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Treatment of Olive Oil Processing Wastewater by Ultrafiltration, Nanofiltration, Reverse Osmosis and Biofiltration

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This paper deals with the possibility to purify olive mill wastewater streams from olive mills by means of coagulation, membrane technology and bio filtration.
In the last decade, membrane processes have gained a main role to seek for a viable process to treat olive mill wastewater streams due to their capability to eliminate almost all of the pollutants in the water. One main drawback to this approach is the severe membrane fouling issues, that reduces sensibly these capabilities within a short period of time. In order to inhibit the fouling formation, in this work the boundary flux approach was used, that is the determination of proper operating conditions that do not promote fouling formation by specific measurements and modelling. Nevertheless, membranes may not be sufficient to reach the desired purification grade of the wastewater stream for a harmless disposal in the environment.
Novelty of this work is the last process step, that is bio filtration and was accomplished by means of a biofilter. This step is necessary in order to guarantee the achievement of a treated water to a quality grade compatible to the discharge in superficial aquifers. The adopted system is compact, have small residence times and is capable to treat the RO permeate to the target values. The experimental work will be discussed and reported in this paper.

1. Introduction

Olive oil production is one of the main agriculture activities in many Mediterranean countries, that give rise, in case of the 3 phase production process, to the by-production of large quantities of wastewaters, called olive mill wastewaters (OMW), and some solid wastes. The management, treatment and safe disposal raise serious environmental problems. The characteristic properties of OMW include its dark color, strong odor, acid pH and high organic content, mainly composed by pollutants such as polyphenols that may exhibit antimicrobial, ecotoxic and phytotoxic properties, and that are the main responsible to generally not permit the treatment by biotechnologies. Moreover, olive oil production is a seasonal activity and a huge amount of OMW are produced in the framework of some months, making a storage of the wastewater costly.
A medium sized olive oil mill produces around 10 m^3/day of OMW, which represents a major threat for the environment and high cost for its disposal, and is associated to an equal amount of potable water consumption. Type of olives, area under cultivation, the use of pesticides and fertilizers, the climate conditions, the harvest time and the harvest year are factors that may change the quality of OMW sensibly.
A treatment process of OMW must therefore be very flexible concerning capacity, capable to uptake high incoming flow rate values for short period of time, and selectivity, due to the changing nature of the feedstock within and between the different olive harvest location and time.

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Membrane processes is one of the most promising treatment processes for OMW. Only a small amount of concentrates (waste) are produced, reducing the initial volume of OMW down to 10%. The permeate stream generally reaches a quality near the legal discharge in municipal sewer system, making the disposal of the wastewater cheap. The main problem of membranes is that fouling may occur, leading to a reduction of the membrane efficiency. It is necessary to try to remove these substances by means of some pretreatment processes and to control the operating conditions to inhibit fouling formation.

Nowadays, proper membrane process design can be a difficult task to accomplish when fouling is present and must be considered. The presence of fouling, and the consequent reduction of permeate fluxes as a function of time, forces the designer to over-design the membrane plant in order to guarantee sufficient operating autonomy to conduct the process for a certain period of time at or above the permeate project values (Saad, 2005). In most cases the over-design is performed a forfeit or by past experience of the designer, starting only from the knowledge of the permeate project value, without considering in detail the entity and nature of fouling. Some examples of existing overdesigned membrane plants are reported in bibliography, when membranes are used as stand-alone technology (Hassan et al., 2010) or in combined processes such as membrane bio-reactors (Pirokova, 2006). In other cases, even worse, engineers underdesign the membrane plant, depending on higher operating conditions, which are not sustainable for long period of time.

For liquid-liquid separation processes, (Field et al., 1995) introduced the concept of critical flux for microfiltration, stating that there is a permeate flux below which fouling is not promptly observed. Afterwards, it was possible to identify critical flux values on ultrafiltration (”UF”) and nanofiltration (“NF”) membranes systems, too (Mänttäri and Nystörm, 2000). Nowadays, the critical flux concept is well accepted by both scientists and engineers as a powerful membrane process optimization tool as long critical fluxes apply. In case of most real waste water streams (Le Clech et al., 2006) noticed that operations below the critical flux may not be sufficient in order to have zero fouling rates. To overcome this limitation in the definition of critical flux, in a recent paper, (Field and Pearce, 2011) introduced for the first time the concept of the threshold flux. Summarizing briefly the concept, the threshold flux is the flux that divides a low fouling region, characterized by a nearly constant rate of fouling, from a high fouling region, where flux dependant high fouling rates can be observed. Finally, some research on this topic by using olive mill wastewater streams was performed, both exiting the 2-phase with (Ochando-Pulido et al., 2014) and without (Ochando-Pulido and Stoller, 2014) and the 3-phase olive oil production processes, again with (Stoller et al., 2014) and without (Stoller and Ochando-Pulido, 2012) pretreatment processes. As a research output, the Authors merged the two separate concept together, pointing out their mathematical and qualitative similarity, into the concept of the boundary flux (Stoller and Ochando-Pulido, 2014). Moreover, the relationship between a proper pretreatment tailoring and boundary fluxes was further investigated by using coagulation and photocatalysis as a pretreatment step, by adopting magnetic core (Ruzmanova et al., 2013a) or doped titania nanoparticles (Ruzmanova et al., 2013b)

But all the adopted pretreatment processes and membranes may not be sufficient: after treating OMW by filtration, adsorption, coagulation, gridding and settling as suitable pretreatments and membranes to remove solids, color, odor and certain classes of compounds like polyphenols in OMW, thus reducing the initial polluting load considerably, the output stream may not meet discharge limits. In this case, further effluent mineralization usually requires chemical, further physicochemical and/or biological oxidation methods. In this work, for the first time, the use of biofilters will be adopted as a final addition to the treatment process of OMW as a cheap and cost effective alternative able to guarantee if necessary the desired purification targets.

2. Experimental

The proposed process to treat OMW is as follows (Stoller, 2013):

Gridding: This technique is used to separate coarse particles higher than the cut-size (300 micron).

Coagulation: During operation the charge of the suspended fine particles are destabilized. Coagulants with charges opposite to those of the suspended solids are added to the water to neutralize the negative charges on dispersed solids such as clay and organic substances. Once the charge is neutralized, the small-suspended particles are capable of sticking together. This process leads to the formation of larger particles called flocks capable to sediment. The choice of the chemical coagulant depends upon the raw water conditions, the nature of the suspended solid to be removed, the cost of the amount of chemical necessary to produce the desired result and the facility design. In this work, nitric acid (HNO_3) was used as a coagulant in order to avoid further addition of metal salts to the waste water stream.

Sedimentation: The created flocks in the vegetation water have to be settled out before continuing the treatment, performed by a 24h long lasting sedimentation step. The sludge formed by this process is removed from the bottom of the tank.

Ultrafiltration (UF): as a first separation step of finer suspended solids.
Nanofiltration (NF): as a second separation step of organic matter macromolecules.
Reverse Osmosis (RO): as a last separation step to eliminate salts and ions.

The used pilot plant is shown schematically in Figure 1.

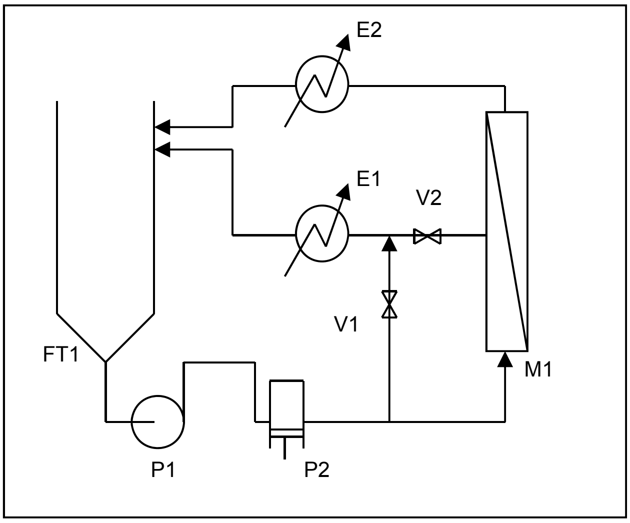

Figure 1: The scheme of the pilot plant

The plant consists of a 100 liter feed tank FT1, in which the pretreated feedstock is carried. The centrifugal booster pump P1 and the volumetric pump P2 drive the wastewater stream over the used spiral wounded nanofiltration membrane, supplied by Osmonics, fitted in the housing M1, at an average flow rate equal to 600 l/h, the maximum one that can be obtained constantly on this system.
The membranes, ultrafiltration model GM2540F, nanofiltration model DK2540F and reverse osmosis model SC2540F, are characterized by a mean pore size value of 2nm, 0.5 nm and no pores, respectively. All modules were used for more than 1000 h of operation time. The active membrane area of one module is equal to 2.51 m^2 and the maximum allowable operating pressure is equal to 16bar, 32 bar and 80 bar for UF, NF and RO, respectively. Acting on the regulation valves V1 and V2 it is possible to set the desired operating pressure P_{EXT} over the membrane maintaining the feed flow rate constant with a precision of 0.5 bar.
Both permeate and concentrate streams are cooled down to the feedstock temperature, mixed together and recycled back to the feedstock. In this way, the feedstock composition is kept constant during each experimental batch run. The temperature was controlled for all experiments at the value of 20°C ± 1°C.
After each experiment the membrane was rinsed with tap water at least 30 min. If not necessary, the membrane module was stored directly in the membrane housing filled with fresh tap water, else put in a fresh tap water filled external storage tank.

Biofilter: this treatment step is necessary if membranes alone were not capable to meet the requirements of purification. The last pollutants, generally dissolved small chained organic molecules in the RO permeate, are eliminated by means of biomasses which may successfully purify the stream since all the phytotoxic substances (in first line polyphenols) were separated beforehand.

3. Results and Discussion

After gridding the OMW was processed by the coagulation process. Table 1 reports the obtained results in terms of some key parameters, such as COD (Chemical Oxygen Demand) and pH.

Table 1: Results obtained after coagulation

Stream	COD [g/l]	ΔCOD	pH	Volume [l]
Initial OMW	21.83		4.2	40
OMW after coagulation	12.50	42.7%	3.0	35

The obtained results are in line with those reported elsewhere. Up to 80 ml of nitric acid were used for the required acidification of the initial 20 liters of OMW.
The supernatant was then processed by membranes. The measurement of the boundary flux is key to operate the membrane process without promoting the formation of irreversible fouling. The boundary flux J_b divides the operation of membranes in two different regions: a lower one, where no or a small, constant amount of fouling triggers, and a higher one, where fouling builds up very quickly. In case of sub-boundary flux conditions, eq.1 holds:

$$dm/dt = - \alpha; \; J_p(t) \leq J_b \qquad (1)$$

where α, expressed in [L h^{-2} m^{-2} bar^{-1}], represents the constant permeability reduction rate suffered by the system and will be hereafter called the sub-boundary fouling rate index. α is a constant, valid for all flux values. For each step, boundary flux measurements were performed. The measurement was performed by following the indications reported by Stoller and Ochando-Pulido (2015). The obtained results were shown in Table 2.

Table 2: Results obtained by membranes

Stream	Jb [l/hm^2]	α [l/h^{2}m^{2}bar]	COD [g/l]	ΔCOD total	Volume [l]
UF feed	-	-	12.50	42.7%	35
UF permeate / NF feed	3.83	1 10^{-4}	11.80	45.8%	20
NF permeate /RO feed	5.70	3 10^{-5}	7.60	65.1%	15
RO permeate	6.92	9 10^{-3}	1.82	99.1%	10

A main difference to recent previous works was the elimination of the cost inefficient photocatalysis step as a pretreatment process to OMW (Stoller et al., 2013a). As a consequence, the obtained final value of COD of the RO permeate, that is 1828 mg L^{-1}, is rather high and do not allow the discharge of the purified water either in municipal sewer systems (limit equal to 500 mg L^{-1}) nor superficial aquifers (limit equal to 125 mg L^{-1}). Therefore, additional treatment is required. In Figure 2, a photograph of the obtained samples during the experimental work were shown.

Figure 2: Photograph of the obtained samples
(from left to right: raw OMW, after coagulation, UF permeate, NF permeate, RO permeate)

In this work as an additional post-treatment process biofiltration was adopted. The biofilter was of cylindrical shape, having 40cm and 19cm of high and diameter, respectively. The effective liquid volume in the reactor was equal to 2L. Moreover, some adhered biomass was stitched to an immersed support in the liquid; temperature and oxygen concentration was controlled by a control system at a set-point of 25°C and 8-9 mg L^{-1}, respectively. The feed flow rate of OMW was continuously fed to the biofilter and equal to 500 mL day^{-1}. The performances of the biofilter were evaluated by analysis of one sample each day at different residence times. The constant characteristics of the feed stream and obtained results of this preliminary work on the biofilter were reported in Table 3.

Table 3: Results obtained by the biofilter

Residence Time [days]	FEED	1	2	3
pH	4.0	5.9	7.2	7.0
COD [mg L^{-1}]	1828	1227	594	529
COD reduction [%]	0.0	16.1	59.3	63.8

The biofilter performances were promising. After 2 days of residence time, one of the highest COD values of the RO permeate in years of research encountered here, that is 1828 mg L^{-1}, were sensibly reduced in the 500 mg L^{-1} range. RO permeates in past experimental works were as high as 1000 mg L^{-1}, therefore the biofilter appears generally capable to achieve the result to have a purified water stream exiting the process well below 500 mg L^{-1} within 2 days of operation.

Although RO was not capable to meet the purification requirements, this process eliminates all the polyphenols from the permeate stream, thus permitting the subsequent biological operation without the presence of phytotoxic substances leading to a biofilter to work efficiently and characterized by high performances. This technique appears therefore promising to qualify as a proper, cheap post-treatment process to membranes to meet disposal requirements, and will be further investigated in the next months. This appears to be an important progress compared to previous adopted methods such as photocatalysis towards overall cost reduction of the process (Stoller et al., 2013a).

4. Conclusions

The proposed treatment process based on coagulation, membranes technology and biofilter appears to be suitable to purify olive mill wastewater streams at least to a grade compatible to the discharge in the municipal sewer system. This may be possible as soon as the RO permeate exhibits COD values lower than those encountered during this work. A COD value of 1500 mg L^{-1} of the RO permeate should be sufficient to guarantee success. Operating the membrane processes below boundary flux conditions permits long period operations assisted by a periodical washing with water without addition of cleaning chemicals. The boundary flux values are sensibly increased by the proposed pretreatment process, that is coagulation.

The addition of the biofilter as a post-treatment process to the RO membrane is strongly suggested and possible since all phytotoxic substances, such as polyphenols, were removed. In the next future, the processes will be optimized to target a total purification of OMW compatible to the disposal in superficial aquifers.

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