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Membrane process enhancement of 2-phase and 3-phase olive mill wastewater treatment plants by photocatalysis with magnetic-core titanium dioxide nanoparticles

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ABSTRACT

In this work, the benefit of using photocatalysis as a pretreatment step for a subsequent olive mill wastewater (OMW) treatment process by membranes will be discussed.

Membrane processes appear to be suitable to purify aqueous wastewater streams polluted by organic matter such as OMW, but suffer severe fouling. In order to avoid fouling, the use of operating conditions below the boundary flux is suggested. The problem is that in many cases, boundary flux values are extremely low, making the process economically not feasible. In order to overcome this limitation, pretreatment steps are necessary to increase boundary flux values accordingly. Photocatalysis appears to be capable to achieve these requirements: on one hand, the process is capable to reduce the organic load of the feedstock and on the other hand, particle size distributions of the suspended organic matter are changed. Both principles are known in literature to lead to boundary flux value changes.

In this paper the authors report the obtained results of the experimental work concerning photocatalysis and membrane performances.

Introduction

As an indication of the popularity of membrane fouling problems, the growing evolution over the last 5 years has led to more than 3000 papers published in international journals trying to satisfy this research criteria [1]. Despite this incredible effort by researchers, the reduction of membrane fouling remains nowadays one of the main challenges of the broad applied membrane technology [2]. The reason for this is that fouling on membranes does not only lead to sensible investment losses, due to the need of a premature module substitution, but also gives rise to unexpected increases of investment costs during the development and design of membrane plants: therefore engineers tend to design membrane processes with an excessive oversized capacity, up to 35% [3].

This applies especially on wastewater purification processes [4]. This latter situation has a great economic impact on the process since the permeate, that is purified water with a quality grade compatible with irrigation use, has limited economic value.

Field et al. [5] introduced the concept of critical flux for microfiltration (MF), stating that there is a permeate flux below which fouling is not promptly observed. It was immediately clear that the new developed concept could be a powerful optimization tool for this kind of separation operations. Afterwards, it was possible to identify critical flux values on ultrafiltration (UF) and nanofiltration (NF) membranes systems, too [6]. Nowadays, the critical flux concept is well accepted by both scientists and engineers [7].

The main drawback of this concept is that the determination of critical flux values cannot be theoretically predicted, but only experimentally measured by time consuming experiments. Critical flux depends on various factors, such as hydrodynamics, feed stream composition and membrane surface characteristics [8–12]. In many cases, concerning agricultural wastewater streams, the entering feedstock quality is not constant during time. Moreover, batch membrane processes are preferred in order to limit the amount of required membrane area, and the overall investment costs, as well. Again, during the batch operation, the feedstock quality sensibly changes. As a consequence, critical flux values never remain constant, which represent a major difficulty in fine-tuning optimal operating conditions.

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In case of real wastewater streams Le Clech et al. noticed that operations below the critical flux may not be sufficient in order to have zero fouling rates [13]. Therefore it appears that membrane systems treating real wastewater streams do not exhibit a critical flux in strict way. To overcome this limitation in the definition of critical flux, in a recent paper, Field and Pearce introduced for the first time the concept of threshold flux [14]. Summarizing briefly the concept, the threshold flux is equal to the permeate flux above which short-term fouling can be observed and below it only long-term fouling is triggered.

In the past years, before the concept of the threshold flux was introduced, many papers on olive vegetation wastewater (OVW) purification by membranes, mainly UF and NF, always determining critical fluxes, were published by the authors [15–19]. Irreversible fouling arises quickly on the membranes due to the high concentration of pollutants when wastewater is purified without any pretreatment, and different pretreatment processes influence to a variable extent the critical flux values [20–22]. Therefore, proper and optimal designed pretreatment processes on the given feedstock must be developed in order to maximize productivity and minimize fouling: this objective will be referred from now on as the concept of pretreatment tailoring of membrane processes. The Authors observed in previous research works the change of the fouling regime by using olive mill wastewater [19,20,23]. Despite the applied optimization methods were based on modified critical flux measurements, before the threshold flux concept ever existed, successful fouling control was accomplished on this system, and in detail justified by means of the threshold flux in 2013 [24].

In fact, critical and threshold flux concepts share many common aspects which merge perfectly into a new concept, that is the boundary flux and was introduced 2013 by the authors [25]. Increasing the boundary flux values, thus the process productivity values without triggering severe membrane fouling, appears to be mandatory to reach the economic feasibility of the treatment process.

In case of OMW, pretreatment processes are necessary to achieve this result. Beside gridding and flocculation, on the basis of the data reported in this paper, photocatalysis appears suitable to sensibly help reach these results. In order to achieve economic feasibility of the process, the recovery of the catalyst has to be taken into account, since immobilized systems may not be used due to the high opacity of the wastewater. This fact restricts to operate with suspended photocatalitic particles. For this purpose, magnetic core titania particles were developed, capable to be recovered by means of a magnetic trap. The produced particles have a dimension in the range of tens of nanometers, in order to maximize their efficiency due to the high surface to volume ratio they exhibit [26].

In this work, both wastewater streams exiting 2-phase (OMW2) and 3-phase (OMW3) olive oil production processes were taking into account.

Experimental

The olive mill wastewater stream

Olive mill wastewater is a heavy polluted liquid stream exiting the olive oil production process. In case of OMW3, it is characterized by an acid value (pH value equal to 4), very high COD value (up to 200 g L^{-1}) and a high concentration of phenols (up to 10 g L^{-1}). A medium sized olive oil mill gives rise to several tenths of cubic meters per day of this wastewater, which represents a major threat for the environment, a great cost for its disposal and a huge amount of potable water consumption. This wastewater has antimicrobial and phytotoxic properties, cannot be disposed throughout the years for irrigation purpose and is resistant to biological degradation, thus biological treatment is a hard task and right now not applied in a large scale. Moreover, irreversible fouling quickly arises on the membranes due to the high concentration of pollutants when the wastewater is purified without any pretreatment, and zero flux conditions are met within days of operation. The same applies to OMW2, although this wastewater stream is less polluted.

At the beginning, OMW2 and OMW3 were subjected to a roughing step by means of sieving with cut-size equal to 300 μm in order to remove thick materials and coarse particles. In Table 1, the average composition values of the wastewater streams are reported. Considering that in the two-phase olive oil extraction process water injection is only practiced in the final vertical centrifugation step, the volume of liquid effluent derived from the decanting process (OMW2) is reduced by one third on average if compared to the amount required for the three-phase system. Moreover, much of the organic matter remains in the solid waste, which contains more humidity than the pomace from the three-phase system (60–70% in two-phase systems *vs*. 30–45% in three-phase ones, OMW3) and hence OMW2 exhibits lower pollutants degree, too [27] (Table 1).

Pretreatment processes

The wastewater streams were then processed by a flocculation process, based on adjusting the pH and temperature (*T*) values (pH-T flocculation).

Laboratory scale experiments were first carried out in order to find the best pH and temperature conditions for the flocculation process. Samples of 200 mL of OMW2 and OMW3 were poured into 0.5 L beakers fitted with magnetic stirring. Experiments at different pH values ranging from 2 up to 7 by using 70% w/w HNO_3 and 1 N NaOH, respectively, and different temperature values (15, 25 and 50 °C) were performed and the results are reported elsewhere [28].

The optimized flocculation process was therefore carried out on a pilot scale tank with dimensions 0.2 m diameter × 0.8 m height (approximately 25 L capacity) at a starting high stirring rate mixing (90 s, 1000 rpm) followed by slow stirring for a longer period of time (20 min, 320 rpm), at pH equal to 2.5 and 25 °C (ambient temperature, thus no additional costs of cooling).

The photocatalyst production process

The production process of the photocatalyst, developed in the framework of the European project PHOTOMEM (Contract FP7-SME-2010-1 no. 262470), was performed in three subsequent steps. First, magnetite was produced by using a spinning disk reactor (Fig. 1) at 1440 rpm. This technology allows obtaining nanomaterial by a chemical precipitation process continuously. Two reactants were used: on one side an aqueous solution of $FeCl_3$, HCl and Na_2SO_3 and on the other side an aqueous solution of NH_4OH. As pointed out previously by Stoller et al. the location of the feed points over the disk influences the precipitation outcome [26]. In this case, the first reactant was fed at the center of the disk, whereas the second one was injected at 2 cm of distance.

The second step consists of a coating of silica by a sol–gel procedure, performed by adding the dried magnetite particles to a

Table 1
Composition of raw OMW2 and OMW3 after gridding.

Parameters	OMW2	OMW3
pH	4.9–5.1	5.1–5.2
EC (mS cm^{-1})	1.76–1.84	6.33–6.37
Tss (g L^{-1})	3.1–5.8	32.6–33.0
COD (g L^{-1})	16.4–16.6	32.1–32.4
TPh (mg L^{-1})	181–184	915–921