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Determination of fouling mechanisms in polymeric ultrafiltration membranes using residual brines from table olive storage wastewaters as feed

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In this work, the fouling mechanisms that dominate the ultrafiltration of residual brines from table olive packing plant wastewaters were investigated. For that purpose, Hermia's models adapted to crossflow filtration, resistance-in-series model and a model combining intermediate blocking and cake formation mechanisms were fitted to the experimental data. Tests were performed with a 5 kDa polyethersulfone membrane at transmembrane pressures between 1 and 3 bar and crossflow velocities between 2.2 and 3.7 m s^{-1}. Results demonstrated that the resistance-in-series model was the most accurate to predict permeate flux evolution with time. The predominant fouling mechanism was cake formation followed by intermediate blocking/adsorption. The fouling resistances that were determined by means of the resistance in series model were tested using a well-established mathematical model proposed by Mondal and De that also combines both fouling phenomena (intermediate pore blocking and cake formation). Results demonstrated that the predicted resistances are consistent with those determined by Mondal and De's model.

1. Introduction

Spain is the main producer of table olives with 57,3,500 t $year^{-1}$, which is around 22.1% of the total world production (International Olive Oil Council, 2014). During the production process, large amounts of water are used, generating high volumes of wastewater. Three types of wastewater are obtained: debittering, washing and fermentation brines (Benitez et al., 2003). Fermentation brine wastewater is characterized by an acidic pH (around 4), a high conductivity (80–115 mS cm^{-1}), a high concentration of total suspended solids (0.2–2 g L^{-1}), dissolved chemical oxygen demand (COD: 10–35 g $O_2 \cdot L^{-1}$) and phenolic compounds (4.0–6.0 g of tannic acid L^{-1}) (Garrido Fernández et al., 1997). Ultrafiltration (UF) is one of the most used techniques in industry to: concentrate, separate or purify macromolecules, colloids and suspended particles from liquid streams (Wang and Song, 1999; Barredo-Damas et al., 2012). In this work, UF is considered to remove suspended particles and macromolecules from residual brines from table olive production plants. A subsequent nanofiltration (NF) step could be performed to recover the phenolic compounds.

Currently there are many studies focused on membrane treatment of wastewaters from olive oil production, such as, olive mill wastewater (OMW) residue from a three-phase production method and alperujo residue from a two-phase production method. These residues have a high chemical oxygen demand and a high phenolic compound concentration, but unlike fermentation brine, its conductivity is much lower (between 4.00 and 13.98 mS cm^{-1} for OMW and 0.88–4.76 mS cm^{-1} for alperujo) (Paredes et al., 1999; Alburquerque et al., 2004). Nanofiltration (NF) processes have been considered by most of the authors to recover and concentrate high added value compounds from olive oil production wastewaters. In order to improve the performance of the NF process, a pretreatment with UF has also been proposed (Galanakis et al., 2010; Paraskeva et al., 2007). However, the number of studies on the

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treatment of fermentation brine wastewater by membrane technology is very limited. Nowadays, the technologies that have shown more favorable results for recovering desirable compounds from the brines have been membrane processes. This can be combined with adsorption processes using active carbon or ion exchange resins (Bódalo et al., 2008). The rejection of total suspended solids, dissolved COD and phenolic compounds in UF process treating olive mill wastewater (OMW) and table olive wastewaters was investigated by El-Abbassi (El-Abbassi et al., 2014).

Membrane fouling is one of the major problems of UF processes, reducing the permeate flux and decreasing its economic and technological viability (Cheryan and Alvarez, 1995). During an UF process where fouling occurs, the initial permeate flux shows a sharp decline which is followed by a long and gradual flux decline over time (Field et al., 1995). Therefore, the study of the evolution of permeate flux over time during UF is an important factor to be considered when selecting the optimum operating conditions (Vincent-Vela et al., 2010). In order to predict the UF membrane fouling and its performance, mathematical models have been developed by several authors. In literature, empirical and theoretical models that describe the permeate flux decline, with time in UF, can be found. Empirical models provide high precision, but they cannot satisfactorily explain the fouling mechanisms involved in membrane filtration. Theoretical models can help to better understand the phenomenon of fouling, but if experimental data is not used to estimate some of the parameters their predictions are not very precise. Thus, semi-empirical models whose parameters have a physical meaning are usually preferred to explain the fouling phenomena that takes place in membrane processes and to achieve an accurate prediction of permeate flux decline (Vincent Vela et al., 2009; Mah et al., 2012). Depending on the fouling mechanism, four situations may be described: (a) if the solute particle size is higher than the membrane pore; particles are deposited on the surface of the membrane blocking the entrances of the pores completely; (b) if solute particle and membrane pores size are similar, some membrane pores can be partially blocked; (c) if solute particle size is smaller than membrane pores, inside pores of membrane can be blocked and irreversible fouling may appear; (d) sometimes the fouling layer deposited on the membrane surface may form a cake layer (Ruby Figueroa et al., 2011; Corbatón-Báguena et al., 2013).

Among the different theoretical models available in the literature to determine fouling mechanisms, one of the most widely used is the one developed by Ho and Zydney (Ho and Zydney, 2000). The general equation of this model accounts for the combination of pore blockage and cake formation without time division of the permeate flux curve. The authors fitted the model to the BSA microfiltration experimental data. Based on the Ho and Zydney's model, recent works have used their mathematical assumptions to fit the experimental data of different UF processes and also, modify the original model (Muthukumaran et al., 2005; Peng and Tremblay, 2008; Karasu et al., 2010; Corbatón-Báguena et al., 2013; Liu et al., 2014; Tien et al., 2014; Astaree et al., 2015). For instance, Astaree et al. studied membrane fouling mechanisms caused by BSA, dextran and humic acid solutions by fitting the model proposed by Ho and Zydney and modifying it to consider the hydrophilic nature of the membranes used and the pre-filtration effect of the foulant deposit layer. With these two new factors, they demonstrated that better agreements were obtained in comparison to the original mathematical model (Astaree et al., 2015). On the other hand, Tien et al. used the experimental data presented by Ho and Zydney to validate their new rational model, which was based on the deep bed filtration theories and the equations for particle retention within membrane media. Their model was able to predict the experimental data provided by Ho and Zydney and its general equation was simpler than the original one (Tien et al., 2014).

In the same way as Ho and Zydney, some other authors combined two different fouling mechanisms providing a model with strong theoretical background. For instance, Mondal and De published two different articles which describe in detail a generalized model for steady state continuous filtration (Mondal and De, 2009, 2010). The proposed model resulted from the combination of two different fouling mechanisms: on their first article, Mondal and De took into account the resistance due to complete pore blocking and that related to the formation of a cake on the membrane surface (Mondal and De, 2009); while the second article combined the resistances due to intermediate pore blocking and cake formation mechanisms (Mondal and De, 2010). In addition, Bolton et al. developed five new models based on the four classical fouling mechanisms (standard blocking, complete and intermediate blocking and cake formation mechanisms) and the Darcy's law for both constant pressure and constant flow operation modes (Bolton et al., 2006). Their theoretical hypotheses resulted in general equations with two fitting parameters that were much simpler than those taken as references by the authors. Their results also demonstrated that the new models predicted with good accuracy the experimental data. Using the equations developed by Bolton et al., other authors, such as Rezaei et al., fitted those general equations for the combined models to the experimental data obtained during whey crossflow microfiltration (Rezaei et al., 2011). They also compared the fitting accuracies of the combined models with the classical ones that account only for one fouling mechanism at a time. Their results demonstrated that the combined models were able to better predict the permeate flux decline at low time scales, but classical models provided higher accuracies at those experimental conditions where cake resistance was the predominant fouling mechanism.

Although there are several mathematical models available in the literature to determine fouling mechanisms, Hermia's models and their adaptations to crossflow filtration as well as resistance-in-series models are the most accepted. These have also been used to predict permeate flux decline, with time, by other authors (Carrère et al., 2001; Turano et al., 2002; Vincent Vela et al., 2009). Vincent Vela et al. (2009) fitted the Hermia's models adapted to crossflow to the experimental data of permeate flux versus time obtained during the UF of polyethylene glycol solutions. They demonstrated that at high transmembrane pressures and low crossflow velocities, the intermediate blocking was the predominant fouling mechanism. Corbatón-Báguena et al. (2015a) fitted different models to the experimental data obtained during the UF of whey model solutions. They reported that the combination of complete blocking and cake formation mechanisms resulted in more accurate predictions of the permeate flux decline. Carrère et al. (2001) proposed a resistance-in-series model that considered the membrane resistance, the cake resistance and the adsorption and concentration polarization resistance. This was done to estimate permeate flux decline in the crossflow microfiltration of lactic acid fermentation broths. They reported that the adsorption and concentration polarization resistances dominated the filtration process. Turano et al. (2002) also interpreted the experimental data of permeate flux variation with the time obtained during the UF of olive mill wastewaters by using a resistance-in-series model. They indicated that higher values of turbulence and thus higher crossflow velocities resulted in lower values of specific cake resistance.

In this work, the effect of transmembrane pressure (TMP) and crossflow velocity (CFV) on flux decline when UF was used to treat residual brine from a table olives packing plant (TOPP) was investigated. The samples were previously filtered through a 60 μm cartridge filter. In order to understand the predominant fouling