Experimental Design Optimization Of A Reverse Osmosis Membrane For Olive Mill Wastewater Purification After Advanced Oxidation

Ochando-Pulıdo, Javıer M.[1,*] Stoller, M.[2] And Martínez-Férez, A.[3]

[1] University of Granada, Dept. of Chemical Engineering, Granada, Spain

[2] University of Rome La Sapienza, Dept. of Chemical Materials Environmental Engineering, Rome, Italy

*corresponding author:

e-mail: jmochandop@ugr.es

Abstract

Although membranes are a mature technology, many aspects are still in development. The main handicap is membrane fouling, investigated by a plethora of researchers in the last years to convince investors to implement membranes as substitutes of a range of unit operations at industrial scale. In the field of wastewater treatments, this is especially problematic, given the low economic value of the product, that is, treated water.

The management of the effluents generated by olive oil industries represents an ever-increasing problem still unresolved. Within this framework, the prediction of the performance of a selected membrane is mandatory for its operation when implemented in a treatment process at industrial scale. The core of the present work was the modelling and optimization of a reverse osmosis (RO) membrane operation for the purification of a tertiary-treated olive mill wastewater stream (OMW2TT). Statistical multifactorial analysis was employed to examined the variables including the operating pressure (P_{TM}), tangential velocity (v_t) and operating temperature (T). Upon the optimized parameters, namely ambient temperature (24 º C), moderate operating pressure (31.5) and turbulent flow (4 m s^{-1}), the standards to reuse the purified effluent for irrigation, discharge to sewers or even reused in the production process were ensured.

Keywords: Wastewater reclamation; Membrane processes; Reverse osmosis; Modelization; Olive mill wastewater.

1. Introduction

Membrane technology can be a potential tool for the reclamation of OMW. However, fouling is always present in the treatment of wastewater streams by membranes and it is imperative to control it in order 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). During operation, fouling leads to an increase in the energy costs to maintain the target permeate production, and also the operating costs due to frequent plant shut-downs for in-situ membrane cleaning procedures. What is more, the longevity of the membranes can be irretrievably shortened due to irreversible fouling.

It is clear that inhibition and control of fouling is vital to definitely achieve the competitiveness of membrane technology at industrial scale (Field and Pearce, 2011; Stoller and Chianese, 2006a, b and 2007; Stoller, 2009, 2011; Stoller *et al.*, 2013a, b). In this sense, OMW2 contains high concentrations of a wide range of solutes in the form of suspended solids and colloidal particles which are all very prone to cause membrane fouling, such as organic pollutants comprising phenolic compounds, organic acids, tannins and organohalogenated contaminants, as well as inorganic matter.

To solve this handicap in order to achieve adequate steady operation, engineers erroneously tend to whether overdesign excessively the membrane plants in industrial scale facilities, resulting in sensible but useless increment of total costs, or under-design them due to misunderstood and underestimation of the fouling issues, in this latter case operating above the threshold conditions, which are not technically and economically feasible for long periods of time (Field *et al.*, 1995; Field and Pearce, 2011; Stoller, 2009, 2011; Stoller *et al.*, 2013a, b).

The olive oil industrial sector has experienced in the recent decades a great boost. Therefore, the effluents generated, commonly known as olive mill wastewater (OMW), have also been triggered, because the change of technology from the initial batch press method to continuous centrifugation based ones, needed to cope with the increasingly growing demand of olive oil all over the world.

The reclamation of the effluents generated by olive oil industries is a task of global concern, representing an ever-increasing problem still unresolved and not constrained to a specific region anymore. The first centrifuges used in continuous olive oil extraction mills were three-phase ones, but later the technology evolved and two-phase centrifuges appeared. In the two-phase extraction the volume of liquid effluent by-produced in the decanting process (OMW2) is one third on average of that of the three-phase procedure, given that the addition of water needed to fluidize the olive paste is reduced in that proportion. This also results in lower organic pollutants concentration in OMW2, because 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 vs. 30 - 45 % in three-phase ones, OMW3). Two-phase continuous centrifugation based processes have been strongly promoted in countries like Spain, but still not in other countries due to lack of financing (Paraskeva and Diamadopoulos, 2006).

The core of the present work was the optimization and modelling of a reverse osmosis (RO) membrane operation for the purification of olive-oil washing wastewater previously treated by advanced oxidation. The optimization of the performance of a selected membrane is the key for its feasibility when implemented at industrial scale. Fouling issues have been investigated by many research groups in the last years to convince investors to implement membranes as substitutes of a range of unit operations at industrial scale. In the wastewater treatment field, this is especially problematic, given the low economic value of the product, treated water.

Statistical multifactorial analysis was performed with Statgraphics Centurion software to examined the impacts of the main variables of the process including the operating pressure, tangential velocity and operating temperature have a significant effect on the membrane performance. Finally, the compliance of the quality standards that would permit reusing the purified effluent for irrigation, discharge to sewers or even reused in the production process were checked

2. Experimental

2.1. Effluent

The raw feedstock was olive mill wastewater samples collected during the winter campaign from olive mills operating with the two-phase centrifugation technology (OMW2) in the region of Andalucia, the major olive oil producer world-wide. The samples were then taken to the laboratory and analyzed.

In first place, the raw OMW2 was subjected to a pretreatment process previously examined in former research by the Authors (Martínez Nieto *et al*., 2011a, b). The characteristics of the OMW2TT feedstream to the RO membrane unit are hereafter reported in Table 1.

2.2. Membrane plant

The membrane bench-scale plant, from Prozesstechnik GmbH (**Fig. 1**), 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).

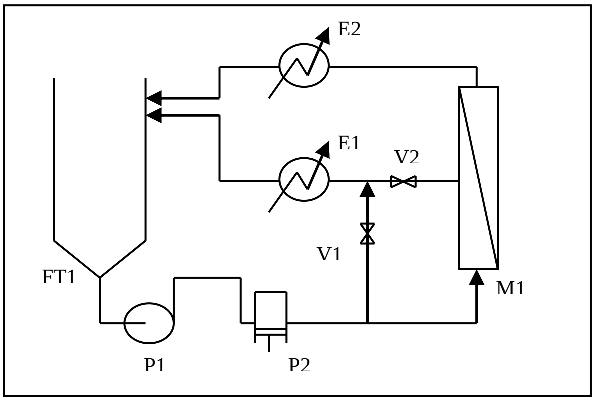

Fig. 1. Flow diagram of the membrane pilot plant. FT1: feedstock tank, P1: booster pump, P2: volumetric pump, V1: bypass regulation valve, V2: concentrate regulation valve, E1 and E2: plate heat exchangers, M1: membrane housing provided membrane.

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 OMW2TT 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} (NRe = $1.3 \cdot 10^4$). 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*., 2015).

2.3. Physico-chemical analyses

Analyses of the chemical oxygen demand (COD), total suspended solids (TSS), ashes, total phenolic compounds, total iron, electrical conductivity (EC) and pH were performed in both the influent (OMW2TT) and in the permeate of the RO unit, following standard methods (Greenberg *et al*., 2005).

A Helios Gamma UV-visible spectrophotometer (Thermo Fisher Scientific) was used for the analyses of the COD, total phenols and total iron. An ion chromatograph (Dionex DX-120) was used to measure the ionic concentrations. EC and pH were analyzed with a Crison GLP31 conductivity-meter and a Crison GLP21 pH-meter, provided with autocorrection of temperature (25 °C), previously calibrated with buffer standard solutions for EC (1,413 µS/cm and 12.88 mS/cm) and pH (pH 4.01, 7.00 and 9.21) purchased as well from Crison. For the measurement of the total iron concentration, all iron ions were reduced to iron ions (II) in a thioglycolate medium with a derivative of triazine, forming a reddish-purple complex that was determined photometrically at 565 nm (Standard German methods ISO 8466-1 and German DIN 38402 A51) (Greenberg *et al*., 2005). Ionic concentrations were analyzed with a Dionex DX-120 ion chromatograph (Ochando-Pulido *et al*., 2012).

2.4. Optimization and modeling

In order to optimize the OMW2TT RO purification process, a Box-Behnken experimental design (BBD) was chosen, which involved a total number of 15 experiments and 3 central points. The experimental results obtained were interpreted by means of the response surface methodology (RSM). Three levels, corresponding to the minimum (-1), medium (0) and maximum (+1), were considered for each variable, that is, operating pressure (15, 25 and 35 bar), temperature (15, 25 and 30 °C) and crossflow (2.5, 3.8 and 5.1 m s^{-1}). The optimization of the model was performed with Statgraphics Centurion XV.

Table 1: OMW2TT physicochemical characterization.

Parameter	Raw
pH	7.8 ± 0.2
EC, mS cm^{-1}	3.3 ± 0.2
TSS, g L^{-1}	14.5 ± 1.5
COD, g L^{-1}	190.0 ± 40.9
Total phenols, mg L^{-1}	0.7 ± 0.3
Total iron, mg L^{-1}	0.0 ± 0.2
Cl^-, mg L^{-1}	1020.0 ± 29.5
Na^+, mg L^{-1}	635.5 ± 95.5

* EC: electrical conductivity; TSS: total suspended solids; COD: chemical oxygen demand; AOP: advanced oxidation process.

RSM is a set of mathematical and statistical technics to develop, improve and optimize a wide range of processes. It can be used to assess the relative significance of different affecting factors. This methodology permits to collect an important quantity of information from the least number of data values. In this case, the key objective of RSM is to resolve the optimal operational conditions for the system or to determine a region that complies with the operating specifications.

Upon using the RSM method, the system is represented in the form of an empirical equation, on the basis of the data points gathered within the set of experiments studied, which serves to adjust each particular coefficient. Second order polynomial models are normally used, including crossed terms that permit to describe satisfactorily the concavities or convexities of the surface. The 'Response Surface' represented by a polynomial model function (RF) comprising three variables x_1, x_2 and x_3 examined.

Table 2: Specifications of selected membrane

Membrane type	Model series
Membrane type	RO
Model series	SC
Material	PA/PS
Effective surface area, m^2	0.02
Membrane structure	TFC
Membrane surface	Hydrophilic
Pore size, nm	< 0.1 nm
Permeability (m_0), L $h^{-1}m^{-2}$ bar^{-1}	1.9 ± 0.2
Salt rejection, %	99 ± 0.2
Max. P, bar	40
Max. T, °C	50
Spacer configuration	Flat, 45 mil parallel

* PA: polyamide; ** PS: polysulfone; ++ TFC: thin-film composite.

The resolution of the first-grade three-equational system leads to the determination of the values adopted by the variables x_1, x_2 and x_3 at the optimal point. A statistical multifactorial analysis was implemented additionally using the same software, with the aim of quantifying all the possible complex conjugated effects of the input parameters considered in the OMW2TT RO purification process.

3. Results and discussion

The p-values of the different operating variables studied for the proposed RO purification process indicated that all three the T, the P and the v_t have a remarkable influence on the Jpss of the membrane, since they present a p-value below 0.05 (practically equal to zero). Therefore, there is a statistically significant relationship among the examined variables at the 95 % confidence level.

Moreover, both the T and P exhibit a heavier influence than the vt, per the p-values withdrawn from this analysis, and the squared effects were found to be significant too (p-values below 0.05), but more significant in the case of T and P. The statistic R^2 indicates that the fitting model, adjusted in this way, explains up to 95.3 % of the variability in the Jpss. Otherwise, the measure of fit as per the adjusted R^2, the most adequate to compare models with different number of independent variables, was satisfactorily found to be equal to 90.7. The results derived from the optimization of the model were interpreted by means of the response surface methodology (**Fig. 2**). High and steady permeate flux can be yielded within the ambient temperature (24 - 29.5 º C), moderate operating pressure (31.5 - 35 bar) and turbulent crossflow (4.1 - 5.1 m s^{-1}).

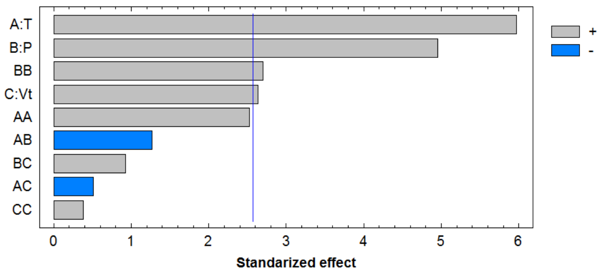

Fig. 2. Standarized Pareto chart for the d RO purification process: effect of the operating variables - T (A), P (B) and v_t (C) - and squared effects.

An increment of the operating pressure within the examined range (up to the maximum of the membrane minus a safety margin δ_p), did not compromise the Jp_{ss} yielded by the membrane. On the hand, an increase of the tangential velocity v_t implied a positive effect: the steady-state value of the permeate flux yielded by the RO membrane was found to be enhanced at increased v_t and had the shape of a plateau.

The turbulence over the membrane surface was satisfactorily promoted at the higher v_t (Reynolds number NRe $2.6 \cdot 10^4$ in contrast with $1.3 \cdot 10^4$). As a result of this, concentration polarization and the fouling deposits could be swept, such that the increase of v_t exhibited a patent benefit to reduce fouling. This can be explained on the basis that the enhanced shear force makes the fouling layer thinner, and there is a selective settlement of molecules as a result of the appropriate crossflow conditions, as stated by Choi *et al*. (2005). The operating temperature (T) also helped increase the Jpss yielded by the membrane. An increase in the T of the stream in contact with the membrane induces two main effects in the membrane-feed binomial: on one hand, it carries changes in the physical structure of the membrane surface, and on the other it makes the solvent less viscous. The results of the optimization of the OMW2TT RO purification process are briefly reported in Table 3. Upon these conditions, the rejection towards COD could be maintained at 99.9 % and the permeate flux production in the order of 34-36 L $h^{-1}m^{-2}$. Finally, the parametric quality standards to reuse the purified effluent for irrigation purposes were checked. COD values in the purified effluent below 17.5 mg L^{-1} were measured. This would enable obtaining an effluent with excellent quality according to the standard recommendations of the Food and Agricultural Association (FAO) with the goal of reusing the regenerated water for irrigation purposes. It would also comply with the water quality standard values established by the Guadalquivir Hydrographical Confederation (Spain) for discharge into public waterways, and it also may be reused in the proper olive oil production process, as sanitary water, closing the loop.

4. Conclusions

In the present work, optimization of the performance of a RO membrane for the purification of olive mill wastewater after advanced oxidation was carried out. Statistical multifactorial analysis showed all the studied operating variables including the operating pressure, tangential velocity and operating temperature have a significant effect on the membrane performance. The obtained contour plots and response surface support these results. The optimized operating conditions permitted a high and stable performance of the RO membrane (range 34-36 L $h^{-1}m^{-2}$), which could comply with the quality standards that would permit reusing the purified effluent for irrigation, discharge to sewers or even reused in the production process. Finally, the compliance of the standards to reuse the purified effluent for irrigation purposes throughout the proposed treatment process was checked. At this… thus permitting reusing the final treated effluent in the proper olive oil production process to close the loop at industrial scale.

Acknowledgements

Spanish Ministry of Science and Innovation is acknowledged for funding the project CTM2014-61105-JIN.

Table 3: Optimum operating conditions

Factor	T, º C	P, bar	v_t, m s^{-1}	Predicted final Jp_{ss}, L $h^{-1}m^{-2}$	R-Square (R^2)
Optimal value	29.6	35	5.1	38.1	95.3

References

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

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

Greenberg, A.E., Clesceri, L.S., Eaton, A.D., 2005. Standard Methods for the Examination of Water and Wastewater. APHA/AWWA/WEF, 22nd ed., Washington DC. Cabs.

Martínez Nieto, L., G. Hodaifa, Rodríguez Vives, J.A. Giménez Casares, J. Ochando, 2011. Degradation of organic matter in olive oil mill wastewater through homogeneous Fenton-like reaction, Chem. Eng. J. 173 (2), 503-510.

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

Ochando-Pulido, J.M., Víctor-Ortega, M.D., Martinez-Ferez, A., 2015. On the cleaning procedure of a hydrophilic reverse osmosis membrane fouled by secondary-treated olive mill wastewater. Chemical Engineering Journal, 260, 142-151

Paraskeva, P., Diamadopoulos, E., 2006. Technologies for olive mill wastewater (OMW) treatment: A review. J. Chem. Technol. Biotechnol. 81, 1475-1485.

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

Stoller, M., Chianese, A., 2006b. Technical optimization of a batch olive wash wastewater treatment membrane plant. Desalination 200 (1-3), 734-736.

Stoller, M., Chianese, A., 2007. Influence of the adopted pretreatment process on the critical flux value of batch membrane processes. Ind. Eng. Chem. Res. 46, 2249-2253.

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

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

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

Stoller, M., Bravi, M., Chianese, A., 2013a. Threshold flux measurements of a nanofiltration membrane module by critical flux data conversion. Desalination 315, 142-148.

Stoller, M., De Caprariis, B., Cicci, A., Verdone, N., Bravi, M., Chianese, A., 2013b. About proper membrane process design affected by fouling by means of the analysis of measured threshold flux data. Sep. Purif. Technol. 114, 83-89.

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