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Are pharmaceuticals removal and membrane fouling in electromembrane bioreactor affected by current density?

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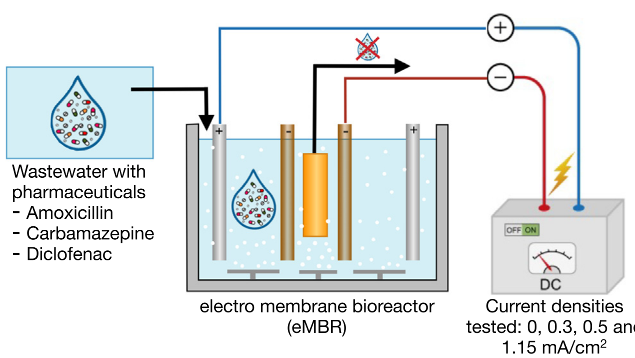
HIGHLIGHTS

- eMBR technology was used to treat pharmaceuticals in simulated municipal wastewater.
- Higher current densities improved removal efficiencies for AMX, DCF and CBZ.
- Removal efficiencies for COD, DOC and phosphate reached 100%.
- Membrane fouling rate in eMBR at highest current density was 45% lower than in MBR.

GRAPHICAL ABSTRACT



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ABSTRACT

Pharmaceutical active compounds (PhACs) have been detected at significant concentrations in various natural and artificial aquatic environments. In this study, electro membrane bioreactor (eMBR) technology was used to treat simulated municipal wastewater containing widely-used pharmaceuticals namely amoxicillin (AMX), diclofenac (DCF) and carbamazepine (CBZ). The effects of varying current density on the removal of PhACs (AMX, DCF and CBZ) and conventional pollutants (chemical oxygen demand (COD), dissolved organic carbon (DOC), humic substances, ammonia nitrogen (NH_4-N), nitrate nitrogen (NO_3-N) and orthophosphate (PO_4-P) species) were examined. High COD and DOC removal efficiencies (~100%) were obtained in all the experimental runs regardless of applied current density. In contrast, enhanced removal efficiencies for AMX, DCF and CBZ were achieved at high current densities. Membrane fouling rate in eMBR with respect to conventional MBR was reduced by 24, 44 and 45% at current densities of 0.3, 0.5 and 1.15 mA/cm^2, respectively. The mechanism for pharmaceutical removal in this study proceeded by: (1) charge neutralization between negatively-charged pharmaceutical compounds and positive electro-generated aluminium coagulants to form larger particles and (2) size exclusion by membrane filtration.

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1. Introduction

The global occurrences of pharmaceutical active compounds (PhACs) in various environmental matrices and the different ecological and health hazards associated with them have rendered these compounds as emerging organic pollutants (Lonappan et al., 2016; Pal et al., 2014). Effluent discharge from wastewater treatment plants (WWTPs) remains the main significant pathway for PhACs to enter the aquatic environment (Gros et al., 2010; Santos et al., 2007). As consumption of pharmaceutical products has increased and their elimination by conventional WWTPs is often incomplete due to their poor biodegradation, these products are frequently being detected in surface waters, sediments and sludges (Clarke and Smith, 2011; Vieno and Sillanpää, 2014). Although detected at miniscule concentrations (from ng/L to μg/L) (Koba et al., 2018), their adverse effects cannot be disregarded, given that pharmaceuticals cause biological toxic effects even at very low concentrations (Kim et al., 2007; Liu and Wong, 2013; Santos et al., 2007).

Various physical, biological and chemical technologies have been proposed as alternative approaches to achieve complete removal of recalcitrant compounds from WWTP effluents (Cruz-Morató et al., 2013; Deng et al., 2017; Prado et al., 2017; Vasiliadou et al., 2014). Of these, membrane bioreactor (MBR) technology has gained significant popularity as a superior technology compared to conventional activated sludge process. The main advantages of MBR include enhanced solids concentration in the reactor, reduced sludge production and clarified wastewater effluent with significant elimination of pathogens and viruses (Karaolia et al., 2017; Nguyen et al., 2017; Serrano et al., 2011). However, membrane fouling remains a major limitation of the MBR process (Li et al., 2015). Thus, MBR systems have been combined with other technologies to extend its effectiveness in treating a wide range of contaminants and to improve fouling control.

Recently, electrochemical processes have been integrated into MBR systems (i.e. electro-membrane bioreactor or eMBR) to address the issues on membrane fouling and abatement of recalcitrant micropollutants (Borea et al., 2017; Ensano et al., 2016; Giwa et al., 2016; Hasan et al., 2012). In a conventional MBR, pollutant removal depends on biodegradation, sorption, hydrolysis and membrane filtration. The integration of an electric field into MBR allows the hybrid system to utilize electrochemical processes such as electrocoagulation, electroosmosis and electrophoresis which enhance both the treatment performance and membrane fouling control (Ensano et al., 2019, 2016).

Several studies have reported the effectiveness of electrochemical processes in MBR. Jiang et al. (2017) used stainless steel mesh electrodes to treat coke wastewater and results showed that the removal efficiencies for chemical oxygen demand (COD), phenol, pyridine and quinolone were significantly higher in eMBR than the corresponding sum for conventional MBR and electrocatalytic process during a long-term treatment. In another study, García-Gómez et al. (2016) showed that combining MBR and electro-oxidation (EO) with Ti/PbO_2 anode resulted in carbamazepine (CBZ) removal at 99.99%. In our previous study (Ensano et al., 2017b), we have shown the superiority of eMBR, removing as much as 80% of the selected pharmaceuticals when 0.5 mA/cm^2 current density was applied, compared to only ~50% when the control MBR was used.

The extent of pollutant removal and fouling control in an eMBR highly depends on the current density applied. However, it also affects the bacterial viability in the mixed liquor and increases energy consumption. At higher voltage, denitrification rate decreases (Li et al., 2001), breakage of bacterial cells occurs and fouling precursors increase which are all detrimental to the treatment and fouling mitigation performance of eMBR (Bani-Melhem and Elektorowicz, 2011; Li et al., 2001; Wei et al., 2011). Recent studies revealed that application of minute electric field at an intermittent mode is proven safe for the microbial community and is similarly effective in pollutant removal as that with continuous electric field application (Akamatsu et al., 2010; Bani-Melhem and Elektorowicz, 2010). It also significantly reduces the operational cost. For example, intermittent cycle (5 min ON and 20 min OFF) of electric field used in a previous study (Ensano et al., 2019) consumes 96% less energy yet the difference in treatment efficiencies compared to that of continuous mode is around 15% only. In the study of Ma et al. (2015) the energy balance analysis showed a reduction by 20% of total energy consumption of the eMBR compared to that of the conventional MBR.

Based on the extensive literature review of the authors, no study has reported an in-depth analysis/discussion on the effect of varying eMBR current density on the removal of conventional pollutants pharmaceutical compounds and on membrane fouling parameters. In our previous studies (Ensano et al., 2019, 2017a), pharmaceuticals removal from synthetic and real municipal wastewater was investigated using electrocoagulation process alone via batch experimental runs. The significant results obtained from these studies were then used in the present work to explore the influence of different current densities in the performance of a continuously operated eMBR system which employs not only electrochemical but also biological and filtration processes in one hybrid reactor. The study was focused on membrane fouling control and on the removal of conventional and pharmaceutical compounds from simulated municipal wastewater with a statistical analysis of the obtained results at the different investigated current densities. The current density values (i.e. 0.3, 0.5 and 1.15 mA/cm^2) were determined based on the preliminary studies (Ensano et al., 2019, 2017b). In any electrochemical system, the current density is a key parameter as it affects both process performance and energy consumption. In the hybrid eMBR reactor, where there are complex inter-dependencies among the electrochemical, biochemical and membrane separation processes, the effect of current density is even more important. Amoxicillin (AMX), diclofenac (DCF) and CBZ were chosen as representative PhACs as they cover different types of pharmaceutical products (broad spectrum antibiotic, anti-inflammatory analgesic, anticonvulsant and mood-stabilizer, respectively) and also due to their widespread occurrence in the aquatic environment (Elizalde-Velázquez et al., 2016; Hai et al., 2018; Vieno and Sillanpää, 2014). A conventional MBR was operated as a control test.

2. Experimental

All experiments were carried out at the laboratory of Sanitary and Environmental Engineering Division (SEED) of Civil Engineering Department of the University of Salerno (Italy).

2.1. Chemicals and materials

A laboratory scale eMBR, developed by Borea et al. (2017), was used in all experiments. The perforated cylindrical aluminium anode and stainless-steel mesh cathode were placed inside a cylindrical bioreactor with a working volume of 13 L. The electrodes, separated by a distance of 6 cm, were connected to a digital external DC power supply (CX400, TTi, 0–6 V, 0–20 A). A ZeeWeed-1 (ZW-1) submerged hollow fibre ultrafiltration module (SUEZ WTS Italy S.r.l.), characterized by an average pore size of 0.04 μm and an effective membrane surface area of 0.047 m^2, was placed vertically at the centre of the bioreactor.

Membrane air scouring and the required level of oxygen were supplied by air diffusers placed at the bottom of the reactor under the membrane module and around the electrodes. The reactor was continuously fed with a synthetic solution, simulating real municipal wastewater, characterized by the following composition (in mg L^{-1}), according to previous studies (Li et al., 2013, 2005; Yang et al., 2002): $C_6H_{12}O_6$ (200), $C_{12}H_{22}O_{11}$ (200), protein (68.33), $(NH_4)_2SO_4$ (66.73), NH_4Cl (10.91), KH_2PO_4 (4.43), K_2HPO_4 (9.0), $MgSO_4 \cdot 7H_2O$ (21), $MnSO_4 \cdot H_2O$ (2.68), $NaHCO_3$ (30), $CaCl_2 \cdot 6H_2O$ (19.74) and $FeCl_3 \cdot 6H_2O$ (0.14). The characteristics of the synthetic wastewater were reported in a previous study (Borea et al., 2017). AMX ($C_{16}H_{19}N_3O_5S \cdot 3H_2O$), DCF ($C_{14}H_{10}Cl_2NNaO_2$) and CBZ ($C_{15}H_{12}N_2O$), produced by Sigma-Aldrich, were selected as target compounds since they are highly consumed and among the most frequently detected pharmaceutical compounds in the effluents of WWTPs (Prado et al., 2017; Secondes et al., 2014). They were spiked in the synthetic wastewater at a concentration of 0.01 mg L^{-1} to simulate the average detected concentrations of these compounds in various wastewaters (Ensano et al., 2017a, 2017b; Naddeo et al., 2009; Teijon et al., 2010). All solutions were prepared without pH adjustment and using ultra-pure water obtained from a Millipore Milli-Q system with resistivity >18 MΩ cm at 25 °C. Sludge for the inoculum was taken from secondary clarifier of the wastewater treatment plant in Salerno (Italy) and acclimatized for over a month until the operation parameters became stable. Sludge was discharged only for the necessary analyses.

2.2. Electro MBR experiments

The reactor was operated continuously with a hydraulic retention time (HRT) of 19 h and at constant flux of 15 L/m^2/h (LMH) with the effluent being extracted by a metered pump (qdos30; Watson-Marlow Pumps Group). The filtration cycle was composed of 14 min 30 s filtration with permeate production and 30 s backwashing. The reactor was operated as follows: in run 1, as a conventional MBR and in runs 2, 3 and 4, as an eMBR with a current density of 0.3, 0.5 and 1.15 mA/cm^2, respectively. The values of current density used in this study were obtained from the results of our previous preliminary study on batch electrochemical tests (Ensano et al., 2019). The current was applied intermittently (5 min ON/20 min OFF) in order to reduce inhibitory effects on the biomass and, at the same time, decrease energy consumption. Each run lasted for ~35 days. The application of the electric field along with the filtration cycles were controlled by a programmable electronic controller. Chemical membrane cleaning was conducted after each run and whenever the transmembrane pressure (TMP) reached ~30 kPa. The membrane module was first washed with tap water for 20 min to remove the attached cake layer then soaked for 8 h in a sodium hypochlorite solution (1000 ppm Cl_2 concentration) (Ensano et al., 2017b).

2.3. Analytical methods

Influent, supernatant and effluent samples were collected every 48 h from the feed tank, reactor and permeate tank, respectively. A total of 18 samples were obtained for each experimental run. These samples were analysed for COD, NH_4-N, NO_3-N and PO_4-P according to standard methods (APAT and CNR-IRSA, 2003). Mixed liquor suspended solids (MLSS) and mixed liquor volatile suspended solids (MLVSS) were also measured using the same standard methods. A multiparametric probe (Hanna Instruments, HI769828) was used for the analysis of dissolved oxygen (DO) concentration, pH, temperature, conductivity and redox potential (ORP). DOC was determined, after filtration over 1.2 μm membrane filter, using a total organic carbon (TOC) analyser. A Lambda 12 spectrophotometer (Perkin Elmer, Germany) was used to quantify the humic substances in terms of the UV absorbance of the aqueous samples at 254 nm (UV_{254}). AMX, DCF and CBZ concentrations were analysed using 4000Q Trap LC–MS/MS System (Applied Biosystems, Foster City, USA) in ESI-positive mode characterized by a mobile phase composed of A: 0.1% formic acid in water and B: acetonitrile–water (1:1, v/v) solution (limit of quantification <1 ng L^{-1}) (Ensano et al., 2019). The method detection limit (MDL) was between 0.9 and 8 ng L^{-1} in spiked water samples and the precision of the method, calculated as relative standard deviation, ranged from 0.9 to 3.0% (Ensano et al., 2019).

Fouling rate, zeta potential, particle size diameter (PSD) of the activated sludge, along with the concentrations of membrane fouling precursors, namely extracellular polymeric substances (EPS), soluble microbial products (SMP) and transparent exopolymeric particles (TEP) were measured in order to evaluate membrane fouling formation. TMP variation over time was monitored continuously through a pressure transducer (PX409-0-15VI, Omega) connected to a datalogger (34972A LXI Data Acquisition/Switch unit, Agilent) which recorded the data. Membrane fouling was assessed through the fouling rate which was evaluated for each cycle of a single run as the TMP variation over time, ΔTMP/dt. PSD and zeta potential were measured by Malvern Mastersizer 2000 instrument.

SMP and EPS were extracted from the sludge flocs according to the heating method (Le-Clech et al., 2006; Morgan et al., 1990). SMP and EPS were characterized by their relative content of proteins (SMPp - EPSp) and carbohydrates (SMPc - EPSc), measured by photometric methods according to Frølund et al. (1995) and DuBois et al. (1956), respectively, using bovine serum albumin (BSA) (Sigma, USA) and D-glucose (Sigma, USA) as standards. TEP concentration was analysed according to the method developed from previous study (Borea et al., 2018, 2017; De la Torre et al., 2008). The concentrations of EPS, SMP and TEP were then normalized for MLVSS content.

In order to determine whether there were statistically significant differences between experiments conducted under different current densities, an Analysis of Variance-ANOVA parametric test was performed for all parameters assuming that all the samples were drawn from normally distributed populations with the same standard deviations (variances). The null hypothesis tested was based on no difference among the populations from which the samples were drawn. If the normality test showed that the data was from non-normal populations, the Kruskal-Wallis ANOVA on Ranks test was performed as a non-parametric test which does not require the assumption that all samples are drawn from normally distributed populations with equal variances. The null hypothesis tested was based on no difference in the distribution of values between the different groups. Once ANOVA test found a significant difference and, thus, only when the P value was significant ($P < 0.05$), multiple pairwise comparison tests were also conducted, isolating the differences by running comparisons between the experimental groups. In detail, Dunnett's and Dunn's tests were applied comparing the differences of the experimental tests, conducted with the application of different current densities (eMBR), versus the control group conducted in conventional MBR setup (at 0 mA/cm^2 current density).

The relationship between pharmaceutical removal as dependent variable affected by changes in current density as independent variable was modelled using polynomial regression function analysis. Polynomial regression is a parametric test, that is, for a given independent variable value, the possible values for the dependent variable are assumed to be normally distributed and have equal variance. An ANOVA test for the polynomial regression models was also performed.

3. Results and discussion

3.1. Effects of current density on the removal of conventional pollutants

Fig. 1 shows the conventional pollutant removal efficiencies obtained from different runs. The high COD and DOC removal efficiencies (~100%) achieved in all runs are attributed to the highly biodegradable sucrose and glucose components of the synthetic wastewater. These results are consistent with the findings reported in previous studies (Borea et al., 2017; Ensano et al., 2017b) and confirm them. Evidently, there was no statistical significant variation found in the COD and DOC removal performances among the different current densities tested. Meanwhile, the presence of electric field in the bioreactor improved the removal of humic substances. The application of the ANOVA test for the UV_{254} removals revealed that there was a statistically significant difference among the experiments conducted ($P < 0.026$). Application of the Dunnett's test revealed that the removals obtained in the conventional MBR at 0 mA/cm^2 current density are significantly different ($P < 0.05$) from the removals found in the eMBR at current density of 0.3, 0.5 and 1.15 mA/cm^2. The removal of humic substances in eMBR is a result of the synergistic effects between biosorption, biodegradation and

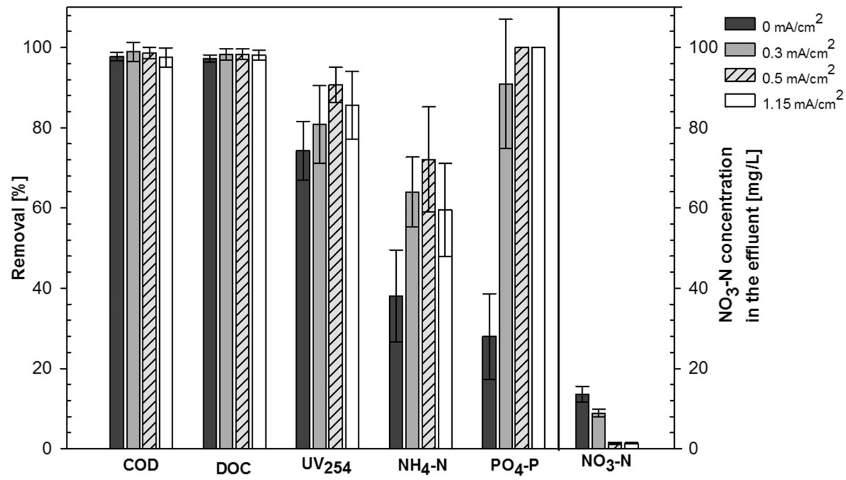

Fig. 1. COD, DOC, humic substance, NH_4-N, PO_4-P removals and nitrate concentration at different eMBR current densities (n = 18).

electrocoagulation processes. High molecular weight humic substances (HS), those that cannot be easily degraded by aerobic bacteria, are first sorbed onto the activated sludge biomass before enzymatic hydrolysis breakdown and biological uptake (Esparza-Soto and Westerhoff, 2003). Those that are not degraded biologically are removed via electrocoagulation process. Ulu et al. (2015) reported that during electrocoagulation, the functional groups of humic acid were attracted to the positive Al species. From Fig. 1, 70% of humic substances characterized by UV_{254} was removed using conventional MBR. When 0.3 and 0.5 mA/cm^2 current densities were applied, the removal efficiencies improved by 7% and 16%, respectively. This accounted the action of electrocoagulation in the system. Higher current density produces greater amount of aluminium hydroxide which improves electrocoagulation. However, as the current density was further increased to 1.15 mA/cm^2, removal efficiency slightly declined due to the reduced population of affected microbial community. Wei et al. (2011) revealed that current densities equal to 6.2, 12.3 and 24.7 A/m^2 caused 10%, 15% and 29% death percentage for heterotrophic bacteria, respectively. COD and DOC removal efficiencies were not affected by the increasing current density due to the usage of highly biodegradable glucose and protein which are the main components of the synthetic wastewater.

The applied electric field in eMBR also caused an increase in NH_4-N removal. The enhancement in NH_4-N removal was attributed to the synergistic effects of the electrocoagulation process (Giwa et al., 2016), the oxidation of NH_4-N at the anode to nitrate (Lin and Wu, 1996), the stripping at the cathode (Zhang et al., 2012) and the biological degradation of NH_4-N via nitrification (Wei et al., 2009). In this study, the low current densities (0.3 and 0.5 mA/cm^2) did not affect the viability of nitrifying bacteria compared to when 1.15 mA/cm^2 was used, as shown by the decrease of NH_4-N removal from 72% to ~60% when the current density was increased from 0.5 to 1.15 mA/cm^2. The application of the ANOVA for NH_4-N removals revealed that there was a statistically significant difference among the experiments conducted ($P < 0.001$). Dunnett's test showed that the removals obtained at 0 mA/cm^2 current density in the conventional MBR are significantly different ($P < 0.05$) from the removals obtained in the eMBR at current density of 0.3, 0.5 and 1.15 mA/cm^2.

This study revealed that current density of 1.15 mA/cm^2 could produce high concentration of aluminium ion complexes which accumulated in the bioreactor forming a barrier that impeded the transmission of enzymes and nutrients through the microbial cell membrane (Bani-Melhem and Elektorowicz, 2011). Furthermore, considerable portion of ammonia removal could also be attributed to ammonia stripping at the cathode. The generation of OH^- at the cathode via the electro-reduction of water caused an increase in pH near the cathode surface. High pH combined with excess aeration results in the release of ammonia to the atmosphere (Zhang et al., 2012).

Meanwhile, reduction of NO_3-N values in the eMBR effluent by 35, 90 and 90% corresponding to current density values of 0.3, 0.5 and 1.15 mA/cm^2, were observed with respect to the effluent value of 13.55 ± 5.63 mgL^{-1} in the conventional MBR. Due to the anoxic conditions created when the electric field was applied, the denitrification process progressed in agreement with the findings of previous studies (Borea et al., 2017). In the presence of electric field, reduction reactions proceeded at the cathode which consumed DO in the reactor subsequently generating anoxic conditions (Borea et al., 2017; Millanar-Marfa et al., 2018). This was validated by the reduction of ORP and DO values in the eMBR. Improved nitrification and denitrification were evident at lower current densities. In addition, eMBR at current densities of 0.5 and 1.15 mA/cm^2 showed complete PO_4-P removal compared to 91% at 0.3 mA/cm^2 and only 28% for conventional MBR (Fig. 1). The results are in agreement with the findings of previous studies and are attributed to electrocoagulation and precipitation of $AlPO_4$ and $Al(OH)_3$ (Attour et al., 2014; Borea et al., 2017; Ensano et al., 2019). The application of the Kruskal-Wallis ANOVA on Ranks analysis of variance for PO_4-P removal revealed that there was a statistically significant difference among the experiments conducted ($P < 0.001$). Dunnett's test showed that the removals obtained in the conventional MBR at 0 mA/cm^2 current density are significantly different ($P < 0.05$) from the removals obtained in the eMBR at current density of 0.3, 0.5 and 1.15 mA/cm^2. The oxidation and reduction reactions at the anode and cathode, respectively, led to the formation in the mixed liquor of $Al(OH)_3(s)$ "sweep flocs" through the reaction between the Al^{3+} ions produced at the anode with hydroxide ions OH^- formed at the cathode in agreement with previous studies (Borea et al., 2017; Ensano et al., 2019, 2017b). In addition, PO_4-P ions reacted with aluminium ions released from the anode to form $AlPO_4$ precipitates (Kim et al., 2010). Marginally lower PO_4-P removal at 0.3 mA/cm^2 can be attributed to the relatively lower coagulant production at this current density. The increase of current density from 0.5 mA/cm^2 to 1.15 mA/cm^2 did not result in a decrease of PO_4-P removal efficiency since it is not influenced by the bacteria viability but it is correlated to electrocoagulation and precipitation mechanisms which were positively affected by the increase of the electric field applied due to higher coagulant productions.

3.2. Effect of current density on the removal of PhACs

Since eMBR is a hybrid reactor combining the actions of electrochemical processes, biodegradation and membrane filtration, the removal mechanism of PhACs using eMBR would be a combination of these processes. DCF and CBZ, in particular, are known to be persistent to biodegradation owing to the electron withdrawing functional groups attached to their molecular structure (i.e. DCF has halogen, amine and carboxylic groups; CBZ has amide) (Tadkaew et al., 2011). Meanwhile, compounds with strong electron donating group (e.g. AMX has hydroxyl groups) are susceptible to electron attack by aerobic bacteria, which is considered to be the rate limiting step during aerobic biodegradation (Fan et al., 2014).

Fig. 2 shows that increasing current densities improved the removal efficiencies for selected PhACs compared to the conventional MBR. Applying 0.3 mA/cm^2 current density to the eMBR resulted to a notable increase in removal efficiency to 65.79 ± 8.37%, 65.23 ± 9.64%, 60.92 ± 7.37% for DCF, CBZ, and AMX, respectively. When the current density was increased to 0.5 mA/cm^2, even higher removals were achieved for DCF = 76.15 ± 8.68%, CBZ = 74.52 ± 9.12% and AMX = 73.10 ± 9.88% in agreement with the previous study (Ensano et al., 2017b).

Finally, further increase in current density to 1.15 mA/cm^2 led to additional PhACs removal (DCF = 79.04 ± 8.51%, CBZ = 77.21 ± 8.30% and AMX = 76.47 ± 9.46%).

During membrane filtration in the conventional MBR, AMX, DCF and CBZ, with molecular mass equal to 419.45, 318.13 and 236.27 g mol^{-1}, respectively, would readily pass through the 0.04 μm PVDF ultrafiltration membrane having a molecular weight cut-off of about 400 kDa. However, upon application of electric field in eMBR, the generation of positive monomeric and polymeric Al species and amorphous $Al(OH)_3$, due to electrocoagulation mechanism, facilitated neutralization of the negatively-charged pollutants and their subsequent agglomeration significantly improved their membrane retention and, thus, their removal. The charge neutralization of the negatively-charged pollutants and their subsequent agglomeration was validated in separate studies (Ensano et al., 2019, 2017a). Indeed, the octanol partition constants (K_{ow}) for AMX and DCF at 0.87 and 0.70, respectively, indicate that these pharmaceuticals are highly hydrophilic ($k_{ow} < 3.2$) and are less likely to be adsorbed on the hydrophobic sludge flocs (Ensano et al., 2017b; Yang et al., 2016). CBZ, on the other hand, having a K_{ow} value of 2.45 is moderately hydrophobic which means it has the highest tendency among the selected PhACs to be adsorbed onto the sludge. Meanwhile, DCF (pKa = 4.15) and AMX (pKa = 2.68, 7.49, 9.63) are anionic at neutral pH (pH = 7–8). Hence, electrostatic repulsion is highly likely to occur between them and the negatively charged activated sludge flocs prevent its adsorption. The charge on CBZ (pKa = 2.3) is quite independent of the solution pH and is, therefore, not affected by electrostatic interaction (Nghiem et al., 2006).

The extent of anodic dissolution of aluminium increases at higher current densities (Sun et al., 2017) resulting in greater concentration of coagulants for pollutant removal (Can and Bayramoglu, 2010; Ouaissa et al., 2014) and, thus, to higher removal efficiencies found in the present study. Hence, the enhanced removal of PhACs in eMBR is mainly contributed by (1) charge neutralization between negatively-charged pharmaceutical compounds and positive electro-generated coagulants to form larger particles (Liu et al., 2015) and (2) size exclusion by membrane filtration and it is not influenced by the bacteria viability which could have been affected at 1.15 mA/cm^2.

From Fig. 2 and Table 1, the high coefficients of determination ($R^2 >$ 0.99) obtained from fitting second order polynomial equation to PhAC removal data as a function of current density shows the applicability of the equation provided in Eq. (1):

$$y = y_0 + \alpha x + \beta x^2 \quad (1)$$

where y is the dependent variable, x is the independent variable, and y_0, α and β are the regression coefficients. The second-order polynomial equation was found to correlate well with the experimental results in agreement with previous studies which analysed electrocoagulation process statistically also for the removal of pharmaceutical compounds (Karichappan et al., 2014; Kermet-Said and Moulai-Mostefa, 2015). The F value and the P value obtained from the ANOVA test for this model are

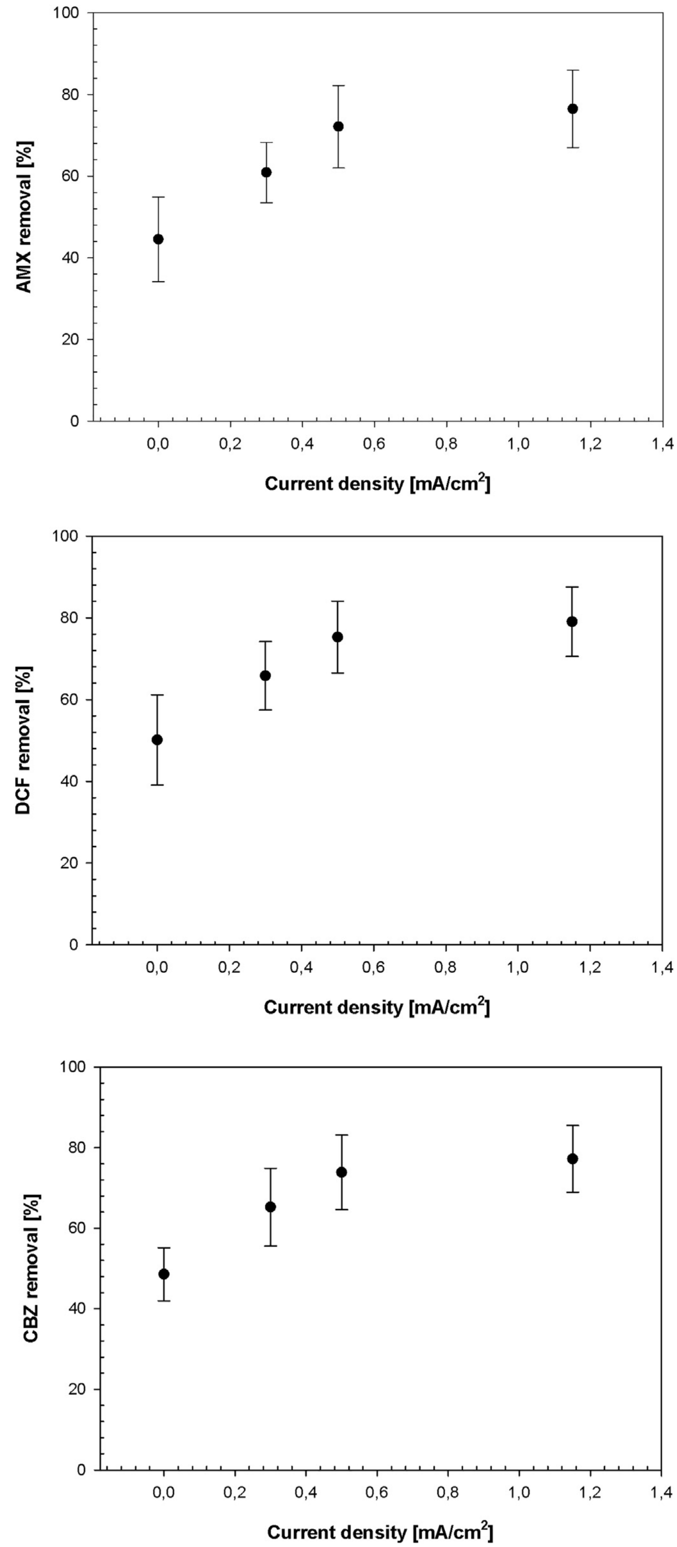

Fig. 2. AMX, DCF and CBZ removals at varying eMBR current densities (n = 18).

reported in Table 1. The F test statistic gauges the contribution of the independent variable in predicting the dependent variable (Borea et al., 2018). Since the values of F obtained are much higher than 1, it can be concluded that the current density as independent variable contributes to the prediction of PhACs removal. This has been also confirmed, except for AMX, by the values obtained for the P value which represents the probability of being wrong in concluding that there is an association between the dependent and independent variables (Borea et al., 2018).

Table 1
Coefficients of the second order model equation.

	y_0	α	β	R^2	F value	P value	First derivative of the function
AMX	44.0776	73.0948	−38.9718	0.9930	71.3772	0.0834	0.94
DCF	49.7950	67.6870	−36.6820	0.9965	143.6558	0.0489	0.92
CBZ	48.4289	69.2340	−38.4132	0.9991	557.9156	0.0299	0.90

Since a confidence level of 95% ($\alpha = 0.05$) was fixed, the P values obtained lower than 0.05 indicate that the independent variable can be used to predict the dependent variable (Borea et al., 2018). In addition, the first derivative of each of the three functions gives the optimal operating conditions (in terms of current density) to achieve maximum pharmaceutical removal. The average value of the optimal current density obtained is 0.92 mA/cm^2.

The application of the ANOVA analysis of variance revealed for all the three PhACs, there was a statistically significant difference among the experiments conducted ($P < 0.001$) at the different current densities. Applying the Dunnett's and Dunn's tests showed that the PhACs removals obtained in the conventional MBR at 0 mA/cm^2 current density are significantly different ($P < 0.005$) from the removals obtained in the eMBR at current density of 0.3, 0.5 and 1.15 mA/cm^2.

Other current densities values will be tested in future pilot studies for further validating the polynomial regression function analysis.

3.3. Effect of current density on membrane fouling

Table 2 shows that membrane fouling rate in eMBR, with respect to conventional MBR, was reduced by 24, 44 and 45% at current densities of 0.3, 0.5 and 1.15 mA/cm^2, respectively. The decline in fouling rate at higher current density is largely attributed to electrocoagulation, the predominant electrochemical process in the bioreactor. Higher current densities produced more aluminium coagulant species per unit time, which enhanced the aggregation of negatively-charged foulants (Sun et al., 2017). These results are validated by the corresponding decline in the magnitude of zeta potential for the colloidal system and the increase in floc size as shown in Table 2 (Ensano et al., 2017b; Ibeid et al., 2015). The modal average diameter (Dv_{50}) of the flocs in the MBR increased from 73.57 μm to 80.35, 91.39 and 100.64 μm at current densities of 0.3, 0.5 and 1.15 mA/cm^2, respectively. The formation of larger flocs by electrocoagulation controlled fouling by (1) minimizing the forward transport velocity of the foulants to the membrane and (2) restricting the adherence of the flocs to the membrane surface (Ensano et al., 2017b; Hong et al., 2013). Moreover, higher current densities significantly enhanced electrophoresis and electroosmosis mechanisms in the bioreactor. With the application of electric field, the negatively-charged foulants such as activated sludge flocs and secreted polymers, drifted towards the anode and away from the membrane via electrophoretic motion (Akamatsu et al., 2012; Ensano et al., 2016). Hence, electrophoresis created strong repulsion of foulants from the membrane surface and resulted in the formation of loose cake layer (Ho et al., 2017). Electroosmosis mechanism caused the removal of bound water from the microbial flocs' electrical double layer which decreased the sludge specific resistance to filtration and improved fouling control (Ibeid et al., 2013).

The electric field also altered notable mixed liquor properties that contribute to membrane fouling. EPS, SMP and TEP are known as membrane fouling precursors. EPS, mainly composed of polysaccharides and proteins, are the construction materials for biofilms, flocs and activated sludge liquor. These are found outside cell surfaces and in the intercellular opening of microbial aggregates. SMPs are organic compounds produced during microbial activities such as substrate metabolism, biomass growth and biomass decay. Like EPS, SMPs are mainly composed of carbohydrates and proteins. SMPs are responsible for the pore blockage of the membrane and the high COD and DOC levels of the effluent. Studies have shown that SMPs act as a "glue" and facilitate the formation of an apparent slime layer (Hong et al., 2013). SMPs contribute to 26 to 52% of the membrane fouling in MBRs (Bani-Melhem and Elektorowicz, 2011). TEPs, on the other hand, are gel-like organic particles consisting predominantly of acidic polysaccharides (Arruda Fatibello et al., 2004). Studies revealed that TEP is a primary parameter that contributes to biofilm growth on membrane surfaces and its concentration is highly related to membrane filtration efficiency (de la Torre et al., 2008).

Fig. 3 shows the normalized concentrations of SMP and EPS in terms of carbohydrates and proteins as well as of TEP in the mixed liquor. A reduction of SMPc in eMBR with respect to conventional MBR by 59, 80 and 92% was found at current densities of 0.3, 0.5 and 1.15 mA/cm^2, respectively. Similar reductions in SMPp by 9, 52 and 90%; in EPSc by 37, 70 and 93%; in EPSp by 43, 58 and 94%; in TEP by 86, 97, 93% were obtained with the application of current densities at 0.3, 0.5 and 1.15 mA/cm^2, respectively. The membrane fouling precursors have a net negative surface charge due to the broken edges of hydroxyl groups in alkaline medium (Ibeid et al., 2017). Hence, aluminium hydroxide with a net positive charge, formed at the anode due to electrolytic oxidation of the aluminium anode, destabilized, neutralized and adsorbed the negatively-charged fouling precursors (SMP, EPS and TEP) leading to a reduction in membrane fouling (Borea et al., 2017). The results obtained are consistent with the decline in fouling rate at higher current densities. The higher removal of polysaccharides in SMP over protein through electrocoagulation, as reported by Ibeid et al. (2017), can be explained by the higher molecular weight and larger surface area of the former which facilitated coagulation with other solid surfaces in the sludge liquor. The application of the Kruskal-Wallis ANOVA on Ranks analysis of variance revealed for all membrane fouling parameters that there was a statistically significant difference among the experiments conducted ($P < 0.001$) at the different current densities. Applying the Dunn's test showed that the concentrations of membrane fouling precursors obtained in the conventional MBR at 0 mA/cm^2 current density are significantly different ($P < 0.05$) from that obtained in the eMBR at current density of 0.3, 0.5 and 1.15 mA/cm^2.

With reference to electrode dissolution and electrode fouling due to the deposition of organic and inorganic sludge components, based on laboratory scale assessment, the maximum anode consumption was found equal to 27 g of electrode for m^3 of wastewater treated with an energy consumption of 0.6 kWh/m^3 in agreement with previous studies

Table 2
Fouling parameters.

Run	Current density (mA/cm^2)	Fouling rate ΔTMP/dt (kPa/day)	Zeta potential (mV)	Average particle size diameter (PSD) (μm)		
				Dv10	Dv50	Dv90
1°- MBR	0	8.08	−16.87 ± 0.75	31.84	73.57	152.5
2°- eMBR	0.3	6.10	−13.56 ± 0.55	32.05	80.35	175.66
3°- eMBR	0.5	4.52	−9.92 ± 0.29	34.08	91.39	204.9
4°- eMBR	1.15	4.41	−7.54 ± 0.92	35.66	100.64	259.8

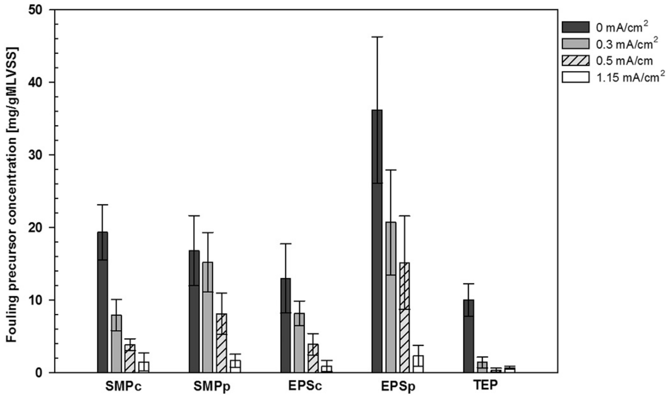

Fig. 3. Concentrations of membrane fouling precursors in the bioreactor at varying eMBR current densities (n = 18).

(Hasan et al., 2014; Hou et al., 2019; Ibeid et al., 2013). A comprehensive study on the cost analysis will be conducted in further pilot scale studies.

4. Conclusions

The present study demonstrated better removal of conventional and emerging pollutants and enhanced membrane fouling control when the eMBR current density was increased from 0.3 to 1.15 mA/cm^2. The magnitude of applied current density affects not only microbial viability but also the synergy between microbial and electrochemical processes for effective wastewater treatment and membrane fouling control. Therefore, microbial analysis in the MBR mixed liquor is highly recommended to determine which bacterial community thrives in the reactor as minute electric field is applied over time. Assessment of pharmaceutical degradation pathway and the related resulting degradation products also need to be examined. Application of this process in treating real municipal wastewater as well as high strength industrial wastewater can also be explored. Overall, the eMBR process is a significant advancement in the "chemical-free" treatment of organic pollutants in water.

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