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Optimization Study of the Fouling Build-Up on a RO Membrane for Pretrated Olive Mill Wastewater Purification

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Even though membranes are considered in many aspects a mature technology, a range of features are still in development and under investigation. Regarding this, the main handicap of this technology is inevitably membrane fouling. Fouling issues have 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, that is, treated water.
On another hand, the management of the effluents generated by olive oil industries, olive mill wastewaters (OMW), is a task of global concern not anymore constrained to a specific region. These wastewaters represent an ever-increasing problem still unresolved.
The present work was aimed for the modelling and optimization of a reverse osmosis (RO) membrane operation for the purification of pretreated olive mill wastewater, with a focus on the dynamic fouling development minimization on the selected membrane as a function of the set-up of the operating conditions. For this goal, beforehand a factorial design was implemented for the optimization of the RO treatment of the OMW stream. The results gathered were thereafter interpreted by means of the response surface methodology. A significant impact was noted to be driven by the operating pressure and the tangential velocity on the fouling rate on the RO membrane. The response surfaces withdrawn from the experimental data support the previous results, and the optimised parameters - ambient temperature range (24 - 25 º C), moderate operating pressure (25 - 30 bar) and turbulent tangential flow (3.1 - 3.5 m s^{-1}) - were found to provide a stable permeate flux of 32.3 - 38.5 L $h^{-1}m^{-2}$. These results reveal the proposed process could be operated successfully at ambient temperature conditions and medium operating pressure, boosting the economic efficiency of the RO purification of this effluent. Finally, the parametric quality standards stablished to reuse the purified effluent for irrigation purposes were checked and found to be satisfactory.

1. Introduction

The olive oil industrial sector has experienced in the recent decades a very significant boost. As a result of this trend, the effluents generated, commonly known as olive mill wastewater (OMW), have also experienced a considerable increase, because of the change of technology from the initial batch press method to continuous centrifugation based ones, which were 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 olive oil sector has stood since many decades as one of the most important industrial activities in the countries of the Mediterranean Basin, and is becoming a problem of global scale as it is now implemented or emerging in countries with a relevant potential in Europe, China, the USA, South/Central America and Australia.
The first centrifuges used in continuous olive oil extraction mills were three-phase ones, but later the technology evolved and two-phase centrifuges appeared.
The difficulty in treating these wastewaters relies on their high concentration in refractory organic compounds, most of which are recalcitrant to conventional and biological treatment processes (Paraskeva and

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Diamadopoulos, 2006). Because of this fact, many treatments have been proposed in the last decades (Aktas et al., 2001; Al-Malah et al., 2000; Hodaifa et al., 2013; Sarika et al., 2005; Tezcan et al., 2006), but their complexity or lack of cost-efficiency have difficulted their implementation at industrial scale.

In this direction, the European Union is currently committed with the regeneration of the used resources, and this implies the treatment of wastewaters of diverse sources (Vilardi et al., 2017; Vilardi and Di Palma, 2017).

In the two-phase centrifugation process, 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).

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 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 energy costs increase to maintain the target permeate production, and also the operating costs due to frequent plant shut-downs for in-situ membrane cleaning. 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, 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 and Ochando, 2012; Stoller et al., 2013c; Stoller et al., 2016, 2017).

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, with a focus on the dynamic fouling development minimization on the selected membrane as a function of the set-up of the operating conditions. Finally, the parametric quality standards stablished to reuse the purified effluent for irrigation purposes were checked. For this goal, a factorial design was beforehand applied for the optimization of the RO purification unit operation of the OMW stream. The results gathered were then interpreted by means of the response surface methodology.

2. Experimental

2.1 Analytical proceedings

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).

2.2 OMW 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 secondary-tertiary treatment on a pilot scale (Ochando-Pulido et al., 2012; Martínez Nieto et al., 2011a, b).

The effluent stream after the secondary-tertiary treatment, hereafter referred as OMW-TT, presents the physico-chemical characteristics reported in Table 1, and was the feed to the final NF purification operation.

Table 1: Physicochemical characterization of OMW-TT[a]

Parameter	OMW-S
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] OMW-TT: olive mill wastewater after pre-treatment.

2.3 Membrane operation

The membrane bench-scale plant, from Prozesstechnik GmbH, is shown in Fig. 1. The system 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).

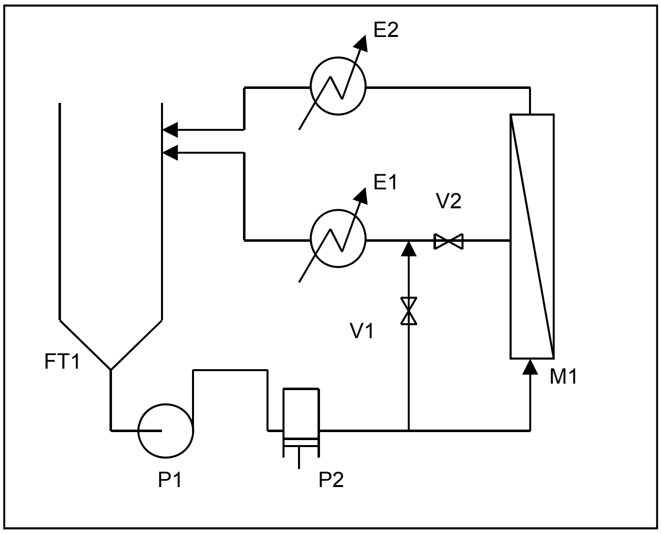

Figure 1 Flow diagram of the membrane pilot plant. FT1: feedstock tank, P1: booster pump, P2: volumetric pump, V1: bypass regulation valve, V2: concentrate regulation valve, E1 and E2: plate heat exchangers, M1: membrane housing provided membrane.

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 OMW-TT 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 cleaning of the membrane was performed as reported elsewhere (Ochando-Pulido et al., 2015).

Table 2: Specifications of the selected membrane

Membrane type	Model series
Membrane type	RO
Model series	SE
Material	PA/PS
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
Max. P, bar	40
Max. T, °C	50

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

3. Results and discussion

In order to optimize the OMW-TT RO purification process, a Box-Behnken experimental design (BBD) was implemented. This 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 software.

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 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 examined.

The p-values of the different operating variables studied for the proposed RO purification process indicated that all three the temperature, the operating pressure and the tangential velocity have a remarkable influence on the steady-state permeate productivity (flux, Jp_{ss}) 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.

Concretely, both the temperature and the operating pressure exhibit a heavier influence than the tangential velocity, 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 the temperature and the operating pressure.

The statistic R^2 indicates that the fitting model, adjusted in this way, explains up to 95.3 % of the variability in the Jp_{ss}. 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}).

The turbulence over the membrane surface was satisfactorily promoted at the higher tangential velocity (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 tangential velocity brought 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 resulting from the appropriate crossflow conditions, as stated by Choi et al. (2005).

The operating temperature also helped increase the Jpss yielded by the membrane. An increase in the temperature 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.

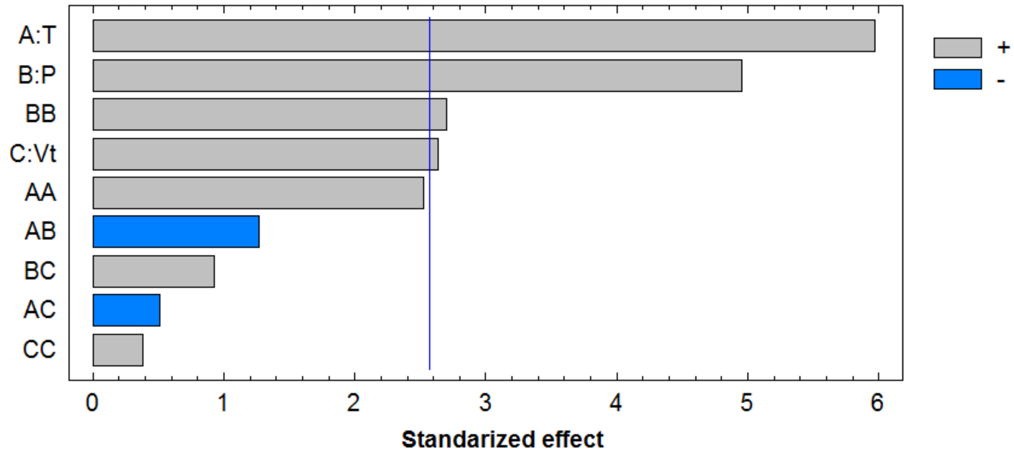

Figure 2. Standarized Pareto chart for the d RO purification process: effect of the operating variables - T (A), P (B) and v_t (C) – and the squared effects.

The results of the optimization of the OMW-TT 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 34-38 L h-1m^{-2}.

Table 3: Optimum operating conditions for the RO purification of OMW

Factor	T, ° 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

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. A focus was intended on the dynamic fouling development minimization on the selected membrane as a function of the set-up of the operating conditions.
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, thus permitting reusing the final treated effluent in the proper olive oil production process to close the loop at industrial scale.

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