

Effects of electrochemical processes application on the modification of mixed liquor characteristics of an electro-membrane bioreactor (e-MBR)

André Aguiar Battistelli, Rayra Emanuely da Costa,
Leonardo Dalri-Cecato, Tiago José Belli and Flávio Rubens Lapolli

ABSTRACT

This study evaluated the effects of electrochemical processes on the mixed liquor characteristics of an electro-membrane bioreactor (e-MBR) applied to municipal wastewater treatment. A laboratory-scale e-MBR was assessed under two experimental runs: without the electric field (run I) and with electric field, controlled by the application of an electric current set in 10.0 A m^{-2} under intermittent exposure mode of 6 minutes ON/18 minutes OFF (run II). The electric field caused approximately 55% removal of both soluble microbial products (SMP) and extracellular polymeric substances (EPS), whereas the proteins/carbohydrates ratio in EPS was increased from 1.9 in the run I to 2.9 in run II, leading to an increment of flocs' hydrophobicity. Additionally, the sludge floc size average value was reduced from $42.2 \mu\text{m}$ in run I to $24.6 \mu\text{m}$ in run II, which led to a significant enhancement in the sludge settleability. As a result, the membrane fouling rate was always less than 3.80 mbar d^{-1} in run II, whereas in run I these values reached up to 34.7 mbar d^{-1} . These results demonstrated that the electrochemical processes enhanced the mixed liquor filterability. Therefore, their implementation represents a great alternative to improve the operational stability of membrane bioreactors.

Key words | electrocoagulation, electro-membrane bioreactor, extracellular polymeric substances, fouling control, soluble microbial products

André Aguiar Battistelli (corresponding author)

Rayra Emanuely da Costa

Leonardo Dalri-Cecato

Flávio Rubens Lapolli

Department of Sanitary and Environmental Engineering,

Federal University of Santa Catarina, Trindade, Florianópolis, SC 88040-900, Brazil

E-mail: andreambiental@live.com

Tiago José Belli

Department of Sanitary Engineering,

State University of Santa Catarina,

Ibirama, SC 89140-000,

Brazil

INTRODUCTION

Membrane bioreactors (MBR) are currently considered a well-established technology for treatment and reuse of municipal and industrial wastewater due to their several advantages over the conventional active sludge treatment process, such as smaller footprint, lower sludge production and higher effluent quality (Krzeminski *et al.* 2017). However, despite the rapid development of this technology in recent years, membrane fouling is still considered an obstacle for the universal application of MBR, and this process may increase the energy consumption and the frequency of membrane cleaning and replacement (Guo *et al.* 2012; Meng *et al.* 2017).

In general, membrane fouling in MBR occurs due to physical and chemical interactions between the membrane surface and the mixed liquor constituents. Regarding these constituents, it is widely accepted that extracellular polymeric substances (EPS) and soluble microbial products

(SMP) are the major membrane foulants (Drews 2010; Lin *et al.* 2014; Meng *et al.* 2017). EPS and SMP consist of a complex matrix of products excreted from bacterial cells, composed mainly of humic substances, nucleic acids, proteins and carbohydrates (Guo *et al.* 2012). Bound EPS is the fraction of these compounds that is on the cell surface or in the intercellular space of microbial aggregates. It is responsible for the aggregation and adhesion of the flocs, whereas SMP is a soluble compound resulting from the dissolution of bound EPS that is related to membrane pore blocking and the initial formation of a gel layer (Lin *et al.* 2014).

In this sense, several studies with an emphasis on changing the mixed liquor characteristics have been performed, in order to reduce the concentrations of SMP and EPS and thereby control the membrane fouling (Drews 2010). Among these alternatives, the electric-assisted fouling

mitigation has been receiving great attention in recent years (Meng *et al.* 2017). This process consists of the application of an electric field between two metallic electrodes installed inside the MBR, causing anode oxidation that solubilizes metallic cations in the mixed liquor (Bani-Melhem & Elektorowicz 2010). This type of reactor is usually referred to as an electro-membrane bioreactor (e-MBR).

The current density and electrodes' material are considered important factors that affect the e-MBR performance (Ensano *et al.* 2016). Therefore, it is recommended to use an intermittent exposure mode and to apply a current density that does not exceed 25.0 A m^{-2} , in order to improve the mixed liquor filterability and maximize the pollutant removal without interfering with the microbial activity (Wei *et al.* 2011). Regarding the electrode material, the most suitable metal to use in this process is aluminum, due to the high surface area of the aluminum hydroxides generated (Ensano *et al.* 2016). Thus, when aluminum anodes are used, the following reactions occur inside the reactor.

At the anode : $\text{Al(s)} \rightarrow \text{Al}^{3+} + 3\text{e}^{-}$

At the cathode $2\text{H}_2\text{O} + 2\text{e}^{-} \rightarrow \text{H}_2(\text{g}) + 2\text{OH}^{-}$

In the solution $\text{Al}^{3+} + 3\text{OH}^{-} \rightarrow \text{Al(OH)}_3(\text{s})$

Due to their high load-neutralizing capacity, the metallic complexes formed are highly effective in the removal of negatively charged organic materials. Besides, such complexes also have a wide surface area, capable of adsorbing and capturing colloidal particles and soluble organic pollutants, forming flocs that can be easily removed by membrane filtration processes (Mollah *et al.* 2004).

It is also important to highlight that the application of an electric field induces the occurrence of other electrochemical processes, such as electroosmosis and electrophoresis, which help to decrease the deposition of foulants onto the membrane surface (Bani-Melhem & Elektorowicz 2011). Moreover, the oxidation of some pollutants may also occur due to their deposition at the anode surface and their reaction with the hydroxyl radicals ($\cdot\text{OH}$) that can be generated due to the application of the electric field (Zeyouidi *et al.* 2015; Ensano *et al.* 2016). Thus, the positive role of the application of electrochemical processes in MBR may occur mainly due to three mechanisms: (i) charge neutralization and sorption of soluble compounds by dissolved metallic cations; (ii) deposition control of foulants onto the membrane surface; and (iii) chemical oxidation of bound biopolymers (Bani-Melhem & Elektorowicz 2011; Hua *et al.* 2015).

Although previous studies have evaluated the use of an electric field as an alternative to improve the mixed liquor filterability and to mitigate membrane fouling (Hasan *et al.* 2014; Ibeid *et al.* 2015; Tafti *et al.* 2015; Zhang *et al.* 2015), specific information about the effect of such electric processes on SMP and bound EPS content is scarcely reported in the literature. Furthermore, experimental results are often obtained based on synthetic wastewater, not representing real scenario conditions, which points to the need for more investigation in this field.

Therefore, the aim of this study was to evaluate the effects of the electrochemical processes on the mixed liquor characteristics of an e-MBR applied to municipal wastewater treatment. For this purpose, the reactor performance was assessed under two experimental runs: without application of the electric field (run I) and with application of the electric field (run II). Mixed liquor filterability was monitored according to the transmembrane profile and on the basis of sludge properties (particle size distribution, zeta potential, capillary suction time and EPS). Batch assays (sludge volume index and specific resistance to filtration) were performed to better characterize the settleability and filterability of the mixed liquor, respectively.

MATERIAL AND METHODS

Experimental set-up

This study was conducted in a laboratory-scale e-MBR (Figure 1). The e-MBR consisted of a cylindrical tank with 16 L working volume, constructed based on the previous study of Bani-Melhem & Elektorowicz (2010). A submerged

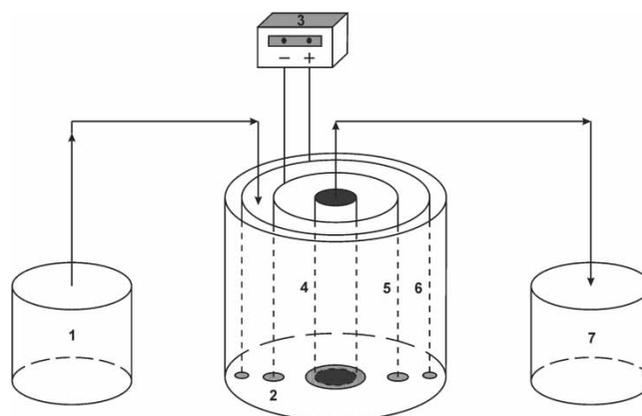


Figure 1 | Schematic of MBR experimental setup. (1) wastewater tank; (2) aeration system; (3) direct current power supply; (4) membrane module; (5) stainless steel cathode; (6) aluminium anode; and (7) permeate tank.

hollow fiber membrane module (Pam membranes Co., Brazil) was installed in the reactor's center. The membrane was made of polyetherimide (PEI), with nominal pore size of 0.3 μm and total surface filtration area of 0.178 m^2 . The e-MBR was also equipped with two cylindrical electrodes spaced 5.0 cm apart. The aluminum anode, with a total surface area of 0.18 m^2 and 45% perforation, was installed around the inner surface of the reactor wall. Moreover, a fine stainless steel cathode, with a total surface area of 0.12 m^2 , was installed between the membrane and the anode.

Operating conditions

The e-MBR performance was evaluated under two experimental runs. During the first 30 operating days, the bioreactor was operated as a conventional MBR, without application of the electric field (run I). Thereafter, during the next 30 days of operation, an electric current controlled at 10.0 A m^{-2} under an intermittent exposure mode of 6 minutes ON/18 minutes OFF was applied to generate an electric field, using an adjustable source of DC digital power (PSA-305D) with a variation of 0–30 V and 0–5 A (run II). Such experimental conditions were previously determined in batch assays, taking into account the results reported by Ibeid *et al.* (2013b). Air was provided by means of a sparger installed at the bottom of the reactors. This aeration system was used to supply oxygen for the microorganisms, scour the membrane surface to minimize biofouling and to mitigate the electrode passivation phenomenon by particle deposition. The airflow rate was kept at 0.5 $\text{m}^3 \text{h}^{-1}$, which corresponds to a specific aeration demand (SADm) of 2.8 $\text{m}^3 \text{m}^{-2} \text{h}^{-1}$. During the whole experimental period, the mixed liquor temperature was controlled to be 20 °C, the pH ranged between 7.1 and 7.8 and the dissolved oxygen level was always higher than 6.4 mg L^{-1} . The solids retention time (SRT) was kept at 30 days by removing part of the sludge daily. The e-MBR was continuously fed with municipal wastewater taken from a sewage collection system, with the help of a submerged pump. This pump was installed inside a PVC pipe with its surface covered by 0.01 m holes to avoid intake of large solid materials into the system. The wastewater characteristics are shown in Table 1.

Two peristaltic pumps (Watson Marlow 323) performed the feeding and the permeation under a flux of 5.25 LMH and intermittent mode (400 s ON/60 s OFF), which resulted in a hydraulic retention time (HRT) of 20 h. The inoculation sludge was obtained from the aeration tank of a municipal wastewater treatment plant located in Florianópolis, Brazil.

Table 1 | Municipal wastewater characteristics. The concentrations represent the average of 15 collection campaigns

Parameter	Unit	Mean \pm SD
Chemical oxygen demand (COD)	$\text{mgO}_2 \text{L}^{-1}$	628 \pm 102
Soluble chemical oxygen demand (sCOD)	$\text{mgO}_2 \text{L}^{-1}$	237 \pm 53
Dissolved organic carbon (DOC)	mg L^{-1}	66.2 \pm 18.6
Total nitrogen (TN)	mgN L^{-1}	89.5 \pm 20.6
Ammonium nitrogen ($\text{NH}_4^+\text{-N}$)	mgN L^{-1}	48.4 \pm 14.7
Total phosphorus (TP)	mgP L^{-1}	9.2 \pm 2.9
Alkalinity	$\text{mgCaCO}_3 \text{L}^{-1}$	452 \pm 103
pH	–	7.8 \pm 0.7

This sludge was acclimated for 1 month before the start of e-MBR monitoring. It is important to highlight that this study addresses the start-up operational period, and thereby the reactor may not reach a steady state condition, particularly over experimental run II, the period in which the electrochemical process was applied.

Experimental procedures and statistical treatment

The municipal wastewater used to feed the e-MBR was characterized in terms of dissolved organic carbon (DOC), chemical oxygen demand (COD), soluble chemical oxygen demand (sCOD), total nitrogen (TN), ammonium nitrogen ($\text{NH}_4^+\text{-N}$), total phosphorus (TP), alkalinity and pH. COD, TN, $\text{NH}_4^+\text{-N}$ and TP were measured by spectrophotometry (Hach DR5000), according to the manufacturer's instructions, using the Hach 10127, 10072, 8000 and 10031 methods, respectively. Alkalinity was determined by titration (Eaton *et al.* 2005) and pH was monitored using a digital pH meter (Thermo Scientific Orion). DOC measurements were performed on a total organic carbon analyzer (TOC-LCSH/Shimadzu). Given the fact that our study was focused on the fouling investigation, the reactor treatment performance was based only on the DOC removal.

Transmembrane pressure values were recorded continuously through a pressure sensor (VDR-920). The energy consumption was monitored with an electronic meter (Kienzle KMC11D50). The mixed liquor properties were evaluated twice a week through the normalized capillary suction time (CSTn) (CST – Triton Electronics Type 304M), zeta potential (Zetasizer Nano, Malvern, UK), particle size distribution (PSD – Mastersizer 2000, Malvern, UK) and viscosity (Brookfield DV-I). The mixed liquor suspended solids (MLSS) was determined by the gravimetric method (Eaton *et al.* 2005).

The settleability of mixed liquor was evaluated by the diluted sludge volume index test (DSVI) (Eaton *et al.* 2005). The DSVI was measured using a 1 L graduated cylinder, where the diluted sludge sample was allowed to settle for 30 min. The fouling propensity of the mixed liquor was determined as specific resistance to filtration (SRF) using a dead-end filtration system at a constant pressure (Ibeid *et al.* 2015). To perform the test, the filtrate volume V (m^3) versus time t (s) was recorded and the SRF was calculated as:

$$SRF = \frac{2b A^2 TMP}{\mu C}$$

where: b (s m^{-6}) was the slope of filtrate volume over time versus time; A is the filtration area (m^2); TMP is the vacuum pressure (Pa), μ is the dynamic viscosity of the filtrate (mPa s) and C is the mass of solids per unit volume (kg m^{-3}).

SMP and EPS were measured twice a week. SMP was obtained by mixed liquor centrifugation (10,000 rpm for 10 min) followed by filtration (0.45 μm acetate filter). EPS was extracted using the heating method at 80 °C for 30 min, followed by centrifugation and filtration as performed for SMP. SMP and EPS were measured as proteins and carbohydrates by spectrophotometric analysis, according to the methods described by Lowry *et al.* (1951) and Dubois *et al.* (1956), respectively. The statistical data treatment

involved the normality test of Kolmogorov-Smirnov. Then, to compare the means obtained in each treatment, the Tukey test was applied with a 95% level of significance. Pearson's coefficient was used to identify the significance of the linear correlations between membrane fouling rate (MFR) and mixed liquor properties. Correlations were considered statistically significant at a 95% confidence level. These analyses were performed using the ActionStat software.

RESULTS AND DISCUSSION

TMP evolution

A faster TMP increase was found during run I (Figure 2(a)), indicating a poor filterability of the mixed liquor in this period. Consequently, higher values of MFR were noticed over run I, starting with 11.25 mbar d^{-1} and reaching up to 34.7 mbar d^{-1} . On the other hand, during run II, the MFR exhibited a more stable behaviour, showing values lower than 3.80 mbar d^{-1} over this entire experimental period (Figure 2(b)). As a result, the maximum value of TMP (0.6 bar) was achieved with only 22 operating days in run I, which led to performing the membrane cleaning

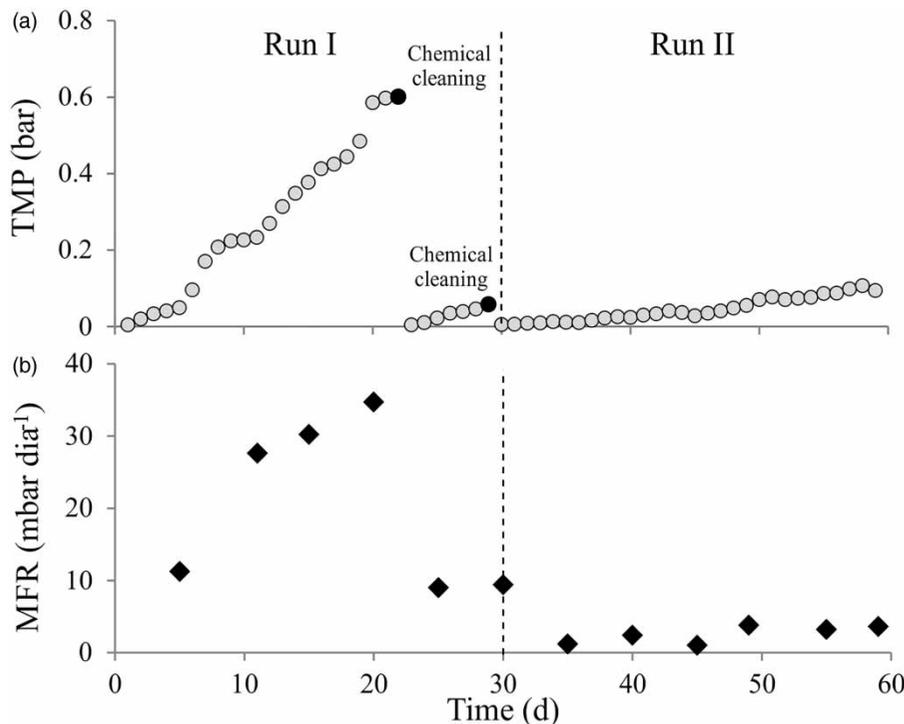


Figure 2 | Evolution of transmembrane pressure (TMP) (a) and membrane fouling rate (MFR) (b) during the whole experimental period.

procedures to recover its permeability, whereas for run II such procedures were not necessary, since the maximum value of TMP was only 0.10 bar.

The membrane fouling behaviour observed in run I meets with the profile usually observed in conventional MBRs operated under subcritical flow conditions. In this scenario, membrane fouling is not significant during the first days; however, it is substantially increased after a certain period of operation (Judd 2011). On the other hand, such behaviour was not observed during run II, suggesting that the application of the electric field may lead to changes in the mixed liquor characteristics and contribute to improving its filterability. Borea *et al.* (2017) observed similar results in a comparative study between a conventional MBR and an e-MBR treating synthetic wastewater. They reported an average MFR 54.3% lower in the e-MBR, evidencing that the integration of the electrochemical process with the MBR system enables a better mixed liquor filterability.

Mixed liquor characteristics analysis

In order to obtain a better understanding of the characteristics of the mixed liquor, more detailed tests were also carried out, including CSTn, SRF, zeta potential, PSD and DSVI.

CSTn is an indicator parameter of the mixed liquor dewaterability and can be strongly related to their filterability; a higher CSTn value usually means poor mixed liquor filterability (Scholes *et al.* 2016). As can be seen from Figure 3(a), the CSTn average values were 9.2 ± 2.6 and 3.9 ± 0.3 s sL mg⁻¹ for run I and II, respectively ($p < 0.05$). These results suggest that mixed liquor filterability was substantially enhanced in run II.

SRF is another parameter widely used to predict the fouling propensity in MBRs, as it is considered a reliable mixed liquor filterability indicator. The average SRF obtained were $18.4 \cdot 10^{12} \pm 5.9 \cdot 10^{12}$ m kg⁻¹ for run I, and $1.24 \cdot 10^{12} \pm 0.3 \cdot 10^{12}$ m kg⁻¹ for run II (Figure 3(b)). These results indicate that SRF was reduced at about 15 times in run II, supporting that mixed liquor filterability was substantially enhanced in this period. Similar results were obtained by Ibeid *et al.* (2015). These authors operated an MBR and an e-MBR simultaneously and verified an average SRF of $24 \cdot 10^{12}$ m kg⁻¹ for the MBR, while the e-MBR exhibited an average SRF equal to $3.2 \cdot 10^{12}$ m kg⁻¹.

The better mixed liquor filterability can be attributed to the release of Al³⁺ from the anode plate, leading to the destabilization of negatively charged colloids. As result, the sludge flocculation process becomes more effective,

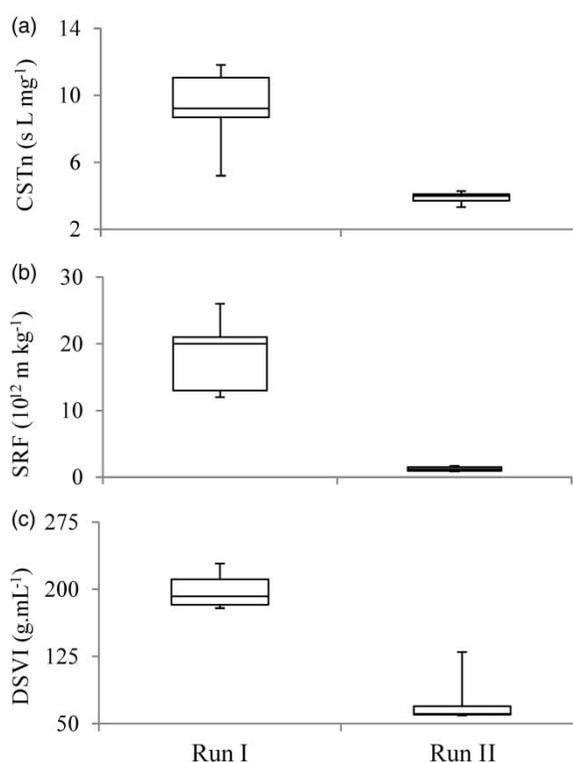


Figure 3 | Boxplot of capillary suction time (a), specific resistance to filtration (b) and diluted sludge volume index (c) for each experimental run.

reducing its resistance to the filtration process (Bani-Melhem & Elektorowicz 2011). In fact, the results from mixed liquor zeta potential (16.1 ± 2.3 mV to run I and 2.3 ± 0.4 mV to run II), indicated a reduction in the repulsive forces between sludge particles, resulting in a strong tendency for aggregation during the period within the application of the electric field. However, although the zeta potential was substantially reduced, it did not result in an increase in the mean size of the flocs. On the contrary, the mean value of PSD was reduced from 42.2 ± 10.8 μm in run I to 24.6 ± 6.4 μm in run II. This reduction of PSD may be related to the electroosmosis phenomenon, which consists of the release of bound water from the sludge flocs caused by application of the electric field (Giwa Ahmed & Hasan 2015). Furthermore, the inorganic suspended solids formed with aluminium hydroxides in the e-MBR are of smaller size and higher density compared to the biological flocs, which may also contribute to the reduction of PSD mean value (Ibeid *et al.* 2013a).

Due to the higher sludge density and the lower PSD, the DSVI exhibited lower values within the operating period in which the electric current was applied. For run I, the average DSVI value obtained was 198.2 ± 19.9 whereas for run II the corresponding value was

$71.5 \pm 24.1 \text{ mL g}^{-1}$ ($p < 0.05$) (Figure 3(c)). These results indicated an improvement in mixed liquor settleability, which can contribute to improved sludge filterability and reduced membrane fouling (Sun *et al.* 2007). Overall, the results from this specific analysis are in accordance with the TMP profile and indicate that application of an electric field can change the physicochemical properties of the flocs, playing an important role in enhancing the settleability and filterability of the mixed liquor.

Effects of MLSS and viscosity on mixed liquor filterability

The MLSS concentration showed no significant variation during run I, whereas a substantial increase in MLSS concentration was observed during experimental run II, from 2.85 g L^{-1} to 13.2 g L^{-1} (Figure 4). The increase in the MLSS values may be attributed to the chemical interaction between Al^{3+} released by anode oxidation and the wastewater's dissolved organic pollutants, which contributed to the formation of inorganic complexes (Bani-Melhem & Elektorowicz 2011; Hasan *et al.* 2014; Hua *et al.* 2015). As a result, the average value of mixed liquor viscosity increased from 1.97 cP at run I to 2.98 cP at run II ($p < 0.05$).

Some studies have reported that higher viscosity and greater MLSS values can intensify the membrane fouling process (Chang & Kim 2005; Wang *et al.* 2007; Lousada-Ferreira *et al.* 2015). However, this behaviour was not observed in our study, as the MFR was less expressive in run II, while the MLSS concentration was higher. Actually, a strong negative correlation was observed between MLSS and MFR ($r = -0.79$, $p < 0.05$), suggesting that the higher membrane fouling observed in run I was not related to the solids concentration (Table 3). A possible explanation is that other

factors were more important in the fouling process than the mixed liquor viscosity in the present study, such as the concentration and composition of the SMP and EPS fractions.

Effects of DOC on mixed liquor filterability

The e-MBR influent DOC values showed significant variation, ranging from 42 to 93 mg L^{-1} (Figure 5). Despite this, the reactor presented high DOC removal performance during the whole experimental period, attaining average removal efficiencies of 84% and 94% in run I and II, respectively ($p < 0.05$). The effluent DOC concentration always remained less than 15 mg L^{-1} , with average values of 9.7 ± 2.2 and $4.2 \pm 0.6 \text{ mg L}^{-1}$ for run I and II, respectively. The higher DOC removal performance within the second experimental period can be attributed to the occurrence of electrochemical processes (Bani-Melhem & Elektorowicz 2011).

The DOC concentration in the mixed liquor of MBR systems can play an important role in this reactor configuration, as the organic compounds from this group are prone to adsorb onto the membrane surface and initiate organic fouling and subsequent biofouling (Judd 2011). In the present study, the average DOC concentration in the mixed liquor was substantially reduced from 19.8 ± 8.5 to $6.6 \pm 1.3 \text{ mg L}^{-1}$ ($p < 0.05$) as the electrocoagulation process was employed during run II. Therefore, a higher amount of DOC was retained by the membrane in run I (16%) than run II (4%). As a result, a strong positive correlation was observed between DOC and MFR ($r = 0.84$, $p < 0.05$) (Table 3), indicating that the soluble fraction of the mixed liquor in fact contributed to the membrane fouling process.

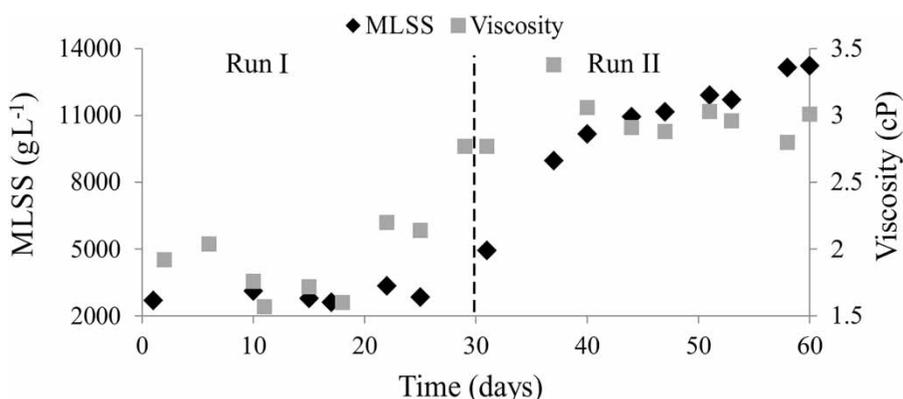


Figure 4 | Evolution of MLSS and viscosity during the whole experimental period.

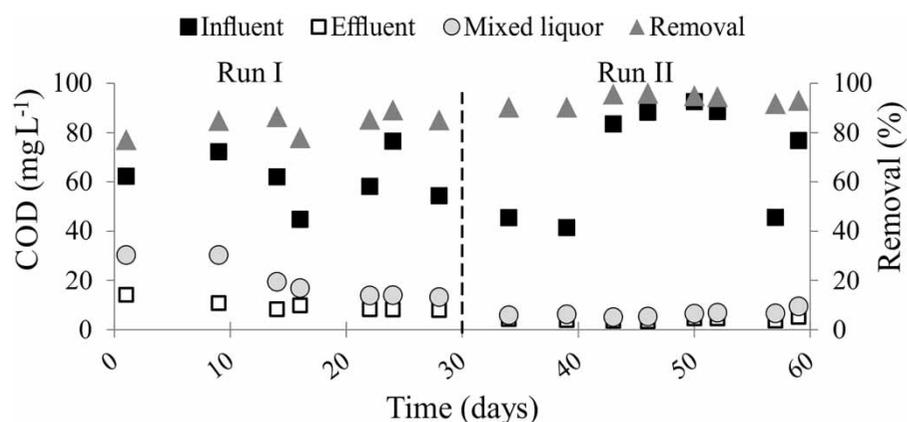


Figure 5 | Dissolved organic carbon concentration in influent, mixed liquor and effluent, as well as the average removal efficiencies of the e-MBR during the whole experimental period.

Effects of SMP and EPS on mixed liquor filterability

As shown in Table 2, the average concentration of SMP was significantly reduced from 23.8 mg L^{-1} in run I to 10.6 mg L^{-1} in run II ($p < 0.05$). On the other hand, the average protein/carbohydrate ratio of SMP ($\text{SMP}_p/\text{SMP}_c$) did not show significant variation ($p > 0.05$), indicating that both proteins and carbohydrates were removed equivalently due to the application of the electric field.

Considering that SMP is the soluble fraction of EPS, some authors report that their removal may occur in e-MBR through complexation with the aluminum ions released during the application of the electric field, leading such compounds to agglomerate with the flocs as bound EPS (Hua *et al.* 2015; Tafti *et al.* 2015). However, in our study, no increase in EPS was observed in run II. On the contrary, the average values of EPS were $22.1 \text{ mg gVSS}^{-1}$ at run I and 10.6 gVSS^{-1} at run II ($p < 0.05$), leading to an average reduction of 55% (Table 2). It was also observed that the average value of protein/carbohydrate ratio of EPS ($\text{EPS}_p/\text{EPS}_c$) increased significantly in run II, indicating that bound carbohydrates were removed more easily compared to the proteins. This significant reduction of

EPS in run II indicates that electrocoagulation was not the main mechanism of SMP removal.

A possible explanation for the high simultaneous removal of SMP and EPS is that hydroxyl radicals are also generated during the application of the electric field, which act as strong oxidants and may also enhance the removal of these organic compounds (Zeyouidi *et al.* 2015). Hua *et al.* (2015) evaluated the mixed liquor characteristics of an e-MBR compared with a conventional MBR and also verified that SMP and EPS are reduced in the reactor with application of the electric field. According to these authors, the $\cdot\text{OH}$ generated may break down the carbohydrates and proteins into lower molecular weight compounds, thereby increasing their biodegradability.

Besides that, as the EPS fraction is composed of organic substances (e.g. carbohydrates, proteins, humic acids, lipids and nucleic acids), these compounds can also be used as a carbon source for the metabolic activity of bacteria when there is a lack of substrate (Sheng *et al.* 2010; Lin *et al.* 2014). Thus, considering that food/microorganism (F/M) ratio was $0.34 \pm 0.06 \text{ gDQO gSSV}^{-1} \text{ d}^{-1}$ at run I and $0.15 \pm 0.03 \text{ gDQO gSSV}^{-1} \text{ d}^{-1}$ at run II, we do not discharge that such a condition may also have contributed to the reduction of EPS in the second strategy.

The high concentrations of SMP and EPS in run I is in accordance with the high membrane fouling observed in this period. Statistical analyses indicate that a positive moderate correlation was obtained between SMP and MFR in the e-MBR ($r = 0.55$, $p < 0.05$), while no significant correlation was observed between the $\text{SMP}_p/\text{SMP}_c$ ratio and MFR (Table 3). These results indicated that the higher the concentration of SMP, the faster the membrane fouling. Zhang *et al.* (2015) operated a conventional MBR and an

Table 2 | Total SMP and EPS concentrations as well the average $\text{SMP}_p/\text{SMP}_c$ and $\text{EPS}_p/\text{EPS}_c$ ratio

Run	SMP mg L^{-1}	$\text{SMP}_p/\text{SMP}_c$	EPS mg gVSS^{-1}	$\text{EPS}_p/\text{EPS}_c$
I	23.8 ± 9.0	1.2 ± 0.6	22.1 ± 13.2	1.9 ± 0.5
II	10.6 ± 0.8	0.9 ± 0.1	10.0 ± 2.5	2.9 ± 0.4

SMP_p , proteins in SMP; SMP_c , carbohydrates in SMP; EPS_p , proteins in EPS; EPS_c , carbohydrates in EPS.

Table 3 | Pearson's correlation coefficient (*r*) for linear correlations between MFR and mixed liquor properties in e-MBR

		MLSS mg L ⁻¹	COD mg L ⁻¹	SMP mg L ⁻¹	SMP _p /SMP _c	EPS mg gVSS ⁻¹	EPS _p /EPS _c
MFR bar d ⁻¹	<i>r</i>	-0.79*	0.84*	0.55*	0.51	0.28	-0.57*
	<i>p</i>	0.003	0.001	0.04	0.08	0.38	0.04

*Significant correlation.

e-MBR and verified that the concentration of SMP in the mixed liquor is directly correlated with MFR in both reactors. Therefore, these authors inferred that a reduction of SMP in the mixed liquor results in a decrease in membrane fouling, which is in agreement with our results.

On the other hand, no correlation was observed between EPS and MFR, while a negative moderate correlation was observed between the EPS_p/EPS_c ratio and MFR ($r = -0.57$, $p < 0.05$) (Table 3). These results indicated that the contents of EPS contributed to membrane fouling more than the concentration of EPS. Furthermore, they also indicated that the higher the EPS_p/EPS_c ratio, the less the membrane fouling. Some authors also reported that carbohydrates contributed to a higher fouling propensity than proteins (Li *et al.* 2012; Deng *et al.* 2016; Jørgensen *et al.* 2017). A possible explanation is that EPS_c has more hydrophilic characteristics, while EPS_p is responsible for hydrophobicity of mixed liquor (Guo *et al.* 2012). Thus, the lower the EPS_p/EPS_c ratio, the more hydrophilic are the mixed liquor flocs. According to Drews (2010), the high hydrophilicity of flocs is assumed to cause larger membrane fouling due to stronger interactions with the typically hydrophilic membranes used in MBRs.

Therefore, we believe that the lower membrane fouling observed in run II may be associated mainly with two factors: (1) lower SMP concentrations and (2) less interaction between hydrophobic mixed liquor flocs and the hydrophilic polyetherimide membrane used in this study.

Energy consumption analysis

The reactor exhibited an energy consumption per volume of permeate equal to 74.5 and 84.9 KWh m⁻³ during run I and II, respectively. Thus, the application of electric current used over run II increased the energy consumption by around 14%. Similarly, Zhang *et al.* (2015) operated an MBR and an e-MBR in parallel and observed that the latter reactor has exhibited an energy consumption only 10% higher. In the present study, we hypothesized that the occurrence of the electrodes passivation process may lead to a slight increase in the observed energy consumption (Mollah

et al. 2004). Therefore, the implementation of other techniques to control this process could contribute to the reduction of energy consumption.

It should be highlighted that the energy consumption observed in both runs was much higher than that usually reported for real-scale MBR, which generally does not exceed 5.0 KWh m⁻³ (Krzeminski *et al.* 2017). The high energetic consumption observed in the present study is likely related to the laboratory-scale reactor used in our experiments, in which the equipment employed does not necessarily represent the conditions applied in real scale. Taking into account the real scenario, the slight increase in the operating costs related to the application of the electric current in the e-MBR could be abated by the lower MFR and, consequently, by the lower demanding of membrane cleaning procedure (Ibeid *et al.* 2013a).

CONCLUSION

This research evaluated the modification of the e-MBR mixed liquor characteristics caused by the application of electrochemical processes. For this purpose, the reactor was assessed under two experimental runs: without the electric field (run I) and with the electric field (run II). It was observed that the CSTn and SRF average values were reduced by about 57 and 93%, respectively, indicating that the mixed liquor filterability was substantially improved during the period in which the electrochemical process was applied. This behaviour was attributed to the lower concentrations of COD (19.8 mg L⁻¹ in run I and 6.6 mg L⁻¹ in run II) and SMP (23.8 mg L⁻¹ in run I and 10.6 mg L⁻¹ in run II) as well as the higher EPS_p/EPS_c ratio (1.9 in run I and 2.9 in run II), which increased the hydrophobicity of the sludge flocs. Moreover, the DSVI was reduced from 198.2 mL g⁻¹ in run I to 71.5 mL g⁻¹ in run II, indicating that the settleability of mixed liquor was also improved. This behaviour may be related to the reduction by about 42% of mean floc size, caused by the electroosmosis phenomenon. Thus, it was concluded that the application of the electrochemical processes can change the

physicochemical properties of the flocs, playing an important role in enhancing the settleability and filterability of the mixed liquor. Additionally, the application of the electric current was responsible for an increase of less than 15% in energy consumption, demonstrating that this process can be an interesting alternative to improve the operational stability of MBR for municipal wastewater treatment.

ACKNOWLEDGEMENTS

The authors would like to acknowledge the Brazilian National Council for Scientific and Technological Development (CNPq) and Coordination of Superior Level Staff Improvement (CAPES) for their financial support.

REFERENCES

- Bani-Melhem, K. & Elektorowicz, M. 2010 Development of a novel submerged membrane electro-bioreactor (SMEBR): performance for fouling reduction. *Environmental Science & Technology* **44** (9), 3298–3304.
- Bani-Melhem, K. & Elektorowicz, M. 2011 Performance of the submerged membrane electro-bioreactor (SMEBR) with iron electrodes for wastewater treatment and fouling reduction. *Journal of Membrane Science* **379** (1–2), 434–439.
- Borea, L., Naddeo, V. & Belgiorno, V. 2017 Application of electrochemical processes to membrane bioreactors for improving nutrient removal and fouling control. *Environmental Science and Pollution Research* **24** (1), 321–333.
- Chang, I. S. & Kim, S. N. 2005 Wastewater treatment using membrane filtration – effect of biosolids concentration on cake resistance. *Process Biochemistry* **40** (3–4), 1307–1314.
- Deng, L., Guo, W., Ngo, H. H., Du, B., Wei, Q., Tran, N. H., Nguyen, C. N., Chen, S. S. & Li, J. 2016 Effects of hydraulic retention time and biofloculant addition on membrane fouling in a sponge-submerged membrane bioreactor. *Bioresource Technology* **210**, 11–17.
- Drews, A. 2010 Membrane fouling in membrane bioreactors – characterisation, contradictions, cause and cures. *Journal of Membrane Science* **363** (1–2), 1–28.
- Dubois, M., Gilles, K. A., Hamilton, J. K., Rebers, P. T. & Smith, F. 1956 Colorimetric method for determination of sugars and related substances. *Analytical Chemistry* **28** (3), 350–356.
- Eaton, A., Clesceri, L. & Greenberg, A. 2005 *Standard Methods for the Examination of Water and Wastewater*, 21st edn. American Public Health Association (APHA), Washington, DC, USA.
- Ensano, B., Borea, L., Naddeo, V., Belgiorno, V., de Luna, M. D. & Ballesteros Jr., F. C. 2016 Combination of electrochemical processes with membrane bioreactors for wastewater treatment and fouling control: a review. *Frontiers in Environmental Science* **4**, 57.
- Giwa, A., Ahmed, I. & Hasan, S. W. 2015 Enhanced sludge properties and distribution study of sludge components in electrically-enhanced membrane bioreactor. *Journal of Environmental Management* **159**, 78–85.
- Guo, W., Ngo, H. H. & Li, J. 2012 A mini-review on membrane fouling. *Bioresource Technology* **122**, 27–34.
- Hasan, S. W., Elektorowicz, M. & Oleszkiewicz, J. A. 2014 Start-up period investigation of pilot-scale submerged membrane electro-bioreactor (SMEBR) treating raw municipal wastewater. *Chemosphere* **97**, 71–77.
- Hua, L. C., Huang, C., Su, Y. C. & Chen, P. C. 2015 Effects of electro-coagulation on fouling mitigation and sludge characteristics in a coagulation-assisted membrane bioreactor. *Journal of Membrane Science* **495**, 29–36.
- Ibeid, S., Elektorowicz, M. & Oleszkiewicz, J. A. 2013a Novel electrokinetic approach reduces membrane fouling. *Water Research* **47** (16), 6358–6366.
- Ibeid, S., Elektorowicz, M. & Oleszkiewicz, J. A. 2013b Modification of activated sludge properties caused by application of continuous and intermittent current. *Water Research* **47** (2), 903–910.
- Ibeid, S., Elektorowicz, M. & Oleszkiewicz, J. A. 2015 Electro-conditioning of activated sludge in a membrane electro-bioreactor for improved dewatering and reduced membrane fouling. *Journal of Membrane Science* **494**, 136–142.
- Jørgensen, M. K., Nierychlo, M., Nielsen, A. H., Larsen, P., Christensen, M. L. & Nielsen, P. H. 2017 Unified understanding of physico-chemical properties of activated sludge and fouling propensity. *Water Research* **120**, 117–132.
- Judd, S. 2011 *The MBR Book: Principles and Applications of Membrane Bioreactors in Water and Wastewater Treatment*, 2nd edn. Elsevier Ltd, Oxford, UK.
- Krzeminski, P., Leverette, L., Malamis, S. & Katsou, E. 2017 Membrane bioreactors – a review on recent developments in energy reduction, fouling control, novel configurations, LCA and market prospects. *Journal of Membrane Science* **527**, 207–227.
- Li, J., Yang, F., Liu, Y., Song, H., Li, D. & Cheng, F. 2012 Microbial community and biomass characteristics associated severe membrane fouling during start-up of a hybrid anoxic–oxic membrane bioreactor. *Bioresource Technology* **103** (1), 43–47.
- Lin, H., Zhang, M., Wang, F., Meng, F., Liao, B. Q., Hong, H., Chen, J. & Gao, W. 2014 A critical review of extracellular polymeric substances (EPSs) in membrane bioreactors: characteristics, roles in membrane fouling and control strategies. *Journal of Membrane Science* **460**, 110–125.
- Lousada-Ferreira, M., van Lier, J. B. & van der Graaf, J. H. 2015 Impact of suspended solids concentration on sludge filterability in full-scale membrane bioreactors. *Journal of Membrane Science* **476**, 68–75.
- Lowry, O. H., Rosebrough, N. J., Farr, A. L. & Randall, R. J. 1951 Protein measurement with the Folin phenol reagent. *Journal of Biological Chemistry* **193** (1), 265–275.

- Meng, F., Zhang, S., Oh, Y., Zhou, Z., Shin, H. S. & Chae, S. R. 2017 Fouling in membrane bioreactors: an updated review. *Water Research* **114**, 151–180.
- Mollah, M. Y., Morkovsky, P., Gomes, J. A., Kesmez, M., Parga, J. & Cocke, D. L. 2004 Fundamentals, present and future perspectives of electrocoagulation. *Journal of Hazardous Materials* **114** (1–3), 199–210.
- Scholes, E., Verheyen, V. & Brook-Carter, P. 2016 A review of practical tools for rapid monitoring of membrane bioreactors. *Water Research* **102**, 252–262.
- Sheng, G. P., Yu, H. Q. & Li, X. Y. 2010 Extracellular polymeric substances (EPS) of microbial aggregates in biological wastewater treatment systems: a review. *Biotechnology Advances* **28** (6), 882–894.
- Sun, Y., Wang, Y. & Huang, X. 2007 Relationship between sludge settleability and membrane fouling in a membrane bioreactor. *Frontiers of Environmental Science & Engineering in China* **1** (2), 221–225.
- Tafti, A. D., Mirzaei, S. M. S., Andalibi, M. R. & Vossoughi, M. 2015 Optimized coupling of an intermittent DC electric field with a membrane bioreactor for enhanced effluent quality and hindered membrane fouling. *Separation and Purification Technology* **152**, 7–13.
- Wang, X. M., Li, X. Y. & Huang, X. 2007 Membrane fouling in a submerged membrane bioreactor (SMBR): characterisation of the sludge cake and its high filtration resistance. *Separation and Purification Technology* **52** (3), 439–445.
- Wei, V., Elektorowicz, M. & Oleszkiewicz, J. A. 2011 Influence of electric current on bacterial viability in wastewater treatment. *Water Research* **45** (16), 5058–5062.
- Zeyoudi, M., Altenaiji, E., Ozer, L. Y., Ahmed, I., Yousef, A. F. & Hasan, S. W. 2015 Impact of continuous and intermittent supply of electric field on the function and microbial community of wastewater treatment electro-bioreactors. *Electrochimica Acta* **181**, 271–279.
- Zhang, J., Satti, A., Chen, X., Xiao, K., Sun, J., Yan, X., Liang, P., Zhang, X. & Huang, X. 2015 Low-voltage electric field applied into MBR for fouling suppression: performance and mechanisms. *Chemical Engineering Journal* **273**, 223–230.

First received 24 August 2018; accepted in revised form 11 December 2018. Available online 24 December 2018