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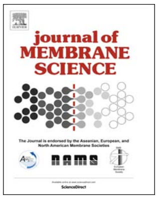

Electro-oxidation as efficient pretreatment to minimize the membrane fouling in water reuse processes

Rafael Gonzalez-Olmos*, Aida Penadés, Gerard Garcia

IQS School of Engineering, Universitat Ramon Llull, Via Augusta 390, 08017 Barcelona, Spain

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ABSTRACT

The effluent from a wastewater treatment plant was pretreated with an electrochemical cell using boron doped diamond (BDD) electrodes in order to control the fouling of an ultrafiltration membrane. The results showed that the electrochemical pretreatment decreased 36–67% the transmembrane pressure (TMP), and consequently the membrane fouling, with increasing applied current densities. The removal of dissolved organic carbon (DOC) and turbidity by the membrane process was enhanced 40% and 41% respectively using the electro-oxidation pretreatment. The removal of DOC in the pretreatment stage correlated well with the maximum TMP reached. The application of electro-oxidation as a pretreatment stage points out to be a promising alternative to reduce the membrane fouling and increase the water quality for water reuse applications.

1. Introduction

In the last years, in many regions with water scarcity problems such as Spain [1–3], water reclamation plants (WRP) have been constructed with the objective of reusing urban and industrial wastewater in different applications such as for recreational, agriculture or industrial uses [4]. WRPs mainly use biological processes as secondary treatment for the removal of suspended solids, organics and nutrients followed by membrane filtrations (low and high pressure) as tertiary treatment in order to produce high quality water suitable for reuse and/or reclamation purposes [5]. The most advanced WRPs include combinations of ultrafiltration (UF) and reverse osmosis (RO) [6].

One of the most important problems working with UF is the membrane fouling which is caused by the presence in the wastewater of suspended solids, microorganisms and dissolved organic matter. Suspended solids form cake layers on the membrane that are likely reversible and it can be removed through backwash cleaning, while biofouling can be controlled using chemicals such as chlorine. Then, one of the major issues of the membrane-based tertiary treatments is the irreversible fouling which results in the reduction of productivity and in the increase of backwashing and membrane replacement cost [7]. It is well known that the less charged macromolecular and/or colloidal organic components (humic acids, fulvic acids, soluble microbial products,…) in the effluent organic matter (EfOM) are the major foulants of UF membranes [8,9]. So, pretreatment strategies for the removal of these compounds is of crucial interest since it can reduce the cleaning operations and increase the operational life of the membranes [10].

Many pretreatments, such as coagulation [7], adsorption [11], ionic exchange [11] and oxidation [12–16] have been previously investigated for the removal and/or transformation of EfOM to prevent the fouling on the membranes. Among them, oxidation based on UV, H_2O_2 [16] and Ozone [12] has shown a good potential for the reduction of membrane flux decline by organic foulants. Electro-oxidation, as an effective advanced oxidation process (AOP) for oxidation of organic matter, offers many advantages over other AOP including simple instrumentation, versatility, additional chemicals such as H_2O_2 are not involved, compatibility to other unit processes, and operational flexibility [17]. Despite of all these advantages, there are not many studies about the use of electro-oxidation to prevent the fouling in membrane processes. The literature have been mainly focused on the use of electro-oxidation to treat the concentrates of RO [18–22] or nanofiltration (NF) membranes [23] with the objective of reducing the concentration of organic matter and micropollutants.

EfOM in wastewater can be degraded with electro-oxidation through three different types of mechanisms: (i) direct electron transfer to the anode surface. (ii) Reactive oxygen species (ROS) produced as intermediates of oxidation of water, including hydroxyl radical (•OH). (iii) Other weaker oxidant agents produced electrochemically from ions existing in the bulk such as chlorine, hypochlorite, persulfate, perphosphate or percarbonate [24,25].

Studies performed during the last twenty years have shown strong influence of the anode material nature on both efficiency and selectivity of electro-oxidation [24]. Typical anodes used for the removal of

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* Corresponding author.
E-mail address: rafael.gonzalez@iqs.url.edu (R. Gonzalez-Olmos).

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organic matter include lead dioxide (PbO_2), tin dioxide (SnO_2), Pt, DSA, boron-doped diamond (BDD) and substoichiometric TiO_2 electrodes. BDD electrodes are considered as the most powerful anodes for anodic oxidation, and also the most suitable due to their remarkable corrosion stability even in strongly acidic media. The extremely high O_2-evolution overvoltage on a BDD anode (2.2–2.6 V/SHE) [24,25] favors the generation of high amounts of reactive •OH in comparison with other anodes [26]. Furthermore, besides •OH formation on the electrode surface, BDD electrodes also increase mediated oxidation by other electrochemically formed compounds [25]. BDD electrodes have also other interesting properties that make their use advantageous for the treatment of EfOM over other materials: they have high chemical inertness, hardness, extended lifetime and efficient use of electrical energy [23].

This work is the first study that reports electro-oxidation using BDD electrodes as a promising pretreatment to reduce the membrane fouling in UF membranes used for wastewater reuse.

2. Materials and methods

2.1. Electro-oxidation set-up

Electro-oxidation experiments were conducted in a single compartment electrochemical cell manufactured by Waterdiam (DiaCell 106). BDD on silicon was used as anode and cathode and both were circular with a surface area of 70 cm^2 each one with 1 mm gap. The electric power required during the electro-oxidation experiments was provided by a power supply (Diaclean-PS 220VAC-48VDC) that had a maximum output of 30 A and 48 V. The electrochemical cell was operated in batch mode. The wastewater was stored in a glass tank and circulated with a flowrate of 120 $L\,h^{-1}$ in a close circuit through the electrochemical cell by a peristaltic pump (See Fig. 1). Continuous pumping and the electro-oxidation process itself caused a temperature increase of the water so, a cooler was used to keep constant the wastewater temperature at around 20 ºC.

2.2. Ultrafiltration set-up

The experimental UF set-up, which is shown in Fig. 2, was based on the experimental set-up used by Oschmann et al. [27] and in our previous study [16] to determine the fouling behavior in submerged hollow fiber UF membranes. It consists of an UF membrane module, a pump, and a pressure gauge. The membrane was placed in a feed tank filled with 2 L of wastewater. The system was equipped with a peristaltic pump which supplied the membrane with negative pressure. The pressure [transmembrane pressure (TMP)] was continuously measured by the pressure gauge and the feed solution was constantly stirred using a magnetic stirrer.

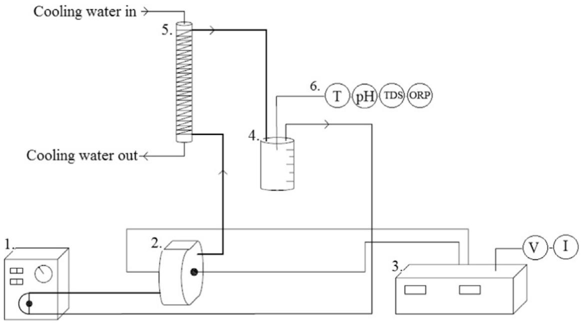

Fig. 1. Diagram of the electro-oxidation set-up: 1. peristaltic pump; 2. electrochemical cell; 3. power supply; 4. feed tank; 5. cooling system; 6. multiparameter probe.

2.3. Membrane module

A ZeeWeed®- 1 (ZW- 1) submerged hollow fiber UF module supplied by Xylem was used in this study. This module operates in an "outside-in" configuration and has a nominal pore diameter of 0.04 µm, with an effective membrane surface area of 0.047 m^2. The membrane, at the conditions of this study, had a pure water flux of 53.97 $L\,m^{-2}\,h^{-1}$ with a TMP of 0.125 bar and a clean membrane resistance of $8.34 \times 10^{11}\ m^{-1}$ The membrane was chlorine resistant and common household bleach was used for membrane cleaning at the end of each experiment. The active constituent was 3.5% sodium hypochlorite.

2.4. WWTP effluent

The WWTP effluent used in this work was collected from a wastewater treatment plant (WWTP) from Catalonia (Spain). It was collected from the outlet of the secondary clarifier in a process line without nutrient removal and it was kept at 4 ºC in the fridge during the study. The characterization of the wastewater effluent can be observed in Table 1. The effluent was used without any additional pretreatment.

2.5. Experimental procedure

Firstly, 2 L of the WWTP effluent was pretreated in batch, with the electro-oxidation system using different current densities (from 7 to 33 $mA\,cm^{-2}$) during 3 h. Samples were taken for analysis at the beginning and at different times of the pretreatment. Secondly, 2 L of the pretreated wastewater were introduced into the feeding tank of the UF set-up and the filtration was conducted at a constant flow rate of 42 $mL\,min^{-1}$ during approximately 3 h. The TMP was recorded at different times as a fouling indicator. Feed and permeate samples of the membrane were taken for analysis at the beginning and at the end of each filtration experiment. All the experiments were carried out by duplicate.

Membrane cleaning was conducted at the end of each experiment according to the following cleaning protocol. First, the membrane was aerated for 5 min in deionized water removing most of the particles. Then, the membrane was soaked in a 160 $mg\,L^{-1}$ sodium hypochlorite solution for at least 3 h followed by another backwash aeration for 5 min. After the membrane cleaning process, it was checked that the initial pure water flux was completely recovered.

2.6. Analytical methods

A multiparameter probe HI 98194 from HANNA instruments was used to measure pH, oxidation-reduction potential (ORP) and total dissolved solids (TDS). Turbidity was determined with a turbidimeter 6035 from Jenway. Dissolved organic carbon (DOC) was determined by analyzing 0.45 µm pre-filtered samples with a TOC-V CSH/CSN analyzer from SHIMADZU. UV absorbance at 254 nm (UV_{254}) was measured using a UV–Visible Spectrophotometer (UV-1280 spectrophotometer from Shimadzu) with a 1 cm path length quartz cell. The specific UV absorbance (SUVA) was then calculated as the ratio between UV_{254} and DOC.

Chemical oxygen demand (COD) was determined by the dichromate digestion method using kits from Lovibond. Total nitrogen was measured by the persulfate digestion method from Hach. NH_4^+-N concentration was determined with an ion selective electrode probe for ammonium (model ISENH418101 from Hach) and NO_3^--N and NO_2^--N concentrations were determined by the chromotropic acid and diazotization methods from Hach respectively. Phosphates were determined by the molybdovanadate method from Hach.