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Research article

Novel micro/ultra/nanocentrifugation membrane process assessment for revalorization and reclamation of agricultural wastewater

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ABSTRACT

The concentration and recovery of the high-added value phenolic fraction from two-phase olive mill wastewater and the simultaneous effluent treatment by a novel micro/ultra/nanocentrifugation membrane process assessment is addressed, permitting to gather information for a correct and effective screening procedure for the adequate membrane election (MF-UF-loose NF) for the target. Phenolic compounds are the major factor of phytotoxicity of these effluents, but on the other hand they present high antioxidant properties that makes them very relevant for food, cosmetic, pharmaceutical and biotechnological industries. The selection of a membrane MWCO between 100 kDa and 0.45 μm permitted the complete transfer of the phenolic fraction to the permeate, whereas below 3 kDa they would be transferred to the concentrate stream instead, with ~60% COD reduction and EC lowered to 551–662 μS cm^{-1} in the final treated stream ensured, sensibly improving the effluent quality. This would provide a purified effluent with good salinity standards according to the indications given by the FAO for irrigation reuse. This procedure could be quick and reliable for the assessment of the adequate membrane needed for a particular purification process, in contrast with long-term, time consuming common bench-scale procedures.

1. Introduction

Agro-industrial wastewater is a problem increasingly affecting the current availability of water resources worldwide, which are becoming insufficient to satisfy the rising demand of fresh water. This specially concerns agricultural irrigation, which copes with more than three quarters of the total water consumption worldwide (International Olive Oil Council, 2015). The intensive and unsustainable development of industry is causing deterioration of the environmental quality.

One solution in this scenario is the use of regenerated wastewater for irrigation purposes, which could be very positive environmentally, as well as result in economic return. Moreover, industrial effluents are being subjected to increasingly tougher environmental regulations, especially in European countries (https://ec.europa.eu/prog, 2020). Hence, the adequate management of the by-produced effluents in industries is becoming a key task to be accounted for.

In that regard, the treatment of agro-industrial wastewater is an issue that has joined much research effort in the last years. However, the medium to low size of these industries and their dispersity in most cases poses a handicap for the cost-efficient management of their effluents. This is the case of olive mill wastewater (OMW), a deleterious effluent generated during the production process of olive oil in small and geographically dispersed factories called mills (Niaounakis and Halvadakis, 2006). Olive oil, a product that has withdrawn much interest in the market in the last years owed to its nutritional, antioxidant and health-promoting properties, is obtained throughout a process based on physical operations, without implication of chemicals. In this line, this industry is committed to meet the conditions to make the whole production process environmentally friendly, and this comprises the treatment of the residual effluents by-produced (Paraskeva and Diamadopoulos, 2006). Moreover, the important growth of this agro-industry, ancestrally circumscribed in the Mediterranean Basin but now in expansion to very different regions in Europe, Australia, the USA, the middle East and China, is rendering the management of these effluents a task of global concern (International Olive Oil Council, 2015).

A feasible solution for the treatment of OMW is urgent: 10–15 m^3 of OMW are generated daily in average-sized olive mills, which implies the by-production of millions of cubic meters of these phytotoxic effluents yearly and the equivalent potable water consumption (Paraskeva and Diamadopoulos, 2006). A plethora of technologies can be found in the scientific literature addressing the problem of OMW treatment. However, conventional methods imply a series of drawbacks and limitations such as high cost and energy consumption, complicated treatment processes, and secondary pollution. Most processes proposed

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up to the moment for the treatment of OMW are rather cost-inefficient, and olive oil industry, in its present status, cannot assume those costs (Paraskeva and Diamadopoulos, 2006; Ochando-Pulido et al., 2017a; Hodaifa et al., 2013). Among them, advanced oxidation processes comprising the use of novel nanoparticles (Ochando-Pulido et al., 2017a; Hodaifa et al., 2013; Vilardi et al., 2017; Vilardi and Di Palma, 2017), tailored biological treatments (Sampaio et al., 2011; Di Palma et al., 2003; Stoller et al., 2010) and membrane technologies (Ochando-Pulido and Martinez-Ferez, 2012; Cassano et al., 2011; Di Lecce et al., 2014; Garcia-Castello et al., 2010; Ochando-Pulido et al., 2013; Stoller, 2011) seem the most promising solutions.

In this situation, a change of paradigm regarding the economy is being currently experienced, implying that the linear vision is now being replaced by a circular vision, where waste is regarded as a potential resource to be reintroduced in the production cycle. Agro-food production chain is one of the main waste producers.

In this line, OMW has been highlighted as an important potential source of natural antioxidants, mainly by virtue of its rich content in polyphenolic compounds (Obied et al., 2005; Boskou, 2006), which exhibit excellent antioxidant, radical scavenging, antimicrobial and anticarcinogenic properties (Boskou, 2006). However, the vast majority of the processes proposed in the last years aimed for the abatement of the phenolic fraction, which is otherwise the main responsible of the highly phytotoxic and recalcitrant characteristics of these effluents (Paraskeva and Diamadopoulos, 2006; Ochando-Pulido et al., 2017a; Hodaifa et al., 2013; Sampaio et al., 2011). Nevertheless, the recovery of this fraction from OMW can provide not only economic profit but specifically make OMW less toxic and thus easier to be ulteriorly treated, promoting the overall sustainability of OMW management.

Among recent separation and purification technologies effectively transferable at industrial scale, membranes offer a series of advantages if compared to classic separation techniques, mainly the facts that they are modular, compact and less energy-intensive, and capable to offer high separation standards (Ochando-Pulido and Martinez-Ferez, 2012; Cassano et al., 2011; Di Lecce et al., 2014; Garcia-Castello et al., 2010; Ochando-Pulido et al., 2013; Stoller, 2011). This has promoted the use of membrane technologies for the recovery of antioxidants from OMW (Russo, 2007; Zagklis et al., 2015; Conidi et al., 2014; Bazzarelli et al., 2016; Abdel-Shafy et al., 2015; Janangiri et al., 2016; Ochando-Pulido et al., 2017b).

In this work, the concentration and recovery of high-added value compounds (polyphenolic fraction) from two-phase OMW and the simultaneous treatment of the effluent by a novel micro/ultra/nanocentrifugation membrane process assessment is proposed, aimed to gather information for a correct, effective and reliable screening procedure for the election of the adequate membrane (MF-UF-loose NF) for the target purpose, sensibly quicker than bench-scale membrane experiments. The minor specific energy consumption (SEC) of membranes, if compared with conventional separation processes, have paved the way for their implementation at industrial scale facilities in multiple applications, and particularly as tertiary treatments in wastewater plants (Ochando-Pulido and Martinez-Ferez, 2012; Cassano et al., 2011; Di Lecce et al., 2014; Garcia-Castello et al., 2010; Ochando-Pulido et al., 2013; Stoller, 2011). Membrane processes can be technically and economically efficient if the productivity (flux) is enhanced and fouling is strongly inhibited. Moreover, given that the product, that is, purified water, is not a priori of high added value, the recovery of added-value compounds can counter-balance the economic feasibility of the effluent reclamation process. In this regard, the selection of the adequate membrane upon the proposed procedure also puts a focus on membrane fouling. To the authors' knowledge, the combination of membrane filtration and centrifugation is a novel methodology not yet investigated until now for purification and revalorization of these agro-industrial effluents, targeted to membrane treatment screening for recovery of added-value compounds.

2. Experimental

2.1. The effluent stream: olive mill wastewater

Samples of OMW were collected from various olive oil mills in the Andalusian provinces of Jaén and Granada (Spain), operating with the most up-to-date two-phase olive oil production technology (hereafter referred as OMW2). The raw OMW2 was taken directly from the vertical centrifuges in-situ during the production process of olive oil.

After gathering, the raw OMW2 was readily used for the experiments, with the intention to use the effluent as fresh as it is by-produced, to avoid modifying its natural characteristics. On another hand, samples of the raw effluent were kept well refrigerated (- 5 °C) to maintain them in good condition for further research experiments. The main physico-chemical characteristics of the raw OMW2 are hereafter reported in the experimental results section.

2.2. Assessment of MF-UF-loose NF membranes

The equipment used for the micro/ultra/nanocentrifugation membrane process assessment, comprised a vertical centrifuge (Thermo Fischer Scientific, Sorval ST40 series), Falcon tubes (50 mL) provided with membranes of molecular weight cut-off (MWCO) ranging from 3 to 100 kDa, nitrate cellulose filters (111306-047N Sartorius, 47 mm diameter, Ø, and 0.45 μm mean pore size, D_p), a volumetric flask and a diaphragm pump for vacuum, as well as a precision electronic mass balance (AX -120 Cobos, 0.1 mg accuracy).

The characteristics of the used membranes, purchased from Merck Millipore, are reported in Table 1.

The proposed micro/ultra/nanocentrifugation membrane process aimed to gather information for a correct, effective and reliable screening procedure for the election of the adequate membrane (MF-UF-loose NF) for the target purpose, sensibly quicker than bench-scale membrane experiments (Ochando-Pulido et al., 2013).

The procedure performed consisted, first, in filtering 200 mL OMW2 samples through the 0.45 μm nitrate cellulose filters. After this, 15 mL of the filtered samples were poured into Falcon tubes provided with membranes of different mean pore diameters (MWCO ranging from 100 to 3 kDa: 100, 50, 30, 10 and 3 kDa). The micro/ultra/nanocentrifugation membrane system is shown in Fig. 1. Subsequently, the Falcon tubes were centrifuged at 4000 rpm for 3 min. After this procedure, the permeate and concentrate volumes were taken from the Falcons and weighed on the precision electronic mass balance. The sequence was performed in triplicate.

Then, samples of permeate and concentrate collected were taken at the end of operation for final and readily analysis, comprising the total polyphenolic fraction (TPhs) concentration, COD, electroconductivity (EC) and pH of all permeate and concentrated volumes of the centrifuged-filtered samples. The observed rejection efficiencies (R_i, %) were calculated with the following expression:

$$R_i(\%) = \left(1 - \frac{C_{p,i}}{C_{f,i}}\right) x\ 100 \quad (1)$$

where $c_{p,i}$ is the concentration of the solute i (mg L^{-1}) in the permeate,

Table 1
Specifications of the used membranes.

Feature	Parametric value
Membrane type	MF-UF-loose NF
Provider	Millipore
Model	Amicon Ultra-15
Material	Regenerated cellulose
MWCO, kDa	3 - 10–30 - 50 - 100

* MWCO: molecular weight cut off.