



# Integration of membrane processes for the recovery and separation of polyphenols from winery and olive mill wastes using green solvent-based processing

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## ABSTRACT

Winery and olive mill industries generate large amounts of wastes causing important environmental problems. The main aim of this work is the evaluation of different membrane separation processes like microfiltration, ultrafiltration, nanofiltration, and reverse osmosis for the recovery of polyphenols from winery and olive mill wastes in aqueous solutions. Membrane processes were tested separately in a closed-loop system, and by an integration in a concentration mode sequential design (open-loop). Feed flow rate was varied from 1 to 10 mL min<sup>-1</sup>, and permeate samples were taken in order to measure the polyphenols concentration. The separation and concentration efficiency were evaluated in terms of total polyphenol content, and by polyphenols families (hydroxybenzoic acids (HB), hydroxycinnamic acids (HC), and flavonoids (F)), using high performance liquid chromatography. Results showed that MF and UF membranes removed suspended solids and colloids from the extracts. NF was useful for polyphenols separation (HB rejections were lower than for HC and F: HB rejections of 50 and 63% for lees filters and olive pomace extracts, respectively), and RO membranes were able to concentrate polyphenols streams (86 and 95% rejection from lees filters and olive pomace, respectively). Membranes sequential designs for lees filters and olive pomace extracts, using a selective membrane train composed by UF, NF and RO membranes, were able to obtain polyphenol rich streams and high-quality water streams for reuse purposes.

## 1. Introduction

Agri-food industries, generate large amount of wastes that represent an important environmental problem due to their toxicity caused by their high organic load (Nunes et al., 2016; Silvan et al., 2019; Zagklis and Paraskeva, 2018). In particular, winery and olive oil industries, two important industries of southern Europe, generate around 30 million tons of wastes per year (20 and 10 million tons, respectively), in different parts of their production process (Bruno et al., 2018; Melo et al., 2015). The main wastes produced by winemaking industries are grape stalk, grape pomace and wine lees. On the other hand, the olive

pomace and olive mill wastewater are the most common residues from olive oil industries (Cassano et al., 2019; Silvan et al., 2019).

This work focuses on two of the most generated residues from winery and olive oil industries: wine lees and olive pomace, respectively. Wine lees are composed of solid and liquid fractions formed after fermentation or filtration processes, and during wine aging. The solid fraction contains all precipitated deposits, which consist of microbial biomass (yeast and bacteria), polyphenols, carbohydrates, lignin, proteins, metals, inorganic salts, organic acids salts (mainly tartrates) and grape residues. The liquid fraction consists of the spent fermentation broth, and is rich in organic acids and ethanol (Cassano et al., 2019; Dimou et al., 2015;

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Pérez-Bibbins et al., 2015). Otherwise, olive pomace is the solid residue produced in the traditional, three-phase and two-phase olive oil extraction systems, being the main difference the amount of water. These residues are composed of olive pulp, skin, stone, water and oil, and their major components are polysaccharides, protein, fatty acids, pigments, and polyphenols (Nunes et al., 2019; Nunes et al., 2016; Pavez et al., 2019).

These wastes are currently used for composting, animal feed or energy production (Langsdorf et al., 2021). Nevertheless, the market value of fertilizers or animal feedstocks is relatively low. Moreover, the presence of polyphenols from these residues, leads to plant germination problems when used as fertilizers, or low digestibility when used as additives in animal feeding (Arboleda Meija et al., 2019). On the other hand, polyphenols are well-known as natural by-products or secondary metabolites of plants, which are present in the daily diet and for their important benefits on human health, e.g., in the prevention or treatment of cancer as well as cardiovascular, inflammatory and neurodegenerative diseases (Nunes et al., 2019; Bazinet and Doyen, 2015; Giacobbo et al., 2018; Panzella et al., 2020). These effects have been attributed to their capacity to act as potent antioxidants by scavenging or preventing the formation of free radicals implied in the oxidative processes (Bazinet and Doyen, 2015). Reported evidence on the great potential of polyphenols against different viruses that cause widespread health problems has been reviewed by Montenegro et al. (Montenegro-Landívar et al., 2021). The potential antiviral properties of families of polyphenols and their action mechanism against various types of viruses (e.g., influenza, coronaviruses, dengue fever and herpes simplex), and rotavirus, among others were critically reviewed.

Therefore, the recovery of polyphenols from natural sources has attracted the attention of the scientific community due to their high market value, and potential use in food, cosmetic, and pharmaceutical industries (Cassano et al., 2018; Panzella et al., 2020).

The valorization of winery and olive mill wastes, opens the opportunity to convert these residues into value-added sources of polyphenols contributing to the circular economy approach, economic growth and environmental protection (Arancon et al., 2013; Sharma et al., 2021; Tapia-Quirós et al., 2020). This is possible by developing innovative green strategies for the extraction, separation and purification of these bioactive compounds, which have become an important challenge for researchers (Sharma et al., 2021; Tapia-Quirós et al., 2020).

The use of water as extraction solvent is a green alternative to toxic, hazardous, and costly solvents, and its efficiency to extract polyphenols from agri-food wastes has been demonstrated (Cassano et al., 2019). Also, aqueous extracts are more suitable for separation and purification processes based on extraction chromatography using polymeric resins. In view of the application of recovered polyphenols in the food, nutraceutical or cosmetic fields, water extraction could be the best option.

Pressure driven membrane separation techniques are the main non-destructive physicochemical techniques applied to separate macromolecules and micromolecules from agri-food industry wastes (Cassano et al., 2016). They are mainly based on the compound separation by their molecular weight cut-off (MWCO) and the use of pressure as driving force. The advantages of membrane separation are high selectivity, low energy consumption, simple equipment and low temperatures (Cassano et al., 2018; Zagklis and Paraskeva, 2015). The most important pressure driven membrane techniques are microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO) (Zagklis and Paraskeva, 2015). The separation efficiency of these methodologies depends on a series of factors: membrane characteristics (material, configuration of the separation module, pore size), physical-chemical composition of the solution (type, weight, polarity, solute load), and operating parameters (feed flow rate, trans-membrane pressure, temperature, permeate flow), among others (Castro-Muñoz et al., 2016). Besides, there are other membrane technologies, like electrically driven processes (e.g., electrodialysis (ED), and hybrid processes (ED with bipolar membranes and ED with filtration membranes)),

in which the electric field is the main driving force in the process. There is no pressure applied in the system, in contrast to the pressure driven filtration process. Molecular transfer and flux depend of the molecule charge and the electric field (Bazinet and Doyen, 2015; Suwal and Marciniak, 2018). Nevertheless, pressure driven membrane separation processes have shown to be a suitable stage of pre-treatment for polyphenol recovery in winery (Díaz-Reinoso et al., 2017; Giacobbo et al., 2015, 2017a, 2017b, 2018; Kontogiannopoulos et al., 2017; Zagklis and Paraskeva, 2015) as well as olive mill residues (Alfano et al., 2018; Nunes et al., 2019; D'Antuono et al., 2014; Hamza and Sayadi, 2015; Ioannou-Ttofa et al., 2017; Kontos et al., 2018, 2016; La Scalia et al., 2017; Ochando-Pulido and Martínez-Férez, 2017; Savarese et al., 2016; Zagklis et al., 2015). However, more studies are needed for the optimization and implementation of these technologies at an industrial level, for solid and liquid wastes. For instance, Cassano et al. (2019) investigated the use of MF polyvinylidene fluoride (PVDF) hollow fiber membranes and NF in flat-sheet configuration (NP010, NP030 and MPF36 membranes), for the clarification and separation of phenolic compounds from red wine lees. The MF hollow fiber membranes completely retained suspended solids; whereas NF membranes rejected more than 93% of anthocyanins and the permeate streams resulted enriched in phenolic compounds like resveratrol. Giacobbo et al. (2015), evaluated MF in a total recirculation mode (V0.2 and MFP5, flat-sheet membranes) and in a concentration mode (plasma associated membranes (PAM) hollow fiber), for the recovery of polyphenols from second racking wine lees. After MF experiments, a sequential design of UF (ETNA01PP and ETNA10PP membranes) and NF (NF270 membrane) was employed in order to fractionate polyphenols and polysaccharides from wine lees (Giacobbo et al., 2017a). MF led to obtain a clean permeate rich in polyphenols. UF has been proven to be effective to separate the polysaccharides of the polyphenols, and NF membrane presented polyphenols rejections higher than 92%, achieving concentrated solutions with high antioxidant activity. Nunes et al. (2019), investigated the performance of NF (NF270 and NF90 membranes) and RO (BW30), for the recovery of phenolic compounds from olive pomace aqueous extracts. Regarding their phenolic contents, no significant differences between NF270 and NF90 concentrates were presented ( $p > 0.05$ ). The BW30 membrane rejected 100% of phenolic compounds, and it was possible to obtain a concentrate stream with high antioxidant capacity. Romani et al. (2016) evaluated MF, UF, NF and RO for the separation and concentration of polyphenols aqueous extracts from green leaves, dried leaves, and pitted olive pulp of *Olea europaea* L. MF stage was carried out with tubular ceramic membranes in titanium oxide; while the UF, NF, and RO stages were conducted with spiral wound module membranes in polyethersulfone (PES). As a result, pitted olive pulp extract was rich in hydroxytyrosol and its derivatives (96.5% of the total polyphenols); green leaves extract contained 67% of oleuropein; and dried leaves extract contained 19.2% of secoiridoids. Zagklis and Paraskeva (2020) proposed an integration of UF (tubular ceramic zirconia membrane), NF (spiral wound polymeric membrane), RO (spiral wound polymeric membrane), and a final adsorption step for the recovery of polyphenols from olive mill wastewater, grape marc, and olive leaves residues. As a result, they obtained  $378 \text{ g L}^{-1}$ ,  $98 \text{ g L}^{-1}$ , and  $190 \text{ g L}^{-1}$  of phenols in gallic acid equivalents (GAE) for olive mill wastewater, olive leaf and grape marc hydroalcoholic extracts, respectively. Also, Bottino et al. (2020) integrated the use of MF (Membralox EP19-40 membrane) and RO (SW30HR membrane) techniques for the treatment of olive mill wastewater. Results demonstrated that, RO technique rejected more than 99.3% of phenolic compounds and produced water with low salinity, chemical oxygen demand, and phytotoxicity. Díaz-Reinoso et al. (2017) proposed a membrane integration of MF, NF and UF centrifugation stages to recover a concentrate of phenolic compounds from white wine vinasses. The experiment allowed the recovery of an enriched phenolic extract with 45% gallic acid equivalents and an ABTS (2,2'-azino-bis(3-ethylbenzothiazoline-6-sulphonic acid)) radical scavenging capacity of 2 g of Trolox (6-hydroxy-2,5,7,

8-tetramethylchroman-2-carboxylic acid) equivalents.

Accordingly, membrane processes provide the possibility of: i) removal of suspended solids and colloids generated in the polyphenols extraction from the winery and olive oil wastes by using MF; ii) a pre-fractionation of the polyphenol families with molecular weights from 0.1 kDa up to 2 kDa, removing other larger molecules (>5 kDa) dissolved in the water extraction stages and non-removed by MF (e.g. sugars, lipids and proteins) using UF membranes; and iii) a separation step of the polyphenols families according to their chemical properties such as hydroxybenzoic acids (HB), hydroxycinnamic acids (HC), and flavonoids (F).

### 1.1. Objective

This study is carried out in the frame of a research program focused on the revalorization of industrial wastes resulting from winery and olive oil processing. Polyphenols have been identified as the most relevant group of phytochemicals from these wastes as a source of antioxidant by-products and their extraction and leaching conditions from the processing wastes was optimized based on experimental design approaches, multi-criteria decision making and response surface methodology. The recovery of remarkable target compounds was targeted and the criteria to assess the content of active antioxidant species by using chromatographic techniques were also set-up. Accordingly, the next stage of the research program to approach the production of pure polyphenol extracts is to identify and screen separation techniques to develop a pre-purification stage removing other components also generated in the waste extraction stages. For all the aforementioned, and taking into account the review of the state of the art, this study focuses in (i) the evaluation of different pressure driven membrane technologies: MF and UF as clarification stage, and NF and RO for the separation and concentration of polyphenols from aqueous extracts of winery and olive mill wastes (lees filters and olive pomace, respectively), and (ii) the development of an integrated membrane process for each extract, in order to obtain streams with high concentrations of polyphenols that could be implemented at an industrial scale in winery and olive mill industries. Taken into account the complexity of the polyphenol containing extracts, chromatographic analytical techniques were used for quantifying: i) the total content of polyphenols and ii) three main families of polyphenols (hydroxybenzoic acids (HB), hydroxycinnamic acids (HC), and flavonoids (F)).

## 2. Materials and methods

### 2.1. Reagents

The polyphenols standards used were: rutin, gallic acid, 3,4-dihydroxybenzoic acid, chlorogenic acid, vanillic acid, syringic acid, ethyl gallate, ferulic acid, 3,4-dihydroxybenzaldehyde, 4-hydroxybenzoic acid, epicatechin, *p*-coumaric acid, naringenin, quercetin, 2,5-dihydroxybenzoic acid and apigenin that were obtained from Sigma Aldrich (St. Louis, USA). 3-hydroxytyrosol, catechin, resveratrol and myricetin were purchased from TCI (Japan). Homogentisic acid and oleuropein were supplied by Extrasynthese (France). Kaempferol and hesperidin were obtained from Glenthams Life Sciences (UK). Caffeic and caftaric acid were purchased from Chengdu Biopurify Pytochemicals (China). Luteolin and 6-hydroxy-2,5,7,8-tetramethylchroman-2-carboxylic acid (Trolox) were supplied by Carbosynth (Berkshire, UK). The solvents used were: ethanol (EtOH) HPLC-UV grade obtained from Honeywell Riedel-de Haën™ (Germany); acetonitrile (ACN) HPLC-UV grade from Fisher Scientific (UK); and formic acid (FA) 98–100% (w/w) from Merck (Darmstadt, Germany). Ultrapure water was obtained from a Milli-Q system (Merck Millipore).

### 2.2. Samples

Lees filters and olive pomace samples were provided by Spanish industries. Lees filters were obtained from red wine production using a combination of Garnacha, Tempranillo, Cabernet Sauvignon and Cariñena grapes. Samples were collected throughout August and October 2018, in a winery located in Barcelona, Spain. Olive pomace samples were obtained from an olive oil two-phase extraction system with Hojiblanca and Picual olives. Sampling was performed in the period between November 2018 and February 2019, in an olive mill industry located in Córdoba, Spain. Both winery and olive mill residues were stored in the freezer at  $-20\text{ }^{\circ}\text{C}$  before used.

### 2.3. Procedures

#### 2.3.1. Polyphenol extraction

Polyphenols were extracted from lees filters and olive pomace according to a previous optimized solid-liquid extraction (SLE) methodology. Ultrapure water was used as the extraction solvent and the stirring rate was set at 300 rpm in a RCT basic hot plate stirrer with temperature controller (IKA, Staufen, Germany). For lees filters, extraction conditions were: 10 min of extraction time,  $70\text{ }^{\circ}\text{C}$  of extraction temperature, and 1:100 (w/v) solid to liquid ratio; whereas for olive pomace, extraction conditions were: 10 min of extraction time,  $25\text{ }^{\circ}\text{C}$  of extraction temperature, and 1:30 (w/v) solid to liquid ratio. The solutions were centrifuged for 15 min at 3500 rpm in a Labofuge 400 centrifuge (Heraeus, Hanau, Germany). Then, the supernatants were filtered through  $0.45\text{ }\mu\text{m}$  nylon syringe filters (Filtros Anovia, Barcelona, Spain) and stored at  $4\text{ }^{\circ}\text{C}$  until the analysis.

#### 2.3.2. Membrane experimental set-up and procedure

The membrane separation was performed in total recirculation mode (closed-loop) and in concentration mode (open-loop), in order to evaluate the variation of the trans-membrane fluxes ( $J_v$ ) with the feed flow rate, the polyphenols rejection percentages, and to design an integration of the membrane systems. For this, a memHPLC membrane cell (MMS AG Membrane Systems, Urdorf, Switzerland) equipped with a 515 HPLC high pressure pump (Waters, Milford, MA, USA) and a MR Hei-Mix L stirring plate (Heidolph, Schwabach, Germany) were used. Membranes characteristics are shown in Table 1. For the MF process, the membranes were mixed cellulose esters of  $0.22\text{ }\mu\text{m}$  and  $0.45\text{ }\mu\text{m}$ ; whereas for UF process, PES membranes of 30 and 50 kDa of MWCO were used. In both cases, the membranes were not dense. Otherwise, in NF and RO processes, the membranes employed were dense membranes. For NF process, three types of membranes were evaluated as follows: polypiperazine thin-film composite (NF270), polyamides (TFC-HR, TFCS and NF90) and a sulfonamide active layer and polysulfone support (Duracid). In the case of RO process, all the membranes tested were polyamide thin-film composite (BW30LE, XLE and SW30HR).

Before experiments, a pre-cleaning procedure was applied to NF and RO membranes in order to (i) remove conservation products and (ii) densify the support layer of the membranes (not required for MF and UF membranes). Each membrane was soaked in Milli-Q water overnight before experiments. Also, the pump was flushed with Milli-Q water for 5 min at  $5\text{ mL min}^{-1}$  to remove impurities from the pump. Then, membrane pressurization was done for dense membranes (NF and RO): the extract was pumped through the system at maximum feed flow rate ( $10\text{ mL min}^{-1}$ ). Conductivity measurements were taken every 10 min until two measurements were equal and the membrane was considered pressurized. Different volume extracts of 30 and 1000 mL were placed in a container (feed tank) on a stirring plate, at constant stirring and room temperature for closed and open-loop experiments, respectively. The extracts were pumped into the membrane cell, with an active area of  $28\text{ cm}^2$ , while feed flow rate was varied from 1 to  $10\text{ mL min}^{-1}$  (one by one), with 5 min of stabilization between each feed flow rate, until reached  $10\text{ mL min}^{-1}$ . After each stabilization, a permeate sample was

**Table 1**  
Employed membranes and characteristics.

Membrane	Manufacturer	Membrane composition
<b>MF</b>		
Filter-Lab 0.45 $\mu\text{m}$ ("Filter-Lab 0.45 $\mu\text{m}$ ," n.d.)	Filtros Anoaia, S. A.	Mixed cellulose esters (MCE)
Filter-Lab 0.22 $\mu\text{m}$ ("Filter-Lab 0.22 $\mu\text{m}$ ," n.d.)	Filtros Anoaia, S. A.	Mixed cellulose esters (MCE)
<b>UF</b>		
Biomax 50 kDa ("Biomax 50 kDa," n.d.)	Merck Millipore	Polyethersulfone (PES)
Biomax 30 kDa ("Biomax 30 kDa," n.d.)	Merck Millipore	Polyethersulfone (PES)
<b>NF</b>		
NF270 ("DuPont-FilmTec™ NF270-4040" n.d.)	DuPont-Filmtec	Polypiperazine Thin-Film Composite
TFC-HR ("KOCH-Fluid Systems," n.d.)	KOCH-Fluid Systems	Proprietary TFC® polyamide
TFCs ("KOCH-Fluid Systems NF TFCs," n.d.)	KOCH-Fluid Systems	Proprietary TFC® polyamide
NF90 ("DuPont-FilmTec™ NF90-4040" n.d.)	DuPont-Filmtec	Polyamide Thin-Film Composite
Duracid ("SUEZ NF Duracid," n.d.)	Suez	Sulfonamide active layer and polysulfone support
<b>RO</b>		
BW30LE ("DuPont FilmTec™ BW30-4040" n.d.)	DuPont-Filmtec	Polyamide Thin-Film Composite
XLE ("DuPont-FilmTec™ XLE-4040" n.d.)	DuPont-Filmtec	Polyamide Thin-Film Composite
SW30HR ("DuPont FilmTec™ SW30-4040" n.d.)	DuPont-Filmtec	Polyamide Thin-Film Composite

to measure the polyphenols concentration. During the experiments, flow rate (Practum513-1S analytical balance Sartorius (Göttingen, Germany)), conductivity (GLP31 conductivity-meter CRISON (Barcelona, Spain)), and pH (GLP22 pH-meter CRISON (Barcelona, Spain)) were monitored. After the membrane processes two streams were obtained, a permeate and a concentrate, which were evaluated by HPLC-UV for the polyphenol analysis. Once the experiment was finished, the pump was purged, and the membrane was removed. All experiments were performed in duplicate, for each membrane tested.

As a summary, the experimental design was the following:

- (i) Closed-loop tests: several MF, UF, NF and RO membranes (described in Table 1) were tested varying the flow rate.
- (ii) Open-loop tests: a sequential design, integrating the best membrane processes for separation and concentration of polyphenols was tested in a concentration mode.

### 2.3.3. High performance liquid chromatography analysis with ultraviolet detection (HPLC-UV)

The chromatographic analysis of the polyphenolic content was carried out by a high-performance liquid chromatography equipment, due to its accuracy and precision to determine polyphenols concentration at low values. In this case, an Agilent Series 1200 system (Agilent Technologies, Palo Alto, CA, USA), equipped with a quaternary pump, an automatic injection system, a diode array detector (DAD), and an AgilentChemStation software for data analysis were employed. The separation was performed with a Kinetex C<sub>18</sub> column (Phenomenex, 100 mm  $\times$  4.6 mm  $\times$  2.6  $\mu\text{m}$ , Torrance, CA, USA), with ultrapure water with 0.1% FA (A), and ACN (B) as the mobile phase components. The gradient program for lees filters extracts was: 0 min, 5% B; 0–38 min, 45% B; 38–40 min, 90% B; 40–42 min, 90% B; 42–42.2 min, 5% B; 42.2–50 min, 5% B; and for olive pomace extracts was: 0 min, 5% B; 0–38 min, 35% B; 38–40 min, 90% B; 40–42 min, 90% B; 42–42.2 min, 5% B; 42.2–50 min, 5% B. The flow rate was 0.4 mL min<sup>-1</sup> and the injection volume 5  $\mu\text{L}$ .

Chromatograms were recorded at 280, 310, and 370 nm. The total polyphenol content (TPC) was estimated from the total peak area in the chromatograms at 280 nm, in the time range between 5 and 36 min. For lees filters, the hydroxybenzoic acids (HB) content was estimated at 280 nm, in the time range between 5 and 15 min; hydroxycinnamic acids (HC) content at 310 nm, in the time range between 15 and 21 min; and flavonoids (F) content at 370 nm in the time range between 21 and 36 min. For olive pomace, the HB content was estimated at 280 nm, in the time range between 7 and 14 min; HC content at 310 nm, in the time range between 14 and 23 min; and F content at 370 nm in the time range between 23 and 42 min. TPC and HB were expressed in terms of mg of gallic acid equivalent per L (mg GAE L<sup>-1</sup>), HC was expressed in terms of caffeic acid equivalent per L (mg CAE L<sup>-1</sup>), and F was expressed in terms of kaempferol equivalent per L (mg KE L<sup>-1</sup>). Calibration curves for gallic acid and caffeic acid were constructed at concentrations from 0.5 to 10 mg L<sup>-1</sup>; and for kaempferol from 1 to 10 mg L<sup>-1</sup>.

### 2.4. Membrane separation operational parameters

The effectiveness of the studied membranes was determined by different parameters. The permeate flow ( $Q_p$ ) was calculated by equation (1) (Mohamad et al., 2019):

$$Q_p (\text{mL s}^{-1}) = M_p / (\rho_E \times t) \quad (1)$$

where  $M_p$  is the permeate mass (g),  $\rho_E$  is the density of the extract (g mL<sup>-1</sup>), and  $t$  is the time taken to obtain the sample (s). The density of lees filters and olive pomace extracts was 0.976 g mL<sup>-1</sup> and 0.983 g mL<sup>-1</sup>, respectively at 21  $\pm$  1 °C.

During the experiments, the trans-membrane flux ( $J_v$ ) was also calculated by equation (2) (Mohamad et al., 2019):

$$J_v (\text{L m}^{-2}\text{h}^{-1}) = Q_p / A \quad (2)$$

where  $Q_p$  is the permeate flow (L h<sup>-1</sup>), and  $A$  is the active membrane area (0.028 m<sup>2</sup>).

Moreover, the rejection ( $R$ ) percentage was calculated by equation (3) (Mohamad et al., 2019):

$$R(\%) = [(C_F - C_P) / C_F] \times 100 \quad (3)$$

where  $C_F$  is the concentration of polyphenols in the feed (mg L<sup>-1</sup>), and  $C_P$  is the concentration of polyphenols in the permeate (mg L<sup>-1</sup>).

Additionally, the concentration factor (FC) was calculated by equation (4) (López et al., 2021):

$$FC = C_C / C_F \quad (4)$$

where  $C_C$  is the concentration of polyphenols in the concentrate stream (mg L<sup>-1</sup>), and  $C_F$  is the concentration of polyphenols in the feed stream (mg L<sup>-1</sup>).

### 2.5. Data analysis

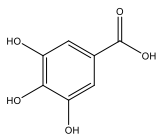
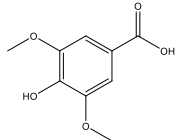
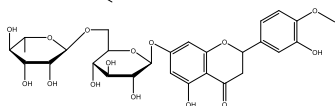
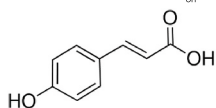
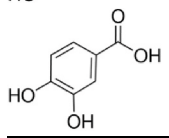
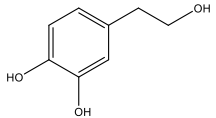
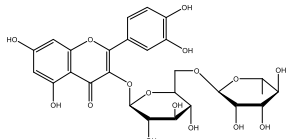
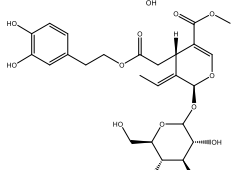
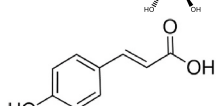
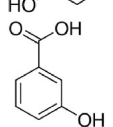
Experiments were done by duplicate and different analysis were performed to be accurate with the measurements. Moreover, an ANOVA test analysis was performed to validate them. One-factor analysis of variance (ANOVA) with replication was applied, at 95% confidence level ( $p < 0.05$ ), to evaluate statistically the differences between the tested membranes. ANOVA was performed with Microsoft Excel 2019.

## 3. Results and discussion

### 3.1. Membrane processes for polyphenol recovery in closed-loop configuration

Polyphenol composition of the extracts generated from a water extraction stage from both lees filters and olive pomace is summarized in

**Table 2**  
Identified polyphenols from lees filters and olive pomace aqueous extracts.

Compound	Structure	Formula	Molecular mass (g mol <sup>-1</sup> )	Concentration (mg L <sup>-1</sup> )
<b>Lees filters extract</b>				
Gallic acid		C <sub>7</sub> H <sub>6</sub> O <sub>5</sub>	170.12	1.7 ± 0.1
Syringic acid		C <sub>9</sub> H <sub>10</sub> O <sub>5</sub>	198.17	4.3 ± 0.1
Hesperidin		C <sub>28</sub> H <sub>34</sub> O <sub>15</sub>	610.1898	3.0 ± 0.2
<i>p</i> -coumaric acid		C <sub>9</sub> H <sub>8</sub> O <sub>3</sub>	164.0473	0.4 ± 0.1
3,4-dihydroxybenzoic acid		C <sub>7</sub> H <sub>6</sub> O <sub>4</sub>	154.12	0.6 ± 0.1
<b>Olive pomace extract</b>				
3-hydroxytyrosol		C <sub>8</sub> H <sub>10</sub> O <sub>3</sub>	154.16	4.1 ± 0.1
Rutin		C <sub>27</sub> H <sub>30</sub> O <sub>16</sub>	610.517	1.8 ± 0.1
Oleuropein		C <sub>25</sub> H <sub>32</sub> O <sub>13</sub>	540.51	17.1 ± 0.7
<i>p</i> -coumaric acid		C <sub>9</sub> H <sub>8</sub> O <sub>3</sub>	164.0473	1.9 ± 0.1
4-hydroxybenzoic acid		C <sub>7</sub> H <sub>6</sub> O <sub>3</sub>	138.12	3.6 ± 0.1

**Table 2.**

For lees filters, at the optimum extraction conditions (e.g. 10 min of extraction time, 70 °C and 1:100 (w/v) solid-to-liquid ratio) the main polyphenols identified were: gallic acid (1.7 ± 0.1 mg L<sup>-1</sup>), syringic acid (4.3 ± 0.1 mg L<sup>-1</sup>), hesperidin (3.0 ± 0.2 mg L<sup>-1</sup>), *p*-coumaric acid (0.4 ± 0.1 mg L<sup>-1</sup>) and 3,4-dihydroxybenzoic acid (0.6 ± 0.1 mg L<sup>-1</sup>). For olive pomace at the optimum extraction conditions (e.g. 10 min of extraction time, 25 °C and 1:30 (w/v) solid-to-liquid ratio) the main polyphenols identified were: 3-hydroxytyrosol (4.1 ± 0.1 mg L<sup>-1</sup>), rutin (1.8 ± 0.1 mg L<sup>-1</sup>), oleuropein (17.1 ± 0.7 mg L<sup>-1</sup>), *p*-coumaric acid (1.9 ± 0.1 mg L<sup>-1</sup>) and 4-hydroxybenzoic acid (3.6 ± 0.1 mg L<sup>-1</sup>).

### 3.1.1. Microfiltration process

Lees filters and olive pomace extracts were driven towards 0.45 and 0.22 µm MF membranes, to evaluate polyphenols separation. The total polyphenol concentration, in the feed stream, for lees filters and olive pomace extracts was 33 and 173 mg L<sup>-1</sup>, respectively. For lees filter extracts permeate flux values achieved were 28.5 L m<sup>-2</sup> h<sup>-1</sup> for both membranes (0.45 and 0.22 µm). Giacobbo et al. (2015) found in wine lees from the second racking of red winemaking, that a MF membrane with a larger pore size of 0.5 µm, showed lower trans-membrane fluxes and consequently, more severe fouling than with a smaller pore size of 0.2 µm at a feed flow rate of 150 L h<sup>-1</sup>. Also, that higher dilution factors with water (10 v/v) showed higher trans-membrane fluxes (in a linear

increase) as well as higher polyphenols recovery rates in the permeate. Results for olive pomace extracts shown permeate flux values of  $8 \text{ L m}^{-2} \text{ h}^{-1}$ . Additionally, the results of polyphenol rejection (%) as a function of  $J_v$  are shown in Fig. 1.

For lees filters extracts, polyphenol rejection percentages were between  $25.1 \pm 9\%$  ( $1 \text{ mL min}^{-1}$ ) and  $12.8 \pm 1\%$  ( $10 \text{ mL min}^{-1}$ ) for the  $0.45 \mu\text{m}$  membrane; and between  $30.3 \pm 5.5\%$  ( $1 \text{ mL min}^{-1}$ ) and  $13.2 \pm 1.8\%$  ( $10 \text{ mL min}^{-1}$ ) for the  $0.22 \mu\text{m}$  membrane (see Fig. 1a). ANOVA results showed that there was no significant difference between the two studied MF membranes on the polyphenols recovery ( $p = 0.71$ ). Rejection results were separated by polyphenol families with the procedure previously described. As a result, the  $0.22 \mu\text{m}$  membrane rejected 23% of HB, 27% of HC, and 54% of F; and the  $0.45 \mu\text{m}$  membrane rejected 22% of HB, 23% of HC, and 24% of F (see Fig. S1, supplementary material).

Rejection results for olive pomace extracts (Fig. 1b), were between  $15.4 \pm 4.6\%$  and  $6 \pm 2.5\%$  ( $1$  and  $10 \text{ mL min}^{-1}$ , respectively) for  $0.45 \mu\text{m}$  membrane; and between  $13.9 \pm 2.6\%$  and  $7.2 \pm 1.3\%$  ( $1$  and  $10 \text{ mL min}^{-1}$ , respectively) for the  $0.22 \mu\text{m}$  membrane. ANOVA results indicated that there was no significant difference between the two studied MF membranes on the polyphenols recovery ( $p = 0.88$ ). Regarding polyphenol families, rejection percentages of 11% of HB, 16% of HC, and 23% of F, for  $0.22 \mu\text{m}$  membrane were found; and 9% of HB, 10% of HC, and 22% of F, for  $0.45 \mu\text{m}$  membrane (see Fig. S1, supplementary material).

Differences between olive pomace and lees filters extracts, is due to olive pomace extracts were more concentrated than lees filter extracts, and therefore the membrane fouling phenomena was greater. The polyphenols rejection values should be due to sorption processes onto to the cake layer formed along the filtration stage and consequently losses of polyphenols of up to 15–20% could be expected. Similar results were reported by Cassano et al. (2019) when using a PVDF based hollow fibre MF-membrane to clarify red wine lees extracts, where 100% of suspended solids were retained, and rejection values for total polyphenols, anthocyanins, and resveratrol were 15, 11, and 14%, respectively. Also, Ochando-Pulido and Martínez-Férez (2017) when using a  $0.45 \mu\text{m}$  MF membrane for the treatment of olive mill wastewater, removed 100% of the suspended solids and rejected 20% of the phenolic fraction of the effluent.

### 3.1.2. Ultrafiltration step

Two UF membranes (50 and 30 kDa), were evaluated for polyphenol separation in lees filters and olive pomace extracts. For lees filters extracts,  $J_v$  maximum values of  $12 \text{ L m}^{-2} \text{ h}^{-1}$  with both membranes (30 and 50 kDa), while for olive pomace extracts, maximum  $J_v$  values achieved where  $6 \text{ L m}^{-2} \text{ h}^{-1}$  at the same trans-membrane pressure values. Polyphenols rejection results, for lees filters and olive pomace extracts, are shown in Fig. 2.

For lees filters extracts, rejection percentages were between  $29.1 \pm 7.3\%$  and  $37.8 \pm 1.3\%$  ( $1$  and  $10 \text{ mL min}^{-1}$ , respectively) for 50 kDa membrane; and between  $41.8 \pm 0.9\%$  and  $38.7 \pm 0.9\%$  ( $1$  and  $10 \text{ mL min}^{-1}$ , respectively) for 30 kDa membrane (see Fig. 2a). ANOVA results showed that there was no significant difference between the two tested

UF membranes on the polyphenols recovery ( $p = 0.80$ ). The rejection results by polyphenols families had a similar behavior for the two membranes (see Fig. S2, supplementary material). The 50 kDa membrane rejected 22% of HB, 48% of HC, and 72% of F; and the 30 kDa membrane rejected 21% of HB, 45% of HC, and 72% of F.

For olive pomace extracts, rejection percentages were between  $44.4 \pm 3.7\%$  and  $35.8 \pm 1.2\%$  ( $1$  and  $10 \text{ mL min}^{-1}$ , respectively) for 50 kDa membrane; and between  $46.4 \pm 0.1\%$  and  $39.9 \pm 1.8\%$  ( $1$  and  $10 \text{ mL min}^{-1}$ , respectively) for 30 kDa membrane (see Fig. 2b). There was no significant difference between the two studied UF membranes on the polyphenol recovery from olive pomace extracts ( $p = 0.26$ ). In agreement with these results, Ochando-Pulido and Martínez-Férez (2017) found that 50 and 30 kDa membranes rejected 43 and 47% of total phenolic content, respectively for olive mill wastewater. When rejection results were separated by polyphenols families, 50 kDa membrane rejected 24% of HB, 39% of HC, and 43% of F; and 30 kDa membrane rejected 27% of HB, 39% of HC, and 51% of F (see Fig. S2, supplementary material).

The 30 kDa membrane, having a smaller pore size, can retain more suspended solids and colloids than the 50 kDa membrane. Hence, 30 kDa membrane was selected for an integrated membrane sequential design for lees filters and olive pomace extracts. Cassano et al. (2013), found also that an UF membrane pretreatment is a critical step for the fractionation of polyphenols from olive mill wastewater in an integrated membrane process, due to the rapid decline of trans-membrane flux and irreversible fouling of the UF membrane obtained in their results.

Retention of polyphenols should be associated mainly to sorption processes linked to the cake layer generated along the filtration stage although it could not be discarded sorption onto the PES structure of the UF membranes. Galiano et al. (2016) proposed the use of a new family of more hydrophobic membranes based on a PVDF structure. Low rejections towards phenolic compounds (<4%) were reported in the clarification of pomegranate juice by using PVDF hollow fiber membranes. PVDF polymer consist of alternating units of  $\text{CF}_2$  and  $\text{CH}_2$  conferring a hydrophobic nature to the membrane filtration structure. Therefore, PVDF chemistry is less prone to undergo weak interactions (e. g., van der Waals and hydrogen bonds) with the hydroxyl groups of polyphenols structures and, therefore, more resistant to fouling and highly permeable to phenolic compounds when compared with polyethersulfone (PES) membranes, as it is the case of those used in this study.

The integration of MF is a robust approach to remove suspended solids of raw lees filters and olive pomace extracts as it has been demonstrated with conventional centrifugation. The next stage by UF allows a complete separation of fats, mainly rejected by the UF membrane, from dissolved electrolytes, sugars and polyphenols, contained in the permeate. Garcia-Castello et al. (2020) demonstrated that a chemical oxygen demand reduction of about 90% for olive pomace wastes was possible through the combination of both processes. In a different approach, the pre-filtration stage of raw olive-oil pomace with a polypropylene screen ( $80 \mu\text{m}$ ) followed by treatment with tubular ceramic UF membranes (pore size  $100 \text{ nm}$ ), produced a separation of high

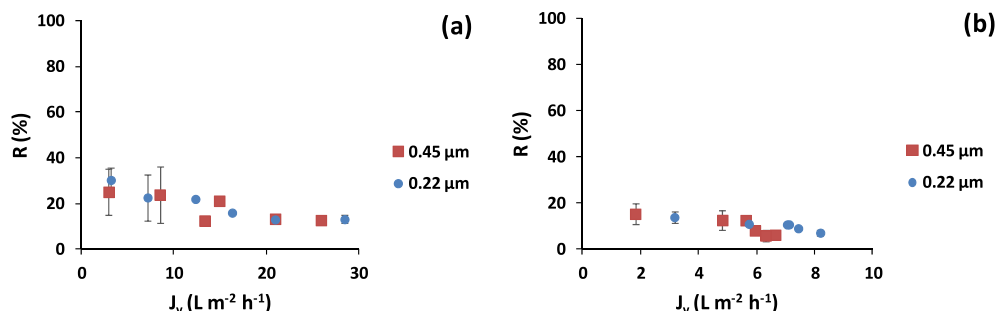


Fig. 1. Total polyphenol rejection evolution with trans-membrane flux for MF membranes ( $0.45$  and  $0.22 \mu\text{m}$ ), in (a) lees filters and (b) olive pomace extracts.

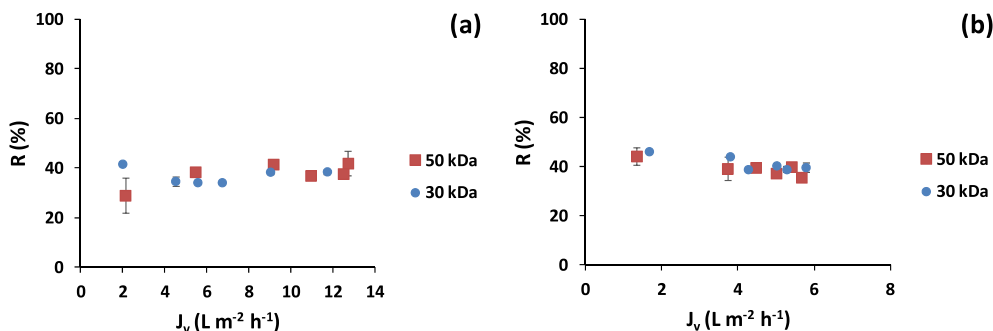


Fig. 2. Total polyphenol rejection evolution with trans-membrane flux for UF membranes (50 and 30 kDa), in (a) lees filters and (b) olive pomace extracts.

molecular weight constituents including fats, lipids and suspended solid particles (Paraskeva et al., 2007).

### 3.1.3. Nanofiltration option

Five NF membranes (NF270, TFC-HR, TFCS, NF90 and Duracid), were studied for NF separation and/or concentration for lees filters and olive pomace extracts. For lees filters and olive pomace extracts,  $J_v$  values ranged from 2 to 8  $L m^{-2} h^{-1}$  at trans-membrane pressure values of 15 bar. The lowest  $J_v$  values were obtained with TFCS membrane for lees filters, while for olive pomace the lowest values were obtained with Duracid membrane. On the other hand, the results of polyphenols rejection in function of  $J_v$  for lees filters and olive pomace extracts are shown in Fig. 3.

For lees filters extracts, TFC-HR and TFCS membranes provided higher rejection values of 86% (average) in all tested flow rate range; for NF270 membrane rejection values were between  $58 \pm 4.7\%$  and  $75.8 \pm 0.9\%$  (1 and 10  $mL min^{-1}$ , respectively); for NF90 membrane between  $76.9 \pm 0.4\%$  and  $78.7 \pm 3.2\%$  (1 and 10  $mL min^{-1}$ , respectively); and for Duracid membrane between  $47.1 \pm 6.8\%$  and  $67.9 \pm 1.0\%$  (1 and 10  $mL min^{-1}$ , respectively) (see Fig. 3a). ANOVA results confirmed the significant difference between the studied NF membranes on the polyphenols recovery ( $p = 1.17 \times 10^{-9}$ ). When evaluating rejection results for each given polyphenolic family (see Fig. S3, supplementary material), TFC-HR and TFCS membranes, showed higher rejection values of 70% for the three studied families. NF270, NF90 and Duracid membranes provided HB rejection values of 65%, 53% and 50%, respectively; and HC and F rejection values were  $>70\%$ . Duracid membrane had the lowest rejection percentage for hydroxybenzoic acids, therefore was selected to separate polyphenols in an integrated membrane sequential design. Giacobbo et al. (2017a) obtained polyphenols rejection values higher than 92% for wine lees extracts by using the NF270 membrane. Also, Kontogiannopoulos et al. (2017) obtained polyphenol rejections of 95% and 98% for NF270 and NF90 membranes, respectively, in bench-scale filtration tests for wine lees extracts.

For olive pomace extracts, NF270 and TFCS membranes gave

rejection percentages between 86 and 90%; TFC-HR between 85 and 95%; NF90 between 91 and 95%; and Duracid between 88 and 94% over all the flow rates evaluated (see Fig. 3b). ANOVA results showed a significant difference between the tested NF membranes on the polyphenols recovery ( $p = 1.10 \times 10^{-3}$ ). When rejection results were focused on each phenolic family, HC and F rejections of 75% and 90% were obtained, respectively, for all the studied membranes (see Fig. S4, supplementary material). Otherwise, the HB rejections were 63% for NF270, 82% for TFC-HR, 73% for TFCS, 79% for NF90, and 75% for Duracid. The NF270 membrane, rejected less percentage of hydroxybenzoic acids, than the other membranes, therefore was selected for an integrated membrane sequential design for olive pomace extracts. In the literature, Ioannou-Ttofa et al. (2017) compared the performance of NF270 membranes in spiral-wound with flat-sheet modules, for olive mill wastewater, and found that the performance of the flat-sheet modules was significantly higher than spiral wound modules, with phenolic compounds removal up to 95%, which is consistent with the results presented in the present work. Also, Cassano et al. (2013), obtained 93% of polyphenols rejection with a NF90 membrane for olive mill wastewater, which is according with the results of this work.

### 3.1.4. Reverse osmosis process

Reverse osmosis process was evaluated with BW30LE, XLE and SW30HR membranes, for the concentration of polyphenols in lees filters and olive pomace extracts. For both extracts  $J_v$  values ranged from 5 to 10.5  $L m^{-2} h^{-1}$  for XLE and BW30LE membranes, while lower  $J_v$  values of 2  $L m^{-2} h^{-1}$  were obtained with SW30HR membrane at the same trans-membrane pressure. Similarly, Nunes et al. (2019) obtained  $J_v$  constant values ( $\approx 15 L m^{-2} h^{-1}$ ) at a higher trans-membrane pressure of 20 bar, for aqueous olive pomace extracts filtered with BW30LE membranes.

Rejection results with trans-membrane flux, for RO membranes (BW30LE, XLE and SW30HR), are shown in Fig. 4.

For lees filters extracts, rejection values were between 70 and 86% for BW30LE membrane; while for XLE and SW30HR membranes

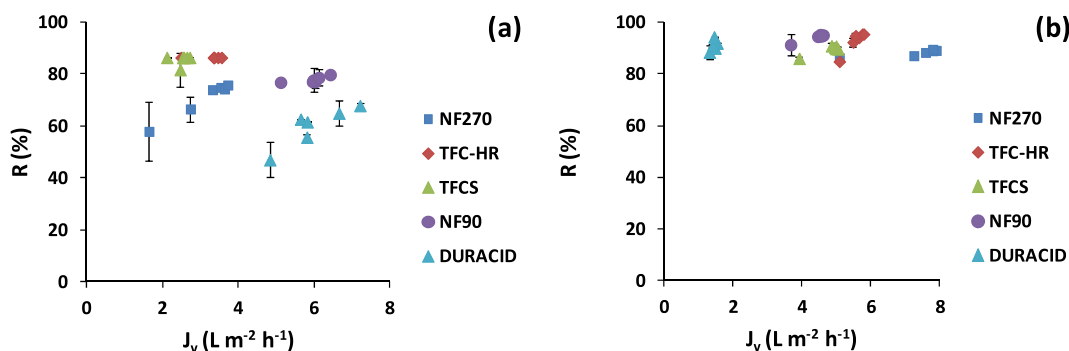


Fig. 3. Polyphenol rejection evolution with trans-membrane flux for NF membranes (NF270, TFC-HR, TFCS, NF90 and Duracid), in (a) lees filters and (b) olive pomace extracts.

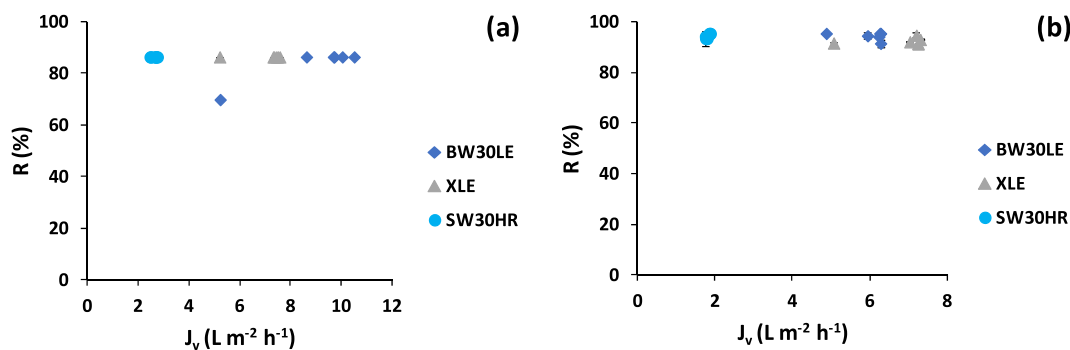


Fig. 4. Polyphenol rejection evolution with trans-membrane flux for RO membranes (BW30LE, XLE and SW30HR), in (a) lees filters and (b) olive pomace extracts.

rejection was an average of 86.4% (see Fig. 4a). ANOVA results confirmed that there was no significant difference between the tested RO membranes ( $p = 0.39$ ). Regarding phenolic families, rejection results were higher than 72% for the three cases (see Fig. S5, supplementary material). Thus, HB were rejected in 80%, HC in 73%, and F in 72%, for the three studied membranes.

For olive pomace extracts, rejection results were between 91% and 95% for the three RO membranes (see Fig. 4b). ANOVA results showed no significant difference between the tested RO membranes ( $p = 0.20$ ). Focusing on the behavior of each family, rejection values were higher than 74% (see Fig. S5, supplementary material). Therefore, HB were rejected in 84%, 74% and 83% for BW30LE, XLE and SW30HR membranes, respectively. The HC and F were rejected in 75% and 90%, respectively, for the three membranes. Likewise, Nunes et al. (2019) obtained rejection percentages of 100% for phenolic compounds and flavonoids from aqueous olive pomace extracts treated with BW30LE membranes. Also, Bottino et al. (2020) found that the SW30HR membrane showed high retention of phenolic compounds (>99.3%), from olive mill wastewater. In addition, the BW30LE membrane was found to be appropriate due to its low fouling index (< 20%), and its effectiveness for phenolic compounds concentration (100%) in olive pomace aqueous extracts (Nunes et al., 2019). Due to the aforementioned above and the obtained results in this work, the BW30LE membrane was selected for an integrated membrane sequential design for lees filters and olive pomace extracts.

The adsorption of phenolic compounds on a thin-film composite polyamide (PA) membranes used in NF and RO applications have been investigated in order to evaluate its relevance upon the solutes retention performance (Arsuaga et al., 2010). The hydrophobicity of polyphenols with molecular weight below the MWCO of the membrane was considered the most relevant parameter defining solutes retention. An increasing of membrane hydrophobicity balance led to an increase of the polyphenol sorption ratios and a consequently to a decrease of membrane retention. Indeed, the increase of the polyphenol sorption onto the PA membrane active layer facilitates their transport through the membrane and hence decreases the retention ratio.

### 3.2. Integrated membrane sequential designs for polyphenol separation and concentration in open-loop configuration

An integrated membrane sequential design, in a concentration mode, was performed for each matrix (lees filters and olive pomace extracts) at

the selected separation conditions resulted from the membrane processes separately (batch systems). Table 3 shows the operational conditions selected for each membrane type as well as the flow rate based on the maximum rejection results by polyphenols families.

#### 3.2.1. Integrated membrane sequential design for lees filters extracts

The integrated membrane sequential design for polyphenols recovery from lees filters extracts is shown in Fig. 5.

A first stage, UF, with a PES membrane of 30 kDa MWCO, was performed with an initial feed extract of 1000 mL at 10 mL min<sup>-1</sup> of feed flow rate. The initial composition of lees filters extract used in this membrane integration process was 6.8 mg L<sup>-1</sup> of HB, 4.5 mg L<sup>-1</sup> of HC, and 4.6 mg L<sup>-1</sup> of F. As a result, suspended solids and colloids were eliminated from the extract. Then, a second stage of NF (using Duracid membrane) was performed with the recovered UF permeate stream at 6 mL min<sup>-1</sup> of feed flow rate. As a result, the NF membrane concentrated the polyphenols families in the rejection stream with concentration factors of 1.2, 1.0 and 1.2 for HB, HC and F, respectively; and obtained a permeate stream with polyphenol concentrations below the limit of quantification (LOQ) of the method. Finally, two RO stages (BW30LE A and B) were performed at 5 mL min<sup>-1</sup> of feed flow rate for the UF rejection (BW30LE A) and the NF rejection streams (BW30LE B). As a result, the three polyphenols families were concentrated in the rejection streams, achieving two polyphenol extracts rich in hydroxybenzoic compounds (more than 8 mg L<sup>-1</sup>). Also, three permeate streams were obtained with polyphenols concentrations below the LOQ of the HPLC-UV. Additionally, the RO concentration factors obtained with BW30LE A were 1.1, 1.0 and 1.0 for HB, HC and F, respectively; and for BW30LE B were 1.3, 1.6 and 1.4 for HB, HC and F, respectively. Díaz-Reinoso et al. (2017) combined a sequence treatment of centrifugation, MF, NF and UF stages, for wine vinasses effluent, which allowed the recovery of a phenolic-enriched product with 45% gallic acid equivalents, and an effluent with reduced pollutant load. Also, Giacobbo et al. (2017a) employed a sequential membrane process with a wine lees MF permeate and a set of UF (ETNA01PP and ETNA10PP membranes) and NF (NF270 membrane) stages. As a result, the UF membranes separated the polyphenols from the polysaccharides in the permeate, and the NF membrane rejected the 100% of anthocyanins (flavonoids) and more than 90% of total polyphenols.

#### 3.2.2. Integrated membrane sequential design for olive pomace extracts

The integrated membrane sequential design for polyphenols

Table 3

Selected conditions for an integrated membrane sequential design for lees filters and olive pomace extracts.

Extract	UF		NF		RO	
	Membrane	Feed flow (mL min <sup>-1</sup> )	Membrane	Feed flow (mL min <sup>-1</sup> )	Membrane	Feed flow (mL min <sup>-1</sup> )
Lees filters	30 kDa	10	Duracid	6	BW30LE	5
Olive pomace	30 kDa	7	NF270	5	BW30LE	5



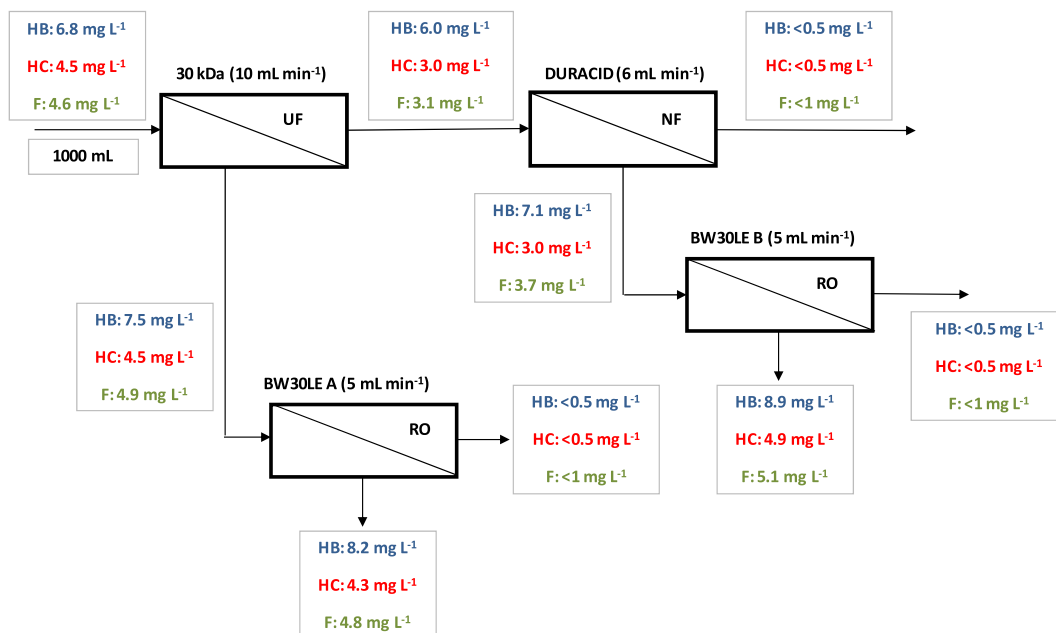


Fig. 5. Integrated membrane sequential design for polyphenols recovery from lees filters extract.

recovery from olive pomace extract is shown in Fig. 6.

First, 1000 mL of olive pomace extract (composed by 23.1 mg L<sup>-1</sup> of HB, 8.2 mg L<sup>-1</sup> of HC, and 37.1 mg L<sup>-1</sup> of F) was driven toward an UF membrane (30 kDa) at 7 mL min<sup>-1</sup> of feed flow rate. Then, the two resulting UF streams (permeate and retentate) were driven toward NF membranes (NF270 A and B, respectively) at 5 mL min<sup>-1</sup>. Finally, the resulting NF streams were driven toward RO membranes (BW30LE A, B and C) at 5 mL min<sup>-1</sup>. As a result, the UF membrane removed suspended solids and colloids from the extract. The NF processes (with NF270 A and NF270 B membranes), concentrated high values of hydroxybenzoic acids (31.8 and 24.3 mg L<sup>-1</sup>, respectively), hydroxycinnamic acids (8.1 and 9.3 mg L<sup>-1</sup>, respectively), and flavonoids (23.9 and 47.5 mg L<sup>-1</sup>, respectively) in the rejection streams. Finally, the RO membranes

concentrated the polyphenol families in the rejection streams. While the permeates from RO membranes had polyphenols concentrations below the LOQ of the HPLC-UV method, except for BW30LE B, with low concentrations of hydroxybenzoic (5.8 mg L<sup>-1</sup>) and hydroxycinnamic (2.5 mg L<sup>-1</sup>) acids. BW30LE membranes were able to obtain permeates of clean water that can be reused in the winery and olive oil production processes.

Therefore, from a UF retentate stream, it was possible to obtain a polyphenol extract, rich in flavonoids compounds (48 mg L<sup>-1</sup>) after a NF step process. On the other hand, from a UF permeate stream, a polyphenol extract, rich in hydroxybenzoic compounds (39 mg L<sup>-1</sup>), was also generated after a NF and RO process. Cassano et al. (2013) integrated a membrane separation system for polyphenols recovery from

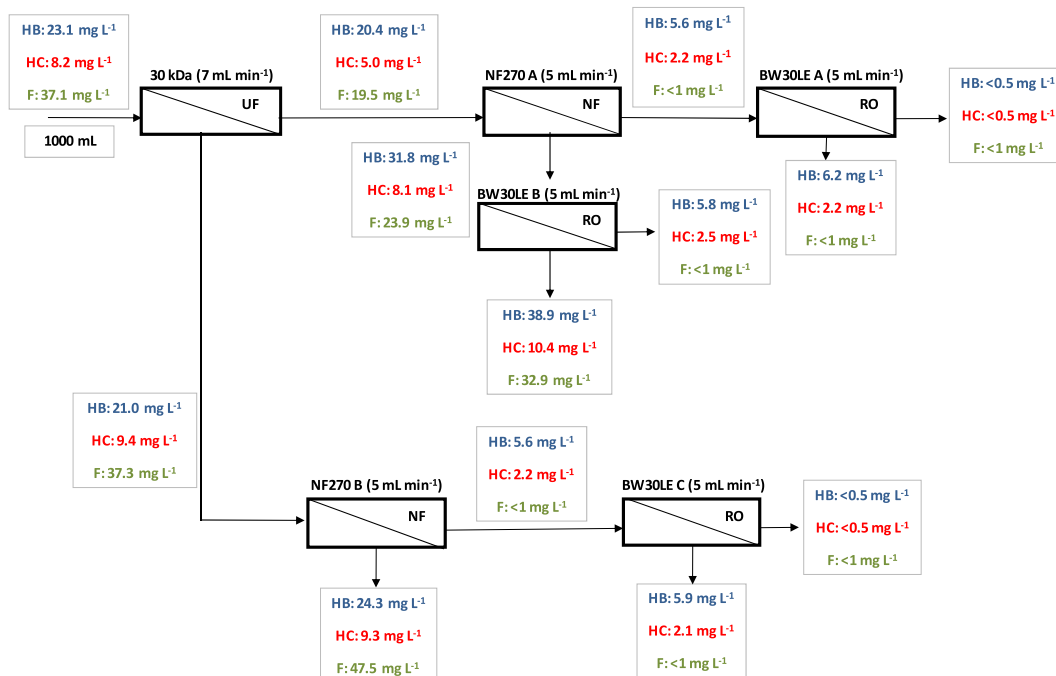


Fig. 6. Integrated membrane sequential design for polyphenols recovery from olive pomace extract.

olive mill wastewaters, using two UF (HFS and Etna 01 PP membranes) processes followed by a final NF (NF90 membrane) step; as a result, the UF membranes recovered the polyphenols in the permeate stream; while the NF membrane concentrated the low molecular weight polyphenols ( $85 \text{ mg L}^{-1}$ ) in the retentate stream. Nunes et al. (2019) obtained olive pomace aqueous extracts with TPC and total flavonoids of  $110 \text{ mg GAE L}^{-1}$  and  $50 \text{ mg of epicatechin equivalents (EE) L}^{-1}$ , respectively; which after their treatment by NF (NF90 and NF270 membranes) and RO (BW30 membrane), concentrated the TPC and flavonoid content in the rejection stream of BW30 membrane (100% of rejection), which was around 15% higher than those achieved with NF270 and NF90 membranes.

From the obtained results, some recommendations could be pointed out for the validation and implementation of the processing stages at full-scale. Results generated along the current experimental study indicates that the processing train evaluated, needs to include a pre-treatment stage, in which MF and UF are critical to assure the operation and performance of the final stages of polyphenol pre-separation by using NF or RO. In the filtration stages, it has been observed that filtration cycles with UF and MF generated a cake layer on the membrane surface that could contain up to 30–40% of the total content of polyphenols. The streams generated during the physical cleaning stages as back wash, forward wash or air scoring should be recirculated to the polyphenol extraction stage using water as solvent. Recently, the “force field-assisted methods” (including electrical, magnetic and/or sonic fields) have been postulated as alternative solutions to modify the filtration performance and prevent fouling (Aktij et al., 2020; Sun et al., 2020; Du et al., 2021). However, the state of development is still far from industrial applications.

Selection of the final post-treatment stages with NF and RO will depend on the selected applications and the target objective of the groups of polyphenols to be recovered. In the case of the olive oil wastes, one of the main interests is centered on the streams containing 3-hydroxytyrosol. Phenolic compounds are rejected based on more than one mechanism. The MWCO of the membrane and the fact that hydrophobic compounds, generally include aromatic ring structures that have aliphatic carbon groups, are important parameters for the performance of NF and RO tests. For that, if the working pH is lower than their acidity constants (e.g., pKa) phenolic compounds can be readily adsorbed in the hydrophobic active layer of these evaluated membranes. The performance of organic polymeric membranes in the separation, purification and concentration of polyphenols from their original sources is strongly related to the nature of the interactions of the solutes (e.g., phenolic molecules) and the polyamide active layer. Indeed, hydrophobic, and electrostatic interactions, adsorption phenomena, steric hindrance as well as solution effects on the membrane, solute/membrane properties and operating conditions play a key role on the recovery efficiency and/or permeation of phenolic compounds through the membrane active layer. A way to improve the selectivity factors could be the use of molecularly imprinted membranes, that combine the advantages of molecularly imprinted polymers and membranes, that are capable to distinguish between the targeted molecules and their structural analogs, thus improving the process of separation. As a relevant example, it could be mentioned the work done by Mansour et al. (2018) using a hybrid molecularly imprinted membrane combining both molecularly imprinting technology and membrane technology, for the recovery of polyphenols from lemon, orange, and onion peel extracts.

#### 4. Conclusions

Pressure driven membrane-based technologies have shown a robust approach to promote recovery schemes of added value by-products from two big families of agro-food industries (e.g., olive oil and winery wastes) in the southern European Countries (e.g., Portugal, Spain, France, Italy, and Greece). The factor moving changes from solving an environmental problem is the introduction of the concept of the bio-

based economy, fixing the interest for natural compounds with biological activities. Solutions to convert such natural compounds is totally linked to the recovery, separation and fractionation of phenolic compounds from these by-products. Results of this study demonstrated the suitability of pressure driven technologies to achieve the objectives. Purification of polyphenols by membrane-based technologies, in aqueous extracts generated by mechanical stirring as a cost-effective technique where water is used as a solvent from winery and olive oil wastes has been demonstrated effective. The recovery of polyphenols by integration of a membrane clean-up/clarification stage by using MF/UF and a membrane-based separation and/or concentration processes based on NF and RO was successfully explored with winery and olive mill industrial residues (specifically lees filters and olive pomace extracts) in closed and open-loop configurations. From batch systems, MF ( $0.45$  and  $0.22 \mu\text{m}$ ) and UF ( $50$  and  $30 \text{ kDa}$  of MWCO) membranes were suitable to remove impurities and suspended solids from samples. Results have demonstrated that the rejection of phenolic compounds usually increases by increasing the transmembrane pressure. This phenomenon is associated to the so-called film layer formation theory assuming the growth of a thin layer of a specific thickness in the zone adjacent to the membrane surface, where the concentration decreases from the surface to the bulk. At higher transmembrane values the concentration polarization and fouling phenomena are more severe, leading to the formation of an additional layer on the membrane surface increasing the retention coefficient. Results have shown that this layer is associated to the complete separation of fats and large amino acids and proteins, promoting the undesired adsorption of a portion of the polyphenols expected to be permeated. For an industrial scale-up, the cake layers formed along the clarification stages could be recovered by a membrane cleaning method (e.g., back-flush, forward-flush and air-scouring) and recirculated to the extraction stage to recover the adsorbed polyphenols.

Concerning NF process, Duracid and NF270 membranes were more selective for polyphenol separation in lees filters and olive pomace extracts, because of their low rejection of hydroxybenzoic acids (rejections of 50 and 63%, respectively). NF membranes shown the possibility of introducing separation factors between families of polyphenols that need to be extended to a second stage where individual compounds in each family is under quantification in on-going studies using HPLC coupled MS. Identification and quantification of the concentrations in feed, retentate and permeate streams will be used to determine the selectivity and separation factors of the NF membranes evaluated. Such membrane data characterization has not been reported in the literature and it is clearly a need for future research and development.

RO membranes (BW30LE, XLE and SW30HR) concentrate polyphenols with rejection percentages of 86% and 95% for lees filters and olive pomace extracts, respectively. From dynamic systems, it can be concluded that the most selective membrane train for polyphenol separation and concentration for lees filters extracts was:  $30 \text{ kDa}$  (UF), Duracid (NF) and BW30LE (RO), and for olive pomace extracts was almost the same membrane train but changing the type of NF membrane by NF270. Therefore, integrated membrane sequential designs for lees filters and olive pomace extracts, were able to separate and concentrate polyphenols, and could be implemented in industries to obtain polyphenol rich streams and clean water for reuse purposes.

Agri-food wastes as olive oil and winery processing residues, considered traditionally highly polluting wastes because of their high organic load and phytotoxic and antibacterial phenolic substances resistant to biological degradation are a suitable source to produce new products. Results as the generated in this study suggests that these waste streams should be regarded as a valuable resource for the recovery of fine chemicals and for different biotechnological applications, such as the production of important metabolites. Thus, agro-industrial by-products can be considered a promising alternative to chemically synthesized antioxidants used in food, cosmetics, and pharmacy, since they are an inexpensive source of valuable compounds, mainly polyphenols

to take profit on their antioxidant properties.

The membrane processing results strength the polyphenols recovery route where the use of a cheap and green extraction procedure for the recovery of polyphenols, combining water as the solvent with the mechanical stirring is valuable. The compatibility of water-based extracts with most of the MF, UF, NF and RO are highlighted. Products obtained in this way will be fully compatible with applications to animal feed, functional foods, dietary supplements or cosmetics, thanks to their polyphenolic content and antioxidant activity. If their use is linked to the need of specific claims on specific polyphenol molecules, the success of these new application will be based on the identification of separation routes using extraction chromatographic techniques. In this direction, cosmetic and pharmaceutical applications related to the need of using claims could be found. However, when the objective is the use of the extracts on products commercialized by both sectors (e.g., winery and olive oil) the blending of the rich extracts could not be linked to so strict needs on purity and the regulations to be follow are not so limiting.

### Credit author statement

**Tapia-Quirós:** Formal analysis, Investigation, Methodology, Writing Original Draft. **Montenegro-Landívar:** Investigation, Methodology. **Reig:** Conceptualization, Formal analysis, Validation, Writing–Review & Editing. **Vecino:** Conceptualization, Formal analysis, Validation, Writing–Review & Editing. **Saurina:** Investigation, Supervision. **Granados:** Investigation, Supervision. **Cortina:** Conceptualization, Investigation, Resources, Funding acquisition, Project administration, Supervision, Writing– Review & Editing.

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### 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.

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### Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jenvman.2022.114555>.

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