Design optimization of a polymeric nanofiltration membrane for olive mill wastewater valorization plus purification

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Abstract
The core of this work was to model and optimize an environmentally friendly nanofiltration (NF) treatment process for two-phase olive mill wastewater (OMW) valorization throughout concentration and recovery of its phenolic fraction and the obtention of a purified permeate stream. A statistical multifactorial analysis was performed to quantify the potential complex conjugated effects of the input parameters. Quality standards to reuse the purified stream in irrigation or in-site discharge were checked. To the author's knowledge, no previous work on the optimization and statistical modelling of membrane processes for OMW purification and valorization can be found up to the present. The optimized data are very relevant for the feasible scale-up of the proposed process, since the NF membrane was highly efficient at ambient temperature conditions and raw effluent pH. A permeate stream that could be reused for irrigation and a retantate stream concentrated in phenols (1315.7 mg/L) was provided.

Keywords: Wastewater reclamation; Membranes; Nanofiltration; Modelling; Olive mill wastewater.

1. Introduction

Membrane technology can be a potential tool for wastewater reclamation. However, fouling is present in the treatment of wastewater streams by membranes and it is imperative to control it to ensure the appropriate operation and design of the plant. Fouling is complex and involves different mechanisms such as pore blocking and plugging, cake, gel and biofilm formation (Field and Pearce, 2011). During operation, fouling leads to an increase in energy costs to maintain the target permeate production, and the operating costs due to frequent plant shut-downs for in-situ membrane cleaning procedures. Inhibition and control of fouling is vital to definitely achieve the competitiveness of membrane technology at industrial scale (Stoller and Ochando, 2016).

Olive oil industrial sector has experienced in the recent decades a great boost. The reclamation of the effluents generated by olive oil industries is a task of global concern, representing an ever-increasing problem still unresolved and not constrained to a specific region anymore. Two-phase continuous centrifugation based processes have been strongly promoted in countries like Spain, Greece, Portugal and now in Italy (Paraskeva and Diamadopoulos, 2006).

The core of the present work was the optimization and modelling of a NF membrane for purification and revalorization of olive mill wastewater (OMW). Statistical multifactorial analysis was performed to examine the impacts of the main variables of the process. Finally, compliance of quality standards for reuse of the purified effluent were checked.

2. Experimental

2.1. Membrane plant

The membrane bench-scale plant (**Fig. 1**) was provided with a jacketed tank (5 L) and a diaphragm pump (Hydra-Cell) to drive the feed to a plate-and-frame membrane module (3.9 x 33.5 cm). The main operating variables were measured and displayed: a constant pressure strategy was adopted. A commercial flat-sheet (200 cm^2) NF membrane (GE Water & Process Tech.) was selected. Tangential-flow NF experiments were run in batch. Full details of the system can be found elsewhere (Ochando-Pulido et al., 2012).

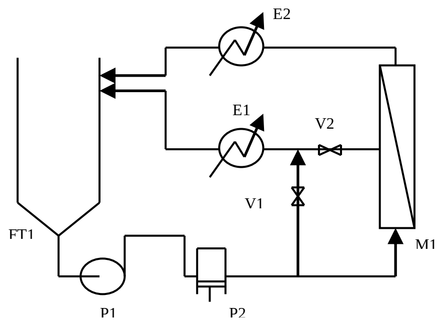

Fig. 1. Flow diagram of the membrane pilot plant.

2.2. Effluent

Raw OMW was collected during winter campaign from olive mills operating with two-phase centrifugation technology (OMW2) in the region of Andalucia, the major olive oil producer world-wide (**Table 1**).

2.3. Physico-chemical analyses

Analyses of chemical oxygen demand (COD), suspended solids (TSS), phenolic compounds, iron, electrical conductivity (EC) and pH were performed following standard methods (Greenberg et al., 2005). A Helios Gamma UV-visible spectrophotometer (Thermo Fisher) was used for COD, total phenols and total iron analyses.

2.4. Optimization and modeling

Statistical impact of the main operating variables - pressure (P), temperature (T), tangential velocity (v_t) and feedstream pH - on the membrane performance in terms of dynamic and steady-state permeate flux (Jp(t) and Jpss, L/hm^2) was examined. Statistical software Statgraphics Centurion XV was used to prepare a design of experiments based on Box-Behnken with four factors.

Table 1: OMW2 physicochemical characterization.

Parameter	Raw
pH	5.0 - 5.2
EC, mS cm^{-1}	1.8 - 2.1
COD, g L^{-1}	13393.0 - 13964.5
Total phenols, mg L^{-1}	749.03 - 775.86

3. Results and Discussion

It was confirmed that all four input variables T, P, v_t and pH present a statistical significance on Jp_{ss} at 95 % confidence level: T and v_t exhibit the highest significance according to the p-values withdrawn from this analysis (p-values → 0), and also the squared effects of T, P and pH (p-values below 0.05) (**Fig. 2**).

Jp_{ss} variation with the operating P presented a convex curve, with a maximum permeate flux above the central point (≈ 0.1), corresponding to 27 bar. At this P the critical permeate flow is reached, and beyond it fouling is promoted (Field and Pearce, 2011; Stoller and Ochando, 2016). Tangential v_t positively affected in almost directly proportional trend to the flux, due to the greater shear effect and drag force caused by the increase in turbulence. The variation of T had practically a linear effect on the increase of the steady-state permeate flux. The effect of the pH presents a concave curve respect to Jp_{ss}. A minimum is observed near the central point corresponding to the pH value of the sample (5.13), this point being very close to the PZC of the membrane (5.97). Durbin-Watson statistic was 2.204 (p-value = 0.689), very close to 2, confirming that the residuals vary randomly and there is no indication of serial autocorrelation among them at 95.0 % confidence level. Also, Lag 1 residual autocorrelation of -0.115, near to zero, means no significant structure unaccounted by the proposed statistical model.

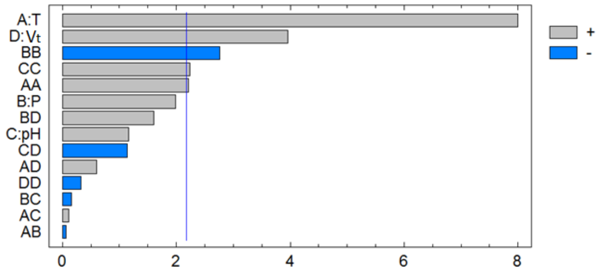

Fig. 2. Standarized Pareto chart.

The optimised parameters for the proposed process were estimated to be 26.5 bar, 32.7 m s^{-1}, 35 º C and pH of 3.7. These conditions ensured a high and stable Jp_{ss} up to 106.2 L $h^{-1}m^{-2}$. This would have an important impact in the proposed NF process for OMW valorization and purification from a cost-efficiency point of view.

4. Conclusions

Optimization of the performance of a NF membrane for purification and valorization of OMW was carried out. The optimised parameters for the proposed process ensured very high and stable flux of the membrane. The obtained optimized data are key for the feasible scale-up of the process in the mills, since the NF membrane was highly efficient at ambient T conditions and raw effluent pH. The effluent may be driven directly from the outlet of the vertical centrifuges at their exiting temperature to the NF membrane, without heating or cooling, enhancing the process cost-efficiency.

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