Desalination 343 (2014) 162–168

Contents lists available at ScienceDirect

Desalination

journal homepage: www.elsevier.com/locate/desal

Fouling control by threshold flux measurements in the treatment of different olive mill wastewater streams by membranes-in-series process

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HIGHLIGHTS

- Optimum treatment sequence: pH–T flocculation + UV/TiO_2 photocatalysis + UF + NF.
- UF and NF membranes exhibit threshold fluxes with 54.5% less fouling on the latter.
- Fouling control of membranes-in-series process for olive mill wastewater treatment.
- Required membrane area, overdimension and constant fouling parameter reduced.
- Steady-state permeate flux and membrane longevity enhanced by the adopted sequence.

ARTICLE INFO

Article history:
Received 8 June 2013
Received in revised form 24 August 2013
Accepted 1 October 2013
Available online 19 October 2013

Keywords:
Olive vegetation wastewater
Modeling
Fouling
Nanofiltration
Ultrafiltration
Wastewater reclamation

ABSTRACT

This paper deals with the measurement of the critical and threshold flux for modelization, prediction and control of the fouling issues of batch membranes-in-series processes, in detail ultrafiltration (UF) followed by nanofiltration (NF) and reverse osmosis (RO), for the reclamation of olive mill wastewater (OMW-2). Results suggest the existence of threshold flux values for both UF and NF membranes, with minimum constant fouling attained on the latter, that is 54.5% lower. UF + NF in series after pH–T flocculation process followed by photocatalysis with ferromagnetic-core titanium dioxide under ultraviolet irradiation (UV/TiO_2) as pretreatment to inhibit fouling issues guarantees COD values in the permeate of 1.3 g L^{-1}. This value complies with irrigation water quality standards. Moreover, the adoption of this treatment sequence helps reducing the required membrane area, equal to 104.6 m^2 and 81.4 m^2 for the UF and NF membranes, respectively, leading to a limited need of overdesign of the membrane plant. In addition, especially the use of the applied UV/TiO_2 photocatalysis process not only enhances the productivity but also ensures minimization of the constant fouling build-up on both membranes. This latter effect sensibly increases the longevity of the membranes, reducing the capital and operating costs of the treatment.

1. Introduction

Since the development and commercialization of the first cellulose acetate asymmetric membranes by Loeb and Sourirajan in 1962, and after much effort invested to attain novel membranes capable of offering higher technical and economical performances, membrane technology has gained ground to classic separation processes. Pressure-driven membrane processes have experienced a huge boost and are nowadays widely applied for water purification and wastewater reclamation treatments [1–10]. Microfiltration (MF) and ultrafiltration (UF) membranes are principally used as secondary treatments for the removal of microorganisms, high molecular weight organic pollutants and macromolecules, whereas nanofiltration (NF) and reverse osmosis (RO) membranes can effectively reduce the concentration of micropollutants, low molecular weight organic matter and dissolved inorganic compounds.

Nevertheless, despite the lower investment and maintenance costs and high efficiency of membrane processes, membrane fouling remains still today as one of the main challenges of this broad applied technology, especially concerning liquid–liquid separation processes as in the case of wastewater treatment [11–13]. During operation, fouling leads not only to an increase in the energy costs to maintain the target permeate production, but also in the operating expenses due to frequent plant shut-downs for in-situ membrane cleaning. Moreover, the longevity of the membranes can be irretrievably shortened due to irreversible fouling.

To face this handicap in industrial scale facilities and to achieve steady operation, engineers erroneously tend to overdesign excessively the membrane plants, resulting in sensible but useless increment of total costs. On the other hand, under-design due to underestimation of the fouling issues leads to operation above threshold conditions,

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http://dx.doi.org/10.1016/j.desal.2013.10.002

which are technically and economically unfeasible for long periods of time [14,15].

Hence, inhibition and control of fouling are keys to membrane technology in order to definitely achieve competitiveness. The first theoretical model giving explanation to membrane transport phenomena of colloidal particles was proposed by the research group of Bacchin et al. [16]. The existence of the critical flux was theoretically proven and physically explained by the authors, who gave a first definition of the critical flux, stating that it is the point at which the repulsive barrier is overcome, and below which no fouling occurs [16]. Afterwards, Field et al. [17] gave an empirical approach of the concept of the critical flux for MF membranes, defining it as the permeate flux which can be attained without incurring in fouling formation during operation time. Later on, this concept was also extended to UF and NF membranes [18–23].

However, some authors noted that this pattern is not always strictly observed in all membrane separation processes, underlining that fouling cannot be completely inhibited during the operation of some liquid–liquid membrane systems such as in the treatment of wastewater [24–26]. These researchers noticed that fouling was unavoidable to a certain extent at every operating condition, and thus the concept of the threshold flux was introduced [26,27]. In contrast with the critical flux, the threshold flux instead makes reference to the maximum permeate flux at which fouling builds up at a very low and constant rate, and above which the rate of fouling becomes exponentially increased. In other words, the threshold flux divides a low fouling region from a high fouling region of pressure-driven membrane processes. Recently, Stoller and Ochando [28] verified the validity of this theory in the treatment of the effluent of the olive oil industry (olive mill wastewater, OMW) by UF and NF membranes.

The main difficulty in determining the critical or threshold flux lies in the impossibility of theoretical prediction, thus experimental estimation is necessary [15,29]. Furthermore, several factors influence these values, such as the membrane type, the membrane surface roughness and mean porosity, the hydrodynamic conditions and the effluent composition and concentration. In regard to the latter, direct treatment by membranes of raw effluents has been reported to lead to rapid emergence of membrane fouling. An optimized pretreatment process, specifically tailored to the application, is essential for the design of an appropriate fouling inhibition strategy [12–15,30–32].

In the present paper, fouling inhibition and control by means of the critical and threshold flux theory of a batch membranes-in-series process for the reclamation of OMW is discussed. The raw OMW was processed by two different pretreatment procedures previously optimized in other works by the authors, that is pH–temperature flocculation stand-alone or followed by photocatalysis by means of ferromagnetic-core nanoparticles under irradiation of UV light [33].

The different degrees of influence of these secondary treatments on the operation of the subsequent membrane stages, that is UF, NF and RO in series, were studied. The core of this present research paper is to validate the critical and threshold flux theory for the accurate prediction and control of the fouling behavior of the membranes through modelization of the permeate flux profiles for the treatment of OMW streams exiting the olive oil production industry.

A medium-sized modern olive oil factory working with the two-phase continuous extraction procedure gives rise on average to around 10 m^3 of OMW-2 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.

2. Experimental

2.1. The feedstock and the applied pretreatment processes

The raw feedstock employed in this work was an effluent stream produced by an olive mill located in Jaén, Spain, operating with a two-phase olive oil extraction procedure (OMW-2). The samples of OMW-2 were taken directly from the vertical decanters and rapidly analyzed before the set-up of the proposed reclamation treatment. Otherwise, the samples were refrigerated for future research works.

These mill effluents typically exhibit strong odor nuisance, acid pH, intensive violet-dark color, very heavy organic pollutants load and also considerable saline toxicity reflected by the high electroconductivity (EC) values [34]. These characteristics make the reclamation of OMW-2 by conventional physicochemical treatments extremely difficult, and the presence of phytotoxic refractory pollutants – such as phenolic compounds, organic acids, tannins and organohalogenated contaminants – inhibits the efficiency of biological processes and therefore their biological degradation. Moreover, the physico-chemical composition of these effluents is also extremely variable as it depends on several factors comprising not only the extraction process, but also edaphoclimatic and cultivation parameters, as well as the type, quality and maturity of the olives [34–36]. Additional difficulties such as small size and geographical dispersion of olive oil mills as well as seasonality of olive oil production are encountered in the management of these agro-industry effluents.

Taking all this into account, membrane technology can represent a cost-effective solution for the reclamation of the olive mill effluents, due to its versatility and modular nature. Nevertheless, to avoid rapid incurrence of fouling on the different membrane stages, the raw feedstock (OMW-2) was processed by two different pretreatment steps on pilot scale: the first one consisting in a pH–T flocculation process 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 conducted in a stirred batch reactor (20 L) provided with a turbine impeller stirrer; the second one further comprising a photocatalysis process (residence time $\tau = 4$ h) by means of 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) and carried out in a photocatalysis reactor (8 L) provided with an UV lamp on top (45 W, 365 nm) and an overhead stirrer. The description of the fabrication of the ferromagnetic nanocatalyst (sol–gel process conducted in a spinning-disc reactor) as well as both pretreatment procedures is described in detail in former works [33].

2.2. Analytical methods

All analytical methods were applied in triplicate with analytical-grade reagents, including 70% (w/w) HNO_3, 98% (w/w) NaOH, 98% (w/w) Na_2SO_3, 30% (w/w) NH_4OH, 37% (w/w) HCl and 30% (w/w) $FeCl_3$, supplied by Panreac.

Chemical oxygen demand (COD), total phenols (TPh), total suspended solids (TSS), electroconductivity (EC) and pH measurements were performed following standard methods [37]. Finally, particle size distribution analysis of the suspended and colloidal matter was carried out with a Plus90 nanosizer supplied by Brookhaven.

2.3. Pilot-scale membrane plant

A scheme of the flow-diagram of the proposed batch membranes-in-series process (UF + NF + RO) is given in Fig. 1, and a photograph of the membranes pilot plant used for the experiments of the present study is shown in Fig. 2. The membrane pilot plant consisted mainly of a 100 L feedstock tank (FT_1) where the pretreated OMW-2 was loaded, and two different pumps – centrifugal booster (P_1) and volumetric piston (P_2) types respectively – that served to drive the effluent to the spiral-wound (SW) membrane module inserted in housing M_1.

Operating pressure and crossflow velocity over the membrane were set independently by means of regulation valves V_1 and V_2 (precision of 0.5 bar and 10 L h^{-1} each), and both variables were also measured and displayed by analogue manometers and a turbine flow meter respectively. Operating temperature and feed flow rate were controlled during the filtration experiments at fixed values equal to ambient conditions