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On the Purification of Agro-Industrial Wastewater by Membrane Technologies: The Case of Olive Mill Effluents

Javier Miguel Ochando-Pulido and
Antonio Martinez-Ferez

Additional information is available at the end of the chapter

Abstract

The olive oil production is one of the main industrial activities in the Mediterranean Basin: Italy, Portugal, Greece, and Northern African countries—Syria, Algeria, Turkey, Morocco, Tunisia, Libya, Lebanon, and Egypt. Also, France, Serbia and Montenegro, Macedonia, Cyprus, Turkey, Israel, and Jordan produce a considerable annual yield. Moreover, it is an emergent agro-food industry in China, the USA, Australia, the Middle East, and China, which is expected to develop a considerable production potential. Hence, the treatment of olive mill effluents is a task of global concern. In this context, advanced separation technologies comprising membranes and adsorption resins have been a breakthrough in terms of advanced separation and purification technologies, but many aspects are still in development or under investigation. In this chapter, a focus on the use of membrane and ion adsorption technologies for the purification of these wastewaters will be given. The effect of different factors comprising the type of membrane, i.e., ultrafiltration, nanofiltration, and reverse osmosis; the type of adsorbent (waste material, resins); and the operating conditions will be addressed. Conventional treatments are not able to abate the high concentration of dissolved species present in these effluents. The use of these technologies can be a feasible solution if properly engineered.

Keywords: olive mill effluents, membranes, adsorption, ion exchange, wastewater treatment

1. Introduction

The scarcity of water particularly concerns agricultural irrigation, which demands more than 70% of the total water consumption worldwide. In this scenario, however, there is a big potential to use regenerated wastewater for irrigation purposes. Reuse of used regenerated wastewater could be a very positive solution regarding environmental and economic impacts.

In the last decades, new advanced separation technologies, less intensive in terms of specific energy consumption than conventional separation procedures and "greener" regarding the minor use of chemicals and reagents to achieve the desired separation, have been more and more implemented. Concretely, membrane technology, adsorption, and ion-exchange (IE) processes can take the lead for these purposes.

Adsorption technology implies relatively low operation costs and long service life because adsorption materials can be regenerated and reused or raw materials can be used. Indeed, adsorption is attractive for its simplicity of design, avoidance of toxic solvents, and minimization of the transformation of the target substances [1]. On another hand, ion exchange is considered a green and simple technology, capable of achieving high removal efficiencies and targeted selectivity, with application for species from wastewaters [2].

Otherwise, membrane technology is modular, easy to design, thus easily scalable to the industry, requires low maintenance, and is environmentally friendly, providing high purifying capacity and selectivity [3–10]. There has been a significant boost in the use of membranes for a plethora of applications and particularly in the field of water and wastewater treatments in the last years. This impulse has been a result of the new membrane materials, modules designs, and optimization of the operating conditions, in specific those for the minimization of fouling issues.

In fact, membrane processes are becoming increasingly used in purifying processes for water and groundwater, to replace classic separation processes, as well as for the reclamation of effluents of different origins, especially those by-produced in agro-industries [6–15].

Among agro-industrial effluents, olive mill wastewater (OMW), generated during the production of olive oil in factories called "mills," is one of the most hardly polluted, depending on the procedure used, reaching chemical oxygen demand (COD) which values up to 100,000 mg/L. The volumes of these effluents have increased markedly in the last decades. Currently, average-sized modern olive oil mills generate several tenths of cubic meters of OMW daily, which raises several millions of cubic meters a year. This can be explained by two linked facts: the increase in the demand of olive oil worldwide due to its health-promoting features (nutritional, antioxidant, anti-inflammatory, cosmetic) and the adoption of continuous production procedures as a response to cope with that demand. Now, the affected countries are not only those in the Mediterranean region, where these industries are ancestral and represent an important sector of the industrial economy, i.e., Spain, Italy, Portugal, Greece, and Northern African countries—Syria, Algeria, Turkey, Morocco, Tunisia, Libya, Lebanon, and Egypt, but also France, Serbia and Montenegro, Macedonia, Cyprus, Turkey, Israel, and

Jordan, as well as the USA, the Middle East, and China, with important production capacities nowadays.

The treatment of the olive mill effluents includes wastewater from the washing of the olives (OWW), as well as olive mill wastewater (OMW-3, for three phases of mills), wastewater from olive oil washing (OMW-2), as well as from other activities in the facility, including cleaning and sanitation. OWW includes high concentration of suspended solids (mainly, peel, pulp, ground, branches, and leaves debris) dragged during the olive fruit washing process but low concentration of dissolved organic matter—depending on the water flow exchange rate in the washing machines during the fruit cleaning procedure—usually lower than the standardized limits to discharge the effluent on superficial land suitable for the purpose.

OMW is characterized by strong odor nuisance, acid pH, intensive violet-dark color, and high saline toxicity, exhibiting considerable electroconductivity (EC) values [16]. Uncontrolled disposal of these effluents represents an environmental hazard, causing soil contamination, underground leakage, and water body pollution. Due to this presence of high COD load including refractory compounds, as well as fats and lipids, direct discharge of these wastewaters to the municipal sewage treatment plants is forbidden. Legal limits are set to prevent difficulties to keep the biomasses alive on which the municipal sewer treatment plants rely.

Discharge of untreated OMW to the ground fields and superficial waters bodies is currently prohibited in Spain, whereas in Italy as well as in other European countries, only partial discharge on suitable terrains is allowed; otherwise, in Portugal OMW can be stored and used for irrigation of arbustive cultures under control manner. Straight discharge of OMW has been reported to cause strong odor nuisance, soil contamination, plants growth inhibition, underground leaks, water body pollution, and hindrance of self-purification processes, as well as severe impacts to the aquatic fauna and to the ecological status [16–20].

The two-phase system appears to be more ecological, thus has been strongly promoted in Spain, and is now being implemented in Portugal and Greece. Nevertheless, the three-phase system is still surviving in other countries where scarcity of financial support has not permitted the technological switch. Considering that in the two-phase extraction water injection is only practiced in the final vertical centrifugation step, the volume of liquid effluent derived from the decanting process (OMW-2) is reduced by one third on average if compared to the amount required for the three-phase system. Moreover, much of the organic matter remains in the solid waste, which contains more humidity than the pomace from the three-phase system (60–70% in two-phase systems versus 30–45% in three-phase ones, OMW-3) and hence OMW-2 exhibits lower pollutants degree, too (**Table 1**).

In this chapter, a focus on the use of membrane and adsorption technologies for the purification of OMW will be given. The effect of different factors comprising the type of membrane, that is, microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO), the type of adsorbent (waste material, resins), and the operating conditions will be addressed. The problem of membrane fouling for these systems will also be covered.

Parameter	OMW-P	OMW-3	OMET-2	OMW-2	OWW
pH	4.5	5.4	7.2	4.9	6.3
Moisture, %	93.0	93.4	99.4	99.3	99.7
Total solids, %	12.0	6.6	0.59	0.6	0.27
Organic matter, %	10.5	5.8	0.39	0.49	0.10
Ashes, %	1.5	0.9	0.21	0.11	0.17
BOD_5, mg/L	90.0	42.0	0.29	0.79	0.50
COD, mg/L	180.0	151.4	7.1	7.8	0.8
Total phenols, mg/L	2,400	921.0	86.0	157.0	4.0
EC, mS·cm^{-1}	9.0	7.9	1.9	1.3	0.9

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

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

Conventional physicochemical treatments are not effective to eliminate the significant salinity of these wastewaters, reflected in their high electric conductivity values. These treatments are not able to abate the high concentration of dissolved species present in these effluents, which present hazardous salinity levels per guideline established by the FAO for irrigation purposes or discharge into public waterways. The use of membrane and adsorption technologies can be a feasible solution if properly engineered.

2. Membrane processes for olive mill effluent purification

Membrane technology, in particular pressure-driven membrane processes comprising MF, UF, NF, and RO, can offer a series of advantages in contrast with other separation processes, making them very promising and environmentally friendly for the purification and remediation of OMW: needless of chemicals and reagents, e.g., solvents—to accomplish the desired separation and concentration; minor costs (capex and opex) and specific energetic requirements than most conventional separation alternatives, upon significant purification potentiality, selectivity, and recovery factors; and also easy scaling to the industry, low space necessities as they are modular, design simplicity, easy operation, and low maintenance needs [5–10].

Fouling mechanisms are very important to fully understand what is taking place between the membrane and the effluent, in view of the adoption and implementation of adequate decisions for the successful design of the membrane plant. This comprises the setup of specifically tailored pretreatment process and optimized operating conditions. Irreversible fouling arises quickly on the membranes due to the high concentration of pollutants when wastewater is purified without

any pretreatment [5–12]. Therefore, adequate and optimally designed pretreatment processes on each particular feedstock, in other words, pretreatment tailoring of membrane processes, must be developed in order to maximize productivity and minimize fouling.

2.1. Microfiltration and ultrafiltration membranes

Canepa et al. [21] conducted a study on OMW-3 (average COD = 90 g/L) treatment based on a combined UF membrane followed by adsorption and RO process at pilot scale. The UF membrane was made of polysulfone, the permeate was treated with adsorbing polymers, and the resins eluate with RO polypiperazine-amide membranes. A rapid decline of the UF permeate flux was observed by the authors, and a daily washing was necessary. The fact that there was a flux decline of 80% after 20 h of UF and 70% after 15 h for the RO membrane was a capital handicap for the feasibility of the proposed process. UF was also examined by Borsani and Ferrando [22]. They proposed a pretreatment consisting of oil removal and suspended solid settling, achieving a final 50% organic matter removal with respect to the raw OMW-3 (COD = 70 g/L). Turano et al. [23] proposed centrifugation as pretreatment, simple, and mechanical operation which does not need addition of chemicals and is available in the production line, before UF—polysulfone, molecular weight cutoff (MWCO) 17 kDa—for the treatment of OMW-3. The centrifugation pretreatment removed 80% of the suspended solid concentration, and 90% COD reduction was achieved at the outlet of the integrated process. Paraskeva et al. [24] examined the treatment/fractionation of OMW-3 by a combination of polypropylene filter screening (80 μm), UF (zirconia, mean pore size 100 nm) followed by NF (polymeric, 200 Da) and RO. In particular, UF removed suspended solids and solid fat/lipid components (90%).

Stoller and Chianese [14] studied the purification of olive washing wastewater (OWW) to comply with municipal sewer discharge standards in Italy. In contrast with OMW, this effluent presents moderate organic pollutant load but high concentration of suspended solids. The authors proposed a coagulation-flocculation pretreatment with polyelectrolytes (aluminum sulfate (AS) or aluminum hydroxide (AH)) before UF and NF in series (composite thin-film spiral-wound membranes). Both pretreatment processes yielded similar COD and biological oxygen demand (BOD$_5$) rejection efficiencies, but higher productivity was observed in the subsequent membrane-in-series process after flocculation with AS. The same procedure was applied by these researchers to OMW-3 [8, 10]. In this case, they also compared the results with two additional pretreatments, heterogeneous photocatalysis with titania nanocatalysts and aerobic digestion. They noted that major pollutant removal by the pretreatment, e.g., COD, is not sufficient to state the suitability of the adopted pretreatment for the downstream membrane operation, but the fact that the pollutant particle size is shifted away from the size of the membrane pores is relevant to enhance steady-state flux.

On another hand, Akdemir and Ozer [25] applied pH adjustment (acidic or alkaline) and cartridge filtration (20 μm) as pretreatment before UF (MWCO 30–100 kDa) and reported the best performance for the 100 kDa UF membrane, pointing for 1 bar as the critical pressure to reduce fouling issues. Also, Coskun et al. [26] examined UF as part of an integral membrane process for OMW-3 reclamation, but did not consider the entity of fouling in the performance

of the membranes. Zirehpour et al. [27] examined a lab-made UF membrane for the purification of OMW-3, preceded by a MF membrane (50, 5, and 0.2 μm). The commercial UF membrane provided higher flux than the lab-made one, but the antifouling properties and rejection efficiency of the latter were better.

On another hand, Ochando-Pulido et al. [28, 29] tested a polymeric UF membrane for the reclamation of both OWW and OMW-2, separately or mixed. As pretreatments, three different processes were examined: (i) first, gridding (cut size equal to 300 μm) of the raw effluent was carried out in order to remove the coarse particles; (ii) then, pH-temperature (T) flocculation (pH-T F) was performed by adding HNO_3 (70% w/w) under continuous stirring (320 rpm); and (iii) the supernatant phase of the pH-T F process after the separation of the mud was either directly conducted to the UF unit and thereby referred to as OMWW-F or further pretreated by photocatalysis (PhC) under ultraviolet irradiation (UV) with lab-made ferromagnetic-core TiO_2 nanoparticles (UV/TiO_2 PhC), thus named OMWW-F/PhC. Finally, the differently pretreated streams were driven to the UF and NF membrane units. The lab-made ferromagnetic photocatalyst nanoparticles were produced in three consecutive steps, following the procedure fully reported elsewhere [30]. Briefly, in the first place, magnetite was synthesized by a sol-gel process in a spinning disk reactor, using tetraethylorthosilicate and tetraisopropoxide as precursors. Moreover, threshold flux-based methods, as previously pointed by Stoller [9], were applied for to optimize the design of the plant and control of the operation.

The first studies on the experimental and theoretical behavior of fouling in MF and UF membranes were performed by Belfort et al., Field and Aimar [31, 32]. The first theoretical model that shed light on membrane transport phenomena of colloidal particles was elaborated by the research groups of Field et al. [3, 32], Bacchin et al. [33], and Mänttäri and Nystörm, [34]. The concept of the critical flux, as the flux which can be successfully attained by a given membrane without incurring in fouling formation during operation time, was explained and proven by these scientists for MF membranes. The insight into the different fouling typologies was addressed by Bacchin et al. and Ognier et al. Fouling was explained because of local conditions that may trigger liquid/gel phases over the membrane layer and in the membrane pores caused by concentration polarization profiles [35, 36]. Later, this concept was also extended to UF and NF membranes [4] and complemented with the concept of the threshold flux. In many cases, it was observed that it was not possible to completely inhibit fouling during the operation of some liquid-liquid membrane systems, as is the case of wastewater [4–7, 37]. The threshold flux divides a low fouling region from a high fouling region. Stoller et al. [38] worked on a reliable methodology to convert previously measured critical flux data into threshold flux values in his studies on OMW-3 purification with polymeric NF membranes. Stoller underlined the key necessity to develop quick and reliable methods capable to allow the estimation of threshold flux conditions and for the conversion of previously available critical flux measurement data into threshold flux data. Finally, both concepts were merged by Stoller and Ochando [39] into a new concept, the boundary flux. The knowledge of real-time boundary flux values is a key factor to design stable control systems for membrane processes (**Figure 1**).
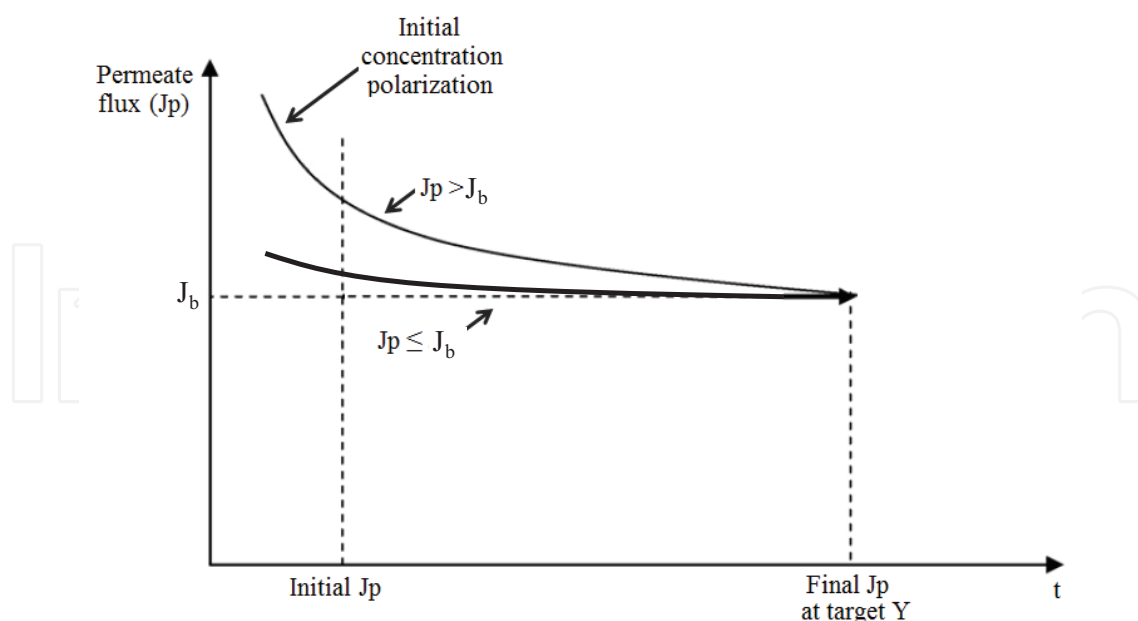
Figure 1. Operation strategies for membranes: above (curve line) or upon boundary flux (J_b) (straight line) conditions; J_p: permeate flux at any time t [29].

2.2. Nanofiltration and reverse osmosis membranes

The specific selectivity toward small solutes and the lower energy consumption of NF membranes have boosted their use as tertiary treatment in integrated wastewater treatment processes. On the other hand, RO membranes permit complying with the most stringent regulations for public health and environment protection. Both types of membranes are already applied in the management of industrial effluents of very different sectors, such as stainless steel [40], energy cogeneration [41], nuclear power [42], textile and tannery [43–47], coking [48, 49], carwash [50], pulp and paper [34, 51], pharmaceutical [52], and agro-food industries, such as dairy [13], tomato [12], and olive oil [5–10, 24], among others. However, again, the problem of fouling is always present in the treatment of any kind of effluent by NF and RO membranes. The critical, threshold, and boundary flux theories are, nonetheless, applicable as well for the design and control of the membrane plant.

Paraskeva et al. [24] used NF after MF/UF for the purification of OMW-3, achieving flux values up to 100–120 L/h and 95% phenol removal. Moreover, better efficiency was achieved by applying RO after NF, ensuring a significant conductivity, salinity, and turbidity decrease and nearly 30 L/h flux and 75–80% recovery of the initial feed volume. However, the permeate flux data regarding fouling was not discussed by the authors. The post-treated effluent was suitable for disposal in aquatic receptors or for irrigation purposes, and the inorganic part (including nitrogen, phosphorus, magnesium, potassium, and metal traces) and the organic fraction (hydrocarbons, nitrogenous compounds, organic acids, polyalcohols) may be potential plant nutrients, mixed with other inorganic or organic fertilizers, for instance, manure or sludge from biological treatments of other sorts of wastes. Zirehpour et al. (2012) evaluated

the performance of a NF membrane at the end of a treatment line comprising MF and UF for OMW-3 purification. A specific arrangement of the integrated membrane system was found 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. Analysis of the fouling behavior of the used membranes was performed, per the recovery ratio and degree of the total flux loss during volume reduction factor experiments.

Di Lecce et al. [53] used polyamide thin-film composite spiral-wound NF at pilot scale for the fractionation of OMW-3 after MF. The purified NF permeate obtained presented COD and phenolic loads in the range of the standards for discharge into surface waters, with a rejection of 98% for COD, dry matter, and phenolic compounds. However, again, the performance of the NF membrane regarding its fouling was not reported.

On another hand, Ochando-Pulido et al. [28, 29] tested polymeric NF and RO membranes for the reclamation of OWW and OMW-2. The NF membrane was downstream of an UF one, and the effluent was initially pretreated by flocculation and/or heterogeneous photocatalysis (pH-T F and/or UV/TiO$_2$ PhC). This treatment sequence helped reducing the required membrane area for both membranes, and the applied UV/TiO$_2$ photocatalysis process enhanced the productivity and longevity of both membranes, achieving a final treated effluent stream compatible for irrigation. Moreover, the threshold flux theory was applied successfully to determine the threshold operating conditions for the process. In a similar line, Stoller [10] worked during 3 years continuously with a NF membrane for the treatment of OMW-3 with the goal to check for the reliability of threshold flux optimization methodologies for the fouling control on the used membrane in the long run. The author reported the successful operation of the NF membrane for the used period of pilot-scale work. Stoller highlighted that this was possible if adequately targeted fouling minimization control methods were carried out, based on the estimation of the critical flux for the optimal operation of the plant. These theories were successfully applied to this system, which could be explained by the threshold flux model.

Ochando-Pulido et al. [6, 7] studied the reclamation of OMW-2 (Spain) by RO, with the goal of "closing the loop," as is the trend of the current "circular economy." the quality to recirculate the final effluent to the olive washing machines of the manufacture process to finally close the loop. The effluent was firstly treated by means of an advanced oxidation process (AOP) which consisted in homogeneous catalysis with Fenton's reagents [16]. The authors noticed the importance of an operating variable of the RO process, the recirculation of a fraction of the permeate. The adoption of this operating sequence permitted enhancing the permeate production of the membrane, which was also stabilized, and resulted as well in a steady rejection of the target species, comprising suspended solids, phenols, and iron removal total rejection, as high as 99.4 and 98.2% of the COD and conductivity, respectively.

3. Adsorption processes for olive mill effluent purification

Adsorption technology has several advantages such as simple handling, relatively low operation costs, and long service lifetime because adsorption materials can be regenerated and reused. Also, adsorption is attractive for its simplicity of design, avoids toxic solvents,

and minimizes the transformation of the target substances [1]. On the contrary, it can present limited purification efficiency and the loss of capacity depending on the feed solution [54].

Among the adsorption methodologies tested with OMW, there are some studies using so-called biosorbents (those of biological origin) as alternatives to other expensive adsorbents. Achak et al. [55] investigated the performance of a low-cost biosorbent made of banana peel. They examined various parameters including adsorbent dosage, pH, and contact time. After optimization, adsorption of phenols from 60 to 88% was achieved upon the equilibrium reached after 3 h of contact time. These authors also tested low-cost biosorbent, wheat bran, which is inexpensive and an available biomaterial. This biosorbent material yielded adsorption efficiencies toward phenolic compounds up to 67%, and the equilibrium was reached in 4 h of contact time. Moreover, both materials were found to provide better performances upon alkaline pH environments.

Another biosorbent, olive stone biomass, by-product of olive oil industry, was addressed by as adsorbent for iron from secondary-treated OMW [18, 56, 57]. The OMW effluent was pretreated by an advanced oxidation process based on Fenton's reaction, which uses iron-based catalysts. The equilibrium adsorption capacity was found to increase when the particle size decreased (from < 1 to 4.8 mm). The percentage of iron adsorption increased from 30 to 70% when the initial concentration of biomass increased from 25 to 125 g/L. These authors demonstrated that direct reuse of olive pitches or a simple washing with cold and hot water can be sufficient for the adsorption process, which was fast and spontaneous within the first 10–20 min. The experimental data supports both pseudo-first and pseudo-second order models. Also, the adsorption capacity became incremented with the temperature, pin pointing for an endothermic adsorption process. In addition, the values of thermodynamic parameters of the process were reported: the activation energy ($Ea = 8.04$ kJ mol^{-1}), the standard enthalpy ($\Delta H_0 = 8.86$ kJ mol^{-1}), the standard free energy ($\Delta G_0 = -19.51$ kJ mol^{-1}), and the standard entropy ($\Delta S_0 = 91.4$ J mol^{-1}K^{-1}). Furthermore, column regeneration studies were carried out for various adsorption-desorption cycles [56], and the column performance was confirmed to permit multiple service and regeneration cycles, thus enabling the treatment of considerably large volumes of wastewater. A negligible loss in bed height and olive stone mass was observed. After adsorption, the olive stone biosorbent could be used as a biofuel for domestic or industrial uses. The present process was highlighted to be environmentally friendly and capable to reduce the iron load from other different effluents, providing an affordable technology for these small- and medium-scale industries.

Dried *Azolla caroliniana*, a freshwater aquatic fern, and granular activated carbon (AFC-LS activated with phosphoric acid) were studied to evaluate their adsorption and desorption capacities by Ena et al. [58]. Granular activated carbon (GAC) showed better efficiency, although total phenols were more than twice as concentrated in Azolla as those found in the GAC powder. Other studies with activated carbon, in this case in powdered form, for OMW treatment were performed by Sabbah et al. [59], after sand filtration, achieving 95% removal of the phenolic compounds present in OMW. Also, Azzam et al. [60] examined powdered activated carbon in one-stage, two-stage, and three-stage countercurrent adsorption system series in stirred batch vessels. The three-stage countercurrent adsorption process could reduce the phenol concentration in 96%, and the equilibrium was reached within 2–3 h.

Another adsorption material used is adsorption resins. Novel ion-exchange (IE) resins developed over the past few decades have promoted this technology as a suitable separation and purification process for wastewater treatment and fractionation purposes. In this sense, IE is considered a green and simple technology, capable of achieving high removal efficiencies and targeted selectivity [2].

IE technology is very attractive because of its relative simplicity of application as well as due to the low cost and the effectiveness to remove target species from wastewaters, particularly from diluted solutions. IE resins have also found an increasing application in the drinking water treatment sector over the last few decades, especially when there is a high concentration of natural organic matter (NOM) since high percentages on the removal efficiency of NOM by IE process are found (Comstock and Boyer) [61]. The efficient use of IE depends on several operating factors such as the contact time, operating temperature, pH, flow rate, initial pollutant concentration, and resin characteristics [62].

Canepa et al. [21] used a resin-bed column for the final purification of OMW-3 previously treated by UF, and performed good regarding the retention of polyphenols, and could treat around 3000 L until saturation.

Mineral resins, such as zeolites, have been reported to be useful mineral materials for reducing the phenolic compound concentration from OMW compared to other substrates, such as clay soil and bentonite. The regeneration of zeolite was easy after treatment either by simple settling or light centrifugation procedures. Moreover, this material could be easily regenerated by a very interesting eco-friendly technique known as low-temperature ashing (LTA) [63].

On another hand, Amberlite XAD16, a nonpolar resin, was used by Scoma et al. [64] as the adsorbent phase and ethanol as biocompatible desorbing phase. This process could remove until the 60% of the phenolic compounds from OMW. Ferri et al. [65] studied the adsorption and desorption efficiency of five resins with different physical properties (Amberlite XAD4, XAD7, XAD16, IRA96, and ISOLUTE ENV+) toward an aqueous solution of 10 typical phenolic compounds occurring in OMW. The desorption solvents tested were water, methanol, and ethanol under basic and acidified conditions. IRA96 polar resin reached the highest phenol adsorption (76%). However, the maximum desorption ratios achieved (60%) was achieved with ENV + resin and ethanol as the desorbing phase.

Zagklis et al. [66] tested the fractionation of OMW-3 exiting a previous membrane process comprising NF and RO by a three-step resin process. The nonionic XAD4, XAD16, and XAD7HP resins were selected. The proposed three-step resin process enabled at high extent the separation of phenols from carbohydrates, which hinder further concentration of phenols from the RO concentrate. After this, vacuum distillation was implemented for the concentration of phenols, facilitated by the carbohydrate removal and the change of solvent from water to ethanol. The final product had phenol concentration of 378 g/L in gallic acid equivalents, from an initial content in the raw OMW of 2.64 g/L. Kaleh and Geißen [54] studied the behavior of 16 commercial resins, and they demonstrated that the reduction and selective uptake of phenols from OMW are feasible by choosing the appropriate sorbents, conditions, and pretreatment.

Víctor-Ortega et al. [67] studied the removal of phenols from synthetic olive mill aqueous solutions with two different anionic resins: a strong-base resin (Amberlyst A26) and a weak-base one (Amberlite IRA-67). The effect of the phenolic load in the raw effluent and the recirculation time were studied. The equilibrium data were modeled with Langmuir, Freundlich, and Temkin isotherms, and the best correlated one was found to be Langmuir isotherm for both resins. Kinetics of the IE process was examined with the pseudo-first order, pseudo-second order, and intraparticle diffusion models. Both second-order and intraparticle diffusion models could describe the IE mechanism accurately. On the other hand, results revealed that phenol uptake is a spontaneous process for Amberlyst A26 anionic resin ($\Delta G° = -1.55$ kJ mol^{-1}), whereas it was found to be non-spontaneous for Amberlite IRA-67 ($\Delta G° = 3.06$ kJ mol^{-1}). Finally, Amberlyst A26 resin was confirmed to be considerably more efficient (80–98%) than Amberlite IRA-67 for the potential removal of phenols from olive mill industrial effluents.

In addition to this, Víctor-Ortega et al. [68] examined a continuous-flow IE process for the purification of OMW-2. They compared the performance of strong-base and weak-base anionic resins. They found that the pH of the feed affected the IE process. This permitted to achieve up to 98% removal of phenols upon an increment of the pH up to 7 with the strong-base resin. The efficiency was noted to be maintained constant at higher pH value. Otherwise, with the other resin, a similar behavior was observed, and the phenolic concentration could be removed up to 57% at pH around 7. With the aim to predict the performance of the resins bed break breakthrough curves, the experimental data were fitted to various models for varying effluent concentrations (5–100 mg/L) under the optimal simulated operating conditions. The authors found an enhancement of the IE efficacy with major concentration of phenols in the feed. For the different model equations tested, Thomas model yielded utmost accuracy, above that of Yoon-Nelson and Clark models. To sum up, and as a very important fact, column regeneration studies showed that almost 100% phenol recovery efficiencies were ensured. The proposed IE process led to a phenol solution susceptible to be concentrated and used in food, cosmetic, or pharmaceutical sectors and a purified effluent for irrigation purposes.

4. Conclusions

The production of olive oil is becoming global, and thus the treatment of the derived effluents from this industry includes wastewater from olive washing (OWW), olive mill wastewater (OMW, for three phases of mills), and wastewater from olive oil washing (OOW).

Conventional physicochemical treatments are not effective to eliminate the significant salinity of OME, reflected in their high electric conductivity values. In this context, advanced separation technologies comprising membranes and adsorption resins have been a breakthrough in terms of advanced separation and purification technologies, but many aspects are still in development or under investigation.

In this chapter, a focus on the use of membrane and ion adsorption technologies for the purification of OMW is reported. The effect of different factors comprising the type of membrane, i.e., ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO); the type of

adsorbent (waste material, resins); and the operating conditions will be addressed. The problem of membrane fouling for these systems will also be covered. The use of membrane and adsorption technologies can be a feasible solution if properly engineered, to comply with the guidelines established, e.g., by the Food and Agricultural Organization (FAO) for irrigation purposes or discharge into public waterways.

Author details

Javier Miguel Ochando-Pulido* and Antonio Martinez-Ferez

*Address all correspondence to: jmochandop@gmail.com

Department of Chemical Engineering, University of Granada, Granada, Spain

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