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Analysis of the Fouling Build-up of a Spiral Wound Reverse Osmosis Membrane in the Treatment of Two-phase Olive Mill Wastewater

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In the present work, modelization and plant dimension for batch reverse osmosis (RO) purification of olive mill wastewater from a two-phase olive oil mill (OMW2) is carried out through analysis of the fouling build-up the by means of the threshold flux theory, for fouling control and appropriate plant dimension.

Inhibition and control of fouling is vital to definitely achieve the competitiveness of membrane technology at industrial scale. The fouling index was found to considerably increase when shifting the P_{TM} from 20 to 30 bar, that is, 31.3 %. However, there is no significant difference with regard to the fouling build-up within the range 10 – 20 bar. Therefore, it is recommended to work upon an operating pressure (P_{TM}) around 20 bar to maximize both the productivity (13.3 – 13.5 L $h^{-1}m^{-2}$) together with the rejection efficiency (R_{COD}, %) whereas on the other hand minimizing the flux decay during the operation time. Finally, a required membrane area (A_m) equal to 95 m^2, that means an overdesign of 48%, is calculated on the basis of the obtained results at a P_{TM} of 20 bar.

Finally, the compliance of the standards to reuse the purified effluent for irrigation purposes throughout the proposed treatment process was checked. At this operating pressure value, the organic matter rejection efficiency reaches 90.5 %, thus permitting reusing the final treated effluent in the proper olive oil production process to close the loop at industrial scale.

1. Introduction

The effluents generated by olive oil industries, commonly known as olive mill wastewater (OMW), have sensibly augmented in the last decades as a result of 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 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 OMW-2, 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 (Cañizares et al., 2009; 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 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; Bacchin et al., 2006). During operation, fouling leads to an increase in the energy costs to

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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, 2006; 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 either 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).

In the present work, analysis of the fouling build-up for the modelization and plant dimension for batch RO purification of OMW2 by means of the threshold flux theory are addressed for fouling control and appropriate plant design. Finally, the compliance of the standards to reuse the purified effluent for irrigation purposes throughout the proposed treatment process was checked

2. Materials and methods

2.1 Membrane pilot plant

The membrane pilot plant (Fig. 1) consists of a 100 liter feed tank (FT1), from which the wastewater stream is carried either by a centrifugal booster pump (P1) or a volumetric pump (P2) to a spiral wounded reverse osmosis (SW RO) membrane, supplied by Osmonics, fitted in the housing (M1), at an average tangential flow rate of 600 L h^{-1}. The selected membrane (SC-785277), previously used for more than 1000 h of operation time in experiments with OMW3 and OMW2, presents an active membrane area of 2.51 m^2, and the characteristics reported in Table 1. Acting on the regulation valves (V1 and V2) it is possible to set the desired operating pressure (P_{TM}) over the membrane, maintaining the feed flow rate constant with a precision of 0.5 bar. The temperature was controlled during all experiments at ambient value (20°C ± 1°C).

Both permeate and concentrate streams were cooled down to the feedstock temperature, mixed together and recycled back to the feedstock, thus keeping constant the feedstock composition during each experimental batch run.

After each experiment the membrane was rinsed with tap water for at least 30 min to recovery its permeability for further runs. If not necessary, the membrane module was stored directly in the membrane housing filled with fresh tap water, else put in a fresh tap water filled external storage tank, as suggested by Ochando-Pulido et al. (2015).

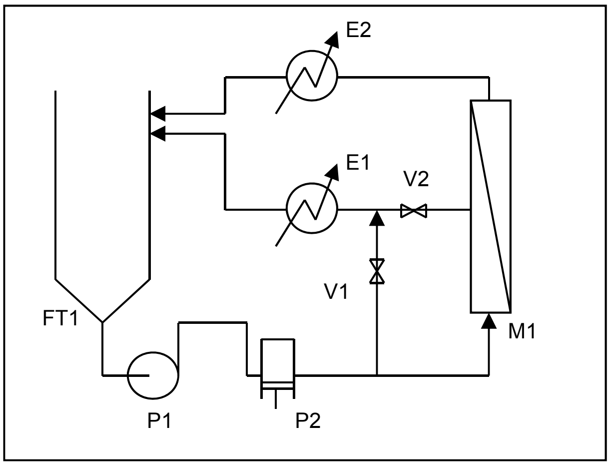

Figure 1. Flow diagram of the membrane pilot plant. FT1: feedstock tank, P1: booster pump, P2: volumetric pump, V1: bypass regulation valve, V2: concentrate regulation valve, E1 and E2: plate heat exchangers, M1: membrane housing provided with spiral-wounded membrane.

Table 1: Specifications of the selected membrane

Membrane type	Model series
Membrane type	RO
Model series	SC785277
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.

2.2 Analytical methods

All the analytical methods were applied in triplicate following standard methods (Greenberg et al., 1992), using analytical-grade reagents supplied by Panreac: 70% (w/w) HNO3, 98% (w/w) NaOH, 98% (w/w) Na2SO3, 30% (w/w) NH4OH, 37% (w/w) HCl and 30% (w/w) FeCl3.

Chemical oxygen demand (COD) was measured by photometric determination of the concentration of chromium (III) after 2 h of oxidation with potassium dichromate/sulfuric acid/silver sulfate solution at 148 ± 2 °C (German standard methods DIN 38 409-H41-1 and DIN ISO 15 705-H45) (Greenberg et al., 1992).

2.3 The effluent stream

The raw feedstock was an OMW stream from an olive mill operating with the two-phase decanting technology (OMW2) in Spain. Firstly, the raw OMW2 was subjected to a pretreatment process previously examined and discussed in former research by the Authors (Ochando-Pulido et al., 2014): (i) gridding (cut-size 300 μm) to remove the coarse particles, (ii) pH-T flocculation by adding HNO_3 (70% w/w), (iii) photocatalysis of the supernatant under ultraviolet irradiation (UV) with lab-made ferromagnetic-core TiO_2 nanoparticles (UV/TiO_2 PC), and (iv) UF and (NF) in series. The physicochemical characteristics of the raw and pretreated OMW2 are reported in Table 2.

Table 2: Physicochemical characterization of raw and pretreated OMW2

Parameter	Raw	After pretreatment
pH	4.9	3.1
EC, mS cm^{-1}	1.7	1.2
TSS, g L^{-1}	5.6	0
COD, g L^{-1}	16.4	0.9
Total phenols, mg L^{-1}	181	38.9

EC: electrical conductivity; TSS: total suspended solids; COD: chemical oxygen demand.

3. Results and discussion

In Fig. 2, the initial vs. steady-state permeate flux values attained on the selected RO membrane by setting the net operating pressure (PTM) at different values within its admissible range are given (R2 = 0.99).

It is essential to operate the plant under the appropriate operating framework. An error commonly committed by engineers is to excessively overdesign the membrane plants, resulting in sensible increment of the total costs. On the contrary, underdesign due to underestimation of the fouling issues leads to operation above the threshold conditions, unfeasible technically and economically in the long run.

Therefore, the RO membrane was fitted to empirically derived threshold flux equations (Field et al., 1995; Field and Pearce, 2011). This fitting process then allowed for the fouling parameters to be calculated as follows:

$$J_p\,(t) = J_{p\,0} - a \cdot t\ ;\ J_p\,(t) \le J_{p\,th} \qquad (1)$$

$$Jp\ (t) = (Jp\ 0 - Jp\ th) \cdot e\text{-}b \cdot t + Jp\ th - a \cdot t;\ Jp\ (t) > Jp\ th \qquad (2)$$

where Jp (t), Jp 0 and Jp th are the permeate flux at a given time, the initial permeate flux and the threshold permeate flux respectively (L h-1m-2), whereas a and b are fouling parameters, obtained by the model by non-linear parameter estimation method (Ochando-Pulido et al., 2012a,b and 2014; Stoller and Chianese, 2006; Stoller, 2011).

The threshold flux can be correlated as a function of a key parameter (KP) defining the fingerprint of the feedstream to the membrane module, which depends mainly on the organic pollutants load (COD) and the particle size distribution (vp) of the feedstock solution (Stoller et al., 2013b). The proposed fitting curve is based on the general relationship between permeate flux Jp and the applied PTM, that is:

$$Jp(KP,t) = m(KP,t) \cdot PTM(KP) \qquad (3)$$

where m(KP,t) is the permeability at any time and PTM(KP) the transmembrane pressure as a function of the chosen key parameter KP (i.e. COD or EC), where both m and PTM can be approximated by a linear function:

$$m(KP,t) = m0(t) - m1 \cdot KP \qquad (4)$$

$$PTM(KP) = P - R \cdot T \cdot KP \qquad (5)$$

where m0 is the pure water permeability at t = 0 (see Table 1), P is the applied operating pressure, R is a constant, T is the temperature, and m1 is a fitting parameter. The pure water permeability m0(t) is a function of time, since it would change depending on the amount of irreversible fouling formed over the membrane (Stoller et al., 2013b).

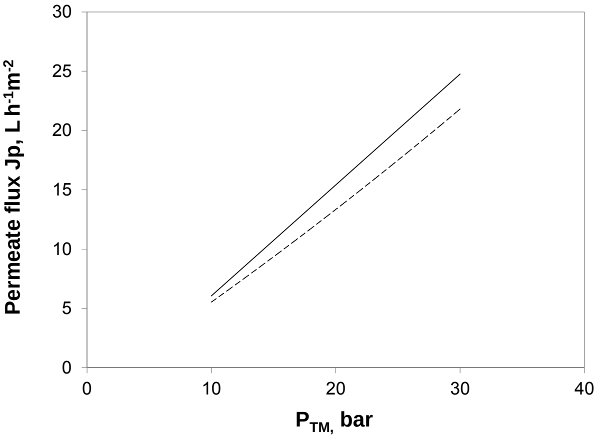

Figure 2. Initial (▬▬) vs. steady state (- - -) RO permeate flux (J_p) as a function of the applied net operation pressure (P_{TM}).

The threshold flux makes reference to the flux point which establishes the barrier between the low fouling and high fouling operating regime of a membrane. It is a result of physical phenomena, such that further applied pressure increment does not result in higher stable fluxes. Above the threshold conditions, the permeate flux is observed to start decaying exponentially just from the beginning of operation.

The results of the experimental RO membrane performance as function of the chosen net operating pressure (PTM) are given in Table 3, where the initial vs. steady state permeate flux values (Jp 0 vs. Jp ss) and organic matter rejection (RCOD) are reported (also see Fig. 3), and also the fouling index (a) and threshold flux value (Jp th) calculated with the threshold flux equations.

Table 3: RO membrane performance as function of the chosen net operating pressure

P_{TM}, bar	$J_{p\,0}$, L h^{-1}m^{-2}	$J_{p\,ss}$, L h^{-1}m^{-2}	$J_{p\,th}$, L h^{-1}m^{-2}	a·10^{-3}, L h^{-1}m^{-2} bar^{-1}	R_{COD}, %
10	6.3	5.6	5.5	0.10	91.6
20	14.9	13.3	13.5	0.11	87.4
30	25.0	21.8	21.6	0.16	90.5

$J_{p\,0}$: initial experimental permeate flux; $J_{p\,ss}$: steady-state experimental permeate flux; $J_{p\,tth}$: calculated threshold flux; a: calculated fouling index; R_{COD}: organic matter rejection.

As it can be observed, there is a different flux loss gap (Jp 0 - Jp ss) depending on the selected PTM as it is increased. On the other hand, the organic matter rejection is also observed to be enhanced upon augmenting the operating PTM, thus a compromise solution should be taken between both parameters. Moreover, the calculated long term fouling parameter a is key for the selection of the operating framework of the membrane. It can be seen that the value of this fouling index increases considerably when shifting the PTM from 20 to 30 bar, that is, 31.3 %.

However, within the range 10 – 20 bar there is no significant difference with regard to this fouling parameter. Therefore, it is justified to work upon a PTM around 20 bar to maximize both the productivity (Jp ss, L h-1m-2) together with the rejection efficiency (RCOD, %) whereas on the other hand minimizing the flux decay during the operation time.

This aspect is important for proper membrane plant design, since the advantage to operate at sub-threshold flux conditions is the minimization of irreversible fouling although reversible fouling may not be avoided.

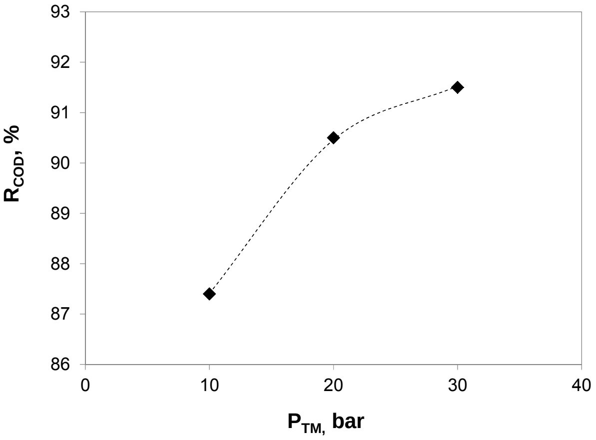

Figure 3. Organic matter rejection (R_{COD}) provided by the selected RO membrane as a function of the applied P_{TM}.

Moreover, since threshold flux changes accordingly to the value of the fitting parameter ‘‘a’’ as a function of time, design should consider to control the process at the lowest threshold flux value obtained before the membrane washing procedure.

Therefore the value of parameter ‘‘a’’ and the operating period of time, equal to the period of time lasting between two washing procedures “t_w”, have direct influence on the needed overdimension of membrane plants (OD,%) to permit one complete process operation at the project permeate flux value, which has very important implications in the capital costs and may be set equal to $J_{p\ th}$ at the end of operation (Stoller et al., 2013b).

An additional percentage of over-design (expressed as percentage as OD_i, %) is needed in order to take into account the irreversible fouling, measured by ‘‘-Δm_w” (%)’, which permits to complete a longer operating period of time, equal to “N_w”.

Mathematically, the equations needed to estimate the required total over-design OD_T, %, once “t_w” and “N_w” are fixed, are as follow (Stoller et al., 2013b; Stoller and Ochando-Pulido, 2015):

$$OD = 100\cdot[1 - (J_{th} - a\cdot P_{TM}\cdot t_w)] / J_{th}^{-1} \quad (6)$$

$$OD_i = t_w\cdot(N_w-1)\cdot(-\Delta m_w) \quad (7)$$

$$OD_T = OD + OD_i \quad (8)$$

Finally, a required membrane area (A_m) equal to 95 m^2, that means an overdesign of 48 % and three membrane modules of 32 m^2 each, is calculated on the basis of the obtained results at a P_{TM} of 20 bar (Stoller and Ochando-Pulido, 2015).

Table 4: Required membrane area and overdimension

P_{TM}, bar	Required A_m, m^2	Overdimension, %
20	95	48

A_m: required membrane area.

4. Conclusions

Fouling analysis, modelization and plant dimension for batch RO purification of olive mill wastewater from a two-phase olive oil mill (OMW2) by means of the threshold flux theory showed that the fouling index increases considerably when shifting the P_{TM} from 20 to 30 bar (31.3 %). On the contrary, in the range 10 - 20 bar there is no significant difference with regard to the fouling rate. Therefore, it is justified to work upon a P_{TM} of 20 bar to maximize both the productivity ($J_{p\ ss}$, L $h^{-1}m^{-2}$) as well as the rejection efficiency (R_{COD}, %) whilst minimizing the flux decay during the operation time. Finally, a required membrane area (A_m) equal to 95 m^2, which represents an overdesign of 48 %, was calculated on the basis of the obtained results at a P_{TM} of 20 bar. At these operating pressure conditions, fouling control and appropriate plant dimension were ensured, and the rejection efficiency towards organic pollutants reached 90.5 %. This permitted reusing the final treated effluent in the olive oil production process, as water for cleaning procedures or in the centrifuges, to close the loop at industrial scale.

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