A study of the osmotic membrane bioreactor process using a sodium chloride solution and an industrial effluent as draw solutions

M.J. Luján-Facundo[1*], J.L. Soler-Cabezas[1], J.A. Mendoza-Roca[1], M.C. Vincent-Vela[1], A. Bes-Piá[1], S. Doñate-Hernández[2].

[1]Instituto de Seguridad Industrial, Radiofísica y Medioambiental, Universitat Politècnica de València, Camino de Vera, s/n, Valencia 46022 (Spain).

[2]Depuración de Aguas del Mediterráneo (DAM). Avenida Benjamín Franklin, 21. 46980 Parque Tecnológico, Paterna, Valencia (Spain).

Tel. +34963876386

e-mail: malufa@etsii.upv.es

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Abstract

Osmotic membrane bioreactor (OMBR) is an emerging membrane process which has gained interest in the recent years because of the low energy consumption and the high effluent quality. The osmotic membrane bioreactor combines a forward osmosis (FO) membrane and a biological treatment. However, salt reverse flux is the main problem because of the negative effect of the salt concentration increase in the reactor on the microbial activity. This is the reason why the study of a suitable draw solution (DS) is very important in the overall performance of the reactor. This study compares the process performance using two draw solutions: a 53 $g \cdot L^{-1}$ NaCl solution and a real waste water solution (waste water from an absorption column consisting mainly of SO_4^{-2} and NH_4-N with concentrations of 153 $g \cdot L^{-1}$ and 19 $g \cdot L^{-1}$, respectively). The comparison is focused on the salt reverse flux during the reactor operation, the mixed liquor characteristics, the membrane fouling and the overall performance. The results indicated that the industrial wastewater showed a higher salt reverse flux, but also a less severe fouling and a higher the osmotic pressure difference in comparison with the NaCl solution. In terms of chemical oxygen demand (COD) removal efficiencies, both draw solutions attained values higher than 80%, though the efficiency was slightly lower when the industrial effluent was used as DS. This was related to the higher conductivity reached in the bioreactor when the industrial effluent was used as draw solution. In spite of it, the use of this industrial effluent as draw solution is strongly recommended because of the high permeate fluxes yielded, the low membrane fouling and the lack of necessity of regenerating the draw solution.

1. Introduction

Water scarcity is further intensified due to climate change, high population growth, and environmental pollution. Nowadays, it already affects billions of people around the world [1]. Overall, efforts for developing and improving novel wastewater treatments and reclamation processes have been progressively introduced, focusing efforts on reusing water even achieving pa drinking water quality [2]. In the recent years, membrane bioreactors (MBR) have gained importance for the municipal and industrial wastewater treatment [3]. Whereas a conventional MBR uses ultrafiltration (UF) or microfiltration (MF) membranes, an OMBR works with FO membranes.

Thus, the OMBR is an emerging wastewater treatment technique that combines FO membranes and a biological reactor [4]. In this way, integrating FO membranes in a biological reactor offers many advantages, such as excellent water quality and very low energy consumption (since OMBR process works without applying mechanical pressure) [5,6]. A common OMBR includes a bioreactor, a FO separation unit and a DS system that makes possible the regeneration of the DS or the provision of fresh DS. FO membranes allow water permeation across the FO membrane from activated sludge feed solution to the DS [4,7,8]. The osmotic pressure difference from one membrane side to the other, due to the low-salinity of activated sludge and the high-salinity of the DS, is the driven force of the OMBR [9]. The selection of the DS is of paramount importance, since the salt concentration difference between feed and draw solutions can cause the salt reverse flux due to the Fick's law.

The main advantage of the FO nonporous membranes is the high rejection capacity for trace organic compounds [10], pathogens [11] and ions [12]. However, membrane fouling, salinity build-up in the bioreactor and cellular debris accumulated in the mixed liquor are key issues on the OMBR performance. On the one hand, membrane fouling is due to organic fouling, inorganic fouling and biofouling [13]. Organic fouling is due to the adsorption of organic compounds (such as SMP) on the membrane surface or in the membrane pores [13]. The organic substances accumulation together with reversible and irreversible attachment of bacterial cells and extracellulars polymeric substances (EPS) on the membrane surfaces drives to biofilm formation (biofouling) [9]. Inorganic fouling is caused by salts precipitation onto the membrane surface [14]. Membrane fouling implies a water flux reduction, a membrane life decrease and an increase of the operational costs [15–17].

In order to mitigate the membrane fouling, a suitable and periodic membrane cleaning is required. The cleaning of FO membranes installed in an OMBR is more complex than the one of the UF or MF membranes in a MBR. UF or MF membranes are usually cleaned by means of hydraulic or chemical backflushing, whereas FO membrane requires an osmotic backflushing. This type of cleaning needs invert the membrane water flux across the membrane. For it, the hypersaline solution is located in the feed tank, whereas distilled water is placed in the DS tank. In this way, water will flow from the DS to the feed side of the membrane, removing organic and inorganic substances from the membrane active layer [9].

One of the most important problems described in the OMBR operation is the high increase of the salt concentration in the bioreactor. This phenomenon is due to the rejection of the feed ions by the FO membrane and, at the same time, by the salt reverse flux (salt passage from the DS to the bioreactor). The control of the salt reverse flux is a key factor for the reactor performance. The salt concentration increase in the bioreactor will reduce the effective driving force for water permeation through the membrane, change the microbial community characteristics, rise the SMP and EPS in the bioreactor [18]. Recently, several authors have investigated these critical issues in OMBR technology to improve its application. Luo et al. [19] studied the salt reverse flux for water reuse in a OMBR using different draw solutions. They concluded that ionic organic draw solutes can mitigate salinity build-up in the mixed liquor. Bell et al. [9] compared the fouling behavior of two different FO membranes, cellulose triacetate membranes and polyamide thin film composite (TFC) membranes. This group of authors published that TFC membranes were more prone to fouling during a long-term OMBR study. However, more studies both in pilot and in full-scale plants are necessary to gain knowledge leading to achieve a better OMBR performance.

This work aims to study the performance of an OMBR comparing the use of two DS in terms of water flux, reverse salt flux, biological stability and membrane fouling. For it, two OMBR experiments were carried out at the same experimental conditions but using different draw solutions, a sodium chloride solution and an actual industrial wastewater solution of ammonium sulphate. The use of actual industrial effluents in OMBR has been hardly reported in the bibliography. Until now, previous studies have reported results with synthetic wastewater as draw solution. Particularly, the use of a residual ammonia absorption solution has already been not described.

2. Materials and methods

2.1. Synthetic wastewater

The simulated wastewater used for the experiment consisted of bacteriological peptone, meat extract (both supplied by Panreac, Spain) and tri-sodium phosphate 12-hydrate (from Panreac, Spain). The concentrations of these chemicals were selected in order to achieve a COD:N:P relation of 100:5:1 mg·L^{-1} to ensure the appropriate nutrients amount. Chemicals were mixed and dissolved in tap water. The wastewater solution (influent to the OMBR) was prepared three times per week. COD of the simulated wastewater was 4,000 mg·L^{-1}.

2.2. Draw solutions

In this study, the performance of two different DS was compared. On the one hand, a sodium chloride solution with a concentration of 53 g·L^{-1} and conductivity of 68 mS/cm was used in test 1. This sodium chloride concentration was selected in order to mimic the saline characteristics of a wastewater from the table olive processing according to Malheiro et al. [20] and Ferrer-Polonio et al. [21]. On the other hand, a liquid effluent from an absorption process for ammonia removal was the DS in the test 2. This wastewater was generated in an industrial wastewater treatment plant and its composition mainly consists of ammonium sulphate (SO_4^{-2} and NH_4-N concentrations of 153 g·L^{-1} and 19 g·L^{-1}, respectively). This waste water had a conductivity of 130 mS/cm and pH very low (1.2). Therefore, pH was increased up to 4.0 to ensure that the FO membrane was not chemically damaged.

2.3. FO membrane and OMBR plant

The FO membrane used in this study was CTA-NW membrane from HTI (USA). The commercial membrane material is cellulose triacetate (CTA) supported by an embedded polyester screen. According to previous research in OMBR (Lay et al. [14] and Wang et al. [18]), active layer was placed in the membrane module facing feed solution (FO mode) to carry out the experiments in order to prevent membrane fouling, especially pore clogging in support layer.

Fig. 1 shows a scheme of the OMBR laboratory plant used in this study. The plant was equipped with a separated bioreactor with an effective volume of 1 L. The bioreactor contained a mechanical stirrer (Velp Scientifica, Spain) to agitate the mixed liquor (feed solution to the FO membrane) and a air pump EHEIM 100 (Spain) to provide air in order to keep an oxygen concentration in the bioreactor around 2 mg·L^{-1}.

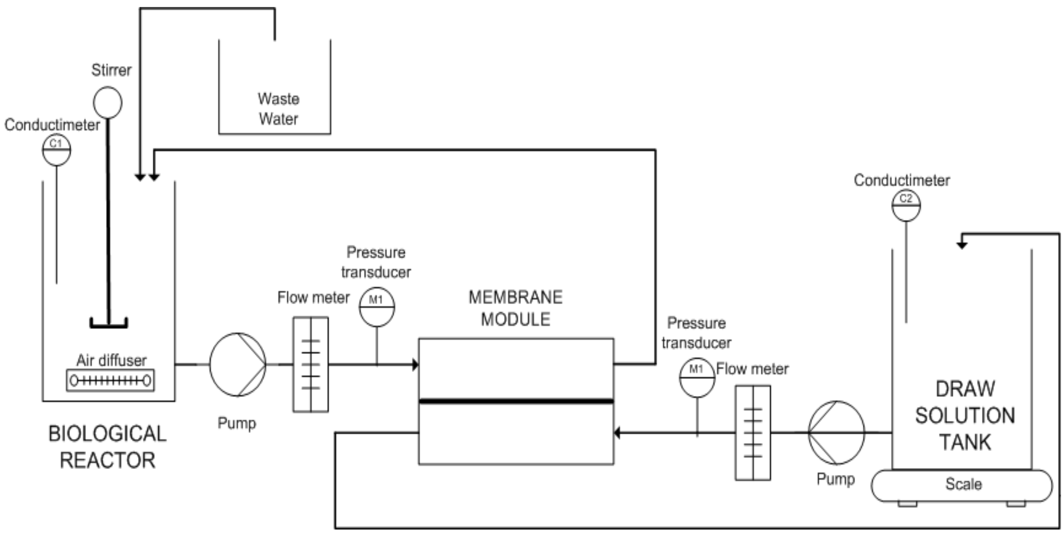


Figure 1: Schematic diagram of the OMBR plant.

The membrane module was CF042-FO (Sterlitech, USA) with capacity for a flat sheet membrane with an effective area of 42 cm^2. The flow rate in both channels of the FO module was 30 $L \cdot h^{-1}$. The feed and the draw solutions were pumped through the system by means of two peristaltic pumps (Pumpdrive 5006, Heidolph, Germany). In addition, the conductivity values both in the feed and draw solutions were registered using two conductivity meters model CDH-DS1 from Omega Engineering (United Kingdom). The water mass permeation through the membrane was monitored by the measuring of the evolution of the draw solution weight with the time. Thus, a digital scale PKP (Kern Instruments, Germany) was employed and mass measurements were registered every 15 minutes, using the software "Kern Balance Connection SCD-4.0".

2.4. Experimental sep-up

As commented in Section 2.2, two DS were tested under the same experimental conditions. To carry out the start-up of the OMBR, secondary sludge of a municipal wastewater treatment plant (located in Valencia, Spain) was used to seed the bioreactor. The mixed liquor suspended solids (MLSS) concentration was adjusted to 5 $g \cdot L^{-1}$ for both tests. The initial pH and conductivity of the mixed liquor were 7.10 and 1.35 $mS \cdot cm^{-1}$, respectively.

The initial hydraulic retention time (HRT) was calculated from the initial membrane water flux (2.65 days and 3.02 days for test 1 and 2, respectively). The food to microorganisms (F/M) ratio tested for the test 1 was 0.12 g $COD \cdot g\ SS^{-1} \cdot d^{-1}$ (for the three first weeks) and 0.24 g $COD \cdot g\ SS^{-1} \cdot d^{-1}$ (for the last three weeks). Test 2 was operated at F/M ratio of 0.24 g COD·g SS^{-1}·d^{-1}. This parameter was calculated according to Eq. 1:

$$\frac{F}{M}(g\ COD \cdot g\ SS^{-1} \cdot d^{-1}) = \frac{Q \cdot COD_e}{SSLM \cdot V} \quad (1)$$

In addition, an anoxic phase was introduced in test 2 after each bioreactor feeding to study the overall nutrients removal. With respect to the cleaning procedure, when membrane water flux was lower than 1 LMH, around 1 LMH or every four days instead, a membrane cleaning step was conducted applying a backflushing with deionized water as DS and a sodium chloride solution of 50 g·L^{-1} (for test 1) and 70 g·L^{-1} (for test 2) as feed solution. After each membrane cleaning step, new fresh DS was supplied for the OMBR operation.

2.5. Analytical methods

2.5.1. Measurement of membrane water flux and reverse salt flux

The membrane water flux and reverse salt flux were measured in order to characterize the pristine FO membrane tested. For it, deionized water was used as FS and sodium chloride solutions as DS. The experimental water flux J_w (LMH) was calculated at different sodium chloride concentrations in the DS by measuring the weight variation of the draw solution over time as it is described in Eq.2.

$$J_w = \frac{\Delta V}{A \cdot \Delta t} \quad (2)$$

Where, ΔV is the total volume increase in the draw solution tank (L) in a Δt (h) period, and A is the active FO membrane area (m^2). The reverse salt flux Js ($g \cdot m^{-2} \cdot h^{-1}$) was calculated following Eq. 3.

$$J_s = \frac{V_t \cdot C_t - V_{t-1} \cdot C_{t-1}}{A \cdot \Delta t} \quad (3)$$

Where, V_t and C_t are the volume and the concentration of sodium chloride in the feed solution measured at time t.

2.5.2. Wastewater characterization

Water quality parameters were analyzed in the bioreactor. These parameters were: COD, total nitrogen (TN), total phosphorous (TP), ammonium nitrogen (NH_4^+-N), nitrate nitrogen (NO_3-N) and nitrite nitrogen (NO_2-N). In addition, when ammonium sulphate was used as DS (test 2), sulphate (SO_4^{-2}) content was also measured in the mixed liquor. Before the analyses, the samples were centrifuged at 10,000 rpm for 15 minutes and the supernatant was filtered using a 0.45 µm filter reference 16555 from Sartorius (Spain). In this way, these measurements corresponded to the soluble fraction of the reactor, indicating the quality of the treated water. COD was measured three times per week using kits from Merck (Spain) and SO_4^{-2}, TN, TP, NH_4^+-N, NO_3-N and NO_2-N was evaluated weekly by means of kits from Merck (Spain). In addition, COD was also measured in the prepared wastewater in order to check its properties and calculate the COD removal efficiency of the OMBR.

2.5.3. Biomass characterization

The measurement of MLSS and mixed liquor volatile suspended solids (MLVSS) was carried out following the methodology described in [22]. In addition, capillary suction time of the mixed liquor was measure weekly to study the sludge filterability using the equipment 304M from Triton Electronics Ltd (United Kingdom). Each sample was taken from the bioreactor each 10 days and CST was determined, values were normalized against MLSS concentration and the result was expressed in units of $s \cdot gMLSS^{-1}$.

Extracted extracellular polymeric substances and soluble microbial products were measured weekly through the experiment by means of analyze proteins and carbohydrates concentrations. Deoxyribonucleic acid (DNA) in SMP was also measured. Thus, eEPS in the sludge were extracted using a cation exchanger resin (Dowex Marathon C, Sigma Aldrich, Spain) following the procedure described by Zuriaga et al. [23]. Proteins content was evaluated using Bicinchoninic acid (BCA) assay test from Novagen. Carbohydrates content was measured with Antrone method [24]. Finally, DNA was determined using Quant-it™ dsDNA HS (0.2–100 ng) kit from Invitrogen (Spain). The three procedures were described extensively in [23].

2.6. Membrane microscopy characterization

Fouled membrane surfaces morphology were examined for the observation of eventual damages and fouling with a Field Emission Scanning Electron Microscope Ultra 55 (Zeiss, Oxford instruments, United Kingdom). In addition, the composition of the fouling layer was characterized by energy diffusive X-ray (EDX) analyzer with the same microscopy. Membrane samples were air-dried in a desicator before being covered with graphite.

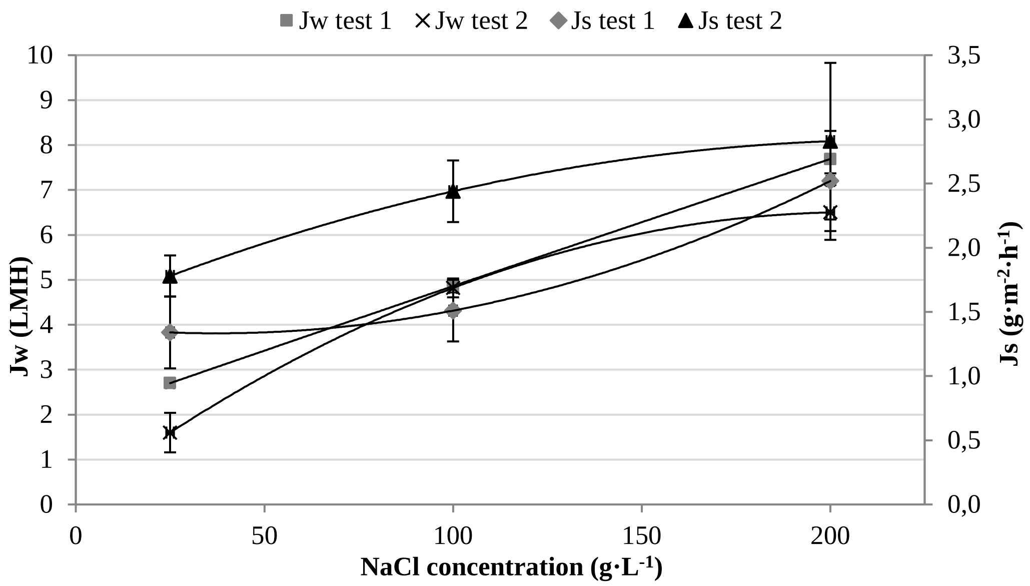
2.7. Statistical analysis

A statistical analysis was carried out by means of the software STATGRAPHICS Centurion XVI to study the relation between the COD removal efficiencies and the feed solution conductivity values. For that, a simple linear regression analysis was conducted. In addition, ANOVA simple analysis was carried out to research if there is any difference between both DS tested in terms of COD removal efficiencies.

3. Results and discussions

3.1. Characterization of the virgin membranes used in the OMBR

Fig. 2 shows the J_w and J_s of the CTA-NW virgin membrane samples used in both tests. The variations in the water flux and reverse salt flux for different NaCl concentrations in the DS when deionized water was used as feed solution can be observed. As expected, both membranes samples had practically the same J_w. Slightly higher values were reported by Yang et al. [25] (4.79 LMH using 58.44 $g \cdot L^{-1}$ of NaCl as DS) and Takahashi et al. [26] (4.8 LMH using 58.44 $g \cdot L^{-1}$ of NaCl as DS). Unlike J_w, J_s values were slightly different for the two tested membranes since they were different membrane pieces. For example, Takahashi et al. [26] published a higher J_s (about 11 $g \cdot m^{-2} \cdot h^{-1}$), employing the same membrane type.

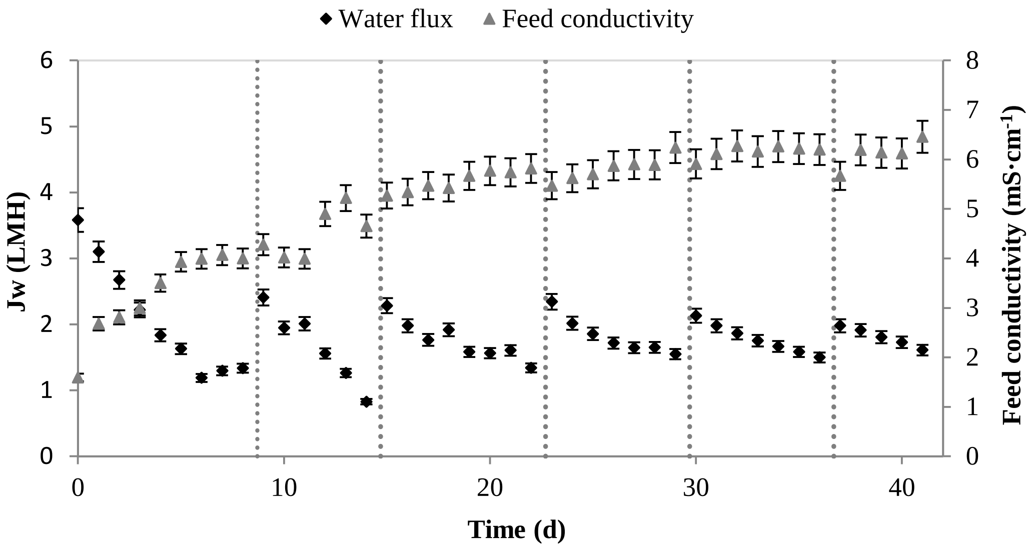


3.2. Water flux and mixed liquor salinity

The evolutions of the FO membrane water flux and of the conductivity of the mixed liquor over the testing period for each test have been represented in Fig. 3. Each vertical line corresponds with a backflushing cleaning step. The variation of the FO membrane water flux over time for test 1 (Fig. 3.a) can be divided into two stages. In the first stage (days 0-10), the water flux significantly decreased from 3.6 LMH to around 1 LMH. This fact could be explained due to the fast deposition of foulants on the membrane surface [27]. After that, when the fouling layer was formed, membrane water flux was more constant varying between 2.2 LMH and 0.9 LMH. In addition, this behavior was very similar to that shown by Wang et al. [28] in their work. Regarding membrane water flux evolution over time for test 2, a similar trend was observed as it is shown in Fig. 3.b. However, fouling layer was formed more slowly since the first backflushing of test 2 achieved a better flux recovery than the first one carried out in test 1.

As commented above, the salinity build-up in the bioreactor is a key factor since this phenomenon is an inherent problem associated with OMBR operation. As it can be observed in Fig. 3, the mixed liquor conductivity increased significantly within the first 15 days of the OMBR operation for both experiments. For test 1 (Fig. 3.a), thereafter feed conductivity increased slightly until reaching a final value around 6.5 $mS\cdot cm^{-1}$. This trend was also observed by Qiu et al. [29]. This fact could be associated with the decrease in the reverse draw solute flux due to the water flux decline. In addition, the fouling layer formed and the daily sampling carried out (sludge withdrawal) helped control salinity build-up. By contrast, for test 2 (Fig. 3.b), a greater increase of the reactor conductivity was observed after the 15^{th}day of operation. More details are given in Section 3.3 in that SO_4^{-2} and NH_4^+ concentrations evolution are showed. In comparison with test 1, more salinity build-up was found in the reactor in test 2 since membrane was less fouled and the osmotic pressure difference was higher, enhancing the salt reverse flux. Thus, the resistance for the reverse salt passage was lower. At the end of the test 2 the feed conductivity slightly decreased due to the sludge withdrawal carried out in this period in order to control the MLSS concentration increase and the salinity build-up. In this way, Luo et al. [30] studied the salinity build-up in a OMBR operated with a DS of 1M of NaCl. They reported a stable feed conductivity value of around 6 mS·cm^{-1} after the 8th operation day due to the biofilm formed on the membrane side facing the mixed liquor.

a)



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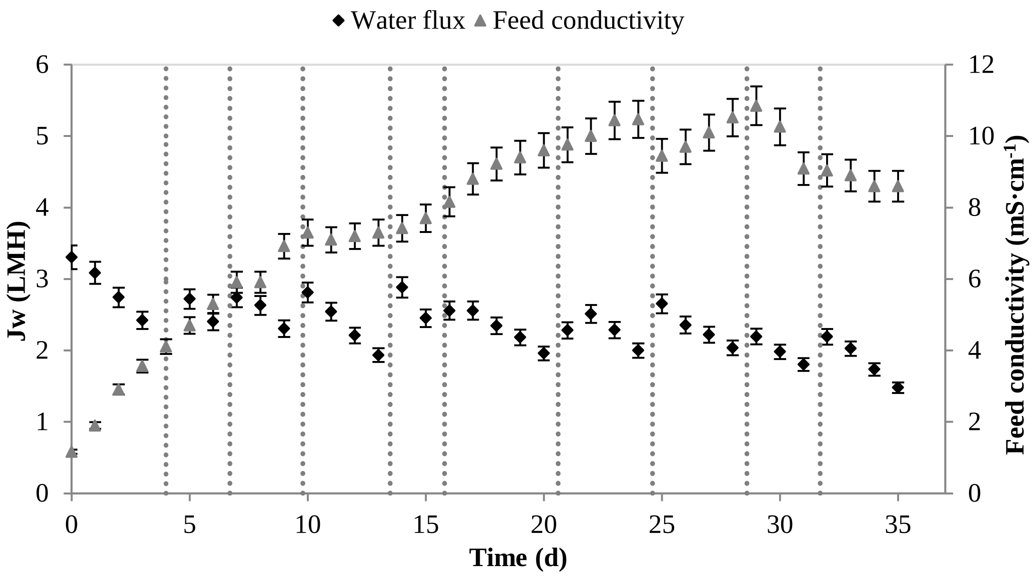


Figure 3: Water flux and feed solution conductivity evolution for a) test 1 and b) test 2.

3.3. Performance of the OMBR experiments

Organic matter and nutrients content in the mixed liquor supernatant were evaluated in order to assess the OMBR performance. Fig. 4 shows COD removal efficiencies for both tests during the experimental period. It is important to highlight that the COD removal was measured on the basis of the soluble COD in the bioreactor instead of calculating the COD content in the DS, since it is considered that FO membrane also rejects organic matter. For test 1, COD removal efficiencies were higher than 90% and slightly decreased at the end of the experiment. By contrast, test 2 had COD removal efficiencies lower than test 1 (between 97.65% and 77.92%). The accumulation of non-biodegradable organic matter (in this case cellular debris since the wastewater influent was a solution of peptone and meat extract) in the biological reactor due to its rejection by the FO membrane (practically 100%) led to a slight and gradual decrease of the COD removal efficiency during the experiment [31,32]. In addition, this decrease was higher in the test 2 than in the test 1, since the conductivity increase in the reactor was higher, leading to biomass inhibition. These results were in concordance with previous studies, such as Huang et al. [33], Qiu et al. [34] and Pathak et al. [35] , who reported COD removal efficiencies operating forward OMBR around 90%.

Nutrients removal was not studied in test 1 since no anoxic phase in the OMBR was included. However, NH_4^+-N and TP content in the supernatant were measured to ensure that there were enough nutrients to carry out the biological process and also to detect their eventual accumulation in the reactor. The NH_4^+-N and TP concentration ranges in the supernatant were 3-8 mg·L^{-1} and 1-4 mg·L^{-1}, respectively.

By contrast, the removal of nutrients was analyzed in test 2 as it is shown in Fig. 5. Thus, this test was divided into two stages: a first aerobic stage (until 18th-day of operation) and a second anoxic/aerobic stage (from 18th-day of operation on). The study of the nutrients removal in tests 2 was of special interest due to the reverse ammonium-nitrogen flux increasing its concentration in the biological reactor.

On the one hand, during the first stage (only aerobic reaction) it is observed an increase of the TN concentration. This was due to the TN rejection by the membrane in spite of the nutrient biomass assimilation. Nitrification process occurred in the reactor since NO_3-N concentration increased. Finally, these nitrogen compounds were rejected by FO membrane and, as a result, TN concentration increased in the bioreactor [36] as it is observed in Fig. 5. This trend was also observed by Luo et al. [19], who operated an OMBR and nitrification process was developed in the biological treatment.

On the other hand, from 18th-day of operation, when anoxic phase was included, both NO_3-N and TP concentration decreased indicating that there was denitrificaction and that phosphorous assimilation was enhanced. Specifically, the removal of TP was 80.5%. Similar results were published by Pathak et al. [35] who obtained a TP removal in the bioreactor of 81.22%.

Focusing on SO_4^{-2} and NH_4^+-N, i.e. the main components of the DS, it has to be highlighted that their high reverse flux due to Fick's law was responsible for the conductivity increase in the biological reactor. The periodical sludge withdrawals seem to be critical in order to avoid the sulfates precipitation (mainly as calcium sulfate) on the membrane surface due to the high sulfates concentration (Fig. 3.b).

Concerning the pH, a slight increase (0.94 and 0.78 units for test 1 and 2, respectively) was observed during the OMBR operation mainly due to reverse draw solute flux. The forward diffusion of protons from the bioreactor into the DS, in combination with the reverse transport of cations (like sodium in the case of test 1) to maintain the electroneutrality of the mixed liquor, led to a pH rise in the biological reactor [19]. However, this did not affect the biological process (pH values remained in the appropriate range for biological activity).

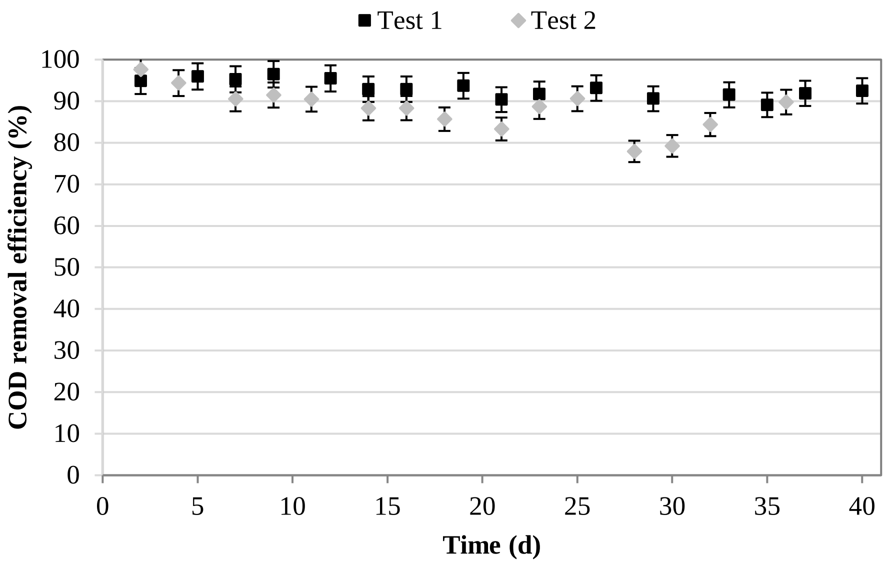


Figure 4: COD removal efficiency during the experimental period for both experiments.

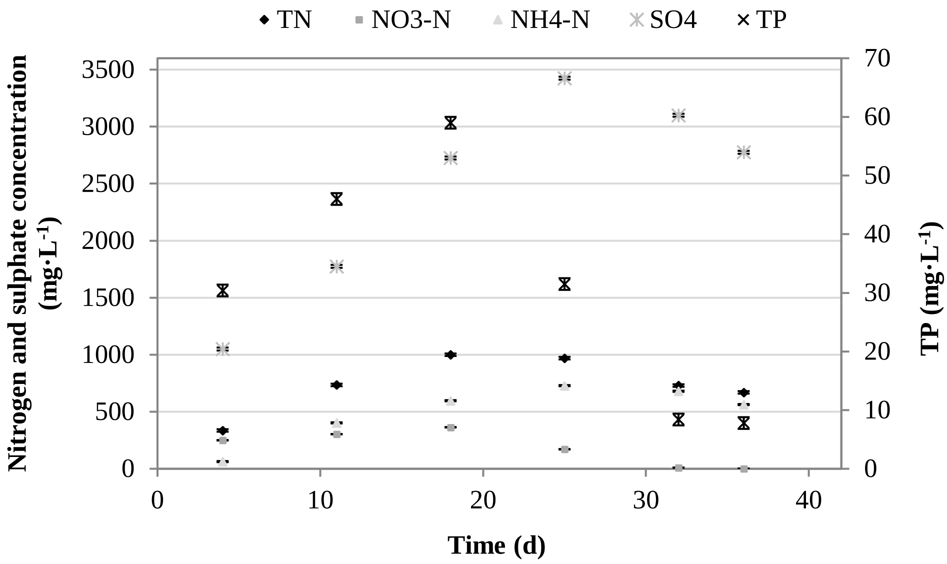


Figure 5: Nutrients and SO_4 evolution in the feed solution during the experimental period.

3.4. Biomass characteristics

Salinity build-up in the bioreactor could alter the biomass characteristics during OMB operation. Previous studies [31,37] have reported that higher salt concentrations could increase the endogenous respiration of microorganisms. The biomass could increase the secretion of organic cellular substances, which would lead to an enhancement of SMP and eEPS production with the aim of cell protection. Fig. 6 represents the SMP and eEPS concentrations in terms of proteins and carbohydrates during the experimental period. DNA has also been included in the SMP in order to evaluate eventual cell lysis. It can be clearly observed that SMP (proteins, carbohydrates and DNA) concentrations were higher in test 2 than in test 1. This result confirms the higher stress of the biomass in test 2 caused by the higher salinity than in test 1 (Fig. 3) [38]. By contrast, this fact had no influence on the eEPS concentration, which was stable and very similar in both tests probably due to the low working organic loads. Similar results were published by Luo et al. [19] related with EPS content in a OMBR. These authors reported that there was no significant variation in the EPS content probably due to a balance between its release and hydrolysis.

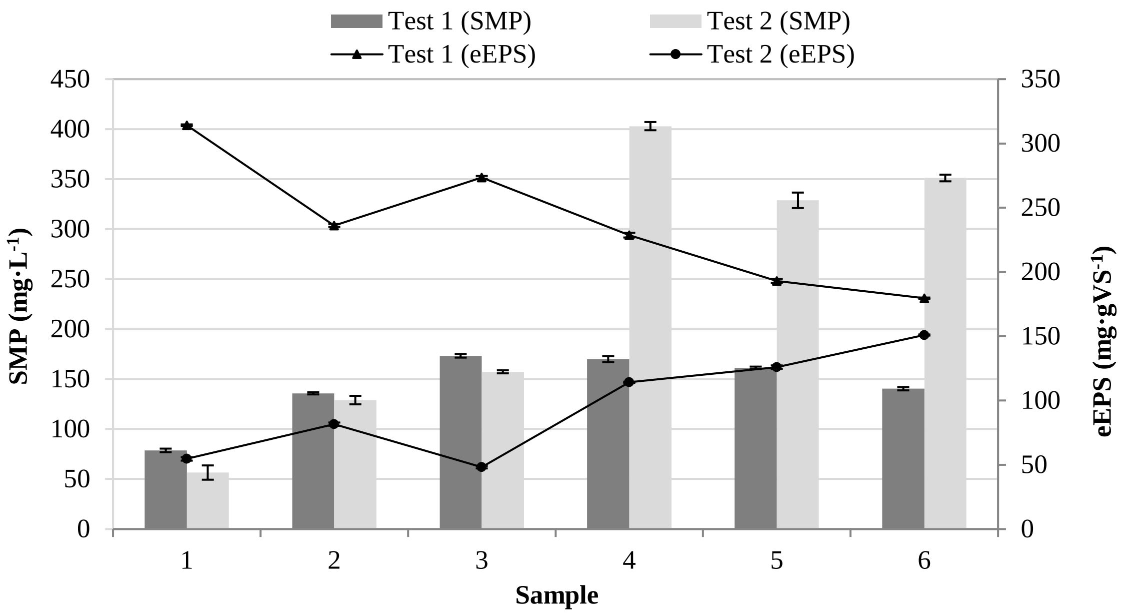
However, for test 1 and from sample 3 (at that time the F/M ratio was increased to 0.24 g COD·g $SS^{-1}·d^{-1}$), SMP concentrations were constant and eEPS decreased with the operation time. This indicates that biomass was adapted to salinity build-up. Thus, the increase of the organic load resulted in a lower eEPS release. These results agree with those reported by Wang et al. [39].

From Fig. 6.a and 6.b, it has to be highlighted that the concentration difference between proteins and carbohydrates was high. In this way, Sabia et al. [40] published that the ratio between proteins and carbohydrates in SMP dramatically increased with the sludge retention time (SRT). These results were in agreement with those obtained in this study, since in both tests the SRT was increasing since the only sludge withdrawals were carried out to take the samples.

Finally, Fig. 6.c relates the measured DNA concentrations in the supernatant from both tests. DNA content indicates that cell lysis occurs [41]. Cell lysis was much higher in test 2, which is in concordance with the above explained results. The high stress caused by the quick conductivity increase and the high increase of the ammonium nitrogen concentration were responsible for the cell lysis. Furthermore, it was detected a direct relation between DNA and protein concentrations, what corroborates that measured proteins could come from the released cellular material from the bacteria, as previously published Zuriaga et al. [42].

Regarding to physic-chemical properties of sludge, CST is an interesting index for sludge filterability [43]. Normalized CST with respect to TSS (nCST) was calculated to investigate the effect of salts concentration on the filterability of the sludge as shown in Table 1. In general terms, the low CST values obtained for both tests indicated good sludge quality from the point of view of its filterability and dewaterability. Thus, it was observed that the presence of salts concentration in the mixed liquors did not affect the filterability of the sludge since the values were very similar during the experimental period for both tests. According to Zhang et al. [44], EPS concentration is considered to be an important factor affecting sludge filterability. These authors published that CST decreased as increases EPS concentration. This fact was due to the improvement of sludge dewaterability as a consequence of the increase of flocs size. The same trend was observed in results detailed in Table 1 when CST values of samples 1 and 2 are compared.

a)



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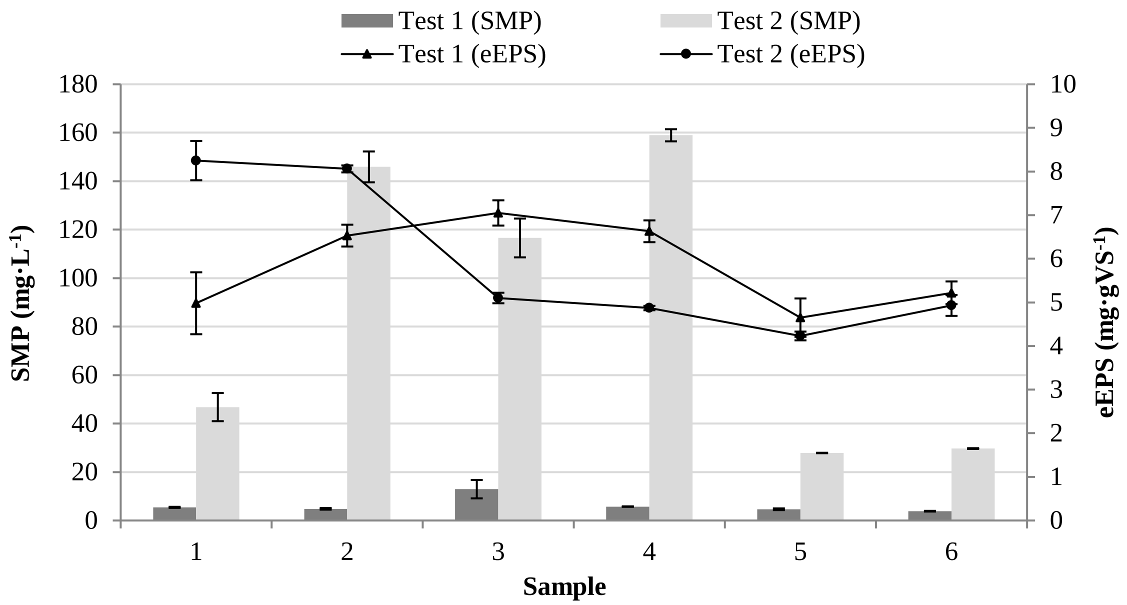

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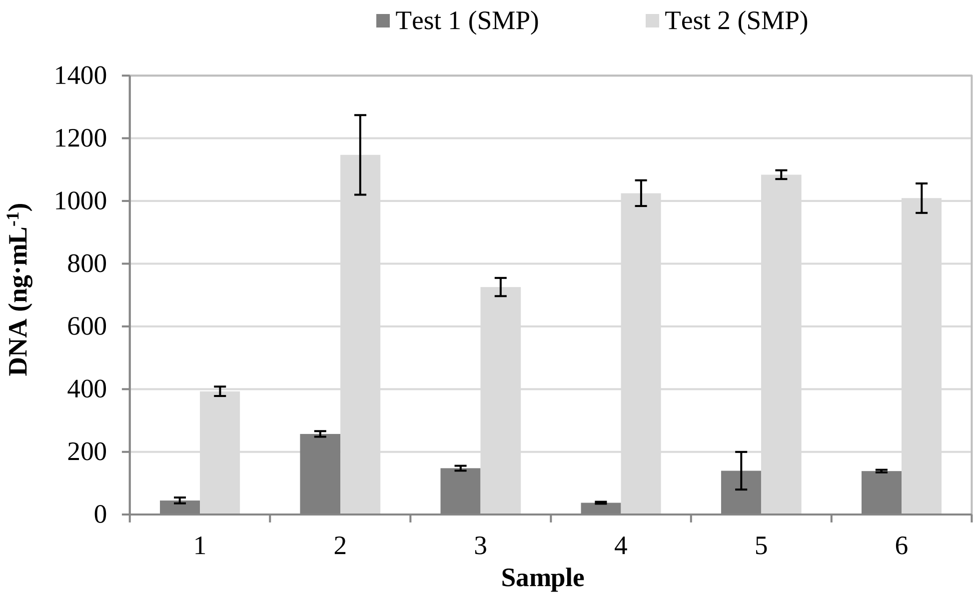


Figure 6: SMP and eEPS concentrations in terms of a) proteins, b) carbohydrates and c) DNA.

Table 1: nCST for both test during the experimental time.

nCST ($s \cdot L \cdot gTSS^{-1}$)	
Test 1	Test 2

Sample 1	3.08 ± 0.15	2.51 ± 0.11
Sample 2	4.92 ± 0.20	2.19 ± 0.10
Sample 3	4.79 ± 0.21	1.98 ± 0.08

3.5. Membrane microscopy analysis

According to Gu et al. [45], CTA FO membranes were covered by a fouling layer during the process but foulants could be easily removed applying a backflushing step. However, in this study and for both tests, FO membranes were fouled and the foulants after 40 operation days could not be totally removed by backflushing (the water flux was not totally restored up to the initial value). To check the membrane fouling, surface morphology of the fouled FO membrane used for test 1 is illustrated in Fig. 7since no significant differences were found between the two used membranes. Besides, an elemental composition of fouling layer is shown in Fig. 8, Fig. 8.a for membrane used in test 1 and Fig. 8.b for membrane used in test 2.

From FE-SEM images it was observed that a fouling layer was detected on the fouled FO membrane after the experimental period and foulant clusters were distributed over the membrane surface. EDX results are illustrated in Fig. 8. In addition to the high peaks of C and O coming from the membrane material, low peaks for nitrogen, phosphorous, calcium, magnesium, chloride, sulphur and sodium were also detected. It has to be highlighted that the S and Ca peaks are slightly higher in the membrane of the tests 2 due to a higher sulphate reverse flux that entailed the accumulation of sulphates in the reactor with the subsequent calcium sulphate precipitation.

According to Zhao et al. [46], inorganic compounds could also form precipitates in the organic fouling layer, even forming bridges between divalent cations and organic molecules (e.g. proteins, carbohydrates) on the membrane surface.

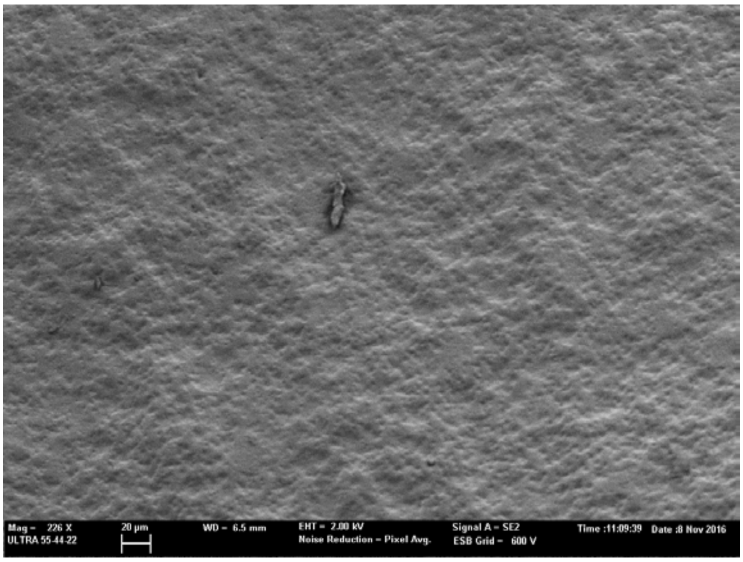
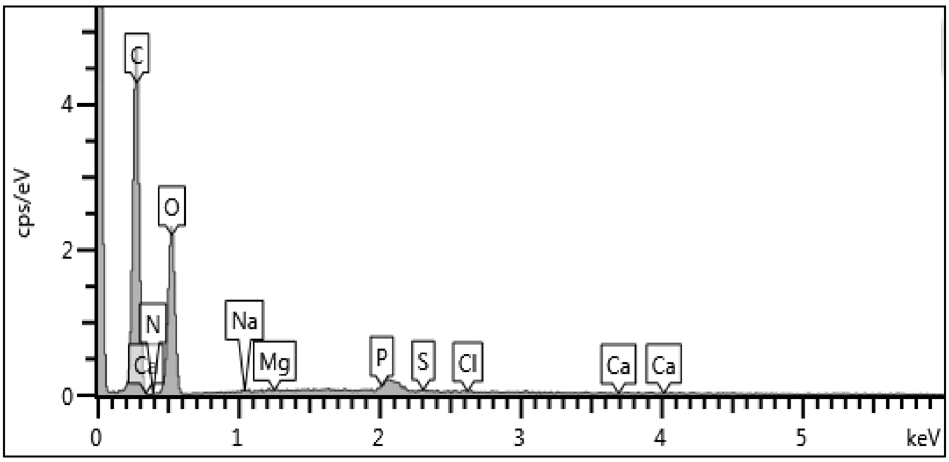


Figure 7: FE-SEM image of active layer of fouled membrane used in test 1.

a)



b)

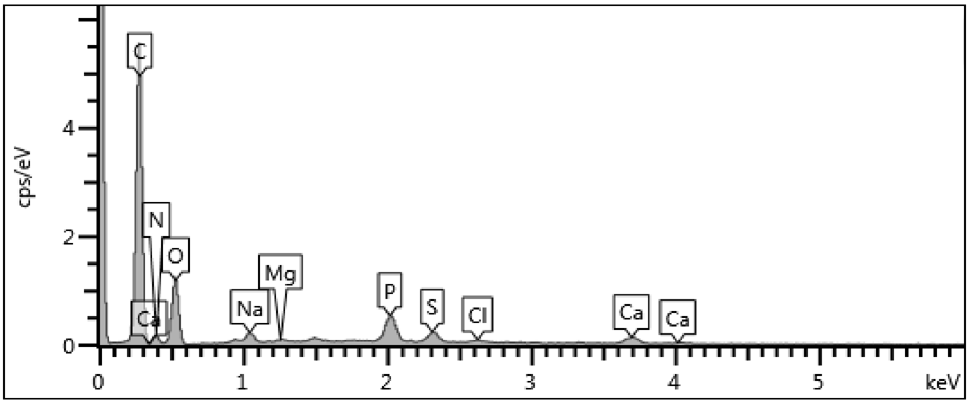


Figure 8: EDX analysis of fouled membranes a) test 1 and b) test 2.

3.6. Statistical analysis

A simple linear regression analysis was calculated with the software STATGRAPHICS to confirm that there is relationship between COD removal efficiency (dependent variable) and the feed solution conductivity (independent variable). The coefficient R^2 shows the variability in the response that is represented by the fitted model, indicating how well the model fits the response variable. Eq. 4 and 5 shows a linear regression between the COD removal efficiency and the feed solution conductivity for test 1 and 2, respectively. The R^2 for Eq. 4 and 5 were 56.66% and 65.13%, respectively. In addition, the sign of the effect indicates if it produces an increase (+) or a decrease (−) of the variable response.

$$\text{COD removal (\%)} = 99.46 - 1.24 \times \text{Feed Conductivity (mS/cm)} \quad (4)$$

$$\text{COD removal (\%)} = 105.55 - 2.27 \times \text{Feed Conductivity (mS/cm)} \quad (5)$$

Finally, if p-values were lower than 0.05, it was considered that independent variables (in this case, feed solution conductivities) were statistically significant at the 95.0% confidence level. In this case, for both tests, feed solution conductivity is statistically significant since p-values were lower than 0.05 (0.0005 and 0.0002 for test 1 and 2, respectively).

In addition, one-way ANOVA was analyzed to study if COD removal efficiencies (response variable) and the draw solution tested (named factor) were independents or not. In this way, from STATGRAPHICS results it can be concluded that there were statistically significant differences between the mean COD removal efficiency value from test 1 and from test 2 since p-value was 0.0011. In addition, the F-ratio differs significantly of 1 (F-ratio was 12.9959) indicating that the null hypothesis of equality of means of the COD removal efficiencies was rejected.

Conclusions

Results reported here demonstrate that both DS tested were useful to carry out an OMBR process for treating simulated wastewater, since results in terms of COD removal efficiencies were always higher than 80% in spite of the salt concentration increase in the reactor. Comparing both DS, salt reverse flux was higher when the industrial wastewater was used as DS. With industrial waste water as DS, the COD removal efficiency was slightly lower since SMPs were produced at a higher extent due to the cellular stress caused but the sharper salt concentration increment. The SEM and

EDX observations on the FO fouled membrane indicated the presence of a fouling layer combining organic and inorganic scaling.

Nevertheless, the less membrane fouling and the higher water flux in comparison with the NaCl solution make the use of the ammonium absorption effluent as DS attractive for the OMBR operation. In addition, the ammonium-nitrogen from the DS could be eliminated at a certain extent, since after its permeation through the membrane nitrogen could be nitrified and finally denitrified in the reactor.

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