Chapter 4

The Use and Performance of Nanofiltration Membranes for Agro-Industrial Effluents Purification

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Abstract

Nanofiltration (NF) technology offers several advantages over classic separation processes. NF membranes have been increasingly implemented in water treatment processes (e.g., desalination of brackish water and seawater) and for wastewater (e.g., textile, pulp and paper, pharmaceutical, and agro-industrial). The specific selectivity toward small solutes and the lower energy consumption of NF membranes have enhanced their use. However, some drawbacks need to be faced when NF is applied on an industrial scale. The main drawback is fouling that reduces the production capacity of the plant and shortens the membrane service lifetime if of irreversible nature, thus increasing the operating and capital costs. Moreover, fouling alters the selectivity of the membrane and thus the rejection efficiency. This chapter focuses the use of NF for the treatment of different agro-industrial effluents (such as dairy, tomato, and olive oil) and addresses membrane fouling as the main drawback against NF competitiveness.

Keywords: dairy wastewater, olive mill wastewater, tomato wastewater, artichoke wastewater, nanofiltration, wastewater treatment

1. Introduction

In the last decades, new advanced separation technologies, less intensive in terms of specific energy consumption than conventional separation ones and "greener" regarding the minor use of chemicals and reagents to achieve the desired separation, have been developed. Concretely, membrane technology can take the lead for these purposes.

In the current scenario, scarcity of water particularly concerns agricultural irrigation, which demands more than 70% of worldwide water consumption [1]. Nevertheless, wastewater regeneration for several purposes such as irrigation stands as a solution to reduce environmental and economic impacts.

Besides, due to population increase, food production has become a major concern worldwide. Food industries are quickly multiplying all over the world because of globalization of markets and the lifting of trade barriers, thus contributing to the large-scale manufacture of a vast range of food and beverage products. Consequently, the high volumes produced, environmental impact, and nutritional value of its by-products/wastes are an enormous challenge that the food industry is facing, with the goal of valorization.

Membrane technology is modular and scalable, is environmentally friendly, requires low maintenance, and can provide high purifying standards [2–4]. In the last years, there has been a significant trend in the use of membranes for a wide range of applications, and particularly in the field of water and wastewater treatments to replace classic separation unit operations, as well as for the reclamation of effluents of different origins, especially those by-produced in agro-industries. This impulse has been a result of the new membrane materials, module designs, and the optimization of the operating conditions, in specific those for minimization of fouling [2–12].

Concretely, nanofiltration (NF) provides a series of advantages over classic separation processes. For example, for clean water production, NF technology has been replacing or working alongside reverse osmosis in water treatment processes for clean water production (e.g., desalination of brackish water and seawater) and for wastewater treatment (e.g., textile, pulp and paper, pharmaceutical, and agro-industrial) due to the cost-benefit analysis of lower-pressure operations. The specific selectivity toward small solutes and the lower energy consumption of NF membranes have enhanced their use. By contrast, in the food industry, the use of nanofiltration is too low, despite this sector has been the first one to introduce membrane technology in dairies, especially to recover cheese whey. Membrane processes that have been predominantly used are microfiltration and ultrafiltration, e.g., for removal of bacteria or to produce whey protein concentrates from ultrafiltration [13]. So, while research about using nanofiltration for by-products recovery from agro-food industry is increasing, real applications are still very low [14]. Some drawbacks must be inevitably faced when NF is applied on an industrial scale. The main drawback is fouling that reduces the production capacity of the plant and shortens the membrane service lifetime if of irreversible nature, thus increasing the operating and capital costs. Moreover, fouling alters the selectivity of the membrane and thus the rejection efficiency.

This chapter focuses the use of NF for the treatment/valorization of different agro-industrial effluents or by-products, mainly dairy, tomato, artichoke, and olive oil, and addresses membrane fouling as the main drawback against NF competitiveness.

Among agro-industrial effluents, olive mill wastewater (OMW), generated during the production of olive oil in factories commonly known as "mills," is one of the most heavily polluted wastewater, depending on the procedure used, reaching chemical oxygen demand (COD) values up to 100,000 mg O_2 L^{-1}. The volumes of these effluents have increased in the last decades due to the marked increment of olive oil consumption worldwide given its well-proven health-promoting properties (nutritional, antioxidant, anti-inflammatory, cosmetic). This fact led to the change in the extraction technology from batch to continuous production procedures as a response to cope with this higher demand. Currently, average-sized modern olive oil mills generate several tens of cubic meters of OMW daily, which sums up several millions of cubic meters a year.

The same applies to other agro-industrial effluents like tomato and artichoke ones. Moreover, one critical aspect in the treatment management of these types of agro-industrial effluents relies on the high variability in volume and organic load, as well as on the seasonality of by-production. This poses an additional handicap to find efficient treatments focused on this type of effluents.

Otherwise, in dairies, NF has been mostly used for the demineralization of salted and acid whey, substituting reverse osmosis, or to produce desalted lactose-containing whey in a single process. The performance of NF is mainly affected by concentration polarization due to an accumulation of solutes at the membrane surface and, simultaneously, to the increase of osmotic pressure, which reduces the effective transmembrane pressure. The resulting boundary layer is usually the reversible part of NF fouling, in which its characteristics are related to the wall shear stress and the driving force (average transmembrane pressure). Besides, that boundary layer can give rise to irreversible adsorption or precipitation of foulants, namely, calcium phosphates, at the membrane surface [15]. The mineral fouling depends on environmental conditions, such as pH and temperature, and should be controlled during NF process. The prevention and control of fouling in NF of dairy or other products can be done through selection of an adequate feed pretreatment, choice of membrane and module design, and optimizing operating conditions.

2. Membrane processes for tomato manufacturing and artichoke wastewaters

Wastewater by-produced during tomato manufacturing is characterized by a dark color and bad odor and presents a considerable concentration in organic compounds, suspended solids, and ground particles [16, 17]. This process water, generated during cleaning, sorting, and moving of tomatoes, constitutes the main tomato industry wastewater and deteriorates very quickly. An additional difficulty for the treatment of these effluents, as previously said, relies on the variability in time and space of composition and pollutant concentration, as it is very seasonal, and depends on the geographical zone, type of fruit, composition, as well as changes in the production, among others. The typical composition of this wastewater, reported by Iaquinta and co-workers [18], is pH around 6.6, high electrical conductivity (2.56 mS cm^{-1}), relatively high COD (1200–1700 mg O_2 L^{-1}), and total organic carbon (TOC; 340 mg L^{-1}).

Because of this, tomato manufacturing wastewater cannot be discharged straight in municipal sewage systems, as the high organic content exceeds legal limit standards. Thereby, the treatment of these effluents is needed beforehand. In this framework, Iaquinta and co-workers proposed a combined treatment process comprising a biological treatment followed by NF, at a pilot scale [16, 17]. The used NF membrane was a commercial spiral-wound module (Desal-5 membrane, model DK2540, produced and supplied by Osmonics). NF process optimization was carried out relying on critical flux methods, in order to avoid operating at fouling conditions. Within critical flux conditions, short-term fouling phenomena are drastically reduced, and, consequently, the productivity and the longevity of the membranes are significantly increased. Critical fluxes were measured at different recovery levels. The authors reported purification of the wastewater up to a water compatible with municipal sewer system requirements, with a recovery rate of 90%. A permeate stream with EC of 1778 μS cm^{-1}, COD of 465 mg O_2 L^{-1}, and TOC of 168 mg L^{-1} was attained, and short-term fouling issues could be avoided by operating the system at permeate fluxes about or below 8.2 L hm^{-2}. Moreover, the process was modeled, which permitted the prediction of a final critical flux value equal to 10.1 L hm^{-2}. On the other hand, the authors also prepared a synthetic effluent, by adding mature tomatoes to tap water in a ratio equal to 1:20 and 1:1000, respectively. An analysis performed on the synthetic wastewater confirmed similar chemical characteristics, in line with the real ones. Furthermore, a similar fouling behavior was found for the NF membrane.

Artichoke is cultivated for its immature inflorescence, in which the head flower composes the edible portion. The main producers are Egypt, Italy, and Spain. It is widely consumed as fresh, frozen, or conserved vegetable [18]. Given that just a small part of this vegetable (around 30%) is used in the food industry, artichoke processing generates a huge amount of solid waste (mainly leaves, stems, bracts of the artichoke plant) that is used as animal feedstuff or manure [19] and wastewaters, such as blanching waters, that need to be managed. Nowadays, attempts have been made to reuse waste solid material as a source of health-promoting compounds, leading to improved management of industrial residues and economic benefits for the agricultural and food sector [20, 21].

Artichoke wastewater is the extract from artichoke solid waste. This material contains suspended solids, macromolecules, and prebiotic sugars [18], and it is considered a cheap source of fructo-oligosaccharides. Machado et al. [18] examined the clarification, purification, and concentration of artichoke extract by sequential microfiltration (MF)—aimed to clarify the artichoke extract—followed by NF, to purify and concentrate the prebiotic sugars. The study was performed on a laboratory scale and tested different MF and NF membranes as well as different operation pressures. MF pretreatment achieved total clarification of the extract; that is, 100% prebiotic sugars were reported to be recovered in permeate stream. However, MF membranes presented a certain flux decline (20–40% with respect to the initial values) that the authors attributed to cake layer formation as observed by surface analysis.

Subsequent NF was performed with the permeate of the less fouled MF membrane (polyethersulfone (PES), 50 μm pore size). Three NF membranes were tested for this purpose, that is, NP010 (Microdyn-Nadir, PES, 1 kDa molecular weight cutoff (MWCO)), NP030 (Microdyn-Nadir, PES, 400 Da MWCO), and NF270 (Dow, polyamide, 150–300 Da MWCO). Total retention of prebiotic sugar was achieved with the latter membrane, allowing the obtention of a concentrate pool rich in these compounds, with functional prebiotic properties, which according to the authors could be used as ingredient on foodstuff applications. Nevertheless, the authors pointed that for obtaining a high degree of purification other techniques should be further or alternatively employed.

Moreover, this NF membrane (NF270) was reported to yield a high flux (up to 120 L h^{-1} m^{-2}), as well as the highest retention toward the target species. As reported by the authors, even though NP010 and NP030 membranes present higher MWCO, their filtration fluxes under the given operational conditions were below those yielded by NF270. The former membranes are made of polyethersulfone, which has lower affinity with water than polyamide, the material of which NF270 membrane is made of, and thus lower permeate fluxes were observed.

Another proposal for artichoke wastewater treatment and fractionation was examined recently by Conidi and co-workers [22]. They reported the results of an integrated ultrafiltration (UF) and NF membrane process, at a lab scale. An evaluation of the used membranes was made based on the permeate flux, fouling index and water permeability recovery. Typical chemical composition of artichoke wastewaters reported by these authors is here presented: suspended solids 2.5 ± 0.10 (%), glucose 960 ± 1(mg L^{-1}), fructose 837 ± 1.07 (mg L^{-1}), sucrose 1050 ± 0.41 (mg L^{-1}), total antioxidant activity 8 ± 0.042 (TAA, mM Trolox), chlorogenic acid 251 ± 2.64 (mg L^{-1}), cynarine 164.7 ± 1.41 (mg L^{-1}), and apigenin-7-O-glucoside 101 ± 2 (mg L^{-1}). On the one hand, the used UF membranes were hollow fiber ones and aimed to remove suspended solids from the artichoke extract, to submit the clarified liquor to the NF step. This preliminary UF clarification step permitted the rejection of most suspended solids in the raw water stream. The initial permeate flux was reported to decrease during the UF process by increasing the volume recovery factor (VRF) due to concentration polarization, fouling phenomena, and increased concentration of solutes in the retentate, such that a steady-state permeate flux of 10 kg hm^{-2} was obtained at VRF of 3. Moreover, it is important to highlight that the initial water permeability of the UF membrane could not be completely recovered after the applied cleaning protocol, which comprised two cleaning steps with alkaline (NaOH) and enzymatic solutions: the NaOH solution cleaning recovered just 65% of the initial water permeability, whereas the subsequent enzymatic cleaning step permitted the recovery of up to 88% of the initial water permeability of the UF membrane.

Regarding the NF step, two different spiral-wound membranes (Microdyn-Nadir Desal DL and GE Water & Process Technologies NP030) with different properties were examined. These membranes were noted to present different selectivity toward phenolic compounds and sugars. Both membranes were observed to provide high rejection toward phenolic compounds (chlorogenic acid, cynarine, and apigenin-7-O-glucoside) and, consequently, toward the total antioxidant activity (TAA). On the other hand, the Desal DL NF membrane was capable to provide high rejection (100%) toward sugar compounds (glucose, fructose, and sucrose) in contrast with NP030 membrane (4%).

Furthermore, the Desal DL membrane yielded higher permeate fluxes than NP030 membrane, despite its minor nominal MWCO: the initial permeate flux was around 21 kg h^{-1} m^{-2}, which decreased to 18 kg h^{-1} m^{-2} at a steady state upon VRF of 3, whereas for NP030, a lower steady-state permeate flux was measured (5 kg h^{-1} m^{-2}). The fouling index values measured for both selected membranes on the base of their water permeability before and after the treatment of clarified artichoke wastewaters also supported this: the NP030 membrane showed a higher fouling index (41%) in comparison with the Desal DL (1.7%).

As stated by the authors, the proposed process enabled significant advantages in terms of reduction of environmental impact, recovery of high-added-value compounds, saving of water, and energy requirements. It permitted obtaining different valuable products: a retentate fraction (from NP030 membrane) enriched in phenolic compounds suitable for nutraceutical, cosmeceutical, or food application; a retentate fraction (from Desal DL membrane), enriched in sugar compounds, of interest for food applications; and a clear permeate (from Desal DL membrane) which can be reused as process water or for membrane cleaning.

Fouling mechanisms are very important to fully understand what is taking place between the membrane and the effluent, in view of the adoption and implementation of adequate decisions for the successful design of the membrane plant. This comprises the setup of specifically tailored pretreatment process and optimized operating conditions. Irreversible fouling arises quickly on the membranes due to the high concentration of pollutants when wastewater is purified without any pretreatment [2–12]. Therefore, adequate and optimally designed pretreatment processes on each particular feedstock, in other words, pretreatment tailoring of membrane processes, must be developed in order to maximize productivity and minimize fouling.

3. Membrane processes for olive mill wastewater purification

OMW is characterized by strong odor, violet-dark color, acid pH, high organic matter content, and high saline toxicity, as confirmed by its high EC values [23]. Uncontrolled disposal of these effluents constitutes an environmental hazard, causing contamination of soil and aquifers, underground leaks, water body pollution, strong odor nuisance, plants growth inhibition, hindrance of self-purification processes, as well as negative effects on the aquatic fauna and the ecological status. Due to the presence of high COD load including recalcitrant compounds, as well as fats and lipids, direct discharge of these wastewaters to the municipal sewage treatment plants is not allowed. In fact, as the majority of municipal wastewater treatment plants include biological treatment processes, legal limits for wastewater discharge into sewer system are set to prevent the inhibition of the microbiological activity. Moreover, discharge of OMW to the ground fields and superficial water bodies is currently prohibited in Spain, whereas in Italy as well as in other European countries, only partial discharge on suitable terrains is allowed; otherwise, in Portugal OMW can be stored and used for irrigation of arbustive cultures under controlled manner (Despacho Conjunto 626/2000) [23–28].

Several wastewater streams can be produced in an olive oil mill, wastewater from the washing of the olives (OWW), olive mill wastewater (OMW-3, only for three-phase mills), wastewater from olive oil washing (OMW-2), and wastewater from cleaning processes. OWW has a high concentration of suspended solids (mainly peel, pulp, ground, branches, and leaf debris) dragged during the olive fruit washing process, but low concentration of dissolved organic matter—which varies in function of the water flow exchange rate in the washing machines and ripeness state—usually below standard limits for discharge on suitable superficial land.

Currently, not only the Mediterranean countries, where this industry is ancestral and represents an important sector of the industrial economy (Spain, Italy, Portugal, Greece, and Northern African countries—Syria, Algeria, Turkey, Morocco, Tunisia, Libya, Lebanon, and Egypt), are affected by this problem but also France, Serbia and Montenegro, Macedonia, Cyprus, Turkey, Israel, and Jordan, as well as the USA, the Middle East, and China, where this industry is growing each year.

The two-phase extraction process appeared in the 1990s as a more ecological system, has been strongly promoted in Spain, and is now being implemented in Portugal and Greece.

Nevertheless, the three-phase system is still surviving in other countries where scarcity of financial support has not favored the change of technology. In the two-phase extraction, water injection is only performed in the final vertical centrifugation step (olive oil washing). The effluent volume derived from the decanting process (OMW-2) is thus reduced on average more than 30%, if compared to the three-phase system (OMW-3). On the other hand, OMW-2 contains lower organic load because part of the organic matter remains in the solid waste, which presents higher moisture than the pomace from the three-phase system (60–70 vs. 30–45%). The measured COD in OWW is commonly in the range 4–16 g O_2 L^{-1} in contrast with up to 30–200 g O_2 L^{-1} for OMW-3. Inorganic compounds including chloride, sulfate, and phosphoric salts of potassium, calcium, iron, magnesium, sodium, copper, and traces of other elements are also common traits of OMW and OWW [28]. The average physicochemical composition of the different types of olive mill effluents is briefly reported in **Table 1**.

The major problem in the treatment of OMW relies on the large volumes produced with high concentration of organic matter (polysaccharides, sugars, polyalcohols, proteins, organic acids, tannins, fatty acids, oil, and organohalogenated pollutants) including a wide variety of phenolic compounds [23–28]. Among them, phenolic compounds represent one of the major factors related to the environmental problems caused by this effluent and its low biodegradability. They are highly concentrated and carry different negative effects such as phytotoxicity, toxicity against aquatic organisms, suppression of soil microorganisms, and difficulty to decompose. Despite that fact, phenolic compounds possess high antioxidant activity that makes them interesting for the food, pharmaceutical, and cosmetic industry. Because of that, the recovery of these compounds by different physicochemical methodologies should represent an important objective for the olive oil industry, obtaining added-value extracts of one of the main olive oil industry by-products.

Furthermore, geographical dispersion and the small size of olive oil mills, as well as the previously mentioned seasonality of production, are drawbacks for establishing a cost-efficient

Parameter	OMW-3	OMET-2	OMW-2	OWW
pH	5.4	7.2	4.9	6.3
Moisture (%)	93.4	99.4	99.3	99.7
Total solids (%)	6.6	0.59	0.6	0.27
Organic matter (%)	5.8	0.39	0.49	0.10
Ashes (%)	0.9	0.21	0.11	0.17
BOD_5 (g O_2 L^{-1})	42.0	0.29	0.79	0.50
COD (g O_2 L^{-1})	151.4	7.1	7.8	0.8
Total phenols (mg L^{-1})	921.0	86.0	157.0	4.0
EC (mS cm^{-1})	7.9	1.9	1.3	0.9

OWW: olive washing wastewater; OMW-3 and OMW-2: olive mill wastewater from three-phase and two-phase continuous extraction procedures; OMET-2: mixture of all effluents produced in the olive mill, including OWW, OMW, and from other activities in the facility (e.g., cleaning and sanitation); COD: chemical oxygen demand; BOD_5: biological oxygen demand; EC, electrical conductivity.

Table 1. Average physicochemical composition of the different types of olive mill effluents [23–28].

treatment/management for the produced effluents. Additionally, the physicochemical composition of these effluents is very variable as it depends on the edaphoclimatic conditions of the region and cultivation practices, the processed olives (type, quality, and maturity), as well as the oil extraction process.

Regarding the use of membranes for agro-industrial wastewater stream treatment, characterized by high concentration in colloids and suspended solids, the major technical drawback for implementation is the high fouling potential (**Figure 1**). Membrane fouling is mainly caused by colloids, soluble organic compounds, and microorganisms and, thus, can be of biological, organic, or scaling source. In any case, fouling increases the feed pressure and obliges to frequent plant shutdown for membrane cleaning procedures. In this regard, as this kind of effluents contain not only high concentrations of organic pollutants but also inorganic matter deleterious scaling problems may happen.

Specifically tailored pretreatment processes can be set upstream the membrane module to avoid high fouling rates, especially in cases in which the feed stream would rapidly lead to zero flux conditions if no pretreatment is conducted. Among recent literature on the topic, Stoller and Chianese [11] reported the purification of OWW by batch-sequenced spiral-wound UF and NF polymeric membranes preceded by solid/liquid (S/L) separation by coagulation-flocculation. OWW contains moderate organic pollutant load but is rich in suspended solids. To this end, the authors tested two different polyelectrolytes: aluminum sulfate (AS) or aluminum hydroxide (AH). Despite similar COD and BOD_5 removal efficiencies, the former provided enhanced flux (7.7 L h^{-1} m^{-2} at 10 bar) of the NF membrane, which yielded a treated permeate dischargeable in municipal sewers. Similar results were obtained by using

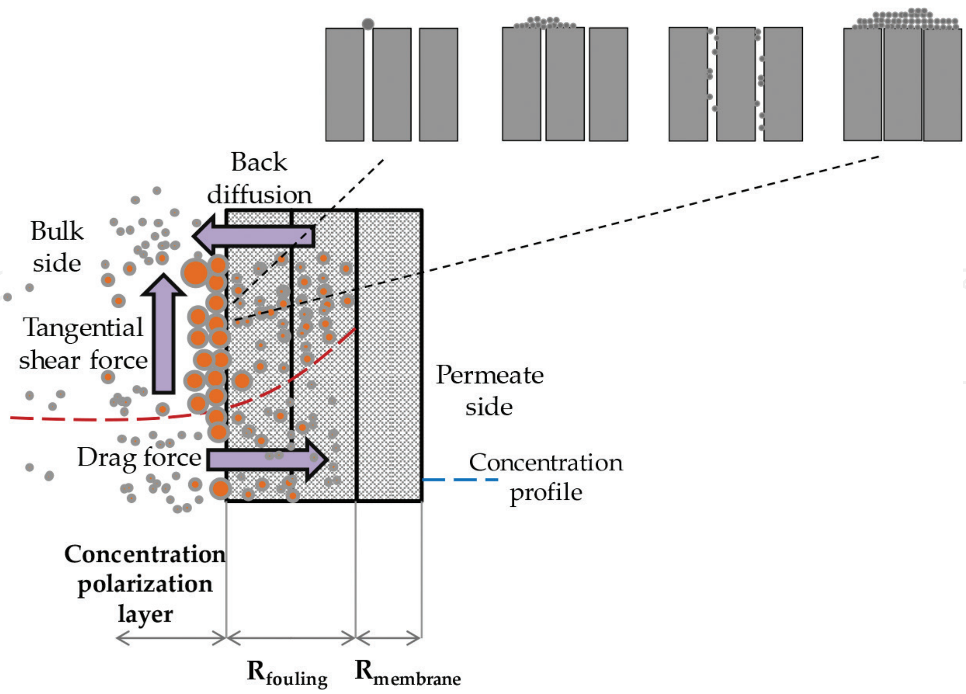

Figure 1. Concentration polarization and membrane fouling mechanisms during membrane filtration: from left to right, (i) pore sealing or complete pore blocking, (ii) intermediate pore blocking, (iii) standard blocking or pore filling/constriction, and (iv) cake or gel layer (adapted from Ochando-Pulido and Martínez-Férez [29]).

the same coagulants-flocculants on OMW-3 [12], much more polluted than the former OWW, up to 55,000 mg O_2 L^{-1} COD, in an integrated process comprising MF, UF, NF, and RO in batch sequence, from which a final stream complying with irrigation standards was attained. Moreover, UV photocatalysis (PC) with titanium dioxide anatase nano-powders and aerobic digestion (AD) was compared with the former pretreatment, also yielding an equivalent outlet stream. PC was more efficient upon the lowest residence time (24 for AS vs. 72 h for PC vs. 7 days for AD) and enabled the highest membrane productivity (13.5 L h^{-1} m^{-2} at 13 bar).

Results obtained by Stoller and co-workers highlight the importance of adequate pretreatment processes, underlining the fact that higher pollutant abatement is not sufficient to ensure the suitability of the pretreatment. It is necessary to confirm that the shift carried by the pretreatment process on the particle size (dp) distribution of the effluent does not lead to a stream with particles of similar size of the membrane's pores (Dp) that would cause deleterious fouling problems by pore plugging and clogging [30–38].

Centrifugation integrated with NF was also tested for OMW-3 [39], permitting to achieve fluxes of up to 21.2–28.3 L h^{-1} m^{-2} and COD removal efficiencies of 59.4–79.2% (at 10 bar). For OMW-3, Zirehpour and co-workers applied MF (50, 5, and 0.2 μm) and UF prior to NF [40]. However, MF membrane showed significant fouling problems, common in MF membranes. On the other hand, the commercial UF membrane examined provided higher permeate flux than the lab-made polyethersulfone (PES) one, but the antifouling properties and rejection efficiency of the latter were reported to be superior. Regarding the use of NF membranes, commercial NF-90 and NF-270, as well as NF-(self-made) one, NF-270 yielded higher permeate flux than NF-90 and NF-(self-made), but major rejection efficiency was found for NF-90. NF-90 and NF-(self-made) membranes are fully aromatic polyamide membranes prepared from interfacial polymerization of m-PDA and TMC. These membranes have relatively rough membrane surfaces. Otherwise, NF-270 is a semi-aromatic piperazine-based membrane with considerably smoother surface, significantly higher water permeability, and lower salt rejection than the former ones, as well as higher hydrophilic and negative charge. COD removals from NF-90 at VRF = 1 and VRF = 2.5 were about 93.4% (COD = 690 ± 10 mg O_2 L^{-1}) and 79% (COD = 2200 ± 10 mg O_2 L^{-1}), respectively. When NF-270 permeation was used as feed to NF-90, the permeate flux of NF-90 was 22.4 L h^{-1} m^{-2} at the beginning of VRF filtration, while permeate flux of NF-90 without NF-270 was 15.1 L h^{-1} m^{-2}, which means that this arrangement with NF-270 followed by NF-90 enhanced the permeate flux (5 L h^{-1} m^{-2} at 5 bar) up to 48%.

Another study by Ochando-Pulido and co-workers [41–43] presented a batch membrane-in-series processes, UF followed by NF, both polymeric in spiral-wound configuration, for the reclamation of OMW-2. Previously, flocculation (pH-T) and UV photocatalysis with ferromagnetic titanium dioxide nanoparticles were performed. The whole pretreatment sequence led to minor membrane area requirements (104.6 and 81.4 m^2, respectively) and enhanced productivity supported by minimized fouling rates. A final treated permeate compatible with irrigation use was obtained. On the other hand, the mix (1:1 v/v) of OMW-2 with OWW enhanced significantly the fluxes observed on both UF and NF membranes, 15.5 and 22.2 L h^{-1} m^{-2}, respectively, which were stable in time [43].

Some authors have also tried to extract added-value compounds contained in these effluents (polyphenols, sugars, pectin) by concentration with membranes. For example, Paraskeva and co-workers fractionated and recovered the phenolic fraction from OMW-3 (Greece) with UF + NF + RO membranes, including 80 μm polypropylene filtration pretreatment [28]. NF spiral-wound polymeric membranes (with 200 Da MWCO) were tested to further purify the UF permeate. In NF tests, a pressure value (TMP) of 20 bar led to satisfactory permeate flow (100–120 L h^{-1}) and 95% rejection of the phenolic concentration. Otherwise, 78% phenolic fraction recovery from OMW-3 (Italy) was achieved by Garcia-Castello et al. [44] with a process comprising ceramic tubular MF (Al_2O_3, 200 nm average pore size) followed by a hydrophobic polyethersulfone spiral-wound NF (Nadir N30F cutoff 578 Da). The NF polyphenol-enriched permeate, with valuable antioxidant properties, could be used in formulations in food, cosmetic, and pharmaceutical industries after the final vacuum membrane distillation (VMD) or osmotic distillation (OD). However, fouling on the membranes was evidenced throughout the whole proposed treatment process: the initial permeability could not be restored after the cleaning procedure and decayed progressively after each working cycle noticing irreversible fouling phenomena on the membrane.

On the other hand, Di Lecce et al. [45] proposed the fractionation of OMW-3 by a two-step MF and NF membrane process, at a pilot scale. The MF membranes were tubular made of polypropylene, whereas the NF membrane was in spiral-wound configuration and consisted of a polyamide thin-film composite. Filtration through cotton fabric filters was performed as pretreatment. In these conditions, the NF membrane achieved 98% rejection of COD, dry matter, and phenols. The quality of the obtained purified NF permeate was close to the standards established for its discharge in surface water bodies, but the dynamic performance of the membranes was not reported.

Recently, Ochando-Pulido and co-workers [46] reported the simultaneous phenol recovery and treatment of OMW-2 by NF. In their work, a polymeric TFC NF membrane was studied. Primarily, different pretreatments (sedimentation, centrifugation, and coagulation-flocculation) upstream the membrane unit were examined, adequating the effluent characteristics, that is, reducing the organic and inorganic concentration without compromising the phenolic content for its ulterior recovery. Among them, centrifugation was the most effective pretreatment in terms of TSS abatement, providing 85.7% recovery of supernatant (only 14.3% sludge), no phenolic compounds loss, and subsequently the highest EC and COD NF rejection. The fact that centrifuges are already available in the olive mills, implying minimization of fixed costs and needless of chemicals (flocculants), reinforces the proposed process. Moreover, this pretreatment enhanced the downstream stable membrane flux, up to 64.52 L h^{-1} m^{-2}, concentrating the feed up to 8.4 times. The obtention of a permeate stream with very good saline quality, 86.8% reduced COD, and practically free of phenolic content, thus minimized in its recalcitrant and phytotoxic potential, and a concentrate pool enriched in high-added-value antioxidant compounds (up to 1315.7 mg L^{-1}) would contribute to the economic feasibility of the reclamation process.

As it can be seen (**Table 2**), interesting added-value compounds contained in OMW may be recovered, concentrated, and fractionated with the aid of the adequate membranes, to counterbalance the treatment process costs of these agro-industrial effluents. Further investigation is still to be done to comprehend, model, control, and minimize associated fouling problems and the selection of optimal membrane materials.

Author/s	Raw OME source	Tretment process target	Scale	Process flow-scheme	Used membranes characteristics	Dynamic fouling-flux behaviour	Achieved standards	Results
Stoller et al. [37]	Continuous 3-phase olive oil extraction	OVW and OVW for sewers discharge or irrigation + fouling inhibition and prediction	Pilot (batch)	(1) Pretreatment among flocculation/ UV-TiO_2 photocatalysis/ aerobic digestion/ MF, followed by (2) UF + NF + RO	Composite SW MF (300 nm), UF (2 nm), NF (0.5 nm) and RO (<0.1 nm); operating below critical pressure	Lowest flux drops MF 17.3–18.9%, UF 23.1%, NF 18.5%, RO 22.9–23.7%; reversible fouling removed after cleaning	Overall COD abatement 98.8–99.4%	Italian standards for municipal sewer system discharge (COD values below 500 mg L^{-1}) achieved
Paraskeva et al. [28]	Continuous 3-phase olive oil extraction	Fractionation of value by-products to and effluent reclamation	Pilot (batch)	(1) 80 µm polypropylene filter, (2) UF, (3) NF and (4) RO	Multichannel UF (zirconia, 100 nm, 1–2.25 bar); polymeric SW NF (200 Da, 20 bar) and SW RO (100 Da, 40 bar)	Fouling data not reported; 100–120 L h^{-1} within NF, 30–32 L h^{-1} with RO	90% lipids and 50% phenols separated by UF; 95% phenols removal	Effluent suitable for irrigation or aquatic receptors
Coskun et al. [39]	Continuous 3-phase olive oil extraction	OMW reclamation for sewers discharge or reuse in process	Pilot (continuous)	(1) Centrifugation, (2) UF, (3) NF and (4) RO	UF cellulose and polyehtersulfone, NF polyamide and RO polyamide	Permeate fluxes up to 21.2–28.3 L m^{-2} h for NF membranes and 12.6–15.5 L m^{-2} h for RO membranes	COD removal 59.4 –79.2% for NF membranes, whereas 96.2–96.3% for RO membranes	Even though these values of conductivities were within acceptable standards for drinking waters, higher effluent COD values were observed, due to fermentation products during storage of the raw effluent
Garcia-Castello et al. [44]	Continuous 3-phase olive oil extraction	OVW reclamation + selective separation of added-value products	Pilot (batch)	(1) MF, (2) NF and (3) OD or VMD	MF ceramic (Al_2O_3, 200 nm, 0.72 ± 1 bar); SW NF (hydrophobic PES, 578 Da, 8 bar)	35% MF initial flux drop and incomplete restore after cleaning (106 L h^{-1} m^{-2} bar); 35% NF initial flux (4.68 L h^{-1} m^{-2}) drop above VRF = 3	MF achieved 91 and 26% TSS and TOC reduction; NF removed 63% TOC and TC reduction in MF permeate	NF permeate stream containing polyphenolic compounds for food, cosmetic or pharmaceutical sectors; 0.5 g L^{-1} free LMW polyphenols, with 56% hydroxytyrosol, obtained by treating the NF permeate by OD

Author/s	Raw OME source	Tretment process target	Scale	Process flow-scheme	Used membranes characteristics	Dynamic fouling-flux behaviour	Achieved standards	Results
Zirehpour et al. [40]	Continuous 3-phase olive oil extraction	OMW reclamation for irrigation reuse purposes	Pilot (continuous)	MF-UF-NF membrane system	MF (50, 5 and 0.2 μm), UF (100–35 kDa) and NF (450–150 Da)	34.1 $L\ h^{-1}\ m^{-2}$ for UF and 9.4 $L\ h^{-1}\ m^{-2}$ for NF	51.2% UF COD rejection and 64% NF salt rejection (VRF = 4)	98.8% COD removal in whole integrated system, with applied pressure for NF lower (5 bar) in comparison with other studies
Ochando et al. [41–43]	Continuous 2-phase olive oil extraction	OMW reclamation for sewers discharge or reuse in process	Pilot (semi-continuous)	(1) UF followed by (2) NF and (3) RO	Composite PA/PS SW	13.2 $L\ h^{-1}\ m^{-2}$ for UF 10.5 $L\ h^{-1}\ m^{-2}$ for NF steady-state performances	90.5% UF and 82.8% NF COD removal	Final treated effluent compliant with standards for reuse in olives washing machines

SW: spiral-wound; LMW: low molecular weight; OD: osmotic distillation; VMD: vacuum membrane distillation; CA: cellulose acetate; PES: polyethersulfone; PS: polysulfone; PA: polyamide; PVDF: polyvinylidenefluoride ; ZO: zirconium oxide; VRF: volume recovery factor.

Table 2. Main research works on olive mill wastewaters treatment by nanofiltration membrane technology.

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4. Membrane processes for recovering and purifying dairy by-products

The largest by-product from the milk processing industry is cheese whey [47]. Worldwide, whey production is estimated at 180–190 million tons per year, which is one of the most challenging and demanding environmental aspects of this activity since only 50% is currently processed into products, such as whey protein concentrates and isolates [48]. Cheese whey contains about 55% of the nutrients of milk, namely, soluble proteins (20% of the milk proteins), lactose, minerals, and vitamins, which give it a high nutritional value [49]. On the other hand, this composition is also responsible by its high environmental impact, with values of BOD_5 and COD in the range 27–60 and 50–102 g L^{-1}, respectively [50].

Due to the physical-chemical composition of ultrafiltration permeates, where lactose is the major compound of the dry matter and several ions are present (sodium, potassium, calcium, magnesium, chloride, phosphate, citrate), nanofiltration can play an important role in separation/valorization of this fraction.

One of the most important uses of nanofiltration is the production of whey-demineralized lactose concentrates for the food industry, or even, if enough purification is achieved, for pharmaceutical purposes. During nanofiltration of these permeates, some problems can occur. The accumulation of solutes of lower molecular weight on the membrane surface leads to an increased osmotic pressure and polarization concentration phenomena, giving rise to a lower performance, with a decrease of permeate fluxes and altering its selectivity. However, the major drawback of this process is the fouling caused by mineral precipitation of calcium phosphates.

Rice and co-workers [51] carried out nanofiltration of ultrafiltration permeates using polyamide membranes NF270. They observed a severe flux decline during filtration at high temperatures and pH, due to calcium phosphate precipitation, because of its lower solubility in these operating conditions. However, washing with an acid solution allowed to recover water flux. Those authors suggested that by changing the pH of the feed, fouling could be avoided, despite changing the separation properties of the membrane.

Cuartas-Uribe and co-workers [52] also studied the concentration of lactose from whey ultrafiltration permeates, combining concentration by nanofiltration with continuous diafiltration modes, and found that the best operating conditions were a transmembrane pressure of 2.0 MPa and a volume dilution factor of around 2.0, because a good removal of chloride was possible with the lowest lactose loss for the permeate. Authors claimed that no fouling problems were detected during NF tests, but experiments at a larger scale to evaluate the economic feasibility of the process are essential.

Dairy wastewaters, generated during production of dairy products (milk, cheese, butter, yogurt), usually contain remains of milk, casein fines, protein, lipids, lactose, starters, enzymes, detergents, and chemicals from the cleaning and disinfection processes used in the plant. Similar to what happens with the recovery of cheese whey nutrients, where membrane technologies have a very prominent place, also in the treatment of wastewater from dairy products, their use has been growing a lot. The most used membrane processes are mainly ultrafiltration, nanofiltration, and reverse osmosis. When nanofiltration or reverse osmosis are directly used to recover the nutrients (proteins, lactose) contained in dairy wastewaters, also chemicals are retained by the membrane, whereby the use of retentates is a major problem. Besides, during this process, the increase of concentration polarization and osmotic pressure phenomena, due to accumulation of small organic molecules and salts near the membrane surface, leads to a sharp decrease of permeate fluxes and change membrane selectivity.

Luo and co-workers [53], based on the knowledge about recovery of nutrients from cheese whey, proposed a two-stage UF/NF process for the treatment of a model dairy wastewater, being in mind that at the first stage (UF) protein was recovered, and at the second one (NF), a retentate rich in lactose and a permeate free of organics was produced. The authors suggested that both UF and NF retentates of UF could be used for bioenergy production. To control the performance of the membranes used in both stages, the authors calculated the membrane hydraulic permeability before and after the trials, the recovery of solutes, the apparent rejections of solutes, and the irreversible fouling. Based on their experimental results, they concluded that a sequence of UF/NF to treat model dairy wastewaters can be a good proposal to solve the problem of the large volumes of these effluents that are produced worldwide. However, it should be emphasized that experiments with real solutions are needed, due to the complex composition of these types of samples, where other compounds, such as casein fines, lipids, microorganisms, detergents, and other cleaning chemicals, are also present, thus affecting membrane performance.

In order to improve the process proposed by previous researchers, Chen and co-workers [54] proposed an integrated process for reclamation of dairy wastewaters using a model solution. This process includes isoelectric precipitation of caseins—ultrafiltration-nanofiltration of the permeates of UF, producing a lactose concentrate which was used for acid lactic production through fermentation by *B. coagulans* IPE22 and a final reusable permeate. The experiments were performed in a dead-end filtration cell and in a pilot-scale plant. For UF, the most hydrophilic membranes were selected for experiments, due to its lower fouling potential by whey proteins, as was also observed by other authors during ultrafiltration of cheese whey [55]. Regarding NF, the results obtained allowed to conclude that the previous separation of casein, before UF, enhanced the performance of subsequent NF process, because irreversible fouling decreased from 44.4 to 11.1%, in the pilot plant test. While this work presents an improvement in relation to the previous work [53], it is important to stress that, with real dairy wastewaters, the major problem in what concerns nanofiltration of the permeates of UF is the concentration of salts, namely, calcium phosphates. In milk, the concentration of calcium and phosphate ions is very close to its solubility constant, and so since during the process of NF, both lactose and calcium phosphates are concentrated, this can lead to mineral precipitation on membranes, thus sharply decreasing the permeate fluxes.

Bertoluzzi and co-workers [55] compared the performance of two double-stage membrane processes for treatment of dairy wastewaters: (i) microfiltration (MF) plus NF and (ii) MF plus OI. For MF, a hollow fiber module was used, being membranes made of poly(ether sulfonate)/poly(vinyl pyrrolidone) (PES/ PVP) mixture with a 0.20 μm pore size. In the NF and RO experiments, polymeric flat-type membranes were used, being these membranes made of polyamide composites. For the NF experiments, they used two different membranes (NF90 and NF), which are made of the same material but have different rejection properties, since NF90 is a tighter membrane, while the other one is a looser membrane, as can also be confirmed by their

Author/s	Byproducts/ dairy wastewaters	Module	Pretreatment	Membrane characterisitics	Achieved standards	Results
Cuartas-Uribe et al. [52]	Cheese whey	Spiral wounded module with an active surface of 2.51 m^2 (batch and continuous)	Pre-concentration by ultrafiltration	Thin film composite (TFC), DS-5DL, with polyamide active surface (cut-off of 150–300 Da)	Both lactose and whey demineralization were achieved with the combined process concentration/continuous diafiltration	NF permeate should be further treated in order to discharge into sewers, due to this COD values
Luo et al. [53]	Model and real dairy wastewaters	Rotating disk module (RDM)	Real effluents pretreated by two sieves with pore sizes of 0.25 and 0.10 mm	NF 270 made of polyamide and with cut-off 150–200 Da	Dairy wastewaters with pH between 7–8 are most suitable to be treated by NF using RDM due to a good compromise between permeate flux, membrane fouling and permeate quality. Membrane fouling is very sensitive to pH in the range 8–10	Similarity between model and real dairy wastewaters can be a valuable tool for process control in industrial applications
Luo et al. [53]	Model dairy wastewater	Dead-end filtration with a stirring cell fitted with a membrane disk	Previous separation of proteins and lipids by ultrafiltration	Several NF membranes were tested: NF270, NF90, Nanomax50, Desal-5 DL and Desal-5 DK, all of them with a surface layer oy polyamide, but with different cut-off´s	A two stage UF/NF for treatment of dairy wastewaters revealed to be a good method to purify dairy wastewaters. The combination of Ultracell for UF followed by NF of permeates with membranes NF270 was the best option, for purification	Retentates of UF were used for production of biofuels; lactose retained in NF was used for biogas production and the final permeate was a reusable water
Chen et al. [54]	Model dairy wastewater	Dead-end filtration cell for UF/NF (lab scale) and pilot plant for NF	Separation between caseins and whey proteins by isoeletric precipitation and centrfugation, followed by UF of supernatants to concentrate whey proteins	Four UF membranes were used: PES5, PES10, PES30 and Ultracell PLGC, made of different surface materials (polyethersulphone and regenerated cellulose) and cut-off´s. Membrane NF270 was used in the pilot scale tests	Both IP pretreatment and membrane surface material contributed to reduce irreversible fouling of UF and NF membranes. The combination of a previous removal of caseins followed by UF with the most hydrophilic membranes (Ultracell PLGC) allowed to drastically reduced the increasing pressure, thus improving the performance of UF and NF	Production of water of a better quality and simultaneous recovery of whey proteins, lactic acid (through lactose fermentation) and cells. Lactic acid and cells can be used for bioplastics production

Table 3. Some research works about the use of nanofiltration for recovery of dairy byproducts and dairy wastewaters purification.

hydraulic permeabilities to pure water. Before the experiments, the dairy wastewater was prefiltrated across a filter of 0.25 μm to remove solids and to avoid a quick fouling of membranes. After that, microfiltration was also used as a pretreatment for the next operation (NF or OI) with the objective of improving their performance. The authors found that the sequence of MF followed by RO allowed a better removal of total solids and organic matter. Besides, the composition of the final permeate was compatible with the discharge on receiving waters according to the Brazilian environmental regulations or could be used in cleaning-in-place processes in the dairy factory. Although the results of this study are a good basis for other similar dairy wastewaters, since the variety of manufacturing processes involved in dairy products used is too large, for each type of sample/desired goal, a previous study is always necessary.

Dairy by-products and wastewaters contain high nutritive, functional, and bioactive compounds, which can be recovered to produce food or other applications (**Table 3**). Nanofiltration, due to its specific characteristics, can play a role in the recovery/valorization of those compounds, allowing at the same time the reuse of its main component, the water. Nevertheless, a deep insight about its separation mechanisms and detailed knowledge on feed composition is necessary to control fouling phenomena.

5. Conclusions

This chapter focused on the use of NF for the treatment of different agro-industrial effluents, dairy, tomato, artichoke, and olive oil. Appropriate pretreatments to avoid membrane fouling have also been addressed as this is the main drawback against NF competitiveness. Among them, other pressure-driven membrane processes, such as microfiltration and ultrafiltration, are used as pretreatment, thus avoiding the use of chemicals. From our review, it was possible to conclude that the implementation of the circular economy vision to the mentioned production chains can be an interesting strategy to balance the investment costs that need to be carried out in order to build treatment plants. In fact, the recovery of added-value molecules (such as lactose and derivatives, polysaccharides, polyphenols, etc.) and of water can be a key aspect for the viability of the treatment processes. As previously said, water scarcity is a growing problem in Mediterranean countries, and therefore alternative sources of water are highly valued. For all of these reasons, it is considered that NF deployment is expected to grow in the forthcoming years.

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