Effect of current density on the efficiency of a membrane electro-bioreactor for removal of micropollutants and phosphorus, and reduction of fouling: A pilot plant case study

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Abstract

Submerged membrane bioreactors (SMBR) are widely known for their advantages in the field of wastewater treatment. However, despite the significant technological advances in recent decades, membrane fouling remains one of the major concerns for its efficient application. Recent studies, carried out with synthetic wastewater, show that the integration of electrochemical processes as electrocoagulation with membranes technologies provides promising advantages.

This research focuses on the performance of a pilot-scale membrane electro-bioreactor (SMEBR) treating real wastewater with an average organic loading rate of 0.91 ± 0.44 mg/L COD from a municipal wastewater treatment plant. Current densities of 5, 10, and 15 A/m² (charge loading of 214.17, 428.34 and 642.42 mA·m⁻³·h respectively) and exposure time of 5’ON/10’OFF were applied to compare the efficiency of the SMEBR system versus the SMBR. The removal efficiencies of COD, nutrients (total nitrogen and total phosphorus) and 10 selected micropollutants (8 pharmaceuticals and 2 pesticides) were studied. The results showed that the SMEBR system improved the treated effluent quality in comparison with the SMBR, mainly regarding phosphorus, increasing its elimination by an average of 34.6%, and the micropollutants acetaminophen, clarithromycin and carbamazepine, which presented an average increase in the removal rates of 19, 43 and 28%, respectively, comparing with those obtained in the SMBR. The optimal operational conditions were obtained when a current density of 5/A/m² was applied. At this stage, the SMEBR showed a significant reduction in the membrane fouling, achieving reductions rates in transmembrane pressure and extracellular polymeric substances of 72.8% and 55.5%, respectively.

Keywords Wastewater treatment; electrocoagulation; submerged membrane electro-bioreactor (SMEBR); current density; membrane fouling; micropollutants.
1. Introduction

The submerged membrane bioreactor (SMBR) is a reliable and promising technology for wastewater treatment and reuse applications. Despite over a decade of significant advances in the development of advanced materials [1] and methods to minimize membrane fouling [2], this remains the most challenging problem in the SMBR operation, resulting in a substantial increase of characterization and scale control studies in the last eight years [[3], [4]].

Several causes are involved in the phenomenon of membrane fouling, as the biofilm (including extracellular polymeric substances –EPS), soluble organic compounds, particles, colloids and dissolved inorganic compounds, which can strongly affect the scaling mechanisms in a membrane filtration system [5]. The three main mechanisms responsible for membrane fouling are: (a) the narrowing of pores, attributed to the adsorption of soluble and micro-colloidal substances that are much smaller than the pore size of the membrane, (b) pore clogging, due to the deposition of particles that are similar in size to the pore size, and (c) formation of cake layer on the membrane surface, due to the deposition of substances [6].

Recently, the implementation of electrocoagulation processes (EC) in SMBR, known as Submerged Membrane Electro-BioReactor –SMEBR, has attracted the attention of the scientific community with regard to the minimization of membranes fouling and the improvement of the effluent quality [[7], [8], [9], [10], [11], [12]]. Several studies (Table 1) show that the configuration of the SMEBR and the operational parameters adopted play a fundamental role in the performance of the integrated system. The materials, distances and configuration of the electrodes [13], the current densities applied [10] and the times of exposure to the electric current [14] are the main variables of the process. Table 1 summarizes the parameters of a range of works concerning the SMEBR systems published in recent years.

### Table 1 Selection of studies using SMEBR

<table>
<thead>
<tr>
<th>Application</th>
<th>Reactor volume</th>
<th>Membrane / pore size</th>
<th>Anode / Cathode</th>
<th>d (cm)</th>
<th>DC</th>
<th>Times (ON/OFF)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Synthetic wastewater</td>
<td>13.4 L</td>
<td>HF / 0.04 μm</td>
<td>Fe / Fe</td>
<td>5.5</td>
<td>1 V/cm</td>
<td>15 /45 min</td>
<td>[12], [15]</td>
</tr>
<tr>
<td>Synthetic / municipal</td>
<td>8.5 L</td>
<td>HF / 0.04 μm</td>
<td>Al / Al</td>
<td>-</td>
<td>1.2 V/cm</td>
<td>10 /30 min</td>
<td>[16]</td>
</tr>
<tr>
<td>Municipal wastewater</td>
<td>235 L</td>
<td>PVDF, HF / 0.1 μm</td>
<td>Al / Stainless steel</td>
<td>-</td>
<td>12 A/m²</td>
<td>5 /10 min</td>
<td>[7]</td>
</tr>
<tr>
<td>Industrial wastewater</td>
<td>32 L</td>
<td>PES, PP / 0.04 μm</td>
<td>Fe / Fe</td>
<td>5</td>
<td>2.5 to 20 mA/cm²</td>
<td>105 min</td>
<td>[17]</td>
</tr>
<tr>
<td>Synthetic</td>
<td>13.5 L</td>
<td>PVDF, HF / Stainless</td>
<td>9</td>
<td>5 to 23</td>
<td>1.7-6.7 /3.3-</td>
<td>[14]</td>
<td></td>
</tr>
</tbody>
</table>
### Table 1: Performance of the SMEBR System

<table>
<thead>
<tr>
<th>Synthetic wastewater</th>
<th>0.1 μm</th>
<th>steel</th>
<th>A/m²</th>
<th>8.3 min</th>
</tr>
</thead>
<tbody>
<tr>
<td>13 L PVDF, HF / 0.04 μm Al / Stainless steel</td>
<td>6</td>
<td>5 A/m²</td>
<td>5 /20 min</td>
<td></td>
</tr>
<tr>
<td>8 L PVDF, HF / 0.04 μm Al / Stainless steel</td>
<td>-</td>
<td>15 A/m²</td>
<td>5 / 20 min</td>
<td></td>
</tr>
<tr>
<td>13 L PVDF, HF / 0.04 μm Al / Stainless steel</td>
<td>6</td>
<td>1 V/cm and 3 V/cm</td>
<td>5 /20 min</td>
<td></td>
</tr>
<tr>
<td>5 L PVDF, PPMA / 0.03 μm Fe/Fe</td>
<td>2</td>
<td>2 A/m²</td>
<td>30°/30°</td>
<td></td>
</tr>
</tbody>
</table>

In the first study ([12], [15]) conducted using SMEBR treating synthetic wastewater (COD = 334 mg/L), a fouling reduction of 16.3% was achieved by using iron electrodes at a fixed distance of 5.5 cm, a voltage gradient of 1 V/cm and an exposure time of 15 min ON/45 min OFF. In another innovative study ([7], [9]) treating municipal wastewater (COD = 316 mg/L), an aluminum anode and a stainless steel cathode were used with a constant current density of 12 A/m² to achieve removal rates of organic matter and nutrients above 92%. Hasan et al. [7] also related the higher performance of the SMEBR with changes in sludge properties (size of flocs, EPS, SVI, zeta potential). Hosseinzadeh et al. [17] studied the efficiency of the pilot plant varying some parameters and observed that the efficiency of COD removal increased when the distance between the electrodes increased from 4 to 5 cm, but decreased when the distance was 6 cm. The research conducted by Tafti et al. [14], with synthetic wastewater (COD = 350 mg/L), concluded that the application of different combinations of current densities and exposure times directly affected the efficiency of the system in terms of effluent quality and reduction of membrane fouling. They observed reduction in membrane fouling and an improvement in organic removal efficiency with the application of a current density of 12.5 A/m² and exposure times of 6.7 min ON/3.3 min OFF. In addition, they reported a reduction in the process efficiency with a density of 20 A/m². Ensano et al. [18] investigated the efficiency of the SMEBR system for the removal of three recalcitrant organic compounds (diclofenac, carbamazepine and amoxicillin). These authors achieved, with the SMEBR, an increase of about 26% in the removals of these organic compounds with respect to conventional SMBR and, in addition, they reported a decrease of 44% in membrane fouling. Ibeid et al. [19], using a constant current density of 15 A/m², demonstrated that the soluble microbial product (SMP) has a more significant effect than volatile suspended solids (VSS) on membrane fouling. In the study conducted by Borea et al. [20] treating synthetic wastewater (COD = 556 mg/L), it was observed that the membrane fouling rate decreased by 15.84% and 54.33% by applying voltage gradients of 1 V/cm and 3 V/cm, respectively. The research carried out by Su et al. [21] allowed a total phosphorus removal and high organic matter removal rates, as well as an alleviation of membrane fouling due to floc size.
enhancement and particle polarization resulting from electrocoagulation and the applied electric field. Previous research reported a significant reduction in membrane fouling [[8], [12]] and an improvement in of the removals of organic matter [17], nutrients [[14], [16]] and pharmaceuticals [18] after the application of electric current. Nevertheless, these studies were carried out using laboratory-scale reactors fed with synthetic wastewater. This is the first study that evaluates the efficiency of a pilot scale submerged membrane electro-bioreactor – SMEBR system (635 L) treating municipal (domestic and industrial) wastewater of medium organic loading rate –OLR.

Consequently, the objectives of the this research were: to study the impact of current density on the removal of ten organic micropollutants from the families of drugs and pesticides by SMEBR system, to evaluate the efficiency of the SMEBR system on the removal of COD and nutrients, mainly phosphorous, from municipal wastewaters, to analyze the influence of current density on the characteristics of the SMEBR sludge and on the membrane fouling compared to the conventional SMBR system, and to estimate the energy consumption of the SMEBR system at the three different current densities.

2. Materials and methods

Experimental setup

The submerged membranes electro-bioreactor (SMEBR) pilot plant was designed and built at the facilities of the University Institute of Water and Environmental Sciences (IUACA). The start-up and operation was carried out at the municipal Wastewater Treatment Plant (WWTP) located in Santomera (Murcia, Spain). The design of the SMEBR system (Figure 1) was based on the scheme patented by Bani-Melhem and Elektorowicz [15].

Figure 1 Scheme of the SMEBR pilot plant
The SMEBR pilot plant consisted of a submerged membrane bioreactor (SMBR) combined with an electrocoagulation (EC) system. The pilot plant was composed of a cylindrical fiberglass tank, 0.70 m in diameter and 2.30 m in height, inside which the membrane module was placed. The maximum and minimum heights reached by the mixed liquor in the reactor were, 1.70 and 1.60 m, respectively. Considering an average height of 1.65 m, the useful volume in the reactor was 635 L.

Two perforated electrodes with 48% of open area were placed inside the tank. The material used for the anode was aluminum and for the cathode stainless steel \([7, 9]\) and the distance between both was 5 cm \([17]\). The electrodes were configured in a cylindrical shape and were concentrically placed with the membrane. Both were connected to a multi-range direct current power supply, model IPS 80-40.5 (ISO-TECH), operating intermittently with exposure time to electric current of 5 min ON / 10 min OFF \([7, 9]\).

A flat membrane module model AMM06011 of Gestión del Valor y Soluciones S.L (A Coruña, Spain) of ultrafiltration polyethersulfone (PES) with a pore size of 0.1 μm and 6.25 m² of total surface area was used. Oxygen supply (4-7 mg O₂/L) was provided by thick bubble diffusers placed below the membranes.

A vortex submersible pump model VXV1100AS of Espa, Innovative Solutions (Banyoles, Spain) and a peristaltic pump model AMP13 of Boyser, S.L. (Barcelona, Spain) were used for the feeding of the SMEBR system and the suction of the permeate. The feeding pump was controlled by a level sensor in order to maintain constant the volume of the tank. All the equipment, as well as the measuring instruments, were connected to a control panel, which provided continuous information on the main process parameters.

Operating conditions

This study was carried out during 173 days, including the time required for stabilization between stages (30 days) and maintenance of the plant. The start-up of the pilot plant began with the seeding of the reactor with sludge from the biological treatment of the WWTP of Santomera, with an MLSS (mixed liquor suspended solids) concentration of approximately 3.0 g/L.

The plant was operated at ambient temperature (between 21 °C in fall/winter and 23 °C in spring) and SMEBR system was operated in four different stages: a first stage operating as a conventional SMBR and the other stages in which electrocoagulation was applied at three different current densities (5, 10 and 15 A/m²).

During all stages of operation, the reactor worked at a constant flux of 5 LMH, dissolved oxygen between 3 and 6 mg O₂/L, filtration/relaxation cycles of 7/3 minutes, electrode materials of aluminum (anode) and stainless steel (cathode), distance between electrodes of 5 cm and electric current exposure times of 5 min ON/10 min OFF. According to Najmi et al. [22], a hydraulic retention time –HRT of 16 hr was set for the entire experimental period.

Regarding the charge loading, which expresses the total charge passing through to the solution by the current [23], it was 214.17, 428.34 and 642.42 mA m⁻³·hr at current densities of 5, 10 and 15 A/m² respectively.

At the end of each stage, the membrane was cleaned with 0.2% sodium hypochlorite solution, according to the manufacturer's instructions. However, at the beginning of the last stage, a chemical cleaning in two phases was necessary, the first one with citric acid (0.2%) and the
second one with sodium hypochlorite (0.2%) in order to achieve a higher recovery level of the membrane.

The plant operated at high sludge retention times –SRT (> 30 days), as no purges were made during the four stages, except for the samples taken for the analytical control and the chemical cleaning of the membrane.

Influent wastewater

The influent of the pilot plant was wastewater collected after the screening unit, but before the degritting unit. Table 2 shows the variability of the influent of the SMEBR plant after the analysis of 35 samples.

**Table 2** Variability of the quality parameters of the influent of the SMEBR pilot system.

<table>
<thead>
<tr>
<th>Water quality parameter</th>
<th>Average value ± standard deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Stage 1 0 A/m³</td>
</tr>
<tr>
<td>pH</td>
<td>7.74±0.26</td>
</tr>
<tr>
<td>Conductivity (µS/cm)</td>
<td>2986±328</td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>25.7±1.8</td>
</tr>
<tr>
<td>COD (mg/L)</td>
<td>894±214</td>
</tr>
<tr>
<td>Total Nitrogen (mg/L)</td>
<td>81.8±12.1</td>
</tr>
<tr>
<td>Total Phosphorus (mg/L)</td>
<td>15.8±2.8</td>
</tr>
</tbody>
</table>

As the influent of the SMEBR system is a domestic and industrial wastewater, which suffers seasonal influences, significant fluctuations in quality parameters were observed.

Analytical methods

The determinations of COD, total nitrogen (TN) and total phosphorus (TP) were made by the MACHEREY-NAGEL digestion vial tests and analyzed by the spectrophotometer model NANOCOLOR® 500 D (Macherey-Nagel). For the pH and conductivity measurements, the BASIC 20 and CM 35 models were used, respectively (Crison instruments-Hach Lange, Spain).

Ten micropollutants commonly present in wastewater were selected ([24], [25], [26]). They were divided into two families: Pharmaceuticals (Acetaminophen, Caffeine, Carbamazepine, Clarithromycin, Diclofenac, Erythromycin Ofloxacin and Trimethoprim) and Pesticides (Acetamiprid and Thiabendazole). For the quantification and analysis of these micropollutants, samples of the influent and effluent were taken in 500 mL sterilized bottles, filtered with 1.2 mm glass fiber filters, and Solid Phase Extraction (SPE) was carried out with the Dionex Auto Trace equipment 280 (Thermo Scientific) using cartridges Oasis HLB 6cc/200 mg according to the method exposed by Almeida et al. [27]. For the SPE of the pharmaceuticals, the solvents ethyl acetate, methanol and water were used, and for the family of pesticides, dichloromethane, acetonitrile and water, all HPLC grade from Sigma Aldrich.
(Steinheim, Germany). The extract collected in each tube was dried with N$_2$ flow and, once the volume was reduced, the samples were transferred to an insert of 200 μL where the process was continued until total drying. Then the samples were reconstituted with 100 μL of internal standard solution for the pharmaceuticals (500 μg/L of carbamazepine d-10 in methanol) and 200 μL of internal standard solution for the pesticides (500 μg/L in triphenyl phosphate and atrazine d-5). For the pharmaceuticals, the samples were reconstituted by adding the derivatization reagent (50 μL of BSTFA: TMCS and 50 μL of pyridine). The samples were analyzed by gas chromatography coupled to mass spectrometry (GC-MS). The equipment used was the Agilent 7890 chromatograph and Agilent 5975 quadrupole mass spectrometer.

Regarding the operational parameters, the concentration of MLSS was analyzed by gravimetric methods according to APHA [28]. The variation of the transmembrane pressure (TMP) during the operation time was continuously registered through a pressure transmitter model TPR 14 of Desin Instruments (Barcelona, Spain). To measure the fouling of the membrane in each stage of operation, the increase in TMP was divided between the period of time (ΔTMP/dt) and this value was normalized according to the concentration of MLSS obtained.

The sludge volume index (SVI) was obtained by measuring the volume occupied by the sludge, in a mixed liquor sample of 1 L, after 30 minutes of sedimentation (V30), divided by the concentration of MLSS. EPS extraction was performed by ion exchange using a cationic resin [29]. For protein determination, a total protein kit (Sigma-Aldrich, TP 0330) was used, according to the method of Lowry et al. [30]. The carbohydrate was determined by the colorimetric method of phenol-sulfuric acid [31]. The determination of humic acids was carried out by colorimetric method [29]. The total EPS were calculated as the sum of the proteins, carbohydrates and humic acids.

3. Results and discussion

The impact of current density on effluents quality

Figure 2 shows the removal rates of COD, total nitrogen and total phosphorus for the different currents densities applied.
Figure 2 COD, total phosphorus and total nitrogen removal in a conventional SMBR (Stage 1) and in the SMEBR system (Stages 2, 3, 4)

COD removal

During the first stage, operating without the application of electricity, an average removal percentage of COD of 96% was reached, while, with the current densities of 5, 10 and 15 A/m$^2$ (stages 2, 3 and 4) average eliminations of 92%, 93% and 96%, respectively, were obtained (Figure 2). The average COD concentration in the SMEBR effluent was 41.9, 39.7 and 27.9 mg/L at current densities of 5, 10 and 15 A/m$^2$ respectively, while in the SMBR (0 A/m$^2$) it was of 39.2 mg/L (stage 1).

The overall efficiency of COD removal after the application of current densities of 5 and 10 A/m$^2$ was lower than that observed in the conventional SMBR (stage 1). This could be attributed, on the one hand, to the lower concentration of organic matter in the influent of the SMEBR system in these two stages (Table 1) and, on the other hand, to the additional resistance to filtration offered by the cake layer on the membrane surface, since it is thicker in the SMBR than in the SMEBR [32]. However, with the application of a higher current density (15 A/m$^2$) this behavior was not observed, since the influence of electrochemical processes was predominant with respect to the contribution of membrane filtration. Borea et al. [20] also observed this behavior when they compared the removals obtained in the SMBR (98%) and 97.5 and 98.2 after applying voltage gradients of 1 and 3 V/cm, respectively. According to Le-Clech et al. [32], permeability of the cake could be affected mainly by the flow, the electrostatic interactions and the size of the particle.

The results obtained by Bani-Melhem & Elektorowicz [12] show that the SMEBR system achieved a COD removal of 85-95%, while the SMBR system reached a removal rate of 75-90%. They reported that the main mechanisms of COD removal during electrocoagulation
were the oxidation and adsorption onto aluminum hydroxides formed by electrostatic attraction, as well as physical entrapment.

Sillanpää & Shestakova [33] reported that the greater the amount of hydroxide formed, which is achieved with the higher current densities applied, the greater the efficiency of the removal of organic matter. However, Tafti et al. [14] verified in their study a reduction of 85% in the removal efficiency when operating at current densities of 20 and 23 A/m², while at densities lower than 5 and 12.5 A/m² efficiencies of around 95% were obtained. According to the efficiencies obtained from this research, the application of electric current did not imply a significant increase in the oxidation of organic matter, since the SMBR technology achieves high rates of COD removal (Figure 2), which corroborates other studies that reported a maximum increase of 5% in the SMEBR system ([20], [17], [14]).

Nutrient removal

A significant influence of electrocoagulation was observed in the removal of total phosphorus. During the first stage, without application of electric current, the SMBR reached a total phosphorus removal rate of 61.4%, while, with the current densities of 5, 10 and 15 A/m² (stages 2, 3 and 4) average removals of 92.4, 97.7 and 97.9% were achieved, respectively (Figure 2).

Other studies report a significant removal of phosphorus by the SMEBR system. Bani-Melhem and Elektorowicz [12] and Hasan et al. [7] achieved over 98% phosphorous removal by the SMEBR system. Wei et al. [16] reached phosphorus removal rates above 90% in SMEBR, compared to 47-61% removal rates in conventional SMBR. In the study conducted by Tafti et al. [14], a conventional SMBR presented a phosphorus removal rate of 38%, while this value increased to 85% with a current density of 12.5 A/m² and exposure times of 3.1 min ON/6.9 min OFF. Wei et al. [16] and Chen et al. [34] described the main chemical reactions that occur in the aluminum anode during electrocoagulation, which explains the high phosphorus removal rates in the SMEBR system:

\[
\begin{align*}
\text{Al} - 3e^- & \rightarrow \text{Al}^{3+} \\
3\text{Al}^{3+} + 2\text{PO}_4^{3-} + 3\text{H}_2\text{O} & \rightarrow (\text{AlOH})_3(\text{PO}_4)_2 + 3\text{H}^+ \\
\text{Al}^{3+} + \text{PO}_4^{3-} & \rightarrow \text{AlPO}_4 \\
\text{Al}^{3+} + 3\text{H}_2\text{O} & \rightarrow \text{Al(OH)}_3 + 3\text{H}^+
\end{align*}
\]

With the application of electrical current, Al³⁺ is generated due to the electrooxidation of the aluminum anode. The newly generated aluminum ions come in contact with the phosphorus present in the biomass, precipitating it as (AlOH)_3(PO_4)_2 and AlPO_4 or adsorbing it by the strong adsorption agent produced, Al(OH)_3. The aluminum hydroxide formed has a very low solubility (Kps=3·10⁻³⁴) and, therefore, an amorphous precipitate is formed for a pH close to neutrality [35].

The phosphorus efficiencies obtained in the present research showed that the SMEBR technology is highly efficient in the removal of this nutrient.

Regarding the removal of total nitrogen, the SMBR reached an average removal rate of 42.5%, while, at current densities of 5, 10 and 15 A/m², average removal rates of 47.3, 37.0 and 43.2% were obtained, respectively (Figure 2). As a result, no significant increase in nitrogen removal efficiency was observed with the application of electrocoagulation. Bani-Melhem & Elektorowicz [12] and Tafti et al. [14] reported a reduction in removal efficiencies...
after the application of higher current densities (37.6-57.7 A/m² and above 20 A/m², respectively). They concluded that a lower removal at higher current densities may be due to partial death (lysis) of the microbial community, leading to an increase in ammonia at the system outlet and, consequently, lower removal efficiencies. In this study, the best removal rates were obtained with the lowest current density, 5 A/m².

Micropollutants removal

During stages 1 and 2 of this research, 10 micropollutants were analyzed. Due to its seasonal uses, the characterization of the influent allowed to distinguish three groups: the first group corresponded to the non-detected compounds (trimethoprim, erythromycin and acetamiprid, with values below the limit of detection 0.05 μg/L), followed by the group of hardly detected compounds (ofloxacin, clarithromycin, thiabendazole and carbamazepine) and finally the third group consisting of frequently detected micropollutants (caffeine, diclofenac and acetaminophen).

The compounds concentrations in the influent of a total of 13 analyzed samples were, in decreasing order, caffeine (0.32 - 37.00 μg/L) diclofenac (0.04 - 20.20 μg/L), acetaminophen (0.09 - 8.64 μg/L), ofloxacin (<0.05 - 2.06 μg/L), clarithromycin (<0.05 - 0.79 μg/L), thiabendazole (<0.05 - 0.40 μg/L) and carbamazepine (<0.05 - 0.27 μg/L).

Figure 3 shows the removal rates of micropollutants in stage 1 (operating as a conventional SMBR system) and in stage 2 (with the application of the current density of 10 A/m²).

![Figure 3](image)

**Figure 3** Micropollutants removal in a conventional SMBR and in the SMEBR system

Through the SMBR system, ofloxacin, acetaminophen and caffeine presented removal rates of 94, 71 and 90%, respectively, while with the SMEBR system operating with a DC current of 10 A/m², rates of 60, 90 and 99%, respectively, were achieved for the same compounds (Figure 3). These compounds, despite their marked hydrophilic character, were possibly removed by the biodegradation since they do not present electron accepting or persistent functional groups [36]. The micropollutant ofloxacin showed higher removal in the SMBR system, however, this high efficiency was due to the increase of this contaminant in the influent in stage 1 (average of 1.43 μg/L). During stage 2, when the current density of 10
A/m² was applied, its removal was also achieved at values below the limit of detection, since its lower concentration in the influent (average of 0.125 μg/L) resulted in a lower removal. Clarithromycin removal rate in SMBR was 42%, which is low percentage compared to the 85% reported by Zheng et al. [37]. In contrast, the SMEBR system showed removal rates of 86% for this compound. This drug has a molecular size of 747.95 Da, greater than the MWCO (membrane cut size) of the ultrafiltration membrane used, which allows its retention by the steric effect. Other possible removal mechanisms are biodegradation, adsorption onto sludge for being a moderately hydrophobic compound (Log K<sub>ow</sub> of 3.16) and the electrochemical effects that generate absorbent coagulants.

Diclofenac, despite of its high hydrophobicity, had a removal rate that did not exceed 40%, both with the SMBR and the SMEBR system. This could be due to the fact that this is an ionizable compound, and its removal efficiency depends on the pH (preferably at pH = 5) [36], since it remains in its hydrophobic form and allows its adsorption onto sludge. This justifies its low removal rate in this study, since the SMBR was operated at pH between 7 and 8.3. Ensano et al. [18], after applying a current density of 5 A/m² and working in a pH range closer to neutrality, reported an increase in the diclofenac removal of 25.16%, with respect to SMBR. In addition, the low removal rate observed for this compound could probably be attributed to persistent functional groups in its molecular structure [39]. The removal of carbamazepine using the SMBR was very low (0.3%), and it increased to 29% with the SMEBR at a DC of 10 A/m². The low removal efficiency of this compound has been reported by many authors [(40), [41], [26]]. Carbamazepine has a very low biodegradability at low concentration [40], so it is difficult for biomass to perform an effective biodegradation. In addition, this compound is adsorbed in the activated sludge and appears in the SMBR effluent due to its hydrophilic character. Ensano et al. [18] also reported an increase in the removal of carbamazepine of 25.26%, with respect to SMBR, after applying a current density of 5 A/m². Thiabendazole showed an average removal of 66% in stage 1, but it was not possible to compare its removal in the SMEBR system since the compound was not detected in the influent in the following stages.

The main mechanisms for the removal of micropollutants in the SMEBR were biological degradation, membrane filtration and the electrochemical action. The application of electrocoagulation generated coagulants capable of absorbing dissolved organic pharmaceuticals and also formed other complexes by neutralizing them and allowing them to join to form larger particles. The increase in their size creates an impediment and they are retained by the membrane [(18), [42]].

The impact of current density on sludge characteristics

To evaluate the influence of the application of the three current densities on the characteristics of the sludge, the concentration of suspended solids –MLSS, the extracellular polymeric substances –EPS and the volumetric index of the sludge -SVI in each stage of operation were analyzed, as shown in Figure 4.
Figure 4 Average concentrations of MLSS, EPS and SVI with standard error of the mean observed in the SMBR (0 A/m$^2$) and in the SMEBR (5, 10 y 15 A/m$^2$).

Variation of SVI

The SVI was used as an indicator of the sedimentation characteristics of the sludge. A lower SVI value, especially below 120 ml/g, suggests a better sedimentation property [17]. A high SVI value is usually attributed to the growth of filamentous bacteria [43]. In Figure 4, without the application of electrocoagulation, an average SVI of 155 ml/g was reached, while with the current densities of 5, 10 and 15 A/m$^2$ averages SVI of 147, 122 and 97 ml/g were obtained, respectively. The study by Hua et al. [44] using both aluminum electrodes fixed at a distance of 5 cm, applying a current density of 20 A/m$^2$ and with exposure times of 15 min ON/45 min OFF, reported average SVI values in the range of 44 - 47 ml/g and 143 - 181 ml/g for the SMEBR and SMBR, respectively. With the application of current densities of 12.5 and 20 A/m$^2$, Tafti et al. [14] reached an SVI of 33 and 36 ml/g, respectively, values lower than 135 ml/g obtained in the SMBR operation. However, by applying a current density beyond 20 A/m$^2$, a reduction the sludge settleability was observed. Hosseinzadeh et al. [17] and Hasan et al. [7] also reported a better settling and compactness of the sludge in the SMEBR system. Ho et al. [45] concluded that the production of cationic coagulants in SMEBR promotes flocs formation of larger sizes and improves the sedimentation rate, thereafter reduces adhesion of foulants on the membrane surface.

Variation of MLSS

The MLSS ranged from 3.3 to 5.4 g/L in the conventional SMBR operation (0 A/m$^2$) and, with the application of current densities of 5, 10 and 15 A/m$^2$, the MLSS concentrations
varied from 5.4 to 6.1 g/L, 5.0 to 7.8 g/L and 7.7 to 10.6 g/L, respectively (Figure 4). The increase in concentration at each stage was attributed to the seasonal fluctuations of the influent and the electrokinetic phenomenon, since it increases the concentration of inorganic components. The increase in the concentration of MLSS after applying the electric current corroborates with that reported by Bani-Melhem & Elektorowicz [15], which observed an increase from 2.1 to 3.5 g/L in the operation of the conventional SMBR and from 3.5 to 5.0 g/L in the SMEBR system, and also with Hasan et al. [7] who reported an increase of 2.4 to 5.0 g/L.

The concentration of MLSS plays an important role in membrane fouling, however, its real impact is still much discussed by the scientific community. Despite controversial findings reported in the literature about the influence of MLSS on membrane fouling, Rosenberger et al. [46] demonstrated an overall MLSS trend: less fouling at very low MLSS concentrations (<6 g/L), no impact at MLSS average concentrations (8-12 g/L), and more fouling at very high MLSS concentrations (> 15 g/L). Le-Clech et al. [47] did not observe a significant difference when the MLSS concentration increased from 4 to 8 g/L, however, at a concentration of 12 g/L a double impact on the permeate flow was verified. Cho et al. [48] concluded that the concentration of MLSS may not play a significant role in the membrane fouling when the SMBR is operated at low flux.

An investigation carried out by Ibeid et al. [19] emphasized that a much more accurate prediction of membrane fouling propensity is achieved by reporting MLVSS concentrations along with EPS concentrations, since the conventional approach of correlating the membrane fouling directly with the MLVSS concentration may cause misunderstandings. Ibeid et al. [19] showed that the membrane fouling rate was approximately four times higher in MLVSS at a concentration of 3.0 g/L than 4.75 g/L, but because of the protein concentrations in the sludge supernatant were 3.2 times higher in MLVSS at 3.0 g/L. However, at MLSS values of 6, 10 and 14 g/L, Dvořák et al. [49] verified similar concentrations of total bound EPS. According to the previous discussion, it was assumed that the MLSS concentration did not contribute significantly to the membrane fouling because the system operated at low flux (5 LMH) and also that the highest fouling (0.81 kPa/day at SMBR) was obtained with the operation at lower MLSS values (from 3.3 to 5.4 g/L).

Variation of EPS

The EPS, composed mainly of proteins, carbohydrates and humic acids, are considered as the greatest impact factor on the membrane fouling [[50], [51], [5]]. Many authors reported that carbohydrates (EPSc) are the ones that most contribute to fouling [[49], [32]] due to their hydrophilic nature [52] and, therefore can interact with the membrane more strongly. Figure 4 suggests that EPSc were affected by electric current, mainly after the application of current densities of 5 and 15 A/m². In the first stage of operation, the total bound EPS presented an average of 152 mg/g MLSS, while with the current densities of 5, 10 and 15 A/m² averages values of 113, 145 and 78 mg/g MLSS were obtained, respectively. An increase in EPSs during the application of a current density of 10 A/m² was detected, which could be caused by a sharp variation in the characteristics of the influent during the citrus
harvesting season, since the microorganisms react to these fluctuations by excreting EPSs as defense mechanism [4], [51].

The fraction of the carbohydrates presented average values of 16, 19 and 10 mg/g MLSS after the application of the current densities of 5, 10 and 15 A/m², respectively, while the conventional SMBR presented an average of 36 mg/g MLSS. The fractions of proteins and humic substances in the mixed liquor (SMBR and SMEBR) were 43% and 41%, respectively. In adequate conditions, the electrokinetic effects in the SMEBR have a considerable contribution in the reduction of EPS. The reduction of EPS in the SMEBR can be attributed to the charge neutralization and adsorption for soluble foulants or electro-chemical oxidation for bound foulants [44]. Soluble EPSs, mostly proteins, carry negative charges that react electrostatically with the cations present (Al³⁺) to form stable flocs [14], [7].

Liu et al. [11] observed that the positive effects of the application of electric current to SMBR included the reduction of EPS. Other investigations [16], [7], reported a reduction in the EPS soluble in the SMEBR operation of 36 and 63%, respectively, with respect to the SMBR. Higher removals were obtained by Ibeid et al. [19] operating an SMEBR at a current density of 10 A/m² and exposure times of 5 min ON/20 min OFF, which managed to remove 55% of proteins and 90% of carbohydrates.

In the research conducted by Tafti et al. [14], when applying a current density of 5 A/m² and an exposure mode of 3.3 min ON/6.7 min OFF, achieved an approximate reduction of 51 and 59% for proteins and polysaccharides, respectively. On the other hand, when applying a density of 20 A/m² and long activation times, a higher EPS content was observed due to cell lysis caused by the electric field.

According to the previous discussion and the results obtained in the present study, it is concluded that the effect of the electric current resulted in a reduction of the EPSc values and, consequently, in a decrease in the membrane fouling rate.

The impact of current density on membrane fouling

As commented in the previous sections, many physical, chemical and biological sludge factors contribute to the membrane fouling, increasing the TMP [9]. To evaluate the impact on membrane fouling after the application of electric current, the evolution of the TMP was analyzed at each stage of operation. Figure 5 shows the evolution of the TMP when the stabilization of each stage of operation was achieved.
In order to analyze the fouling of the membrane in each stage of operation, the increase in TMP over time (\(\Delta\text{TMP/dt}\)) was evaluated, operating with a constant flux of 5 LMH. Figure 5 shows that during the first stage of the study (conventional SMBR) the TMP suffered a significant increase of 0.81 kPa/day during 9 days of operation. In the second stage, with the application of the current density of 10 A/m\(^2\), the TMP increased 0.30 kPa/day after 22 days of operation. With the application of the current density of 5 A/m\(^2\) (stage 3) the TMP increased 0.22 kPa/day after 20 days of operation.

Once the TMP reached -0.40 bar, a chemical cleaning was necessary. Before starting the fourth stage, a two-stage chemical cleaning of the membrane was carried out, the first one with citric acid (0.2\%) and the second one with sodium hypochlorite (0.2\%), which explains the decrease in the starting operating pressure at this stage. With the application of the current density of 15 A/m\(^2\), the TMP increased 0.27 kPa/day after 20 days of operation.

An analogous study in a 235L SMEBR pilot plant treating municipal wastewater with an influent COD between 70-300 mg/L was carried out by Hasan et al. [9]. After operating for over 7 weeks applying a current density of 12 A/m\(^2\) and an exposure time of 5 min ON/10 min OFF, a fouling rate in SMEBR and MBR of 0.018 and 0.371 kPa/d, respectively, was achieved.

Further studies reported on the higher efficiency of SMEBR versus SMBR in reducing membrane fouling. Bani-Melhem & Elektorowicz [12] achieved an average of 16.3\% reduction and Ibeid et al. [8] reached three times less fouling. Tafti et al. [14] observed a lower fouling after applying a current density of 12.5 A/m\(^2\) with an exposure mode of 3.1 min ON/6.9 min OFF. Borea et al. [20], applying a voltage gradient of 3 V/cm, managed to reduce the membrane fouling rate by 54.33\%.

**Figure 5** Variation of transmembrane-pressure –TMP in a conventional SMBR (Stage 1) and in the SMEBR system (Stages 2, 3, 4)
All three current densities applied showed a reduction in TMP compared to the conventional SMBR and, furthermore, the current density of 5 A/m$^2$ showed an even more significant reduction (from 0.81 to 0.22 kPa/day). Compared to the DC of 5 A/m$^2$, the increase in TMP, with DC of 10 and 15 A/m$^2$, suggests that the higher concentrations of Al$^{3+}$ in the mixed liquor contributed to the small increase in membrane fouling. The efficiency of aluminum as a coagulant to minimize membrane fouling is highly reported in the literature [[53], [54], [55], [56]]. However, since coagulation is achieved by charge neutralization and destabilization of negatively charged colloids by cationic Al$^{3+}$ ions hydrolysis products, excess dosage of coagulant can result in charge reversal and colloid restabilization [57]. In a further analysis to understand the fouling observed in the operation of the SMBR and SMEBR systems, Hosseinzadeh et al. [17] investigated the changes in membrane surface morphology. The results revealed that organic matter and colloidal particles mostly contributed to membranes clogging. In the SMBR membrane, organic materials and calcium oxide were found at higher concentrations, while in the SMEBR membrane, a higher percentage of aluminum oxide was detected, as expected. Since the membranes were made of polyethersulfone (PES), their molecular structure had some negative charges, which improve the adsorption of trivalent cations (aluminum) compared to bivalent cations (calcium). Zhu & Elimelech [58] observed that fouling of aluminum oxide colloids seemed to be reversible and this fouling was attributed to the deposition of particles on the surface of the membrane and without pore obstruction, which explains the moderate increase detected with the DC of 10 and 15 A/m$^2$. After a Fourier-transform infrared-FTIR spectroscopy, Akkaya & Bilgili [59] observed the presence of polysaccharides, silicate colloids and organic sulfonic acids as major components of SMBR and SMEBR membrane fouling, and the presence of proteins in the cake layer inside of fouled membranes, concluding that although chemical properties of membranes were similar, the presence of electrical field in SMEBR helped to delay the membrane fouling.

Energy consumption

The electric power requirement and the electrode consumption are the main expenses taking into account the operative cost of the electrocoagulation process. The operating conditions of electrocoagulation, such as current density, pH and influent conductivity, have critical functions in the optimization of the technique. Obviously, an increase in the current density results in increases in energy requirement and electrode consumption [60]. To calculate the energy consumption of the electrocoagulation, the applied electric current (I, amperes), the generated voltage (V, volts) and the treated volume during the time of exposure to the current (Q, m$^3$/h) were considered according to Koby et al. [61]

\[ E = \frac{V \cdot I}{1000 \cdot Q} \]

Considering the operating parameters of electrocoagulation in the pilot plant: exposure time 5 min ON/10 min OFF, permeate flowrate of 38.5 L/h and voltage values registered by the device throughout the study; averages energy consumptions of 0.26, 0.86 and 1.87 kWh/m$^3$ were obtained by applying the current densities of 5, 10 and 15 A/m$^2$, respectively. According to Bayramoglu et al. [62] the operating cost of electrocoagulation, using the aluminum anode, increases constantly with the increase in pH and / or with the reduction of water conductivity. In this study, the pH and conductivity of the mixed liquor showed similar
values in the three operation stages. The average values of pH in the mixed liquor when current densities of 5, 10 and 15 A/m$^2$ were applied were 7.89 ± 0.09, 7.68 ± 0.26 and 7.80 ± 0.16, respectively, while the conductivity presented average values of 2022 ± 125, 1812 ± 85 and 2180 ± 149, respectively.

Hasan et al. [7], applying a current density of 12 A/m$^2$ and exposure times of 5 min ON/10 min OFF, observed that the specific energy consumption of the SMEBR system varied between 1.1 and 1.6 kWh/m$^3$ over 7 weeks of operation, also considering the energy consumed in the air supply. Ibeid et al. [8] reported an energy consumption between 0.6 and 2.0 kWh/m$^3$ operating with a current density of 15-20 A/m$^2$ and with exposure modes of 5 min ON/15 min OFF and 5 min ON/20 min OFF. However, the two studies did not report on the pH and conductivity values of the mixed liquor.

An important aspect to be considered in the operation of the SMEBR is the deterioration of the aluminum anode, which after a certain time of operation must be replaced. The lifetime of the anode depends on the material, thickness, current density and exposure times applied. The lifetime of the anode in this research was 4 months, one month less than that estimated by Hasan et al. [7]. For the stainless steel cathode, a complete physical cleaning was performed after 4 months of operation.

4. Conclusions

The SMEBR system achieved a synergistic effect and excellent results in terms of phosphorus removal, EPSc reduction and minimization of membrane fouling which were attributed to the changes in the physical/chemical properties of the mixed liquor, achieved after application of the electric current. An important potential for the removal of those more recalcitrant micropollutants was verified with SMEBR.

The micropollutants acetaminophen, clarithromycin and carbamazepine showed a significant increase in their removals in the SMEBR system, however diclofenac was highly persistent. Optimal operating conditions were obtained by applying the current density of 5 A/m$^2$ with ON/OFF cycles of 5/10 minutes which, with lower energy consumption, managed to remove 92.4% of the total phosphorus and, compared to SMBR, reduced EPSc and membrane fouling (TMP) by 55.5% and 72.8%, respectively. Nevertheless, an investigation based on an experimental pilot-scale plant fed with municipal wastewater requires an increased number of samples to be more conclusive.

Further studies are required which address the mechanisms of adsorption of micropollutants and phosphorus onto sludge after the application of electrocoagulation, as well as a detailed cost-analysis to determine the feasibility of a full scale SMEBR system treating urban wastewater.
References


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Graphical abstract

Highlights

- A pilot scale submerged membrane electro-bioreactor –SMEBR was designed and operated.
- SMEBR pilot plant was highly efficient (97.9%) in phosphorus removal from municipal wastewater.
- SMEBR increased the removals of pharmaceuticals acetaminophen, clarithromycin and carbamazepine.
- A substantial reduction of extracellular polymeric substances and membrane fouling was reported.
Credit author

- Lyvia Mendes Predolin: Writing-Original Draft, Investigation, Methodology, Software, Visualization.

- M.J. Moya-Llamas: Writing-Review & Editing, Conceptualization, Validation, Visualization.

- Edgardo David Vásquez Rodríguez: Investigation.

- Arturo Trapote Jaume: Project administration.

- Daniel Prats Rico: Funding acquisition, Supervision.
Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in the paper entitled Effect of current density on the efficiency of a membrane electro-bioreactor for removal of micropollutants and phosphorus, and reduction of fouling: A pilot plant case study.

☐ The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: