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Research article

Impacts of operating conditions on nanofiltration of secondary-treated two-phase olive mill wastewater

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ABSTRACT

In the present paper, a thin-film composite polymeric nanofiltration (NF) membrane is examined for the tertiary treatment of secondary-treated two-phase olive mill wastewater, in substitution of the reverse osmosis membrane used in previous work by the Authors. Overcoming the deleterious fouling phenomena persistently encountered in membrane processes managing wastewater streams was indeed pursued. Setting the adequate parameters of the operating variables – that is, operating at ambient temperature upon a net pressure equal to 13 bar (P_c), tangential crossflow in the order of 2.55 m s^{-1} to attain enough turbulence over the membrane, and above the point of zero charge ($pH > 5.8$) of the membrane – ensured high steady-state permeate productivity (59.6 L h^{-1} m^{-2}), also economically sustainable in time owed to minimization of the fouling-build up rate (0.91 h^{-1}). Moreover, these conditions also provided high feed recovery (90%) and significant rejection efficiencies for the electroconductivity (58.1%) and organic matter (76.1%). This led to a purified permeate stream exiting the NF membrane operation exhibiting average EC and COD values equal to 1.4 mS cm^{-1} and 45 mg L^{-1}. This permits complying with the water quality parameters established by different regulations for discharge public waterways and irrigation purposes.

1. Introduction

Great efforts have been made in the last years by scientists and engineers with the goal of providing a suitable solution for the management of the effluents by-produced in olive oil mills, commonly known as olive mill wastewater (OMW). However, the complexity, lack of efficiency or uncertain economic viability of the proposals has up to the date impeded their actual transference to the industrial scale.

Various authors have noticed that common biological treatment processes – active sludge – are not effective for the treatment of OMW (Fountoulakis et al., 2002; Garrido Hoyos et al., 2002; Paraskeva and Diamadopoulos, 2006; Taccari and Ciani, 2011), because of the presence in these effluents of a wide variety of refractory organic pollutants -organohalogenated contaminants, organic acids, tannins and phenolic compounds – which are resistant to biological degradation. The wide variety of other standalone or integrated processes developed for the management of OMW comprises lagooning or natural evaporation and thermal concentration (Annesini and Gironi, 1991; Paraskeva and Diamadopoulos, 2006), composting (Papadimitriou et al., 1997), treatments with clay (Al-Malah et al., 2000) or with lime (Aktas et al., 2001), physico-chemical treatments such as coagulation-flocculation (Sarika et al., 2005), electrocoagulation (Tezcan Ün et al., 2006) and biosorption (Hodaifa et al., 2013a), advanced oxidation processes including ozonation (Cañizares et al., 2009), Fenton's reaction (Hodaifa et al., 2013b) and photocatalysis (Sacco et al., 2012), electrochemical treatments (Papastefanakis et al., 2010) and hybrid processes (Grafias et al., 2010; Khoufi et al., 2006).

Direct discharge of these effluents to the environment involves hazardous pollution consequences and impacts to the ecological status: strong odor nuisance to the surroundings, contamination of soil, pollution of water bodies and inhibition of self-purification processes, as well as phytotoxic damage to the aquatic fauna and hindrance of plants growth (Asfi et al., 2012; Danellakis et al., 2011; Karaouzas et al., 2011; Niaounakis and Halvadakis, 2006; Ntougias et al., 2013; Paraskeva and Diamadopoulos, 2006).

Within this scenario, the European Directive 2000/60/CE took the lead to establish the legal framework in order to confer the utmost protection to water, highlighting the use of regenerated wastewater. Currently, direct discharge of OMW to the soil and

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water bodies is prohibited in Spain, whereas in Italy and other European countries it is only allowed the partial discharge on suitable terrains. Moreover, it is well known that the European Environmental Regulations will become more stringent in virtue of the 'H2020 Horizon' (http://ec.europa.eu/research/participants/portal/desktop/en/opportunities/h2020/calls/h2020-waste-2014-one-stage.html).

The main obstacle for the implementation of cost-effective processes for OMW management relies in the fact that olive mills are typically small factories, geographically dispersed. An average-sized olive oil factory normally by-produces around 10–15 m^3 of OMW daily. A centralized treatment of OMW seems not feasible currently, thus an effective and simple solution is needed for these small plants.

In this regard, membrane technology offers compact modular nature, high efficiency and moderate investment and maintenance expenses. Membrane processes are becoming extensively used in numerous applications, as standalone, integrated or substitutive operations. Membrane technology has effectively replaced many conventional processes in the purification of water and groundwater as well as in the reclamation of wastewater streams of very diverse sources, e.g. agro-industrial activities (Agana et al., 2013; Bódalo et al., 2003; Iaquinta et al., 2009; Luo and Ding, 2011; Ochando-Pulido et al., 2012, 2013; Stoller and Bravi, 2010). The availability of new membrane materials, designs, module concepts and know-how has improved its credibility among investors in the recent years.

In former work, a secondary treatment process based on Fenton's reaction was optimized for the reclamation of OMW in an olive oil mill located in Jaén (Spain) working with the modern two-phase olive oil extraction procedure (OMW2) (Martínez Nieto et al., 2011; Hodaifa et al., 2013a,b). The treatment process comprised a final reverse osmosis (RO) tertiary operation for the removal of the dissolved matter, especially the high electroconductivity (EC) values (up to 3.6 mS cm^{-1}), with the goal of obtaining regenerated water for irrigation purposes (Ochando-Pulido et al., 2012).

In the present paper, a thin-film composite (TFC) polymeric nanofiltration (NF) membrane is examined for the tertiary treatment of the secondary-treated OMW2 (OMW2ST), in substitution of the RO membrane previously examined (Ochando-Pulido et al., 2012). The key advantages of novel NF membranes are the higher permeate fluxes upon sensibly lower operating pressures than RO membranes, but still providing specific selectivity towards small solutes, thus permitting important investment and specific energy consumption savings. However, fouling is a deleterious problem common to all membrane processes, especially in case of NF membranes. If of irreversible nature, it reduces the membrane service lifetime drastically. In any case, fouling alters the selectivity of the membrane and depletes its productivity, making the integration of the membrane operation in integrated wastewater treatment processes economically unfeasible (Field and Pearce, 2011; Le-Clech et al., 2006; Stoller et al., 2013).

Scarce is being published up to now about the application of NF in OMW treatment (Garcia-Castello et al., 2010; Stoller, 2011; Zirehpour et al., 2012), but the least focused on two-phase OMW (Ochando-Pulido et al., 2013). Moreover, there is a noticeable lack of deep analysis of NF operating conditions, especially with an insight into the fouling issues that deeply determine the performance and economic viability of membrane processes.

In the present study, the feasibility of the TFC polyamide/polysulfone NF membrane is fully examined in semicontinuous operation, in contrast with common batch membrane operations, for further purification of OMW2ST. Reduction of the significant conductivity and remaining organic matter concentration in OMW2ST with the purpose of obtaining regenerated water with acceptable quality standards according to the Food and Agricultural Organization (FAO) and the Guadalquivir Hydrographical Confederation (Spain) for irrigation purposes was intended. With this goal, the effects of the main operating parameters on the permeate flux and rejection efficiency of the NF membrane, as well as the dynamic fouling build-up, were assessed in a laboratory scale to find the adequate operating conditions.

2. Experimental

2.1. Analytical methods

Analytical grade reagents (99% minimum purity) were used for the analytical proceedings, which were performed in triplicate. Chemical oxygen demand (COD), total suspended solids (TSS), total phenolic compounds (TPh), total iron and carbonates/bicarbonates concentrations (CO_3^{2-}/HCO_3^-), as well as electroconductivity (EC) and pH analysis, were performed following standard methods (Greenberg et al., 2005). 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) (Greenberg et al., 2005). Ionic concentrations were analyzed by means of a Dionex DX-120 ion chromatograph, as thoroughly described in previous research work by the Authors (Ochando-Pulido et al., 2012).

2.2. OMW2ST samples

Samples of OMW2ST were collected after the secondary treatment of OMW2 set-up by the Authors at pilot and industrial scales and thoroughly described in previous work (Martínez Nieto et al., 2011; Hodaifa et al., 2013a,b). The physico-chemical characteristics of the OMW2ST stream are reported in Table 1.

2.3. Bench-scale filtration plant and membrane characteristics

A bench-scale membrane plant (provided by Prozesstechnik GmbH, Basel, Switzerland), shown in Fig. 1, was used for the experiments. The plant was equipped with a non-stirred double-walled tank (maximum volume equal to 5 L) where the effluent (OMW2ST) was contained, and a diaphragm pump (Hydra-Cell model D-03) which allowed to drive the OMW2ST stream to a plate-and-frame membrane module (M1), with dimensions 3.9 cm width × 33.5 cm length.

The main operating variables were measured, displayed and controlled: the operating pressure could be set accurately by means of a spring loaded pressure-regulating valve located in the concentrate stream outlet (SS-R4512MM-SP, Swagelok), and it was also monitored by a digital pressure gauge (Endress + Hauser,

Table 1
Physicochemical characterization of OMW2ST.[a]

Parameter	OMW2ST
pH	7.4 ± 0.3
EC (cm^{-1})	3.4 ± 0.2
TSS (mg L^{-1})	14.5 ± 1.5
COD (mg L^{-1})	188.7 ± 37.9
Total phenolic compounds (mg L^{-1})	0.7 ± 0.3
Total iron (μg L^{-1})	215.0 ± 185.0
HCO_3^- (mg L^{-1})	131.1 ± 1.8
Cl^- (mg L^{-1})	1018.0 ± 27.1
Na^+ (mg L^{-1})	631.4 ± 97.3

[a] OMW2ST: olive mill wastewater after secondary treatment.