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Treatment of table olive processing wastewaters using novel photomodified ultrafiltration membranes as first step for recovering phenolic compounds

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HIGHLIGHTS

- UF process is a useful tool for reducing colour and organic load from TOPW.
- UV modification was performed to enhance fouling-resistant membrane capability.
- FTIR-ATR and water contact angle were measured to ensure the modification process.
- Effect of PEG and Al_2O_3 on membrane performance was investigated.
- Membranes modified with Al_2O_3 reduced the phenolic content in the concentrate stream.

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ABSTRACT

Table olive processing wastewaters (TOPW) have high salt concentration and total phenolic content (TPC) causing many environmental problems. To reduce them, ultrafiltration (UF) was applied for treating TOPW. However, NaCl, which is the main responsible of salinity in TOPW, and phenols are small molecules that cannot be separated by conventional UF membranes. They have serious problems caused by fouling, which can be overcome using membrane modification techniques. For these reasons, photomodification may be an effective technique to obtain a stream rich in TPC due to the changes in membrane surface properties. UV-modification in the presence of two hydrophilic compounds (polyethylene glycol and aluminium oxide) was performed to achieve membranes with high reductions of organic matter and to keep the TPC as high as possible. Commercial polyethersulfone (PES) membranes of 30 kDa were used. Surface modification was evaluated using FTIR-ATR spectroscopy and membrane performance was studied by calculating the rejection ratios of colour, chemical oxygen demand (COD) and TPC. Results demonstrated that UF is a useful pre-treatment to reduce organic matter from TOPW, obtaining a permeate rich in TPC. PES/Al_2O_3 membranes displayed superior antifouling properties and rejection values, keeping high the TPC (>95%). Therefore, UF using modified membranes is an appropriate and sustainable technique for treating TOPW.

1. Introduction

Obtaining high-added value compounds from food wastewater is based on five distinct recovery stages so-called "Universal Recovery Processing", which progress from a macroscopic pretreatment, a separation process of macro and micromolecules, followed by an extraction process and further purification treatment, and finally, the formation of the target high-added value product. In the second stage, membrane processes are one of the

Abbreviations: ATR, attenuated total reflectance; COD, chemical oxygen demand; FTIR-ATR, Fourier transform IR spectroscopy with attenuated total reflectance; MWCO, molecular weight cut-off; NF, nanofiltration; OMW, olive mill wastewater; PCs, phenolic compounds; PEG, polyethylene glycol; PES, polyethersulfone; TOPW, table olive processing wastewater; TPC, total phenolic content; UF, ultrafiltration; UV, ultraviolet.

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Nomenclature

List of symbols

A_{440}	Absorbance at 440 nm (dimensionless)
A_{700}	Absorbance at 700 nm (dimensionless)
C_f	PCs concentration in the feed stream (mg of tyrosol/L)
COD_f	COD concentration in the feed stream (g of O_2/L)
COD_p	COD concentration in the permeate stream (g of O_2/L)
C_P	PCs concentration in the permeate stream (mg of tyrosol/L)
DC	Decolourisation rate (%)
FD	Fouling degree (%)
FRR	Flux recovery ratio (%)
J_0	Pure water flux at the end of compaction test (L/m^2 h)
J_f	Permeate flux during wastewater ultrafiltration (L/m^2 h)
J_{f1}	Permeate flux obtained at the beginning of wastewater ultrafiltration (L/m^2 h)
J_{f2}	Permeate flux at the end of wastewater ultrafiltration (L/m^2 h)
J_W	Permeate water flux during rinsing process (L/m^2 h)
OD_f	Feed optical density (dimensionless)
OD_p	Permeate optical density (dimensionless)
R_{COD}	Rejection rate of COD (%)
RFR	Relative flux ratio (%)
R_{TPC}	Rejection rate of total PCs (%)
t	Operating time (h)
T	Operating temperature (°C)
ΔP	Transmembrane pressure (MPa)

most widely used techniques to separate macromolecules from food wastewater, especially ultrafiltration (UF). Depending on the nature of the feed solution and the target compounds, permeate or concentrate stream is recovered or rejected. Amongst the several target compounds, the most common are pectins, proteins, lactose, and phenolic compounds [1,2].

Phenolic compounds (PCs) are the most abundant antioxidants in the Mediterranean diet and they play a crucial role in human health and nutrition due to their behaviour as preventative agents against several diseases and oxidative stress [3]. As a natural resource to obtain PCs, the olive fruit and the study of traditional industrial processes used for producing olive oil as well as for preparing table olives are acquiring more and more importance over the years, principally in studies developed in Mediterranean countries (such as Spain, Tunisia, Turkey, Italy and Greece). Some researchers focused their studies on the physiological benefits of PCs due to their important biological properties (such as antioxidant, antimutagenic, anticarciogenic and antiglycemic properties) [4–6], whereas other researchers tried to remove them partially or completely to obtain a palatable final product because PCs can be embittering [7,8].

Olive mill wastewater (OMW) is the most common source to obtain PCs from olive oil. These wastewaters arises from the production of olive oil in olive mills and they are considered one of the most polluting effluents produced by agro-food industry, where their high concentration of organic matter and nutrients (especially reduced sugars and PCs) have adverse effects on the environment such as the inhibition of plant seed germination or the stimulation of microbial respiration [9,10]. Many researchers have studied OMW treatment using UF membranes in order to obtain a stream rich in PCs. Cassano et al. compared the performance of two UF membranes made of polyethersulfone (PES) and regenerated cellulose, where those made by the last material showed good results with a high PCs concentration in the permeate stream [11]. According to Yahiaoui et al. UF membranes are also useful to satisfactorily remove chemical oxygen demand (COD) from OMW in both ways, as an isolated process and as a pre-treatment for other processes such as an electrochemical reactor [12].

Generally, UF process cannot separate low-molecular-weight compounds from water as efficiently as nanofiltration (NF) and reverse osmosis. For this reason, other authors have investigated the application of combined membrane processes for treating OMW. In this way, several papers found in the literature [11,13–15] deal with combining these techniques to achieve COD removal values of about 20–47% and total phenolic content (TPC) recovery values of about 45–70% only in the UF process and 60–80% and 90–95%, respectively, in the combined process (UF and NF). Better separations of TPC may be achieved with the incorporation of reverse osmosis processes [16].

In our case, we study the residual brines from table olive processing or table olive processing wastewaters (TOPW), which are less studied than OMW and they consist of high salt concentrations (sodium chloride and sodium hydroxide), PCs (which affects some properties of the final marketable product such as taste, colour and texture [17]), sugars, acids, tannins, pectins, carotenoids, oil residues and trace amounts of various metals. Due to their high organic content and high concentrations of salt and PCs, these wastewaters show antimicrobial, exotoxic and phytotoxic properties [18,19]. During their discharge to water, TOPW heavily pollute the urban wastewaters, streams and rivers to which they join. Therefore, the treatment of this type of wastewater makes them into an important environmental concern. Amongst all the aforementioned compounds present in TOPW, PCs are powerful organic pollutants and their presence in the environment must be controlled. Thus, it would be very interesting to remove them from TOPW to obtain high-value products, especially hydroxytyrosol and tyrosol, which have a high antioxidant activity [3].

Several technologies based on biological, chemical oxidation and separation processes have been used for treating TOPW by different research groups. Chatzisymeon et al. applied heterogeneous photocatalytic treatments to an effluent from TOPW by which they obtained good efficiencies in decolourisation (>90%) and phenols [19]. Katsoni et al. used wet-air oxidation process for treating TOPWs, obtaining more than 90% of phenol degradation and decolourisation [20]. El-Abbassi et al. studied the application of UF process on both OMWs and TOPWs and they demonstrated that such process can be efficient in recovering PCs (~40%), mainly in acidic wastewaters [21].

This paper deals with the study of the effect and performance of different modified UF membranes that might be used to obtain a stream rich in PCs from TOPW and a stream poor in these compounds with less dangerousness. The aims of this work were to separate high-molecular-weight organic compounds from TOPW with high TPC using UF process as clean technology (with easy and rapid operation) due to the high-added value of PCs in other industries (such as cosmetics, pharmaceuticals and chemical processing); and to reduce the fouling suffered by these membranes and the volume and dangerousness of TOPW generated. Membranes were modified by ultraviolet (UV) irradiating their surface in the presence of two additives from different nature: polyethylene glycol (PEG) of 400 Da and aluminium oxide (Al_2O_3). The influence of both additives on membrane performance was investigated in terms of the presence of TPC in the permeate stream, COD removal, decolourisation and fouling/rinsing experiments.