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# Integrated membrane systems as an innovative approach for the recovery of high value-added compounds from agro-food by-products

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The valorization of available food manufacturing waste with high potential to manufacture value-added products, in line with the main goal of the circular economy, is actually one of the current challenges for scientists.
Membrane-based processes are an emerging tool to improve the currently adopted valorisation protocols of agro-food by-products, within a sustainable biorefinery strategy, with remarkable improvements of the environmental and economical sustainability of the overall approach.
This work aims at providing a critical overview of the on ongoing research studies for the recovery of high value-added compounds from agro-food by-products such as olive mill wastewaters, citrus by-products and wastes from the wine industry by membrane-based operations. In particular, the development of integrated membrane systems on lab-scale unit for the separation, fractionation and concentration of phenolic compounds and their derivatives from these sources will be presented and discussed.
Experimental results clearly indicate that the combination of membrane unit operations in integrated systems offers interesting perspectives in terms of recovery of primary resources, reduction of the environmental impact, formulation of innovative food products and rationalization of conventional food manufacturing processes.

## 1. Introduction

The food industry yearly produces a considerable amount of solid and liquid wastes that mainly result from production, preparation, consumption and disposal processes. The characteristics of a specific waste depend mainly on the product being processed (e.g., fruit, vegetable, oils, dairy, meat and fish) and the processing methods. Generally, these wastes contain large amount of macro-pollutants and are only partially recycled for specific uses such as spread on land, animal feeding and composting, whereas the main volumes are managed as waste of environmental concern, with relevant negative effects on the overall sustainability of the food processing industry (Federici et al., 2009). On the other hand, many of these residues are a precious resource of potentially useful chemical substances after either direct recovery or chemical transformation and can be potentially reused into other production systems, trough e.g. bio-refineries (Mirabella et al., 2014), and for developing new products with a market value (i.e. functional foods). In this view, the exploitation of vegetable by-products as a source of bioactive compounds represents a promising opportunity to obtain added-value products for food or pharma industries.
Pressure-driven membrane operations such as microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO) have become key technologies in the food processing industry over the last 35 years. The basic properties of these processes make them ideal for the treatment of both food products and by-products; high selectivity, possibility to operate under mild conditions of temperature, low energy consumption, modularity, easy scale-up, no phase change and no use of chemical additives are typical advantages over conventional separation technologies. The large variety of membrane materials available, as well as the diversity of membrane processes developed, underlines one of the strengths of membrane separations: the possibility of

designing and fine-tuning the membrane and the membrane process for a specific task. Relatively new membrane processes, such as membrane distillation (MD), osmotic distillation (OD) and membrane emulsification (ME), offer new interesting solutions for the concentration and encapsulation of target compounds.

In this work, an overview of some applications of membrane-based operations recently investigated on laboratory scale for the recovery of high value-added compounds from agro-food wastewaters is given. In particular, case studies related to the implementation of membrane processes in integrated systems for the recovery of bioactive compounds from olive mill wastewaters (OMWs), citrus and wine by-products are reviewed and discussed.

## 2. Olive mill wastewaters

Intensive researches in the field of OMWs management suggest that these effluents are an useful resource for the recovery of fine chemicals and for different biotechnological applications such as the production of important metabolites. In particular, OMWs are characterized by presence of more than 30 different types of biophenols and related compounds including tyrosol, hydroxytyrosol and oleuropein well recognized for their antioxidant, cardioprotective, antiatherogenic, chemopreventive and anti-inflammatory activities (Obied et al., 2005). Therefore, utilizing OMWs as potentially cheap source of pharmacologically active compounds ensures sustainability in terms of material recovery, reduced new material consumption and prevention of environmental pollution.

Driven by economic factors, environmental concern and technological advancement, membrane-based processes have been largely investigated over the last 30 years for the valorization of OMWs. Integrated systems based on the use of selected membrane operations in a sequential design provide significant improvements of the performance thanks to the synergistic effect among the different unit operations. In this approach, MF or UF membranes are mostly employed as a pre-treatment step to remove suspended particles and colloids while allowing the polyphenols and other soluble contaminants to pass through. Tight UF membranes and NF membranes are useful to fractionate the permeate stream in order to improve purity of phenolic compounds. Phenolic fractions can be finally concentrated by RO or OD.

The selection of proper membranes in terms of membrane material, pore size and module design as well as the optimization of operating and fluid-dynamic conditions are key factors to improve permeation fluxes and selectivity towards target compounds which are both highly dependent on concentration polarization and membrane fouling phenomena.

Flat-sheet UF membranes with different molecular weight cut-off (MWCO) (4, 5 and 10 kDa) and polymeric material (regenerated cellulose and polyethersulfone) were evaluated for their retention coefficients towards phenolic compounds, total antioxidant activity and total organic carbon. All selected membranes showed lower rejection towards free low molecular weight phenolic compounds in comparison with values observed for total polyphenols. This was in agreement with the molecular weight of the investigated phenols which is in the range 138-284 g/mol and hence lower than the MWCO of each UF membrane. For example, regenerated cellulose membranes with MWCO of 5 e 10 kDa exhibited lower rejections towards phenolic compounds, higher permeate fluxes and lower fouling index when compared with polyethersulfone membranes having a similar MWCO. Indeed polyphenols, also aggregated with polysaccharides, has a higher affinity for the polyethersulfone membranes leading to severe fouling by pore narrowing and blocking under UF conditions (Cassano et al., 2011).

In the process implemented by Cassano et al. (2013), raw OMWs were pretreated by hollow fiber UF membranes (with a pore size of 0.02 $\mu$m) in order to remove suspended solids and colloids; then the UF permeate was processed with a flat-sheet UF membrane with a MWCO of 1000 Da. This step allowed to remove most part of organic substances from phenolic compounds in agreement with the reduced total organic carobon (TOC)/polyphenols ratio (from 9.2 in the original UF feed to 3.8 in the UF permeate). A concentrated phenolic solution containing more than 85 mg/L of low MW polyphenols was produced by treating the UF permeate with a spiral-wound NF membrane having a MWCO of about 200 Da. The hybrid process allowed to produce three different valuable fractions: a concentrated solution containing high MW organic substances (retentate of both UF processes) which can be submitted to an anaerobic digestion for the production of biogas; a concentrated solution (NF retentate) enriched in polyphenolic compounds suitable for cosmetic, food and pharmaceutical industries as liquid, frozen, dried or lyophilized formulations; a water stream (NF permeate) which can be reused for irrigation, membrane cleaning and as process water (Figure 1).

By referring to the sustainability of the process, membrane filtration has been considered as one of the most effective processes in terms of organics reduction and economic viability among different investigated methods of OMWs treatment, thanks to the profit derived from the exploitation of phenolic content and the fraction rich in nutrient components (Zaklis et al., 2013).

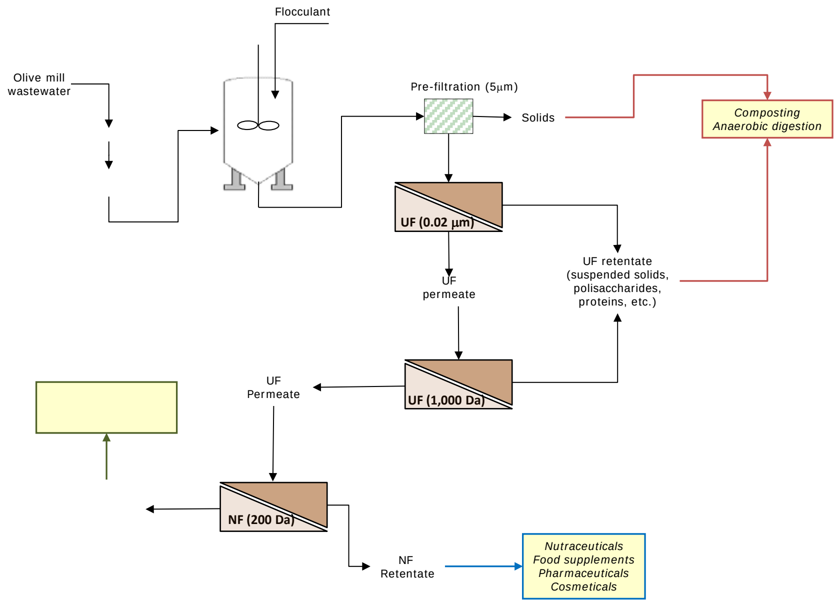


*Figure 1: Schematic of the integrated membrane process proposed for the recovery of flavonoids from orange press liquor (UF, ultrafiltration; NF, nanofiltration; OD, osmotic distillation) (adapted from Cassano et al., 2014)*

In another approach, raw OMWs were submitted to an acidification/MF pretreatment and then processed by NF before a final concentration by OD (Bazzarelli et al., 2016). Relatively high fluxes, with respect to literature data, were obtained in both MF and NF steps (60 and 7 L/m$^2$h, respectively); by referring to low MW polyphenols the NF membrane exhibited rejections higher than 90% for cathecol, tyrosol, caffeic acid and vanillic acid and of 83% for hydroxytyrosol. The concentration of the NF retentate by OD produced an enriched fraction of low MW polyphenols according to a concentration factor of 7. This fraction was also formulated by membrane emulsification for the production of a W/O emulsion with an encapsulation efficiency of 90%. According to the process mass balance, related to the treatment of 1000 L of OMWs, 1463 g of phenolic compounds (85% of the initial phenolic content) and 800 L (80% of the initial volume) of purified water can be recovered, respectively.
Recently, Tundis et al. (2020) analysed the phenolic composition and the antioxidant, hypoglycaemic and hypo-lipidemic properties of OMWs fractions obtained to a combination of MF, NF and RO membranes in order to prospect a potential use in pharmaceutical, nutraceutical, and cosmeceutical industries. As reported in Table 1, hydroxytyrosol, oleuropein, tyrosol and 4-hydroxyphenyl acetate were the most abundant phenolic compounds in the raw wastewaters. All compounds were highly recovered in the MF permeate. For the NF membrane, the measured rejections were strongly correlated with the molecular weight of phenolic compounds. In particular, the retention towards tyrosol was 4.8%, while phenolic compounds with MW higher than 194 g/mol were completely retained.

*Table 1: Analysis of phenolic compounds (mg/L) in samples of olive mill wastewaters treated by integrated membrane process (Tundis et al, 2020)*

| Phenolic Compounds | Feed | MF-P | NF-R | NF-P | RO-R | RO-P |
|---|---|---|---|---|---|---|
| Caffeic acid | 8.1 ± 0.5 | 7.6 ± 0.5 | 27.7 ± 1.4 | 1.8 ± 0.2 | 45.7 ± 1.2 | 0.5 ± 0.03 |
| p-Coumaric acid | 6.4 ± 0.4 | 4.3 ± 0.2 | 12.2 ± 0.8 | 2.6 ± 0.2 | 35.9 ± 1.6 | nd |
| Ferulic acid | 6.9 ± 0.6 | 6.3 ± 0.3 | 20.1 ± 1.1 | nd | 51.3 ± 1.4 | nd |
| Luteolin | 15.2 ± 0.6 | 13.7 ± 1.1 | 71.5 ± 2.7 | nd | 82.8 ± 3.1 | nd |
| 4-Hydroxyphenyl acetate | 72.6 ± 1.8 | 67.0 ± 2.6 | 29.6 ± 1.2 | 64.0 ± 3.2 | 57.1 ± 1.2 | nd |
| Hydroxytyrosol | 373.3 ± 4.8 | 320.1 ± 5.8 | 1017.5 ± 8.8 | 268.3 ± 1.2 | 1522.2 ± 7.3 | 18.8 ± 1.2 |
| Oleuropein | 106.8 ± 4.0 | 85.2 ± 2.7 | 263.2 ± 4.2 | nd | 510.0 ± 5.5 | nd |
| Tyrosol | 89.7 ± 2.1 | 68.1 ± 5.1 | 157.3 ± 4.3 | 64.8 ± 1.2 | 519.0 ± 6.2 | 5.0 ± 0.6 |
| Vanillic acid | 29.4 ± 0.3 | 27.8 ± 1.7 | 97.0 ± 2.5 | 6.5 ± 0.9 | 116.2 ± 3.1 | 1.4 ± 0.1 |
| Verbascoside | 26.7 ± 1.1 | 18.0 ± 1.3 | 82.8 ± 3.4 | nd | 130.9 ± 1.2 | nd |

*MF, microfiltration; NF, nanofiltration; RO, reverse osmosis; P, permeate; R, retentate; nd, not detectable.*

As expected, all compounds were completely or almost completely rejected by the RO membrane. Therefore, the RO retentate (RO-R) exhibited the highest bioactive compounds content. In particular, the hydroxytyrosol content (1522.2 ± 7.3 mg/L) was about five times higher than the MF feed. In the RO permeate (RO-P) only hydroxytyrosol (18.8 ± 1.2 mg/L), tyrosol (5.0 ± 0.6 mg/L), vanillic acid (1.4 ± 0.1 mg/L), and caffeic acid (0.5 ± 0.03 mg/L) were identified. Accordingly, the RO retentate showed the highest antioxidant activity in the ABTS test (IC50 6.9 ± 1.9 μg/mL), while NF permeate and RO permeate were the less active. Similar results were found in samples analysed by the DPPH test and for hypoglycaemic activity.
The set of results suggested that RO polyphenol-enriched fractions are effective in scavenging radicals and protecting lipid-oxidations and in inhibiting key enzymes such as lipase, α-amylase, and α-glucosidase, useful therapeutic targets for the development of functional products for obesity and diabetes type 2 prevention.

## 3. Citrus wastewaters

Citrus by-products are enriched in bioactive compounds, such as flavonoids and phenolic acids, recognized for their beneficial implications in human health due to their antioxidant activity and free radical scavenging ability. The UF process allows to recover these compounds in a permeate stream having a total soluble solids content and an acidity level approximating similar to that of the press liquor; suspended solids, such as proteins and fibers and high molecular weight carbohydrates such as pectins associated with cloud, are retained by the UF membrane. Polysulphone (PS) UF membranes in hollow fiber configuration and a MWCO of 100 kDa produced steady-state value of about 45 $L/m^2h$ when the raw press liquor was processed according to a bath concentration configuration in selected operating conditions up to a volume reduction factor (VRF) of 14. Operating conditions were optimized, according to the response surface methodology in order to maximize permeate flux and improve the recovery of phenolic compounds in the clarified liquor (Ruby-Figueroa et al., 2012). NF membranes can be used to fractionate the clarified liquor producing a retentate stream enriched in phenolic compounds. In particular, polyethersulphone (PES) membranes with MWCO of 1,000 Da were able to produce a pre-concentrated liquor at 32 °Brix from the clarified liquor exhibiting rejections of 97.4 % and 98.9 % towards flavanones and anthocyanins, respectively. The final concentration of the NF retentate by OD produced a concentrated solution at 47 °Brix. OD was performed at an operating temperature of 28 °C by using polypropylene hollow fiber membranes with a pore size of 0.2 μm. The NF retentate was recirculated in the shell side of the membrane module, while calcium chloride dehydrate was recirculated in the lumen side. The concentration factor of phenolic compounds in the OD retentate resulted in agreement with the concentration factor of total soluble solids due to the water removal. The final product, containing about 20 g/L of anthocyanins and about 100 g/L of flavanones, showed interesting perspectives for its use as natural colorant and/or for nutraceutical applications. The conceptual design proposed for the recovery of phenolic compounds from citrus press liquor is depicted in Figure 2.

## 4. Wastes from wine industry

The winemaking industry generates a large amount of solid and liquid by-products in a short period of time, including grape pomace, wine lees, spent filter cakes, vinasses and winery wastewater that must be treated, disposed of or reused properly in order to avoid negative environmental impacts. These by-products constitute a valuable source of phenolic compounds and, therefore, can be used for valorization of functional ingredients or bioactive phytochemicals that can be devoted to the generation of pharmaceutical, food, and cosmetic ingredients (Teixeira et al., 2014).
Traditional extraction methods, based on the use of maceration assisted by solvent extraction, are characterized by several limitations such as loss of compounds due to hydrolysis and oxidation during extraction, long extraction time and potential environmental pollution due to large volumes of organic solvent used. In this context, the development of “green” extraction and separation procedures is of great importance into industrial processes to reduce or eliminate the use and generation of hazardous substances.
Sustainable extractive technologies, such as ultrasound- and microwave-assisted extraction, followed by membrane separation methods represent a promising tool for the recovery of high-added value compounds from winery wastes and by-products.
Arboleda Mejia et al. (2019) investigated a combination of microwave/hydro-alcoholic extraction and membrane operations for the recovery of phenolic compounds from red wine lees. The hydro-alcoholic extract was previously microfiltered in order to reduce its turbidity and then fractionated with different flat-sheet polymeric membranes with MWCO in the range of 150-1,000 Da. Among the selected membranes, the 1,000 Da membrane exhibited the highest productivity in selected operating conditions (in agreement with its higher MWCO) but lower retention of phenolic compounds and sugars in comparison with the other membranes. On the other hand, the 150 Da membrane presented retention coefficients higher than 70% for all detected free low

molecular weight phenolics (Figure 3). Therefore, an integrated process based on the combination of microwave-extraction, microfiltration (polyvinylidene fluoride membrane, pore size 0.15 μm) and nanofiltration (polyamide membrane, MWCO 150 Da) was considered of practical interest for the production of concentrated fractions of bioactive compounds from red wine lees.

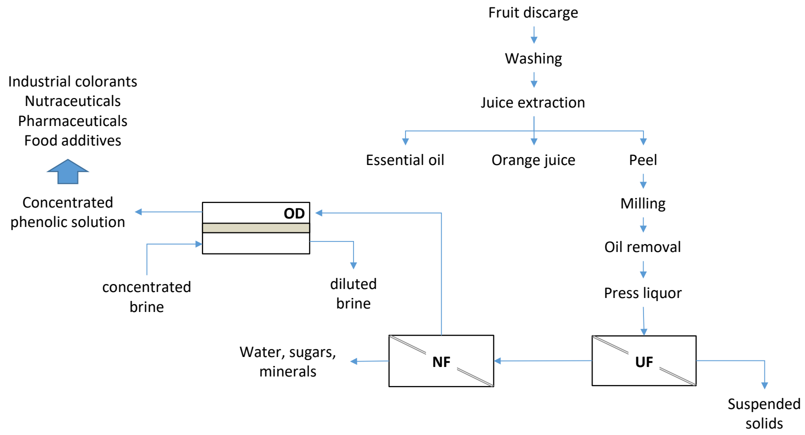


*Figure 2: Schematic of the integrated membrane process proposed for the recovery of flavonoids from orange press liquor (UF, ultrafiltration; NF, nanofiltration; OD, osmotic distillation) (adapted from Cassano et al., 2014)*

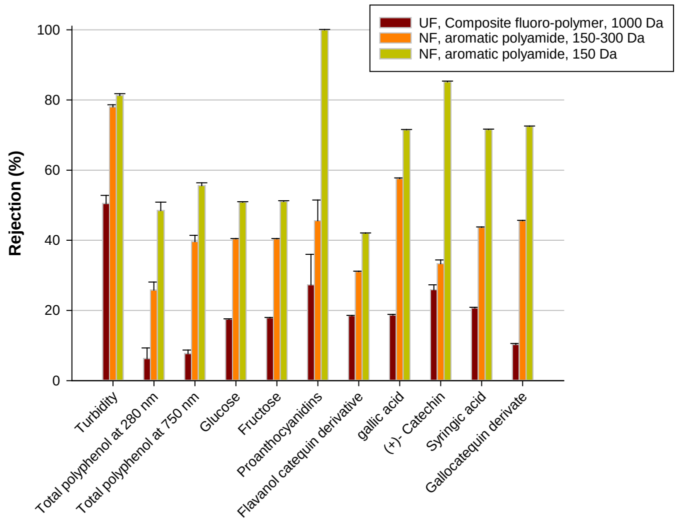


*Figure 3: Rejection of polymeric membranes towards specific compounds of clarified red wine lees extract (adapted from Arboleda Meija et al., 2019)*

Recently, cellulose acetate NF membranes were prepared and investigated for the recovery of phenolic compounds from red grape pomace extract obtained through ultrasound-assisted enzymatic extraction (Arboleda Mejia et al., 2020). The average permeate flux of prepared membranes measured in selected operating conditions (operating pressure and temperature of 20 bar and 25 °C, respectively) resulted higher than that of the NF90 membrane, an aromatic polyamide commercial membrane with a MWCO of 200 Da. These results were in agreement with the rejection values measured for different solutes and data of water permeability. In particular, it was inferred a strong correlation between the solute retention and the permeate flux values (Table 2). Among the prepared membranes, the CA400-22 membrane showed a rejection of about 73% to the total polyphenols and a rejection of about 60-70% to the antioxidant capacity. This membrane showed almost a total retention towards proantocyanidins (about 93%) and allowed to recover most part of glucose and fructose in the permeate stream (rejection values of 19.5% and 12.5%, respectively) obtaining a permeate rich in sugars. Therefore, this membrane offered the best performance in terms of separation between sugars and phenolic compounds.

*Table 2: Nanofiltration of grape pomace extract. Permeate flux ($J_p$) (at 20 bar and 25 °C) and rejection of selected membranes towards specific solutes*

| Membrane type | $J_p$ (L/m$^2$h) | Glucose rejection (%) | NaCl rejection (%) | $Na_2SO_4$ rejection (%) |
|---|---|---|---|---|
| NF90 | 26.09 ± 1.25 | 100 | 95 | 99 |
| CA316-70 | 43.38 ± 0.9 | 95 | 77 | 97 |
| CA316 | 44.44 ± 1.05 | 50 | 27 | 86 |
| CA400-22 | 50.58 ± 2.55 | 11 | 10 | 47 |

## 5. Conclusions

Pressure-diven membrane operations, also combined in a sequential design, has been investigated for the treatment of agro-food by-products according to a logic of circular economy. Tailor made processes for specific by-products have been identified through a proper selection of membrane characteristics (membrane material, pore size, geometry) as well as through the optimization of operating and fluid-dynamic conditions in order to reduce and control membrane fouling phenomena which have a strong influence on membrane productivity and selectivity towards target compounds. Experimental results indicate that these processes successfully meets the requirements for the recovery, purification and concentration of phenolic compounds with the production of concentrated fractions of potential applications in the food, pharmaceutical and cosmetic industries.

New perspectives and potentialities in this field are expected from the development of superior membranes and process engineering breakthroughs as well as through the combination of membrane operations and conventional separation technologies (i.e. adsorption, centrifugation, evaporation).

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