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Boundary flux optimization of a nanofiltration membrane module used for the treatment of olive mill wastewater from a two-phase extraction process

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ABSTRACT

The boundary flux theory was used to modelize the performance of a nanofiltration (NF) membrane in the treatment of the effluents exiting a two-phase olive oil extraction process, in particular olive mill (OMW) and olives washing (OWW) wastewater streams. The results obtained from the pressure-cycling experiments exhibit a boundary flux pattern with very low long-term fouling for all analyzed feedstocks. This observation is confirmed by the low values of the sub-boundary fouling parameter (α) obtained by the fitting of the experimental flux data measured during batch-run operation to the boundary flux model. Reduced long-term fouling (28.6–33.3%) occurred during NF operation of the effluents after the proposed secondary treatment, which comprised pH-temperature flocculation followed by ultraviolet (UV) photocatalysis with ferromagnetic-core nanocatalyst and an ultrafiltration separation step (UF). Otherwise, a decrease of long-term fouling in the range of 57.1–60% was observed by using the secondary-treated 1:1 (v/v) mixture of OMW and OWW as feedstock. Moreover, processing both feedstocks to the complete secondary treatment led to increased feed recovery rates (85–90%) and boundary flux values (12.3–19.6 L h^{-1} m^{-2}). Finally, the standard limits to reuse the purified effluents for irrigation were successfully achieved.

1. Introduction

In the last decade, nanofiltration (NF) membranes have been increasingly implemented in water treatment processes such as groundwater and surface water [1,2], desalination of brackish water and seawater [3,4] and decontamination of wastewater of very diverse nature including coking [5,6], carwash [7], textile and tannery [8–10], pulp and paper [11,12], pharmaceutical [13] and agro-food industries such as dairy [14], tomato [15] and olive oil [16–18], among others.

The specific selectivity towards small solutes and the lower energy consumption of NF membranes have boosted their use as tertiary treatment in integrated wastewater treatment processes. However, some drawbacks have to be faced when NF is applied on an industrial scale [19]. The main drawback still to be solved to definitely permit competitiveness of NF technology is fouling. Membrane fouling reduces the production capacity of the plant and also shortens the membrane service lifetime if of irreversible nature, thus increasing the operating and capital costs. Moreover, fouling alters the selectivity of the membrane and thus the rejection efficiency.

Several factors influence deeply the performance of NF membranes: the feedwater composition – such as the pH, the ionic strength and the divalent ions concentration, the organic matter load and the particle size distribution – as well as the operating conditions, that is the applied net driving pressure, the crossflow velocity (turbulence) over the membrane and the operating temperature.

Among the strategies to control fouling in pressure-driven membrane systems for wastewater applications, pretreatments specifically tailored to the membrane and feedstock have been highlighted to be essential in fouling inhibition protocols, given the fact that direct treatment of the raw effluents by membranes has been reported to lead to rapid emergence of membrane fouling [16,17,20–23]. A common error typically committed by engineers is to overdesign excessively the membrane plants, which results in sensible but useless increment of the total costs. On the contrary, under-design due to underestimation of the fouling issues leads to operation above threshold conditions, unfeasible technically and economically in the long run.

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The existence of a critical flux, defined as the point at which the repulsive barrier of a membrane is overcome and below which no fouling occurs, was first theoretically proven by Bacchin et al. Research Group for microfiltration (MF) membranes [24]. This was a breakthrough in the know-how of pressure-driven membrane systems, and afterwards other researchers further worked on this concept in MF, ultrafiltration (UF) and NF membranes [25–31].

Some authors further observed that during the operation of some liquid–liquid membrane systems fouling cannot be completely inhibited [32], such as in the treatment of wastewater [33–36]. A new concept was therefore introduced to modelize the performance of membrane systems in these cases, called the threshold flux, providing more proper design and operating guidelines [32]. The threshold flux makes reference to the flux point which establishes the barrier between the low fouling and high fouling operating frame of a membrane, and it is a result of physical phenomena only, such that further applied pressure increment does not result in greater stable fluxes. Above the threshold conditions, the permeate flux starts to decay exponentially just from the early stages of operation.

The critical and threshold flux theory is an important tool to define the membrane plant operating strategy, which is bounded by the compromise between the capital costs, which are reduced by adopting high permeate flux targets, and the operating expenses, which are principally minimized by restricting the membrane fouling rate.

In a previous work, the critical and threshold flux theories were merged into a new concept, the boundary flux [37]. In the present study, this concept was used to modelize and thus define the operating framework of a NF membrane during batch operation employed in the tertiary treatment of the effluents by-produced by olive oil mills (olive mill effluents, OME).

The raw OME were processed by two different secondary treatment procedures previously optimized in former work by the authors, that is pH-temperature flocculation followed by photocatalysis with a ferromagnetic-core nanocatalyst under irradiation of UV light plus UF or simply pH-temperature flocculation stand-alone followed by UF [18]. Modelization and control of the fouling behavior of the NF membrane was studied by estimating the boundary flux values for the different feedstocks as well as the short-term and long-term fouling, predicted by fitting the permeate flux data to the boundary flux equations.

OME are among the heaviest-polluted existing industrial effluents, exhibiting high toxicity given by the presence of aromatic compounds and a wide range of other organic pollutants not suitable to be biologically managed. For these reasons, OME pose a serious environmental threat for an increasing number of regions, leading to problems in relation to odor nuisance, soil contamination, underground leakage and water body pollution. A medium-sized modern olive oil factory gives rise on average to more than 10 m^3 of OME daily, which means not only a huge amount of potable water consumption, but also a major hazard for the environment as it cannot be directly reused for irrigation purposes, and thus its disposal represents a huge cost for this industry.

The quality standards for reuse of the purified effluents for irrigation or in the olive oil production process, for instance in the olive washing machines, were finally checked.

2. Experimental

2.1. NF membrane feedstock: pretreated olive mill effluents

In the present study, samples of olives washing wastewater (OWW) collected from the washing machines and olive mill wastewater (OMW) exiting the vertical centrifuges were taken from several olive oil mills located in Jaén and Granada (Spain) operating with the modern two-phase olive oil extraction procedure [38–40]. Two different raw feedstocks were used for the study of the fouling behavior of the NF membrane: on one hand OMW whereas 1:1 (v/v) mixture of OMW and OWW on the other hand, hereafter referred to as OWMW.

After gridding in order to remove coarse particles (cut-size equal to 300 μm), both raw feedstocks were subjected to two main secondary treatments at pilot scale prior to the NF process, to avoid quick emergence of irreversible fouling on the membrane when no pretreatment of the raw effluents is conducted [18,20]. The first secondary treatment comprised pH-temperature flocculation followed by photocatalysis with a ferromagnetic-core nanocatalyst under irradiation of UV light plus UF, whereas the second included simply pH-temperature flocculation stand-alone followed by UF [18].

For ease of referral, the effluents exiting the proposed secondary treatment processes were hereafter given the following labels: $FS_{1,\ UF}$ or $FS_{2,\ UF}$ for OMW after the secondary treatment without photocatalysis *vs.* the whole procedure, whereas $FS'_{1,\ UF}$ or $FS'_{2,\ UF}$ for OWMW exiting the same secondary treatment processes.

The two different secondary treatment strategies were performed on the raw feedstocks at pilot scale upon the conditions formerly optimized on lab scale in previous experiments [18]:

(i) pH-T flocculation process was performed at ambient temperature (25 ± 0.5 °C) and acid pH (2.5 ± 0.25) adjusted by the addition of 70% w/w HNO_3 and carried out in a stirred batch reactor (20 L) provided with a turbine impeller stirrer [18].
(ii) UV photocatalysis process (residence time τ = 3 h) was conducted in a photocatalysis reactor (8 L) provided with an UV lamp on top (45 W, 365 nm) and an overhead stirrer by using lab-made ferromagnetic-core nanoparticles (γ Fe_2O_3/SiO_2/TiO_2 with pure anatase phase and some traces of brookite, presenting a final modal particle size equal to 79 ± 2 nm). The description of the fabrication of the ferromagnetic nanocatalyst by sol–gel process in a spinning-disc reactor is thoroughly described in former work [18].
(iii) UF was carried out at ambient operating conditions (20 ± 0.5 °C) and turbulent tangential velocity over the membrane (Reynolds number N_{Re} > 4000), upon operating pressure values equal to 7 and 8 bar for $FS_{1,\ UF}$ and $FS_{2,\ UF}$ whereas 9 and 11 bar for $FS'_{1,\ UF}$ and $FS'_{2,\ UF}$, respectively [41].

The organic pollutants load values of the used feedstocks, measured by the chemical oxygen demand (COD), are reported in Table 1.

The pH-T coagulation–flocculation process performed in this work poses a cost-effective alternative pretreatment for the removal of the organic suspended matter in these effluents if compared to current coagulation–flocculation processes with commercial flocculants, which in our experience provide lower efficiency values upon higher costs.

Otherwise, UV/TiO_2 photocatalysis is a rather potentially cost-effective advanced oxidation process (AOP), able to abate a wide

Table 1
Mean organic matter load of the feedstocks.

Effluent	COD (mg L^{-1})
$FS_{1,\ UF}$	8700
$FS_{2,\ UF}$	5700
$FS'_{1,\ UF}$	2100
$FS'_{2,\ UF}$	840