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On the cleaning procedure of a hydrophilic reverse osmosis membrane fouled by secondary-treated olive mill wastewater

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HIGHLIGHTS

- Cleaning protocol examined for reverse osmosis membrane fouled after OMW treatment.
- HR-SEM analyses of fouled membrane reveal colloidal iron, scaling and organic fouling.
- Citric acid followed by NaOH + SDS (0.1% w/v) provided maximum cleaning efficiency.
- 30–35 °C and 4.01 m s^{-1} tangential velocity for 20–25 min were optimum variables.
- Complete restoration of membrane permeability successfully achieved.

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ABSTRACT

The membrane cleaning protocol has a major importance to permit the economic feasibility and reduce the environmental impacts of industrial scale membrane processes, especially in the treatment of highly polluted industrial effluents like olive mill wastewater (OMW), which typically implies deleterious fouling problems on the used membranes. In the present study, the most adequate cleaning protocol was examined for a hydrophilic reverse osmosis (RO) membrane fouled by organic and inorganic matter after the treatment of OMW previously subjected to a secondary treatment (OMWST). The HR-SEM microphotographs of the fouled RO membrane layer reveal the presence of organic fouling as well as inorganic deposits in the form of residual colloidal iron and scaling mainly due to calcium carbonate, chloride and sulfate. This is supported by the positive saturation index value (0.44–0.90) and the elemental microanalyses performed on the fouled membrane surface. The physical cleaning did not achieve a significant recovery of the initial permeability of the RO membrane. An integrated alkaline-detersive plus acid cleaning procedure consisting in two cleaning stages in series, that is, (i) acid cleaning with citric acid followed by (ii) alkaline-detersive cleaning with NaOH + SDS solution, provided the maximum cleaning efficiency upon 0.1% (w/v) dosage. Finally, by performing the cleaning procedure upon turbulent tangential velocity over the membrane (4.01 m s^{-1}, equivalent to $N_{Reynolds} = 2.1 \cdot 10^4$) at a cleaning operating temperature ranging from 30 to 35 °C during 20–25 min, complete restoration of the membrane permeability was successfully achieved.

1. Introduction

In the recent years, membrane technology has gained ground to classic separation processes in water purification and industrial wastewater reclamation treatments as a result of the development of novel membranes, capable of offering improved technical and economical performances. In particular, reverse osmosis (RO) membranes permit complying with the most stringent regulations for public health and environment protection. RO membranes have already been applied in the management of industrial effluents of very different sectors, such as stainless steel [1], energy cogeneration [2], nuclear-power [3], textile [4,5] and agro-food industries [6–8], among others.

However, membrane fouling remains still today as the main challenge of this broad applied technology, especially in the case of wastewater treatment membrane applications [9–11]. Membrane fouling depends on several factors, and so does the membrane cleaning procedure, comprising the membrane morphology, that is, its surface chemical nature, roughness and mean porosity, as well as the feedwater composition including the pH, ionic strength and divalent ions concentration, the organic matter load and the particle size distribution, and the operating

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conditions, such as the applied net driving pressure, the crossflow velocity (turbulence) over the membrane and the temperature [6].

During operation, the build-up of the fouling layer causes permeate flux loss that leads to an increase in the energy costs to maintain the target permeate production, as well as in the operating expenses due to frequent plant shut-downs for in situ membrane cleaning. The fouling resistance can be divided into reversible and irreversible fouling according to the attachment strength of the foulants to the membrane surface. Reversible fouling is caused by loosely attached foulants easily removable by strong shear force or washing (physical cleaning). Otherwise, irreversible fouling is caused by strong attachment of foulants such as pore blocking and plugging, cake, gel and biofilm, and frequently leads to irretrievable membrane life shortage. Irreversible fouling removal by such physical control methods may be difficult in most cases and hence physicochemical, biological or enzymatic cleaning will be needed.

The membrane cleaning protocol is an integral part of the membrane system that may need long procedure times as well as chemicals consumption, and it also might cause corrosion in the system and membrane degradation, thus it has a major importance on industrial scale membrane process operations [12]. Optimization of the membrane cleaning procedure is therefore essential to permit the economic feasibility and reduce the environmental impacts of membrane processes.

The cleaning procedure should be tailored to the specific membrane-foulant system, and normally a trial and error method shall be performed. The cleaning agents must be able to dissolve the majority of the fouling materials and remove them from the membrane layer without causing surface damage [12]. Among the characteristics that the selected cleaning reagents should present we should pin-point low cost, safety and chemical stability, as well as the ability to be removed with water.

The cleaning reagents may interact with the foulant to weaken the cohesion forces between the foulants along with the adhesion between the foulants and the membrane surface. The chemicals should (1) loosen and dissolve the foulants, (2) keep the foulants in dispersion and solution form, (3) avoid triggering new fouling (secondary fouling) and (4) not attack either the membrane or other parts of the system. In detail, the cleaning reagents can affect the fouling materials present on the membrane surface in different ways, such that foulants may be removed, morphology of foulants may be changed (swelling, compaction) and/or surface chemistry of the deposit may be altered. The possible reactions between the foulants and the cleaning agents comprise hydrolysis, peptization, saponification, solubilization, dispersion (suspension) and chelation [12–14].

The aim of this study was to address the most adequate cleaning protocol for a hydrophilic RO membrane fouled by organic and inorganic materials after the RO treatment of olive mill wastewater (OMW), which typically implies deleterious fouling problems on the used membranes [6–8,10,11]. OMW was previously subjected to a secondary treatment (OMWST) comprising sequentially Fenton-like reaction, flocculation-sedimentation and olive stones filtration, thoroughly described in previous work [7,15,16]. In this regard, pretreatments specifically tailored to the membrane-feedstock binomium have been highlighted to be essential for fouling inhibition protocols, given that direct treatment of the raw effluents by membranes has been reported to lead to critical fouling build-up [6–8,10–12].

A medium-sized modern olive oil factory gives rise on average to more than 10 m^3 of OMW daily, which means not only a huge amount of potable water consumption, but also a major hazard for the environment as it cannot be directly reused for irrigation purposes, and thus its disposal represents a huge cost for this industry. OMW is one of the heaviest-polluted existing agro-industrial effluents, exhibiting high toxicity given by the presence of aromatic compounds and a wide range of other organic pollutants not suitable to be biologically managed. For these reasons, OMW poses a serious environmental threat for an increasing number of regions, leading to problems in relation to odor nuisance, soil contamination, underground leakage and water body pollution.

Biological treatment of OMW is not applied currently at industrial scale because it is not efficient due to the resistance of OMW to microbial degradation [17–20]. A plethora of other reclamation practices and combined treatments have been proposed and developed, but have not led to complete satisfactory results. Among them we can highlight lagooning or natural evaporation and thermal concentration [21], treatments with lime and clay [22,23], composting [24–26], coagulation-flocculation [27–29] and electrocoagulation [30,31]. In this context, chemical remediation strategies – ozonation [32], Fenton's reagent [15,16], photocatalysis [33,34], electrochemical [35–37] and hybrid processes [38–41] – are required for the depuration of these bio-refractory wastewaters. Among them, Fenton's process appears to be the most economically advantageous since it may be conducted at ambient temperature and pressure conditions, and also due its equipment simplicity and operational ease [15,16].

The proposed scope was to find the most appropriate chemical agents and the optimum conditions for the cleaning of the RO membrane fouled by OMWST. For this purpose, the impacts of several chemicals such as acids, bases, surfactants and chelating agents were elucidated, as well as the cleaning operating conditions comprising pressure, temperature, tangential velocity and time. To the Authors' knowledge, no previous work can be found in the scientific literature on the cleaning procedure of membranes fouled after the treatment of these effluents, especially by RO.

2. Materials and methods

2.1. OMW effluent stream

During the production of olive oil, two-phase continuous centrifugation-based olive oil factories lead to the generation of two main wastewater streams, the first one from the washing of the fruit (olives washing wastewater, OWW) and the second one from the olive oil washing (olive oil washing wastewater, OOW) during the vertical centrifugation. These effluents are commonly referred to as olive oil mill wastewater (OMW) [10,11].

Samples of OWW and OOW effluents were collected from several olive oil mills in the Andalusian provinces of Jaén and Granada (Spain) during winter months and rapidly analyzed in the lab and refrigerated for further research when necessary. OWW and OOW were mixed in 1:1 (v/v) proportion to stabilize the average organic matter concentration of the effluent stream (OMW) entering the treatment system and thus avoid sensible fluctuations in the COD parameter. After this, OMW was conducted to a secondary treatment on a pilot scale described in detail in former works by the Authors [15,16]. The OMW effluent after the secondary treatment, hereafter referred as OMWST, was the feedstream to the final RO stage [6,7], and presents the characteristics reported in Table 1.

2.2. Membrane plant, membrane module and RO operation

The bench-scale membrane plant (Prozesstechnik GmbH, Basel, Switzerland) used for the final purification of OMWST and the operating procedure is fully described elsewhere [6,7]. The nominal characteristics of the commercial flat-sheet (200 cm^2 active area) thin-film composite (TFC) RO virgin membrane used in the experiments, provided by the manufacturer (GE Water and Process