Control systems for olive mill wastewater treatment with ultrafiltration and nanofiltration membrane in series based on the boundary flux theory

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ABSTRACT

Proper membrane process design can be a difficult task to accomplish when fouling is present, and must be faced. Engineers usually consider the project variables concerning productivity and selectivity and follow these targets. However, in the presence of fouling, additional parameters must be considered, implying better knowledge of fouling phenomena. One possible solution to increase the reliability of a process is the use of stable control systems. This article reports a suitable method to reach this target, based on the boundary flux theory. The knowledge of the boundary flux values permits avoidance of high fouling operating conditions on a selected membrane. The goal here was to determine the framework for control of an ultrafiltration (UF) and nanofiltration (NF) batch membranes-in-series process treatment for olive mill wastewater, relying on these boundary flux points, which will thereafter serve for the automatic control of the process by an advanced control system. In this work, boundary flux values equal to $10 \text{ Lh}^{-1} \text{ m}^{-2}$ for the UF membrane module and $14.3 \text{ Lh}^{-1} \text{ m}^{-2}$ for the NF one were estimated. Moreover, the membrane constant permeability loss, measured by integrating the sub-boundary fouling index, was estimated to be reduced in the order of 65.4% for the NF membrane after the applied pretreatment and UF. This strategy permitted attaining stable and constant productivity for both membranes. Moreover, it is shown that, relying on the boundary flux modelization, both types of control systems (feed control and pressure control) could be used reliably. The proposed approach could help safely narrow the overdesign of membrane processes due to fouling issues and thus would have an impact on the reduction of the costs for both membrane processes.

Key words | olive mill wastewater, pretreatment tailoring, threshold flux, ultrafiltration, wastewater treatment

INTRODUCTION

The significant boost of the olive oil industrial sector in the last years has brought an undesired side-effect: the amounts of effluents by-produced have also significantly increased, especially due to the change of the batch press method for the modern continuous centrifugation-based olive oil production processes used currently. An average-sized olive oil factory nowadays generates around $10\text{–}15 \text{ m}^3$ of wastewater daily. This amount derives from the oil centrifugation process, called olive mill wastewater (OMWW), in sum to wastewater derived from the washing of the olives (olives washing wastewater, OWWW). This has implications, only in Spain, which is the major producer, for the generation of around ten million cubic meters of these highly contaminated effluents per year, and for potable water consumption.

The direct discharge of these effluents has been reported to cause odor nuisance, soil contamination, plant growth inhibition, underground leaks, water body pollution and hindrance of self-purification processes, as well as severe impacts on the aquatic fauna and to the ecological status (Ena et al. 2007; Danellakis et al. 2011). It is well known that the European Environmental Regulations are becoming more stringent in virtue of the ‘H2020 Horizon’. In countries like Spain, the direct discharge of OMWW to the ground fields and surface waters is currently prohibited, whereas
in Italy and other European countries only the partial discharge on suitable terrains is allowed. Because of the presence of high concentrations of organic pollutants and refractory compounds, the direct disposal of these effluents to the municipal sewage treatment systems is also prohibited. Legal limits are established in order to prevent difficulties for the municipal sewer wastewater treatment plants, which rely on biomasses that must be maintained alive.

Moreover, these effluents contain considerable concentrations of phytotoxic refractory pollutants that make OMWW recalcitrant to biological degradation and thus inhibit the efficiency of biological processes. Furthermore, the physico-chemical composition of these effluents is extremely variable, as it depends on several factors such as the extraction process, edaphoclimatic and cultivation parameters, as well as the type, quality and maturity of the processed olives.

Many reclamation practices and combined treatments for OMWW have already been proposed and developed, but they have not given completely satisfactory results. Some relevant examples are lagooning or natural evaporation and thermal concentration (Annesini & Gironi 1991; Paraskeva & Diamadopoulos 2006), composting (Cegarra et al. 1996), treatments with clay (Al-Malah et al. 2000) or with lime (Aktas et al. 2001), biological processes (Marques 2001; Ena et al. 2007), physico-chemical procedures including coagulation-flocculation (Sarika et al. 2005), electrocoagulation (Tezcan et al. 2006) and biosorption (Hodaifa et al. 2013a), advanced oxidation processes comprising ozonation (Beltrán et al. 2000), Fenton’s reaction (Martínez-Nieto et al. 2011; Hodaifa et al. 2013b) and photocatalysis (PhC) (Sacco et al. 2012), electrochemical treatments (Inan et al. 2004) and hybrid processes (Grafias et al. 2010).

In this regard, membrane technology is compact and modular, presents high efficiency and moderate investment and maintenance expenses (Akdemir & Ozer 2009; Ochando-Pulido et al. 2012a, 2012b, 2013a, 2013b). Still today, the biggest technical drawback for the implementation of membrane technologies in wastewater treatment plants is membrane fouling. Fouling is caused by the accumulation of colloids, soluble organic compounds and microorganisms on the membrane surface and pores. These phenomena are unavoidable, but can be reversible or irreversible. If irreversible fouling forms on the membrane, it cannot be removed by cleaning procedures any more and leads quickly to technical failure of the process (Stoller & Ochando-Pulido 2012). Therefore, the optimal operation of membrane processes should be targeted to attain only the formation of reversible fouling in order to ensure constant performances over a long period of time.

Fouling has notably compromised the reliability of membrane technology. This trend is still patent, since proper membrane process design can be a difficult task to accomplish when fouling is present and must be faced. Engineers normally consider the project variables concerning productivity and selectivity and follow these targets. However, in the presence of fouling, additional parameters, in particular the life-time of the membrane modules and the constancy of the permeate fluxes as a function of time, must be considered, implying better knowledge of fouling phenomena. Fouling leads to loss of membrane productivity and causes a sensible reduction of the membrane module service lifetime, multiplying the operating costs.

A possible solution to increase the reliability of a process is the use of stable control systems. In the case of most membrane processes, this is commonly performed by simple control strategies that do not include the knowledge and control of fouling. The complete lack of advanced control systems in membrane technologies, capable of taking fouling issues into account, limits the reliability of this technology and represents one key problem to be solved to permit its further maturation. In order to achieve this result, the fouling behavior of the system must be defined a priori.

This article will report a suitable method to reach this target, based on the boundary flux theory. The knowledge of the boundary flux values permits avoidance of high fouling rate operating conditions. The core of the proposed method is to increase, if possible, by appropriate pretreatment processes, the boundary flux up to a maximum value, and to design the process control based on this value, which will serve for the automatic control of the process by an advanced control system. The design for the purification of OMWW streams (two phase, OMWW) by membranes will be reported. Two different tailored pretreatments, thoroughly described by the author in former research work (Ochando-Pulido et al. 2014), were applied on the raw OMWW, then driven to an ultrafiltration (UF) membrane process and subsequently to nanofiltration (NF).

**MATERIALS AND METHODS**

**OMWW feedstock and pretreatments**

Samples of OMWW were taken from olive oil mills located in Jaén and Granada (Spain), operating with the continuous
centrifugation-based process, during the 2015 campaign. The highly polluted raw OMWW was subjected to different pretreatment processes studied and thoroughly described in previous work by Ochando-Pulido et al. (2013b): (i) first, gridding (cut-size equal to 300 μm) of the raw effluent was carried out to remove the coarse particles; (ii) then, pH-temperature (T) flocculation (pH-T F) was performed by adding HNO₃ (70% w/w) under continuous stirring (320 rpm); (iii) the supernatant phase of the pH-T F process after the separation of the mud was either directly conducted to the UF unit and thereby referred to as OMWW-F, or further pretreated by PhC under ultraviolet irradiation (UV) with laboratory-made ferromagnetic-core TiO₂ nanoparticles (UV/TiO₂ PhC), thus named OMWW-F/PhC. Finally, the differently pretreated streams were driven to the UF and NF membrane units.

The laboratory-made ferromagnetic photocatalyst nanoparticles were produced in three consecutive steps, following the procedure fully reported elsewhere (Ochando-Pulido et al. 2014). Briefly, in first place magnetite was synthetized by a sol-gel process in a spinning disk reactor, in which an aqueous solution of FeCl₃, HCl and Na₂SO₃ was injected at the centre whereas a NH₄OH aqueous solution was injected at 2 cm of distance from the centre of the disk, respectively. In second place, coating with silica was performed by adding the dried magnetite particles to a tetraethylorthosilicate-ethanol-NH₃ solution. The coated particles were afterwards recovered by magnets, dried at 80 °C and calcined at 450 °C. Finally, TiO₂ coating was carried out by pouring the silica-coated particles into a titanium tetraisopropoxide-ethanol solution, then adding H₂O₂ drop-wise under strong mixing conditions. Again, the recovered particles were dried at 80 °C and calcinated at 450 °C.

**Analytical procedures**

All the analytical methods were carried out in triplicate with analytical-grade reagents: 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, supplied by Panreac. Chemical oxygen demand (COD), total suspended solids (TSS), electroconductivity (EC) and pH were measured following Standard Methods (Greenberg et al. 2005).

**Membrane pilot-scale plant**

The membranes-in-series pilot plant used for the experiments is schematically shown in Figure 1. The operating pressure and the tangential velocity over the membrane were measured and displayed by analogue manometers and a turbine flow-meter, and could be set by regulation valves V₁ and V₂, respectively. The feed flow rate was controlled and fixed at turbulent tangential velocity over the membrane (550 L h⁻¹, to promote N_Re > 4,000), to minimize concentration polarization in the boundary region of the membrane layer. The temperature was kept at ambient conditions (20 ± 0.5 °C), measured by a Pt100 sensor, and two plate heat exchangers (E₁ and E₂) served to keep the temperature of the streams stable. The permeate flux was measured during operation time by a precision electronic mass balance (AX-120 Cobos, 0.1 mg accuracy). The UF and NF modules were supplied by GE Water and Process Technologies, presenting the characteristics reported in Table 1. The experiments were conducted in batch operation: the permeate from the UF membrane was collected in a vessel, and then it was driven to the NF membrane.

**Performance of the membranes relying on the boundary flux determination**

Different extents of fouling can be measured on the same system depending on various factors, mainly the membrane type, the membrane surface roughness and mean porosity, the hydrodynamic conditions and the effluent composition and concentration (Stoller & Ochando-Pulido 2015). It is especially difficult to control fouling when agricultural wastewater streams are purified by membranes, since the entering feedstock composition is not constant during the
campaign. Direct treatment by membranes of raw effluents has been reported to lead to rapid emergence of membrane fouling (Field & Pearce 2014; Ochando-Pulido & Stoller 2014; Stoller et al. 2015). Furthermore, the use of batch membrane processes with the purpose of reducing the amount of required membrane area to save investment costs, leads to sensible feedstock changes during operation. Therefore, flux values never remain constant, a fact that determines a major difficulty in finely tuning the optimal operating conditions for adequate membrane process design and control.

The boundary flux model equations, merged by Stoller & Ochando-Pulido (2014, 2015), can be written as:

\[
dm/dt = -\alpha; \quad J_p(t) \leq J_b
\]

(1)

\[
dm/dt = -\alpha + \beta \cdot (J_p(t) - J_b); \quad J_p(t) > J_b
\]

(2)

where \( dm/dt \) is the membrane permeability change in time, \( J_b \) (L h\(^{-1}\) m\(^{-2}\) bar\(^{-1}\)) is the boundary flux, \( \alpha \) (L h\(^{-1}\) m\(^{-2}\) bar\(^{-1}\)) represents the constant permeability reduction of the membrane, called the sub-boundary fouling rate index. On the other hand, \( \beta \) (h\(^{-1}\) bar\(^{-1}\)) represents the fouling behavior in the exponential fouling regime of the system, hereafter called the super-boundary fouling rate index.

The method to measure the boundary flux is adapted from the one proposed to measure critical flux values by Espinasse et al. (2002). Besides experimental data, the extended method requires the use of Equations (1) and (2) to separate the two different operating regimes, that is, a region where low fouling is formed (and \( \alpha \) is controlling) from another region where a high level of fouling is attained (\( \beta \) is controlling instead). The validity of Equation (1) excludes the validity of Equation (2): as long as Equation (1) holds, sub-boundary flux conditions are met. This approach needs a simple mathematical model to fit pressure-cycle experimental data. The point at which the \( dm/dt \) diverges from constancy is the boundary one (\( J_b \)), and the \( P_{TMb} \) value is therefore equal to boundary pressure value \( P_{TMb} \).

The suggested pressure-stepping method has been proven to be rapid and reliable (Espinasse et al. 2002). Fouling measurements by means of long-term experiments, which need to stop the plant and thus the production, are not feasible for common industrial practices. The method briefly consists of cycling up and down the applied pressure, by a constant \( P_{TM} \) variation equal to \( \Delta P_{TM} \), and to check for the reproducibility of the membrane permeability when the same pressure level is again applied after one cycle. Then, the method requires the integration of Equation (1) in time:

\[
J_b(P_{TM}, t) - J_b(P_{TM}, t') = -\Delta J_b = -\int_t^{t'} \alpha \cdot P_{TM} \cdot dt
\]

(3)

As long as Equation (3) holds, the boundary conditions are determined. The lowest \( P_{TM} \) value at which the difference between the experimental permeate flux gap – \( \Delta J_b \) and the theoretical – \( \Delta J_b^* \) value evaluated from Equation (3) in the same period \( dt \) becomes positive, is the boundary

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Parametric value</th>
<th>Parametric value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Membrane type</td>
<td>UF</td>
<td>NF</td>
</tr>
<tr>
<td>Model</td>
<td>GM</td>
<td>DK</td>
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<tr>
<td>Surface, m(^2)</td>
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<td>2.5</td>
</tr>
<tr>
<td>Permeability, L h(^{-1}) m(^{-2}) bar(^{-1})</td>
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<td>8.0 ± 0.5</td>
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<tr>
<td>Configuration</td>
<td>Spiral-wound (SW)</td>
<td>Spiral-wound (SW)</td>
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<tr>
<td>Chemical structure</td>
<td>Thin film composite (TFC)</td>
<td>Thin film composite (TFC)</td>
</tr>
<tr>
<td>Chemical composition</td>
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<td>Polyamide/polysulfone</td>
</tr>
<tr>
<td>MWCO*, kDa</td>
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<td>0.1–0.3</td>
</tr>
<tr>
<td>Average pore size, nm</td>
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<td>0.5</td>
</tr>
<tr>
<td>Maximum pressure, bar</td>
<td>16</td>
<td>32</td>
</tr>
<tr>
<td>Maximum temperature, °C</td>
<td>50</td>
<td>90</td>
</tr>
<tr>
<td>pH range</td>
<td>1–11</td>
<td>1–11</td>
</tr>
</tbody>
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*MWCO: molecular weight cut off.
pressure $P_{\text{TM}}$, and the corresponding boundary flux value $J_b$.

Subsequently, the boundary flux values were 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$_{BOD}$) and the particle size distribution ($\nu_p$) of the feedstock solution (Stoller & Ochando-Pulido 2014, 2015). The proposed correlation curve is based on the general relationship between the permeate flux $J_p$ and the operating $P_{\text{TM}}$, as follows:

$$J_p(KP, t) = m(KP, t) \cdot P_{\text{TM}}(KP)$$  \hspace{1cm} (4)

where $m(KP, t)$ is the permeability and $P_{\text{TM}}(KP)$ the transmembrane pressure, as a function of the chosen key parameter $KP$ at any given time $t$; $m$ and $P_{\text{TM}}$ can be respectively approximated by linear functions:

$$m(KP, t) = m_0(t) - m_1 \cdot KP$$  \hspace{1cm} (5)

$$P_{\text{TM}}(KP) = P - R \cdot T \cdot KP$$  \hspace{1cm} (6)

where $m_0$ is the pure water permeability of the membrane at $t = 0$ (given in Table 1), $P$ is the applied operating pressure, $R$ is a constant, $T$ is the temperature, and $m_1$ is a fitting parameter affecting the pure water permeability $m_0(t)$, which is a function of time since it depends on the amount of fouling dynamically formed on the membrane (Stoller & Ochando-Pulido 2014, 2015).

Substituting Equation (5) and Equation (6) in Equation (4) at the boundary conditions defined by Equation (1) and re-arranging, the following second order polynomial equation is obtained:

$$J_b(KP, t) = m_0 \cdot P_b - \alpha \cdot t \cdot P_b - (m_0 - m_1) \cdot R \cdot T - \alpha \cdot R \cdot T \cdot t$$

$$+ m_1 \cdot P_b \cdot KP + m_1 \cdot R \cdot T \cdot KP^2$$  \hspace{1cm} (7)

valid in the physical range of $KP = [0, +\infty)$ such that $\lim_{KP \to 0} J_b(KP, t) = m_0(t)$, that is, the pure water flux conditions. This fitting curve has two roots, the first one is $KP^*$, representing the upper limit of the solute concentration in the feed solution that triggers zero flux conditions, and establishes the validity of the fitting curve in the range $[0, KP^*]$; whereas for long-run operation of the membrane $[t \to \infty]$, the minimum point tends to $-\infty$, which means that the relevant $J_b(KP, t)$ values as a function of time becomes lower and lower, that is, the membrane is less productive. There is a time point $t^*$ for a given $KP$ where zero flux conditions are attained, due to the amount of fouling on the membrane.

**RESULTS AND DISCUSSION**

The criterion to ensure the optimum operating strategy in batch operation for a membrane plant is to obtain the target solute recovery in the shortest time possible, without compromising the desired concentration of impurities in the final permeate (in case of wastewater streams determined by the established standard limits). The presence of fouling, and the consequent reduction of the permeate flux values during the operation time, forces engineers to over-design excessively the membrane plant to guarantee the operation of the process for a certain working period. In most cases, the over-design is performed based on the past experience of the designer, starting only from the projected permeate flux value, without considering in detail the nature and actual impact of the specific fouling of the system. In other cases, even worse, engineers underdesign the membrane plant, relying on excessively intensive operating conditions which are unsustainable in the long run. In both cases, the designer partially failed in engineering the process, which becomes at the end cost-inefficient or unfeasible.

Within these framework, the only degree of freedom for the operation of the membrane plant in this case is the permeate flux of the membrane unit. The strategic choice can therefore consist in operating whether upon a permeate flux value lower or higher than the boundary value. The boundary flux ($J_b$) establishes the frontier between the low fouling and high fouling operating framework of a membrane (Bacchin et al. 1996; Field & Pearce 2011; Stoller & Ochando-Pulido 2014, 2015).

The use of stable control systems is a possible solution for the reliability of the membrane operation. In this sense, most membrane processes are typically performed by simple control strategies which do not comprise the knowledge and control of fouling. The lack of advanced control systems in membrane technologies, capable of taking fouling phenomena into account, represents one key problem to be solved. To achieve this result, the fouling behavior of the system must be defined a priori. The knowledge of real-time boundary flux values can be a key factor to design stable control systems for membrane processes, since operation within sub-boundary flux conditions avoids high fouling rates and thus premature technical and economical failures.

The proposed fitting curve (Figure 2) for $J_b$ (Equation (7)), based on the general relationship between the permeate flux $J_p$ and the transmembrane pressure $P_{\text{TM}}$, the membrane permeability $m$ and the osmotic pressure $\pi$ as a function of one or more key parameters and time $t$, can be a successful...
approach if the chosen key parameters are able to give reliable fingerprints of the specific feedstock (Stoller & Ochando-Pulido 2015). For control purposes it appears mandatory that the key parameters are measured on-line, in-situ and real-time. This advanced control system, instead of conventional control ones, could define the appropriate real-time set-points to optimize the process with insight of productivity, selectivity and longevity by avoiding high fouling rates.

The adequate control strategy depends on the membrane and the feedstock characteristics. By simple system-control strategies, changing feedstocks require batch membrane processes. The advanced control system here proposed would permit the measurement of both the feedstock fingerprint and the operating conditions, thus changing feedstreams would not represent a handicap for the membrane performance any more. The model requires some input parameters: membrane area; fitting parameters for selectivity and the osmotic pressure; fitting parameter of membrane permeability and pure water permeability; operating boundary pressure; sub-boundary fouling rate index; initial value(s) of the key parameter(s); initial feedstock volume.

Two main membrane processes control strategies are adopted worldwide: controlling the permeate flow rate by changing the applied pressure value by a regulation valve on the retentate line, or controlling directly the constancy of the applied pressure. The advantage of the ‘constant permeate flow rate’ control strategy (flow control, FC) is the possibility to maintain the productivity of the membrane plant steadily in line with the project values, hereafter referred to as $F_p^*$ (Figure 3). The application of the FC requires the use of a simple proportional-integral (PI) control system. The problem of this strategy is to define correctly the permeate flow rate set-point of the controlled system.

In order to overcome this problem, the proposed model is required to estimate the boundary flux value at the end of the operation. Most membrane processes require FC control strategies. In this case, once the process is designed in a suitable way, the boundary flux model may be integrated within an advanced control system, capable of predicting real-time boundary flux values. With this information, the control system will establish the set-points of the in-line controllers, optimizing the process with insight to productivity, selectivity and longevity, by operating at sub-boundary flux conditions.
Otherwise, the advantage of the ‘constant operating pressure’ control strategy (PC) is its simplicity, but the productivity of the membrane plant may not be in line with the projected one, in particular if the permeate flow rate is not constant (Figure 4). The challenge of this strategy is to define correctly the operating pressure set-point $P_{sp}$ of the controlled system: the osmotic pressure value will dynamically change as a function of time and of the pollutant concentration in the feedstock, and needs to be added to the $P_{TM}$ value. In particular, this problem would have higher impact when applied to batch membrane processes. Nevertheless, the set-point can be defined by analysis of the starting feedstock conditions, and as a consequence, calculations can be performed with ease if compared to the previous control strategy.

To sum up, the optimal control strategy depends on the binomial membrane system-feedstock characteristics. In cases in which the feedstock concentration at the start of operation is nearly constant and the osmotic pressure changes may be neglected (that is, equal to or near zero), the FC strategy may be advantageous concerning ease of control and membrane area requirements. In all other cases, the FC strategy is suggested.

The guidelines for the appropriate design of batch membrane processes control systems based on the boundary flux are hereafter reported (Stoller & Ochando-Pulido 2013):

1. In case of adopting the FC control strategy, the required membrane area $A_f$ ($m^2$) can be evaluated with the following relationship:

$$A_f = F_{sp} \cdot (1 - \delta_p)^{-1} \cdot J_b(KP_c)^{-1} \cdot (1 + (C - 1) \cdot \tau \cdot \Delta w\%)$$

(8)

where $KP_c$ is the final value of the key parameter $KP$ (in this work, the COD value was chosen), estimated from a starting value of $KP(0)$ of the feedstock in worst-case conditions, that is, in total rejection conditions of $KP$, as a function of the feed recovery $Y$; $C$ is the number of desired separation cycles lasting $\tau$ hours, considering the loss of permeability $\Delta w\%$ after every membrane cleaning procedure; and $\delta_p$ represents a safety margin of about 5–10%. If $J_b(KP_c) < 0$ it means the designed process is technically unfeasible. $F_{sp}$ is the set point of the feed flow rate, which should be set to:

$$F_{sp} = V \cdot Y \cdot \theta^{-1}$$

(9)

where $V$ is the feedstock volume and $\theta$ is the desired operation time for one batch, generally equal to $\tau$.

2. The feasibility of the desired operating time $\theta$ should be checked as follows:

$$J_b(0) - \alpha \cdot P_b \cdot \theta^* > 0$$

(10)

3. Moreover, the tangential velocity of the concentrate stream exiting the last module should be checked, since it should be at least equal to the ones where the boundary flux is known. If $A_s$ is the feedstream passage section area of the membrane module, $F_t$ the maximum feed flow rate of the adopted pump, and $v_f$ the minimum desired concentrate stream velocity over the membrane surface at the outlet and equal to that of the chosen boundary conditions, then $N_m$, that is, the parallel membrane module lines connected to the pump, is equal to (the result should be rounded to the lower unity):

$$N_m = 0.001 \cdot (F_t - F_p) \cdot A_s^{-1} \cdot v_f^{-1}$$

(11)

4. If the adopted control strategy is the PC type (control of the operating pressure), the first step is to consider the boundary $P_b$ value, reduced by a safety margin $\delta_p$ of 5–10%. The required membrane area $A_p$ ($m^2$) can be evaluated by the following relationship:

$$A_p = F_p^* \cdot (J_b(0) - 0.5 \cdot \alpha \cdot P_b \cdot (1 - \delta_p) \cdot \tau^{-1} \cdot (1 + (C - 1) \cdot \tau \cdot \Delta w\%))$$

(12)

Starting from Equation (11) it is possible to calculate the value of the set-point operating pressure value ($P_{sp}$), equal to:

$$P_{sp} = P_b \cdot (1 - \delta_p) + \pi(KP)|_{t=0}$$

(13)

5. Finally, it should be checked that the difference between the adopted $P_b$ value and the pressure drop ($\Delta P_m$) across
every single membrane module of the series $N_s$ is positive.

6. A second final check should be performed on the rejection calculated at the end of the membrane-in-series process ($R$), such that the following condition, where $R'$ is the target rejection, must hold:

$$R' < R(P_b - (N_s - 1) \cdot \Delta P_m) \quad (14)$$

If all conditions are complied with, the draft technical design is successfully completed.

In case of the FC control strategy, the sensor is the flowmeter on the permeate stream, which transmits the measured value to the controller that acts on the aperture of the regulation valve on the concentrate outlet (Figure 3). In case of reduced permeate flow rate if compared to the set-point, the valve will increasingly close the $P_{TM}$ of the feedstream and thus the passage across the membrane. At this point, estimation of the boundary flux will be necessary for the integration of the model within advanced control systems. The estimated values of the boundary flux value ($J_b$) and the corresponding operating pressure ($P_b$) for the selected UF and NF membranes following the reported methodology (refer to ‘Performance of the membranes relying on the boundary flux determination’ section) is given in Figure 5. Thereafter, the sub-boundary fouling index $\alpha$ could be estimated by integration in time with Equation (3).

Following this, a second sensor would be capable of measuring $KP$ values, in this case the organic matter load (measured by the COD) of the feedstream. These data are given to the boundary flux model, therefore getting as an output the permeate flow rate value at which to operate the process in sub-boundary conditions. This value is given as the set-point to the previous feedback controller of the permeate flow rate. In case of set-point adjustments, after a certain period of time the feedback controller will automatically adjust the permeate flow rate to the new set-point value. Analogous would be the case of the use of the PC control strategy.

In Table 2 the membrane plant treatment design – comprising the boundary flux, the fouling index and the required membrane area – for OMWW is reported and summarized. Two different tailored pretreatments, thoroughly described by the author in former research works (Ochando-Pulido et al. 2013b) were applied on the raw OMWW feedstreams: gridding (cut-size of 300 $\mu$m) and UV/TiO$_2$ PhC. The feedstock was driven to an UF membrane process and subsequently to NF, reported in Table 1.

The performed calculations are based on the following premises: the membrane processes are batch-wise; inhibition of fouling is mandatory (and, consequently, working always in sub-boundary flux conditions); and the plant capacity is taken to be equal to 10 m$^3$ day$^{-1}$ (the average volume of these effluents by-produced in typical medium-sized olive mills).

The results obtained showed that the boundary flux $J_b$ was found to be 10 L h$^{-1}$ m$^{-2}$ for the UF membrane process whereas it was 14.3 L h$^{-1}$ m$^{-2}$ for the NF operation (Figure 5). The modeled behavior for both membranes fitted quite accurately the experimental dynamic fluxes (Figure 6). Moreover, the sub-boundary fouling parameter $\alpha$ was estimated to be equal to 0.011 L h$^{-1}$ m$^{-2}$ bar$^{-1}$ for the UF membrane and only 0.005 L h$^{-1}$ m$^{-2}$ bar$^{-1}$ for the NF membrane, which means a 65.4% reduction of the membrane constant permeability loss for the latter after the

Figure 5: Estimation of the boundary flux value ($J_b$) and the corresponding operating pressure ($P_b$) for UF (left) and NF membranes (right).
applied pretreatment and UF. Additionally, the calculated required membrane area upon the adoption of feed control FC is reported, showing a reduction of the membrane surface requirement for both UF and NF processes when PC is adopted (5.7–7.3% lower). The number of the necessary membrane modules (32 m² each) would be three UF modules plus two NF ones, which is minimum. These results are determinant for the feasible scale-up of the process to these small and dispersed industries.

The developed model provided with reliable input data can be useful to optimize the process both from a technical and economic point of view. The boundary flux model proposed could help to safely narrow the overdesign of membrane processes as a consequence of fouling phenomena. Moreover, proper process analyses eliminate the risk of wrong plant design by not reaching the desired target project values of productivity and selectivity.

Table 2 | Membrane area and total costs evaluation for the treatment of 1 m³ h⁻¹ of OMWW

<table>
<thead>
<tr>
<th>Feedstock</th>
<th>pH</th>
<th>COD</th>
<th>EC, mS cm⁻¹</th>
<th>COD</th>
<th>TSS, mg L⁻¹</th>
<th>COD</th>
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<td>2.9 ± 0.1</td>
<td>3.2 ± 0.1</td>
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<tr>
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<td>1.8 ± 0.1</td>
<td>1.9 ± 0.1</td>
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<td></td>
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</tr>
<tr>
<td></td>
<td>500 ± 10.5</td>
<td>10.5</td>
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<tr>
<th>Key parameter</th>
<th>Value in feedstream, g L⁻¹</th>
<th>Pretreatments</th>
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<td>11.1 ± 0.3</td>
<td>Gridding and PhC</td>
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<td>6.0 ± 0.2</td>
<td>From UF permeate</td>
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<table>
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<th>Membrane properties</th>
<th>Membrane type</th>
<th>UF</th>
<th>Membrane model</th>
<th>SW</th>
<th>Membrane ID</th>
<th>GM</th>
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<tr>
<td>Pore size, nm</td>
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<td>0.5</td>
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<tr>
<td>m_w, L h⁻¹ m⁻² bar⁻¹</td>
<td>5.2 ± 0.4</td>
<td>2.5 ± 0.2</td>
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</tbody>
</table>

| Process properties | T, °C | 20 ± 0.5 | 20 ± 0.5 |
|                   | v_p, L h⁻¹ | 550 ± 0.1 | 550 ± 0.1 |
|                   | π, bar | 0.0 | 0.0 |
|                   | Operation time, h | 4 | 4 |
|                   | Operation cycles | 500 | 500 |
| R, %              | 48.5 ± 0.2 | 76.6 ± 0.2 |

| Boundary flux data results | α, L h⁻² m⁻² bar⁻¹ | 0.011 | 0.005 |
|                           | Δw%, % | 0.001 | 0.001 |
|                           | J_s, L h⁻¹ m⁻² | 10.0 ± 0.4 | 14.3 ± 0.5 |
|                           | P_{MTf}, bar | 10.0 ± 0.1 | 9.0 ± 0.1 |
| Control type             | FC | PC |
| Membrane area, m²        | 74.2 | 68.8 |

| Membrane area, m² | 50.3 | 47.4 |

m_w: pure water permeability of the membrane; EC: electrical conductivity; TSS: total suspended solids.

Figure 6 | Experimental (o) and modelized (—) dynamic permeate flux for UF (left) and NF membranes (right) under boundary conditions.
CONCLUSIONS

The knowledge of the boundary flux values limits high fouling rate operating conditions. This permits design of the process control based on this value and to rely on the automatic control of the process to an advanced control system. The application for the purification of OMWW streams by membranes is reported.

Two different tailored pretreatments, thoroughly described in former research work, were applied on the raw OMWW, then driven to a UF membrane process and thereafter to NF, in batch. For OMWW, the boundary flux $f_b$ was found to be $10 \ L h^{-1} m^{-2}$ for the UF membrane process whereas $14.3 \ L h^{-1} m^{-2}$ for the NF operation. Moreover, the sub-boundary fouling parameter $\alpha$ was estimated to be equal to $0.011 \ L h^{-2} m^{-2} \ bar^{-1}$ for the UF membrane but only $0.005 \ L h^{-2} m^{-2} \ bar^{-1}$ for the NF membrane, implying $65.4\%$ reduction of the membrane constant permeability loss for the latter after the applied pretreatment and UF.

Additionally, the calculated required membrane area upon the adoption of feed control FC vs. pressure control PC systems pointed to a reduction of the membrane surface required for both UF and NF processes when the latter is adopted (5.7–7.3% lower). However, the advantage of the FC strategy would be the possibility of maintaining the productivity of the membrane plant steadily in line with the project values. The number of the necessary membrane modules ($32 \ m^2$ each) would be three UF modules plus two NF ones, which is minimum. These results are determinant for the feasible scale-up of the process in these small and dispersed industries.

The boundary flux values were reliable as set points for the control loops. This strategy permitted attaining stable and constant productivity for both membranes by operating at sub-boundary flux conditions. Moreover, it is shown that, relying on the boundary flux modelization, both type of control systems (feed control and pressure control) could be used reliably. The knowledge of real-time boundary flux values can be a key factor in designing stable control systems for membrane processes, since operation within sub-boundary flux conditions avoids high fouling rates and thus premature technical and economical failures.

ACKNOWLEDGEMENTS

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