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Treatment of Olive Mill Wastewater by Forward Osmosis

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ABSTRACT

Olive millings periodically release huge volumes of environmentally detrimental wastewater. In this work, Forward Osmosis (FO) is applied to de-hydrate Olive Mill Wastewater (OMWW) within the logic of Zero Liquid Discharge and by-products valorization.

Single-step FO operated with 3.7 m $MgCl_2$ draw solution and 6 cm/s crossflow velocity resulted in a volume reduction of 71%, complete decolorization of the permeate, and more than 98% rejection to OMWW components, including biophenols and ions. This makes FO more attractive than conventional multi-stage treatment processes that may include energy-intensive centrifugation and adsorbent utilization. Moreover, MBR-based pre-treatment prior to FO reduced pectins by 92.3%, thus resulting in 30% flux enhancement.

Cleaning cycle based on osmotic back-flushing, after continuous OMWW dehydration tests carried out over 200 h, resulted in an almost complete removal of the foulant layer and permitted to restore up to 95% pure water permeability of cellulose triacetate (CTA) membranes. The possibility to process FO concentrate by pressure driven processes, such as UF and NF, to recover and fractionate valuable biophenols was also proven.

1. Introduction

Discharging heavily polluted wastewater generated during the extraction of olive oil poses serious economical and environmental concern worldwide. The situation is particularly severe in the Mediterranean region where more than 75% of the world olive oil is produced [1]. The amount of Olive Mill Wastewater (OMWW) generated is about 5 m^3 per ton of produced olive oil with COD around 220 g/L [2–4]. The high variability of feed composition and, in particular, the presence of antibacterial phenolic compounds, makes OMWW difficult to treat [3,5]. The environmental impact due to the toxic load of OMWW is estimated to be more severe than municipal sewage. Rise and expansion in the problem is foreseen due to the health-driven production increase by up to 30% in the last 15 years and the emergence of new producers like US, Argentina and South Africa [2,6,7].

Recently, integrated membrane operations for combined OMWW reclamation and extraction of biophenols have got relevant interest [2,4,5,8–13]. The motivation for treating and reclaiming OMWW arises from legislation which constrains its illegal discharge to the environment [1]. While good quality water reclamation from OMWW is of interest in industrial applications, the biophenolic fractions have antibacterial properties and hold a wide range of antioxidant, cardio-protective and cancer-preventive activities [10,14–16]. Biophenolic exhausted concentrate may also be transformed into syngas for the production of methanol, ammonia and synthetic fuel [17].

So far, occurrence of severe membrane fouling has restricted the large scale applicability of conventional membrane technologies [10,18]. Previous investigations showed that irreversible membrane damage resulted in 57% permeability loss when treating OMWW with 2 kDa polyethersulfone Ultrafiltration (UF) membrane, and in 60% permeability loss while using 0.4 μm polyethylene Microfiltration (MF) membranes [18,19]. Despite the significant efforts made to restore the original membrane performance by chemical cleaning, results obtained are still unsatisfactory. In general, severe fouling affects the investment costs as a result of reduced membrane lifetime and increased chemical cost.

Nowadays, Forward Osmosis (FO) is re-emerging as low-energy demanding membrane operation for dehydration of aqueous solution [20]. FO is a membrane process that uses an osmotic pressure gradient as a driving force to transport water across an ideally

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Nomenclature

List of abbreviation

AHA	humic acid
BMR	biocatalytic membrane reactor
BSA	bovine serum albumin
CTA	cellulose triacetate
DS	draw solution
ECP	external concentration polarization
ICP	internal concentration polarization
OMWW	Olive Mill Wastewater
VRF	volume reduction factor

List of symbols

A_{fl}	fouling layer water permeability (kg/m^2 h atm)
A_m	membrane water permeability (kg/m^2 h atm)
A	overall membrane and fouling layer water permeability (kg/m^2 h atm)
B_{fl}	fouling layer salt permeability (kg/m^2 h atm)
B_m	membrane salt permeability (kg/m^2 h atm)
B	overall membrane and fouling layer salt permeability (kg/m^2 h atm)
D	diffusion coefficient (m^2/s)
d_h	hydraulic diameter (m)
$J_{w,obs}$	experimentally observed flux (L/m^2 h)
$J_{w,ref}$	theoretically predicted flux under zero rate of fouling, salt back diffusion and cake enhanced concentration polarization (L/m^2 h)
J_w	water flux (L/m^2 h)
K_{CECP}	cake enhanced concentration polarization mass transfer coefficient (m/s)
K	draw solute transport resistivity (s/m)
K	feed side mass transfer coefficient (m/s)
L	filtration cell length (m)
L_p	hydraulic permeability (L/m^2 h atm)
ΔP	hydrostatic pressure (atm)
Re	Reynolds number
R	universal gas constant (0.0821 L atm/mol K) (L atm/mol k)
S	membrane structural parameter (m^{-1})
Sc	Schmidt number
Sh	Sherwood number
t	porous support layer thickness (m)
V	crossflow velocity (cm/s)
ρ	density (kg/m^3)
$\Delta\pi$	osmotic pressure gradient between feed and draw solution (atm)
π_{DS}	draw solution osmotic pressure (atm)
μ	dynamic viscosity (kg/m s)
π_{fs}	feed solution osmotic pressure (atm)
η^f	final conductivity (mS/m)
η^i	initial conductivity (mS/m)
$\Delta\pi_b^0$	initial bulk osmotic pressure difference (atm)
$\Delta\pi_b^f$	final bulk osmotic pressure difference (atm)
Θ	osmolality (mOsm/kg H$_2$O)
ε	porosity
φ	recovery (%)
σ	reflection coefficient
τ	tortuosity
ϕ	Van't Hoff coefficient

semi-permeable membrane [21]. FO has been investigated for sea water desalination [22], wastewater treatment and concentration of diluted streams [23], food processing [24], removal of trace organic matter [25] and for use in membrane bioreactor [26]. Interestingly, several studies have shown that fouling occurring in FO in most part is reversible due to low foulant compaction as a result of the negligible hydraulic pressure gradient. Therefore, FO holds a great potential to treat wastewater [27], including OMWW, which has high fouling propensity [28,29].

In this work, the suitability of FO to treat OMWW with the aim to reduce the total processable volume was proven for the first time at the best of our knowledge. FO permitted to purify water in a single step to an extent that it can be released in the environment. Simultaneously, it permitted to concentrate valuable biophenols for further treatments. In particular, the effect of operational parameters on FO performance for the treatment of OMWW was studied. Single-step FO performance was evaluated in terms of transmembrane flux as a function of the osmotic pressure, rejection to individual ions, total phenolics, Total Organic Carbon (TOC), Total Inorganic Carbon (TIC) and Total Suspended Solids (TSS), sensitivity to fouling and effectiveness of cleaning procedures. Moreover, the possibility of integrating FO with different pressure driven membrane operations to recover biophenolic compounds is explored.

2. Materials and methods

2.1. Materials

OMWW (TS = 4.13%, pectin = 0.3–0.46 mg/mL, pH 4.2) was taken from three-phase local olive oil producer (Olearia San Giorgio, Calabria – Italy). Draw solution (DS) was prepared by dissolving $MgCl_2{\cdot}6H_2O$ (Fischer Scientific, Italy) in ultrapure water (USF ELGA Lab water, Fisher scientific) within a concentration range from 1.8 to 7.5 molal (m). This salt was chosen because of its limited back-diffusion tendency and reduced scale forming potential at the pH (4.5) of raw OMWW. The osmotic potential (mOsm/kg H_2O) of $MgCl_2$ at different concentration and feed OMWW was measured using Fiske® 210 Micro-Sample Osmometer (Analytical control De Mori S.r.l, Milan – Italy). Gallic acid and Folin–Ciocalteau reagents were purchased from Sigma Aldrich (Italy).

2.2. OMWW characterization

OMWW characterization was performed according to the following protocols:

- *Total Solids (TS)*: 1 g of OMWW is dried at 105 °C in a thermo-balance (Ohus S.r.l Milan, Italy) until reaching at steady-state weight.
- *Total Dissolved Solids (TDS)*: 1 g of OMWW is filtered through a 0.45 μm filter cartridge and the filtrate is dried in a thermo-balance at 105 °C until reaching at steady-state weight. *Total Suspended Solids (TSS)* is evaluated as difference between TS and TDS.
- *Total phenolic content* is determined using the Folin–Ciocalteau reagent (a mixture of phosphotungstic acid and phosphomolybdic acid) [30]. The partially reduced reagent produces molybdenum–tungsten blue complex, which is measured spectrophotometrically at 756 nm with UV/VIS spectrophotometer (Perkin Elmer, Lambda EZ201). Calibration curve was obtained using standard solutions of gallic acid (0–100 mg/l).