

## On the Effect of pH and Operating Conditions on Nanofiltration of Two-Phase Olive Mill Wastewater

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In the present work, a thin-film composite polymeric nanofiltration (NF) membrane is examined for the tertiary treatment of secondary-treated two-phase olive mill wastewater (OMW2-ST). Overcoming the deleterious fouling phenomena persistently encountered in membrane processes managing wastewater streams was indeed pursued. With this purpose, the point of zero charge (PZC) of the membrane was determined as a key for the operating conditions. This will determine the intensity of the electrostatic interactions between the organic and inorganic solutes present in the OMW2-ST stream and the active surface of the NF membrane, further to the steric effects. Working above the point of zero charge (pH > 5.8) of the membrane ensured high steady-state permeate productivity ( $59.6 \text{ L h}^{-1}\text{m}^{-2}$ ), also economically sustainable in time owed to minimization of the permeate flux decay (5.5 %). Moreover, these conditions also provided high feed recovery (90%) and significant rejection efficiencies for the electroconductivity (58.1%) and organic matter (76.1%). This led to a purified permeate stream exiting the NF membrane operation exhibiting average EC and COD values equal to  $1.4 \text{ mS cm}^{-1}$  and  $45 \text{ mg L}^{-1}$ . This permits complying with the water quality parameters established by different regulations for discharge public waterways and irrigation purposes.

### 1. Introduction

Olive oil industries, one of the principal industrial economic activities in the Mediterranean Countries, comprising mainly Spain, Italy, Portugal, Greece, Cyprus, Morocco, Turkey, Iran, Algeria, Tunisia, Egypt, Israel and Palestine, lead to the by-production of highly polluted effluents known as olive mill wastewater (OMW). The adoption of continuous olive oil production processes in the nineties in order to increase the production capability of olive mills has also led to a sensible increase of the amounts of OMW.

Direct discharge of OMW causes hazardous pollution to the ecological status, namely contamination of soil, pollution of water bodies and inhibition of self-purification processes, strong odor contamination in the surroundings, as well as phytotoxic consequences to the aquatic fauna and hindrance of plants growth (Niaounakis and Halvadakis, 2006; Ntougias et al., 2013).

Great efforts have been made in the last years by scientists and engineers with the goal of providing a suitable solution for the management of OMW. However, the complexity, lack of efficiency or uncertain economic viability of the proposals has up to the date impeded their actual transference to the industrial scale.

Within this scenario, the European Union is committed through the European Commission to increase the vigilance and make European Environmental Regulations more stringent in the near future, as agreed in the 'H2020 Horizon'. Already, the European Directive 2000/60/CE established the legal framework in order to confer the utmost protection to water, in order to impulse the use of regenerated wastewater. Currently, direct discharge of OMW to the soil and water bodies is prohibited in Spain, whereas in Italy, Portugal and other European countries only the partial discharge on suitable terrains is allowed.

The main obstacle for the implementation of cost-effective processes for OMW management relies in the fact that olive mills are typically small factories, geographically dispersed. An average-sized olive oil factory

normally by-produces around 10 - 15 m<sup>3</sup> of OMW daily. A centralized treatment of OMW seems not feasible currently, thus an effective and simple solution is needed for these small plants.

In this regard, membrane technology offers compact modular nature, high efficiency and moderate investment and maintenance expenses. Membrane processes are becoming extensively used in numerous applications, as standalone, integrated or substitutive operations. Membrane technology has effectively replaced many conventional processes in the purification of water and groundwater as well as in the reclamation of wastewater streams of very diverse sources, e.g. agro-industrial activities (Iaquinta et al., 2009; Ochando-Pulido et al., 2014a,b; Stoller et al., 2013a,b). The availability of new membrane materials, designs, module concepts and know-how has improved its credibility among investors in the recent years.

However, concentration polarization and fouling are always present in the treatment of wastewater streams by membranes and it is imperative to control it in order to ensure the appropriate operation and design of the plant. Fouling is a complex phenomenon involving different mechanisms such as pore blocking and plugging, cake, gel and biofilm formation (Field et al., 1995; Field and Pearce, 2011; Bacchin et al., 2006). During operation, fouling leads to an increase in the energy costs to maintain the target permeate production, and also the operating costs due to frequent plant shut-downs for in-situ membrane cleaning procedures. What is more, the longevity of the membranes can be irretrievably shortened due to irreversible fouling.

It is clear that inhibition and control of fouling is vital to definitely achieve the competitiveness of membrane technology at industrial scale (Field and Pearce, 2011; Stoller, 2009, 2011; Stoller et al., 2013a,b). In this sense, OMW2 contains high concentrations of a wide range of solutes in the form of suspended solids and colloidal particles which are all very prone to cause membrane fouling, such as organic pollutants comprising phenolic compounds, organic acids, tannins and organohalogenated contaminants, as well as inorganic matter. To solve this handicap in order to achieve adequate steady operation, engineers erroneously tend to either overdesign excessively the membrane plants in industrial scale facilities, resulting in sensible but useless increment of total costs, or under-design them due to misunderstood and underestimation of the fouling issues, in this latter case operating above the threshold conditions, which are not technically and economically feasible for long periods of time (Field et al., 1995; Field and Pearce, 2011; Stoller et al., 2013a,b).

In the present paper, a thin-film composite nanofiltration (NF) membrane is examined for the tertiary treatment of secondary-treated OMW2 (OMW2ST). The key advantages of novel NF membranes are the higher permeate fluxes upon sensibly lower operating pressures, but still providing specific selectivity towards small solutes, thus permitting important investment and specific energy consumption savings.

However, fouling is a deleterious problem common to all membrane processes, especially in case of NF membranes. If of irreversible nature, it reduces the membrane service lifetime drastically. In any case, fouling alters the selectivity of the membrane and depletes its productivity, making the integration of the membrane operation in integrated wastewater treatment processes economically unfeasible (Le-Clech et al., 2006). Scarce is being published up to now about the application of NF in OMW treatment, but the least focused on two-phase OMW (Ochando-Pulido et al., 2014a,b). Moreover, there is a lack of deep analysis of NF operating conditions comprising the influent pH, especially with an insight into the fouling issues that determines the performance and economic viability. In this study, the feasibility of the TFC NF membrane is examined in semicontinuous operation, in contrast with common batch membrane operations, for OMW2ST purification. Reduction of the significant conductivity and remaining organic matter concentration in OMW2ST with the purpose of obtaining regenerated water with acceptable quality standards according to the Food and Agricultural Organization (FAO) for irrigation purposes was intended. With this goal, the dynamic fouling build-up was assessed in a laboratory scale to find the adequate operating conditions including the impact of the pH on the performance.

## 2. Materials and methods

### 2.1 Analytical methods

Wastewater samples were collected from various olive oil mills during the olive oil production campaign in winter in the Andalusian provinces of Jaén and Granada (Spain), operating with the two-phase centrifugation system (OMW2), and rapidly analyzed in the lab. After this, the OMW2 samples were conducted to a secondary treatment previously optimized by the Authors (Martínez Nieto et al., 2011), prior to the entrance to the final membrane purification process. The physico-chemical characteristics of the OMW2ST stream are reported in Table 1. Chemical oxygen demand (COD), total suspended solids (TSS), total phenolic compounds (TPh), total iron, electroconductivity (EC) and pH were measured in the raw effluents samples and at the end of each depuration step following standard methods (Greenberg et al., 2005). All the chemical reagents used for the analytical proceedings presented analytical grade with purity over 99 %, and the analyses were performed in triplicate.

Table 1: Physicochemical characterization of OMW2ST<sup>a</sup>

Parameter	OMW2ST
pH	7.4±0.3
EC (mS cm <sup>-1</sup> )	3.4±0.2
TSS (mg L <sup>-1</sup> )	14.5±1.5
COD (mg L <sup>-1</sup> )	188.7±37.9
Total phenolic compounds (mg L <sup>-1</sup> )	0.7±0.3
Total iron (mg L <sup>-1</sup> )	0.8±0.3
HCO <sub>3</sub> <sup>-</sup> (mg L <sup>-1</sup> )	131.1 ± 1.8
Cl <sup>-</sup> (mg L <sup>-1</sup> )	1018.0±27.1
Na <sup>+</sup> (mg L <sup>-1</sup> )	631.4±97.3

<sup>a</sup> OMW2ST: olive mill wastewater after secondary treatment.

## 2.2 Membrane bench-scale plant and NF experiments

The membrane filtration tests were carried out in a lab-scale membrane plant (Prozesstechnik GmbH, Basel, Switzerland) schematically showed in Fig. 1. The membrane plant was equipped with a non-stirred double-walled tank (5 L capacity) where the OMW2ST samples (2 L) were poured, then pumped through the flat membrane module (3.9 cm height x 33.5 cm length x 14.2 cm width) by means of a diaphragm pump (Hydra-Cell model D-03). The main process parameters comprising the operating pressure, temperature and tangential velocity were measured and displayed. The operating pressure was accurately adjusted ( $P_{TM} \pm 0.01$  bar) with a spring loaded pressure-regulating valve on the concentrate outlet and monitored by a digital pressure gauge, allowing independent control of the operating pressure and the flowrate. The operating temperature ( $T \pm 0.1$  °C) was regulated automatically via an electronic temperature controller.

The characteristics of the selected NF membrane (GE Water and Process Technologies, USA) are reported in Table 2. The active area of the membrane was 200 cm<sup>2</sup>. In order to promote the adequate turbulence over the membrane to minimize concentration polarization as far as possible, a feed spacer consisting in a polymeric net (2 mm mesh diameter) was inserted into the plate-and-frame membrane module. Before each NF experiment, the corresponding membrane was equilibrated by filtering MilliQ<sup>®</sup> water at a fixed pressure and temperature until a constant and stable flux was observed, to allow for membrane compaction. Once a stable flux was achieved, the hydraulic permeability ( $K_w$ ) of the membrane was determined by measuring the pure water flux within their pressure range, at ambient temperature and turbulent crossflow velocity.

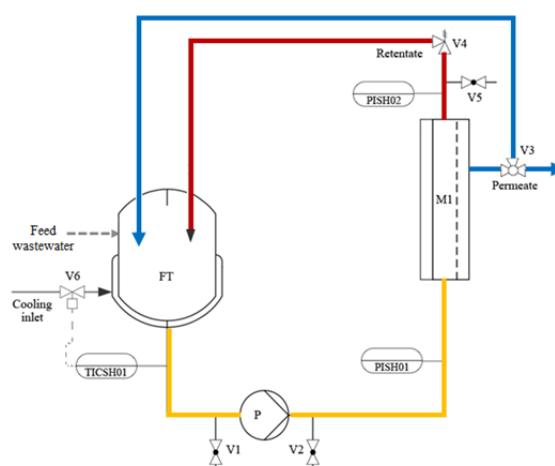


Fig. 1. Flow diagram of the bench-scale membrane filtration unit. M1: flat-sheet membrane module, P: feedstock pump, FT: feedstock tank; V1, V2: emptying valves; V3: permeate flux by-pass valve V4: pressure regulating valve; V5: venting valve; V6: magnetic valve for cooling jacket inlet; PISH01, PISH02: pressure gauges; TICSH01: temperature gauge.

Table 2: Specifications of the NF membrane

Membrane type	Model series
Membrane type	NF
Material	PA/PS
Membrane structure	TFC
Membrane surface	Hydrophilic
Pore size, nm	0.5 nm
MWCO, Da	300
Permeability ( $m_0$ ), $L h^{-1} m^{-2} bar^{-1}$	$6.5 \pm 0.5$
Max. P, bar	40
Max. T, °C	50

\*PA: polyamide; \*\*PS: polysulfone; \*\*TFC: thin-film composite;  
MWCO: molecular weight cut off.

NF experiments were driven in a semicontinuous mode, for a feed recovery rate ( $F_R$ ) of up to 90% of the initial feedstream volume, at ambient temperature ( $22 \pm 0.1$  °C) and turbulent tangential-flow regime over the membrane (tangential velocity equal to  $2.55 m s^{-1}$ , providing  $N_{Re} > 4000$ ) (Mott and Untener, 2014). The  $P_{TM}$  was fixed at the threshold pressure value (Espinasse et al., 2002). The concentrate stream was returned continuously to the feed tank whereas the permeate stream was steadily collected, replacing it with the same volume of fresh pretreated OMW2ST stream.

Samples of permeate were collected and analyzed to evaluate the membrane separation effectiveness with regard to the COD and EC. The permeate flux was continuously measured during operation time by a precision electronic mass balance (AX -120 Cobos, 0.1 mg accuracy). After each NF run, the membrane was recovered for the following experiment by cleaning it in situ with 0.1-0.15% w/v NaOH and 0.1-0.15% w/v sodium dodecyl sulfate (SDS) solutions (provided by Panreac S.A.) (Ochando-Pulido et al., 2015a).

### 3. Results and discussion

The target operating pressure for the NF purification of OMW2ST was addressed by means of the pressure-cycling method, performed in recirculation mode following the guidelines given by Espinasse et al. (2002) as described in previous works by the Authors (Stoller and Ochando, 2012; Stoller, 2013; Ochando-Pulido et al., 2014a,b; Ochando-Pulido et al., 2015b; Ochando and Stoller, 2015). The results of the pressure hysteresis cycle are shown in Fig. 2. The data points reported were the final values of the permeate flux after 15 min when steady-state conditions were achieved.

The observed threshold flux value ( $J_{th}$ ) for the raw OMW2ST was found to be  $63.2 L h^{-1} m^{-2}$ , corresponding to an operating pressure value ( $P_{th}$ ) equal to 13 bar. Above this  $P_{th}$  point, incomplete restoration of the permeate flux started to be observed when the same pressure level was again applied after the pressure-cycle. This point therefore establishes the bound of the low fouling operating framework of the NF membrane from the high fouling build-up range, where a rapid permeate flux loss starts to be controlling. This concept was firstly introduced by Field et al. (1993, 1995) Research Group for microfiltration (MF) membranes. Some years later these Authors also proved it empirically for ultrafiltration (UF) and NF membranes (Bacchin et al., 2006; Field and Pearce, 2011).

On the other hand, the effect of the feedstream pH ( $pH_0$ ) on the measured threshold flux of the membrane system was further investigated. For this purpose, experiments under different  $pH_0$  equal to 5.0, 5.5, 6.5 and 7.5 were performed in order to examine the effect on the threshold flux performance of the NF membrane. Results are summarized and reported in Table 3.

Table 3: NF performance as a function of the feedstream pH

Feedstream $pH_0$	$P_{TM}$ , bar	$J_{th}$ , $L h^{-1} m^{-2}$	$-\Delta J_p$ , %
5	13	26.9	57.3
5.5	13	52.6	16.7
6.5	13	57.8	8.1
7.5	13	59.0	5.5

$P_{TM}$ : operating pressure;  $pH_0$ : feedstream inlet pH;  $J_{p,0}$ : initial permeate flux;  
 $J_{th}$ : threshold flux;  $-\Delta J_p$ : flux loss.

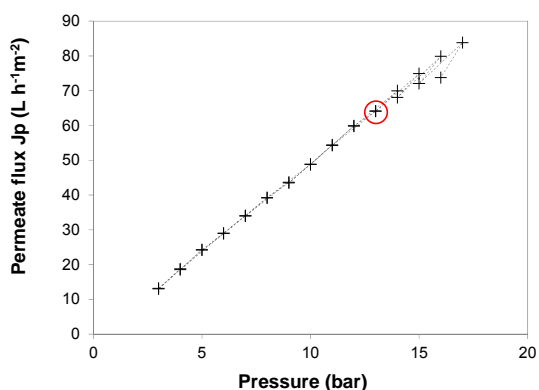


Fig. 2. Determination of the experimental  $J_{th}$  -  $P_{th}$  values (highlighted in circle) of the NF membrane for OMW2ST, recirculation mode; Operating temperature 22 °C, crossflow 2.55 m s<sup>-1</sup>.

A stable value of the permeate flux was attained just from the start of the operation for the NF experiments carried out at the highest pH values, that is, 7.5 and 6.5. For these conditions, a plateau was rapidly reached and maintained during the course of the experiments, revealing minimum fouling development on the NF membrane. Furthermore, the permeate flux loss ( $-\Delta J_p$ ) during the operation time was minor during the NF operation at a pH equal to 7.5 (5.5 %) if compared to the one performed at a pH of 6.5 (8.1 % permeate flux loss). This can be explained on the basis of the point of zero charge value (PZC) of the NF membrane, determined following Mullet et al. (1999). It was found that the membrane exhibited zero surface charge density at a PZC value equal to 5.8. This proves to have important implications in the performance of the NF purification of OMW2ST, because the membrane is therefore negatively charged for pH values above 5.8 ( $pH > PZC$ ), due to the deprotonation of the superficial carboxylic functional groups ( $H_2N\text{-polyamide-COOH} + H_2O \leftrightarrow H_2N\text{-polyamide-COO}^- + H_3O^+$ ), whereas it would present positive surface charge density below that value ( $pH < PZC$ ), as a result of the protonation of the superficial amine functional groups ( $H_2N\text{-polyamide-COOH} + H_3O^+ \leftrightarrow H_3N^+\text{-polyamide-COOH} + H_2O$ ). This determines the intensity of the electrostatic interactions between the organic and inorganic solutes present in the OMW2ST stream and the active surface of the NF membrane, further to the steric effects. Those attraction-repulsion interactions have a deep influence on the approach of the solutes to the interphase, thus affecting the fouling build-up of the NF membrane. When the difference between the pH of the influent (OMW2ST) to the NF operation ( $pH = 5.5$ ) and the membrane PZC ( $PZC = 5.8$ ) is narrow, a much significant decay of the permeate flux during the NF operation time was observed (16.7 %). Furthermore, for a pH value of the influent ( $pH = 5.0$ ) below the PZC of the membrane ( $pH < PZC$ ) the fouling build-up rate was strongly triggered, and the permeate flux was observed to decay abruptly (57.3 % permeate flux loss).

These results were attributed to the absence of electrostatic repulsion among the organic pollutants, and between the organic matter and the active layer of the NF membrane, in virtue of Donnan exclusion (Seidel et al., 2001). For pH values of the OMW2ST influent close to the PZC of the membrane ( $pH \sim PZC$ ) the active layer exhibits zero surface charge density, whereas for  $pH < PZC$  the NF membrane is positively charged. On the contrary, the hydrophilic organic matter and colloidal pollutants of the OMW2ST stream, comprising phenolic compounds and carboxylic organic acids (Ochando-Pulido et al., 2014a,b), are protonated and thus neutrally charged at acid pH ( $pH < PZC$ ). These facts thus enhance the deposition and accumulation of particles on the NF membrane surface, sensibly triggering fouling (Lee et al., 2006; Seidel et al., 2001). Analogously, for a pH of the OMW2ST influent equal to 6.5 the deprotonation equilibrium of the carboxylic functional groups on the active layer of the membrane is minor, and thus the electronegativity of the NF membrane, in comparison with that at a higher pH (7.5). As a consequence, a weaker repulsion between the organic pollutants molecules, which present negative charge at those pH values, and the membrane surface is attained.

Setting the adequate parameters of the operating variables ensured the hydrodynamic conditions favouring the equilibrium between the membrane-particles repulsion and the permeation drag. This led to a purified permeate stream apt for irrigation with good quality according to the recommended standards reported by the FAO.

Table 4: Characterization of the permeate stream

Parameter	Value
EC, $\mu S\ cm^{-1}$	97.0
COD, $mg\ L^{-1}$	3.7

EC: electrical conductivity; COD: chemical oxygen demand

#### 4. Conclusions

In the present work, a thin-film composite NF membrane is examined for the tertiary treatment of secondary-treated two-phase olive mill wastewater (OMW2ST). Setting the adequate parameters of the operating variables ensured the hydrodynamic conditions favouring the equilibrium between the membrane-particles repulsion and the permeation drag, thus minimum membrane fouling. A stable value of the permeate flux was attained upon working at pH values (6.5 - 7.5) above the point of zero charge (PZC = 5.8) of the membrane. For these conditions, a plateau was rapidly reached and maintained, revealing minimum permeate flux decay on the NF membrane. This led to a purified permeate stream exiting apt for irrigation with good quality according to the recommended standards reported by the Food and Agricultural Organization (FAO).

#### Acknowledgements

Spanish Ministry of Economy and Competitiveness is acknowledged for funding project CTM2014-61105-JIN.

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