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A focus on Fouling of Nanofiltration Membranes in the Treatment of Two-phase Olive Mill Wastewater by Boundary Flux and Pore Blocking Theories

Javier Miguel Ochando-Pulido[*a], Marco Stoller[b], Antonio Martínez-Férez [a]

[a]Chemical Engineering Department, University of Granada, Avda. Fuentnueva s/n, 18071 Granada, Spain
[b]University of Rome "La Sapienza", Department of Chemical Engineering, Via Eudossiana, 18-00184 Rome, Italy
jmochandop@ugr.es

The implementation of membranes in water and wastewater treatment processes has significantly increased in the last decades. However, membrane fouling leads to increased expenses if not properly examined and considered, and this is especially problematic in wastewater treatments. For this reason, fouling minimization represents the key factor to make those processes feasible.
The use of NF membranes is especially problematic regarding fouling problems. In first place, adequate fouling inhibition methods should be designed upstream the membrane operation, in order to make the downstream membrane processes for wastewater treatment technically and economically feasible. In the present work, fouling build-up on a nanofiltration (NF) membrane during the treatment of olive mill wastewater coming from Spain (OMW-S) is addressed by the boundary flux theory, and the results were compared and complemented by using the pore blocking models. Fouling mechanisms are important to fully understand what is happening between the membrane and the effluent, to take the adequate decisions with respect to the design of the membrane plant and set-up of optimized operating conditions. The goal is to operate membranes modules by avoiding irreversible fouling for a long period of time, that is, several years of service lifetime. Thereafter, the operating parameters should be carefully chosen to avoid working beyond the conditions that the selected membrane can stand for the specific feedstream.
The followed strategy allows the operation of the membranes system in a controlled framework that permits the stable operation of the plant. Moreover, the required membrane area is minimized and the constancy of the permeate productivity is also narrowed by following the proposed methodology.

1. Introduction

Olive oil industries are one of the principal industrial activities in the Mediterranean Countries, South Europe, Northern Africa, as well as in emerging ones like China, Australia, the Middle East and the USA. These industries by-produce high volumes of strongly polluted effluents (10 - 15 m^3 daily for average-sized mills).
Important efforts have been made in the last decades to provide a solution for the management of olive mill wastewaters (OMW). However, the complexity or low viability of the proposals hinders their transference to an industrial scale. 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, thus a centralized treatment of OMW seems not feasible in the current framework.
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. 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). Currently, the 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.

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Membrane technology, versatile and modular, may be a cost-effective solution for the reclamation of these effluents in these typical small factories. In particular, novel nanofiltration (NF) membranes can yield higher fluxes upon sensibly lower operating pressures than RO membranes, but still providing specific selectivity towards small solutes and thus permitting sensible investment and specific energy consumption savings (Iaquinta et al., 2009).
However, fouling is an actual problem of this technology and it is imperative to control it to ensure the appropriate operation and design of the plant. Fouling is a complex phenomenon involving diverse mechanisms: pore blocking and plugging, cake, gel and biofilm formation (Field et al., 1995; 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,c).
Minimization and control of fouling is key to achieve the competitiveness of membrane technology at industrial scale (Ochando et al., 2014a,b; Stoller and Ochando, 2012). In the present paper, a polymeric nanofiltration (NF) membrane was examined for purification of the secondary-treated OMW2 (OMW-S). Its performance was examined by means of the boundary flux and pore blocking theories.

2. Experimental

2.1 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).

2.2 OMW effluent

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 OMW-S, 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-S[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-S: olive mill wastewater after pre-treatment.

2.3 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) NF membrane (GE Water & Process Tech.) was selected for the experiments. Its characteristics are reported in Table 2. First, 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-S were poured into the feed tank. Tangential-flow NF 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. 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).
The effects of the operating pressure (x - x bar) on the performance of the membrane were studied in terms of permeate flux productivity 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

Table 2: Specifications of the selected NF membrane

Feature	Specifications
Supplier	GE Water & Process Tech.
Membrane type	DK
Active surface, cm^2	200
Material	PA/PS*
Membrane structure	TFC*
Membrane surface	Hydrophilic
Pore size, nm	0.5
MWCO, Da	150-300
Permeability (m_0), L $h^{-1}m^{-2}$ bar^{-1}	6.5 ± 0.5
Max. P, bar	40
Max. T, °C	50
pH range	1-11

* PA: polyamide; PS: polysulfone; TFC: thin film composite;

3. Results and discussion

Fouling mechanisms are also important to fully understand what is happening between the membrane and the effluent, to take the adequate decisions with respect to the design of the membrane plant, adoption of properly-tailored pretreatment process and set-up of optimized operating conditions.
In first place, the performance of the NF membrane was analyzed by the boundary flux theory (Stoller and Ochando, 2015). The pressure-cycling method proposed by Espinasse et al. (2002) was followed to determine the boundary conditions (permeate flux-pressure) of the NF system. The measurement consisted in performing a hysteresis cycle within the operating pressure range of the membrane. Thus, 1 bar increment was chosen. The boundary pressure (P_b) corresponds to the minimum pressure value at which the deviation from the complete restoration of the permeate flux (J_b) is verified when the same pressure level is again applied after the cycle. During these experiments, the tangential flow was fixed at 2.55 m s^{-1} and the permeate and concentrate streams were cooled to the temperature of the feedstock (22 °C), mixed and recycled back to the raw wastewater tank (recycling mode) to maintain the characteristics of the effluent constant. The data points reported were the final values of the permeate flux after reaching 15 min steady-state conditions. The results of the pressure-cycling method are shown in Fig. 1 (left caption).
The J_b value was estimated to be around 63.2 L $h^{-1}m^{-2}$, corresponding to a P_b of 13 bar. Above this point on, deviation of the permeate flux value started to be observed when the same pressure level was again applied after the pressure-cycle. This point stablishes the limit of the low fouling operating framework of the NF membrane from

the high fouling build-up range. In these latter conditions, a rapid flux loss starts to be controlling due to an exponential rate of fouling development on the membrane, as stated by various membrane researchers (Bacchin et al., 2006; Field et al., 2011; Stoller and Ochando, 2015).
The data withdrawn from the pressure-cycling experimental tests were subsequently used for the semicontinuous operation of the NF membrane plant. The performance of the NF membrane, in terms of permeate flux, during the purification of OMW-S in semicontinuous mode upon setting the estimated boundary conditions is reported in Fig. 1 (right caption). The observed profile of the permeate flux during the operating time supported the results formerly obtained in the pressure-cycling experiments (Fig. 1, left caption). Very low fouling development in time was observed for the semicontinuous operation of the NF membrane, with only 5.5 % permeate flux loss. What is more, a plateau of the permeate flux pattern was observed within the initial filtration period, and the permeate flux value registered in the steady-state of the NF membrane ($J_{p,ss}$) was found to be equal to 59.6 L $h^{-1}m^{-2}$, in the same range of the J_b value previously estimated by the pressure hysteresis method.

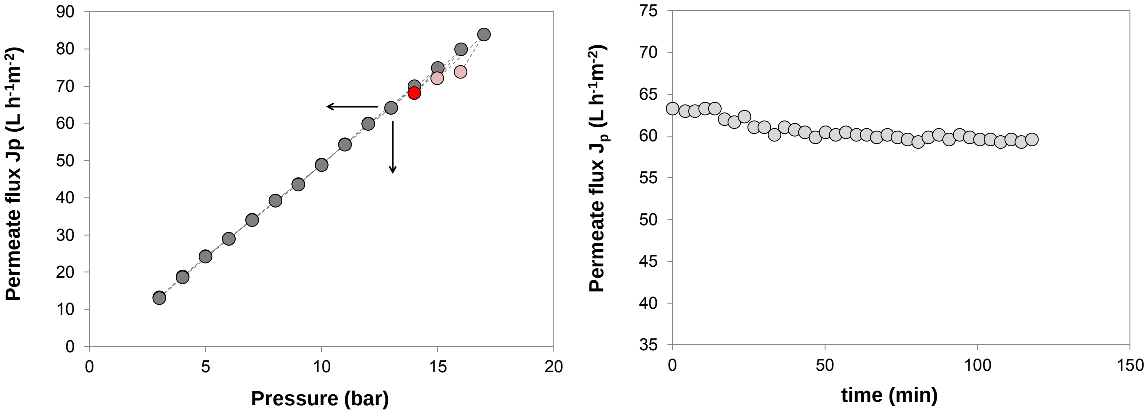

Fig. 1. Determination of boundary conditions (J_b-P_b) of the NF membrane purification of OMW-S, recirculation mode (right caption); performance of the NF membrane in semicontinuous at P_b-J_b (left caption).

The fouling index was additionally calculated by fitting the experimental data of the permeate flux profile to the extended fouling - permeate flux equation (Field and Pearce, 2011; Stoller et al., 2011):

$$Jp_t = (Jp_0 - J_b) \cdot e^{-bt} + J_b \quad (1)$$

where Jp_0 is the initial permeate flux (L $h^{-1}m^{-2}$) and Jp_t is the permeate flux at time t (L $h^{-1}m^{-2}$), whereas J_b represents the boundary flux (L $h^{-1}m^{-2}$), and b is the fouling index (h^{-1}), which quantifies the dynamic fouling build-up on the membrane during operation time. Both J_b and b were estimated simultaneously by a non-linear parameter estimation method (Cheryan, 1998; Field et al., 1995; Stoller and Ochando, 2015).
The obtained value of the fouling index b was found to be 0.9 h^{-1}, that is, a fouling index tending to zero (b→0), which supports that the set conditions on the boundary are actual, whereas the model J_b value resulted to be 59.6 L $h^{-1}m^{-2}$ (Table 3), in the range of those experimentally measured.
In addition to this, the experimental data were examined through the pore blocking models (Field and Pierce, 2011; Hermia, 1982). The complete pore blocking law supposes that each molecule only fouls the membrane by sealing one pore each, and thus no particle deposits over another. The standard blocking law takes into consideration that solutes smaller than the pores' size can enter and thus fill them, provoking their constriction and thus the reduction of the inner volume proportionally to the number of particles deposited or adsorbed into it. The cake or gel layer mechanism considers that the particles get deposited over the membrane surface but do not block any pore.
The experimental results fitted accurately the intermediate blocking mechanism, which responds to the following model equation:

$$Jp_t = \frac{Jp_0 \cdot Jp_{ss} \cdot e^{Ki \cdot J_{p\,ss} \cdot t}}{Jp_{ss} + Jp_0 \cdot (e^{Ki \cdot J_{p\,ss} \cdot t} - 1)} \quad (2)$$

The intermediate pore blocking model assumes the possibility that some solute molecules might not just block pores but settle over others. The parameter K_i represents the membrane surface blocked per unit of total volume permeated through the membrane and unit of initial membrane surface porosity. The modelled permeate flux value in time by the intermediate blocking model equation (eq. 2) is reported in Fig. 2.

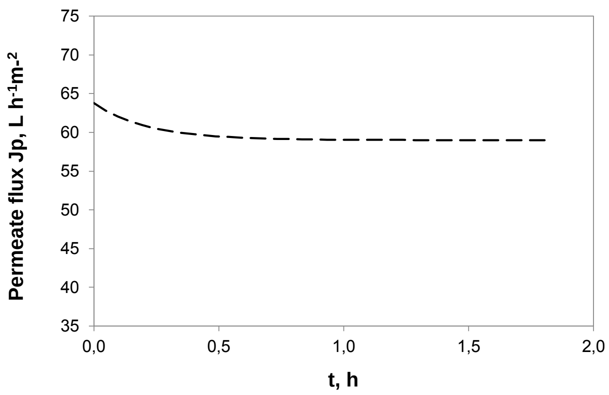

Fig. 2. Modelling of the of the NF membrane purification of OMW-S, recirculation mode (right caption); performance of the NF membrane in semicontinuous at P_b-J_b (left caption).

Table 3: Parameters obtained for intermediate and boundary flux model equations.

Model	K_i, m^{-1}	b, s^{-1}	$J_{p\ ss\ (model)}$, L $h^{-1}m^{-2}$	$J_{b(model)}$, L $h^{-1}m^{-2}$
Intermediate blocking	0.077	-	59.0	-
Boundary flux	-	0.9	-	59.6

[*] Operating conditions: 2.5 m/s, 22 °C.

The obtained values for both parameters were K_i 0.077 (m^{-1}) and Jp_{ss} (model) 59.0 L $h^{-1}m^{-2}$ (reported in Table 3). This latter value is very similar to both the experimental one and also to the J_b value previously estimated through the fitting to the boundary flux model, which supports the goodness of both model equations for the prediction of the performance of the NF membrane, and the complementariness.
In order to take the adequate decisions with respect to the membrane plant design, the adoption of properly-tailored pretreatment process, optimized operating conditions and cleaning protocols, the insight of the mechanisms by which fouling occurs between the membrane and the foulants in the effluent are necessary.
Within this framework, a clear identification and differentiation of the possible membrane fouling mechanisms is imperative to achieve the proper steady-state control of the process and ensure a stable performance of the membrane unit (Ochando-Pulido et al., 2016; Stoller and Chianese, 2006; Stoller, 2011).

4. Conclusion

In the present work, fouling build-up on a nanofiltration (NF) membrane during the treatment of olive mill wastewater coming from Spain (OMW-S) is addressed by the boundary flux theory, and the results were compared and complemented by using the pore blocking models.
Fouling mechanisms are important to fully understand what is happening between the membrane and the effluent, to take the adequate decisions with respect to the design of the membrane plant and set-up of optimized operating conditions. The goal is to operate membranes modules by avoiding irreversible fouling for several years of service lifetime. To achieve this goal, the operating parameters should be carefully chosen to avoid working beyond the conditions that the selected membrane can stand for the specific feedstream.
The obtained model values for the intermediate blocking parameters were found to be K_i 0.077 (m^{-1}) and the $Jp_{ss\ model}$ 59.0 L $h^{-1}m^{-2}$. This latter value is very similar to both the experimental one and also to the J_b value previously estimated through the fitting to the boundary flux model. The results obtained in this work supports the goodness of both models for the prediction of the performance of the NF membrane, and the complementariness.
The followed strategy allows the operation of the membranes system in a controlled framework that permits the stable operation of the plant. Moreover, the required membrane area is minimized and the constancy of the permeate productivity is also narrowed by following the proposed methodology.

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