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Ultrafiltration of residual fermentation brines from the production of table olives at different operating conditions

Carlos Carbonell-Alcaina [a, *], Silvia Álvarez-Blanco [a, b], María Amparo Bes-Piá [a, b], José Antonio Mendoza-Roca [a, b], Laura Pastor-Alcañiz [c]

[a] Research Institute for Industrial, Radiophysical and Environmental Safety (ISIRYM), Universitat Politècnica de València, C/Camino de Vera s/n, 46022 Valencia, Spain
[b] Department of Chemical and Nuclear Engineering, Universitat Politècnica de València, C/Camino de Vera s/n, 46022 Valencia, Spain
[c] Depuración de Aguas del Mediterráneo (DAM), Avda. Benjamin Franklin, 21, Parque Tecnológico, 46980 Paterna, Valencia, Spain

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ABSTRACT

The membrane process of ultrafiltration (UF) has been investigated as a pretreatment previous to the further recovery and concentration of phenolic compounds from residual table olives fermentation brines. Two UF membranes were tested: a permanently hydrophilic polyethersulfone (PES) membrane with a molecular weight cut-off (MWCO) of 30 kDa and a PES membrane with a MWCO of 5 kDa. Transmembrane pressure and crossflow velocity were varied from 1 to 3 bar and from 2.2 to 3.7 m s^{-1}, respectively. The best membrane in terms of permeate flux and selectivity was that with MWCO of 5 kDa and the best operating conditions were transmembrane pressure of 3 bar and crossflow velocity of 2.2 m s^{-1}. In these conditions permeate flux was 21.6 L $h^{-1} \cdot m^{-2}$, while the rejection of COD and phenolic compounds were 50.0% and 21.9%, respectively and the removal of colour and turbidity was almost complete. In addition, an alkaline cleaning protocol was proposed, which was effective to restore the initial permeability of the selected membrane.

1. Introduction

In the last years, there has been a growing interest in obtaining high added value compounds from renewable raw materials and wastes. Some of these compounds have a potential use in food, cosmetic and pharmaceutical industries. Among these compounds, those with antioxidant properties have generated great interest. These compounds, which are abundant in the Mediterranean diet in the form of vitamins C and E, carotenoids and phenolic compounds, have beneficial effects on human health (Sánchez-Moreno et al., 2006) (Zulueta et al., 2007) (Guedes et al., 2011).

Phenolic compounds are present especially in fruits and vegetables. Olive fruit, which is one of the bases of the Mediterranean diet, contains a great quantity of these compounds. The production of olive fruits amounted to 5700 tonnes in the 2014/2015 crop season (International Olive Council, 2015). Olive fruits can be processed to obtain olive oil or treated to be consumed directly as table olives. The number of olive fruits dedicated to the production of olive oil has always been higher than those used to prepare table olives. However, in recent years, such numbers are tending to equalize. The total world production of table olives in 2014 was close to 2600 tonnes. Approximately, 85% of the production takes place in the Mediterranean area, being Spain in 2014 the major producer (around 22.1% of the world production), followed by Turkey and Egypt (around 16.6% and 15.4% of the world production, respectively) (International Olive Council, 2015). According to the Spanish Ministry of Environment, it is estimated that 1.5 kg of wastewater are generated per each kilogram of table olives produced in Spain.

To be consumed as table olives, the olive fruits must be processed to reduce their bitterness. Three types of wastewater streams are mainly generated from this process, which consists of three steps: lye treatment with NaOH, lye washing and olive fermentation in brine (Sánchez Gómez et al., 2006). Each of these three steps approximately generates the same volume of wastewater. According to the Spanish Ministry of Environment, in Spain, per each kilogram of table olive produced, 0.5 kg of fermentation brine wastewater is obtained. This is the wastewater that has been considered to carry out this work. During the fermentation in brine,

* Corresponding author.
E-mail address: carcaral@upvnet.upv.es (C. Carbonell-Alcaina).

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the lactic fermentation of the olives occurs, thus reducing the basic pH of the solution to a pH of about 4. The fermentation of sugars is almost complete. In this process, part of the phenolic compounds from the olive fruits (mainly oleuropein) solubilises into the acid solution (Soler-Rivas et al., 2000). In this solution, most of the phenolic compounds disappeared, while the concentration of hydroxytyrosol and tyrosol increased (Brenes et al., 1995). This is due to the hydrolysis of the phenolic compounds like oleuropein, as an example, that hydrolyzed into hydroxytyrosol (Brenes et al., 1995).

Apart from the acid pH, the fermentation brine wastewater is also characterized by a high salt concentration (conductivity from 80 to 95 mS cm^{-1}) and high soluble chemical oxygen demand (COD), of 15000–30000 $mgO_2 \cdot L^{-1}$. Part of this organic matter corresponds to the phenolic compounds (these concentration varying from 1000 to 2000 mg of tyrosol equivalents$\cdot L^{-1}$) (García-García et al., 2011) (Ferrer-Polonio et al., 2014). The main phenolic compounds present in olive brine are hydroxytyrosol (HTY) and tyrosol (TY) and they show an outstanding antioxidant activity (Brenes et al., 1995) (Fendri et al., 2013). Nevertheless, the presence of these compounds in the wastewater represents one of the major problems for its treatment, primarily because they are hardly biodegradable and secondly because of their significant antimicrobial activity, which reduces the efficiency of the biological processes in wastewater treatment plants (WWTP) (Parinos et al., 2007). Besides, the high salt concentration can also have a negatively impact on the WWTP process as it causes activated sludge deflocculation (Woolard and Irvine, 1994) (Kargì and Dinçer, 1999) (Reid et al., 2006) (Lefebvre and Moletta, 2006). On the other hand, if the organic matter and phenolic compounds are removed, the brine can be reused in the table olive fermentation process. In this perspective, the recovered phenolic compounds, due to their potential antioxidant properties, are an attractive ingredient for the food, cosmetic and pharmaceutical industries (Tripoli et al., 2005).

It is therefore of a great interest the recovery of these valuable compounds from the waste streams from fruits and vegetables processing. Historically, the treatment of the olive brine waste water has been based on the reduction or elimination of the organic matter with the aim of its reuse in later stages of the processing, as in the packaging stage. To this end, the treatments that have been considered were ultrafiltration (UF) (Brenes et al., 1990), UF and active carbon (Garrido et al., 1992), biological treatment (Brenes et al., 2000) (Ferrer-Polonio et al., 2015), advanced oxidation (Rivas et al., 2003) and electro-coagulation (García-García et al., 2011).

Nevertheless, in the literature, there are some works dealing with the recovery of phenolic compounds from olive mill wastewater (OMW), generated during olive oil production. In some of these studies, membrane process have been proposed by several authors (Garcia-Castello et al., 2010) (Cassano et al., 2013) (Zirehpour et al., 2015). These works have shown that the combined utilization of ultrafiltration and nanofiltration (NF) processes for treating OMW is more effective than performing the separation in one single step (Paraskeva et al., 2007) (Garcia-Castello et al., 2010) (Cassano et al., 2013). In these combined processes, UF was applied as pretreatment for COD removal, as this membrane process is not able to separate low-molecular-weight compounds. Then, the UF permeate was treated by NF in order to obtain a permeate rich in phenolic compounds (Cassano et al., 2013). Also, reverse osmosis, osmotic distillation and vacuum membrane distillation were used to concentrate the phenolic compounds from the NF permeate (Paraskeva et al., 2007) (Coskun et al., 2010) (Zagklis et al., 2015) (Garcia-Castello et al., 2010). In these works, it was observed that the ultrafiltration membranes suffered severe fouling, whereas the fouling of the NF membranes was largely reduced when UF was used as pretreatment.

In spite of the number of works aimed to the recovery of the phenolic compounds from OMW, up to now there are very few studies in the literature where the phenolic compounds are recovered from wastewaters resulting from table olive production. El-Abbassi et al., 2014, used UF as a pretreatment for a subsequent extraction process of phenolic compounds from table olive production wastewaters (El-Abbassi et al., 2014). They used a magnetically stirred unit and compared the results obtained at different pH values. The best results in terms of decolorization and COD removal were obtained at acidic pH values. Kiai et al., 2014, considered membrane distillation technology in the treatment of table olive wastewaters for the concentration of phenolic compounds and to obtain high quality water (Kiai et al., 2014).

In this work, membrane processes were used to recover phenolic compounds from the fermentation brine wastewater generated during Spanish-style green table olive processing. For this purpose, an integrated process that combines UF and NF was proposed. This work investigates the UF step as a pretreatment prior to the NF step. Two flat sheet UF membranes and different operating conditions were compared with the objective of reducing the presence of a great amount of total suspended solids (TSS) and soluble COD. Then, the UF permeate would be processed by NF in order to obtain a permeate stream enriched in phenolic compounds, with a low content of soluble COD. Therefore, the UF membrane should show a low rejection of phenolic compounds. In this work, the capability of the UF process to remove TSS and soluble COD with less phenolic compounds rejection from table olive wastewaters has been investigated in order to improve the performance of the subsequent NF process. Therefore, according to this objective, the operating conditions that maximize the phenolic compounds/COD ratio have been sought.

2. Material and methods

2.1. Feed samples

In the present work, different real samples of residual table olive fermentation brine were supplied by a table olive packing plant in Valencia region (Spain). Due to the high content of suspended solids observed in the residual wastewater, a previous filtration step with a polyester cartridge filter of 60 μm pore size (CA-0202-00, model GT, HydroWater, Spain) was performed. The samples were stored at 5 °C.

2.2. Analytical methods

Regarding the analytical methods considered, each parameter was measured in triplicate and the average value was calculated.

The conductivity and the pH were measured with an EC-Meter GLP 31 + conductimeter and a GLP 21+ pH-meter (Crison, Spain), respectively, at room temperature (25 °C). Turbidity was measured with a turbidimeter (D-112, DINKO, Spain) following the UNE-EN ISO 7027 standard method. The colour of the samples was determined from absorbance readings at 440 and 700 nm using a DR600 spectrophotometer (Hach Lange, Germany). The colour value was calculated as the difference between the two absorbance readings in 1 cm pathlength cells as described by (De Castro and Brenes, 2001).

The amount of TSS was determined from 25 mL samples by means of glass microfiber filters (1.2 μm pore size), according to UNE 77034 standard method. After the filtration of the samples, the microfiber filters were dried at 105 °C for 2 h. The amount of TSS corresponded to the difference between the initial weight of the filter and its weight after being dried.