



Review

Phenolic compounds recovered from agro-food by-products using membrane technologies: An overview



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ABSTRACT

Typically, the various agro-food by-products of the food industry are treated by standard membrane processes, such as microfiltration, ultrafiltration and nanofiltration, in order to prepare them for final disposal. Recently, however, new membrane technologies have been developed. The recovery, separation and fractionation of high-added-value compounds, such as phenolic compounds from food processing waste, are major current research challenges.

The goal of this paper is to provide a critical review of the main agro-food by-products treated by membrane technologies for the recovery of nutraceuticals. State-of-the-art of developments in the field are described. Particular attention is paid to experimental results reported for the recovery of polyphenols and their derivatives of different molecular weight. The literature data are analyzed and discussed in relation to separation processes, molecule properties, membrane characteristics and other interesting phenomena that occur during their recovery.

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1. Introduction

Nowadays, the final disposal of agro-food by-products has become a major challenge for food processing industries due its potential impact on the environment. Several methods have been used to deal with this problem, such as decantation separation,

dissolved air flotation, de-emulsification, coagulation and flocculation, all of which aim to reduce the organic load from aqueous waste (Cheryan & Rajagopalan, 1998). More recently, pressure-driven membrane processes, such as micro- (MF), ultra- (UF) and nano- (NF) filtration, have been applied to the treatment of agro-food wastewaters. Pressure-driven membrane processes have several benefits: low energy requirements, high separation efficiency, easy scale-up, simple operation, high productivity in terms of permeate fluxes, and the absence of phase transition. Collectively, these advantages facilitate the recovery of

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Nomenclature

MF	microfiltration	OMWs	olive mill wastewaters
UF	ultrafiltration	NWs	nixtamalization wastewaters
NF	nanofiltration	AWs	artichoke wastewaters
TMP	transmembrane pressure	OPL	orange press liquor
NMWCO	nominal molecular weight cut-off	TOC	total organic carbon
MWCO	molecular weight cut-off	RO	reverse osmosis
MW	molecular weight	OD	osmotic distillation
COD	chemical oxygen demand		

high-added-value components (Cassano, Conidi, & Drioli, 2011). For this reason, these processes have been applied on various scales, ranging from macroscopic pre-treatment (MF) to the use of isolation and purification techniques (i.e. UF, NF) (Galanakis, 2012, 2015). Different types of high-added-value components have been recovered from agro-food by-products, such as antioxidant components, carbohydrates, sugars, pectins, proteins and phenolic compounds (Castro-Muñoz, Orozco-Álvarez, & Yáñez-Fernández, 2015a; Galanakis, 2015). In the case of phenolic compounds in particular, there is great interest in identifying new sources and tangible methods for extracting them from such sources. However methods, such as hot-water extraction, solvent extraction, irradiation-assisted extraction, adsorption, ultrasound-assisted extraction, enzyme-assisted extraction and supercritical fluid extraction, have not produced sufficiently positive results. The degradation of phenolic compounds usually occurs due to their low stability at high temperatures, long extraction times and the need for solvents (Conidi, Cassano, & Garcia-Castello, 2014b). Polyphenols are of particular interest for the food and pharmaceutical industries due to their benefits to human health. With their antioxidant activity, they can offer protection against the development of cancers, cardiovascular diseases, diabetes, osteoporosis and neurodegenerative conditions (Pandey & Rizvi, 2009). As the secondary metabolites of plants, these compounds are widely

found in vegetables (artichoke, olive, maize, etc.), fruits (grapes, apple, pear, cherries, berries, etc.), beverages, cereals and other foodstuffs. However, there is strong evidence that such compounds can also be present in some agro-food by-products, such as artichokes (Conidi et al., 2014b), nixtamalization (Castro-Muñoz & Yáñez-Fernández, 2015), olive mill wastewaters (Cassano et al., 2011, 2013) and orange press liquor (Conidi, Cassano, & Drioli, 2012), to mention just a few. These by-products could be a new source for the recovery of polyphenols leached from both industrially-processed natural products and their wastes.

The aim of this paper is to provide an overview of the phenolic compounds that have been recovered from agro-food by-products by using conventional membrane processes. The most relevant results from recently published studies are analyzed and discussed.

2. Principles of conventional membrane processes

Conventional membrane processes, such as MF, UF and NF, use transmembrane pressure (TMP) as the driving force. As shown in Fig. 1, these pressure-driven membrane processes can separate a bulk solution (feed) into two new streams using a barrier (membrane).

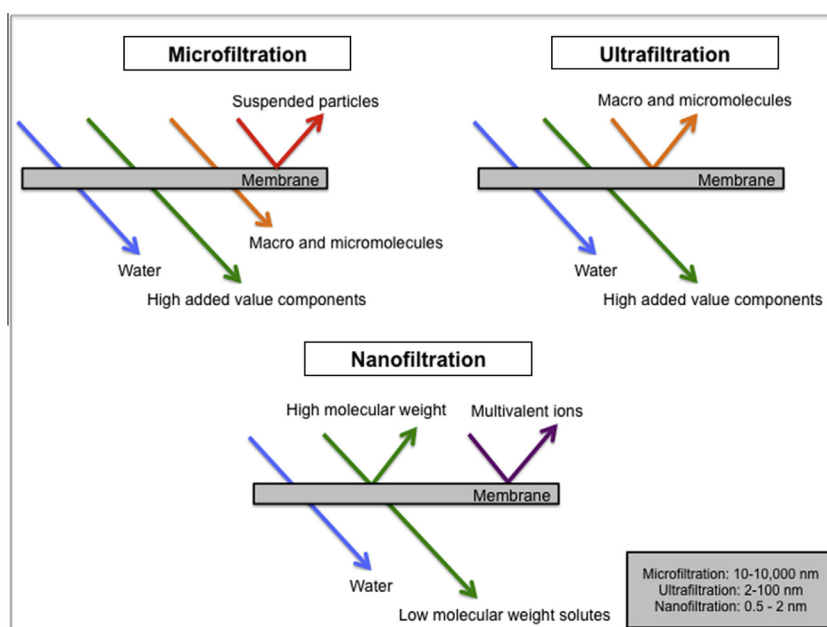


Fig. 1. Scheme for MF, UF and NF technologies.

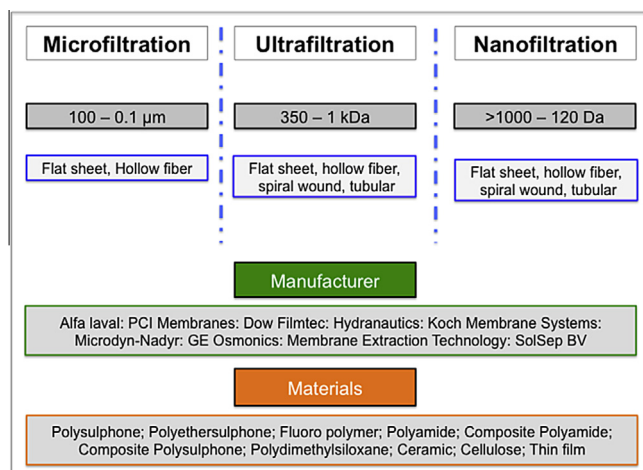


Fig. 2. Classification of conventional membranes according to their MWCO.

The two valuable streams obtained from membrane processing are the permeate and retentate streams. The permeate stream consists of the solvent that passes through the membrane with rich solutes under the nominal molecular weight cut-off (NMWCO) of the membrane. The retentate stream contains particles and dissolved compounds partially retained by the membrane barrier (Van der Bruggen, Lejon, & Vandecasteele, 2003b; Van der Bruggen, Vandecasteele, Van Gestel, Doyen, & Leysen, 2003a). The separation efficiency of these membrane methodologies depends on a number of factors: the physico-chemical composition of the bulk solution (type, weight, polarity, solute charge); the operating parameters (feed flow rate, TMP, temperature, permeate flux); and, certain membrane characteristics (membrane material, configuration of membrane separation module, pore size) (Santos, Mateus, & Cabral, 1991; Van der Bruggen, Schaep, Wilms, & Vandecasteele, 1999). As the characteristic that distinguishes the MF, UF and NF processes, pore size plays a particularly key role in the separation process. Fig. 2 displays the commercial membranes that can be found for conventional membrane technologies according to their pore size. In addition, the most common manufacturers are shown, together with the typical configurations of their membranes and the materials used for making them.

In principle, membrane-based separation methods are able to separate components through a sieving process that is based on their molecular weight. Nevertheless, the MWCO of the membranes is not the absolute barrier to solute recovery. The asymmetric characteristics of the membrane pores do not always reflect a narrow MWCO range (Galanakis, 2015). Moreover, other phenomena such as concentration polarization and membrane fouling, may also contribute to solute retention (Cassano, Donato, & Drioli, 2007b; Cassano, Marchio, & Drioli, 2007a). So too can Coulombic and hydrophobic interactions between the solutes and membrane surface (Crespo & Brazinha, 2010). In the following sections, cases of the treatment of agro-food by-products and of the recovery of polyphenols by conventional membrane processes are analyzed and discussed in detail.

3. Membrane technology: A tool for the treatment of agro-food by-products

In recent decades, pressure-driven membrane processes have been used for the treatment of waste streams, enabling the concentrate to be treated or discharged and, thereby, reducing the contaminants directly or indirectly discharged into wastewater (Van der Bruggen et al., 2003b). The agro-food by-product that

has been most treated by membrane processes is olive mill wastewater (OMW). This extract presents a huge challenge to the olive processing industry due to its high content of chemical oxygen demand (COD). Karakulski, Kozłowski, and Morawski (1995) proposed the use of UF technology to reduce the COD in OMW in order to obtain a clear permeate stream suitable for direct sewer discharge. Using three different membrane materials, they showed that it was possible to reduce the initial COD content by 72.5–89.8%. Such a reduction resulted in clear permeate with a COD content of 35–96 mg O₂ dm⁻³, which is suitable for direct sewage discharge. Some years later, Akdemir and Ozer (2008) evaluated COD removal and permeate fluxes in OMW as a function of various operating parameters such as TMP, feed flow rate and operating time. They used a statistical approach (Box-Wilson design), obtaining a maximum COD removal of 89.5%. Using UF technology under optimal conditions (Akdemir & Ozer, 2009), the removal of organic load in terms of total organic carbon (TOC) can reach at least 85% but COD removal efficiency might be further improved by using other type of agents; for example, surfactants. Using this approach, El-Abbassi, Khayet, and Hafidi (2011) were able to remove over 95% COD.

Nevertheless, UF processes are not the only ones used to reduce the TOC content of various wastes. Castro-Muñoz, Orozco-Álvarez, Cerón-Montes, and Yáñez-Fernández (2015b) used an MF process for the treatment of nixtamalization wastewaters (NWs) in order to reduce their pollutant load. While almost 10% of the initial TOC content was retained, high turbidity rejection (>70%) and total solids content (>25%) were achieved. If industries were only focused on reducing the pollution of their aqueous waste, MF and UF technologies would be most suitable. However, removal efficiency and productivity must also be considered as a function of the type of by-product treated. Recently developed approaches for the treatment of food processing wastes have focused on the separation of functional macro and micromolecules in order to derive extra value. The emergence of membrane technologies as a tool for feedstock production seems to be the most feasible way of deriving such value (Galanakis, 2012, 2013).

4. Membrane processes: An approach to recovering phenolic components from agro-food by-products

Nowadays, pressure-driven membrane applications are not only focused on pollution removal, but also on the recovery of high-added-value components from agro-food by-products. In terms of the latter, polyphenol recovery from OMWs has been the most studied (Mudimu, Peters, Brauner, & Braun, 2012; Rahmanian, Jafari, & Galanakis, 2014). Russo (2007) reported a membrane process for the selective fractionation and recovery of polyphenols from raw OMW extracts. The processing of these extracts using MF and UF operations resulted in permeates with different polyphenol fractions: hydroxytyrosol (134,879–266,679 ppm), tyrosol (7968–11,218 ppm), oleuropein (7765–26,698 ppm), caffeic acid (10,570–21,982 ppm) and protocatechuic acid (8871–22,601 ppm). While this clearly shows that olive by-products are an important source of nutraceutical components, the suggested process was not efficient enough to reject the components due to their molecular weights, which were between 138 and 540 Da (Bendini et al., 2007; Drynan, Clifford, Obuchowicz, & Kuhnert, 2009). As the final processing step, the authors proposed NF and Reverse Osmosis (RO) for the fractionation and concentration of the permeate stream, developing an NF membrane system for fractionation of the extract. A considerable increase in phenol content was achieved using these NF membranes; various fractions with a high polyphenol content (1369–9962 mg L⁻¹) were obtained from a feed solution with a low polyphenol content of about 725 mg L⁻¹.

It is important to note that a UF pretreatment step was necessary prior to NF processing (Paraskeva, Papadakis, Tsarouchi, Kanellopoulou, & Koutsoukos, 2007).

Later, Galanakis, Tornberg, and Gekas (2010) evaluated four different UF membranes for the clarification of OMWs, showing that the membrane most suitable for the removal of the heavier fractions of hydroxycinnamic acids and flavonols was the 25 kDa membrane. Using this membrane, almost all of the initial polyphenols were recovered in the permeate stream (retention coefficient 10%). The same study reported high total polyphenol retention (70% retention, including 99% recovery of the initial hydroxycinnamic acids and flavonols) using an NF membrane of 120 Da. In respect to high flavonol retention, this group of micromolecules is formed by monomers such as procyanidin, quercetin and kaempferol, all of which have hydroxyl groups (OH) that provide negative polarity to the micromolecules. This characteristic, a well-known phenomenon termed 'polarity resistance', enables the attraction of water molecules and the restriction of membrane permeation (Galanakis, 2015). Cassano et al. (2011) also evaluated various UF membranes for the recovery of these valuable compounds. They used MF pretreatment to remove suspended solids that cause fouling phenomena and to enhance UF processing performance. All of the reported membranes showed low rejection of total polyphenols, meaning that the polyphenols were collected in the permeate fraction. Within these nutraceuticals, hydroxytyrosol, protocatechuic acid, caffeic acid, tyrosol and p-cumaric acid were found. Tyrosol was the major component in the OMW extracts, accounting for 53.5–68.2%. In addition, the permeates showed high antioxidant activity ranging from 3.1 up to 7.7 mM Trolox, which is not surprising because these low molecular polyphenols regularly show high antioxidant activity and other health benefits (Tuck & Hayball, 2002).

In Italy, a recognized research group has started to develop an integrated membrane process for the fractionation of agro-food by-products. An integrated membrane process involves the use of multiple membrane operations in sequence, the main aim of the approach being to reduce the occurrence of fouling phenomena in the subsequent membrane steps by prepending high pore size membranes. To test this approach, OMWs were processed by a sequence of two UF operations followed by a final NF step (Cassano, Conidi, Giorno, & Drioli, 2013). The authors were able to fractionate the extract in 3 valuable streams: (i) a concentrated fraction with a high content of organic substances (UF retentate) suitable for biogas production using an anaerobic catalytic process; (ii) a concentrated stream rich in phenolic substances (ca. 960 mg L⁻¹; NF retentate) suitable for food, cosmetic and pharmaceutical applications due to the main polyphenols identified being hydroxytyrosol, tyrosol, caffeic acid, p-cumaric acid, catechol and protocatechuic acid; (iii) water with a low TOC content (95 mg L⁻¹; NF permeate) that can be reused in different ways within the olive oil extraction process. While the complete recovery of these phenolic micromolecules depends on the narrow pore size of the membrane used, the nature of the molecules also plays an important role. Polyphenols present aromatic rings and aliphatic chains that produce a hydrophobic profile which reduces the permeation performance of the membranes (Galanakis, 2015). The last proposal Garcia-Castello, Cassano, Criscuoli, Conidi, and Drioli (2010) has real potential for treating OMWs in a way that not only reduces the organic load, but also recovers valuable components. They conducted a similar study, but obtained different results. In their study, almost all of the initial polyphenols were recovered (319 mg L⁻¹) in permeate from the NF step (the extract was microfiltered in order to reduce the suspended solids). Although the NF membrane rejected about 5% of the initial polyphenols, specific components, including hydroxytyrosol, tyrosol, caffeic acid, p-cumaric acid, protocatechuic acid and oleuropein, were found

in the fraction. Additionally, large quantities of some other low molecular polyphenols were recovered. When valuable components are diluted in large volumes of solvent, other membrane technologies can be applied, such as osmotic distillation. (OD). Using OD, Garcia-Castello et al. (2010) achieved a polyphenol concentration of 985 ppm. In addition, reverse osmosis (RO) has also been used to concentrate total phenolic components, such as 3,4-dihydroxyphenylethanol (3,4-DHPEA), p-hydroxyphenylethanol (p-HPEA), oleuropein-aglycone dialdehyde (3,4-DHPEA-EDA) and verbascoside, as well as some volatile components (aldehydes, alcohols and esters). However, in this scenario, MF and UF technologies are needed to remove other undesirable components from OMWs (Servili et al., 2011a). Conversely, when the concentration of phenolics is not required, the diluted components can be used for the production of other valuable components; for example, Conidi, Mazzei, Cassano, and Giorno (2014a) catalyzed oleuropein (544 mg L⁻¹) obtained from MF and UF operations to produce phytotherapeutics.

While the most widely studied agro-food by-product is OMW, other by-products have been investigated. For example, phenolic substances were extracted from grape seeds using ethanol-water extraction (Nawaz, Shi, Mittal, & Kakuda, 2006). An ethanol solution rich in total polyphenols was processed by UF prior to valuable compounds being concentrated and recovered in the retentate stream. Nawaz et al. suggested that the solubility of bioactive compounds is enhanced in ethanol (organic solvent) mixed with water rather than in just pure water. Furthermore, they corroborated that UF membranes can reject solutes with a MW of around 1000 Da. This supports Galanakis's (2015) idea that it is the asymmetry of the membrane's pores that enable it to reject components under this MW. Moreover, hydrophobic membranes interact when processing aqueous and hydroalcoholic streams containing phenolic compounds that exhibit hydrophilic behavior (Crespo, 2010).

The winemaking industry produces large amounts of various by-products, such as grape seeds, fermented grape pomaces, lees and liquors. Díaz-Reinoso, Moure, Domínguez, and Parajó (2009) worked on the development of a membrane system to recover the antioxidants (phenols) from liquors. They used UF and NF membranes with narrow pores size to concentrate the phenolic fractions, recovering fractions with phenol concentrations of 0.615 to 1.09 mg L⁻¹ from an initial concentration of 0.173 mg L⁻¹. Thus, using such technologies, the extract can be concentrated three- to sixfold. At the same time, the streams showed high antioxidant activity (18–22.5 from 0.27 mmol Trolox). The same authors also reported that such retentates can be processed by polymeric resins in order to slightly increase the phenolic concentration and antioxidant activity (Díaz-Reinoso, González-López, Moure, Domínguez, & Parajó, 2010), both of which are directly associated with the phenolic solutes (Crespo, 2010). Another by-product of the winemaking industry is winery sludge, which is generated during wine decanting. Using UF, Galanakis, Markouli, and Gekas (2013) were able to separate polyphenols from pectins containing waste. Up to 99% retention of the phenols was achieved for the most polar phenolics, such as o-diphenols and hydroxycinnamic acids. These interesting results show that the polarity of the solutes is fundamental to their separation; namely, o-diphenols are more polar (negative) molecules than the other polyphenols due to the presence of more hydroxyl groups (Galanakis, 2015).

Various phenolic compounds have also been recovered from several types of food waste. Using nanofiltration, Aguiar Prudencio et al. (2012) recovered chlorogenic acid (101 µg mL⁻¹), epigallocatechin gallate (882 µg mL⁻¹) and gallic acid (15.7 µg mL⁻¹) from extracts of bark of the mate tree. According to Scalbert and Williamson (2000), phenolic acids, flavonols, catechins, isoflavones, flavanones and anthocyanin are all classified as

Table 1

Main phenolic compounds recovered from agro-food by-products using conventional membrane processes.

Recovered component	Recovery rate	Agro-food by-product	Membrane operation	MWCO/Material/Configuration	References
Total polyphenols	58.30%	Orange press liquor	UF	100 kDa/Polysulphone/Hollow fiber	Ruby-Figueroa, Cassano, and Drioli, (2011) and Ruby-Figueroa, Cassano, and Drioli, (2012) Castro-Muñoz and Yáñez-Fernández (2015)
	45.70%	Nixtamalization wastewaters	Integrated membrane process: MF	0.2 µm/Polysulfone/Hollow fiber	
			UF	100 kDa/Polysulfone/Hollow fiber	
			UF	1 kDa/Polysulfone/Hollow fiber	
	95.00%	Olive mill wastewaters	NF	200 Da/Polymeric/Spiral wound	Paraskeva et al. (2007)
	11.40%	Grape seeds	UF	0.22 µm/Cellulose acetate/Flat sheet	Nawaz et al. (2006)
	>70%	Fermented grape pomace	UF	1000 Da/Thin-film/Spiral wound	Díaz-Reinoso et al. (2009) and Díaz-Reinoso et al. (2010)
	>80%		UF	1000 Da/Ceramic (titania)/Tubular	
	>30%		NF	250 Da/Polyamide-polysulfone/Spiral wound	
	>60%		NF	350 Da/Polyamide-polysulfone/Spiral wound	
	>80%		NF	150–300 Da/Thin-film/Spiral wound	
Hydroxytyrosol, protocatechuic acid, caffeic acid, tyrosol and p-cumaric acid	–	Olive mill wastewaters	MF	0.2 µm/Polypropylene/Tubular	Cassano et al. (2011)
	48.30%		UF	4 kDa/polyethersulphone/Flat sheet	
	21.30%		UF	5 kDa/Regenerated cellulose/Flat sheet	
	8.70%		UF	10 kDa/Regenerated cellulose/Flat sheet	
	33.50%		UF	10 kDa/Polyethersulphone/Flat sheet	
Hydroxycinnamic acids, o-diphenols	81%	Winery sludge from red grapes	UF	100 kDa/Polysulfone/Flat sheet	Galanakis et al. (2013)
	77%		UF	20 kDa/Polysulfone/Flat sheet	
	56%		UF	1 kDa/Composite fluoropolymer/Flat sheet	
3,4-DHPEA, p-HPEA, 3,4-DHPEA-EDA, verbascoside, and total phenols	–	Olive mill wastewater	Integrated membrane process: MF	0.3 µm/Polypropylene/Tubular	Servili et al. (2011a, 2011b)
			UF	7 kDa/Polyamide-polysulfone/Spiral wound	
p-Cumaric	13.3%	Olive mill wastewaters	Integrated membrane process: MF	0.2 µm/Polyvinylidene fluoride/Flat sheet	Conidi et al. (2014a)
			UF	30 kDa/Polysulphone/Hollow fiber	
Chlorogenic acid, Cynarin, Apigenin-7-O-glucoside	100%	Artichoke wastewaters	Integrated membrane process: UF	50 kDa/Polysulfone/Hollow fiber	Conidi et al. (2014b)
			NF	400 Da/Polyethersulfone/Spiral wound	
			NF	150–300 Da/Polyamide/Spiral wound	
	>85%	Artichoke wastewaters	NF	400 Da/Polyethersulphone/Spiral wound	Cassano et al. (2015)
Gallic acid, chlorogenic acid and epigallocatechin gallate	100%	Residues from mate tree	NF	150–300 Da/Thin-film/Spiral wound	Aguiar Prudencio et al. (2012)

(continued on next page)

Table 1 (continued)

Recovered component	Recovery rate	Agro-food by-product	Membrane operation	MWCO/Material/Configuration	References
Free low MW polyphenols, hydroxytyrosol, procatechuic acid, tyrosol, oleuropein, tyrosol and caffeic acid,	>45%	Olive mill wastewaters	UF	1 kDa/Polyethersulphone/Spiral wound	Russo (2007)
Proanthocyanidins	>20%	Defatted milled grape seeds	UF	200 kDa/Polyvinylidene fluoride/Tubular	Santamaría et al. (2002)
Hydroxytyrosol, procatechin acid, catechol, tyrosol, caffeic acid, p-cumaric acid and rutin.	100%	Olive mill wastewaters	Integrated membrane process: UF	0.02 µm/ Polyvinylidene fluoride/ Hollow fiber	Cassano et al. (2013)
			UF	1 kDa/Composite fluoropolymer/Flat sheet	
			NF	Salt rejection > 97%/Thin-film/Spiral wound	
Isoflavones (aglycone and glucoside)	>30%	Soy processing waste	UF	1 kDa/Regenerated cellulose/Spiral wound	Xu et al. (2004)
Hydroxytyrosol, procatechin acid, tyrosol, caffeic acid, p-cumaric acid, oleuropein and some other low MW polyphenols.	78%	Olive mill wastewaters	Integrated membrane process: UF NF	200 nm/Al ₂ O ₃ /Tubular 578 Da/ Polyethersulphone/Spiral wound	García-Castello et al. (2010)
Hydroxycinnamic acids and flavonols.	13%	Olive mill wastewaters	UF	100 kDa/Polysulfone/Spiral wound	Galanakis et al. (2010)
	40%		UF	25 kDa/Polysulfone/Spiral wound	
	71%		UF	10 kDa/Polyethersulfone/Spiral wound	
	81%		UF	2 kDa/Polyethersulfone/Spiral wound	
	99%		NF	120 Da/Polypiperazine/Spiral wound	
Anthocyanins, flavonoids	>90%	Orange press liquor	NF	180 Da/Polyamide-polysulfone/Spiral wound	Conidi et al. (2012)
	>80%		NF	300 Da/Polypiperazine amide thin-film composite/Spiral wound	
	>80%		NF	400 Da/Polyethersulfone/Spiral wound	
	>70%		NF	1000 Da/ Polyethersulfone/Spiral wound	
Anthocyanins (cyanidin-3-glucoside chloride, myrtillin chloride and peonidin-3-glucoside chloride), flavanones	>65%	Orange press liquor	NF	Na ₂ SO ₄ rejection > 25–50%/Polyethersulfone/Spiral wound	Cassano et al. (2014)
Chlorogenic acid, Apigenin-7-O-glucoside	100%	Artichoke wastewaters	NF	200–300 Da/Polyamide/Spiral wound	Conidi et al. (2015)

polyphenols. In relation to anthocyanins and flavonoids, Conidi et al. (2012) used nanofiltration for their recovery and concentration from orange press liquor (OPL), a by-product of the citrus processing industry; the fractions contained 4395 and 465 ppm flavonoids and anthocyanins, respectively. Anthocyanins have a positive polarity that is associated with their high number of aromatic rings and hydroxyl groups (Sikorski, 2002), although the most common monomer (malvidin 3-glucoside) is weakly positive (Giusti, Rodríguez-Saona, Griffin, & Wrolstad, 1999). However, the partial polymerization of anthocyanins, coupled with their hydrophobic nature, affects the process of their separation (Galanakis, 2015). Furthermore, Ruby-Figueroa, Cassano, and Drioli, (2011, 2012) demonstrated that UF membranes can also be used to recover nutraceutical compounds; applying UF processes, they showed that a rejection of up to 57% of the initial content of the components can be reached. However, because the performance of this process is not the best, it is usually applied

as a pre-treatment for solutions with a high content of low molecular weight polyphenols. For example, Cassano, Conidi, and Ruby Figueroa (2014) used NF technology as a pre-concentration step for OPL, obtaining 15.42 and 62.16 g L⁻¹ anthocyanins and flavanones, respectively. Specific solutes, such as cyanidin-3-glucoside chloride, myrtillin chloride and peonidin-3-glucoside chloride, were identified in the anthocyanin fraction. Prior to this study, proanthocyanidins and isoflavones had been recovered by other researchers. Proanthocyanidins were obtained from grape seeds using a UF membrane, but the content was low and the waste was assumed to be the source of this specific solute (Santamaría, Salazar, Beltrán, & Cabezas, 2002). In the case of isoflavones, Xu, Lamb, Layton, and Kumar (2004) separated them from a new agro-food waste, wastewater from the processing of soy. Isoflavone glucoside and isoflavone aglycone were identified and recovered in concentrations of 0.0680 and 0.0168 µmol g⁻¹, respectively.

In Cassano's group, other agro-food by-products have been explored in order to obtain phenolic fractions. Artichoke wastewaters (AWs) were also fractionated using an integrated membrane process (Conidi et al., 2014b). Three valuable streams were produced, in one of which cynarin, chlorogenic acid and apigenin-7-O-glucoside were identified at high concentrations of 412, 612 and 400 mg L⁻¹, respectively. Additionally, this fraction showed high antioxidant activity (almost 40 mM Trolox), which, as a nutraceutical component, the author suggested may be of interest to the cosmetics and food industries. The permeate stream from the final separation step did not contain any phenolic and sugar components that could be reused during membrane processing or cleaning. While chlorogenic acid and apigenin-7-O-glucoside can be purified by specific methodologies, such as the use of polymeric resins, prior treatment is needed. Conidi et al. (2014b) purified the AWs using UF and the permeate samples concentrated by NF membrane processing. High amounts of these valuable compounds were recovered: 1.6 g L⁻¹ chlorogenic acid and 0.3 g L⁻¹ apigenin-7-O-glucoside. In a following study, Conidi, Rodríguez-Lopez, García-Castello, and Cassano (2015) submitted the NF retentate to an adsorption/desorption system in order to obtain purified fractions; these fractions showed similar antioxidant activity (43 mM Trolox) to that reported in their 2014b study. A similar permeate stream was obtained to that from the NF step, but without the presence of phenols. Thus, NF membranes are suitable for the recovery and fractionation of specific polyphenols from other high-added-value compounds. For example, phenolics (apigenin, cynarin, chlorogenic acid) were separated from sugars (sucrose, fructose, glucose) in AWs using a two-step nanofiltration process (Cassano, Conidi, Ruby Figueroa, & Castro-Muñoz, 2015). The first NF step showed high selectivity towards phenols (rejection > 85%), with final concentrations of 814, 898 and 1224 ppm obtained for apigenin, cynarin and chlorogenic acid, respectively. In this study, the MWCO between the used membranes was too close; the first NF membrane had a MWCO of 400 Da while the second of 150–300 Da. These types of membranes are capable of separating specific micro-solutes. In the case of the 400 Da NF membrane, the

hydrophobicity of the material used (polyethersulphone) was able to satisfactorily reject the polyphenols (Susanto & Ulbricht, 2009). However, interaction between phenolic compounds and a polyethersulphone membrane, as well as adsorption fouling, has been reported as possibly increasing the rejection selectivity of such membranes (Galanakis, 2015; Susanto, Feng, & Ulbricht, 2009).

Recently, an integrated membrane process was applied to recover phenolic compounds from a typical by-product of the food processing industry. In America, the nixtamalization process produces large amounts of wastewater, known as 'Nejayote'. This waste was processed and three steps were carried out: (i) an MF step to remove the suspended solids and reduce the organic load (Castro-Muñoz et al., 2015b), (ii) a UF step to recover the carbohydrates (Castro-Muñoz, Cerón-Montes, Barragán-Huerta, & Yáñez-Fernández, 2015c), and (iii) a final narrow UF step to separate the calcium components (Castro-Muñoz & Yáñez-Fernández, 2015). The final permeate from this integrated membrane system had a high total polyphenol content of 951 mg L⁻¹ from an initial phenolic content of 1190 mg L⁻¹. Correspondingly, the fraction had low TOC content. This final permeate can be fractionated by NF membranes and concentrated by other membrane technologies, such as RO.

This review has shown that UF and NF technologies have been successfully employed to recover phenolic compounds from various sources, particularly from agro-food by-products. UF and NF processes have become established technologies for the recovery of high-added-value components from food wastes (Galanakis, 2012). In particular, NF operations seem to be the most viable technology for application in the food processing industry in the near future. Recent studies have reported several potential applications for nanofiltration, such as in water softening, vegetable oil processing, the beverage industry, the dairy industry (whey processing, lactose recovery, lactic acid separation), the sugar industry (sugar beet press water, oligosaccharide filtration) and wastewater treatment (Salehi, 2014). The latter will continue to represent a difficult challenge for industry because, as production demands increase, so

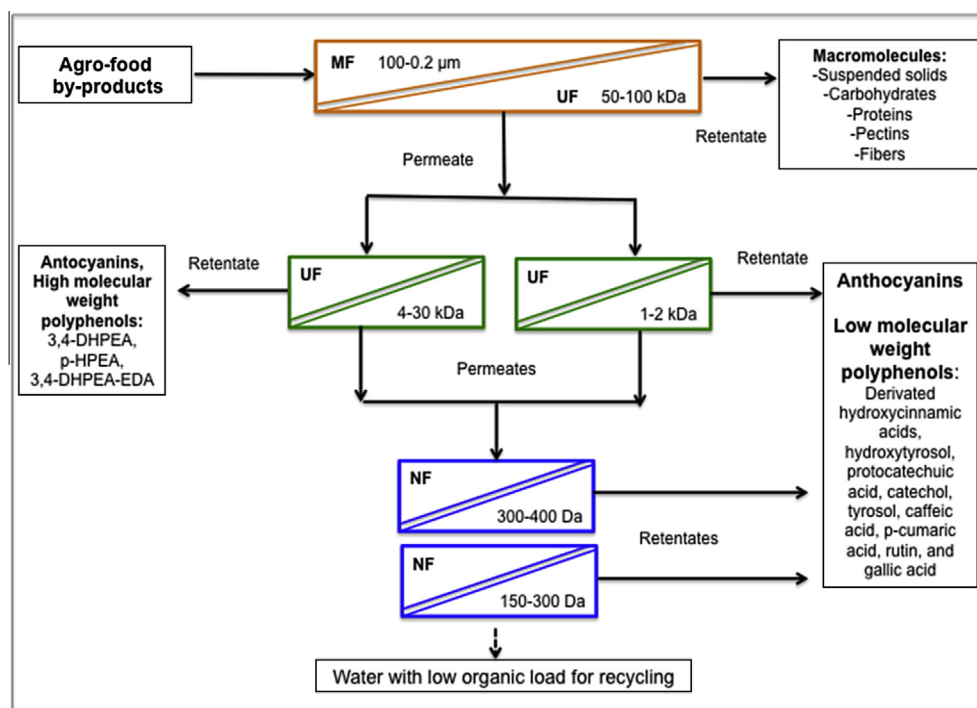


Fig. 3. Integrated membrane system suggested for the fractionation of agro-food wastes.

too will wastewater production. Clearly, the implementation of membrane processes is coming, at least for the treatment of food processing wastewaters. In addition, the recovery of different high-added-value compounds will strongly support the application of more conventional membrane processes (Galanakis, 2015; Rahmanian et al., 2014). Table 1 summarizes the main phenolic compounds recovered from agro-food by-products using the conventional membrane operations reviewed in this paper; it also presents some specifications of the process type and membranes used for such recovery.

In the future, it is likely that the more conventional technologies, such as pressure-driven membrane processes, will be focused on the recovery of high-added-value components. They have more advantages for separation than typical methods, such as thermal processes and chromatographic applications, which give low yields at high operational costs. The environment will also welcome the continuing application and exploration of target solutes by UF and NF. It just remains to optimize and reduce the energy consumption of filtration systems, an area both researchers and manufacturers have been focusing on in recent years (Bennett, 2015). Despite this energy consumption issue, membrane operations such as NF have been named as emerging technologies for the production of nutraceuticals from agro-food by-products (Galanakis, 2013, 2015). In the case of phenolic compounds, it seems more economically beneficial for industry to focus on processing by-products that represent mainly valueless garbage (Galanakis & Schieber, 2014), the disposal of which can be avoided by the agro-food industries through the recovery of solutes. Finally, for food-processing companies aiming to implement an integrated membrane system in order to fractionate their wastewaters, Fig. 3 provides a clear overview of how to recover specific phenolic compounds according to the highlighted studies reported in this review.

Basically, this scheme meets the first four stages needed to achieve the “Universal Recovery Process” described by Galanakis (2015): (i) macroscopic pre-treatment, (ii) the separation of macro- and micromolecules, (iii) extraction, and (iv) isolation-purification. The fifth stage, product formation, is missing. However, the recovery efficiency of these membrane techniques depends on some other parameters being pre-defined. Table 2 summarizes the commercial membranes tested for the separation of high and low molecular weight polyphenols, thereby providing a clear and simple overview of the application and limits of each membrane in terms of operating parameters.

The use of integrated membrane operations for recovering bioactive compounds has been consolidated, at least for OMWs. Typically, this recovery strategy involves fractionation using MF, UF and NF membranes in sequence. The MF step is used to try to prevent the removal of suspended solids that can produce operational issues (early fouling) in the subsequent steps. The application of UF technology supports the removal of the macromolecules in the retentate stream while conserving the polyphenols in the permeate stream. Finally, the NF step improves the recovery process by concentrating the solutes in the retentate (Cassano, Conidi, Galanakis, & Castro-Muñoz, 2016). This approach enables the recovery of at least 70% of the water volume of the starting total volume of OMWs. It is proposed that, following concentration, the permeate from these narrow membranes can be reused in industrial processes; namely, in water processing, membrane cleaning and the processing of olive mill wastewater (see Fig. 3). Furthermore, these integrated membrane systems are capable of recovering other types of high-added-value compounds, such as carbohydrates, proteins, pectins and peptides (Galanakis, Castro-Muñoz, Cassano, & Conidi, 2016). Regarding polyphenols, they can be separated depending on their molecular weight and

Table 2
Specifications of membranes used for recovering polyphenols from waste.^a

Operation	Commercial membrane	Manufacturer	Membrane material	Configuration	pH range	Maximum operating temperature (°C)	NMWCO (kDa)/% Retention
UF	UFP-1-E-4A	Amersham Biosciences	Polysulphone	Hollow fiber	2–14	50	1
UF	DCQ III-006	China Blue Star Membrane Technology	Polysulphone	Hollow fiber	2–13	40	100
UF	GR40PP	Alfa Laval	Polysulphone	Spiral wound	2–10	75	100
UF	GR51PP	Alfa Laval	Polysulphone	Spiral wound	2–10	75	50
UF	GR60PP	Alfa Laval	Polysulphone	Spiral wound	2–10	75	25
UF	GR70PP	Alfa Laval	Polysulphone	Spiral wound	2–10	75	20
UF	GR81PP	Alfa Laval	Polyethersulphone	Spiral wound	2–10	75	10
UF	GR95PP	Alfa Laval	Polyethersulphone	Spiral wound	2–10	75	2
UF	ETNA01PP	Alfa Laval	Fluoro polymer	Flat sheet	1–11	60	1
NF	AFC99	PCI Membranes	Polyamide	Tubular	1.5–12	80	99, NaCl
NF	AFC80	PCI Membranes	Polyamide	Tubular	1.5–10.5	70	80, NaCl
NF	AFC40	PCI Membranes	Polyamide	Tubular	1.5–9.5	60	60, NaCl
NF	AFC30	PCI Membranes	Polyamide	Spiral wound	1.5–9.5	60	75, NaCl
NF	NF-90	Dow Filmtec	Polyamide	Spiral wound	2–11	45	92, NaCl
NF	NF-270	Dow Filmtec	Polyamide	Spiral wound	3–10	45	70.6, NaCl
NF	NF-200-400	Dow Filmtec	Polyamide	Spiral wound	3–10	45	35–50, CaCl ₂
NF	NF-2540	Dow Filmtec	Polyamide	Spiral wound	3–10	45	98, MgSO ₄
NF	ESNA1-LF2	Hydranautics	Composite Polyamide	Spiral wound	3–10	45	73–92, CaCl ₂
NF	ESNA1-LF	Hydranautics	Composite Polyamide	Spiral wound	3–10	45	84–96, CaCl ₂
NF	ESNA1-LF-LD	Hydranautics	Composite Polyamide	Spiral wound	3–10	45	86–95, CaCl ₂
NF	ESNA1-LF2-LD	Hydranautics	Composite Polyamide	Spiral wound	3–10	45	83–90, CaCl ₂
NF	MPS-34	Koch Membrane Systems	Composite polysulphone	Spiral wound	0–14	70	0.2
NF	MPF-44	Koch Membrane Systems	Polydimethylsiloxane	Spiral wound	–	40	0.25
NF	MPF-55	Koch Membrane Systems	Polydimethylsiloxane	Spiral wound	–	40	0.7
NF	NP030	Microdyn-Nadir	Polyethersulphone	Spiral wound	0–14	95	0.4
NF	NP010	Microdyn-Nadir	Polyethersulphone	Spiral wound	0–14	95	1
NF	Desal-5-DK	GE Osmonics	Polyamide	Spiral wound	0–14	50	98, MgSO ₄
NF	Desal-5-DL	GE Osmonics	Polyamide	Spiral wound	0–14	50	96, MgSO ₄
NF	StarMem-120	Membrane Extraction Technology	Polyimide	–	0–14	50	0.2

^a Adapted from Galanakis C.M., Castro-Muñoz R., Cassano A. and Conidi C. (2016). *Recovery of high-added-value compounds from food waste by membrane technology*. Membrane technologies for biorefining, (A. Figoli, A. Cassano, & Basile A.), Elsevier, UK.

the membrane used; low molecular polyphenols are normally recovered from NF retentate.

5. Current practices of polyphenols extracted from agro-food wastes

Throughout this review, many studies have been reported in which phenolic solutes were recovered successfully using conventional membrane systems. Despite their limited post-recovery application, some studies have proposed particular uses. For instance, Servili et al. (2011b) enriched milk beverages with phenolic compounds recovered from OMWs. The phenolic content of virgin olive oil has also been improved (Servili et al., 2011a). And polyphenols have been added during the processing of vegetable oils (Esposto et al., 2015). It is important to highlight that food rich in bioactive compounds has become an important choice for consumers aiming to reduce the risk of contracting specific diseases or to treat certain minor illnesses. Polyphenols are also important for improving the utilization of food and agricultural products (El-Shourbagy & El-Zahar, 2014). This emerging approach of re-using of polyphenols can provide a better outlook on the utilisation of valuable solutes in the food industry. Consequently, phenolic extracts have started to be evaluated according to their biological properties; polyphenols recovered from OMWs (Cassano et al., 2013), NWs (Castro-Muñoz, Barragán-Huerta, & Yáñez-Fernández, 2016) and AWs (Cassano et al., 2015) have all been tested against oxidative radicals. Thus, polyphenol recovery is of great interest to pharmaceutical companies looking for ways to produce new nutraceuticals, cosmetics and food supplements (Conidi et al., 2014b).

6. General remarks

Over the course of this deep review, membrane processes have been shown to be able to recover functional compounds, known as nutraceuticals, from new sources; namely, agro-food by-products. Methodologies such as UF and NF can be used to recover, separate and fractionate specific phenolic compounds that, according to their biological activity, have potential applications in the food and pharmaceutical industries. Furthermore, compared with traditional methods, these separation processes are economically viable not only in terms of recovery, but also because they do not require the use of other agents or of destructive components. Thus, the recovery of high-added-value solutes from agro-food wastes is both industrially sustainable and environmentally friendly. Furthermore, the high costs of waste disposal make it necessary for industries that use large-scale production processes to focus on waste recycling. In the future, it is quite possible that governments will legislate to ensure the use of approaches such as those described herein in order to reduce water and environmental pollution.

It is likely that research and development will be focused on new implementations of NF technology as the primary tool for the recovery and concentration of phenolic compounds. However, when purification is required, the use of another technology, such as OD, RO or adsorption processes, is also needed. Currently, though, market opportunities for the natural extracts obtained from such processes are missing. Thus, it is high time that industry started to address this challenge in order to achieve the fifth stage of the “Universal Recovery Process”.

Conflict of interest

The authors declare no conflict of interest.

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