A Study of Nanfiltration and Ultrafiltration Membranes for The Recovery Polyphenols

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Abstract

Pressure-driven membrane-based technologies represent a valid approach to reduce the environmental pollution of several agro-food by-products. Recently, in relation to the major interest for natural compounds with biological activities, their use has been also addressed to the recovery, separation and fractionation of phenolic compounds from such by-products. In particular, tight ultrafiltration (UF) and nanofiltration (NF) membranes have been recognized for their capability to recover phenolic compounds from several types of agro-food by-products. The separation capability of these membranes, as well as their productivity, depends on multiple factors such as membrane material, molecular weight cut-off (MWCO) and operating conditions (e.g., pressure, temperature, feed flow rate, volume reduction factor, etc.). This paper aims at providing a critical overview of the influence of these parameters on the recovery of phenolic compounds from agro-food by-products by using tight UF and NF membranes. The literature data are analyzed and discussed in relation to separation processes, molecule properties, membrane characteristics and other phenomena occurring in the process. Current extraction methodologies of phenolic compounds from raw materials are also introduced in order to drive the implementation of integrated systems for the production of attractive phenolic formulations of potential interest as food antioxidants.

Keywords: *Polyphenols; Biologically Active Compounds; Ultrafiltration; Nanofiltration; Agro-Food By-Products.*

1. INTRODUCTION

Today, the recovery of biologically active compounds from natural sources has attracted great attention due to their potential uses such as ingredients in foodstuff, pharmaceutics, and cosmetic formulations. Among these compounds, polyphenols (PPs), secondary metabolites ubiquitously distributed in all higher plants, have been recently the most searched ones [1]. PPs represent a wide variety of compounds, which are classified in several classes, such as hydroxycinnamic acids, hydroxybenzoic acids, anthocyanins, flavonols, proanthocyanins, flavonols, flavanones, isoflavones, flavones, stilbenes and lignans [2–4]. More than 8000 phenolic structures are currently known, and among them, over 4000 flavonoids have been identified [5]. These plant metabolites are characterized by the presence of several phenol groups (aromatic rings with hydroxyls), which are derived from L-phenylalanine or tyrosine. Typically, all these compounds present the basic chemical structure based on cinnamic acids (C6–C3) and benzoic acids (C6–C1) (Figure 1).

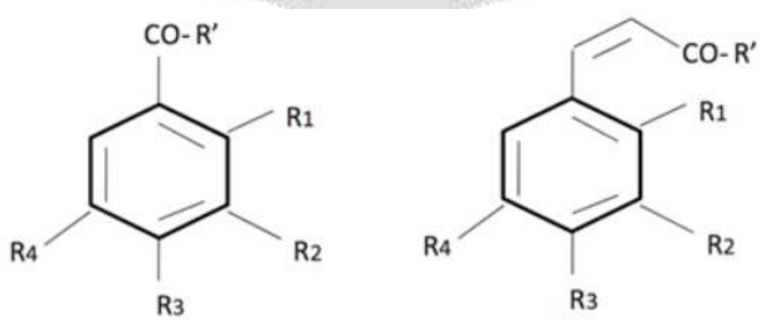

Figure 1. Molecular structure of benzoic and cinnamic acid derivatives

Over the course of the last decades, phenolic compounds have been deeply studied for their great protective activities as antioxidants, free radical scavengers, and metal chelators, as well as to the ability to reduce and inhibit different types of enzymes (telomerase, lipoxygenase, cycloxygenase) [1,6]. They also contribute to the prevention of several types of human diseases, such as cardiovascular disease, cancer, osteoporosis, diabetes, and neurodegenerative diseases. In particular, some phenolic compounds (e.g., flavan-3-ol; flavonol, tannin, neolignan) have demonstrated specific health protective effects such as antimicrobial activity (against virus, bacteria, and fungi) [1] and oral health [4]. Basically, these health-protective activities of PPs are directly attributed to the phenolic hydroxyl groups that are good H-donating antioxidants, and then, they scavenge reactive oxygen species and break the cycle of generation of new radicals [2]. Thereby, the PPs inhibit the oxidation of lipids, proteins, and DNA. Furthermore, they inhibit the production of enzymes involved in radical-type generation, which are related to the development of diseases [7]. Phenolic compounds have been identified in a wide class of plant-derived foods such as fruits (berries and berry products), seeds, cereals, leaves, and vegetables, and the list is constantly growing [8]. The required mean daily PPs intake from fruits and vegetables among adults is 219 mg (males) and 193 mg (females) from fruit and 78 mg (males) and 67 mg (females) from vegetables [9]. However, there is a need for looking for new sources aiming to satisfy this intake and industry demand. Thereby, scientists have focused their attention on potential sources of PPs, including agro-food by-products, such as wastewaters (from olive, artichoke, maize, and winemaking processing industries), residues (orange press liquor, winery effluent, fruit seeds, fermented grape pomace, grape marc, etc.) and some other derivative by-products [10,11]. On the other hand, there is great interest in identifying tangible methods for extracting them from such sources, based on the limitation that the degradation of phenolic compounds generally occurs due to their low stability at high temperatures, presence of solvents, and long extraction times [12]

2. EXTRACTION METHODOLOGIES OF POLYPHENOLS (PPS)

Agro-residues produced during the handling and processing of fruits, vegetables and forest resources are characterized by a complex composition of phytochemicals such as vitamins, tocopherols, PPs, and carotenoids, along with complex carbohydrates and fiber which have been associated with the alleged health-promoting effects of fruits and vegetables consumption.

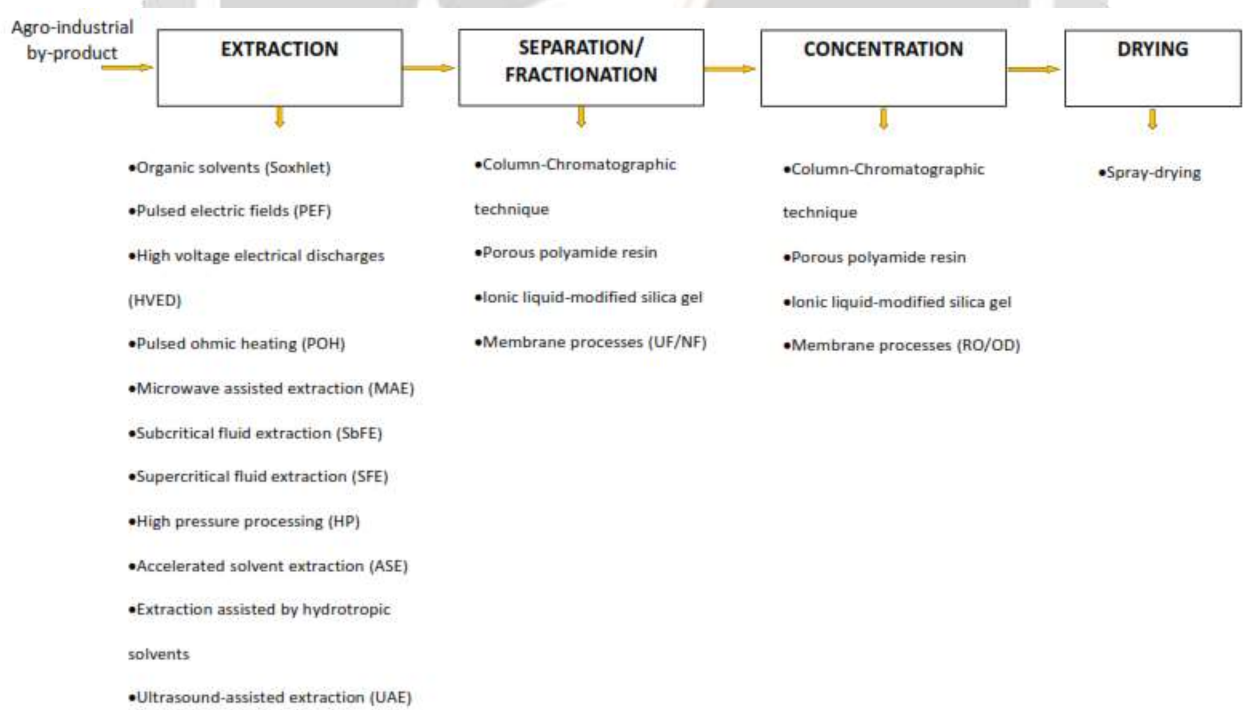

Figure 2. Layout of operation steps for recovering bioactive phenolic from agro-industrial by-products

Therefore, their extraction from residues and agro-industrial by-products, as an alternative to the synthetic substances commonly used in the food, pharmaceutical, and cosmetic industries, has been strongly encouraged [13] The development of adequate methods for the recovery of phenolic compounds from their original sources is crucial and can be accomplished through several steps (Figure 2). The processes employed should be environmentally sustainable and efficient, resulting in high yields.

Extraction is the first and crucial step and plays an essential role in the final characteristics of the product. The traditional process to extract PPs from by-products is the conventional extraction by solvent (Soxhlet extraction); however, drawback of leaving trace amounts of solvents or causing thermal degradation has driven to find new technologies to avoid that [14]. In this regard, several non-conventional processes have been reported as alternatives, much of them friendly in an environmental way, to improve the extraction of valuable compounds from agro-industrial by-products. Pulsed electric fields (PEF) [15], high voltage electrical discharges (HVED), pulsed ohmic heating (POH), microwave-assisted extraction (MAE), subcritical fluid extraction (SbFE), supercritical fluid extraction (SCFE), high pressure processing (HP), accelerated solvent extraction (ASE), extraction assisted by hydrotropic solvents, and ultrasound-assisted extraction (UAE) are typical examples. Independent of the selected type of extraction, there are some common objectives, including selectivity and efficiency in the release of the target phytochemicals and a reproducible method regarding variations in the sample matrix. Several factors are involved in the extraction yield. They include mixture components, such as the proportion of residue to be treated and the type of solvent used (water, acetone, ethyl acetate, alcohols as methanol, ethanol, and propanol, and their mixtures), as well as operating conditions such as temperature, pressure, extraction cycles, operating time, etc. The definition of the mixture and operating conditions will depend primarily on the residue characteristics, mainly by the type of PPs, and consequently by their solubility which will lead to the selection of specific solvents.

3. GENERAL ASPECTS OF MICROFILTRATION (MF), ULTRAFILTRATION (UF) AND NANOFILTRATION (NF) PROCESSES

Membrane-based technologies, such as MF, UF and NF, are physical separation processes allowing the separation of different compounds from a feed solution under a hydrostatic pressure difference applied between the two sides of a perm selective barrier. As a result, the feed solution is divided into a permeate fraction containing all components that have permeated the membrane and a retentive fraction containing all compounds rejected by the membrane, within some of the solvent. The separation is determined by the pore size-range of the membrane, which is mainly related to its molecular weight cut-off (MWCO), and to a lesser extent on molecular shape, charge and hydrophobicity. Typically, a membrane's MWCO refers to the smallest average molecular mass of a known solute that will not effectively diffuse across the membrane. MF membranes have large pore sizes ranging from 100 to 10,000 nm (separating particles), while UF membranes have pore sizes between 2 and 100 nm which are able to retain molecules with molecular weights ranging from 350,000 to 1000 Da. NF membranes are characterized by narrow pore sizes from 0.5 to 2 nm, retaining micro molecules with molecular weights from 120 to 1000 Da. Wide UF membranes, with MWCO ranging between 50 and 100 kDa, can fundamentally be used to recover different types of macromolecules (such as suspended solids, carbohydrates, proteins, and pectins). UF membranes from 4 to 30 kDa are effective to concentrate high molecular weight components (such as tannins, proteins, hydrolysates, and some high molecular weight phenolic fractions), while tight UF membranes, from 1 to 3 kDa, are highly effective to concentrate low molecular weight compounds (such as anthocyanins, low molecular weight PPs, low molecular weight sugars, and peptides); indeed, these membranes are in the molecular limit of the NF process. Low nominal MWCO NF membranes (ranging from 350 to 400 Da) can practically retain the same molecules recovered by tight UF membranes (1–3 kDa); however, high separation efficiency in NF membranes is expected. On the other hand, fine NF membranes (120–300) are the best ones to selectively recover and concentrate low-molecular weight compounds (like low molecular weight PPs). Thus, tight UF and NF membranes are the most suitable ones to meet the recovery of PPs.

A schematic representation of MF, UF and NF processes is illustrated in Figure 3. Typical operating pressures related to these processes are specified in Table 1.

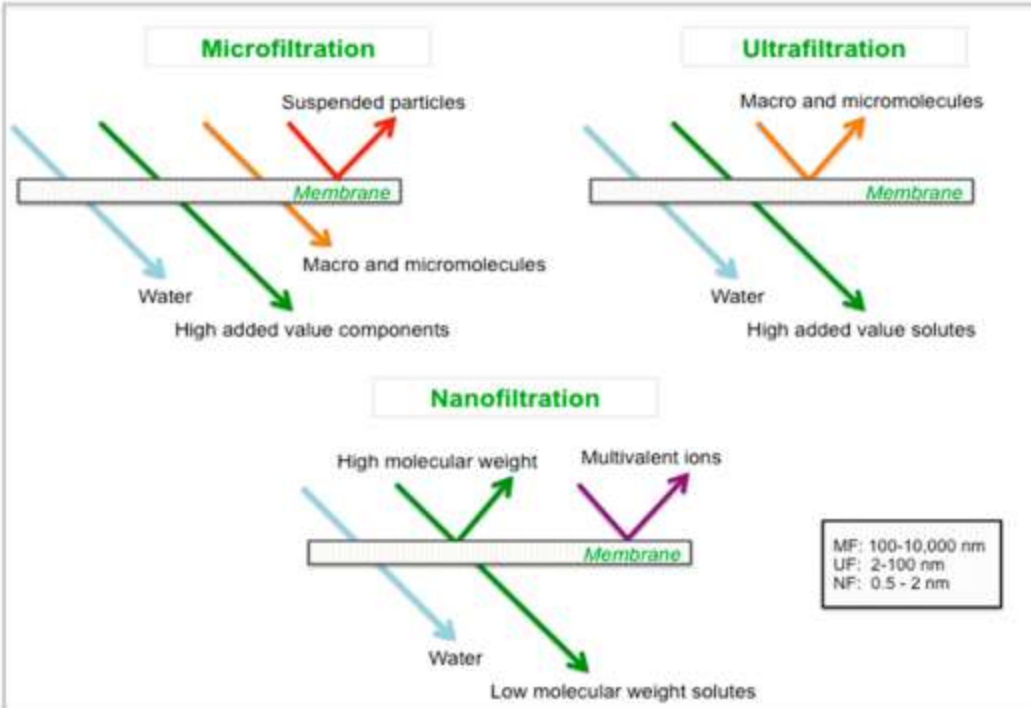

Figure 3. Schematic description of MF, UF and NF membranes MF, ultrafiltration; UF, ultrafiltration; NF, nanofiltration

Table 1. Pressure requirements and separation mechanisms of MF, UF and NF

Membrane Process	Required Pressure (Bar)		Typical Separation Mechanism
	Min.	Max.	
Microfiltration	0.1	2	Sieving
Ultrafiltration	0.1	7	Sieving
Nanofiltration	3	25	Sieving & charge effect

4. RECOVERY OF PPs BY TIGHT UF AND NF MEMBRANES

In principle, separation processes using tight UF and NF membranes are able to separate specific compounds through a sieving mechanism based on the MWCO; however, the membrane's MWCO is not the only criterion that has to be taken into account. For instance, the asymmetric manufacture of membrane pores does not always reflect a narrow MWCO range; in addition, some other phenomena (e.g., concentration polarization, membrane fouling, coulombic and hydrophobic interactions) also contribute to the phenolic retention. In the following sections, the influence of membrane material, MWCO and operating parameters on the recovery of PPs by tight UF and NF membranes is analyzed and discussed together with the contribution of specific pre-treatments of feed solutions aimed at limiting the formation of fouling layers which are the main cause of reduced membrane performance.

Effect of Pre-Treatment on the Membrane Performance

Agro-food wastewaters contain considerable amounts of high molecular weight solutes in the shape of suspended solids and colloidal particles identified as detrimental from a bioactivity perspective. Physical and physico-chemical processes (screening, sedimentation, centrifugation, adsorption, etc.) are used as primary separation (as pre-treatment) to remove suspended solids or other impurities. Because of this purpose, the use of UF and MF processes has been often introduced in integrated systems for recovery of phytochemicals from agro-industrial by-products as preliminary step, in alternative to the use of conventional systems based on the use of adsorbents and filter aids, before a fractionation step performed by using tight UF and/or NF membranes.

Effect of Operating Conditions on the Membrane Performance

The membrane performance is influenced by a series of factors which should be controlled not only to maximize the permeate flux but also to improve selectivity towards target compounds. Transmembrane pressure (TMP) plays an important role in the membrane performance because it has a direct effect on membrane fouling which can be reversible or irreversible. Increasing TMP produces a linear increase in the permeate flux; however, there is a critical point, defined as critical trans membrane pressure at which this linear relationship is lost. The limiting point is where the maximum flux value is obtained under some operating conditions and it cannot be increased by varying TMP. Therefore, to keep a continuous process the TMP selected must be lower than the critical value, this means work under the critical zone in which the fouling effect is minimum. The rejection of phenolic compounds usually increases by increasing the TMP. This phenomenon can be described by the so-called film layer theory assuming the formation 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 TMP values concentration polarization and fouling phenomena are more severe, leading to the formation of an additional selective layer on the membrane surface increasing the retention coefficient.

5. CONCLUSION

Fruit and vegetable processing residues are considered highly polluting wastes because of their high organic load and phytotoxic and antibacterial phenolic substances resistant to biological degradation. On the other hand, intensive research in the field of agro-food waste management suggests that these effluents should be regarded as a useful resource for the recovery of fine chemicals and for different biotechnological applications such as the production of important metabolites. In particular, agro-industrial by-products can be considered a promising alternative to synthetic antioxidants used in food, cosmetics and pharmacy since they are an inexpensive source of valuable compounds, mainly polyphenols which are known for their antioxidant properties. Pressure-driven membrane operations are well-known established technologies for the treatment of high strength wastewaters aimed at the production of purified water for recycle or reuse and the recovery of valuable compounds. The use of tight ultrafiltration and nanofiltration membranes has been reviewed in the light of their growing use for the separation and purification of phenolic compounds from agro-food by-products and extracts. Tailor made processes for specific by-products can be identified through an appropriated selection of membrane typology as well as optimization of operating and fluid-dynamic conditions which are key parameters influencing both productivity and selectivity towards target compounds. The combination of tight UF and NF membranes with conventional extraction systems and/or membrane pre-treatment of raw agro-food wastewaters offer new opportunities for the formulation of nutraceutical products while reducing the environmental pollution of these effluents.

6. REFERENCES

1. Daglia, M. Polyphenols as antimicrobial agents. Curr. Opin. Biotechnol. 2012, 23, 174–181.
2. Tapiero, H.; Tew, K.D.; Nguyen Ba, G.; Mathé, G. Polyphenols: Do they play a role in the preventions of human pathologies? Biomed. Pharmacother. 2002, 56, 200–2007.
3. Manach, C.; Williamson, G.; Morand, C.; Scalbert, A.; Rémésy, C. Bioavailability and bioefficacy of polyphenols in humans. I. Review of 97 bioavailability studies. Am. J. Clin. Nutr. 2005, 81, 230S–242S.
4. Petti, S.; Scully, C. Polyphenols, oral health and disease: A review. J. Dent. 2009, 37, 413–423.
5. Tsao, R. Chemistry and biochemistry of dietary polyphenols. Nutrients 2010, 2, 1231–1246.
6. Wojdyło, A.; Oszmianski, J.; Czemerys, R. Antioxidant activity and phenolic compounds in 32 selected herbs. Food Chem. 2007, 105, 940–949.
7. Tripoli, E.; Gianmmanco, M.; Tabacchi, G.; Di Majo, D.; Giammanco, S.; La Guardia, M. The phenolic compounds of olive oil: Structure, biological activity and beneficial effects on human health. Nutr. Res. Rev. 2005, 18, 98–112.
8. El Gharras, H. Polyphenols: Food sources, properties and applications—A review. Int. J. Food Sci. Technol. 2009, 44, 2512–2518.

9. Scalbert, A.; Williamson, G. Dietary intake and bioavailability of polyphenols. J. Nutr. 2000, 1, 2073S–2085S.
10. Galanakis, C.M.; Castro-Muñoz, R.; Cassano, A.; Conidi, C. Recovery of high-added-value compounds from food waste by membrane technology. In Membrane Technologies for Biorefining; Figoli, A., Cassano, A., Basile, A., Eds.; Woodhead Publishing: Cambridge, UK, 2016; pp. 189–215, ISBN 978-0-08-100451-7.
11. Castro-Muñoz, R.; Barragán-Huerta, B.E.; Fíla, V.; Denis, P.C.; Ruby-Figueroa, R. Current role of membrane technology: From the treatment of agro-industrial by-products up to valorization of valuable compounds. Waste Biomass Valoriz. 2017, 1–17.
12. Castro-Muñoz, R.; Yáñez-Fernández, J.; Fíla, V. Phenolic compounds recovered from agro-food by-products using membrane technologies: An overview. Food Chem. 2016, 213, 753–762.
13. Moreira, M.M.; Morais, S.; Delerue-Matos, C. Environment-friendly techniques for extraction of bioactive compounds from fruits. In Soft Chemistry and Food Fermentation—Handbook of Food Bioengineering; Grumezescu, A.M., Holban, A.M., Eds.; Academic Press: London, UK, 2017; Volume 3, pp. 21–48, ISBN 978-0-12-811412-4.
14. Shilpi, A.; Shivhare, U.S.; Basu, S. Supercritical CO2 extraction of compounds with antioxidant activity from fruits and vegetables waste—A review. Focus Mod. Food Ind. 2013, 2, 43–62.
15. Brianceau, S.; Turk, M.; Vitrac, X.; Vorobiev, E. Combined densification and pulsed electric field treatment for selective polyphenols recovery from fermented grape pomace. Innov. Food Sci. Emerg. Technol. 2015, 29, 2–8.
16. Barba, F.J.; Brianceau, S.; Turk, M.; Boussetta, N.; Vorobiev, E. Effect of alternative physical treatments (Ultrasounds, pulsed electric fields, and high-voltage electrical discharges) on selective recovery of bio-compounds from fermented grape pomace. Food Bioprocess Technol. 2015, 8, 1139–1148.