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Kinetics and boundary flux optimization of integrated photocatalysis and ultrafiltration process for two-phase vegetation and olive washing wastewaters treatment

J.M. Ochando-Pulido [a],*, M. Stoller [b]

[a] Chemical Engineering Department, University of Granada, 18071 Granada, Spain
[b] Department of Chemical Engineering, University of Rome "La Sapienza", Via Eudossiana, 18-00184 Rome, Italy

HIGHLIGHTS

- Simultaneous treatment of effluents of olive mills operating with two-phase technology.
- pH-T flocculation + UV/TiO_2 photocatalysis + UF yields effluent apt for irrigation.
- Significant and stable flux (26.5% increment) and minor fouling (28.6% reduction).
- Proposed boundary model fits accurately the UF membrane performance.

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ABSTRACT

In many of the studies available on the treatment or fractionation by membrane technology of the effluents by-produced by olive oil factories, the problem of fouling is not correctly approached or not even addressed. In the present study, the operating framework of a spiral wound polymeric ultrafiltration (UF) membrane module was optimized by the boundary flux theory, which merges both the critical and threshold flux theories for simplification purpose and was formerly validated by the Authors. The raw wastewater, a mixture of olive washing and olive vegetation wastewaters, was pretreated by two processes developed in prior research: pH-temperature flocculation (pH-T F) and photocatalysis with lab-made ferromagnetic-core titanium dioxide nanoparticles under ultraviolet light (UV/TiO_2 PC). The organic matter removal during UV/TiO_2 PC fitted accurately a two-step first-order kinetic model. Also, the proposed boundary model fits the membrane experimental data with accuracy. Higher boundary flux values were confirmed for batch UF when the feedstream is further pretreated by UV/TiO_2 PC (23.3–23.6% increment), and also slightly higher feed recovery and significant minor sub-boundary fouling index α. Moreover, the higher rejection of the organic pollutants (53.3%) permits achieving the standard limits to reutilize the purified effluent for irrigation purposes.

1. Introduction

As a sample of the popularity of ultrafiltration (UF) membranes for effluents tertiary treatments, a plethora of scientific papers have been published in international scientific journals in the last decade [1]. Currently, UF membranes have replaced many conventional separation operations in wastewater treatment processes, provided their lower specific energy consumption, minor investment and maintenance costs as well as higher efficiency. UF membranes have already been employed in the decontamination of wastewater from very different sources, including metalworking industry [2], oil field wastewater [3], refinery wastewater [4], pulp and paper [5], textile wastewater [6], dairy effluents [7], protein production [8], olive mills wastewater [9–11], restaurant wastewater [12] and municipal sewage [13], among others.

Much effort has been invested to attain novel membranes capable of offering higher technical and economical performances since the development and commercialization of the first cellulose acetate asymmetric membranes. However, there is an important lack of knowledge concerning membrane fouling still to be fulfilled.

Fouling is a complex phenomenon which involves different mechanisms comprising pore blocking, plugging or constriction, cake, gel and biofilm formation as well as cake-enhanced

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* Corresponding author. Tel.: +34 958241581; fax: +34 958248992.
E-mail address: jmochandop@ugr.es (J.M. Ochando-Pulido).

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concentration polarization [14–16]. Moreover, several variables influence to different extent the type and rate of fouling formation on UF membranes, related to the membrane (layer and support chemical nature, roughness and mean porosity), the hydrodynamic conditions inside the membrane module (net operating pressure, turbulence and temperature) and also the characteristics of the feedstream (physico-chemical composition, concentration, particle size distribution, pH, ionic strength and divalent ions concentration).

In the present work, UF treatment of the effluents by-produced by olive oil industries (OME), in particular olive washing (OWW) and olive vegetation wastewaters (OVW), is discussed. In most of the studies available on the treatment of these effluents by membranes, and also in others in which the fractionation of OME has been studied [17,18], the problem of fouling is not correctly approached or not even addressed. Fouling is always present in the treatment of wastewater streams by UF membranes and its control is imperative to assure the appropriate operation and design of the plant. During operation, fouling soars on one hand the energy costs to maintain the target permeate production, and on the other the operating costs associated to frequent plant shut-downs for in situ membrane cleaning procedures. Furthermore, the longevity of the membranes might be irretrievably shortened if irreversible fouling arises.

In this regard, OME contain 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, as well as inorganic matter, which may also lead to deleterious scaling problems.

Concerning this, the Authors have observed in previous works that an optimized membrane plant design requires a properly-tailored pretreatment process in order to avoid high fouling rates, which would rapidly lead to zero flux conditions if no pretreatment is conducted on the raw effluent upstream the UF operation [19,20]. In particular, it is key to shift the mean particle size distribution of the foulants in the feedstream away from the average pore diameter of the selected membrane to avoid constriction, blocking and plugging of the pores, which often cause irreversible fouling.

On the other hand, it is essential to operate the plant under the appropriate operating framework. Bacchin et al. introduced in 1996 an important concept that has served as a very reliable tool to define the operating framework of membrane operations, the critical flux [21]. They observed for microfiltration (MF) membranes that there is a permeate flux below which fouling is not promptly attained, but above which fouling becomes critically triggered. This pattern was also confirmed in UF membranes afterwards [22,23], as well as for nanofiltration (NF) [24,25].

Lately, a new concept was introduced, the threshold flux. In this case, the concept evaluates the maximum permeate flux that can be yielded by a membrane upon a low constant fouling rate regime [26,27]. This concept is a novel practical tool for membrane process designers, more than the critical flux, especially in those cases where the presence of fouling is unavoidable even below the critical conditions, such as in wastewater treatments by membranes [16,26–32]. Subsequently, both concepts were merged by Stoller and Ochando in a recent paper for ease of application [33].

In the present manuscript, the operating framework of a spiral wound (SW) polymeric UF membrane module was optimized by means of the boundary flux theory. Membrane fouling control was addressed by this model, and also for this purpose the raw wastewater stream was pretreated by two processes developed in previous work by the Authors, that is, pH-temperature flocculation (pH-T F) and photocatalysis with lab-made ferromagnetic-core titanium dioxide nanoparticles under ultraviolet light (UV/TiO_2 PC) [12,34], for which the kinetics was also studied. Finally, the parametric quality standards to reuse the purified effluent whether for irrigation purposes or for discharge into public waterways or in municipal sewers were checked.

2. Experimental

2.1. The feedstock to the UF membrane module

As a result of the production of olive oil in olive oil factories working with the modern two-phase continuous centrifugation process, two main effluents are generated. Once received in the olive mills, olives are washed prior to their entrance in the olive oil production line, leading to the generation of olive washing wastewater (OWW). Afterwards, during the vertical centrifugation of the oil, olive vegetation wastewater (OVW) is by-produced.

OWW is a moderately polluted effluent, presenting high amount of suspended solids but low concentration of dissolved organic matter. Concentration values depend mainly on the water flowrate employed in the olives washing machines during the cleaning procedure of the fruit, but normally stand below the limits for discharge on suitable superficial terrains (Guadalquivir Hydrographical Confederation, 2006: total suspended solids TSS < 500 mg L^{-1} and chemical oxygen demand COD < 1000 mg L^{-1}). On the other hand, high organic pollutants load in the form of dissolved matter is confirmed in OVW, most of them phytotoxic and recalcitrant to biological degradation [12].

Samples of OWW and OVW were taken from olive oil mills located in Jaén and Granada (Spain) operating with the two-phase olive oil extraction process. Olive oil factories operating with the two-phase extraction technology generate on average a daily amount of more than 1 m^3 of OWW per ton of processed olives and 10 m^3 of OVW, respectively. Thereby, in order to treat OWW and OVW simultaneously, both effluents were mixed in 1:1 (v/v) proportion – hereafter labeled as olive mixed wastewater (OMW) – to stabilize the average organic matter concentration of the stream entering the treatment system and thus avoid sensible fluctuations in the COD parameter.

Subsequently, the OMW stream was subjected to two different pretreatment processes studied and thoroughly described in previous work by the Authors [12,34]. Beforehand, gridding was carried out to remove the coarse particles present in OMW (cut-size equal to 300 μm), then pH-T flocculation (pH-T F) by adding HNO_3 (70% w/w) followed by photocatalysis of the supernatant under ultraviolet irradiation (UV) with commercial Degussa P-25 or lab-made ferromagnetic-core TiO_2 nanoparticles (UV/TiO_2 PC). The feedstream at the end of this pretreatment process will be hereafter assigned as OMW-FPC. The alternative pretreatment process comprised only gridding followed by pH-T F, therefore the feedstream exiting this pretreatment line will be referred to as OMW-F.

The pH-T F experiments were performed at ambient temperature (20 ± 0.5 °C) in a 20 L stirred batch reactor equipped with a turbine impeller stirrer providing short, initial high stirring rate mixing (90 s, 1000 rpm) followed by slow stirring for a longer period of time (20 min, 320 rpm).

UV/TiO_2 PC was carried out in an 8 L agitated batch reactor, provided with an UV lamp on top (nominal power 45 W, wavelength 365 nm), at ambient temperature (20 ± 0.5 °C) and medium agitation speed (500 rpm), lasting 2–4 h residence time. Two different nanometric TiO_2 catalysts were used for the experiments: one commercial catalyst Degussa P-25 (mean particle size 40 nm, crystal phase composition 70% anatase and 30% rutile) and laboratory-made composite photocatalytic nanoparticles with a ferromagnetic core and two subsequent layers of silica and titania.

Different catalysts dosages (0.5–9 g L^{-1} for both catalysts, plus 20 g L^{-1} for the commercial Degussa P-25) were tested and the