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Comparison of Critical and Threshold Fluxes on Ultrafiltration and Nanofiltration by Treating 2-Phase or 3-Phase Olive Mill Wastewater

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In this work, batch membrane processes in series composed by ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO) are used to purify the effluents exiting both the two-phase and tree-phase extraction processes.

One main problem of membrane technology is membrane fouling. In the last years, the threshold flux theory was introduced as a key tool to analyze operating conditions triggering sensible fouling. Operating below threshold flux means to limit fouling formation, and in order to increase the value of threshold flux proper pretreatment processes are required.

1. Introduction

Olive oil industry is actually one of the main agricultural activities of the Mediterranean Basin countries, including Spain, Italy and Greece. During the olive oil production process two main liquid streams are produced as wastewater, the first one from the washing of the fruit (olives washing wastewater, OWW) and the second one from the extraction of the olive oil (olive vegetation wastewater, OVW, a mixture of the proper olive-fruit humidity along with process-added water). These effluents are commonly referred to as olive mill wastewater (OMW). In traditional olive oil mills 0.4 - 0.6 m^3 of OMW were produced per ton of processed olives. This means that an average-sized olive oil factory produces a daily amount of 1 m^3/ day of OWW and 10-15 m^3 of OVW (**Table 1**). In continuous mills, horizontal centrifuges - also known as decanters - are used for solid-liquid separation. There are two types of continuous olive oil extractors: in the three-phase system the olive oil phase is separated from the aqueous stream and the solid phase, whereas in the two-phase system the olive oil phase is straightly separated from the wet solid (commonly named “alpeorujo”).

***Table 1** - Flow rates of the different effluents of the continuous extraction processes*

Effluent, $L \cdot kg^{-1}$	3-phase extraction	2-phase extraction
Washing of olives (OWW)	0.06	0.05
Horizontal centrifuge	0.90	0
Vertical centrifuge	0.20	0.15
Cleaning	0.05	0.05
Total	1.21	0.25

In this work, the purification of the OMW effluent from both the two-phase and three-phase systems is specifically addressed. Summarized composition of OVW and OWW of the samples taken from the two-phase and three-phase olive oil extraction processes are reported in **Table 2**. OVW-2 and OVW-3 are one of the heaviest polluted industrial effluents by organic matter and are characterized by strong odor nuisance, acid pH, intensive violet-dark color and high saline toxicity (exhibiting high electroconductivity (EC) values).

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***Table 2 -** Physico-chemical composition of raw OVW-2 and OVW-3*

Parameters	OVW-2	OVW-3
pH	4.9 - 5.1	5.1 - 5.2
EC, $mS \cdot cm^{-1}$	1.76 - 1.84	6.33 - 6.37
Tss, $g \cdot L^{-1}$	3.1 - 5.8	32.6 - 33.0
COD, $g \cdot L^{-1}$	16.4 - 16.6	32.1 - 32.4
TPh, $mg \cdot L^{-1}$	181 - 184	-

Up to now, various treatment processes for the management and reclamation of OMW have been proposed. Biological treatment of OMW is a hard task and right now not applied on a large scale due to the resistance of OMW to biological degradation. Other treatment practices have been developed, such as lagooning or natural evaporation and thermal concentration, treatments with lime and clay, composting, physico-chemical procedures as coagulation-flocculation and electrocoagulation, advanced oxidation processes including ozonation, Fenton´s reagent and photocatalysis and also electrochemical and hybrid processes (Martinzes Nieto et al., 2011; Stoller, 2009; Martinez Nieto et al., 2011b, Stoller at al., 2010; Iaquinta et al., 2009; Turano et al., 2002).

One main drawback in membrane technologies is membrane fouling, and this is especially true in wastewater purification processes. The organic matter concentrates on the membrane surface by polarization and may lead to fouling, thus decreasing permeate. The decay in productivity increases the operating and energy costs and leads to frequent plant shut-downs for in-situ membrane cleaning, which are not capable to contrast the progressive membrane module deterioration which shortens the membrane lifetime dramatically. The control of fouling is key to increase the profitability and competiveness of this technology.

Pressure-driven membrane processes - in particular ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO) - have been applied in the last years for municipal, agricultural and industrial wastewater reclamation (Stoler, 2008; Ochando-Pulido et al., 2012, Ochando-Pulido et al., 2012b; Ochando-Pulido et al., 2012c). Several works have been conducted in the past by means of membrane technology with the target to reduce the organic load of OMW, but only few focusing on OVW-2 (Stoller et al., 2012; Ochando-Pulido et al., 2012d).

In all this works membrane fouling has been noticed to play a key role during operation. Some research groups have observed that the non-adoption of specifically tailored OMW pretreatment processes leads irretrievably to rapid development of fouling on the membranes (Stoller et al., 2006; Stoller, 2011). Moreover, other factors exhibiting high influence on membranes performances are the feedstock, the hydrodynamic conditions and the membrane type, roughness and porosity.

Field et al. (1995) introduced for the first time the concept of critical flux for MF membranes, defining it as the permeate flux below which fouling is not promptly observed, and afterwards critical flux values were also identified in UF and NF membranes. However, later on some authors noted that this behavior is not always strictly observed in the treatment of real wastewater streams by membrane processes, and thus extends his theory to these cases by introducing the concept of threshold flux (2011). Confirmation of the existence of a threshold flux in the case of the treatment of OMW with membranes has been recently reported by Stoller and Ochando (Ochando-Pulido et al., 2012d). The threshold flux makes reference to the maximum permeate flux at which fouling builds up at a very low and constant rate, and above which the rate of fouling increases exponentially.

Threshold flux values may be increased by proper tailored raw wastewater pretreatment processes and optimized operating conditions.

In this work, the treatment by membranes of both OVW-2 and OVW-3 will be discussed. Both feedstock were treated by a batch membrane process consisting of UF followed by NF and finally RO, in series. Beforehand, both feedstock were processed by the following pretreatment processes:

(i) pH-temperature flocculation
(ii) UV/TiO_2 photocatalysis

At the end, compliance with municipal sewers discharge and irrigation standards were checked.

2. Results and Discussion

2.1 Analytical procedure

Chemical oxygen demand (COD), total phenols (TPh), total suspended solids (Tss), electroconductivity (EC) and pH measurements were performed following standard methods. COD was measured by means of a LASA 100 photometer with the COD cuvettes LCK014 supplied by Dr. Hach Lange, whereas EC was measured by the 8706R1 portable instrument supplied by Delta Ohm. Last, particle size distribution analysis of suspended and colloidal matter was carried out with a Plus90 nanosizer supplied by Brookhaven. All analytical methods were applied at least in triplicate with analytical-grade reagents. The list of reagents used were 70% (w/w) HNO_3, 98% (w/w) NaOH, 98% (w/w) Na_2SO_3, 30% (w/w) NH_4OH, 37% (w/w) HCl and 30% (w/w) $FeCl_3$, supplied by Panreac, whereas 70% (w/w) TiO_2 P-25 nanopowder was provided by Degussa.

2.2 Raw feedstock pretreatment

At first, both raw feedstock (OVW-2 and OVW-3) were processed by gridding at a cut-size of 300 μm, in order to remove coarse particles. Subsequently, two different pretreatment steps were applied on both feedstocks, the first consisting in pH-T flocculation and the other one in photocatalysis with TiO_2 nanopowder under UV light (nominal power 45 W, wavelength 365 nm).

The best operating conditions as well as the optimal chemical dosage for both pretreatment steps are taken from a previous work (Stoller, 2009; Stoller et al., 2010).

The pH-T flocculation process in an inexpensive one if compared with others for the removal of suspended matter, and consisted in adding 70 % w/w HNO_3 or 1 N NaOH to whether reduce or increase the pH values of the feedstock (from 2 up to 7) at various temperatures ranging from 15 to 50 °C, to promote formation of easily-sedimentable flocks.

The UV light/ TiO_2 photocatalysis is an advanced oxidation process suitable to organic matter degradation. The details about the production of the home-made photocatalyst is described elsewhere (De Caprariis et al., 2012; Sacco et al., 2012; Stoller et al., 2012). Briefly explained, the photocatalyst was produced through a sol-gel process by means of a spinning-disk reactor, and consisted of a ferromagnetic core (γ-Fe_2O_3, modal particle size of 30 nm) and two subsequent layers of silica and titania (γ $Fe_2O_3/SiO_2/TiO_2$). This obtained nano-photocatalyst presented a final mean particle size of 79 nm with pure anatase titania phase and traces of brookite. The magnetic property of the photocatalyst permits the recovery from the treated wastewater stream and the reuse, making this procedure extremely cost effective.

The two pretreatment steps used in this work were scaled up: pH-T flocculation was carried out in a 20 L stirred batch reactor provided with a turbine impeller stirrer, whereas photocatalysis was conducted in an agitated 8 L batch reactor, equipped with an UV lamp on top. Finally, achieved reduction of COD, total phenols and suspended solids concentration was measured at the end of each pilot-scale pretreatment step.

2.3 Description of membranes, filtration procedures and pilot scale plant

The membranes pilot plant, schematically represented in **Fig. 1**, is provided with a 100 L feed tank (FT_1) where the various feedstocks were loaded. Two different pumps - a centrifugal booster (P_1) and a volumetric piston (P_2) pumps - served to drive the raw effluents to the spiral-wound (SW) membrane module fitted in housing M_1.

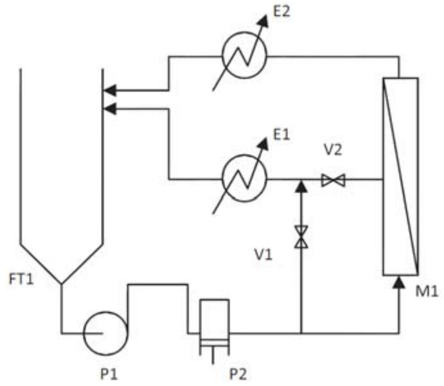

Fig. 1. *Membrane filtration pilot plant flow diagram*

The characteristics of the membranes chosen for this research, all polymeric ones supplied by GE Water and Process Technologies, are reported in **Table 3**. The used membrane modules were model GM for UF, model DK for NF and model SC for RO, all three with an active area equal to 2.5 m^2. These membranes were previously employed in other experiments with raw wastewaters for more than 1000 h of operation time, and thus exhibited low pure water permeability values if compared to virgin ones.

***Table 3** - Membranes characteristics*

Membrane type	Model series	K_w, $L \cdot h^{-1} m^{-2}$ bar	Pore size, nm	Surface, m^2	Max. P, bar	Max. T, °C
UF	GM	5.2	2	2.5	16	50
NF	DK	2.5	0.5	2.5	32	50
RO	SC	1.9	< 0.1	2.5	40	50

Both operating pressure and crossflow velocity over the membrane can be independently set by means of regulation valves V_1 and V_2, with a precision of 0.5 bar and 10 $L \cdot h^{-1}$ each. As well, both variables were measured and displayed by analogue manometers and a turbine flow meter respectively. During all experiments, both temperature and feed flow rate were controlled at fixed values, equal to ambient conditions (20 ° C) and turbulent tangential velocity over the membrane (550 $L \cdot h^{-1}$, to promote $N_{Re} > 4000$). Otherwise, permeate flux was gauged during operation time through a precision electronic mass balance (AX-120 Cobos, 0.1 mg accuracy).

Prior to each filtration run, the corresponding membrane was allowed to equilibrate by filtration of MilliQ® water at constant pressure and temperature until stable flux was observed (approximately after 2 hour time), after which measurement of the pure water permeability coefficient (K_w) of each membrane was performed (**Table 3**).

Then, threshold flux estimation was carried out with one of the methods available in the scientific literature for critical flux measurement. Both critical and threshold flux values cannot be theoretical predicted and experimental determination is needed. The chosen method, proposed by Espinasse et al. (2002), consists basically in a hysteresis cycle for the pressures range of each corresponding membrane, increasing and decreasing stepwise the net driving pressure up and down, in a way that complete restoration of the permeate flux must be observed for the same pressure level after one cycle to stay within threshold flux conditions [20]. Hence, the highest pressure value at which this condition is ultimately observed divides the low fouling region from the high fouling region.

After each measurement, the threshold flux value (J_{th}) and its corresponding operating pressure (P_{th}) were noted. To maintain the characteristics of the feedstock constant during threshold flux measurements, both permeate and concentrate streams were cooled down to the feedstock temperature and then mixed and recycled back to the raw wastewater tank (recycling mode). Finally, the permeate flux profiles during batch runs - that is collecting the permeate stream whereas steadily recirculating the concentrate flow back to the feed tank - were examined for all the membranes.

After each experiment, rinsing of the membrane with tap water for 30 min was performed. If no longer necessary, the membrane module was stored in fresh tap water, after which chemical cleaning of the circuit with 1N NaOH solution was performed in closed loop for 30 min.

3. Results and discussion

The two feedstock were pretreated by flocculation and UV/TiO_2 photocatalysis. The obtained results of the lab scale UV/TiO_2 tests are reported in **Table 4**.

***Table 4** - OVW-2 and OVW-3 physicochemical composition after pretreatment*

Parameters	OVW-2	OVW-3
pH	2.9	3.2
Tss, g/L	1.15	5.1
COD, g/L	11.1	15.2
TPh, mg/L	139	-

Afterwards, threshold flux was determined for each feedstock and membrane process step. The obtained results are reported in **Table 5**.

Table 5 *- Threshold flux determination of the single adopted membrane steps.*

Raw effluent	Membrane	Feedstock	P_{th}, bar	J_{th}, L/hm^2	J_{ss}, L/hm^2	R_{COD}, %	Recovery, %
OVW-2	UF	FS_1	8	7.3	7.6	39.9	87.4
		FS_1'	9	9.4	9.6	48.5	88.1
	NF	$FS_{1, UF}$	7	10.3	10.2	69.4	84.2
		$FS'_{1, UF}$	8	12.5	12.3	76.6	85.0
	RO	$FS_{1, UF+NF}$	20	-	10.5	82.8	75.8
		$FS'_{1, UF+NF}$	20	-	13.2	90.5	83.3
OVW-3	UF	FS_2'	4	0.8	0.6	28.2	74.5
	NF	$FS'_{2, UF}$	5	6.9	6.6	63.1	76.7
	RO	$FS'_{2, UF+NF}$	20	-	22.6	89.1	80.2

After the determination of the threshold flux values, both UF and NF operations were performed on batch mode. To close the treatment process loop, a final purification stage consisting in a RO membrane was conducted, for which an operating pressure of 20 bar was selected. Results are summarized in **Table 5**, where the threshold flux values (P_{th} - J_{th}) of every membrane step for each feedstock are given, as well as the results referring to the batch membranes-in-series operation including the COD abatement (R_{COD}, %), the recovery rate and the experimental steady-state permeate flux registered (J_{ss}) for each membrane stage.

It can be observed that the steady-state permeate flux values (J_{ss}) observed during the batch membranes sequence were, upon threshold hydrodynamic conditions (P_{th}), in good line with the threshold flux values (J_{th}) previously estimated by the pressure cycling method. Furthermore, high recovery rate values were attained for all membrane steps regardless of the feedstock. However, not only higher steady-state/threshold permeate fluxes were provided for the OVW-2 effluent pretreated by UV/TiO_2 photocatalysis with the ferromagnetic nanoparticles after pH-T flocculation (9.6, 12.3 and 13.2 L/hm^2 *vs.* 7.6, 10.2 and 10.5 L/hm^2) but also major recovery rates (88.1%, 85 % and 83.3 % for UF, NF and RO respectively *vs.* 87.4 %, 84.2 % and 75.8 %) and organic matter rejection efficiencies (R_{COD}) were ensured for every membrane operation (48.5, 76.6 and 90.5 % *vs.* 39.9, 69.4 and 82.8 %).

On the other hand, lower steady-state/threshold flux values were confirmed for the UF and NF membrane stages in the treatment of OVW-3 pretreated by both pH-T flocculation and photocatalysis in contrast to the values corresponding to OVW-2, as well as lower R_{COD} (see **Table 5**), given the higher EC and COD values in the former feedstock. Moreover, slightly minor recovery values were achieved. However, these results are quite satisfactory taking into account the higher pollutants load in the raw OVW-3. What is more, quite higher (41.6 %) steady-state RO permeate flux was registered for $FS'_{2, UF+NF}$ if compared to $FS'_{1, UF+NF}$ upon the same operating pressure (20 bar), owed maybe to the fact that the higher presence of organic matter in $FS'_{2, UF+NF}$ may derive in molecular aggregation leading to bigger particles more easily retained by the membrane, confirmed by similar R_{COD} in spite of its higher organic concentration.

Final COD values equal to 452 mg/L ($FS_{1, UF+NF}$) and 121 mg/L ($FS'_{1, UF+NF}$) were measured in the RO permeate streams after both OVW-2 treatments, whereas 466 mg/L ($FS'_{2, UF+NF}$) for OVW-3. This means the achievement of quality standards for irrigation (values below 1000 mg $O_2/\cdot L^{-1}$) in all cases, as well as for discharge not only in Italian, but also in Spanish sewer systems (values below 500 and 125 mg $O_2/\cdot L^{-1}$, respectively) in case of OVW-2.

4. Conclusions

The pretreatment process including pH-T flocculation followed by UV/TiO_2 photocatalysis with ferromagnetic-core nanoparticles appears to be very promising for efficient pretreatment of olive mill effluents from two-phase (OVW-2) and three-phase (OVW-3) continuous extraction processes before batch membranes-in-series operation consisting of UF followed by NF and finally RO polymeric membrane modules. This pretreatment procedure ensured higher and steady threshold permeate flux values in all membrane separation stages, major COD rejection values and increased recovery rates, enhancing the cost-effectiveness of the management process of both OVW-2 and OVW-3 by the proposed batch membranes sequence.

Moreover, the purified wastewater stream can be discharged in Italian and Spanish sewers.

The concept of the threshold flux is a key tool for controlling fouling problems common to all large-scale membranes applications, giving valuable information regarding optimal hydrodynamics to ensure safe design and steady operation of the plant.

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