A focus on pressure-driven membrane technology in olive mill wastewater reclamation: state of the art

J. M. Ochando-Pulido and A. Martinez-Ferez

ABSTRACT

Direct disposal of the heavily polluted effluent from olive oil industry (olive mill wastewater, OMW) to the environment or to domestic wastewater treatment plants is actually prohibited in most countries, and conventional treatments are ineffective. Membranes are currently one of the most versatile technologies for environmental quality control. Notwithstanding, studies on OMW reclamation by membranes are still scarce, and fouling inhibition and prediction to improve large-scale membrane performance still remain unresolved. Consequently, adequately targeted pretreatment for the specific binomium membrane-feed, as well as optimized operating conditions for the proper membranes, is today’s challenge to ensure threshold flux values. Several membrane materials, configurations and pore sizes have been elucidated, and also different pretreatments including sedimentation, centrifugation, biosorption, sieving, filtration and microfiltration, various types of flocculation as well as advance oxidation processes have been applied so far. Recovery of potential-value compounds, such as a variety of polyphenols highlighting oleuropein and hydroxytyrosol, has been attempted too. All this research should constitute the starting point to proceed with OMW purification beyond recycling for irrigation or depuration for sewer discharge, with the aim of complying with standards to reuse the effluent in the olive oil production process, together with cost-effective recovery of added-value compounds.

Key words | olive mill wastewater, olive vegetation wastewater, olive washing wastewater, membrane processes, wastewater reclamation, wastewater reuse

INTRODUCTION

Olives and olive oil processing represent one of the most important agro-industries in the Mediterranean countries since ancient times. Moreover, there has been a growing interest worldwide regarding olive oil consumption in recent years owing to its nutritional, antioxidant and heart-healthy properties. In response to this, the ancestral olive oil pressure-based discontinuous extraction procedure, although more ecological, has been replaced in the last decades by the more efficient two-phase and three-phase continuous centrifugation-based processes. On the other side of the coin, this change has resulted in a gross increase in the amount of effluents derived from the production of olive oil, which consist of olive vegetation wastewater (OVW) and olives washing wastewater (OWW), together called olive mill wastewater (OMW). This problem concerns not only the Mediterranean countries, which cope with 97% of the total olive oil world production, but also other countries in which olives are cultivated, such as the USA, Argentina, Australia and the Middle East. In Spain, the main olive oil producer worldwide, there are more than 1,700 olive oil factories, which gave rise to more than 1,400,000 tons of olive oil during the 2010 campaign. Olives and olive oil production increase year by year and so does OMW in parallel.

The olive oil production process usually yields around 20% olive oil, 30% semi-solid waste and 50% aqueous polluted OVW (Niaounakis & Halvadakis 2006). The latter means 0.5–1.5 m³ of this liquid waste per ton of olives, depending on the adopted process (Paraskeva & Dia- madopoulos 2006). An average-sized olive oil factory produces more than 10 m³/day of OVW, equivalent to 1 m³ of OWW per ton of washed olives. In the two-phase-based system (OVW-2), due to the minor water injection in the horizontal centrifugation step (10–25% vs. 55–60%...
in three-phase-based ones, OVW-3), the volume of OVW becomes reduced by 25–50%, as well as the pollutants load (Hermoso et al. 1998). Acidic pH, extremely high concentration of suspended and dissolved solids, as well as one of the heaviest organic loads including organic acids, sugars, pectins and a major content of phenols and tannins confer on OMW phytotoxic and antimicrobial properties and low biodegradability (Garrido Hoyos et al. 2002). Also, OMW exhibits significant electrical conductivity (EC) mainly attributed to considerable concentration of chloride and potassium, as well as other inorganic compounds such as sulfate and phosphoric salts of calcium, iron, magnesium, sodium, copper and traces of other elements (Di Giovacchino 1985; Rozzi et al. 1988). Moreover, OMW composition is not constant and varies greatly depending on several factors, among which we can highlight climatic and cultivation parameters, and the milling method applied for the olive oil production (Table 1). This results in a great cost for its disposal and a huge amount of potable water consumption.

Due to the fact that most olive oil production plants are small and decentralized, a centralized treatment of OMW seems not feasible; therefore an effective and simple solution ought to be found for the small plants. Direct disposal of these effluents for irrigation purpose or to surface waters, although still practiced, is both hazardous and illegal, resulting in severe pollution consequences such as underground leakage, soil contamination and water body pollution (Voreadou 1989). In 1981 the Spanish Government, as in other Mediterranean countries, prohibited the direct discharge of these waters into rivers and subsidized the construction of ponds for their separate storage and natural evaporation (Annesini & Gironi 1991). Over the years, this rule has proved inefficient as a consequence of the low evaporation potential of these ponds, together with the hazardous leaks derived from frequent deficiencies in their construction. Among the plenty of methods suggested for the management of OMW we can list thermal treatments (Paraskeva et al. 2006), composting (Bouranis et al. 1995; Cegarra et al. 1996; Papadimitriou et al. 1997), treatments with lime (Aktas et al. 2001) and clay (Al-Malah et al. 2000), advanced oxidation processes (AOPs) (Espuglas et al. 2002; Martínez Nieto et al. 2009, 2011), biological treatments (Marques 2001; Fountoulakis et al. 2002; Garrido Hoyos et al. 2002; Ammary 2005), electrochemical treatments (Papastefanakis et al. 2010), electro-coagulation (Inan et al. 2004; Tezcan Ün et al. 2006) and hybrid processes (Rizzo et al. 2008; Lafi et al. 2009; Grafias et al. 2010). Complexity and efficiency of the listed treatments vary considerably, as well as the operating, energy and installation costs involved, which in sum represent the key drawback for not having adopted them.

In this sense, pressure-driven membrane processes are currently one of the most versatile and efficient technologies for environmental quality control, and particularly ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO) membranes have experienced a significantly increasing interest for reclamation of municipal, industrial and agricultural wastewaters (Almulla et al. 2003; Nicolaisen 2003). Since the invention of the first cellulose acetate (CA) asymmetric membrane by Loeb and Sourirajan in the early 1960s, a plethora of research over better materials, optimized membrane elements and well-defined operating regimes has led to important improvements in membrane performance and cost-effectiveness. Among the advantages of membrane technologies in comparison with classic separation processes are lower capital and operating costs than many conventional treatment systems, lower energy consumption, no thermal degradation of substances as extreme temperatures are not required, no addition of solvents, possibility of being used in conjunction with other treatment processes, high purifying capacity and recovery rates, easy industrial scaling as a result of their modular nature and ease of design and operation and low maintenance requirements.

First steps in OMW treatment by pressure-driven membrane processes

Incipient development of membrane technology has resulted in the introduction of tangential pressure-driven
membrane processes for wastewater treatment (Bódalo-Santoyo et al. 2005), which have already been applied for the management of the effluents derived from industries of various sectors, e.g. pulp and paper (Pizzichini et al. 2005), stainless steel (J. Lee et al. 2006), nuclear-power (Samodurov et al. 2006), energy cogeneration (Epimakhov et al. 2004), agro-food industry (Iaquinta et al. 2009). Particularly concerning OMW management through membrane technology, limited studies have been conducted and thus literature data with regard to this theme are still scarce (Table 2).

One of the first research studies attempting OMW depuration by membrane processes was conducted by Pompei & Codovilli (1974), who evaluated the depuration of OVW from a three-phase centrifugation olive oil production plant through RO. Results showed high reduction of the chemical oxygen demand (COD). As a next step, Carrieri (1978) applied UF of OVW with CA membranes of different porosities, coupled with other depuration methods such as biological depuration, RO and distillation. Actually, CA-type membranes are no longer widely in use in industrial applications.

Later on, Canepa et al. (1988) conducted a study on OMW treatment based on a combined membranes and adsorption process on a pilot scale, for recycling and agricultural irrigation purposes. OMW samples were taken from batch or continuous olive oil extraction processes and presented an average COD equal to 90 g O2/L. The treatment at issue comprised UF on polysulfone membranes, after which the UF permeate was treated with adsorbing polymers, and treatment of the resin eluate with RO poly-piperazine-amide membranes. The UF pilot unit consisted of four multiple modules in series containing three tubular membranes each – 2 m² total filtering area, each module working at 102 kPa and 20 °C.

A rapid decline of the UF permeate flux was observed, with a plateau after around 20 h of work. Hence, a daily washing period was necessary to obtain the best performance of the UF plant, attaining up to 63% COD reduction and a final volume reduction factor (VRF) of about 11. The UF permeate was then percolated through a resin-bed column, with a flow rate equal to 250 L/h. The resin bed showed good performance with regard to the retention of polyphenols, which could be subsequently used for alimentary and pharmaceutical industrial purposes, and its saturation was not achieved until around 3,000 L. Ultimately, the eluate coming out of the resin bed was treated through two RO units in series, equipped with one spiral-wound module each, working at 20 °C and 40 MPa. Flux reduction, due to deleterious fouling on the RO membranes, became important after about 30 h of work. Therefore, also in this case a daily washing period was needed to attain the best performances in terms of total permeate flow.

Results demonstrated up to 93% COD rejection and 99% total dissolved solids removal upon a VRF of about 6. To sum up, total COD abatement of around 99% could be accomplished at the end of the whole process. The authors also proposed using the whole waste obtained from the UF retentate and the RO concentrate for oil extraction, furfural production or combustion for energy recovery. They also evaluated the economical feasibility of an industrial scaling. However, the fact that there was a flux decline of 80% after 20 h of UF and nearly 70% after 15 h of RO operations constituted a capital handicap, despite the satisfactory permeate flow rates attained initially.

Borsani & Ferrando (1996) proposed a method to purify OVW coming from batch or continuous olive oil extraction (average BOD₅: 18 g O₂/L, COD: 70 g O₂/L). The purifying method was conducted in a wastewater treatment plant and consisted of: (1) oil removal and suspended solids settling, (2) tangential UF on polysulfone membranes, and (3) a final double-stage biological treatment of the permeate fraction collected from the UF step.

They studied the type and quantity of polyelectrolyte to get the best suspended solids sedimentation possible, and the correct quantity of caustic soda to neutralize OVW acidity, also taking into account to create the best conditions for the polyelectrolyte action and the further UF step. The UF step was performed at 30 °C and 10 bar, and consisted of 220 modules subdivided into three batteries, each module composed of 18 tubular type membranes (MWCO 30 kDa), resulting in a total filtering surface of 2 m².

Before feeding the first oxidation step of the biological post-treatment, pollutant concentration in the UF permeate was 50% lower than the one relevant to the crude OVW. After that, UF permeate was mixed with sewage (average BOD₅: 250 mg O₂/L, COD: 450 mg O₂/L) entering the first step of the biologic plant, complying with 1:16 flow rate ratio. Average BOD₅ and COD load abatement of about 65–70% was achieved until this point in the process. Finally, after the second step of the biological treatment, BOD₅ and COD values in the water leaving the plant always complied with Italian standard limits for discharge in superficial waters (BOD₅: 40 mg O₂/L, COD: 160 mg O₂/L), with an average daily amount of treated OVW of 150 m³/d.

Turano et al. (2002) proposed a new approach in the depuration of OMW, consisting of a preliminary centrifugation step for the removal of suspended solids, followed by a selective separation phase carried out by UF of the
<table>
<thead>
<tr>
<th>Author/s</th>
<th>OMW derivation</th>
<th>Pursued goal</th>
<th>Scale of study</th>
<th>Process scheme</th>
<th>Type of membranes</th>
<th>Fouling – flux decline</th>
<th>Depuration achieved</th>
<th>Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>Canepa et al.</td>
<td>Batch or continuous 3-phase olive oil extraction</td>
<td>Recycling and agricultural irrigation + added-value products recovery</td>
<td>Pilot (continuous)</td>
<td>(i) UF, (ii) treatment with adsorbing polymers and (iii) RO</td>
<td>Tubular UF (PS, 102 kPa; MWCO 20 kDa); SW RO (polyvinylpyrrolidone, 40 MPa)</td>
<td>80% UF flux decline after 20 h and nearly 70% after 15 h of RO</td>
<td>COD reduction (UF) up to 63%, 95% (RO) and 99% total</td>
<td>Good retention of polyphenols by resin bed, for alimentary and pharmaceutical purposes; UF retentate and RO concentrate for oil extraction, furfural production or combustion for energy recovery</td>
</tr>
<tr>
<td>Borsani &amp; Ferrando</td>
<td>Batch or continuous 3-phase olive oil extraction</td>
<td>Discharge on superficial waters</td>
<td>Pilot (continuous)</td>
<td>(i) Oil removal and TSS solids settling, (ii) UF, (iii) permeate mix with sewage and (iv) double-stage biological treatment</td>
<td>Tubular UF (PS, 10 bar, MWCO 10 kDa)</td>
<td>Not reported</td>
<td>50% COD load decrease after UF and up to 70% after biological treatment</td>
<td>Effluent compliance of Italian standards for superficial waters discharge, 150 m$^3$/d average</td>
</tr>
<tr>
<td>Turano et al.</td>
<td>Continuous 3-phase olive oil extraction</td>
<td>Pollution reduction + selective separation of added-value products from OMW</td>
<td>Laboratory (batch)</td>
<td>(i) Centrifugation and (ii) UF of centrifuge supernatant</td>
<td>Flat-sheet UF (PS, MWCO 17 kDa)</td>
<td>Above 80% flux decline after 30 min, 83% initial flux recovery after cleaning</td>
<td>55% COD and 80% ashes and TSS reductions after centrifugation, 90% final COD abatement</td>
<td>Effluent COD (5 g O$_2$/L) still high for European legislation; complete fats rejection, separated from salts, sugars and polyphenols, contained in permeate stream</td>
</tr>
<tr>
<td>Paraskeva et al.</td>
<td>Continuous 3-phase olive oil extraction</td>
<td>Fractionation into streams rich in potential-value by-products to compensate high OMW treatment costs</td>
<td>Pilot (batch)</td>
<td>(i) 80 μm polypropylene filter, (ii) UF, (iii) NF and (iv) RO</td>
<td>Multichannel UF (zirconia, 100 nm, 1–2.25 bar); polymeric SW NF (200 Da, 20 bar) and SW RO (100 Da, 40 bar)</td>
<td>Fouling data not reported; 100–120 L/h within NF, 30–32 L/h with RO</td>
<td>90% lipids and 50% phenols separated by UF; 95% phenols removal</td>
<td>Effluent suitable for irrigation or aquatic receptors; inorganic (N, P, Mg, K) and organic solutes (hydrocarbons, N compounds, organic acids, polyalcohols) as plant nutrients combined with other fertilizers</td>
</tr>
<tr>
<td>Russo (2007)</td>
<td>Continuous 3-phase olive oil extraction</td>
<td>Selective recovery of added-value products from OWW</td>
<td>Pilot (batch)</td>
<td>(i) MF, (ii) UF and (iii) RO</td>
<td>MF ceramic (ZO, 0.8 and 0.45 μm) and PES SW (500 kDa); UF SW polymeric (80, 20 and 6 kDa; PS or PES) and ceramic (ZO, 1 kDa); composite SW RO</td>
<td>High flux drop and incomplete membranes permeability restore after cleaning procedure</td>
<td>RO 99.9% nitrogen substances, sugars and polyphenols rejection and 83–99% respect ionic species</td>
<td>MF 0.45 μm high free LMW polyphenols concentration (349 pm); UF 6 kDa 45% free LMW polyphenols rejection; RO retentate enriched in LMW polyphenols for food, pharmaceutical or cosmetic industries; MF and UF retentates as fertilizers or for biogas yield</td>
</tr>
<tr>
<td>Author/s</td>
<td>OMW derivation</td>
<td>Pursued goal</td>
<td>Scale of study</td>
<td>Process scheme</td>
<td>Type of membranes</td>
<td>Fouling – flux decline</td>
<td>Depuration achieved</td>
<td>Results</td>
</tr>
<tr>
<td>------------------</td>
<td>-----------------------------------------------------</td>
<td>---------------------------------------------------</td>
<td>---------------------------------</td>
<td>----------------</td>
<td>----------------------------------------------------</td>
<td>------------------------------------------------</td>
<td>------------------------------------------------</td>
<td>------------------------------------------------------------------------------------------------------------------------------------------</td>
</tr>
<tr>
<td>Garcia-Castello et al. (2010)</td>
<td>Continuous 3-phase olive oil extraction</td>
<td>OVW reclamation + selective separation of added-value products</td>
<td>Pilot (batch)</td>
<td>(i) MF, (ii) NF and (iii) OD or VMD</td>
<td>MF ceramic (Al2O3, 200 nm, 0.72 ± 1 bar); SW NF (hydrophobic PES, 378 Da, 8 bar)</td>
<td>35% MF initial flux drop and incomplete restore after cleaning (106 L/hm² bar); 35% NF initial flux (4.68 L/hm²) drop above VRF = 3</td>
<td>MF achieved 91% and 26% TSS and TOC reduction; NF removed 63% TOC and TC reduction in MF permeate</td>
<td>NF permeate containing polyphenols susceptible of being concentrated and used in food, cosmetic or pharmaceutical sectors; 0.5 g/L free LMW polyphenols, with 56% hydroxytyrosol, obtained by treating the NF permeate by OD</td>
</tr>
<tr>
<td>Stoller (2009, 2011), Stoller &amp; Bravi (2006, 2007)</td>
<td>Continuous 3-phase olive oil extraction</td>
<td>OWW and OVW for sewer discharge or irrigation + fouling inhibition and prediction</td>
<td>Pilot (batch)</td>
<td>(i) pretreatment among flocculation/UV-TiO₂ photocatalysis/ aerobic digestion/ MF, followed by (ii) UF + NF + RO</td>
<td>Composite SW MF (300 nm), UF (2 nm), NF (0.5 nm) and RO (&lt;0.1 nm); operating below critical pressure</td>
<td>Lowest flux drops MF 17.3–18.9%, UF 23.1%, NF 18.5%, RO 22.9–23.7%; reversible fouling removed after cleaning</td>
<td>Overall COD abatement 98.8–99.4 %</td>
<td>Italian standards for municipal sewer system discharge (COD values below 500 mg/L) achieved</td>
</tr>
<tr>
<td>Akdemir &amp; Ozer (2009)</td>
<td>Continuous 3-phase olive oil extraction</td>
<td>Satisfy standards for wastewater discharge to sewers</td>
<td>Laboratory (batch)</td>
<td>(i) pH adjustment, (ii) cartridge filtration and (iii) UF</td>
<td>Flat-sheet UF (polyvinylidene-difluoride, 30 kDa and another Ultrasil 100 kDa, 1 bar)</td>
<td>Highest flux 25.9 L/hm² at 4 bar affected by fouling; 1 bar safest operating pressure</td>
<td>COD, TOC and SS removal ratios 92.3%, 92.7%, 97.1%</td>
<td>Effluent COD, TOC and SS 6.4 g O₂/L, 2.5 g/L, 320 mg/L; although sewer discharge standards not obtained, further investigations on posed pretreatment should be considered</td>
</tr>
<tr>
<td>Ochando-Pulido et al. (2012)</td>
<td>Continuous 2-phase olive oil extraction</td>
<td>OMW reclamation for sewer discharge or reuse in process</td>
<td>Pilot (semi-continuous)</td>
<td>(i) Fenton-like oxidation, (ii) flocculation-sedimentation, (iii) biosorption and (iv) RO</td>
<td>Composite PA/PS flat RO</td>
<td>High and stable permeate flux upon recirculating above 10% permeate</td>
<td>100% TSS, phenols and iron removal, 99.4% and 98.2% COD and conductivity</td>
<td>Effluent COD below 5 mg O₂/L, within standards for reuse in olive washing machines</td>
</tr>
</tbody>
</table>

centrifuge supernatant in a laboratory-scale flat-sheet membrane module (polysulfone, nominal MWCO of 17 kDa, model MPPS U002 supplied by Separem, Biella, Italy). According to the authors, centrifugation was chosen over other pretreatment techniques due to its simplicity and the possibility of operating only mechanically (without any chemical change). Also, its availability in the olive oil production loop posed an economical boost. They fulfilled a preliminary rheological characterization of the waste and analyzed the permeation efficiency by the cake-filtration model as a function of several parameters such as the importance of the pretreatment, the effects of localized turbulence promoted by the UF module geometry, and of the main operating variables, i.e. 30 °C, transmembrane pressure (TMP) (0.5–3 bar) and feed flow rate.

After each experiment, a combined cycle of alkaline (Henkel, P3 Ultrasil 91) and acid (Henkel, P3 Ultrasil 75) cleanings was carried out over the membrane, severely fouled by organic compounds and minerals present in the OMW. Performing that standard cleaning procedure, about 85% of the initial permeability could be recovered when ultrafiltering pretreated OMW, while only 37% was restored when ultrafiltering the raw wastewater. Higher steady-state flux was also ensured for the pretreated OMW and much smoother efficiency decay to its final value, enabling longer working cycles and less frequent plant shutdowns for washing and cleaning. Steady-state values showed that centrifuged wastewater permeate flux was about 13 times higher than raw wastewater one. As final values, 55% COD reduction was achieved after centrifugation, and a significant reduction of the waste pollution of about 80% for ashes and suspended solids and 90% for COD was accomplished throughout the whole process.

Nevertheless, fouling still remained a severe problem even in the presence of a pretreatment step, becoming evident not only from flux decay but also from the decrease of the steady-state UF efficiency at increasing operating pressures, due to the increase of the transport resistance. They attributed membrane fouling to the oil phase that makes agglomeration of macromolecules (suspended solids, ashes, organic particles, etc.) easier. These particles in turn tended to block the membrane pores causing a very steep permeate flux drop (more than 95% after the first 5 min) when no pretreatment was used and a smoother one (70–80% after 30 min) when a great part of the suspended solids had been removed. What is more, 17% of the original permeability of the membrane could not be restored due to irreversible fouling.

These facts highlight the key importance of tailored and cost-effective pretreatments for OMW management by membranes. Fouling mitigation constitutes one of the main challenges of membrane technology, as it increases operating and energy costs, and frequent membrane chemical cleanings are required, thus soaring the consumption of cleaning reagents. What is more, irreversible fouling leads to irretrievable membrane life shortage. Dissolved and suspended organic matter associated with OMW, such as polysaccharides and proteins, also constitutes a breeding ground for microbiological activity, enhancing biofouling. In addition to the production of colloidal particles and sparingly soluble salts, accumulation of insoluble matter, pore plugging and blocking, scale formation and cake-enhanced concentration polarization can occur.

**Targeted OMW pretreatments and sustainable flux**

It still remains very difficult to predict fouling phenomena over the membranes, found in almost all membrane facilities. In regard to this, Field et al. (1995) minted the concepts of critical, threshold and sustainable flux for microfiltration (MF) and extended it subsequently to UF and NF processes (Field & Pearce 2011). The threshold flux is defined as the maximum permeate flux at which fouling builds up at a low and constant rate. Above this value the rate of fouling increases noticeably. The concept of threshold flux is key for membrane separation processes and fouling inhibition purposes. The problem lies in the fact that threshold flux values cannot be theoretically predicted, but must be measured experimentally, and depend on hydrodynamics and solute concentration in the feedstock, among other factors. In many research papers it was pointed out that pretreatment of the feedstock is essential in fouling inhibition strategies, but only if the pretreatment processes were tailored to the feedstock. Proper pretreatment processes can increase threshold flux values, whereas improper ones may not change at all or in worst case reduce them appreciably.

In this regard, Stoller & Chianese (2006, 2007) conducted a series of investigations on OWW purification. With the aim of complying with municipal sewer discharge standards, the proposed treatment consisted mainly of two consecutive steps: pretreatment of the wastewater followed by membrane separation (composite thin-film spiral-wound membranes, Osmonics) on a pilot scale.

The batch membrane process comprised UF followed by NF in series, after a pretreatment step consisting of either coagulation–floculation – using as coagulant aluminum sulfate (AS) or aluminum hydroxide (AH) – or biological (BIO) aerobic digestion by means of fungi in a biological
immobilized bed reactor. The authors aimed to predict the optimum sustainable permeate flux by means of the critical flux theory in order to minimize fouling. They reported that the two pretreatment processes performed similarly with respect to COD and BOD$_5$ reductions, though highlighting a 40% critical flux value increment for the flocculation pretreatment with AS.

Also, Stoller & Bravi (2010) studied the relationship between the particle size distribution and the critical flux values after different pretreatment procedures applied to a three-phase OVW stream. Apart from the previously tested pretreatment steps, they also evaluated photocatalytic (PC) organic matter reduction by means of nanometric titanium dioxide anatase powders irradiated by UV light. The study was also carried out on a pilot-plant scale in batchwise. Once pretreated OVW was filtered through a 50 or 75 μm sieve, results were compared with performances and effects on the critical flux value for MF, UF and NF membranes operating in sequence in batch mode, and a final RO step, each one with a recovery rate of about 90%. They noted that different pretreatment on the same raw wastewater shifted differently the particle size distribution mainly by diverse organic matter degradation, and reported that this influenced heavily the critical flux value and thus the filtration outcome.

Around two-thirds of the organic matter was eliminated by the coagulation–flocculation process with one or the other of the adopted coagulants (residence time 72 h both). Moreover, with both coagulants, a significant reduction of polyphenols and the final dry matter occurred. Nevertheless, the separation process with the AH-pretreated stream was stopped at the UF step as satisfactory permeate flow rates were not observed, due to the similar size of the formed aggregates with respect to the membrane mean pore size, which led to quick fouling on the membrane. This was not the case for AS, which showed higher permeate flow rates and less fouling issues. Results similar to the pretreatment with AH occurred after biodigestion, presumably owing to the residual biomass may give rise to particles of dimension close to that of the MF pores, being therefore discarded despite the comparable COD reduction achieved, and also a much longer residence time equal to seven days was used. Aerobic digestion after coagulation–flocculation with AS was also evaluated but the COD reduction, although higher, was not sufficient to compensate for the critical flux decrease due to pore-blocking particles.

Finally, they noted that photocatalysis met the highest COD reduction at the shortest process time (24 h). Moreover, this result was obtained on the highest polluted wastewater, with lower average performances if compared with AS, but more stable with respect to the recovery factor (Y). Summing up, all pretreatment processes successfully tested down to RO gave rise to final permeate volume recoveries equal to 62% of that of the initial feedstock (COD = 5 O$_2$/L), with a resulting COD value equal to 456, 242 and 385 mg/L for AS, BIO + AS and PC respectively.

In conclusion, a non-linear relationship between the critical flux value and the pore-blocking particle density was noted. In detail, best performances were accomplished by coagulation with AS (highest critical fluxes on all membranes, overall COD reduction equal to 99.2%). Also UV/TiO$_2$ photocatalysis performed efficiently, showing high critical fluxes for all membranes excluding RO, with overall COD reduction equal to 99.4%. Biological treatment was suggested only in combination with coagulation (medium-high critical flux values on all membranes, overall COD reduction equal to 98.6%), as plugging of the MF membrane seemed unavoidable without coagulant and elimination of the bioflocs.

In sum, Stoller (2009, 2011) underlined the key importance of the pretreatment and highlighted that higher pollutant reductions, e.g. in the COD value, do not necessarily mean the pretreatment procedure is the most suitable. The fact that the pretreatment shifts pollutant particle size shift far away from that of the pores is of paramount importance to further enhance threshold flux values.

Following the concept of the pretreatment relevance for OMW management by membrane processes, Akdemir & Ozer (2009) conducted research on the suitability of pressure-driven crossflow UF of previously pretreated OMW (COD: 84 g O$_2$/L; total organic carbon (TOC): 35 g O$_2$/L; suspended solids: 11 g/L; oil and grease: 25 g/L; and pH: 4.8). The authors compared the performance of two different UF polymeric membranes (an Osmonics polyvinylidine-difluoride membrane with a MWCO of 30 kDa and an Ultrafilic membrane with a MWCO of 100 kDa), with the finality to satisfy Turkish standards for wastewater discharge to sewers.

Chemical and physical pretreatment steps consisting of pH adjustment and cartridge filtration were applied to samples before UP in a flat-sheet membrane module. In detail, pretreatment consisted in the first instance of acidic pH adjustment (pH = 2) and then cartridge filter filtration (20 μm), and finally alkaline pH adjustment (pH = 6) and again cartridge filter filtration (20 μm), reaching up to 63% COD removal.
The effects of the main operating parameters TMP, feed flow rate, pH) and membrane type on permeate flux and membrane fouling were examined and rejection coefficients calculated from COD and TOC experimental studies. The final COD, TOC, suspended solids, and oil and grease concentrations of membrane effluent were 6.4 g O₂/L, 2.5 g/L, 320 mg/L and 270 mg/L, respectively, corresponding to removal ratios of around 92.3, 92.7, 97.1, and 98.9%, respectively. Although the pursued standards compliance was not achieved, the pretreatment step should be highlighted as a novel and simple one, effective from the point of view of the organic compounds abatement prior to the UF step. Nevertheless, despite the considerably high COD removal provided by the pretreatment, it did not ensure high threshold flux values, as despite the highest permeate flux (25.9 L/hm²) being obtained with the 100 k Da membrane upon operational conditions of 200 L/h flow rate and operating pressure equal to 4 bar, 1 bar was reported to be the safest operating TMP with respect to fouling issues. However, further investigations on the given pretreatment should be considered.

It is worth pointing out that existing research works on OMW treatment by membranes focus on complying with standards for irrigation or discharge in sewers. In contrast with this, Ochando-Pulido et al. (2012) studied the reclamation of two-phase OMW by RO on a bench scale, so as to achieve the quality to recirculate the final effluent to the manufacture process or at least to the olive washing machines to finally close the loop.

Noticing the importance of pretreatment tailoring for membrane operations, OMW was previously treated through an AOP based on homogeneous Fenton-like reaction. AOPs are widely used for the removal of recalcitrant organic constituents from industrial and municipal wastewater (Martínez Nieto et al. 2009, 2011). This is the case for pesticides as well as polyphenols and tannins besides other organic non-humic and humic solutes associated with OMW. These constituents are not only resistant to biological degradation and toxic to microbial processes, but have also been demonstrated to develop fouling phenomena on the membranes (Childress & Elimelech 1996; S. Lee et al. 2006, Lee et al. 2007).

As previously mentioned, both hydrodynamics and the nature of the feedstock affect membrane steady-state performance deeply. In this sense, the authors addressed the influence of operating temperature and permeate recirculation on fouling minimization and flux enhancement. Augmenting temperature was observed to lead to decreasing viscosity of the solvent, which results in increase of diffusivities of both water and solutes through the membrane (Goosen et al. 2002; Jin et al. 2009). In this regard, Jin et al. (2009) studying dynamic light scattering on particle size distributions of humic acid confirmed lower hydrodynamic diameters of the dissolved and suspended organic matter with increasing temperature. As a result, the specific cake resistance is allowed to decrease as temperature increases. On the other hand, high and stable permeate flux was provided upon recirculation of a fraction of the permeate stream above 10%, ensuring no significant steady-state flux decline. Under those conditions, 100% suspended solids, phenols and iron removal was achieved, in addition to around 99.4 and 98.2% overall COD and conductivity rejection efficiencies respectively. Both the lower increment of the feedstock viscosity and the concentration gradient across the membrane along operation time seemed to keep fouling and cake-enhance concentration polarization under control.

**Compensating for high treatments costs: recovery of potential-value compounds**

Some authors have tried to extract polyphenols, sugars and other added-value compounds contained in this wastewater by concentration with membranes. Notwithstanding, in all these studies it can be noticed that membrane fouling plays an important role. Canepa et al. (1988) had earlier proposed this possibility. Later on, Turano et al. (2002) reported complete separation of fats, completely rejected by the membrane, from salts, sugars and polyphenols, contained in the permeate stream. However, despite the relevant COD reduction, organic matter concentration in the permeate was still too high, containing polyphenols ranging from 0.2 to 0.3 g/L depending on the feed concentration, sugars from 2 to 12 g/L and mineral salts ranging from 3 to 8 g/L. They suggested converting the obtained polyphenols either by means of enzymes (tyrosinase, polyphenoloxidase, peroxidase, etc.) immobilized in a membrane bioreactor (Edwards et al. 1999; Durán & Esposito 2000; Calabro et al. 2002), thus reducing the permeate polluting load, or recovering them in virtue of their high antioxidant and radical scavenging properties (Rice-Evans et al. 1996; Dreosti 2000).

In a similar line, Paraskeva et al. (2007) investigated the treatment and complete fractionation of OMW coming from a three-phase-decanter olive oil mill in Greece, using a combination of different membrane processes. The authors tested UF followed by NF and/or RO in a batch mode, keeping constant the composition of the initial raw wastewater.
Prior to UF, screening with an 80 \( \mu \)m polypropylene filter was performed to remove suspended solids. The UF membrane was made of ceramic material (zirconia, mean pore size 100 nm) in multichannel configuration. Recovery ratio was fixed between 80 and 90% of the initial OMW volume, operating temperature 15–35 °C and TMP between 1.0 and 2.25 bar. UF succeeded in the separation of high molecular weight constituents including suspended solids, as well as the condensation of solid, fat, lipid components (up to 90%) and a large amount of the phenolic compounds (~50%).

Polymeric membranes in spiral-wound configuration were used for either NF (200 Da MWCO) or RO (100 Da MWCO) tests, in order to further treat UF permeate. In NF tests, temperature was kept constant at 20 °C and best TMP turned out to be equal to 20 bar, leading to satisfactory permeate flow rate between 100 and 120 L/h. Following the NF step, phenols were removed to an extent exceeding 95% of the initial value, but even better efficiency was achieved by applying RO after NF, which enabled a significant conductivity, salinity and turbidity decrease and nearly 30 L/h permeate flow rate. Best performances were found to occur at 35 °C and high-pressure values (TMP = 40 bar), which allowed a turbidity value of 14 NTU and a decrease of up to 98.95% of the raw water conductivity to be reached, with a recovery between 75 and 80% of the initial OMW volume.

Finally, they stated not only that the chemical composition of the post-treated effluent was suitable for disposal in aquatic receptors or for irrigation purposes, but also that both the inorganic part of OMW (N, P, Mg, K, metal traces) and the organic (hydrocarbons, nitrogenous compounds, organic acids, polyalcohols) may be used as plant nutrients perhaps in combination with other inorganic or organic fertilizers such as manure or sludge from biological treatments of other types of wastes (Georgakakis 1989; Bais et al. 2002; Harvey et al. 2002), whereas polyphenols and fats ought to be separated, as described before, due to their phytotoxic properties (Capasso et al. 1995; García et al. 2000). Nonetheless, no data on permeate flux decline regarding the operating conditions were reported and fouling was not discussed by the authors.

In the same line, other researchers (Russo 2007; Garcia-Castello et al. 2010) have also noted the potential of integrated membrane processes in recovering polyphenols and other added-value organic compounds from OVW. Russo (2007) studied the reclamation of OVW by preliminary MF followed by two-stepped UF (6 kDa followed by 1 kDa membranes) and final RO operation. Best productivities with lowest fouling were 50 L/hm² for VRF equal to 3 for the ceramic MF membrane, whereas 10–15 L/hm² was obtained for UF with polymeric membranes of the MF permeate and up to 35 L/hm² when ultrafiltrating the UF permeate with 1 kDa ceramic membranes. Finally, 20–25 L/hm² were yielded by the RO membrane. The author reported high concentration of low-molecular-weight (LMW) polyphenols (349 ppm from initial 55 ppm in raw OVW) in the MF permeate, 76% being hydroxytyrosol. Finally, the RO retentate contained enriched and purified LMW polyphenols, proposed for food, pharmaceutical or cosmetic industries, whereas MF and UF retentates were suggested as fertilizers or for production of biogas in anaerobic reactors. Garcia-Castello et al. (2010) proposed a treatment method comprising MF, NF and finally vacuum membrane distillation (VMD) or osmotic distillation (OD). MF ensured 91 and 26% reduction of suspended solids and TOC, respectively, as well as 78% recovery of the initial content of polyphenols in the permeate stream. Further, NF achieved recovery of most polyphenols in the permeate, which was enriched by treatment by OD or VMD. A solution containing about 0.5 g/L of free LMW polyphenols, with hydroxytyrosol representing 56% of the total, was produced by using calcium chloride dihydrate solution as brine. The authors highlighted the interest of these formulations for food, cosmetic and pharmaceutical industries.

Notwithstanding, fouling on the membranes was evidenced throughout the whole posed process. High initial flux decline (35%) was observed similarly in all MF runs. Furthermore, the initial permeability could not be restored after the cleaning procedure; thus the permeate flux was noticed to decay progressively due to irreversible fouling phenomena taking place on the membrane. The polymeric 500 KDa MF membrane suffered more than 70% quick permeate flux drop without reaching steady state and just 40% of the initial permeability could be recovered after the cleaning protocol, and also high fouling indexes for the ceramic MF membranes were stated. Russo (2007) also reported MF as critical due to severe fouling and difficulties in the cleaning procedure, and warned of the necessity of a proper pretreatment. UF membranes suffered from fouling problems too, and only 80% of the initial UF permeability could be restored after the cleaning procedure. For NF operation, also, important initial permeate flux (4.68 L/m²h) decay (35%) occurred for VRF above 3.

**CONCLUSIONS**

OMW reclamation represents an environmental problem still to be resolved, currently affecting especially the
Mediterranean area, where olives are most widely cultivated. Removal of inorganic compounds from, and also a variety of phytotoxic and bacterial growth-inhibiting recalcitrant organic solutes, including polyphenols and tannins, cannot be accomplished by conventional treatments and leads to cost-ineffective results.

In this regard, membrane technologies have been widely applied to drinking water treatment and wastewater reclamation in the last years, proving to be an effective vehicle for removing most organic and inorganic compounds and microorganisms from raw water. However, only a limited number of studies have been published so far regarding OMW treatment by pressure-driven tangential membrane processes. Existing studies focus typically on meeting irrigation or municipal sewer discharge standards, and few attempt the recovery of potential-value compounds such as a variety of polyphenols including mainly oleuropein and hydroxytyrosol.

As can be asserted from the present review, there are still some unresolved problems that slow down large-scale membrane applications with respect to OMW management despite the promising perspectives for NF and RO, similar to as those encountered in drinking water production and also in wastewater treatment and many other industries in relation to membranes. Undoubtedly, the main challenge is the loss of membrane performance due to fouling issues.

With regard to this, the concept of the threshold flux is key to control fouling inhibition in all membrane operations. It is essential to set up an adequate pretreatment upstream of the NF or RO unit. Adequately targeted pretreatment should be chosen for the specific binomium membrane-feed to enhance threshold flux and inhibit fouling on the membranes. Proper pretreatment processes increase threshold flux values whereas improper ones may not improve or even worsen them.

With respect to this, several membranes materials, configurations and pore sizes have been tested up to now, and also different pretreatments including sedimentation, centrifugation, biosorption, filtration, sieving and MF, various types of flocculation as well as AOPs such as Fenton-like oxidation and UV/TiO₂ photocatalysis have been applied prior to NF and RO operations. These pretreatments provide different organic concentration abatement and also shift differently the particle size distribution of the colloidal and suspended matter. The latter is also a relevant factor. According to the pore blocking model, only particles of certain size can lead to fouling issues in a short time, which are those having a size similar to that of pores.

As future tasks, research on cost-effective OMW pretreatments, either new ones or more efficient combinations of those already existing, should continue, to ensure steady-state efficiency. Further research on optimized operating conditions for each integrated pretreatment-membrane operation is also necessary. All this will reduce the frequency of the cleaning cycles and prolong membrane lifetime too, improving process economics as a result.

This review constitutes a starting point to proceed with OMW purification beyond recycling for irrigation or depuration for discharge purposes, with the aim of meeting the standards to reuse OMW in the olive oil production process, as well as the recovery of valuable compounds which would make the OMW reclamation process more economically interesting.

REFERENCES


Calabrò, V., Curcio, S., De Paola, M. G. & Iorio, G. 2002 Membrane bioreactor for the enzymatic oxidation of...


Hermosa, M. 1998 Elaboración de aceites de oliva de calidad. Obtención por el sistema dos fases. Junta de Andalucía, Consejería de Agricultura, Pesca (Elaboration of quality olive oil. Obtained by the two-phase system). Servicio de Publicaciones y Divulgación, Seville.


First received 27 March 2012; accepted in revised form 16 July 2012