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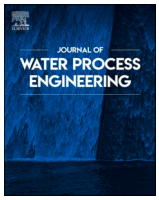

Separation of phenolic compounds from canned mandarin production wastewater by ultrafiltration and nanofiltration

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ABSTRACT

A significant amount of Mandarin Wastewater is generated in the production of canned mandarin segments. To the best of our knowledge, the efficiency of membranes to recover phenolic compounds present in Mandarin Wastewater has never been studied before. The highest added value of polyphenols in cosmetic and pharmaceutical industries greatly encourages its purification as much as possible. In this study, different ultrafiltration and nanofiltration membranes were tested, and the best combination was a 5 kDa PES spiral-wound ultrafiltration membrane at 3 bar, followed by the NF270–2540 flat-sheet polypiperazine-amide nanofiltration membrane at 10 bar. Ultrafiltration was able to retain pigments (R = 90 %), pectins (R = 63 %), and sugars (R = 58 %). Then, phenolic compounds passed to the permeate (R = 5 %), which was used as the feed for nanofiltration. Finally, polyphenols were concentrated in the retentate of nanofiltration (R = 80 %), while sugars were partially separated in the permeate (R = 50 %). For a more detailed phenolic profile, liquid chromatography coupled to mass spectrometry was performed with the initial wastewater and the nanofiltration permeate. The results showed a significant rejection of most of the phenolic compounds (rejection >60 %) and the purity of the chemical family of flavonoids was doubled.

1. Introduction

Mandarin wastewater is a common industrial waste associated with the production of canned mandarin segments, a product that has dominant position in the citrus processing industry. In the production of mandarin segments, wastewater is generated in two different processes. The first process consists of a scalding with water steam to soften the mandarin peels before their removal. From this stage, Scalding Wastewater is generated. The following process consists of separating mandarin segments with hot pressurised water. From this process Segmenter Wastewater is generated. Finally, the membrane surrounding the mandarin segments is removed with acid and alkaline treatment, and the segments are packed in a can inside a brine.

It is known that citrus fruits contain many valuable products, some of which are transferred to the wastewater during the process. Usually, this effluent contains polyphenols, pectin and sugars, which cause a high chemical oxygen demand (COD) [1]. Polyphenols, the most abundant antioxidant compounds in nature, have different valuable properties as they are anti-inflammatory, anti-atherogenic, anti-mutagenic and anti-thrombotic [2]. Lately, there has been an increasing demand for polyphenols market since they represent a natural and valid antioxidant to add to cosmetics and foodstuffs. The polyphenols contained in mandarin fruit are mainly flavonoids such as hesperidin and narirutin, but also phenolic acids such as ferulic acid [3,4].

Abbreviations: GAE, Gallic Acid Equivalent; TPC, Total Phenolic Content; NF, Nanofiltration; UF, Ultrafiltration; MWCO, Molecular Weight Cut-Off; PES, Polyethersulfone; TMP, Transmembrane pressure; VRF, Volume Reduction Factor; LC-MS, Liquid Chromatography – Mass Spectrometry; COD, Chemical Oxygen Demand.

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Another compound present in mandarin wastewater are pectins, which are water-soluble heteropolysaccharides mainly composed of units of methylated D-galacturonic acid; they can be found in different composition, length, ramification and esterification degree [5,6]. Pectins are compounds with various industrial applications, as they can be utilized as food and cosmetic thickeners and are also prebiotics [7]. Moreover, pectins are significantly responsible for membrane fouling due to forming a gel-like structure over the membrane surface, reducing the permeate flux. For this reason, a pretreatment should be considered for recovering the pectins before the polyphenol concentration step [8].

Phenolic compounds represent a problem when treating wastewater in conventional treatment plants due to their relatively low biodegradability and high organic matter content [9]. For this reason, the recovery of polyphenols from wastewater not only obtains a value-added by-product but also reduces the phytotoxicity of the wastewater and enhances its treatment.

The novelty of this work relies on the recovery of phenolic compounds from mandarin wastewater using membrane processes. The separation and purification of phenolic compounds from food industrial wastewaters (spinach, orange, pomegranate, olive) has been widely studied [10–14]. However, the recovery of phenolic compounds from mandarin wastewater has not been studied yet. Both Scalding Wastewater and Segmenter Wastewater were analysed to determine the optimal wastewater for polyphenols purification. Then, centrifugation was used as a pretreatment, and different ultrafiltration and nanofiltration membranes were employed. A crossflow velocity of 1 m/s was set for both UF and NF membrane processes to limit membrane fouling according to previous research [15,16]. The membranes were selected according to previous results [17–19], to separate, purify and concentrate phenolic compounds. The main goal of ultrafiltration was obtaining the lowest rejection to phenolic compounds and the highest rejection to the rest of the organic matter, while NF aimed to concentrate the phenolic compounds and obtain the lowest rejection to sugars. This process follows the directives of the Circular Economy Action Plan for its efforts to improve waste management [20]. All samples were characterised, and the initial feed and the final stream (nanofiltration retentate) of the optimal process (UF 5 kDa + NF 270) samples were analysed with Liquid Chromatography – Mass Spectrometry (LC-MS) to determine the phenolic profile.

Table 1
Ultrafiltration membranes.

Flat-sheet membranes			Spiral-wound membranes		
MWCO	Model, Brand	Material, specific area	MWCO	Model, Brand	Material, specific area
5 kDa	NT E0072/2, Orelis (France)	PES, 90 cm^2	5 kDa	MT-3-2540 M, Synder (USA)	PES, 1.858 m^2
50 kDa	UH050 P, Mycrodin Nadir (Germany)	PES, 90 cm^2	50 kDa	MQ-3-2540HM, Synder (USA)	PES, 1.858 m^2

2. Materials and methods

2.1. Mandarin wastewater

Samples of Scalding Wastewater and Segmenter Wastewater were kindly provided by Agriconsa S.A. (Algemesí, Valencia, Spain). First, Scalding and Segmenter Wastewater samples of 1 L were collected, while both processes were running in constant agitation. According to the total phenolic content, Segmenter Wastewater was selected for the separation processes with membranes. Therefore, Segmenter Wastewater samples were collected and transported in high density polyethylene bottles of 60 L.

2.2. Ultrafiltration

Previous to the ultrafiltration process, wastewater samples were centrifugated (ThermoFisher, USA) at 17200 RCF for 6 min. For the ultrafiltration step, a total of two flat-sheet and two spiral-wound membranes were selected, of two different molecular weight cut-off (MWCO) 5 and 50 kDa (Table 1).

Flat-sheet membrane experiments were performed in an ultrafiltration plant with a tailor-made module of 90 cm^2 and a feed volume capacity of 15 L. Instead, spiral-wound membrane tests were conducted in an ultrafiltration plant with a tailor-made module of 1858 m^2 and a feed volume capacity of 70 L. In Fig. 1 it is presented the diagram of the spiral-wound ultrafiltration 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. On the other hand, spiral-wound membranes were put in the plant and rinsed with water to drag preserving chemicals. Then, all membranes were compacted at a transmembrane pressure (TMP) of 8 bar with a crossflow velocity of 1 m/s, until the flux was stabilized. Once the compaction finished, the hydraulic permeability (K) of the membrane was measured using TMPs 1, 3 and 5 bar, at a crossflow velocity of 1 m/s using the following Eq. (1):

$$J = K \cdot \Delta P \quad (1)$$

where J is the permeate flux and ΔP is the transmembrane pressure. After assessing the hydraulic permeability, a total recycle configuration test was performed using TMPs 1, 3 and 5 bar, at a crossflow velocity of

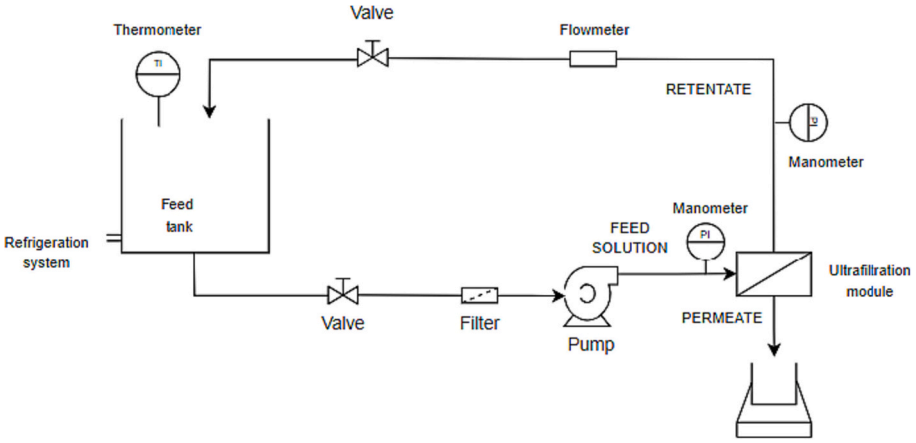

Fig. 1. Diagram of the spiral-wound ultrafiltration plant.

1 m/s with the centrifuged Segmenter Wastewater. Both, the permeate and the retentate were recycled back to the feed tank. Between each TMP the membrane fouling was removed by increasing the crossflow velocity to 1.5 m/s for 5 min. Samples were taken for the initial feed and each pressure permeates. For each sample sugars, colour and TPC were analysed, in order to assess the rejection rate (%R) using the following Eq. (2):

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

where C_p is the concentration in the permeate and C_f is the concentration in the feed. The TMP with the best results (3 bar) was chosen to carry out a batch concentration test at a feed crossflow velocity of 1 m/s, with the spiral-wound membranes, reaching a volume reduction factor (VRF) of 5.93 and 6 for the 50 kDa and 5 kDa UF membranes, respectively. The initial volume used for both UF membranes in the batch concentration test was 60 L. The VRF was calculated using the following Eq. (3):

$$VRF = \frac{V_0}{V_f} \quad (3)$$

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 for each VRF and global permeate (recovered during the whole process) were characterised to determine the rejection values of sugars, colour and TPC. After each essay with wastewater, the membrane fouling was removed by rinsing the plant with water, increasing the crossflow velocity to 1.5 m/s without applying any TMP. Then, a chemical cleaning was performed using Ultrasil 110 1 % (*v*/v) during 15 min at room temperature and a crossflow velocity of 1.5 m/s without applying any TMP.

2.3. Nanofiltration

The permeates obtained with both spiral-wound UF membranes (5 kDa and 50 kDa) in the concentration tests were the feeds for the NF tests (NF270–2540 from Dow Chemical, EEUU). NF270–2540 is a flat-sheet membrane, made of Polypiperazine-amide material, with a MWCO of 200–400 Da [21–23]. The specific membrane area was 72 cm^2. This membrane was selected according to the molecular weight of the target compounds, which were phenolic compounds derived from the mandarin fruit (Table 3). Among them, the most interesting compounds were flavonoids and terpenoids. Therefore, the NF270 membrane was considered suitable to obtain sufficient rejection values without compromising the permeate flux. NF experiments were performed in a 72 cm^2 tailor-made module with a feed tank capacity of 12 L. In Fig. 2 it is summarised the diagram of the nanofiltration plant. The plant was operated under batch operating mode.

Before the tests, the membrane was put in deionised water for 24 h to condition it. Then, the membrane was compacted at 20 bar until the flux was stabilized. Before the batch concentration test, the hydraulic permeability was calculated by Eq. (1) using a crossflow velocity of 1 m/s (feed flow of 140 L/h) and a TMP of 5, 10 and 15 bar. Then, a total recycle configuration test was performed at 5, 10 and 15 bar with the ultrafiltered wastewater using a crossflow velocity of 1 m/s. In this test both, the permeate and the retentate, were recycled back to the feed tank. Samples were taken for the initial feed as well as for each permeate obtained at different operating pressures For each sample sugars, COD and TPC were analysed in order to assess the rejection rate (%R) using the Eq. (2). Between each TMP, the membrane fouling was removed by increasing the crossflow velocity to 1.5 m/s for 5 min. A pressure of 10 of bar was chosen to do the batch concentration test using a crossflow velocity of 1 m/s. A VRF of 2.5 was reached. The initial volume used in the NF batch concentration test was 6 L. Samples of feed and permeate for each VRF and global permeate (recovered during the whole process) were characterised to determine the rejection values of sugars, COD and TPC. After each test with wastewater, the membrane fouling was removed using deionised water as feed and applying a 1.5 m/s crossflow velocity without TMP. Then, a chemical cleaning was conducted using Ultrasil 110 1 % (*v*/v) during 15 min at room temperature and a crossflow velocity of 1.5 m/s without applying any TMP.

In all the tests, the flux calculations were corrected using Synder Filtration Temperature correction factor [24].

2.4. Characterisation of samples

2.4.1. Measurement of the total phenolic content

The total phenolic content (milligrams of gallic acid equivalents per liter) was determined by Folin-Ciocalteau methodology [25]. This analytic technique gives an overall value of the phenolic content.

2.4.2. Determination of the phenolic profile

For a more complete characterisation, Liquid Chromatography – Mass Spectrometry (LC-MS) was carried out with the samples that corresponded to the optimal process tested in terms of polyphenols recovery (raw water and NF retentate).

An analytical methodology based on liquid chromatography (LC) coupled to mass spectrometry (MS) was applied, in order to individually determine the phenolic compounds present in mandarin wastewater. A 1260 Infinity II LC liquid chromatograph was employed (Agilent Technologies, USA). It was coupled to a 6546 quadrupole-time-of-flight

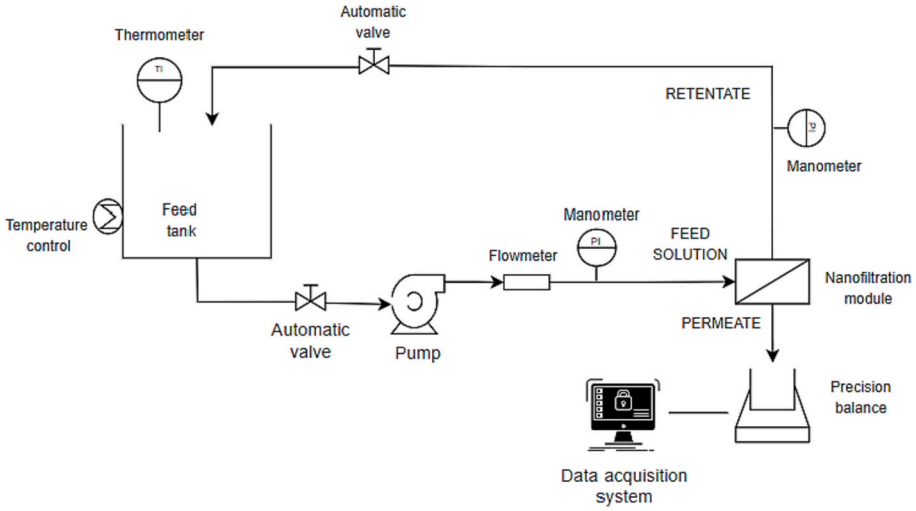

Fig. 2. Diagram of the nanofiltration plant.

Table 2
Characterisation of Raw Mandarin Segmenter wastewater before and after centrifugation.

	Raw wastewater	After centrifugation
pH	3.83 ± 0.10	3.70 ± 0.15
Conductivity (μS/cm)	2580 ± 20	2440 ± 20
Turbidity (NTU)	509 ± 18	378 ± 20
TPC (mg/L)	211 ± 8	176 ± 2
COD (mg/L)	13,015 ± 10	12,695 ± 5
Sugars (mg/L)	4460 ± 10	4346 ± 8
Pectins (mg/L)	673 ± 15	574 ± 20

(QToF) mass analyser (Agilent Technologies, USA), equipped with an electrospray (ESI) interface, which worked in negative ionisation mode. The separation of the compounds was carried out throughout a Zorbax Extend C18 column (4.6 × 100 mm, 1.8 μm) (Agilent Technologies, USA), at 40 °C and a flow rate of 0.6 mL/min, after the injection of 4 μL of each sample. All the injections were performed at least in duplicates. MilliQ water (Direct-Q®, 3UV system (Merck Millipore, USA)) and LC-MS grade acetonitrile (Honeywell, USA) were employed as mobile phases A and B, respectively. Both phases were acidified with 0.5 % acetic acid (*v*/v) (VWR chemicals, USA). The initial conditions were 95 % A and 5 % B. Later, a gradient was performed, achieving the following concentrations of phase B: 11 % B at 2.5 min, 20 % B at 7 min, 90 % B at 16 min, and 95 % B at 17 min. The latter was maintained for two minutes and, afterwards, three minutes were employed for the column re-equilibration before the following injection. The temperature of the drying gas in the mass spectrometer was 200 °C and its flow was fixed at 8 L/min. The nebuliser was set at 30 psi, and the capillary voltage was 3500 V.

The obtained chromatograms were inspected by means of the software MassHunter Qualitative and MassHunter Quantitative (Agilent Technologies, USA). To identify the compounds, the spectral data of the pure standards, LC-MS accurate mass data, and literature information [26–29] were employed. An external calibration was performed to conduct the quantification of the compounds, according to pure standards of caffeic acid (y = 747,196.9× – 1,540,115.2, to quantify organic and phenolic acids), narirutin (y = 1,674,606.5× + 1,067,495.3, to quantify flavonoids and terpenoids) and hesperidin (y = 228,050.7 + 670,324.1). The standard solutions were prepared in the range 0.4–25 mg/L.

2.4.3. Other techniques applied for the characterisation of the samples

The electrical conductivity (Conductimeter GLP31+, Crison, Spain), pH (pHmeter GLP31+, Crison, Spain) and turbidity (Turbidimeter TL2310, Hach, USA), were measured for Segmenter Wastewater and Scalding Wastewater. For the UF and NF samples, COD ($mg{\cdot}L^{-1}$) was measured by means of the 1.14541.0001 kit (Merck, Germany). The pectin content (mg galacturonic $acid{\cdot}L^{-1}$) was determined with the galacturonic acid method [30]. The total sugars content was determined by the Anthrone method [31]. It must be noted that this method measures carbohydrates of high (polysaccharides) and low molecular (monosaccharides) weight. Colour was determined, according to ISO 7787:2022 method B [32] by measuring absorbance at three different wavelengths (436 nm, 525 nm and 620 nm) using a UV-VIS DR 600 spectrophotometer (Hach, Germany), The colour was calculated using Eq. (4):

$$Colour = \frac{A^2_{\lambda=436} + A^2_{\lambda=525} + A^2_{\lambda=620}}{A_{\lambda=436} + A_{\lambda=525} + A_{\lambda=620}} \quad (4)$$

3. Results

3.1. Characterisation of mandarin wastewater

First, the total phenolic content (TPC) of both samples Segmenter Wastewater and Scalding Wastewater was analysed. The results showed 4.5 ± 0.6 mg GAE/L for Scalding Wastewater, and 454 ± 40 mg GAE/L for Segmenter Wastewater. For this reason, Segmenter Wastewater was selected for the separation and purification processes. The selected wastewater was characterised in terms of pH, conductivity, turbidity, TPC and COD (Table 2) before and after centrifugation:

According to Table 2, Segmenter Wastewater contained a remarkable concentration of phenolic compounds. The COD was also remarkably high, as well as the conductivity and turbidity. The acidic pH was expected, due to the characteristics of the citrus products and their content in citric acid [33,34].

The TPC concentration determined in this by-product suggested a more detailed study in order to know which specific phenolic compounds are contained in the wastewater. The lack of information about the specific polyphenol content in Mandarin Segmenter Wastewater made it necessary to characterise it thoroughly. Therefore, a powerful LC-MS methodology (detailed in Section 2.4.2) was applied to determine each phenolic compound present in this by-product. Table 3 contains the information about all the determined compounds, along with their concentration in the Segmenter Wastewater. Furthermore, a

Table 3
Identity, molecular weight, retention time (t_R), *m/z*, concentration, and chemical class of all the compounds determined in the Segmenter Wastewater.

N°	Compound	Molecular weight (g/mol)	t_R (min)	*m/z*	Concentration (mg/L)	Chemical class
1	Quinic acid	192	1.759	191.0555	33.0 ± 0.6	Organic acids
2	Citric acid	192	1.875	191.0191	76 ± 2.0	Organic acids
3	Malic acid	134	1.892	133.0150	65 ± 2	Organic acids
4	Citramalate	148	2.176	147.0303	61 ± 4	Organic acids
5	Succinic acid	118	2.627	117.0199	163 ± 4	Organic acids
6	Methyl-protocatechuic acid-O-sulfate	248	5.215	246.9907	14.8 ± 0.1	Phenolic acids
7	Methyl-vanillate	182	5.833	181.0511	15.5 ± 0.1	Phenolic acids
8	Dehydrophaseic acid hexoside	444	6.151	443.1923	9.8 ± 0.1	Phenolic acids
9	Feruloyl-aldaric acid	386	6.451	385.0761	33.1 ± 0.2	Phenolic acids
10	Isopropyl malic acid	176	6.852	175.0613	24.2 ± 0.5	Organic acids
11	Luteolin rutinoside	594	7.587	593.1516	87 ± 2	Flavonoids
12	Naringenin glycoside derivative	742	8.105	741.2255	4.7 ± 0.4	Flavonoids
13	Apigenin-7-O-malonylapyosil-hexoside	650	10.109	649.2529	18.04 ± 0.03	Flavonoids
14	Phloretic acid	166	10.393	165.0558	29.0 ± 0.8	Phenolic acids
15	Narirutin	580	10.626	579.1721	28.0 ± 0.8	Flavonoids
16	Hesperidin	610	10.960	609.1819	152.7 ± 0.8	Flavonoids
17	Nomilinic acid-17-O-glucoside	712	11.311	711.2866	4.1 ± 0.2	Terpenoids
18	Nomilin-17-O-glucoside	694	11.411	693.2756	18.9 ± 0.1	Terpenoids
19	Dydimin	594	11.929	593.1885	12.8 ± 0.2	Flavonoids
20	$C_{35}H_{59}O_{14}$ (score 99.39)	703	13.148	702.3811	2.3 ± 0.1	Unknowns
21	$C_{28}H_{34}O_{10}$ (score 99.61)	530	14.484	529.2082	7.5 ± 0.1	Unknowns

chromatogram obtained during the characterisation of this stream is presented in Fig. 3.

Table 3 and Fig. 3 collect 21 compounds analysed by LC-ESI-QToF-MS (see section 2.4.2.). They belong to four different chemical families, including organic acids, phenolic acids, flavonoids, and a miscellaneous family which comprised two compounds whose identification was not possible. In this case, a molecular formula was proposed for these compounds, as well as the score provided by the software MassHunter. This score reflects the accuracy of the assigned molecular formula, considering the spectral data from the LC-MS.

Among the organic acids, compounds that are normally found in agri-food matrices, such as quinic acid, citric acid, succinic acid, and their derivatives were found [35,36]. The detected phenolic acids included derivatives of protocatechuic acid, ferulic acid, and vanillin. Phloretic acid was also determined. In the Segmenter Wastewater, the most interesting phenolic family was entitled by the flavonoids. Citrus flavonoids have demonstrated to have relevant and beneficial bioactivities. For example, they contribute to reduce the risk of obesity [37] and prevent several diseases [38]. In Mandarin Segmenter Wastewater, the flavonoids included valuable compounds, such as narirutin or hesperidin, among others. In fact, hesperidin was by far the most concentrated phenolic compound from the matrix, which remarked the potential of this residue. Some terpenoids, specifically limonoids, were also detected. They were derivatives of nominilic acid and its aldehyde form, nomilin. Citrus limonoids also have strong antioxidant capacity, which has been related to interesting properties, including anticarcinogenic and antidiabetic effects [39].

According to the obtained results, the Mandarin Segmenter Wastewater was considered a source of high added-value compounds. Therefore, the recovery of phenolic compounds from this by-product was pursued.

Table 4
Polyphenols and sugars concentration in the ultrafiltration and nanofiltration streams (a) 5 kDa membrane, (b) 50 kDa membrane.

	Feed UF	Retentate UF	Permeate UF (Feed NF 270)	Retentate NF 270	Permeate NF 270
(a)					
TPC (mg/L)	176 ± 2	226 ± 6	166 ± 4	366 ± 2	32 ± 1
Sugars (mg/L)	4346 ± 8	17,061 ± 22	1803 ± 12	3160 ± 9	899 ± 11
(b)					
TPC (mg/L)	176 ± 2	231 ± 3	165 ± 4	383 ± 3	20 ± 2
Sugars (mg/L)	4346 ± 8	8086 ± 17	3598 ± 13	8167 ± 6	555 ± 10

3.2. Ultrafiltration

The water permeability for the flat sheet ultrafiltration membranes was 21.78 $L{\cdot}h^{-1}{\cdot}m^{-2}{\cdot}bar^{-1}$ and 52.13 $L{\cdot}h^{-1}{\cdot}m^{-2}{\cdot}bar^{-1}$ for the 5 and 50 kDa membranes, respectively. Arénillas et al. [40] obtained a permeability of 20 $L{\cdot}h^{-1}{\cdot}m^{-2}{\cdot}bar^{-1}$ with a 5 kDa PES UF membrane, while Proner et al. [41] obtained a permeability of 56 $L{\cdot}h^{-1}{\cdot}m^{-2}{\cdot}bar^{-1}$ with UH050 membrane (50 kDa). On the other hand, the hydraulic permeability observed for the spiral-wound membranes was 17.10 $L{\cdot}h^{-1}{\cdot}m^{-2}{\cdot}bar^{-1}$ and 42.03 $L{\cdot}h^{-1}{\cdot}m^{-2}{\cdot}bar^{-1}$ for Synder MT 5 kDa and MQ-3 50 kDa membranes, respectively. Comparing to literature, Mohanadas et al. [42] reported a permeability of 29.13 $L{\cdot}h^{-1}{\cdot}m^{-2}{\cdot}bar^{-1}$ and Zaouk et al. [43] 108 $L{\cdot}h^{-1}{\cdot}m^{-2}{\cdot}bar^{-1}$ for Synder MT 5 kDa and MQ-3 50 kDa membranes, respectively.

3.2.1. Total recycle configuration test

The rejection rate (Fig. 4a) showed that UF spiral-wound membranes retained mainly colour, since the pigments in mandarins are mostly carotenoids, which have a larger area compared to the ultrafiltration membrane pores [44]. On the other hand, they also significantly eliminated sugars, especially the 5 kDa membrane, while TPC shows very little rejection with both the 5 and 50 kDa membranes. Regarding the permeate flux (Fig. 4b), the tendency with TMP was to increase linearly between 1 and 3 bar, but, at 5 bar, the line is softened due to membrane fouling. It must be noted that the permeate flux values are an average value of the permeate flux obtained at the end of the test with each pressure (Fig. S1 of supplementary data) when the flux reaches the steady state. As indicated in Fig. 4b, the fouling phenomenon was more relevant for the 50 kDa membrane. It has been previously observed that ultrafiltration membranes with higher MWCO suffer from more severe fouling than tighter membranes, such as the 5 kDa membrane [15]. This can be attributed to a higher internal fouling, because a wider range of compounds are likely to penetrate the pores, blocking them and reducing their internal area [45–47]. For this reason, 3 bar was selected for the following concentration tests with both membranes.

The effect of increasing the TMP on the rejection of sugars and TPC was the opposite for both membranes (Fig. 4a). In the case of the 5 kDa membrane, the evolution of the rejection values with TMP was highly affected by concentration polarization. An increase in the TMP led to a

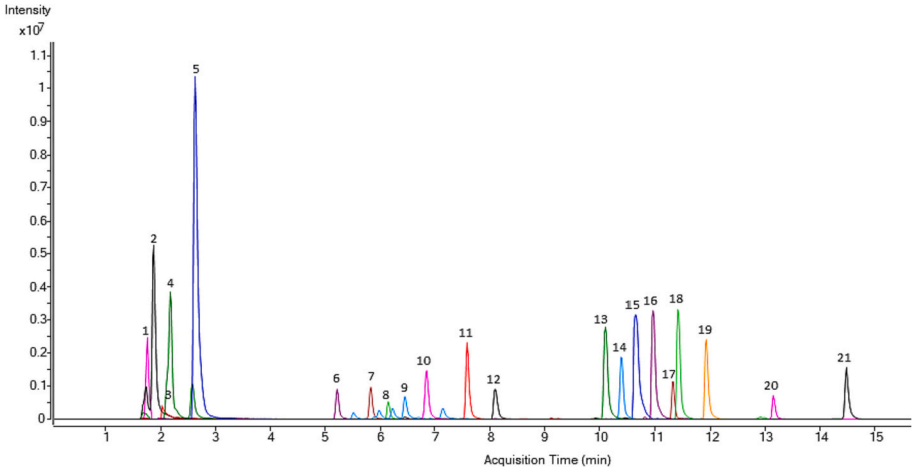

Fig. 3. Extracted ion chromatogram (EIC) of the compounds determined in Mandarin Segmenter Wastewater by LC-ESI-QToF-MS.

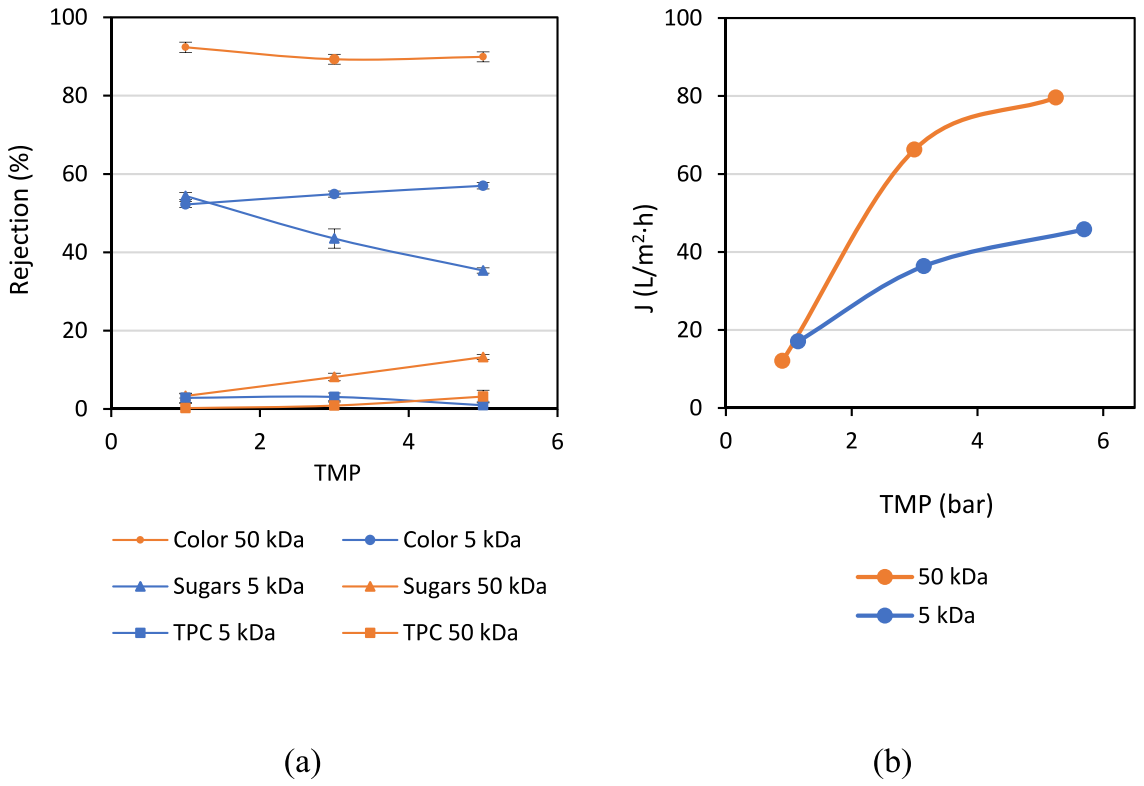

Fig. 4. Rejection rate (a), and permeate flux (b) for UF spiral-wound membranes in the total recycle configuration test at 1, 3 and 5 bar using a crossflow velocity of 1 m/s. The permeate flux values are an average value of the permeate flux obtained at the end of the test with each pressure (Fig. S1) when the flux reaches the steady state.

higher concentration of solutes at the membrane surface, which favoured their passage [18]. In this case, solute flux showed a greater increment with TMP than permeate flux. Then, the concentration of sugars and TPC in the permeate stream was higher, conducting to a decrease in the rejection values. Giacobbo et al. [48] observed the same trend for the rejection of pharmaceutical compounds by UF membranes and reported that, when solute rejection is dependent on pressure, its permeation is dominated by convection. However, the higher fouling of the 50 kDa membrane led to an opposite evolution of the rejection when the TMP was increased. In this case, a higher TMP implied a greater membrane fouling and the thickening of the cake layer [49], which reduced the passage of solutes across the membrane, resulting in higher rejection values for the sugars and TPC as the TMP increased. In any case, UF membranes were a successful way to treat mandarin wastewater by removing sugars and pigments without retaining polyphenols.

In the case of flat-sheet membranes, the permeate flux was between 22 and 36 $L{\cdot}h^{-1}{\cdot}m^{-2}$ for the 5 kDa membrane and 37–40 $L{\cdot}h^{-1}{\cdot}m^{-2}$ for the 50 kDa membrane. The values were notably lower due to a higher membrane fouling, especially in the 50 kDa membrane. Regarding the rejection rate, TPC was 1–3 % for 5 kDa and 1–2 % for 50 kDa, being in the same range than the spiral-wound membranes. The rejection rate of the colour was 92–93 % for 50 kDa and 93–95 % for 5 kDa. Finally, the rejection rate of sugars was 35–55 % for 5 kDa and 18–32 % for 50 kDa. In general, the rejection rate was similar for both flat-sheet and spiral-wound membranes but, since the membrane fouling was less significant and the permeate flux was higher for the spiral-wound membranes, the batch concentration test was performed with them.

3.2.2. *Batch concentration test*

After studying the performance of the ultrafiltration membrane maintaining a constant concentration in the feed solution, the ultrafiltration process was carried out (with the same membranes) in concentration mode by collecting the permeate stream (VRF of 6 was reached).

The rejection rates (Fig. 5a) achieved in this test showed a remarkable decrease of the colour and a partial reduction of the sugars content. Thus, the permeate stream was enriched in phenolic compounds. The rejection rate increased with the VRF due to membrane fouling, especially for sugars and to a lesser extent with the colour, while TPC remained almost constant. This tendency was also observed by Sun et al. [50]. The global rejection rate of pectins, in the batch concentration test at 3 bar, between the initial feed and the final permeate is presented in Fig. 6. From the results obtained, it can be concluded that both UF membranes separated a significant amount of pectins (61–63 %), preventing the fouling caused by pectins for the next NF step. Moreover, the concentrated pectins in the retentate stream could be separated and enriched, since they have many interesting industrial applications, such as food and cosmetic thickeners and also prebiotics. The difference in the rejection between TPC and sugars may be explained since UF membranes retained mainly high molecular weight carbohydrates (polysaccharides), which have a higher molecular weight than polyphenols.

The permeate flux (Fig. 5b) decreased notably with the VRF in both membranes, due to concentration polarization. This reduction was more notable with the 50 kDa membrane, since fouling was more severe in this membrane because larger pores tend to be blocked easier.

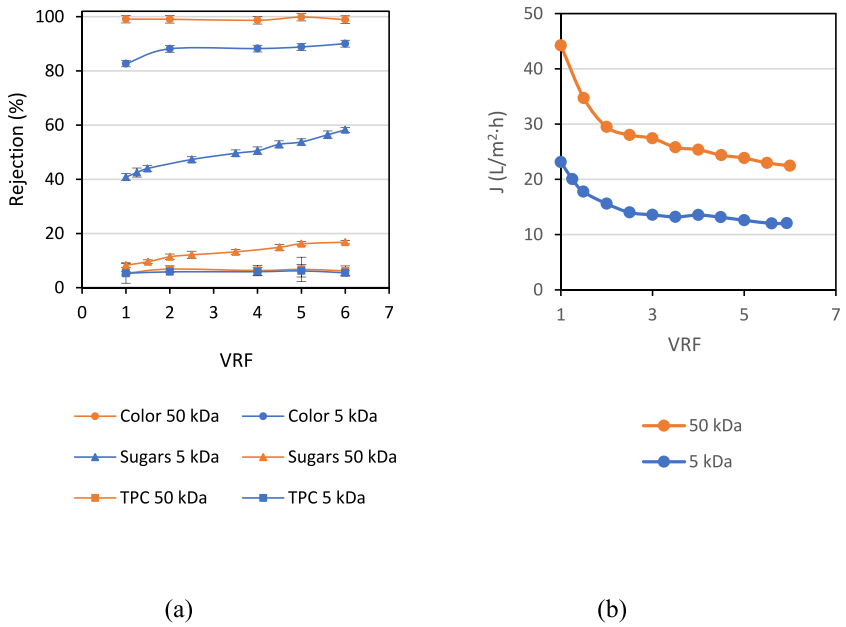

Fig. 5. Rejection rate (a) and permeate flux (b) for UF spiral-wound membranes in the batch concentration test at 3 bar using a crossflow velocity of 1 m/s.

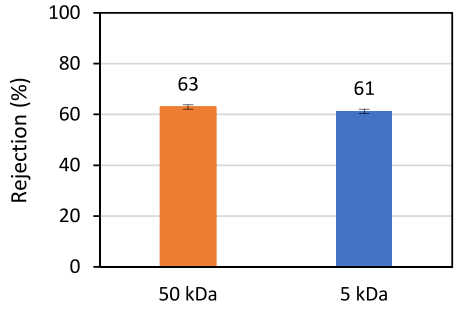

Fig. 6. Pectins global rejection rate for UF spiral wound membranes in the batch concentration test at 3 bar.

3.3. Nanofiltration

The water permeability for the NF270 membrane was 10.047 $L{\cdot}h^{-1}{\cdot}m^{-2}{\cdot}bar^{-1}$ for the membrane coupon used to filter the permeate from the 5 kDa membrane and 9.988 $L{\cdot}h^{-1}{\cdot}m^{-2}{\cdot}bar^{-1}$ for the membrane coupon used to filter the permeate from the 50 kDa. The water permeabilities were slightly different since two different parts of the same membrane were used to perform the experiments with the permeates of 5 and 50 kDa membranes, respectively. Comparing to literature, Nghiem et al. [51] obtained a permeability of 13.5 $L{\cdot}h^{-1}{\cdot}m^{-2}{\cdot}bar^{-1}$ for this membrane.

3.3.1. Total recycle configuration test

The NF total recycle configuration test was performed with the global permeate stream from the batch concentration test with both 5 kDa and 50 kDa spiral-wound membranes. In Fig. 7 the results of rejection of sugars, COD and TPC and permeate flux were calculated:

Fig. 7a shows that polyphenols were retained by the NF membrane. For both tested feeds (from 5 kDa and 50 kDa membranes) the rejections were higher than 70 %, highlighting that for the 50 kDa feed, the value achieved was close to 90 %. Sugars were separated and passed mainly to the permeate stream in the case of the feed from the 5 kDa membrane (R = 24–33 %), while for the feed from the 50 kDa one, the NF membrane was not able to separate phenolic compounds from sugars (R = 85–90 %), and both of them were concentrated in the retentate stream. The 5 kDa UF membrane rejected most of the high molecular weight carbohydrates. Therefore, the NF feed (UF permeate) contained mainly monosaccharides, which have a lower molecular weight than polyphenols and were recovered in the NF permeate. On the other hand, the 50 kDa UF membrane did not retain all the high molecular weight carbohydrates and they were recovered in the UF permeate (the feed stream for NF). In this case, the NF membrane retained both high molecular weight carbohydrates and polyphenols. The COD was notably reduced in both cases, but especially in the feed from the 50 kDa membrane, due to the high rejection rate of high molecular weight carbohydrates. In general, the rejection rate increased with TMP, which is in agreement with the solution diffusion and Spiegler–Kedem–Katchalsky models [48]. Regarding the permeate flux, the values presented in Fig. 7b are an average value of the permeate flux obtained at the end of the test with each pressure (Fig. S2 of supplementary data) when the steady state was reached. The highest permeate flux was obtained at 15 bar, both when the permeates from the 5 kDa and the 50 kDa membranes were treated. However, at 10 bar, the process was already highly productive, with a permeate flux higher than 60 $L{\cdot}h^{-1}{\cdot}m^{-2}$. Considering the higher energy consumption required to apply the highest TMP, 10 bar was selected as a proper pressure to perform the following experiments.

3.3.2. Batch concentration test

Fig. 8 shows the rejection of sugars, COD and TPC and the permeate flux, using both permeates from spiral-wound ultrafiltration membranes (5 and 5 kDa) as the feed for the NF batch concentration test (a VRF of 2.5 was reached).

The phenolic compounds were concentrated in the retentate (Fig. 8a), following the same tendency as the total recycle configuration test. In the case of the feed from 50 kDa, sugars were not separated from polyphenols and they were concentrated in the retentate as well. However, when the permeate from the 5 kDa membrane was employed as the nanofiltration feed, the sugars passed mainly to the permeate (as it was explained previously, they are mainly monosaccharides of lower molecular weight) and the polyphenols were concentrated in the retentate, achieving the main goal of this work. Even though the COD rejection rate was higher for the feed from 50 kDa, the COD was retained notably in both cases. The final COD value after the nanofiltration of the ultrafiltration permeate obtained with the 5 kDa and 50 kDa membranes was 8875 mg/L and 11,425 mg/L, respectively, which are much lower than the initial COD of the Mandarin Segmenter Wastewater (see Table 2).

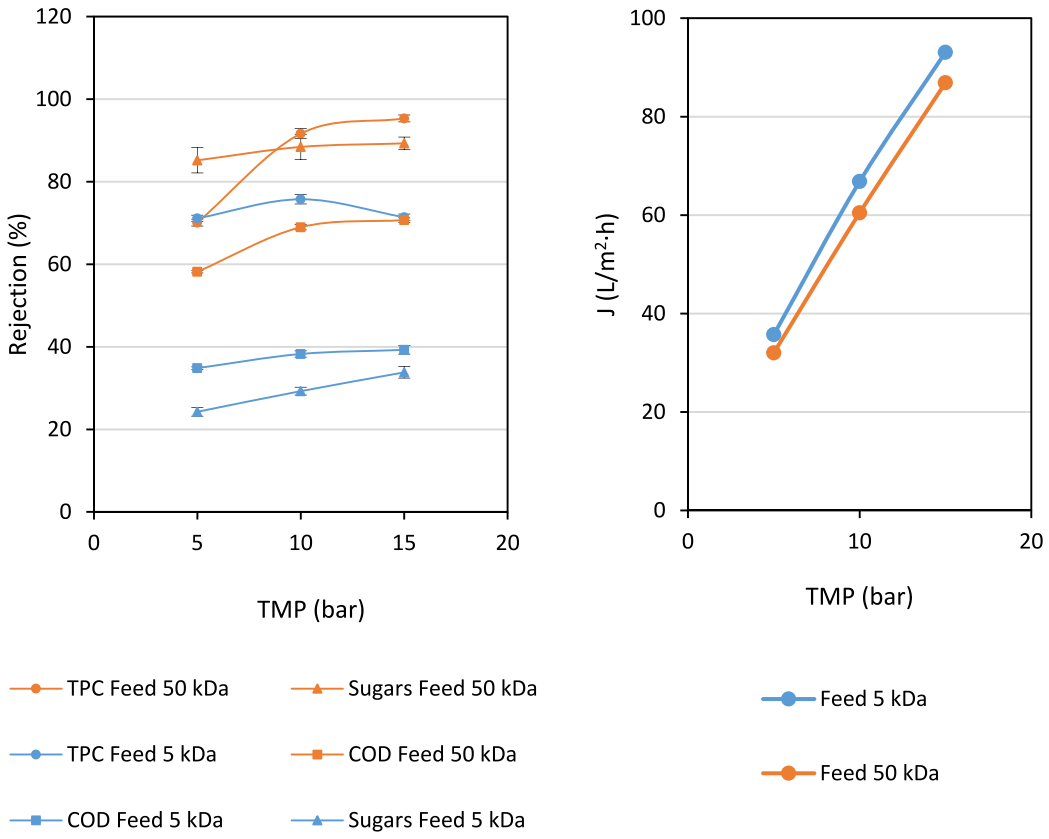

Fig. 7. Rejection rate (a), and permeate flux (b) for the NF 270 membrane in the total recycle configuration test at 5, 10 and 15 bar using a crossflow velocity of 1 m/s. The permeate flux values are an average value of the permeate flux obtained at the end of the test with each pressure (Fig. S2) when the flux reaches the steady state.

The rejection rate increased with the VRF, due to the formation of a denser fouling layer on the membrane surface that leads to the reduction in the mean pore size of the membrane [50,52]. In the case of the permeate flux (Fig. 8b), 5 kDa showed a higher permeate flux comparing to 50 kDa and, in both cases, it was sharply reduced at the beginning of the concentration process, followed by a gradual reduction with the VRF.

Table 4 summarizes the concentration of target compounds (polyphenols) and sugars in the UF and NF streams.

According to Table 4, the optimal process was a combination of an ultrafiltration with the UF spiral-wound 5 kDa membrane, followed by a nanofiltration with the NF 270 membrane to treat the UF permeate. As a result, the polyphenols were purified and concentrated in the retentate stream of the nanofiltration. Sugars were separated in the permeate, as shown in Fig. 8a. As the nanofiltration retentate was the desired product, a thoughtful characterisation of this stream was pursued. Therefore, the metabolites present in the nanofiltration retentate were determined by LC-MS. The individual rejection of the 21 detected compounds in the Mandarin Segmenter Wastewater is presented in Fig. 9. The final concentration in the nanofiltration retentate, in mg/L, is presented at the right of the bars.

As can be seen in Fig. 9, the rejection of all phenolic compounds surpassed 60 % (except for methyl-vanillate and phloretic acid, which were the only two compounds with a molecular weight (MW) below the MWCO of the NF270 membrane and were rejected in 50.16 ± 0.03 % – 50.67 ± 0.07 %, respectively). These high rejection values were satisfactory, as they allowed the concentration of the compounds of interest. Furthermore, the purity of the phenolic compounds was enhanced during the integrated membrane process, considering the concentration of phenolic compounds and the COD of the initial wastewater (20,200 mg O_2/L) and those of the final nanofiltration retentate (COD of 8875 mg O_2/L). According to this data, the purity of the recovered phenolic content was doubled. Furthermore, the ratio of total phenolic content to total sugar content was increased by three times. This result was achieved due to the efficient removal of non-desired compounds (previously discussed) and the concentration of the purified polyphenols.

In the case of the chemical family of flavonoids, which is very relevant, as it was previously commented, because it includes highly valued molecules, such as narirutin and hesperidin [53,54] the purity increased by two times as well. Therefore these compounds can be efficiently recovered from Mandarin Segmenter Wastewater. This implies an improvement with respect to the current state-of-the-art related to the extraction and purification of phenolic compounds, not only in the field of membrane technology [55,56] but also regarding methodologies such as solid-liquid extraction or ultrasound-microwave synergistic extraction [57,58]. For instance, Polidori et at., 2018, where able to successfully recover hesperidin from citrus juice by means of microfiltration, but the proposed process was not efficient for the recovery of narirutin [53]. Balyan and Sarkar, 2016, also proposed a UF/NF integrated membrane process for the purification and concentration of aqueous

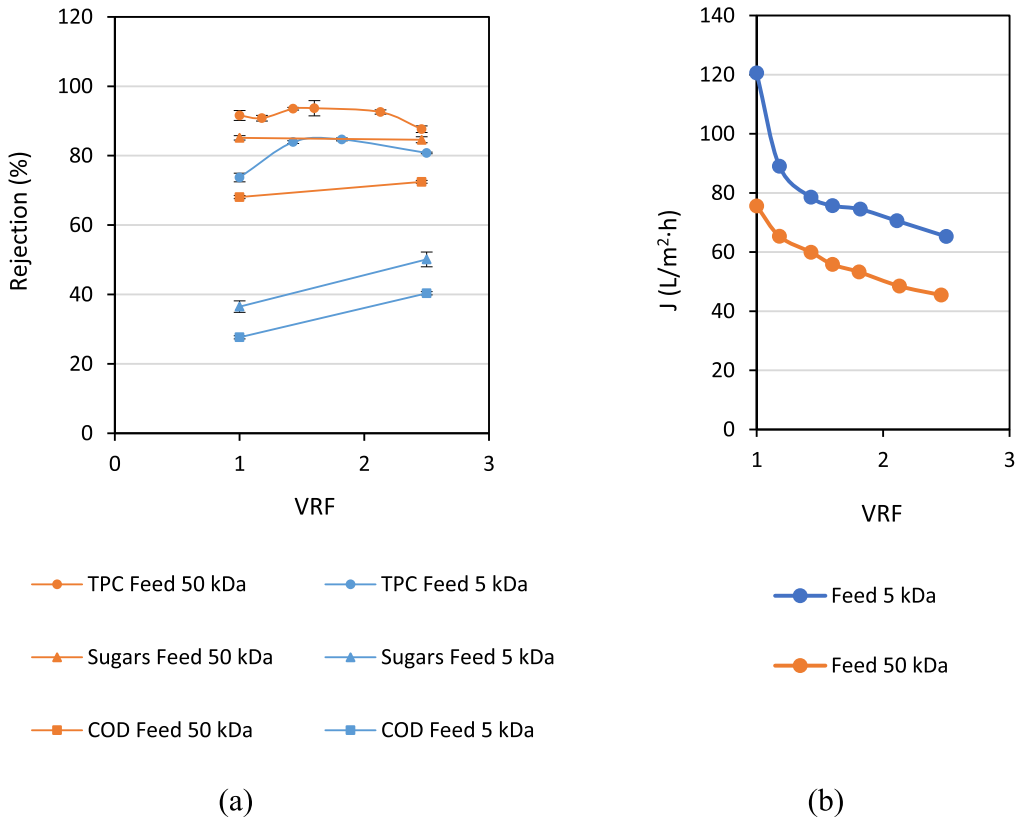

Fig. 8. Rejection rate for TPC (a) and permeate flux (b) for the NF 270 membrane in the batch concentration test at 10 bar using a crossflow velocity of 1 m/s.

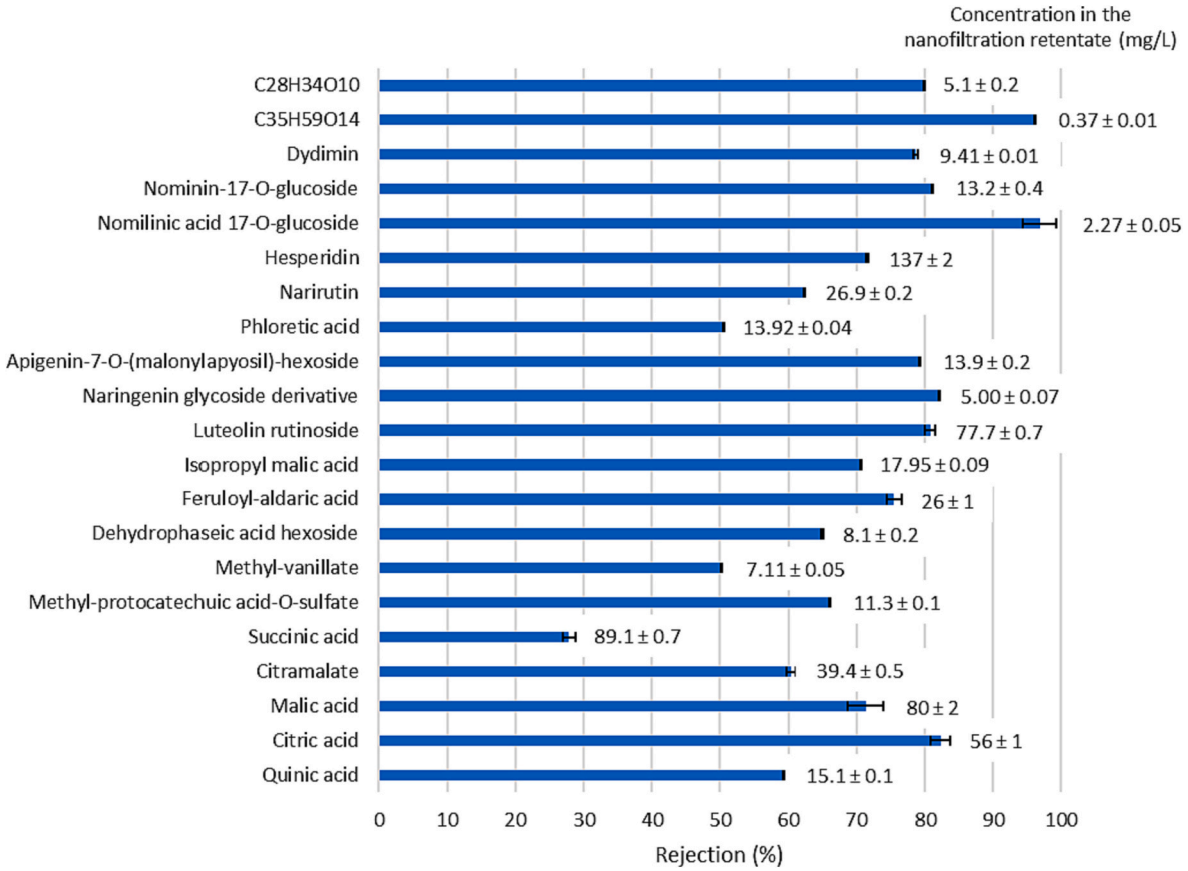

Fig. 9. Rejection of every compound determined by LC-ESI-QToF-MS in the NF 270 retentate, at a VRF of 2.5 at 10 bar.

Syzygium cumini (L.) seed extract. However, after the process the purity was only increased by 0.35 % [59].

According to previous research Cifuentes-Cabezas et al. [60], applying non-ionic resins to the nanofiltration retentate could efficiently separate the phenolic compounds from carbohydrates. Previously to the scaling up, pilot plant tests with larger membrane area for both UF and NF membranes must be performed to check if the results and the operating conditions are reproducible.

4. Conclusions

A separation procedure combining membranes processes has been developed to recover phenolic compounds from Mandarin Segmenter Wastewater. The optimal combination processes consisted of a centrifugation pretreatment (6 min at 17200 RCF) followed by 5 kDa PES spiral-wound UF membrane (crossflow velocity of 1 m/s and a pressure of 3 bar) and a NF270–2540 flat-sheet membrane (crossflow velocity of 1 m/s and a pressure of 10 bar). The UF process was able to retain in the retentate stream pigments (R_{Colour} = 90 %), pectins ($R_{Pectins}$ = 63 %), and sugars (R_{Sugars} = 58 %). Polyphenols passed to the permeate stream (R_{TPC} = 5 %), which was the feed for next NF membrane process. The NF process achieved satisfactory rejections for phenolic compounds (R_{TPC} = 80 %) and sugars (R_{Sugars} = 50 %). As a result, the final product (NF permeate) was enriched in phenolic compounds. The initial wastewater sample and the NF permeate were analysed with LC-MS to obtain the detailed phenolic profile pointing out that the rejection of almost all phenolic compounds surpassed 60 % and specifically the purity of the chemical family of flavonoids was increased from 1.5 % to 3 %. The results presented demonstrate the suitability of membrane technology to recover polyphenols from mandarin wastewater. The subtraction of phenolic compounds contributes to the decontamination of the wastewater and also to the revalorisation of the product obtained, in the pharmaceutical and cosmetic industries.

CRediT authorship contribution statement

Pablo Alonso-Vázquez: Data curation, Investigation, Methodology, Writing – original draft. **Carlotta Valle:** Data curation, Investigation, Methodology. **Carmen Sánchez-Arévalo:** Conceptualization, Methodology, Supervision, Writing – review & editing. **Beatriz-Elena Cuartas-Uribe:** Conceptualization, Methodology, Supervision, Writing – review & editing. **María-Cinta Vincent-Vela:** Conceptualization, Methodology, Supervision, Writing – review & editing. **Amparo Bes-Piá:** Conceptualization, Methodology, Supervision, Writing – review & editing. **Silvia Álvarez-Blanco:** Conceptualization, Methodology, Supervision, Writing – review & editing.

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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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jwpe.2024.105041.

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