Chapter

SECONDARY RAW MATERIALS FROM AGROINDUSTRIAL BY-PRODUCTS AND WASTE THROUGH NANOFILTRATION

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ABSTRACT

The adoption of a new economic model, the Circular Economy, that promotes closing the loop of products life-cycles based on greater recycling and reuse, is driving attention to by-products and waste valorisation. Food production chain is considered one of the main waste producers. Therefore, several studies on its by-products and waste valorization have been carried out, producing a wide range of secondary raw materials. Membrane technologies are increasingly used for the recovery of valuable compounds such as fibers, pectin, sugars, proteins

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and phenolic compounds from agroindustrial waste. In Mediterranean countries olive oil, wine and cheese production chains are of special interest, having an important economic and social impact in these countries, often associated with the production of high quality products, such as the PDO (Protected Designation of Origin) olive oils and cheeses and the VQPRD (Quality Wines Produced in Demarcated Wine Region) wines. The current chapter gives an overview regarding nanofiltration (NF) application for recovering high added-value compounds from the above mentioned agroindustrial by-products and waste streams. For example, in cheese making production, NF has been recently used to recover the components of cheese whey ultrafiltration (UF) permeates of a molecular weight lower than 1000 Da, aiming for its selective separation, concentration and/or demineralization, with advantages over other techniques. Compared with reverse osmosis it enables an energy saving of 20 to 45%, due to the use of lower transmembrane pressures. NF technology has also been lately examined to recover valuable antioxidant compounds from the wastes of olive oil industry, particularly low-molecular-weight polyphenolic compounds from olive mill wastewater. To sum up, NF is a technology that, if properly optimized, can offer a series of advantages in contrast to classic separation processes for the recovery of highly valuable components from the waste streams of these industries, core of the agro-industrial sector.

Keywords: circular economy, nanofiltration, olive mill waste, wine industry, cheese production.

1. INTRODUCTION

The scarcity of water concerns especially agricultural irrigation, which demands more than 70% of the total water consumption worldwide (Food and Agricultural Association, 2013). In this scenario, however, there is a potential opportunity to use regenerated wastewater for irrigation purposes, posing a very appealing solution regarding environmental and economic impacts.

On another hand, the adoption of a new economic model, the Circular Economy, that promotes closing the loop of products life-cycles based on greater recycling and reuse, is driving attention to by-products and waste valorisation. Food production chain is considered one of the main waste producers. Therefore, several studies on its by-products and waste valorization have been carried out, producing a wide range of secondary raw materials.

In the last decades, new advanced separation technologies, less intensive in terms of specific energy consumption than conventional separation procedures and also ‘greener’ regarding the minimum use of chemicals and reagents to achieve the desired separation, have been more and more implemented. Concretely, membrane technology can take the lead for these purposes.

Membrane technology is modular and easy to design and thus easily scalable to the industry, requires low maintenance and is environmentally friendly, providing high purifying capacity and selectivity (Field et al., 1995, 2011; Le-Clech et al., 2006; Ochando-Pulido et al., 2012a,b, 2013; Stoller, 2011, 2013). In the last years, there has been a significant boost in the use of membranes for a wide range of applications. This impulse has been a result of the new membrane materials, fabrication procedures, modules designs, and the optimization of the operating conditions, in specific those for the minimization of fouling issues.

In particular, membrane processes are becoming increasingly used in the purification of water and groundwater, in replacement of many conventional processes, as well as in the reclamation of wastewater streams from diverse sources, such as those generated by agroindustrial activities (Bódalo et al., 2003; Iaquinta et al., Luo and Ding, 2011; Ochando-Pulido et al., 2012a,b; Stoller and Chianese,, 2006; Stoller and Bravi, 2010). Furthermore, membrane technologies can be used for recovering valuable compounds such as fibers, pectin, sugars, proteins, and phenolic compounds from agroindustrial waste.

The specific selectivity towards small solutes and the lower energy consumption of NF membranes have boosted their use as tertiary treatment in integrated wastewater treatment processes. This type of membranes has already been applied in the management of industrial wastewaters of very different sectors, such as textile and tannery (Ellouze et al., 2012; Gönder et al., 2011; Liu et al., 2011; Stoller et al., 2013), coking (Korzenowski et al., 2011; Yin et al., 2011), carwash (Boussu et al., 2007), pulp and paper (Mänttäri et al., 2000; Pizzichini et al., 2005), pharmaceutical (Wei et al., 2010). Especially concerning agroindustrial sector, NF membranes have already been implemented in agrofood industries such as dairy (Luo et al., 2011; Lipnizki F., 2010), tomato (Iaquinta et al., 2009), olive oil (Ochando-Pulido et al., 2012a,b; Paraskeva et al., 2007; Stoller and Chianese, A., 2006; Stoller and Bravi, 2010), among others.

On another hand, the problem of fouling is a drawback to wastewater treatment by NF and RO membranes. Fouling mechanisms are very important to fully understand what is happening between the membrane and the feedstream, to take the adequate decisions with respect to the design of the membrane plant, the adoption of properly-tailored pretreatment process and the set-up of optimized operating conditions. (Iaquinta et al., 2009 ; Le-Clech et al., 2006; Ochando-Pulido et al., 2012a,b, 2013; Stoller, 2011, 2013). The first phenomenon that triggers over the membrane surface is concentration polarization, caused by the increasing concentration of solutes near the membrane boundary region. It may also reach such high values to enable the formation of gel layers. In this state, the solutes will deposit over the membrane, and cleaning may be difficult although not impossible (reversible). If the concentration within the gel layer exceeds solubility concentration values, a solid cake starts to precipitate and stick to the membrane surface. This impermeable layer may represent irreversible fouling that cannot be washed away anymore. Membrane fouling is complex, and can involve membrane pore blocking, plugging and clogging, chemical degradation and/or cake formation on the membrane surface caused by microorganisms as well as organic and inorganic material (Chen, 2007; Cheryan, 1998). Nevertheless, the result is always a reduction of the membrane performances in terms of permeability, selectivity and longevity.

In the past, fouling has sensibly compromised the reliability of membrane technology. This trend is still actual, since proper membrane process design can be a difficult task to accomplish when fouling is present and must be faced. Fouling leads to a reduction of the membrane productivity and causes a sensible reduction of the membrane module service lifetime, multiplying the operating costs. The presence of fouling, and the consequent reduction of permeate fluxes as a function of time, forces the engineers to over-design the membrane plant in order to guarantee the conduction of the process for a certain period of time at or above the permeate project values (Saad, 2005). The critical, threshold and boundary flux theories (Field et al., 1995, 2011; Le-Clech et al., 2006; Ochando-Pulido et al., 2012a,b, 2013; Stoller, 2011, 2013) are, as well as concentration polarization-based models (Macedo et al., 2011), among other, suitable tools applicable for the adequate design and control of the membrane plant in these cases.

2. NF Membrane Technology for Added-Value Compounds Recovery from OMW

Olive oil mill wastewater (OMW) is one of the main wastes generated during the production of olive oil and represents the principal environmental problem of this production process. The treatment of OMW is extremely difficult due to its great volume and the high concentration of organic matter. Its principal components are polysaccharides, sugars, polyphenols, polyalcohols, proteins, organic acids, and oil. Among them, phenolic compounds represent one of the major factors related to the environmental problems caused by this effluent and its difficulty to be treated. 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 represents an important objective for olive oil industry that will help to obtain interesting extracts and diminish the volume of one of the main olive oil industry by-products.

Membrane technology, which includes microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO) pressure-driven membranes, provide a series of advantages in contrast with classic separation technologies, making them very promising and environmentally friendly for recovering polyphenolic compounds and the remediation of OMW: no need to use chemical reagents - solvents - to achieve separation, fractionation and concentration; lower capital and operating costs and specific energy requirements than conventional separation procedures, but still capable to achieve high purifying capacity, selectivity and recovery; and also easy industrial scaling because they are modular, ease of design and operation and low maintenance (El-Abbassi et al., 2014; Garcia-Castello et al., 2010).

Paraskeva et al. (2007) research group addressed the treatment of OMW from a three-phase olive oil mill in Greece, with the goal of ulteriorly recovering and fractionate its phenolic fraction, combining several types of membranes in batch, including NF preceded by UF and finally RO. As a pretreatment before UF, an 80 µm polypropylene filter was chosen aiming for suspended solids removal. Thereafter, the UF membrane was able to effectively separate the high molecular weight compounds in the effluent including suspended solids, solid lipid components (up to 90%) and a certain amount of the phenolic compounds (~50%). Then, NF and RO spiral-wounded polymeric membranes, with a MWCO of 200 and 100 Da respectively, were targeted to further purify the UF permeate. In NF tests, a pressure value (TMP) of 20 bar led to satisfactory permeate flow between 100–120 L/h. In this membrane stage, 95% of the phenolic concentration could be rejected, and subsequently the RO membrane permitted the purification of the stream in terms of salinity and turbidity (around 98.9% for a TMP equal to 40 bar and

35°C), with 30 L/h permeate flow yield and a recovery of 75–80% in volume. Garcia-Castello et al. (2010) achieved up to 78% recovery of the phenolic fraction of OMW from a three-phase mill (Italy) with a process comprising a ceramic (Al_2O_3, 200 nm average pore size) tubular MF membrane followed by a hydrophobic polyethersulphone spiral-wound NF membrane. Moreover, the MF membrane provided the reduction of 91% of the suspended solids concentration and together with 26% of the organic matter (TOC). The NF permeate, enriched in polyphenols with valuable antioxidant properties, could be used in formulations in food, cosmetic and pharmaceutical industries. For this purpose, a final vacuum membrane distillation (VMD) or osmotic distillation (OD) was examined, further enriching the obtained stream in the target compounds.

VMD and OD belong to the membrane contactors family. Most of the experiences with membrane contactors have focused on the concentration of fruit juices and other food applications, and for the addition or removing of gas compounds to or from liquid streams (Garcia-Castello et al., 2010). The membranes modules used for VMD or OD are usually microporous and symmetric and can be both hydrophobic and hydrophilic. Membrane contactors do not offer any selectivity for a particular species with respect to another, but they perform simply as a barrier between the phases involved, such that the species are transferred from one phase to the other by simply diffusion, as reported by Drioli et al. (2006).

During the VMD experiments performed by Garcia-Castello et al. (2010), the feedstream (the NF permeate), warmed up to the desired temperature (20-40°C), was recirculated at atmospheric pressure at different flow rates to one side of the membrane while a vacuum of about 30 mbar was applied at the other side. Due to the difference of partial pressure established across the membrane, water migrated as vapour through the micropores and condensed in a trap immersed in liquid nitrogen located between the module and the vacuum pump. Two commercial flat-sheet PVDF and PP membranes were chosen. The PVDF membrane showed the lowest swelling degree and, therefore, it was chosen for VMD tests. The evaporation flux gradually decreased in the first 200 min and then reached an asymptotic value of 8 L/m^2 h.

On the other hand, in the OD process, the feed solution (NF permeate) was recycled into the shell side of the membrane module while the stripping solution ($CaCl_2 \cdot 2H_2O$ 60% w/w) was recycled in counter-current into the lumen of the membrane fibres, at a temperature for both the feed and brine of 30 ± 2°C, and 0.43 bar average TMP. Results showed 3.4 L of NF permeate were reduced to 1.1 L. The initial brine concentration of 60% w/w produced an evaporation flux of about 1.0 kg/m^2 h, but the evaporation flux decreased due to the reduction of the driving force of the process, reaching a value of about 0.35 kg/m^2 h when the brine solution concentration was around 42%. A final solution containing about 0.5 g/L free LMW polyphenols, with hydroxytyrosol representing 56% of the total amount, was produced by using calcium chloride dihydrate solution as brine.

Concerning the efficiency of the two concentration processes analysed, even if the VMD has the advantage of higher transmembrane fluxes, it is remarkable that the energy consumptions should be lower in OD since it does not use a vacuum pump neither needs a refrigeration step to condensate the permeate. However, the $CaCl_2$ consumption and the treatment of the stripping solution (e.g., by evaporation) must be taken into account for an overall comparison between the two processes.

Cassano et al. (2013, 2011) evaluated the performance of a system integrating two UF membranes followed by final NF. Three different fractions were obtained: a concentrated stream from the retentate of both UF membrane processes, containing high molecular weight organic substances, which depleted of polyphenolic compounds may be subjected to an anaerobic digestion for biogas production; another concentrated stream derived from the NF retentate, enriched in LMW polyphenolic compounds suitable for cosmetic, food and pharmaceutical industries as liquid, frozen, dried or lyophilized formulations; and a final treated water stream (NF permeate), apt to be reused as process water or in the integrated membrane system as membrane cleaning solution. However, only 87% flux could be recovered after cleaning, revealing deleterious irreversible fouling build-up on the membrane.

Zirehpour et al. (2012) synthetized a lab-made polyethersulfone (PES) UF membrane and tested it in an integrated MF-UF–NF membrane system for the purification of three-phase OMW. The effluent was pre-filtered by three-step MF in series, with nominal pore sizes of 50, 5 and 0.2 µm, in concentration mode, subsequently followed by two and three UF and NF membranes. However, the MF membrane showed determinant fouling problems, very common in MF membranes. Otherwise, the commercial UF membrane tested provided higher permeate flux than the lab-made one, but the antifouling properties and rejection efficiency of the latter was significantly better. A specific arrangement of the integrated membrane system was concluded to be the UF membrane followed by two-step NF membranes in series, the first NF step providing high flux while the second one providing high rejection.

Di Lecce et al. (2014) recently proposed the fractionation of OMW (three-phase, Italy) by means of a two-step MF and NF membrane process, and the study was carried out at 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. As pretreatment before the membranes-in-series process, filtration of the raw OMW through cotton fabric filters was performed. This ensured the reduction of 3.8 - 5.4% (w/w) of the suspended solids concentration in the effluent. Within this working conditions, the rejection of the NF membrane was enhanced up to 98% in terms of COD, dry matter, phenols concentration and antioxidant activity, disregarding the volume concentration factor. The quality of the obtained purified permeate of the NF membrane unit was close to the standards stablished for its discharge in surface water bodies, in terms of organic load (COD) and phenols concentration. One aspect lacking in this study was the assessment of the dynamic performance of the membranes involved in the membranes-in-series system, that is, the permeate flux and fouling behaviour during the operation time of the process. These are aspects of paramount importance for the scale-up of the process, and thus to evaluate the economic feasibility of the proposed system.

As it can be seen, interesting added-value compounds contained in OMW may be recovered, concentrated and fractionated with the aid of the adequate membranes, in order to counterbalance the costs of the treatment process of these agroindustrial effluents. However, further investigation is still to be done in order to comprehend, model, control, and minimize the fouling problems associated, and the optimal membrane materials.

3. NF Membrane Technology for Added-Value Compounds Recovery from Dairy By-Products

Dairies are one of the major food processing industries and manufacture different products over the world. Consequently, it generates large volumes of by-products during the processing of milk and manufacture of varied products and, therefore, it deals with problems of management/utilization of by-products. During processing, large amounts of by-products and wastes of high biological oxygen demand (BOD) and chemical oxygen demand (COD) are produced from dairy industries. Traditionally, they are valorised into different added-value products only partially, such as for animal feed and compost. However, the nutritional, biological, functional and nutraceutical value of the components present, such as proteins, sugars and lipids, vitamins and minerals, could be an inexpensive and abundant source for developing new added-value products (e.g., foods, pharmaceuticals, energy).

The main by-products and wastes from the dairy industry are: whey, buttermilk and several types of effluents, such as washing water of rennet casein precipitate, and white and pre-rinsing waters from the first step of cleaning-in-place processes (CIP) (Daufin et al., 2001).

Whey is a co-product of the cheese-making and casein industry. Typically, every 100 kg of milk can lead to the production of 10-20 kg of cheese, depending on the variety, and about 80-90 kg of liquid whey (Cheryan, 1998). According to the Food and Agriculture Organization Corporate Statistical Database (FAOSTAT), more than 114 million tonnes of whey were produced worldwide in 2013, with Europe producing 63 million tonnes in that year (FAOSTAT, 2013). Data from European Whey Products Association (EWPA) indicated that about 6 million tonnes of whey (dry matter) were produced in the European Union in the year 2015 (EWPA, 2016). It contains about 65 g of dry matter/L, being lactose the main component (70–80%), proteins (9%), corresponding to 20% of all milk proteins, and minerals (8–20%) and, to a much lesser extent, hydrolysed peptides from casein-*k*, lipids and bacteria, which resulted from cheese manufacturing (Daufin et al., 1998; Walstra, 2001). Two types of whey are produced, sweet and acid, defined by reference to their final pH, which depends on the mode of milk coagulation. Sweet whey (pH of approximately 6.0) is produced from the milk clot, obtained by enzymatic hydrolysis of caseins by chymosin, at a pH of not less than 5.6 (Morr, 1989; Daufin et al. 1998). The acid whey (pH of approximately 4.6) is obtained after the coagulation of the caseins by biological acidification, due to the microbial fermentation of milk lactose in lactic acid, and/or chemical, by the addition of mineral or organic acids, up to pH isoelectric of the caseins, which is about 4.6 (Daufin et al., 1998). Another whey (sweet) is generated during production of ovine whey cheeses through thermal aggregation of whey proteins, named second cheese whey (SCW). SCW contains about a half of the dry matter of the initial cheese whey, also carrying out a high organic load, with BOD_5 and COD values of about 10,200 and 69,500 mg

O_2 L^{-1} (Macedo, 2005). Most of this whey has no current use and because of the larger volumes generated (approximately 18 L of SCW by kg of whey cheese produced) it constitutes a serious environmental problem (Macedo et al., 2015). The low solids content of whey, associated with a very unfavorable lactose/protein ratio makes it difficult for direct utilization (Cheryan, 1998).

Buttermilk is a liquid by-product of the manufacture of butter from cream. The chemical composition of buttermilk varies greatly, depending of the amount of water added. Generally, its composition is virtually identical to the skim milk, except for the high amounts of phospholipids and milk fat-globular membrane proteins (Mandal et al., 2013). Worldwide, approximately 50 ton of butter are produced daily, which in turn lead to the by-production of 950,000 kg of buttermilk (MacCarthy et al., 2002). However, its nutrient richness makes this by-product, currently treated as waste, a potential source of added-value compounds, a challenge that this industry must face as a resource and not as a waste problem.

Membrane separation processes play a role in recovering by-products/wastes from agro-food industries, allowing:

(i) innovation in processes and/or development of new products that meet consumer needs in terms of safety, novelty, diversity and quality.
(ii) in environmental terms, these processes are considered clean, because they can replace the use of chemicals; they can add value to by-products or wastes and are very suitable for the treatment of effluents (evaporation condensates, ultrafiltrates, brines and cleaning solutions used in CIP and wastewater).

Among membrane separations processes, pressure driven membranes processes, such as microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO), have been the most used by food industry.

In the dairy industry, the use of NF to pre-concentrate and partially demineralize whey and milk ultrafiltration permeates (MUF) has grown recently, appearing as an interesting alternative to other processes such as reverse osmosis (RO), electrodialysis (ED) and ion exchange (IE) (Lipnizki, 2010; Salehi, 2014). The demineralization of dairy fluids is very important to reduce their high salt content (8-20% of dry matter) (Daufin et al., 2001; Suaréz et al., 2006), which causes several difficulties in processing. It leads to slow lactose crystallization rate, fouling of MF and UF membranes during manufacturing of whey protein concentrates (WPC) and whey protein isolates (WPI), as well as nutritional imbalance in human and infant food (Daufin et al., 2001).

Compared to other processes of demineralization of whey used by the industry, such as reverse osmosis (RO), electrodialysis and ion exchange (IE), NF presents several advantages. Through NF it is possible to achieve in a single operation the concentration of dry matter in the range 20-22% (at a volume reduction ratio of 4-5) and a partial demineralization between 25-50%, and even more, if diafiltration is used (Daufin et al., 2001). In relation to reverse osmosis, energy savings of 20-45% are feasible, due to the use of lower transmembrane pressures (Garem and Jeantet, 1995).

Besides, NF is more selective than the other processes, allowing a reduction of monovalent (40-90%) and divalent nutritional value of about 5-20%, for calcium and phosphates ions, as compared to 62% and 43%, respectively, for 50% demineralization in ED (Kelly and Kelly, 1995). Other applications of NF for partial demineralization of whey, aiming to valorize this by-product and minimize its adverse effects on the environment, were described by Kelly et al. (1992). These include removal of salt from salty whey, generated during the production of several types of cheese (Cheddar, ovine and caprine PDO cheeses); pre-concentration and partial demineralization (up to about 50%) of sweet whey for manufacture of lactose; conversion of acid whey into “sweet” whey, of low chloride content, through partial demineralization and concentration; treatment of cheese pickles for re-use; partial demineralization of the mother liquor from the crystallization of lactose, which can then be used in animal feed.

Recently, NF of whey UF permeates has been applied in the separation of bioactive peptides, present naturally in whey and/or released by the proteins during cheese processing (Pouliot et al.; 1999, Pouliot et al., 2000; Butylina et al., 2006).

Milcent and Carrere (2001) studied the performance of NF and RO for removing lactic acid from fermentation broths and observed an improvement in the fermentation yield, suggesting that these processes may be promising in biotechnological separations.

A complete recovery of the whey should, necessarily, involve the recovery of lactose. This component, in addition to its several industrial applications, is mainly responsible for the high COD and BOD values of this product. Industrially, lactose is produced from sweet whey (or whey permeate from UF), which is concentrated by evaporation (or in combination with reverse osmosis and evaporation), crystallized, decanted (for separation of the crystals), purified and dried. Prior to the evaporation step, calcium is precipitated to be used as a nutritional supplement and simultaneously to increase the yield in lactose production. In the production of pharmaceutical grade lactose, the concentration should be carried out until the dry matter content reaches 60%, and furthermore the purification, crystallization and separation steps of the crystals must be repeated until the final concentrate contains 92% dry matter, which is then dried for use. Guu et Zall (2006) found that the application of NF for sweet whey or UF permeates allowed to increase the production of lactose crystals by about 10% and 8%, respectively, for a VRR of 3.0. This behavior was attributed to the partial demineralization of the permeate, especially in terms of the monovalent ions sodium and potassium. These results raise the interest for the integration of NF membranes in the lactose production plants at industrial level.

Some research works have been developed using NF to recover the organic fraction (namely lactose) and, at the same time, to avoid the environmental impact of sweet whey. Magueijo et al. (2005) studied the recovery of lactose and organic matter from second cheese whey (SCW) through NF, using two different polymeric NF membranes (NFT50 and HR95 PP) in a plate-and-frame module. Membrane NFT50 was selected due to the higher permeate fluxes, a good rejection of organic matter and lactose, leading to a water recovery of approximately 80% (for a VRR of 5). However, permeate fluxes sharply decreased during the concentration process, probably due to the increasing osmotic pressure or, eventually, mineral precipitation of calcium phosphates.

Lactose and derivatives have many applications, in particular in the food industry (bakery and confectionery, milk, yogurts, ice creams, fruit juices, soups and sauces), pharmaceutical and fermentation industries. In addition, it can also be used to obtain added-value chemicals such as lactitol and sorbitol, glycols (propylene glycol and ethylene glycol) and glycerol, used as sugar substitutes, antifreeze or for making food containers (Elliot et al., 2001). Other lactose products with interesting applications in the industry are, for example, lactulose, lactobionic acid and galactooligosaccharides used by the pharmaceutical industry for therapeutic purposes and/or by the food industry as additives, mineral sources or as nutritional supplements (Elliot et al., 2001). In addition, lactose can also be used to obtain added-value chemicals such as lactitol and sorbitol, glycols (propylene glycol and ethylene glycol) and glycerol, used as sugar substitutes, antifreeze or for making food containers (Elliot et al., 2001).

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Despite the growing interest in the use of NF in the dairy industry, the performance of this process is frequently affected by losses of lactose and nitrogen compounds to the permeate, which contributes to the reduction of its selectivity (Van der Horst, 1995; Garem and Jeantet, 1995). The loss of these compounds into the permeate depends on the membrane characteristics (pore diameter and length, membrane charge at the pH of the feed), the characteristics of the feed (pre-treatments, ionic strength, valence of the ions present, viscosity, pH) and the process conditions (Van der Horst et al., 1995; Alkhatim et al., 1998).

The phenomena of concentration polarization and membrane fouling can also be important, leading to a decrease in the productivity of the operation (Garem and Jeantet, 1995). Among the factors that affect NF productivity, it seems that the concentration polarization (reversible phenomenon) dominates the behavior of this operation during the NF of the whey, contributing between 92-95% for the total fouling (Garem and Jeantet, 1995; Jeantet et al., 2000). Similar results were found by Eckner and Zottola (1993) during NF of skimmed milk, in which the phenomenon of concentration polarization and irreversible fouling contributed in about 67-95% and 5-30%, respectively, to the decline in permeation fluxes, depending on the pH and temperature. The permeation fluxes grew between 0.5-2.7% for each °C of temperature increase and decreased about 2.4% by the decrease of 0.1 pH units, between pH 6.8 and 5.6.

In the NF of whey UF permeates, as proteins are almost absent because they were removed by UF, permeates render even more vulnerable to mineral precipitation, since the proteins have a stabilizing function of calcium phosphate in solution (Marshall and Daufin, 1995). The mineral precipitation depends mainly on the pH, temperature and ionic strength, being more likely when any of these factors is high (Marshall and Daufin, 1995). Kelly et al. (1992) observed a severe fouling caused by the precipitation of calcium phosphate, when the acid casein whey pH was raised above the isoelectric pH of the whey proteins, 5.2. However, the permeation of Cl^- ions through the membrane was improved. Kelly and Kelly (1995) observed during whey NF a much more severe fouling when the calcium phosphate concentration exceeded saturation. Lactose and the small nitrogen compounds present as peptides, amino acids and urea have a minor contribution in the construction of the layer (Jeantet et al., 2000). So, to enhance the performance of NF with whey all these factors should be controlled.

4. NF Membrane Technology for Added-Value Compounds Recovery from Winery By-Products

Wine production is an important economic activity all over the world. In 2016 the global wine production reached 259.5 million hectolitres (OIV, 2016).

NF has been applied along the winemaking process with several and different objectives, for example as an alternative method for tartaric acid stabilization of wines, grape juice concentration and dealcoholizing wine.

Tartaric stabilization of wines is commonly achieved by cold precipitation, which is a time and energy consuming process that leads to loss of aromatics and wine. Electrodialysis has come up as an alternative and more recently a two-step process, NF followed by MF, has been proposed (Salehi, 2014).

One of the impacts of global warming in grape development is the increase of sugar content, leading to wines with higher alcoholic degree. Several studies have shown that NF can be effective in removing sugar from musts, and consequently producing wine with lower alcohol content (Catarino and Mendes, 2011; Garcia-Martin et al., 2010; Salgado et al., 2015 and 2017).

On another hand, NF has been applied to grape juice and wine must for enriching tannins and organoleptic components (Banvolgyi et al., 2006; Ferrarini et al., 2001; Massot et al., 2008).

In addition to the above-mentioned NF applications in winemaking process, this technology can be useful for recovering added-value bioactive compounds from winery by-products. The main winemaking by-products are grape pomace (62%), wine lees (14%), stalk (12%) and wastewater (1.2 times greater than the production of wine) (Naziri et al., 2014).

Syed et al. (2017) developed a process for recovering bioactive monomeric flavan-3-ols from grape pomace. The authors compared two operation modes, NF and diananofiltration (operated in the diafiltration mode), using a Duramem 900 membrane with a transmembrane pressure of 8 bar.

Results showed that the diafiltration operation mode was more effective for fractionating monomeric and oligomeric phenolic compounds into the permeate stream than simply NF.

Giaccobo et al. (2017) studied the use of lees from second racking of red wine as a source for recovering polyphenols and polysaccharides. They tested several UF and NF membranes, evaluating the permeation fluxes and solute rejection coefficients in terms of transmembrane pressure variation. They concluded that the best strategy would be to establish a sequential process, UF-NF, as UF was effective in separating polysaccharides from polyphenols, with polyphenols going preferentially into the permeate stream that could be thereafter concentrated by NF (NF270 membrane presented polyphenols rejections above 92%).

As mentioned, winemaking process generates large amounts of wastewater mainly resulting from the cleaning processes and wine losses. The physico-chemical composition of the wastewater varies along the winemaking activities taking place in the winery, achieving the highest organic content when resulting from rackings (due to the presence of lees). This wastewater has high organic load and is rich in polyphenolic compounds. Phenolic compounds are phytotoxic and antibacterial and therefore are inhibitory for biologic treatment of the wastewater produced. But on another hand, we can look at the wastewater as a source of bioactive compounds with added value, and efforts can be made to recover them before further treatment of the wastewater.

Giaccobo et al. (2016) assessed the recovery of polyphenols and polysaccharides from first racking wastewater using membrane technologies and proposed an integrated process that uses MF for suspended solids removal, UF to concentrate polysaccharides and NF to concentrate polyphenols, also resulting water that can be reused. Operated at the best conditions this sequential treatment allowed recovering 1 g of polyphenols and 1 g of polysaccharides per liter of raw wastewater processed.

From the above stated it can be concluded that wine production by-products and wastewater can be used as a secondary raw material for the production of nutraceuticals and bioactive compounds.

This strategy can contribute to the economic development of the wine production chain and for mitigating the environmental impact of this activity, as polyphenols are the key recalcitrant compounds present in waste and wastewater streams from winemaking process.

5. Conclusion

The current chapter presented an overview on the application of nanofiltration for recovering high added-value compounds from agroindustrial by-products and waste streams. Focus was given to cheese, olive oil and wine production chains, as they are of considerable economic and social relevance in Mediterranean countries.

From our review, it was possible to conclude that the mentioned production chains are interesting study cases for illustrating the implementation of the circular economy vision. In fact, different combinations of membrane technologies allow recovering molecules such as lactose and derivatives, polysaccharides, polyphenols, water, etc.

NF also has the advantage of enabling energy saving when compared to other membrane technologies, due to the use of lower transmembrane pressures. To sum up, NF is a technology that, if properly optimized, can offer a series of features in contrast to classic separation processes for the recovery of high added-value components from the waste streams of these industries, core of the agro-industrial sector.

References

Alkhatim, H. S., Alcaina, M. I., Soriano, E., Iborra, M. I., Lora, J. & Arnal, J. (1998). Treatment of whey effluents from dairy industries by nanofiltration membranes. *Desalination*, *119*, 177-184.

Belfort, G., Davis, R. H. & Zydney, A. L. (1994). The behavior of suspensions and macromolecular solutions in crossflow microfiltration. *J. Membr. Sci*., *96*, 1-58.

Borsani, R. & Ferrando, B. (1996). Ultrafiltration plant for olive vegetation waters by polymeric membrane batteries. *Desalination*, *108*, 281-286.

Boussu, K., Kindts, C., Vandecasteele, C. & Van der Bruggen, B. (2007). Applicability of nanofiltration in the carwash industry. *Sep. Purif. Technol*., *54* (2), 139-146.

Bódalo, A., Gómez, J. L., Gómez, E., Máximo, F. & Hidalgo, A. M. (2003). Application of reverse osmosis to reduce pollutants present in industrial wastewater. *Desalination*, *155*, 101-108.

Butylina, S., Luque, S. & Nyström, M. (2006). Fractionation of whey-derived peptides using a combination of ultrafiltration and nanofiltration. *Journal of Membrane Science*, *280*(1-2), 418–426.

Castro-Muñoz, R., Yáñez-Fernández, J. & Fíla, V. (2016). Phenolic compounds recovered from agro-food by-products using membrane technologies: An overview. *Food Chemistry*, *213*, 2016, 753-762. http://dx.doi.org/10.1016/j.foodchem.2016.07.030.

Catarino, M. & Mendes, A. (2011). Dealcoholizing wine by membrane separation processes. *Innovative Food Science and Emerging Technologies*, *12*, 330–337. http://dx.doi.org/10.1016/j.ifset.2011.03.006.

Cheryan, M. (1998). Ultrafiltration and Microfiltration Handbook (2nd ed.). Boca Raton, Florida, USA: CRC Press.

Coskun, T., Debik, E. & Demir, N. M. (2010). Treatment of olive mill wastewaters by nanofiltration and reverse osmosis membranes. *Desalination*, *259*, 65-70.

Danellakis, D., Ntaikou, I., Kornaros, M. & Dailianis, S. (2011). Olive oil mill wastewater toxicity in the marine environment: Alterations of stress indices in tissues of mussel Mytilus galloprovincialis. *Aquat. Toxicol*., *101* (2), 358-366.

Daufin, G., Bérot, S., Fillaudeau, H. L. & Escudier, J. R. (2001). Recent and emerging applications of membrane processes in the food and dairy industry. *Institution of Chemical Engineers*, *79*, 80-89.

Di Lecce, G., Cassano, A., Bendini, A., Conidi, C., Giorno, L. & Gallina, T. (2014). Characterization of olive mill wastewater fractions treatment by integrated membrane process. *J. Sci. Food Agric.*, *94*, 2935–2942.

Daufin, G., René, F. & Aimar, P. (1998). Les séparations par membrane dans les procédés de l’industrie alimentaire. *Collection Sciences et Techniques Agroalimentaires*, Paris.

Eckner, K. F. & Zottola, E. A. (1993). Effects of temperature and pH during membrane concentration of skim milk efficiency. *Milchwissenschaft*, (48) 187-191.

Elliot, D. C., Wend, C. F. & Alnajjar, M. S. (2001). Lactose processing technology-creating new utilization opportunities. *In “Proceedings of the 38th Annual Marschall Cheese Seminar” (Proceedings compiled by the California Dairy Research Foundation)*, pp. 1-8.

Ellouze, E., Tahri, N. & Ben Amar, R. (2012). Enhancement of textile wastewater treatment process using Nanofiltration. *Desalination*, *286*, 16-23.

Espinasse, B., Bacchin, P. & Aimar, P. (2002). On an experimental method to measure critical flux in ultrafiltration. *Desalination*, *146*, 91-96.

EWPA, (2016). Economic Report 2016/17. In European Whey Products Association.

FAOSTAT, (2013). FAO Statistical Databases. Retrieved December 27, 2017, from http://www.fao.org/faostat/en/#data/BL.

Ferrarini, R., Versari, A. & Galassi, S. (2001). A preliminary comparison between nanofiltration and reverse osmosis membranes for grape juice treatment. *Journal of Food Engineering*, *50*, 113–116.

Field, R. W. & Aimar, P. (1993). Ideal limiting fluxes in ultrafiltration: comparison of various theoretical relationships. *J. Membr. Sci.*, *80*, 107-115.

Field, R. W., Wu, D., Howell, J. A. & Gupta, B. B. (1995). Critical flux concept for microfiltration fouling. *J. Membr. Sci.*, *100*, 259-272.

Field, R. W. & Pearce, G. K. (2011). Critical, sustainable and threshold fluxes for membrane filtration with water industry applications. *Adv. Colloid Interface Sci.*, *164*, 38-44.

Garcia-Castello, E., Cassano, A., Criscuoli, A., Conidi, C. & Drioli, E. (2010). Recovery and concentration of polyphenols from olive mill wastewaters by integrated membrane system. *Water Res.*, *44*, 3883–3892.

García-Martín, N., Perez-Magariño, S., Ortega-Heras, M., González-Huerta, C. Mihnea, M., González-Sanjosé, M. L., Palacio, L., Prádanos, P. & Hernández, A. (2010). *Sugar reduction in musts with nanofiltration membranes to obtain low alcohol-content wines*, *Separation and Purification Technology*, *76*, 2, 158-170. http:// dx.doi.org/10.1016/ j. seppur.2010.10.002.

Garem, A. & Jeantet, R. (1995). Fouling occurring in nanofiltration of dairy products. In "Fouling and cleaning in pressure driven membrane processes" (International Dairy Federation ed.) *Special issue*, *9504*, 71-79.

Giacobbo, A., Meneguzzi, A., Bernardes, A. M. & Pinho, M. N. (2016). Pressure-driven membrane processes for the recovery of antioxidant compounds from winery effluents, *Journal of Cleaner Production*., http://dx.doi.org/10.1016/j.jclepro.2016.07.033.

Gönder, Z. B., Arayici, S. & Barlas, H. (2011). Advanced treatment of pulp and paper mill wastewater by nanofiltration process: Effects of operating conditions on membrane fouling, *Sep. Purif. Technol.*, *76* (3), 292-302.

Guu, Y. K. & Zall, R. R. (2006). Nanofiltration concentration effect on the efficacy of lactose crystallization. *Journal of Food Science*, *57*(3), 735-739.

Jeantet R., Rodríguez, J. & Garem, A. (2000). Nanofiltration of sweet whey by spiral wound organic membranes: impact of hydrodynamics. *Lait*, *8*, 155-163.

Iaquinta, M. & Stoller, M. (2009). Optimization of a nanofiltration membrane for tomato industry wastewater treatment. *Desalination*, *245*, 314-320.

Karaouzas, I., Skoulikidis, N. T., Giannakou, U. & Albanis, T. A. (2011). Spatial and temporal effects of olive mill wastewaters to stream macroinvertebrates and aquatic ecosystems status. *Water Res*., *45* (19), 6334-6346.

Kelly, R. M., Horton, B. S. & Burling, H. (1992). IDF Special Issue No. 9201 - New Applications of Membrane Processes. *International Dairy Federation*, Brussels, Belgium, 130-140.

Kelly, J. & Kelly, P. (1995). Nanofiltration of whey: quality, environmental and economical aspects. *J. Soc. Dairy Technol*., (48) 20-25.

Korzenowski, C., Minhalma, M., Bernardes, A. M., Ferreira, J. Z. & de Pinho, M. N. *Purif. Technol*., *76* (3), 303-307.

(2011). Nanofiltration for the treatment of coke plant ammoniacal wastewaters, Sep. Le-Clech, P., Chen, V., Fane, T. A. G., 2006. Fouling in membrane bioreactors used in wastewater treatment. *J. Membr. Sci*., *284* (1-2), 17-53.

Leopoldo, Martínez Nieto., Saloua, Ben Driss Alami., Gassan, Hodaifa., Catherine, Faur., Salvador, Rodríguez., José, A. Giménez. & Javier, Ochando. (2010). Adsorption of iron on crude olive stones. *Industrial Crops and Products*, *32*, 467–471.

Liu, M., Lü, Z., Chen, Z., Yu, S. & Gao, C. (2011). Comparison of reverse osmosis and nanofiltration membranes in the treatment of biologically treated textile effluent for water reuse, *Desalination*, *281*, 372–378.

Lipnizki, F. (2010). *Membrane Technology*, Volume *3*, Membranes for food applications. Wiley-Vch Verlag GmbH&Co. kGaA, Weinheim1.

Luo, J., Ding, L., Wan, Y. & Jaffrin, M. Y. (2012). Threshold flux for shear-enhanced nanofiltration: experimental observation in dairy wastewater treatment. *J. Membr. Sci.*, *409*, 276-284.

Macedo, A. (2005). Application of membrane technology for valorization of by-products from Serpa cheese making. Final report of Agro Project nº 327, Measure 8, Action 8.1. (experimental development and demonstration e demonstração-DE&D), from Ministry of Agriculture and Fisheries from Government of Portugal.

Macedo, A., Duarte, E. & De Pinho, M. N. (2011). The role of concentration polarization in ultrafiltration of ovine cheese whey. *Journal of Membrane Science*, *381*, 34-40.

Macedo, A., Duarte, E. & Fragoso, R. (2015). Assessment of the performance of three ultrafiltration membranes for fractionation of ovine second cheese whey, *International Dairy Journal*, *48*, 31-37.

MacCarthy, D. A., Fitzpatrick, J. J. & Cronen, K. (2002). Encyclopedia of dairy sciences (1st ed.), ed. S1 Elsevier.

Magueijo, V. Minhalma, M., Queiroz, D., Geraldes, V., Macedo, A. & Pinho, M. N. (2005). Reduction of wastewaters and valorisation of by-products from "Serpa" cheese manufacture using nanofiltration. *Water Science & Technology*, *52* (10-11), 393-399.

Mandal, S., Puniya, M., Sangu, K. P. S., Dagar, S. S., Singh, R. & Puniya, A. K. (2013). Dairy by-products: wastes or resources? - the shifting perception and valorization, chap. 21. In: Valorization of food processing by-products. Edited by M. Chandrasekaran, Fermented Food and Beverages Series, CRC Press, Boca Raton, USA, pp. 617-648.

Mänttäri, M. & Nystörm, M. (2000). Critical flux in NF of high molar mass polysaccharides and effluents from the paper industry. *J. Membr. Sci.*, *170*, 257-27.

Marshall, A. D. & Daufin, G. (1995). Physico-chemical aspects of membrane fouling by dairy liquids. *In "Fouling and cleaning in pressure driven membrane processes"* (Special Issue 9504), pp. 8-35. International Dairy Federation, Brussels.

Massot, A., Mietton-Peuchot, M., Peuchot, C. & Milisic, V. (2008). Nanofiltration and reverse osmosis in winemaking. *Desalination*, *231* (1–3), 283–289.

Milcent, S. & Carrere, H. (2001). Clarification of lactic acid fermentation broths. *Separation and Purification Technology*, *22*, 393-401.

Morr, C. V. (1989). *Whey Proteins: Manufacture In "Developments in Dairy Chemistry"*, vol. *4* (P. F. Fox ed.), pp. 245-284. Elsevier Applied Science, London and New York.

Naziri, E., Nenadis, N., Mantzouridou, F. T. & Tsimidou, M. Z. (2014). Valorization of the major agrifood industrial by-products and waste from Central Macedonia (Greece) for the recovery of compounds for food applications, *Food Research International*, Volume *65*, Part C, 350-358. http://dx.doi.org/10.1016/j.foodres.2014.09.013.

Ntougias, S., Gaitis, F., Katsaris, P., Skoulika, S., Iliopoulos, N. & Zervakis, G. I. (2013). The effects of olives harvest period and production year on olive mill wastewater properties - Evaluation of Pleurotus strains as bioindicators of the effluent's toxicity. *Chemosphere*, *92*, 399-405.

Ochando-Pulido, J. M. S., Rodriguez-Vives, J. M. & Martinez-Ferez, A. (2012a). The effect of permeate recirculation on the depuration of pretreated olive mill wastewater through reverse osmosis membranes. *Desalination*, *286*, 145-154.

Ochando-Pulido, J. M., Hodaifa, G., Rodriguez-Vives, S. & Martinez-Ferez, A. (2012b). Impacts of operating conditions on reverse osmosis performance of pretreated olive mill wastewater. *Water Res.*, *46* (15), 4621-4632.

Ochando-Pulido, J. M., Hodaifa, G., Victor-Ortega, M. D., Rodriguez-Vives, S. & Martinez-Ferez, A. (2013). Effective treatment of olive mill effluents from two-phase and three-phase extraction processes by batch membranes in series operation upon threshold conditions. *J. Hazard. Mater.*, *263* (1), 168-176.

Ochando-Pulido, J. M. & Stoller, M. (2014). Boundary flux optimization of a nanofiltration membrane module used for the treatment of olive mill wastewater from a two-phase extraction process Separ. *Purif. Technol.*, *130*, 124-131.

Ochando-Pulido, J. M., Verardo, V., Segura-Carretero, A. & Martinez-Ferez, A. (2015). Technical optimization of an integrated UF/NF pilot plant for conjoint batch treatment of two-phase olives and olive oil washing wastewaters. *Desalination*, *364*, 82-89.

Ognier, S., Wisniewski, C. & Grasmick, A. (2004). Membrane bioreactor fouling in sub-critical filtration conditions: a local critical flux concept. *J. Membr. Sci*., *229*, 171-177.

Paraskeva, C. A., Papadakis, V. G., Tsarouchi, E., Kanellopoulou, D. G. & Koutsoukos, P. G. (2007). Membrane processing for olive mill wastewater fractionation. *Desalination*, *213*, 218-229.

Pizzichini, M., Russo, C. & Di Meo, C. (2005). Purification of pulp and paper wastewater with membrane technology for water reuse in a closed loop. *Desalination*, *178*, 351-359.

Pouliot, Y., Wijers, M. C., Gauthier, S. F. & Nadeau, L. (1999). Fractionation of whey protein hydrolysates using charged UF/NF membranes. *Journal of Membrane Science*, *158*, 105-114.

Pouliot, Y. & Gauthier, J. L´Heureux. (2000). Effect of peptide distribution on the fractionation of whey protein hydrolysates by nanofiltration membranes. *Lait*, (80), 113.

Saad, M. A. (2005). Membrane desalination for the Arab world: overview and outlook, *Arab Water World*, *1*.

Salehi, F. (2014). Current and future applications for nanofiltration technology in the food processing. *Food and Bioproducts Processing*, *92*, 161-177.

Salgado, C. M., Palacio, L., Prádanos, P., Hernández, A., González-Huerta, C. & Pérez-Magariño, S. (2015). Comparative study of red grape must nanofiltration: Laboratory and pilot plant scales, *Food and Bioproducts Processing*, *94*, 610-620, http://dx.doi.org/10.1016/j.fbp.2014.08.007.

Salgado, C. M., Fernández-Fernández, E., Palacio, L., Francisco, J., Carmona, F. J., Hernández, A. & Prádanos, P. (2017). Application of pervaporation and nanofiltration membrane processes for the elaboration of full flavored low alcohol white wines, *Food and Bioproducts Processing*, *101*, 11-21, http://dx.doi.org/10.1016/j.fbp.2016.10.001.

Stoller, M. & Chianese, A. (2006). Optimization of membrane batch processes by means of the critical flux theory. *Desalination*, *191*, 62-70.

Stoller, M., 2009. On the effect of flocculation as pretreatment process and particle size distribution for membrane fouling reduction. *Desalination*, *240*, 209-217.

Stoller, M. & Bravi, M. (2010). Critical flux analyses on differently pretreated olive vegetation waste water streams: some case studies. *Desalination*, *250*, 578-582.

Stoller, M. (2011). Effective fouling inhibition by critical flux based optimization methods on a NF membrane module for olive mill wastewater treatment. *Chem. Eng. J.*, *168*, 1140-1148.

Stoller, M., Bravi, M. & Chianese, A. (2012). Threshold flux measurements of a nanofiltration membrane module by critical flux data conversion. *Desalination*, *315*, 142–148.

Stoller, M. & Ochando-Pulido, J. M. (2012). Going from a critical flux concept to a threshold flux concept on membrane processes treating olive mill wastewater streams. *Procedia Eng.*, *44*, 607–608.

Stoller, M., Sacco, O., Sannino, D. & Chianese, A. (2013). Successful integration of membrane technologies in a conventional purification process of tannery wastewater streams. *Membranes*, *3*, 126-135.

Stoller, M. (2013). A three-year long experience of effective fouling inhibition by threshold flux based optimization methods on a NF membrane module for olive mill wastewater treatment. *Membranes*, *32*, 37-42.

Stoller, M. & Ochando-Pulido, J. M. (2015). The boundary flux handbook: a comprehensive database of critical and threshold flux values for membrane practitioners. Elsevier, Netherlands.

Suárez, E., Lobo, A., Alvarez, S., Riera, F. A. & Alvarez, R. (2006). Partial demineralization of whey and milk ultrafiltration permeate by nanofiltration at pilot plant scale. *Desalination*, *198*, 274-281.

Syed, U. T., Brazinha, C., Crespo, J. G. & Ricardo-da-Silva, J. M. (2017). Valorisation of grape pomace: Fractionation of bioactive flavan-3-ols by membrane processing, *Separation and Purification Technology*, *172*, 1, 404-414. http://dx.doi.org/10.1016/j.seppur.2016.07.039.

Szilvia, Banvolgyi., Istvan, Kiss., Erika, Bekassy-Molnar. & Gyula, Vatai. (2006). Concentration of red wine by nanofiltration, *Desalination*, *198*, 1, 8-15. http://dx.doi.org/10.1016/j.desal.2006.09.003.

Turano, E., Curcio, S., De Paola, M. G., Calabrò, V. & Iorio, G. (2002). An integrated centrifugation–ultrafiltration system in the treatment of olive mill wastewater. *J. Membr. Sci.*, *206*, 519-531.

Van der Horst, H. C. (1995). Fouling of organic membranes during processing of dairy liquids. *In*: "Fouling and cleaning in pressure driven membrane processes" (International Dairy Federation ed.), *Special Issue*, *9504*, 36-52.

Walstra, P., Geurts, T. J., Noomen, A., Jellema, A. & van Boekel, M. A. J. S. (2001). "Ciencia de la Leche y Tecnologia de los Productos Lácteos". Editorial Acribia, S. A., Zaragoza.

Wei, X., Wang, Z., Fan, F., Wang, J. & Wang, S. (2010). Advanced treatment of a complex pharmaceutical wastewater by nanofiltration: Membrane foulant identification and cleaning. *Desalination*, *251*, 167-175.

Yin, N., Yang, G., Zhong, Z. & Xing, W. (2011). Separation of ammonium salts from coking wastewater with nanofiltration combined with diafiltration. *Desalination*, *268*, 233-237.

Zagklis, D. P., Vavouraki, A. I., Kornaros, M. E. & Paraskeva, C. (2015). Purification of olive mill wastewater phenols through membrane filtration and resin adsorption/desorption. *J. Hazard. Mater*., *285*, 69–76.

Zirehpour, A., Jahanshahi, M. & Rahimpour, A. (2012). Unique membrane process integration for olive oil mill wastewater purification, Separ. *Purif. Technol*., *96*, 124-131.

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