the CFO42 module manufactured by Sterlitech Corporation (USA) and the FTSH2O™ (Fluid Technology Solutions, USA) flat sheet membrane made of cellulose triacetate (CTA) with an active area of 0.0042 m^2. High density polyethylene tanks with a volume capacity of 5 L were used as containers for feed and draw solutions. DS mass was continuously measured by a digital balance (EW, Kern, Germany). The water flux (J_w) was measured as a volume difference due to the water volume transferred from the FS tank to the DS tank using the following Eq. (4).

$$J_w = \frac{\Delta V}{A_m{\cdot}\Delta t} \tag{4}$$

where ΔV corresponds to the volume change of the DS, A_m is the membrane area, and Δt is time between volume measures. Two conductivity meters (CDH-SD1, Omega Engineering) were used for continuously measuring the electrical conductivity, one for each solution. Calibration lines of salt concentration-conductivity were performed with each conductivity meter. Hence, the concentration of salt was continuously registered in both FS and DS for the membrane characterisation. The reverse salt flux (J_s) was determined measuring the variation of salt concentration in the FS using the following Eq. (5).

$$J_s = \frac{V_t{\cdot}C_t - V_{t-1}{\cdot}C_{t-1}}{A_m{\cdot}\Delta t} \tag{5}$$

where V_t and C_t are the volume and the salt concentration of the feed solution, respectively, at time t. FS tanks were placed on magnetic stirrers (SBS, Spain) to prevent particle precipitation. Counter-current mode was selected, according to Sanahuja-Embuena et al. [30]. They reported that the counter-current operation increases the driving force compared to co-current operation. The FS faced the active layer for all the experiments. Before using the membrane, it was immersed in

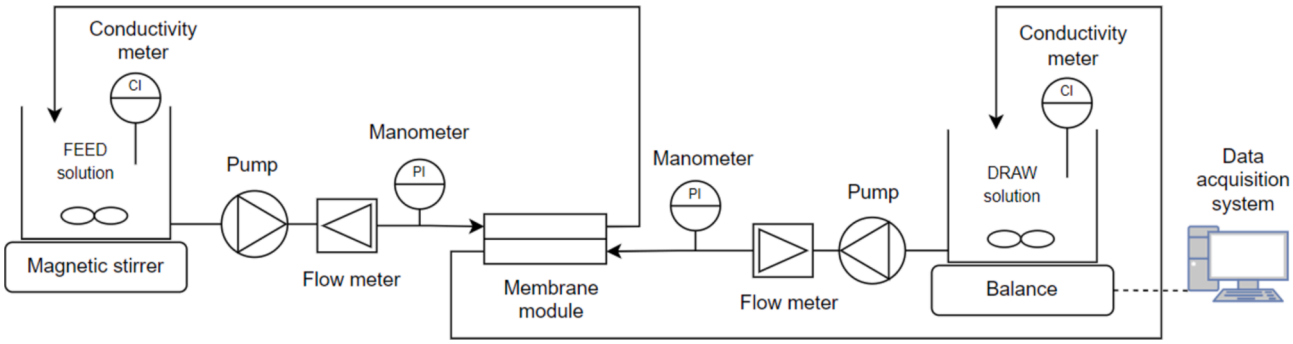

Fig. 3. Diagram of the forward osmosis plant.

Table 2
Characterisation of the orange peel waste extract obtained by ultrasound assisted extraction with water as solvent. Extraction conditions: solid–liquid ratio of 1:10 (w/v), at 80 °C for 10 min. TPC: Total Phenolic Content, COD: Chemical Oxygen Demand.

Parameter	Value
TPC (mg·L^{-1})	243 ± 9
COD (mg·L^{-1})	10600 ± 41
Sugars (mg·L^{-1})	5258 ± 64
Pectins (mg·L^{-1})	738 ± 33
Color	0.82 ± 0.04
pH	4.33 ± 0.10
Conductivity (μS·cm^{-1})	553 ± 6
Total solids (g·L^{-1})	4.8 ± 0.1

deionised water for 24 h to be conditioned. The pristine membrane was characterised measuring the J_w and J_s using sodium chloride (NaCl) at different concentrations (50, 100, 150 and 200 g·L^{-1}) in the DS and distilled water in the FS. Then, the concentration experiment was performed for 5 days using the ultrafiltered orange extract as FS. The DS consisted of a 58 g·L^{-1} NaCl solution. The concentration of NaCl was selected simulating a seawater desalination brine [23]. Samples of FS and DS were taken every 24 h. Flow rates of 25 L·h^{-1} were applied for both FS and DS in all the experiments. After the experiment, a membrane cleaning was performed. First, a rinsing during 30 min using distilled water at room temperature, in both FS and DS, was performed. Flow rates of 25 L·h^{-1} were applied for both FS and DS in the first rinsing and 35 L · h^{-1} in the second rinsing. Then a backflushing was performed, using distilled water in the DS and NaCl at a concentration of 50 g·L^{-1} in the FS. Finally, a third rinsing was conducted with hot water at 40 °C and a flow rate of 35 L·h^{-1}, in both FS and DS. All the experiments were performed in batch operating mode. In Fig. 3 the diagram of the forward osmosis plant is presented.

2.4. Characterisation of samples

2.4.1. Phenolic content measurement

Folin-Ciocalteau methodology [31] was performed to determine an overall value of the phenolic content expressed as milligrams of gallic acid (GA) equivalents per liter. A calibration curve relating the absorbance (y) and GA concentration (x) was performed in the range 0–500 mg·L^{-1} GA (y = 2.44·10^{-03}x) with a regression coefficient (r^2) above 0.9993.

Additionally, an analytic methodology based on LC-MS was applied to determine the phenolic profile of the UF samples. This allowed, not only to characterize the samples in detail, but also the evaluation of the individual rejection index of each phenolic compound found in the UF streams. Thus, 4 μL of each sample were injected in an Agilent 1260 Infinity II liquid chromatograph coupled to a 6546 quadrupole-time-of-flight (QToF) mass analyser (Agilent Technologies, Santa Clara, CA, USA). The analytes were separated throughout a Zorbax Extend C18 column (4.6 × 100 mm, 1.8 μm) (Agilent Technologies, USA), at a flow rate of 0.6 mL·min^{-1}. Mobile phase A was pure water, whereas mobile phase B was acetonitrile. Both mobile phases were acidified with 0.5 % acetic acid and they underwent the following gradient: 5 % B (initial conditions), 11 % B at 2.5 min, 20 % B at 7 min, 90 % B at 16 min, 95 % B at 17 min. 95 % B was maintained until 19 min and then the equipment took 3 min to return to the initial conditions. The temperature in the column oven was kept at 40 °C. A previous study was employed to select the parameters for the MS, which worked in negative polarity. To quantify the compounds, standard calibration curves were employed. They were prepared in the range 1–25 mg·L^{-1}.

2.4.2. Complete characterisation of samples

To characterise the samples, electrical conductivity (Conductimeter GLP31+, Crison, Barcelona, Spain), and pH (pHmeter GLP31+, Crison, Barcelona, Spain) were assessed. The COD (mg·L^{-1}) was measured by means of the 1.14541.0001 kit from Merck (Darmstadt, Germany) and chloride content (mg·L^{-1}) was measured using the 1.14720.0001 kit (Merck, Darmstadt, Germany). Total sugars content was determined by the Anthrone method [32]. Pectin content (mg galacturonic acid·L^{-1}) was determined with the galacturonic acid (GA) method [33]. Calibration curves for sugars and pectins, relating the absorbance (y) and concentration (x), were performed in the range of 0–100 mg glucose·L^{-1} for sugars (y = 1.37·10^{-02}x − 7.88 ·10^{-03}) and 0–300 mg GA·L^{-1} for pectins (y = 4.86·10^{-03}x). All regression coefficients (r^2) were above 0.9998. Color was determined by measuring the absorbance at three different wavelengths (436 nm, 525 nm, and 620 nm) using a UV–VIS DR 600 spectrophotometer (Hach, Düsseldorf, Germany), according to ISO 7787:2022, method B [34]. Total color was calculated using Eq. (6):

$$Color = \frac{A_{\lambda=436}^2 + A_{\lambda=525}^2 + A_{\lambda=620}^2}{A_{\lambda=436} + A_{\lambda=525} + A_{\lambda=620}} \quad (6)$$

3. Results

First of all, the orange extract was characterised. As can be seen in Table 2, OPW contained a significant amount of TPC that enable the utilisation of this residue as a source of high added-value compounds. Among these interesting phenolic compounds, the molecules of narirutin and hesperidin are notable because of their beneficial bioactivities [35,36]. In a previous work by our research group [29], they were determined in the aqueous extract of OPW, motivating its utilisation. Considering that mostly flavonoids were present in the extract, an underestimation of TPC is plausible, as the interaction of several flavonoids (such as hesperidin, narirutin, apigenin, luteolin, etc.) and Folin-Ciocalteu reagent is limited by the absence of a catechol group [37]. Nevertheless, the TPC content is adequate to validate the antioxidant content of OPW and to allow the comparison of the results with other studies in the literature, as Folin-Ciocalteu is the preferred analytical method when agri-food effluents are processed by means of membrane

Table 3
Initial water permeability (measured with osmotized water) and permeate flux (J_p) at the end of the run in the total recycle batch configuration test at 3 bar. The permeate flux values are average values of the permeate flux obtained at the end of the test performed with the orange peel waste extract (Fig. S1) when the flux reached the steady state.

Membrane type	Initial water Permeability ($L{\cdot}m^{-2}{\cdot}h^{-1}{\cdot}bar^{-1}$)	J_p ($L{\cdot}m^{-2}{\cdot}h^{-1}$) at 3 bar
NP010	17.48 ± 0.34	10.37 ± 0.15
UH004	10.52 ± 0.15	18.01 ± 0.24
UP005	10.53 ± 0.18	10.80 ± 0.26
UP010	59.07 ± 0.20	22.99 ± 0.25

technology.

It must be remarked the large values of COD, total solids and pectin content (Table 2), which made necessary to perform a pretreatment before the polyphenol concentration. The presence of sugars, pigments, solids and pectins in the OPW extract was also reported previously [29,38,39].

3.1. Ultrafiltration

Total recycle batch configuration test was performed with different UF membranes and the best membrane was selected for the batch concentration test.

3.1.1. Total recycle batch configuration test

The initial water permeability of the tested UF membranes is presented in Table 3. Comparing to literature, Restolho et al. [40] obtained a permeability of 15 $L{\cdot}m^{-2}{\cdot}h^{-1}{\cdot}bar^{-1}$ with the NP010 membrane, Antón et al. [41] obtained a permeability of 13 $L{\cdot}m^{-2}{\cdot}h^{-1}{\cdot}bar^{-1}$ with the UH004 membrane and Zhang et al. [42] reported permeability values of 10 $L{\cdot}m^{-2}{\cdot}h^{-1}{\cdot}bar^{-1}$ and 50 $L{\cdot}m^{-2}{\cdot}h^{-1}{\cdot}bar^{-1}$ for the UP005 and UP010 membranes, respectively. The values obtained in this work are similar to the reported ones, but it must be also considered that different flat-sheet membrane pieces could present slightly different permeability values [43]. The highest permeate flux in the total recycle batch configuration with the orange extract was obtained with the UP010 membrane. However, membrane fouling was more relevant for this membrane, since permeate flux decline was the largest and it took more time to reach the steady state (Fig. S1). It has been previously reported that membranes with greater pores suffer from more severe fouling than membranes with smaller pores [44]. This can be related to a higher pore blockage, since a wider range of compounds are likely to penetrate the pores, reducing their internal area [45–47]. Moreover, the UH004 membrane showed higher permeate flux than the UP005 membrane, even though they have a similar molecular weight cut-off (MWCO). This could be attributed to the higher hydrophilicity of the UH004 active layer, which favoured water permeation.

The rejection of different compounds for each membrane is presented in Fig. 4. The rejection of pectins varied from 54 to 59 % for NP010, UH005 and UP005 membranes. However, these membranes also rejected a significant amount of phenolic compounds ($R_{polyphenols}$ = 21–41 %), which was undesired. As published before, the majority of the phenolic compounds present in orange-derived aqueous streams are flavonoids [18], whose molecular weight is high (579–649 g/mol) compared to pectins (194 g/mol). This prevalence of flavonoids was later confirmed when the permeate of the batch concentration experiment was characterized in detail by LC-MS, as can be observed in Table 4, which will be commented in detail later. On the other hand, the UP010 membrane, which presents larger pores, rejected a low fraction of phenolic compounds ($R_{polyphenols}$ = 4 %) being notably higher the rejection of pectins ($R_{pectins}$ = 29 %). Moreover, the color of the samples was notably reduced (R_{color} = 70 %) and the COD was also reduced

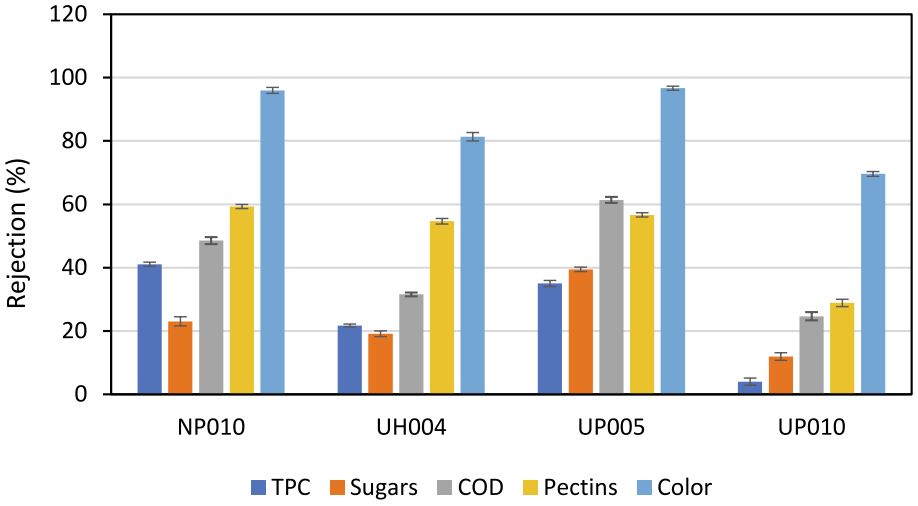

Fig. 4. Rejection rate for the ultrafiltration membranes in the total recycle batch configuration tests at 3 bar and a crossflow velocity of 1 $m{\cdot}s^{-1}$.

Table 4
Compounds determined by LC-MS, including their *m/z*, retention time, chemical class, and their concentration in the ultrafiltration (UF) permeate.

Compound	*m/z*	Retention time (min)	Concentration in the global UF permeate ($mg{\cdot}L^{-1}$)	Chemical class
Methyl-protocatechuic acid-O-sulfate	246.9907	4.95	2.77 ± 0.08	Phenolic acids
Dehydrophaseic acid	443.1923	5.70	1.26 ± 0.02	Terpenoids
Narirutin	579.1721	10	16 ± 3	Flavonoids
Luteolin rutinoside	593.1516	6.97	12.04 ± 0.07	Flavonoids
Hesperidin	609.1819	10.35	323 ± 32	Flavonoids
Apigenin-7-O-(malonylapyosil)-hexoside	649.2529	9.40	11.94 ± 0.06	Flavonoids
Nomilin-17-β-d-glucoside	693.2756	10.83	7.1 ± 0.1	Terpenoids
Nomilinic acid 17-O-β-d-glucoside	711.2866	10.76	0.51 ± 0.01	Terpenoids

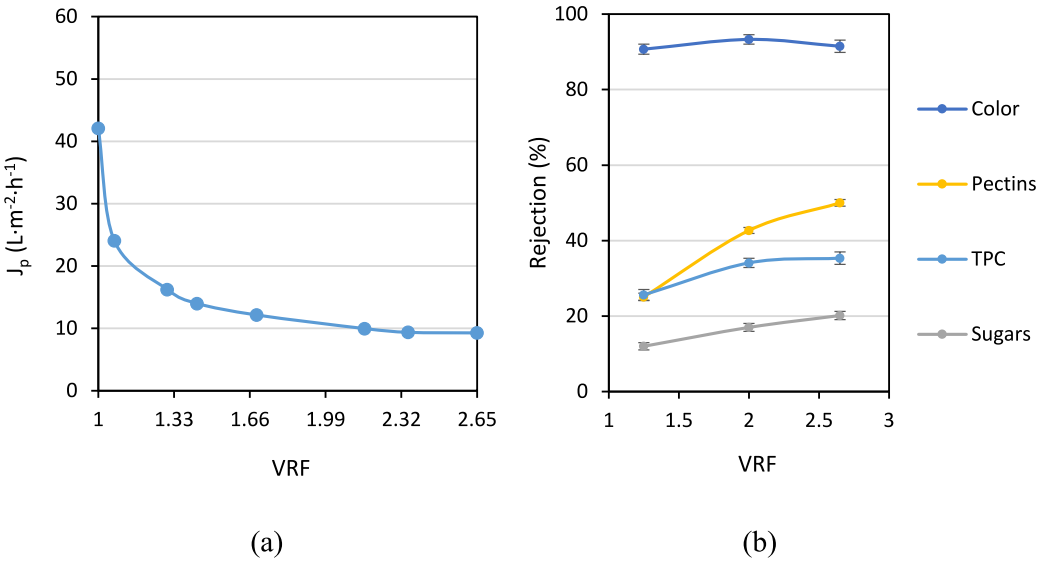

Fig. 5. Permeate flux (a), and rejection rate (b) in the batch concentration test using the UP010 membrane at 3 bar and a cross-flow velocity of 1 m·s^{-1}.

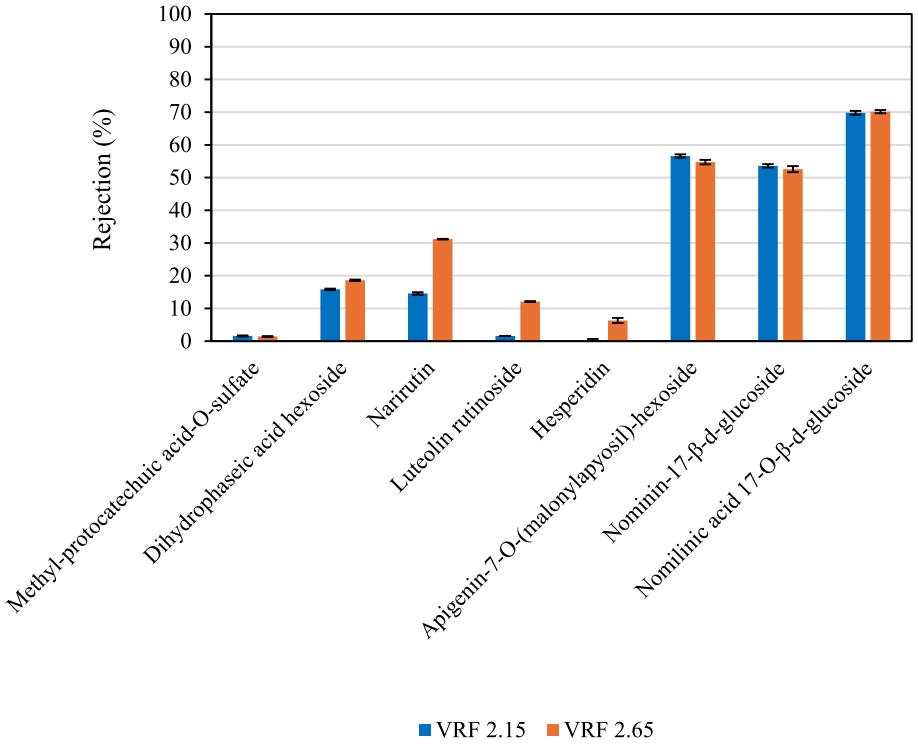

Fig. 6. Individual rejection of each compound determined by LC-MS in the aqueous extract of orange peel waste after ultrafiltration with the UP010 membrane, at 3 bar and 1 m·s^{-1}.

Table 5
Membrane cleaning and water permeability recovery in the batch concentration test with the UP010 membrane.

Cleaning type	Water 20 °C 30 min 1.5 m/s	Water 35 °C 30 min 1.5 m/s	Ultrasil 110 0.7 % v/v 15 min 1.5 m/s
Initial Permeability (L·m^{-2}·h^{-1}·bar^{-1})	59.07	59.07	59.07
Final Permeability (L·m^{-2}·h^{-1}·bar^{-1})	27.45	39.79	59.07
% Recovery	47 %	67 %	100 %

(R_{COD} = 25 %). Therefore, UP010 membrane was selected because of a higher permeate flux, a better separation of pectins, COD and color, and a very small rejection of phenolic compounds. Gökmen et al. [48] also reported a negligible removal (up to 7 %) of total phenols in the clarification of apple juice using a 10 kDa polyethersulphone membrane.

The membrane cleaning (Table S1) revealed that the permeability was recovered by more than 90 % for the UP005 and UH004 membranes only with water rinsing. However, for the NP010 and UP010 membranes, a chemical cleaning with Ultrasil 110 0.7 % v/v was necessary. It has been reported that gel layer formation is more likely to occur in membranes with higher permeate flux (such as the UP010 membrane) [49], as the accumulation of solids on the membrane surface is favoured.

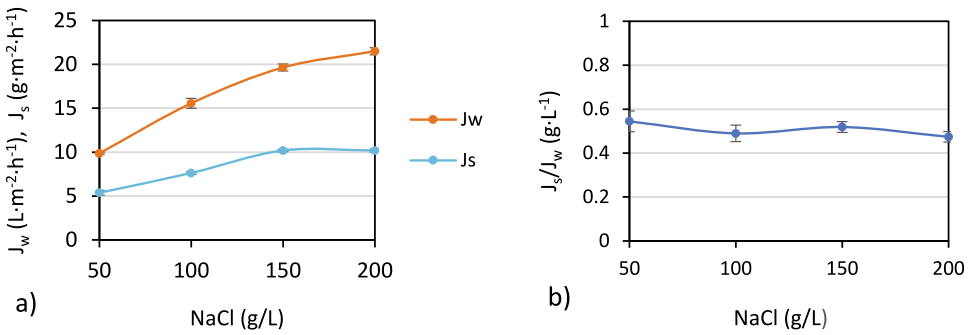

Fig. 7. Characterisation of the forward osmosis membrane: (a) water flux (J_w) and reverse salt flux (J_s), (b) specific reverse salt flux (J_s/J_w).

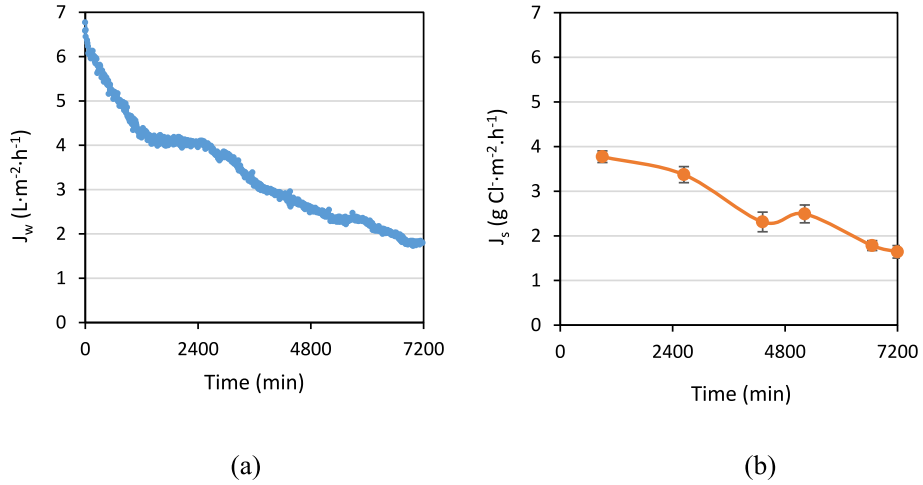

Fig. 8. Forward osmosis concentration test using ultrafiltered orange extract as feed and 58 $g{\cdot}L^{-1}$ NaCl as draw solution: (a) water flux, (b) reverse salt flux.

Table 6
Membrane cleaning: (a) water flux recovery, (b) initial and final membrane characterisation using NaCl as draw solution at a concentration of 50 $g{\cdot}L^{-1}$. (a).

Cleaning type	J_w ($L{\cdot}m^{-2}{\cdot}h^{-1}$)	J_w recovery (%)
Initial (pristine membrane)	9.86	–
After test (fouled membrane)	4.72	47 %
After rinsing 25 $L{\cdot}h^{-1}$, 25 °C	5.78	57 %
After rinsing 35 $L{\cdot}h^{-1}$, 25 °C	6.02	60 %
After backflushing	8.00	80 %
After final rinsing 35 $L{\cdot}h^{-1}$, 40 °C	9.18	93 %

(b)

	J_w ($L{\cdot}m^{-2}{\cdot}h^{-1}$)	J_s ($g{\cdot}m^{-2}{\cdot}h^{-1}$)	J_s/J_w ($g{\cdot}L^{-1}$)
Initial (pristine membrane)	9.86	5.37	0.54
Final after rinsing 35 $L{\cdot}h^{-1}$, 40 °C	9.18	5.60	0.60

Therefore, the reduction in the permeate flux is greater and membrane cleaning is hindered. It must be noted that the permeability was recovered by a 100 % for the UP010 membrane so that it could be used for the subsequent batch concentration test.

3.1.2. Batch concentration test

The ultrafiltration process was carried out with the UP010 membrane in concentration mode by continuously collecting the permeate stream (VRF of 2.65 was reached). The permeate flux (Fig. 5a) decreased with the VRF in the batch concentration test due to membrane fouling. It drastically declined at the beginning of the concentration test, followed by a gradual reduction with the VRF, attributed to the progressive concentration of the feed stream. Finally, steady state was reached at VRF of 2. The rejection rates (Fig. 5b) achieved in this test derived in a notable decrease of the colour and a partial reduction of the pectin content in the permeate stream. The rejection rate increased with the VRF due to membrane fouling, especially for pectins, while the increase was much smaller in the case of TPC and sugars and the color rejection remained almost constant. This tendency was also observed by Sun et al. [50], who studied the treatment of phenolic wastewater from a paper mill using 1, 2 5 and 7 kDa polyethersulfone membranes. Moreover, as it has been reported, the retention of gelling substances (pectins) causes the formation of a second or dynamic membrane that increases the retention of lower molecular weight compounds such as phenols or sugars [51].

From the results obtained, it can be confirmed that the UF membrane separated a significant amount of pectins (50 %). Therefore, a smaller fouling caused by these compounds in the subsequent FO stage was expected. Jin et al. [52] reported a similar pectin rejection of 50–60 % using a 10 kDa UF membrane at a VRF of 2 for citrus pectin extract purification. In addition, the concentrated pectins in the retentate stream could be separated and recovered, since they also have many interesting industrial applications, such as food and cosmetic thickeners and also prebiotics.

In order to assess the individual rejection of each phenolic compound present in the OPW extract, a thoughtful characterisation of the UF streams was performed by LC-MS. Before submitting the ultrafiltration permeate to a concentration stage by means of forward osmosis, it was considered necessary to give more details about the exact compounds that were recovered from the wastewater, at which percentage they were rejected, and their individual concentration in the ultrafiltration

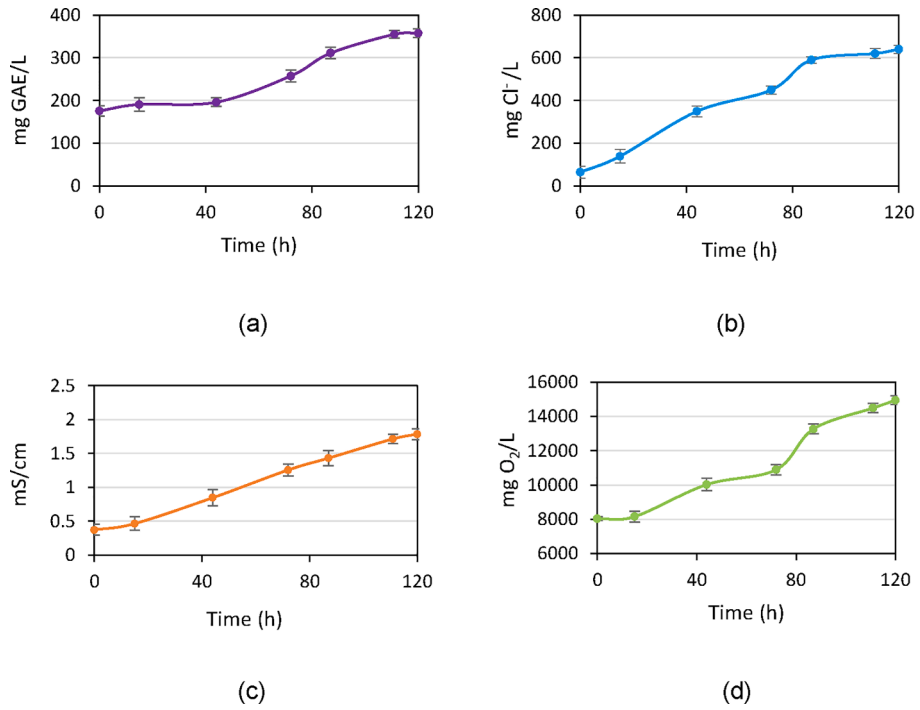

Fig. 9. Characterisation of feed solution samples in the forward osmosis concentration test: a) total concentration of phenolic compounds, (b) concentration of Cl^-, (c) conductivity, (d) chemical oxygen demand.

permeate. The individual rejection of each detected compound can be found in Fig. 6. Also, more details about the molecular weight, *m/z* and chemical class of the determined molecules have been included in Table 4. Three chemical families of phenolic compounds were found in OPW: derivatives of phenolic acids, flavonoids and terpenoids. In Fig. 6, all the compounds have been listed in an increasing order of molecular weight. As can be seen in Fig. 6, increasing rejection values were obtained as the molecular weight of the compounds was higher.

First, the aqueous OPW extract contained a derivative of phenolic acids, which was tentatively identified as methyl-protocatechuic acid-O-sulfate [53]. Due to the small molecular weight of this compound in comparison with the MWCO of the UP010 membrane (10 kDa), its low rejection was expected. The second chemical family derived from OPW was entailed by flavonoids. They included several compounds, such as narirutin, luteolin rutinoside, hesperidin, and apigenin-7-O-(malonylapyosil)-hexoside. Narirutin and hesperidin are the major and more important flavonoids from citrus-derived matrices, and their presence highly increases the interest of OPW. Flavonoids also experienced low rejection values, being preferentially recovered in the UF permeate. For these compounds, the rejection increased with the VRF, as it is normally observed in batch concentration UF processes, due to the increasing concentration of the feed stream and membrane fouling [54,55]. In any case, a satisfactory passage was observed. Finally, several terpenoids were detected too, including dehydrophaseic acid hexoside, nomilinic acid 17-O-β-d-glucoside, and nominin-17-β-d-glucoside. Dehydrophaseic acid hexoside is the second phenolic compound represented in Fig. 6 due to its reduced molecular weight, which also explains its low retention rate. On the contrary, nomilinic acid 17-O-β-d-glucoside, and nominin-17-β-d-glucoside are the largest compounds determined in the UF streams. These compounds are the last molecules eluting from the chromatographic column during the LC-MS analysis, which indicates that they are the most non-polar compounds among the detected analytes. This relatively reduced polarity can result in an interaction with the UP010 membrane, whose active side is composed of polyethersulfone [49]. This fact, together with the higher molecular weight of nomilinic acid 17-O-β-d-glucoside, and nominin-17-β-d-glucoside can explain the observed higher rejection.

The final concentrations of phenolic compounds that were obtained in the UF permeate after its purification are detailed in Table 4, together with some analytical information. The concentrations presented in Table 4 should not be compared with the TPC data, as the analytic strategy was different in each case. Due to the discrepancies between specific and non-specific methodologies, a cautious correlation should be considered [56,57]. According to Table 4, the highest concentration corresponded to narirutin and hesperidin, which are the most valuable phenolic compounds present in the extract. Therefore, the interest of the purified extract of OPW increased after the UF step as the purity of these compounds was enlarged. Later, as will be presented in section 3.2, this permeate was submitted to a concentration stage by forward osmosis in order to increase the concentration of the obtained polyphenols.

After the concentration test, the UP010 membrane was cleaned, obtaining the results described in Table 5. In this case, the rinsing with water at room temperature recovered much less of the initial permeability (47 %) than in the total recycle batch test (84 %) (results presented in Table S1). This could be attributed to the more severe fouling in the concentration test, due to the progressive feed concentration and the largest duration of the test. [58] also reported a remarkable membrane fouling in the purification of phenolic compounds from pomegranate juice using a 4 kDa polyethersulfone ultrafiltration membrane in a concentration test, obtaining only a 12 % of the initial water permeability after being measured with the fouled membrane.

After the cleaning with water at room temperature, a cleaning with hot water at 35 °C was performed and a permeability recovery of 67 % was achieved. Finally, a chemical cleaning using Ultrasil 110 at 0.7 % (v/v) was necessary. The chemical cleaning permitted 100 % recovery of the initial water permeability. Cifuentes-Cabezas et al. [49] reported similar results for the cleaning of a UH050 membrane used for the recovery of phenolic compounds from olive-oil washing wastewater. In that case, a rinsing with water at 25 °C permitted a permeability recovery of 83 %, then at rinsing with hot water at 35 °C recovered an 88 %, and finally a cleaning with Ultrasil 110 1 % (v/v) recovered 95 % of the initial water permeability.

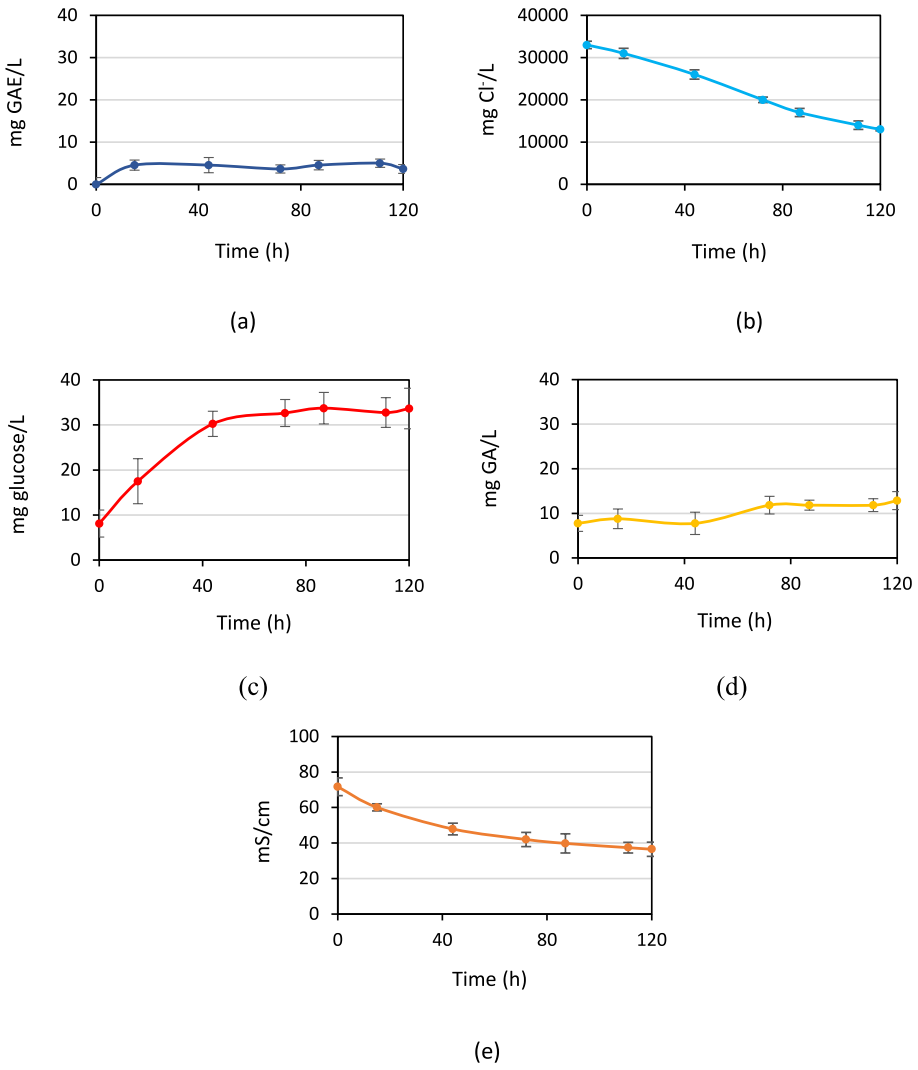

Fig. 10. Characterisation of draw solution samples in the forward osmosis concentration test: a) total concentration of phenolic compounds, (b) concentration of Cl^-, (c) concentration of sugars, (d) concentration of pectins, (e) conductivity.

Table 7
Total polyphenols concentration (TPC) and individual concentration of hesperidin and narirutin in the ultrafiltration and forward osmosis streams.

	UF Feed	UF Retentate	UF Permeate (FO Feed)	FO Concentrate
TPC ($mg{\cdot}L^{-1}$)	243 ± 10	337 ± 9	176 ± 8	358 ± 11
Hesperidin ($mg{\cdot}L^{-1}$)	306 ± 5	423 ± 4	323 ± 32	–
Narirutin ($mg{\cdot}L^{-1}$)	15.7 ± 0.2	24 ± 4	16 ± 3	–
Sugars ($mg{\cdot}L^{-1}$)	5258 ± 64	6724 ± 46	5369 ± 69	10543 ± 86
Pectins ($mg{\cdot}L^{-1}$)	738 ± 33	1187 ± 26	593 ± 19	1094 ± 37

3.2. Forward osmosis

Forward osmosis was employed as an efficient, low-energy technology to concentrate the obtained UF permeate, which consisted in a polyphenols-enriched extract of OPW.

Before processing the UF permeate, the forward osmosis membrane was characterised. The membrane characterisation (Fig. 7) showed a linear increase of water flux and reverse salt flux with NaCl concentration in the range 0–150 $g{\cdot}L^{-1}$. In the 150–200 $g{\cdot}L^{-1}$ range, the increment of J_w and J_s was lower, reaching roughly a steady state. The specific reverse salt flux (J_s/J_w) rate remained almost constant around 0.5. Cifuentes-Cabezas et al. [59] reported the same tendency of J_w and J_s and a SRSF of 0.41 $g{\cdot}L^{-1}$ with the FTSH2O membrane.

The concentration test was performed using the UF permeate as feed solution. A sharp decrease in water flux was observed initially (Fig. 8a). After this initial decrease, flux decline was smoothed and J_w became steadier. The overall decrease in water flux was from 6.77 $L{\cdot}m^{-2}{\cdot}h^{-1}$ to 1.80 $L{\cdot}m^{-2}{\cdot}h^{-1}$, in 120 h. The great decline in J_w may be due to the formation of a fouling layer caused by the accumulation of the pectins remaining in the FS. García-Castelló et al. [17] observed a similar water flux drop in an orange press liquor dewatering process by forward osmosis and they reported that it was directly influenced by the presence of pectins in the FS. The reverse salt flux (Fig. 8b) decreased also from 3.77 $g{\cdot}m^{-2}{\cdot}h^{-1}$ to 1.64 $g{\cdot}m^{-2}{\cdot}h^{-1}$, due to the decrease in the driving force associated to the progressive dilution of the DS. The decrease in the driving force also influences the water flux drop. It must be noted that the specific reverse salt flux was maintained in the range of 0.82–0.89 $g{\cdot}L^{-1}$. The ratio was larger than that observed in the membrane characterisation performed with distilled water, since water flux in the concentration test with the ultrafiltered extract was much smaller due to the membrane fouling.

After the concentration test, J_w was evaluated using distilled water as

FS. It was observed that it decreased by a 47 % compared with the pristine membrane (Table 6a). Therefore, a membrane cleaning protocol was performed. Hydraulic flushing (rinsing) and backflushing are techniques reported in the literature to be efficient up to 90 % in removing organic fouling from membrane in forward osmosis processes [60,61]. The water flux was not highly recovered when rinsing with water at room temperature (recovery of 57 % and 60 % for water flow of 25 and 35 $L{\cdot}h^{-1}$, respectively). Then, backflushing significantly improved the water flux recovery (80 %), but did not reach the minimal recovery desired of 90 %. Finally, the rinsing with hot water at a flow of 35 $L{\cdot}h^{-1}$ recovered a 93 % of the initial J_w, without notably affecting the specific reverse salt flux (Table 6b).

Samples of FS and DS were characterised in the concentration experiment (Figs. 9 and 10). Regarding the FS, polyphenols were concentrated until 358 ± 10 $mg{\cdot}L^{-1}$, achieving a concentration factor of 2.03 (Fig. 9a). The evolution in water flux with time observed in Fig. 8a can explain the increase in TPC concentration until the fourth day of experiment and the tendency to stabilize at the end of the test. Pei et al. [20] observed a higher rejection of polyphenols when water flux was larger. The COD also increased notably from 8035 ± 120 $mg{\cdot}L^{-1}$ to 14950 ± 258 $mg{\cdot}L^{-1}$ (Fig. 9d). In addition, due to the observed reverse salt flux chloride concentration in the FS raised (Fig. 9b). Hence, the FS presented a higher conductivity at the end of the test (Fig. 9c). The decrease in the reverse salt flux at the end of the concentration test (Fig. 8b) might explain the smoothing on the curves of chloride concentration and conductivity.

The characterisation of DS samples revealed that a tiny fraction of phenolic compounds (Fig. 10a) passed through the membrane to the DS. The passage of phenolic compounds to the DS has also been reported by Cifuentes-Cabezas et al. [59], Xiao et al. [62]. The same tendency was observed for sugars, and pectins (Fig. 10c and 10d, respectively). The increase was sharp at the beginning, but it tended to soften at the end, especially for sugars and TPC. Pectin fouling could explain this tendency, since the fouling layer represents an additional resistance to permeation. On the other hand, the decrease of chloride concentration and conductivity (Fig. 10b and 10e, respectively) can be explained by the progressive dilution of the DS, but it is also due to the reverse salt flux [59]. In addition, an insignificant amount of pigments was able to pass through the membrane, being the colour coefficient of the DS lower than 0.002 in all cases. Thus, the value of the colour coefficient in the DS at the end of the test can be almost neglected.

Finally, the concentration of phenolic compounds obtained in each stream of the whole integrated membrane process is presented in Table 7. Inevitably some phenolic compounds were retained in the UF step, as reflected by the data of TPC, Hesperidin and Narirutin. Nevertheless, the similar concentration of these compounds between the feed and permeate streams indicted a low rejection index, as aimed. Furthermore, considering the difference in the concentration values of the UF feed stream and the FO concentrate stream, polyphenols were globally concentrated by a factor of 1.47, eliminating a significant amount of sugars, pigments and pectins in the preliminary UF step.

4. Conclusions

After a preliminary screening, a 10 kDa UF membrane was selected from the experiments performed in the total recycle batch configuration mode to separate phenolic compounds ($R_{polyphenols}$ = 4 %) from pectins ($R_{pectins}$ = 29 %), color (R_{color} = 70 %), and COD (R_{COD} = 25 %).

Then, a batch concentration test was performed and the results showed that UF separated a significant amount of pectins (50 %). Thus, the fouling caused by pectins in the next FO step was expected to be reduced. A volume reduction factor of 2.65 was reached in the UF step. The LC-MS analysis showed low rejection values for flavonoids, being preferentially recovered in the UF permeate. The most concentrated polyphenols in the UF permeate were hesperidin and narirutin, with concentration values of 323 ± 32 $mg{\cdot}L^{-1}$ and 16 ± 3 $mg{\cdot}L^{-1}$, respectively.

Regarding the membrane cleaning of the UF UP010 membrane, the rinsing with water at room temperature recovered only a 47 % of the initial permeability. Then a cleaning with hot water at 35 °C allowed a recovery of 67 %. Finally, a chemical cleaning using Ultrasil 110 at 0.7 % (v/v) was necessary. The chemical cleaning permitted a recovery of 100 % of the initial water permeability.

The concentration test with forward osmosis increased phenolic compounds concentration by a factor of 2.03. On the other hand, the reverse salt flux raised the salt concentration in the FS notably increasing its conductivity at the end of the test. In addition, a negligible amount of phenolic compounds, sugars and pectins passed through the membrane to the DS.

After the concentration test, the cleaning protocol performed showed that the rinsing with water at room temperature was not enough to recover the permselective properties of the membrane. Backflushing was not able either to reach the minimal water flux recovery considered of 90 %, achieving a J_w recovery of 80 %. The optimal cleaning protocol consisted of rinsing with hot water (40 °C) at a flow rate of 35 $L{\cdot}h^{-1}$, recovering a 93 % of the initial J_w, without notably affecting the specific reverse salt flux.

Finally, the phenolic compounds were globally concentrated by a 1.47 factor in the whole integrated membrane process.

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.

Acknowledgments

The authors thank the Regional Government of Valencia for the financial support (Reference of the project: CIAICO/2021/333), and Agriconsa S.A. for providing the orange waste samples.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.seppur.2024.131228.

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