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On the optimization of a flocculation process as fouling inhibiting pretreatment on an ultrafiltration membrane during olive mill effluents treatment

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HIGHLIGHTS

- Flocculation process UF pretreatment was examined for suspended solids (TSS) removal.
- Modelization and optimization of pretreatment process are addressed at pilot scale.
- Statistical multifactorial analysis shows pH and temperature influence TSS removal.
- Optimized parameters 21.4 °C and pH 2.2 yield 98.4–98.6% TSS reduction.
- Boundary flux 9.7 L/hm^2 and significant fouling reduction ($3.4\cdot10^{-2}$ min^{-1}) ensured.

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ABSTRACT

In this work, a simple and cost-effective pretreatment upstream an UF membrane operation for the purification of the main olive mill effluent streams (OME) is examined. The raw wastewater was processed by a pH-temperature (T) flocculation process formerly studied at lab scale in previous work. In the present paper, modelization and optimization of the pretreatment process are addressed at pilot scale. Statistical multifactorial analysis showed both pH and T remarkably influence the suspended solids concentration removal efficiency (p-value practically equal to zero), confirming a statistically significant relationship between the variables considered at 95% confidence level. Moreover, the pH exhibits a deeper influence than the T, according to the p-values withdrawn from the analysis, and the squared effects are significant too, but more significant in the case of the pH. Contour plots and response surface support the previous results, and the optimized parameters were 21.4 °C and pH equal to 2.2, yielding 98.4 − 98.6% TSS reduction and 90.5% *v*/*v* recovery of clarified water. Finally, a boundary flux value of 9.7 L/hm^2 and a significant reduction of the fouling index ($3.4\cdot10^{-2}$ min^{-1}) were ensured, and a permeate stream reusable for irrigation, boosting the cost-efficiency of the integral process.

1. Introduction

Membrane fouling is a problem of cost efficiency, especially in wastewater treatment applications, which must imply low operating costs. Appropriate fouling inhibition methods should assure this result, thus making membrane processes for the treatment of residual liquid effluents both technically and economically feasible.

The use of membranes for the treatment of wastewater streams began several decades ago. However, initially the technology was not capable of maintaining the performances as a function of time, mainly due to membrane fouling. The consequence was a lack of confidence in membrane technologies during the last two decades. The recent availability of new membrane materials, membrane design methods, module configurations and the improvement of the know-how in general, and in particular on membrane fouling mechanisms, has permitted membrane technologies gain credibility among engineers and investors for wastewater treatment purposes. Moreover, the rapid boost of wastewater volumes produced worldwide is opening a new market for membranes, which have a significant potential to take the role as the leading technology for these applications. In fact, today an increasing number of municipal wastewater treatment facilities are using membrane technologies, and this number is growing every year [1,2]. Membrane processes exhibit high selectivity values required to achieve high water quality standards, are more cost-effective than other conventional processes, require less area and can replace several treatment units by a single one.

In particular, ultrafiltration (UF) membranes have nowadays replaced a wide range of conventional separation operations in wastewater treatment processes, from very different sources including metalworking industry [3], oil field [4], refinery wastewater [5], pulp and

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paper [6], textile wastewater [7], dairy effluents [8], protein production [9], olive mills wastewater [10–12], restaurant wastewater [13] and municipal sewage [14], among others.

In order to successfully design a membrane process for a specific application at industrial scale, the constancy of the performances is mandatory. The difficulty in achieving this task is due to the deleterious fouling phenomena occurring over the membrane dynamically during the operation time, which reduce the membrane performances as a function of time.

Membrane fouling is complex, and may involve pore blocking, plugging and clogging, chemical degradation and/or cake formation on the membrane surface caused by microorganisms, organic matter and inorganic material [15,16]. The result is always a reduction of the membrane performances in terms of permeability, selectivity and longevity.

The presence of fouling, and the consequent reduction of the membrane productivity as a function of time, force engineers to over-design the membrane plants in order to guarantee the conduction of the processes for a certain period of time at or above the permeate project target values [17].

The feed stream composition is the main responsible of ever changing flux values, and this is especially true for agricultural wastewater streams treatment by membranes, since the entering feedstock composition is not constant during the campaign. Furthermore, the use of batch membrane processes in order to limit the amount of required membrane area, and thus saving investment costs, leads to sensible feedstock load changes during operation.

In this regard, olive mill effluents (OME), generated during the industrial production of olive oil in so called olive mills, contain high concentrations of a wide range of solutes in the form of suspended solids, dissolved matter and colloidal particles which are all very prone to cause membrane fouling, such as organic pollutants, as well as inorganic matter that may also lead to deleterious scaling problems [18–25].

Direct treatment by membranes of raw effluents has been reported to lead to rapid emergence of membrane fouling build-up [26–29]. Appropriate fouling inhibition methods should be designed upstream the membrane operation, in order to make the membrane processes for wastewater treatment both technically and economically feasible [20,25,30–32].

In this research work, a simple and cost-effective pretreatment upstream an UF membrane operation for the purification of the main olive mill effluent streams (OME) of olive oil factories is examined. The raw wastewater was processed by a pH-temperature (T) flocculation process formerly studied at lab scale in previous work by the Authors [12].

The core of the present paper is the optimization and modelization of the proposed pretreatment process, addressed at pilot scale. For this purpose, a factorial design was applied for the optimization of the pH-T flocculation pretreatment, and the results were interpreted with the response surface methodology. A statistical multifactorial analysis with the aim of quantifying all the possible complex conjugated effects of the input parameters considered in the pH-T flocculation process was performed. The process was also successfully modelized by means of a second-grade quadratic fitting model equation. Ulteriorly, the boundary flux theory, successfully validated by the Authors in previous works [33–35], was used to assess the operating conditions for the subsequent UF batch membrane operation, and the results were contrasted with the treatment of raw and untreated OME. Finally, the parametric quality standards to reuse the purified effluent for irrigation purposes were checked.

2. Experimental

2.1. Effluent stream

For this research work, samples of the two main residual liquid effluents by-produced in two-phase centrifugation technology-based olive mills were taken in the Andalusian provinces of Jaén and Granada, which are the main producers of olive oil in Spain and thus the most representative. Samples of olives washing wastewater (OWW) were directly withdrawn from the olives washing machines, and olive oil washing wastewater samples (OOW) were taken at the outlet of the vertical centrifuges. Thereafter, both effluents were mixed in 1:1 *v*/*v* proportion for their subsequent treatment. The physicochemical characteristics of both effluents and the mixed stream (OMW) are hereafter reported in Table 1.

2.2. Pilot-scale flocculation plant and experiments proceeding

The raw wastewater stream was processed by a solid/liquid (S/L) separation process formerly studied at lab scale in previous work by the Authors, based on flocculation by adjusting the pH and temperature (T) conditions (pH-T flocculation) [12]. In the present work, experiments were performed with the aim of optimizing the pH-T flocculation process at pilot scale.

The flocculation process was carried out in a pilot scale tank (vertical cylindrical vessel with flat bottom) with dimensions 0.2 m diameter × 0.8 m height (approximately 25 L capacity), provided with an overhead impeller stirrer. Samples of 20 L of OMW were poured into the flocculation tank. Experiments were conducted at different pH values ranging from 2 up to 7 by using 70% *w*/*w* HNO_3 and 1 N NaOH, respectively, at different temperature values (15, 25 and 40 °C). During all pH-T flocculation experiments, a starting high stirring rate mixing was set (90 s, 1000 rpm), followed by a slower stirring for a longer period of time (20 min, 320 rpm). The initial quick mixing stage aimed to promote uniform dispersion of the flocculant and particles collisions, whereas the subsequent weak mixing was focused on ensuring the ideal conditions for the movement of the flocks in suspension, without destroying them.

Once the mixing was completely stopped, the sample was left to settle for 24 h, after which the mud was extracted from the bottom of the flocculation tank and finally dried, in order to calculate the sludge fraction and the fraction of clarified water (% *v*/*v*). In addition to this, the achieved reduction of suspended solids was measured in the clarified supernatant at the end of the pilot-scale experiment.

2.3. Pilot-scale membrane plant and filtration procedures

The membrane pilot plant, as shown schematically in Fig. 1, was provided with a 100 L feedstock tank (FT_1), where the pretreated OMW stream was loaded through a feed line. A pumping system consisting of a centrifugal booster pump (P_1) and a volumetric piston pump (P_2) was available to drive the wastewater stream to the spiral-wound (SW) membrane module fitted in housing M_1.

The desired operating pressure within the membrane module and the feed cross-flow rate could be set by acting on regulation valves V_1 and V_2, with an accuracy of 0.5 bar and 10 L/h, respectively. The operating pressure and the feed flow rate were respectively measured by analog manometers and a turbine flow meter. The permeate flux was gauged during the operation time by continuously weighing the mass of collected permeate on a precision electronic mass balance (AX-120

Table 1
Physicochemical composition of raw OWW, OOW, and 1:1 (*v*/*v*) mixture (OMW).

Parameters	OWW	OOW	OMW
pH	6.4 ± 0.1	4.8 ± 0.2	6.1 ± 0.2
EC, mS/cm	1.5 ± 0.2	2.5 ± 0.1	1.8 ± 0.1
TSS, g/L	10.4 ± 1.3	2.9 ± 0.9	6.5 ± 0.9
COD, g/L	0.8 ± 0.1	7.3 ± 0.1	4.2 ± 0.1
TPh, mg/L	2.4 ± 0.9	166.9 ± 4.2	84.6 ± 2.5

EC: electroconductivity; TSS: total suspended solids; COD: chemical oxygen demand; TPh: total phenol.ic compounds.