Analysis of Fouling Resistances under Dynamic Filtration of Pretreated Olive Mill Wastewater on a Loose Reverse Osmosis Membrane

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In this work, a loose reverse osmosis (RO) membrane (Osmonics AK model), capable of offering beforehand higher fluxes under lower operating pressure than typical tight reverse osmosis membranes but still offering similar rejection, was used for the final purification of olive mill wastewater. However, the output that a membrane may offer when it is virgin and readily used will change in time due to membrane fouling. If not properly considered, the advantages that a chosen membrane may offer in contrast with others would quickly and often irreversibly vanish, with the consequences in terms of capital expenses that this will represent.

One approach to meet the investor's needs to trust membrane technology is to guarantee that fouling will be inhibited as much as possible, but to overcome the loss of performance that fouling carries engineers overdesign the membrane plants by using too wide safety margins that trigger the costs sensibly. Since the mechanisms by which fouling phenomena are triggered are always complex, the osmotic-pressure resistances-in-series model can be a simple but reliable model to describe the membrane response and predict its performance in time.

In this context, the normalized fouling measured on the examined RO membrane was found to be minimum in the operating pressure range between 5 and 8 bar (0.65-0.98, respectively), and it decreased down to 0.51 upon increasing the crossflow up to 5.09 m s^{-1}, avoiding irreversible fouling. Moreover, significantly minor fouling (0.33) was attained at the lowest temperature, regularly experienced during the olive oil production campaign. On another hand, the rejection towards organic solutes was maintained above 97%.

1. Introduction

Great efforts have been made in the last years by scientists and engineers with the goal of providing a suitable solution for the management of olive mill wastewaters (OMW), but given the complexity or low viability of the proposals their actual transference to the industrial scale has not been feasible yet.

Olive oil industries are one of the principal industrial activities in the Mediterranean Countries, comprising Spain, Italy, Portugal, Greece, Cyprus and Northern African countries - Morocco, Turkey, Iran, Algeria, Tunisia, Egypt, Israel and Palestine - as well as in emerging ones like China, Australia, the Middle East and the USA. These industries by-produce high volumes of strongly polluted OMW. Direct discharge of OMW causes hazardous pollution: contamination of soil and water bodies and inhibition of self-purification processes, strong odor in the surroundings, phytotoxic consequences to the aquatic fauna and hindrance of plants growth (Niaounakis and Halvadakis, 2006; Paraskeva and Diamadopoulos, 2006).

Within this scenario, the European Union is committed to increase the vigilance and make European Environmental Regulations, as agreed in the 'H2020 Horizon'. The European Directive 2000/60/CE established the legal framework to confer the utmost protection to water, to impulse the use of regenerated wastewater. Currently, direct discharge of OMW to the soil and water bodies is prohibited in Spain, whereas in Italy, Portugal and other European countries only the partial discharge on suitable terrains is allowed.

One of the main obstacles for the implementation of cost-effective processes for OMW management relies in the fact that olive mills are typically small factories, geographically dispersed. An average-sized olive oil

factory normally by-produces around 10 - 15 m^3 of OMW daily. A centralized treatment of OMW seems not feasible currently, thus an effective and simple solution is needed for these small plants.

Membrane technology, given its versatility and modular nature, can represent a cost-effective solution for the reclamation of these effluents in these typical small factories. Membrane processes are becoming extensively used in numerous applications, as standalone, integrated or substitutive operations, also in the purification of water and groundwater, and in the reclamation of wastewater of very diverse sources, e.g. agro-industrial (Iaquinta et al., 2009; Ochando-Pulido et al., 2014a,b; Stoller et al., 2013a,b). The availability of new membrane materials, designs, module concepts and know-how has improved its credibility among investors in recent years.

On the hand, concentration polarization and fouling are always present in the treatment of wastewater streams by membranes and it is imperative to control them to ensure the appropriate operation and design of the plant. Fouling is a complex phenomenon involving different mechanisms such as pore blocking and plugging, cake, gel and biofilm formation (Field et al., 1995; Field and Pearce, 2011; Bacchin et al., 2006). During operation, fouling leads to an increase in the energy costs to maintain the target permeate production, and the operating costs due to frequent plant shut-downs for membrane cleaning procedures. Also, the longevity of the membranes can be irretrievably shortened due to irreversible fouling. To solve this in order to achieve adequate steady operation, engineers erroneously tend to either overdesign excessively the membrane plants in industrial scale facilities, resulting in sensible and useless increment of total costs, or under-design them due to underestimation of fouling issues, in this latter case operating above threshold conditions, not feasible technically and economically for long periods of time (Field and Pearce, 2011; Stoller et al., 2013a,b).

Minimization and control of fouling is key to achieve the competitiveness of membrane technology at industrial scale (Field and Pearce, 2011; Stoller and Ochando, 2012; Stoller et al., 2013a,b,c). In this sense, OMW contains high concentrations of a wide range of solutes in the form of suspended solids and colloidal particles which can tend to cause membrane fouling, such as organic pollutants comprising phenolic compounds, organic acids, tannins and organohalogenated contaminants, as well as inorganic matter.

In the present work, a polymeric loose reverse osmosis (RO) membrane was selected for the purification of OMW coming from modern two-phase continuous centrifugation mills. The effluent was previously conducted to a physicochemical primary-secondary treatment (OMW2ST) at pilot and industrial scale, as thoroughly described in previous works by the Authors (Ochando-Pulido et al., 2012). Within this framework, the effects of the operating conditions on membrane fouling build-up were examined by conducting well-controlled dynamic RO experiments. In case of membrane fouling, when triggered, the consequences are in most cases negative. One approach to answer the investor's need to trust this technology is to guarantee that fouling will be strongly inhibited. Since the description of fouling phenomena may be difficult and complex, engineers may avoid the consequences altogether by limiting the causes. In this work, the osmotic-pressure resistances-in-series model is used as a simple but efficient tool to describe the membrane process in time, with a focus on the fouling resistances occurring on the RO membrane during OMW2ST purification.

2. Experimental

2.1 The effluent stream

Samples of OMW were collected from different olive oil mills in Andalusia region (Spain) during the olive oil production campaign in winter, then rapidly analyzed in the lab and refrigerated for further research. After this, the samples were subjected to the primary-secondary treatment on a pilot scale (Ochando-Pulido et al., 2012). The effluent stream after the primary-secondary treatment, hereafter referred as OMW2ST, presents the physico-chemical characteristics reported in Table 1, and was the feed to the final RO purification operation.

Table 1: Physicochemical characterization of OMW2ST[a]

Parameter	OMW2ST
pH	7.5±0.3
EC (mS cm^{-1})	3.4±0.2
TSS (mg L^{-1})	14.5±1.5
COD (mg L^{-1})	195.0±30.0
Total phenolic compounds (mg L^{-1})	1.0±0.3
Total iron (mg L^{-1})	0.8±0.3
HCO$_3^-$ (mg L^{-1})	131.5±2.5
Cl$^-$ (mg L^{-1})	1020.0±25.1
Na$^+$ (mg L^{-1})	640.5±98.5

[a] OMW2ST: olive mill wastewater after pre-treatment.

2.2 Membrane operation

The membrane bench-scale plant (Prozesstechnik GmbH), was provided with a non-stirred jacketed tank (5 L) where the effluent was contained, and a diaphragm pump (Hydra-Cell) to drive the feed to a plate-and-frame membrane module (3.9 cm width x 33.5 cm length). The main operating variables were measured and displayed: the pressure, for which a constant pressure strategy (PC) was adopted, adjustable with a spring-loaded pressure-regulating valve on the concentrate outlet (Swagelok) and monitored by a digital pressure gauge (Endress+Hauser). This permitted the independent control of the applied pressure ($P_{TM \, set \, point}$ ± 0.01 bar) and the flowrate (0.1 L h^{-1} precision), regulated by a feed flow rate valve to fix the tangential velocity over the membrane; the operating temperature was regulated automatically ($T_{set \, point}$ ± 0.1 °C) via a proportional-integral-derivative (PID) electronic temperature controller (Yokogawa), connected to a chiller (PolyScience).

A commercial flat-sheet (200 cm^2 active area) RO membrane (GE Water & Process Tech.) was selected for the experiments. Its characteristics are reported in Table 2. Prior to each experiment, the membrane was equilibrated by filtering MilliQ® water at fixed pressure and temperature until a stable flux was observed, to allow for membrane compaction. Then, the hydraulic permeability of the membrane was determined by measuring the pure water flux over the admissible pressure range, at ambient temperature and turbulent flow. Thereafter, 2 L of OMW2ST were poured into the feed tank. Tangential-flow RO experiments were run in semicontinuous, recycling the concentrate stream back to the feedwater tank while steadily collecting the permeate stream and replacing the permeate outlet volume by pumping fresh effluent into the feed tank.

The effects of the operating pressure (3 - 8 bar) on the performance of the membrane were studied in terms of concentration polarization and fouling build-up. The temperature was controlled at 22 ± 0.5 °C and the tangential velocity at turbulent flow, 2.55 m s^{-1} (N_{Re} = 1.3·10^4). Fluctuations in the feed composition made the evaluation of the membrane performance difficult, thus experiments were replicated twice. After each run the membrane was fully cleaned in situ with 0.1 - 0.5 % w/v NaOH, sodium dodecyl sulfate (SDS) and citric acid solutions (Panreac S.A.) to recover it for the next experiment (Ochando-Pulido et al., 2015a,b,c).

Table 2: Specifications of the RO membrane

Feature	Specifications
Membrane type	AK
Material	Aromatic PA
Membrane structure	Asymmetric
Membrane surface	Hydrophilic
Pore size, nm	-
Permeability (m_0), L h^{-1}m^{-2} bar^{-1}	5.5 ± 0.5
Max. P, bar	8.7
Max. T, °C	50

[*]PA: polyamide; T: temperature; P: pressure.

2.3 Analytical methods

Analytical grade reagents were used for the analytical proceedings, which were triplicated. Chemical oxygen demand (COD), total suspended solids (TSS), total phenols (TPh), total iron concentrations, electroconductivity (EC) and pH analysis, were performed following standard methods (Greenberg et al., 2005). EC and pH were measured with a Crison GLP31 conductivity-meter and a Crison GLP21 pH-meter. A Helios Gamma UV-visible spectrophotometer (Thermo Fisher Scientific) was used for the COD, TPh and total iron measurements (Standard German methods ISO 8466-1 and German DIN 38402 A51). Ionic concentrations were analyzed with a Dionex DX-120 ion chromatograph (Ochando-Pulido et al., 2012).

3. Results and discussion

3.1 Osmotic-pressure resistances-in-series model

Concentration polarization and fouling were estimated by the osmotic-pressure resistances-in-series model:

$$J_p = K \cdot (\Delta P - \Delta \pi) = \frac{\Delta P - \Delta \pi}{\mu \cdot R_t} \tag{1}$$

where Jp (L h^{-1} m^{-2}) represents the permeate flux which is a function of the transmembrane pressure of the system (bar), that is, the difference between the applied pressure (ΔP) and the osmotic pressure gradients ($\Delta \pi$) between the feed side and the permeate, whereas inversely proportional to the dynamic viscosity of the

feed μ (Pa·s) and the total filtration resistance across the membrane R_t (m^{-1}). The π of the feed was calculated with Van't Hoff 's equation $\pi_f = \Sigma c_i, f RT$, where $c_{i,f}$ is the feed molar concentration (mol L^{-1}), R is the ideal gas constant (8.314 J K^{-1} mol^{-1}) and T the absolute temperature (K), and the π of the permeate was negligible.

The driving force and the total filtration resistance (R_t) may change in time because of concentration polarization and membrane fouling, leading to a decay in the permeate flux (Cheryan, 1998):

$$R_t = R_m + R_{cp} + R_{ad} + R_f \tag{2}$$

comprising the intrinsic resistance of the membrane R_m, the concentration polarization resistance R_{cp}, the adsorption resistance R_{ad} and the fouling resistance R_f.

To determine the R_m, the pure water flux was measured in recirculation mode at turbulent flow (5.09 m s^{-1}, that is $N_{Re} = 2.6 \cdot 10^4$) and ambient temperature (22 ± 0.1 °C). R_m was calculated from the inverse of the slope of the pure water flux J_w vs. P fitting, given that for pure water the following simplified equation results:

$$J_w = K_w \cdot \Delta P \Rightarrow R_m = \frac{\Delta P}{\mu \cdot J_w} \tag{3}$$

Following Choi et al. (2005), R_{cp} was defined as the filtration resistance of the system corresponding to the change in the permeate flux when the feed solution is replaced with deionized water, such that additional effects like gel and cake layer on the flux decline can be attributed to the fouling resistance R_f. The feed was thereby replaced with MilliQ® water and the R_{cp} was obtained as follows:

$$R_{cp} = \frac{\Delta P - \Delta \pi}{\mu \cdot J_{pt}} - R_m \tag{4}$$

In the present study, as a simplification assumption, the adsorption resistance R_{ad} was considered to be included within the fouling resistance R_f, given that some authors have concluded by conducting comparative static vs. dynamic filtration experiments, that R_{ad} in the absence of permeate flux is negligible in comparison with the other resistances (Choi et al., 2005). Therefore, R_f was determined per the following expression:

$$R_f = \frac{\Delta P - \Delta \pi}{\mu \cdot J_{pt}} - R_m - R_{cp} \tag{5}$$

where J_p (L h^{-1} m^{-2}) is the permeate flux at t during operation, whereas R_m and R_{cp} are previously estimated.

3.2 Analysis of the concentration polarization and fouling resistances

In first place, the intrinsic resistance of the selected RO membrane (R_m) was calculated (Table 3). It can be observed that the value of R_m was reduced with an increment in the operating temperature. R_m was found to decrease 31.1 % by increasing the temperature from 15 to 22 °C, whereas up to 24.7 % upon an increment from 22 to 30 °C. This shall be attributed to the increase of the water diffusivity through the membrane thickness as a result of the lower viscosity of the solvent, in sum to swelling changes in the physical properties of the membrane, leading to higher permeability and thus minor mass transfer resistance (Jin et al., 2009).

Table 3: Membrane resistance (R_m) and permeability (K_w) of AK membrane.

T, °C	K_w, L h^{-1}m^{-2}bar^{-1}	R_m, m^{-1}
15	4.2	$8.1 \cdot 10^{13}$
22	6.1	$5.9 \cdot 10^{13}$
30	8.1	$4.4 \cdot 10^{13}$

*Operating conditions: 2.5 m/s and 3-8 bar.

On another hand, the osmotic pressure of the feedstream was found to be in the range 1.45 - 1.52 bar for 15 - 30 °C, respectively. In Table 4, the experimental data of the RO runs carried out for OMW2ST purification upon the operating conditions examined are reported, with a focus on the initial (J_{p0}) and the steady-state permeate flux values (J_{pss}). A similar pattern was noted for the permeate flux during operation time: an initial sharp decay for a short period driven by concentration polarization and incipient fouling as a result of the rapid accumulation of solutes within the boundary region, and then a more gradual decrease (-ΔJ_p) until steady state, as the equilibrium between the foulants accumulation on the membrane surface and their sweeping back to the bulk upon the appropriate operating conditions was being approached.

The resistances due to concentration polarization and membrane fouling upon the different conditions examined are reported in the same table. Those values were normalized with respect to the intrinsic hydraulic permeability of the membrane (R_{cp}/R_m and R_f/R_m) to ensure accuracy of the results. As it can be noted, the concentration polarization resistance was found to be very similar at the lowest operating pressure values (3-5

bar), that is, 0.62-0.64, whereas it was found to decrease at the highest operating pressure conditions (8 bar). This was explained by the major hydrodynamic force at this pressure resulting in a higher permeation of both solvent and solutes through the membrane.

Otherwise, the fouling build-up during RO of OMW2ST depended on the selected values of the operating parameters for the specific RO membrane-OMW2ST feedstream binomium. Further increments of the transmembrane pressure (P_{TM}) up to a value of 8 bar led to significantly increased e flux values, that is, 44.4% for an increment of the operating pressure from 3-5 bar and 54.6% when the operating pressure was increased from 5 to 8 bar, respectively.

However, membrane fouling is evident not only from the flux decay (-ΔJp, %) but also from the decrease of the steady state filtration performance at increasing P_{TM} (Table 4). This fact is supported by the major R_f/R_m values reported at increasing operating pressure, that is, 8.8% and 6.3% increment of the fouling rate on the membrane for increment from 3-5 bar to 5-8 bar, respectively. Under certain operating conditions such as high P_{TM} values, the permeation drag may be high enough to overcome the double layer repulsion, thus favoring the deposition of particles and triggering membrane fouling.

Table 4: Membrane resistance (R_m) and permeability (K_w) of AK membrane.

P, bar	Jp_0, L h^{-1}m^{-2}	Jp_{ss}, L h^{-1}m^{-2}	Jp_c, L h^{-1}m^{-2}	R_{cp}/R_m	$\Delta(R_f/R_m)/dt$, min^{-1}
3	9.4	5.5	6.2	0.64	4.1·10^{-3}
5	14.2	9.9	7.7	0.62	4.5·10^{-3}
8	29.5	21.8	14.8	0.44	4.8·10^{-3}

[*] Operating conditions: 2.5 m/s, 22 °C and 3-8 bar.

Finally, the irreversible fouling on the RO membrane was calculated as a function of the operating conditions. The fouling resistance R_f can be divided into reversible and irreversible fouling depending on the attachment strength of the foulants to the membrane surface. The reversible fouling resistance R_{rf} is built-up by loosely attached foulants easily removable by a strong shear force or washing. On the other hand, the irreversible fouling resistance R_{if} is caused by foulants strongly attached to the membrane, in the form of pore blocking, plugging and/or clogging, as well as cake, gel and biofilm formation, and it can be difficultly removed in a successful way by such physicochemical control methods.

The irreversible fouling resistance was evaluated by measuring the recovery of the membrane pure water permeability (K_w, L m^{-2}h^{-1}bar^{-1}) once performed the cleaning protocol: at the end of each experimental RO run the membrane was cleaned following the described procedure (Ochando-Pulido et al., 2015a), after which the K_w was measured and compared with its initial value ($K_{w,0}$). The loss of membrane permeability (ΔK_w%) after each corresponding RO experimental semicontinuous run ($K_{w,0}$- $K_{w,0}$/ K_w) which could not be restored was therefore attributed to irreversible fouling occurring on the membrane.

Table 5: Irreversible fouling measured on the AK membrane.

P, bar	FR_{Kw}, %	R_{if}/R_f, %
3	82.5	17.5
5	82.4	17.6
8	85.3	14.7

[*] Operating conditions: 2.5 m/s, 22 °C and 3-8 bar.

The results obtained from the controlled dynamic RO experiments were also analyzed by means of the critical flux model. The fouling index was calculated as a function of the operating conditions by fitting the experimental permeate flux profiles data to the fouling - permeate flux equation (6):

$$Jp_t = (Jp_0 - Jp_c) \cdot e^{-bt} + Jp_c \tag{6}$$

where Jp_0 is the initial permeate flux (L h^{-1}m^{-2}) and Jt is the permeate flux at time t (L h^{-1}m^{-2}), whereas Jp_c represents the critical permeate flux (L h^{-1}m^{-2}), that is, the permeate flux yielded by the membrane in the steady-state, and b is the fouling index (h^{-1}), which quantifies the dynamic fouling build-up on the membrane during operation time. Both Jp_c and b were estimated simultaneously by a non-linear parameter estimation method (Field and Pearce, 2011; Ochando-Pulido et al., 2014a; Stoller et al., 2013a,b). The obtained results support the ones previously stated (Table 4).

4. Conclusion

In the present work, the effects of the operating conditions on membrane fouling build-up were examined by conducting controlled dynamic RO experiments for pretreated olive mill wastewater purification. Membrane technology, given its versatility and modular nature, can represent a cost-effective solution for the reclamation of these effluents in these typical small factories.

One approach to answer the investor's need to trust this technology is to guarantee that fouling will be strongly inhibited. Since the description of fouling phenomena may be difficult and complex, engineers may avoid the consequences altogether by limiting the causes. In this work, the osmotic-pressure resistances-in-series model was used as a simple but efficient tool to describe the membrane process in time, with a focus on the fouling resistances occurring on the RO membrane during OMW2ST purification. The obtained results are also supported by the critical flux model.

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