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Analysis of the concentration polarization and fouling dynamic resistances under reverse osmosis membrane treatment of olive mill wastewater

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ABSTRACT

In this work, the resistances-in-series plus critical flux models are used as a simple but efficient tool in order to describe and predict the dynamic performance of a reverse osmosis membrane process, aimed for the tertiary treatment of two-phase olive mill wastewater (OMW2ST). To overcome the uncertainty of fouling, engineers overdesign the membrane plants by using wide safety margins that trigger the costs sensibly. One approach to answer the investor's need to trust membrane technology is to guarantee that fouling will be strongly inhibited or avoided. Within this context, concentration polarization and fouling could be accurately addressed by the applied models. Similar concentration polarization and fouling build-up rate on the selected membrane was found in the operating pressure range 15–25 bar (1.20×10^{-1}–1.41×10^{-1} h^{-1}), but increased over 5 times (6.42×10^{-1} h^{-1}) upon incrementing the transmembrane pressure up to 35 bar. Moreover, concentration polarization decreased 22.6% and the fouling build-up rate became reduced 45.5% with an increase of the crossflow up to 5.09 m s^{-1} upon negligible energy penalty, also avoiding irreversible fouling. Finally, significantly minor fouling (52.5–56.2% reduction) was attained at the lowest temperature, regularly experienced during the olive oil production campaign.

Introduction

Today, pressure-driven membrane processes are widely used in a plethora of applications, as stand-alone, integrated or substitutive operations. The availability of new membrane materials, membrane designs, membrane module concepts and general know-how has promoted credibility among investors [1,2]. In particular, membrane technology has replaced many conventional processes aimed for the purification of water and groundwater as well as for the reclamation of wastewater streams of very diverse sources [3–21].

In order to successfully implement a membrane process for a specific application at industrial scale, the prediction of the performance of the selected membrane is mandatory for the appropriate operation of the membrane plant. Here an additional difficulty is given by concentration polarization and membrane fouling phenomena occurring over the membrane during the operation time, which alter the membrane output continuously.

Concentration polarization is caused by the increasing concentration of solutes within the membrane boundary region. It gives rise to an additional resistance and thus raises the operating costs and also affects adversely the quality of the permeate stream. On the other hand, membrane fouling is complex and may involve membrane pore blocking, plugging and clogging, chemical degradation and/or cake formation on the membrane surface. Fouling might be caused by microorganisms as well as organic and inorganic material, and results in loss of the permeate flux and alteration of the membrane selectivity [22,23].

As a main short-term effect, fouling leads to an increase in the energy costs to maintain the target permeate production. Furthermore, it also triggers the operating expenses in the long

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run due to the need of frequent plant shut-downs for in-situ membrane cleaning, as well as irreversible fouling, that shortens the longevity of the membranes irretrievably, incrementing significantly the capital costs because of the need of premature membrane module substitution.

Despite the high efficiency and moderate investment and maintenance expenses of membrane processes as a general rule, concentration polarization and fouling phenomena, somewhat linked to each other, remain still today as the main obstacle for the definite implementation of this technology. This handicap especially affects liquid–liquid separation processes, as is the case of wastewater streams, as reported by different Authors [24–28].

Fouling has perceptibly compromised the reliability of membrane technology. Despite the development, understanding and validation of membrane fouling phenomena theories and their description in order to overcome the knowledge gap, this feeling still persists at industrial scale. In order to overcome this uncertainty, engineers tend to overdimension the membrane plants, in many cases by using wide safety margins or on the basis of past experience [24]. This approach may be considered successful in order to guarantee the process performance, but triggers the costs sensibly.

In the present research paper, a polymeric thin film composite (TFC) reverse osmosis membrane (RO) was selected for the tertiary treatment of the effluent streams coming from olive mills operating with the modern two-phase continuous centrifugation technology, that is, olive mill wastewater (OMW2), which was formerly conducted to a physicochemical primary–secondary treatment (OMW2ST) at pilot and industrial scale, as thoroughly described in previous works by the Authors [29–33]. Membrane technology, given its versatility and modular nature [34], can represent a cost-effective solution for the reclamation of OMW2ST in these typically small factories. Within this framework, the effects of the operating conditions on membrane concentration polarization and fouling build-up were examined and modelized by conducting well-controlled dynamic RO experiments.

In this context, it is not mandatory to define and describe with scientific precision the phenomena of membrane fouling. The causes may be of interest for the process designer, but not for the investor, who will ask about the consequences. In case of membrane fouling, when triggered, the consequences are in most cases negative. One approach to answer the investor's need to trust membrane technology is to guarantee that fouling will be strongly inhibited or avoided. Since the description of the fouling phenomena may be difficult and complex, engineers may avoid the consequences altogether by limiting the causes.

In this work, the osmotic-pressure resistances-in-series model is used as a simple but efficient tool in order to describe the membrane process and predict its performance in time, additionally supported by the critical flux model. Concentration polarization and fouling resistances occurring on the RO membrane during OMW2ST purification were addressed, and the fouled active layer was also examined. To the Authors' knowledge, only one previous work on the analysis of the dynamic fouling resistances occurring during membrane filtration of this kind of wastewater can be found in the scientific literature, that is, the one performed by Turano et al. [35] on OMW coming from olive mills operating with the three-phase centrifugation technology, but none on OMW of two-phase continuous centrifugation process.

Experimental

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) and total iron concentrations, as well as electroconductivity (EC) and pH analysis, were performed following standard methods [36]. 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) [36]. Ionic concentrations were analyzed with a Dionex DX-120 ion chromatograph, as thoroughly described in previous works by the Authors [32,33]. Microphotographs and elemental microanalysis of the active layer of the virgin as well as of the fouled membrane coupons after the RO experiments were performed with a high resolution scanning electron (HR-SEM) microscope (Carl Zeiss SMT model).

The effluent stream

In the production process of olive oil, two-phase continuous centrifugation-based olive oil factories lead to the generation of two main effluent streams, the first one during the washing of the fruit (olives washing wastewater, OWW), whereas the second one is by-produced during the washing of the olive oil in the vertical centrifuges (olive oil washing wastewater, OOW). These effluents are commonly referred to as olive oil mill wastewater (OMW2) [29–33]. An average-sized olive oil factory produces around 1 m^3 of OOW per ton of processed olives and 1 m^3 of OWW per ton of washed olives, which means a daily amount of 10–20 m^3 of OMW2.

Samples of OMW2 were collected from different olive oil mills in the Andalusian provinces of Jaén and Granada (Spain) during the olive oil production campaign in winter, then rapidly analyzed in the lab and refrigerated for further research. After this, OMW2 was subjected to a primary–secondary treatment on a pilot scale comprising Fenton-like advanced oxidation followed by flocculation–sedimentation and olive stones filtration, as described in detail in former works by the Authors [29–33]. The effluent stream after the primary–secondary treatment, hereafter referred as OMW2ST, presents the physico-chemical characteristics reported in Table 1, and was the feed to the final RO purification operation [32,33].

Membrane operation

The membrane bench-scale plant (Prozesstechnik GmbH, Basel, Switzerland), shown in Fig. 1, was provided with a non-stirred double-walled tank (maximum volume equal to 5 L) where the

Table 1
Physicochemical characterization of OMW2ST.

Parameter	OMW2ST
pH	8.0 ± 0.2
EC ($mS\,cm^{-1}$)	3.4 ± 0.2
TSS ($mg\,L^{-1}$)	14.5 ± 1.5
COD ($mg\,L^{-1}$)	188.7 ± 37.9
Total phenols ($mg\,L^{-1}$)	0.7 ± 0.3
Total iron ($\mu g\,L^{-1}$)	215.0 ± 185.0
Cl^- ($mg\,L^{-1}$)	1018.0 ± 27.1
F^- ($mg\,L^{-1}$)	1.1 ± 0.9
Br^- ($mg\,L^{-1}$)	2.4 ± 0.4
NO_3^- ($mg\,L^{-1}$)	7.9 ± 0.6
SO_4^{2-} ($mg\,L^{-1}$)	133.3 ± 5.9
HCO_3^- ($mg\,L^{-1}$)	131.1 ± 1.8
PO_4^{3-}, ($mg\,L^{-1}$)	1.8 ± 1.3
Na^+ ($mg\,L^{-1}$)	631.4 ± 97.3
K^+ ($mg\,L^{-1}$)	59.4 ± 9.9
Ca^{2+} ($mg\,L^{-1}$)	93.9 ± 9.8
Mg^{2+} ($mg\,L^{-1}$)	26.9 ± 5.6

OMW2ST: olive mill wastewater after secondary treatment.