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Control of emerging contaminants by the combination of electrochemical processes and membrane bioreactors

Benny Marie B. Ensano[1] · **Laura Borea**[2] · **Vincenzo Naddeo**[2] · **Mark Daniel G. de Luna**[1,3] · **Vincenzo Belgiorno**[2]

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Abstract This study investigates the removal of selected pharmaceuticals, as recalcitrant organic compounds, from synthetic wastewater using an electro-membrane bioreactor (eMBR). Diclofenac (DCF), carbamazepine (CBZ), and amoxicillin (AMX) were selected as representative drugs from three different therapeutic groups such as anti-inflammatory, anti-epileptic, and antibiotic, respectively. An environmentally relevant concentration (10 μg/L) of each compound was spiked into the synthetic wastewater, and then, the impact of appending electric field on the control of membrane fouling and the removal of conventional contaminants and pharmaceutical micropollutants were assessed. A conventional membrane bioreactor (MBR) was operated as a control test. A reduction of membrane fouling was observed in the eMBR with a 44% decrease of the fouling rate and a reduction of membrane fouling precursors. Humic substances (UV_{254}), ammonia nitrogen (NH_4-N), and orthophosphate (PO_4-P) showed in eMBR removal efficiencies up to 90.68 ± 4.37, 72.10 ± 13.06, and 100%, respectively, higher than those observed in the MBR. A reduction of DCF, CBZ, and AMX equal to 75.25 ± 8.79, 73.84 ± 9.24, and 72.12 ± 10.11%, respectively, was found in the eMBR due to the enhanced effects brought by electrochemical processes, such as electrocoagulation, electrophoresis, and electrooxidation.

Keywords Diclofenac (DCF) · Carbamazepine (CBZ) · Amoxicillin (AMX) · Pharmaceuticals · Electro-membrane bioreactor (eMBR) · Membrane fouling · Fouling precursors

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✉ Vincenzo Naddeo
vnaddeo@unisa.it

[1] Environmental Engineering Program, National Graduate School of Engineering, University of the Philippines, 1101 Diliman, Quezon City, Philippines

[2] Sanitary Environmental Engineering Division (SEED), Department of Civil Engineering, University of Salerno, Via Giovanni Paolo II, 84084 Fisciano, SA, Italy

[3] Department of Chemical Engineering, University of the Philippines, 1101 Diliman, Quezon City, Philippines

Introduction

The pollution brought by emerging contaminants (EC) in our water resources has now become a global environmental problem (Richardson 2009). Pharmaceutical compounds, in particular, are gaining great attention from the scientific community due to their potential environmental risks and adverse effects to human health (Schwaiger et al. 2004, Pan et al. 2008, Vernouillet et al. 2010, Houtman et al. 2014). The considerable amount of pharmaceuticals detected in the effluents of various wastewater treatment plants (WWTPs) confirmed that conventional treatment systems are incapable of degrading completely recalcitrant pharmaceuticals from wastewater (Inyang et al. 2016). This results to their occurrence in the aquatic environment at concentrations ranging from the nanogram per liter up to the milligram per liter level (Verlicchi et al. 2012). More effective treatment methods are, therefore, required in order to minimize the potential impacts of these pollutants to our environment.

Membrane bioreactor (MBR) technology represents a more promising alternative for wastewater treatment over conventional systems due to its number of advantages which include higher effluent quality, small reactor volume, and lower excess sludge production (Han et al. 2015; Díaz et al. 2016). In MBRs, the higher values of biomass concentrations could enhance the biodegradation potential of pharmaceutical compounds while

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the longer sludge retention times (SRT) might promote biota diversity increasing their degradation (Fan et al. 2014). However, membrane fouling still serves as one of the major drawbacks of MBR technology (Lin et al. 2014), and the presence of pharmaceuticals in wastewater was proven to cause severe membrane fouling due to the induced stress on bacteria leading to a significant increase of protein-like substances which is one of the major fouling precursors (Li et al. 2015).

Recently, the application of electrochemical processes to membrane bioreactors (electrically enhanced MBR or eMBR) was investigated and found to improve MBR performance while simultaneously reducing fouling rate (Zhang et al. 2015; Zeyoudi et al. 2015; Ensano et al. 2016; Borea et al. 2017). The application of an electric field inside the bioreactor induces different electrochemical mechanisms such as electrocoagulation, electroosmosis, and electrophoresis that stimulate degradation of organic pollutants and, at the same time, control the mobility and deposition of foulants onto the membrane surface (Bani-Melhem and Elektorowicz 2010; Hasan et al. 2012; Ganzenko et al. 2014; Yuan and He 2015). Ibeid et al. (2015) observed a decrease in the specific resistance to filtration (SRF) and fouling rate by 8–86 times and 6 times, respectively, using eMBR with current density (CD) values ranging from 15 to 35 A/m^2. In another study, removal rates of chemical oxygen demand (COD), nitrogen, phosphorus, nickel (Ni), and chromium equal to 99.3, 90.6, 86.6, 86.1, and 79.3%, respectively, were obtained from eMBR using CD = 15 A/m^2 intermittently supplied at 5 min ON and 15 min OFF (Giwa and Hasan 2015). Wang et al. (2016) achieved an 11.1% higher phenol degradation in eMBR than the sum of two individual processes.

Considerable research efforts have been dedicated to the removal of pharmaceutical compounds from wastewater using MBR or electrochemical processes (Dutta et al. 2014; Phan et al. 2015; Yehya et al. 2015; Padilla-Robles et al. 2015; Liu et al. 2015). However, the removal efficiency of pharmaceutical compounds using the combined system (eMBR) has not been studied yet. To date, most of the studies conducted in eMBRs have been focused on the abatement of bulk organics from wastewater and the control of membrane fouling.

Hence, in this study, the performance of a laboratory scale eMBR was investigated for the removal of conventional pollutants and selected pharmaceuticals in a simulated municipal wastewater. Diclofenac (DCF), carbamazepine (CBZ), and amoxicillin (AMX) were chosen based on the documented occurrence of these compounds in aquatic environment (Ternes 1998; Kim and Aga 2007). A conventional MBR was operated as a comparison test. To the best of the authors' knowledge, this is the first attempt to tackle specifically the effects of combining electrochemical processes, biological degradation, and membrane filtration on selected pharmaceutical removal using initial concentrations as low as 0.01 mg/L per compound and intermittent application of low values of current density.

Materials and methods

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

Chemicals

All reagents were of analytical grade and were used without further purification. A synthetic solution, simulating real municipal wastewater, was used as feed and characterized by the following composition according to previous studies (Yang et al. 2002; Li et al. 2005, 2013): $C_6H_{12}O_6$ (200 mg/L), $C_{12}H_{22}O_{11}$ (200 mg/L), protein (68.33 mg/L), $(NH_4)_2SO_4$ (66.73 mg/L), NH_4Cl (10.91 mg/L), KH_2PO_4 (4.43 mg/L), K_2HPO_4 (9.0 mg/L), $MgSO_47H_2O$ (21 mg/L), $MnSO_4H_2O$ (2.68 mg/L), $NaHCO_3$ (30 mg/L), $CaCl_2$ $6H_2O$ (19.74 mg/L), and $FeCl_36H_2O$ (0.14 mg/L). 0.01 mg/L of DCF, CBZ, and AMX was spiked in the synthetic solution in order to simulate averaged detected concentrations of these compounds. DCF ($C_{14}H_{10}Cl_2NNaO_2$), CBZ ($C_{15}H_{12}N_2O$), and AMX ($C_{16}H_{19}N_3O_5S{\cdot}3H_2O$) were produced by Sigma-Aldrich and were selected as target compounds since they are representative of highly consumed pharmaceuticals and are among the most frequently detected pharmaceutical compounds in the effluents of WWTPs (Prado et al. 2017; Naddeo et al. 2009; Teijon et al. 2010; Secondes et al. 2014).

All solutions were prepared without pH adjustment using ultrapure water obtained from a Millipore Milli-Q system with resistivity >18 MO cm at room temperature.

Experimental setup

The experimental setup of the eMBR, developed by the authors in a previous study (Borea et al. 2017), is shown in Fig. 1. Perforated cylindrical aluminium anode and stainless steel mesh cathode are immersed inside a cylindrical bioreactor (working volume equal to 13 L) at a distance of 6 cm from each other. The electrodes were connected using copper wire to a digital external DC power supply (CX400, TTi, 0–6 V, 0–20 A). A ZeeWeed-1 (ZW-1) submerged hollow fiber ultrafiltration module (GE/Zenon Membrane Solution), characterized by an average pore size of 0.04 μm and an effective membrane surface area of 0.047 m^2, is placed vertically at the center of the bioreactor. Air diffusers are located at the bottom surrounding the membrane module in order to supply the required level of oxygen for biological oxidation, provide good mixing of suspended sludge flocs inside the reactor, and

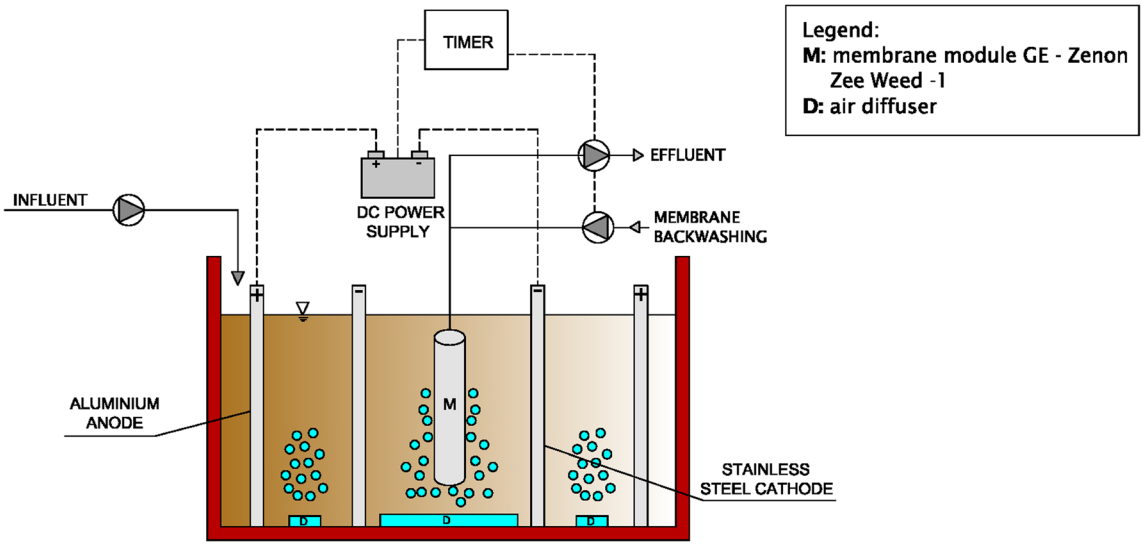

Fig. 1 Experimental setup of the electro-membrane bioreactor

facilitate membrane scouring. The aeration rate used in the experiment was set to 98 L/min in both MBR and eMBR.

Operating conditions

Fresh activated sludge for inoculation was taken from the secondary clarifier at the conventional municipal treatment plant in Salerno (Italy). It was acclimatized for over a month until the operation parameters became stable. No sludge was withdrawn during the entire operation except for the necessary analysis. The eMBR was operated continuously at a hydraulic retention time (HRT) of 19 h and at constant flow rate of 15 LMH, extracting the effluent by a metering pump (Qdos 30; Watson-Marlow Pumps Group). The 15-min filtration cycle is composed of 14 min 30 s permeate production and 30 s backwashing.

There were two stages involved: in stage 1, the reactor was operated as a conventional MBR, and in stage 2, a CD of 0.5 mA/cm^2, calculated by dividing the current by the anode area, was applied intermittently (5 min ON/20 min OFF) to electrodes inside the reactor. The selected intermittent operation mode was according to the previous study (Borea et al. 2017). It was chosen to minimize the inhibitory effects of direct exposure of bacteria to electric current as well as save energy. Each stage lasted for 35 days. A programmable electronic controller controlled both the direct current (DC) application and filtration cycle.

Chemical membrane cleaning was conducted after each stage and whenever the transmembrane pressure (TMP) reached an approximate value of 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). Each stage was therefore characterized by different filtration cycles corresponding to the time span between two chemical cleanings.

Analytical methods

Samples of influent, supernatant, and effluent were analyzed for COD, dissolved organic compounds (DOCs), ammonia nitrogen (NH_4-N), nitrate nitrogen (NO_3-N), and orthophosphate (PO_4-P) following standard methods (APAT and CNR-IRSA 2003). DOC was determined, after filtration over a 1.2-μm membrane filter, using TOC analyzer. 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}). Mixed liquor suspended solids (MLSSs) and mixed liquor volatile suspended solids (MLVSSs) were measured using the same standard methods. Dissolved oxygen (DO) concentration, pH, temperature, conductivity, and redox potential (ORP) were obtained using a multiparametric probe (Hanna Instruments, HI769828). DCF, CBZ, and AMX concentrations were measured using 4000Q Trap LC–MS/MS System (Applied Biosystems, Foster City, USA) in ESI-positive mode with a mobile phase composed of A: 0.1% formic acid in water, and B: acetonitrile–water (1:1, *v*/*v*) solution (limit of quantification lower of 1 ng/L). The method detection limit (MDL) was between 0.9 and 8 ng/L in spiked water samples. The precision of the method, calculated as relative standard deviation, ranged from 0.9 to 3.0%.

The transmembrane pressure (TMP) of the membrane 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 evaluated in order to assess the fouling rate and measuring zeta potential and particle size diameter (PSD) of the activated sludge, along with the concentrations of membrane fouling precursors, namely bound extracellular polymeric substances (EPS), soluble microbial products (SMP), and transparent exopolymeric particles (TEP).

Membrane fouling rate was calculated 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. EPS and SMP were extracted from the sludge floc according to the heating method (Morgan et al. 1990; Le-Clech et al. 2006). Protein and carbohydrate contents of EPS and SMP (EPSp, EPSc, SMPp, SMPc) were then determined using photometric methods adopted from 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 was analyzed according to the method developed from previous study (Borea et al. 2017).

Results and discussion

Effects of applied electric field on membrane fouling

The application of electrochemical processes to the MBR led to a decrease of the fouling rate from 8.08 kPa/day (MBR) to 4.52 kPa/day (eMBR) (Table 1). Moreover, the membrane module of eMBR was cleaned less frequently than that of the conventional MBR. The frequency of chemical cleaning, defined as the number of chemical cleaning divided by the overall filtration time (Borea et al. 2017), was reduced by 18% when a minute electric field of 0.5 mA/cm^2 was applied to the eMBR. Such reduction minimizes possible damage of the membrane by strong chemicals and, hence, prolongs the membrane lifespan.

The reduction of membrane fouling could be attributed to the different electrochemical mechanisms developed inside the bioreactor such as electrocoagulation, electroosmosis, and electrophoresis. Upon application of electricity, various aluminium hydroxide complexes that are positively charged are formed in the solution via electrocoagulation process which destabilize, neutralize, and adsorb the negatively charged flocs (Hua et al. 2015). As a result of electrocoagulation and, hence, of the reduction of negatively charged foulants, the magnitude of zeta potential for the colloidal system in the mixed liquor was shown to reduce from −16.87 to −9.92 mV in terms of absolute value (Table 1). The reduction of sludge surface charge (zeta potential) lessens the repulsive force between the flocs and improves the adhesion ability of bacteria to surfaces (flocculation) resulting in the increase of floc size (Ibeid et al. 2015). From Fig. 2, there is an evident increase of particle size diameter, showed by the shifting of the curve to the right, when electricity was applied to eMBR. From 73.57 μm in MBR, the modal average diameter rose to 91.39 μm in eMBR.

Membrane fouling can be best described by the hydrodynamic and thermodynamic properties of foulants in the eMBR. Foulants move towards the membrane surface through the hydrodynamic drag force (permeation drag) while the binding of foulants to the membrane is caused by the thermodynamic forces (short range physicochemical interactions) (Hong et al. 2013). In connection to sludge floc size, Hong et al. (2013) studied the relationship of floc size with thermodynamic interactions between the sludge and the membrane surface. The results showed that the interaction energy is inversely proportional to the radius of sludge flocs (Hong et al. 2013). In terms of hydrodynamic drag force, the forward transport velocity of the foulants to the membrane increases as the floc size decreases (Hong et al. 2013). Formation of larger flocs due to electrocoagulation, therefore, is conducive to fouling control since it minimizes the forward transport velocity as well as the adherence of the flocs to the membrane surface.

Applied electric field also controls the movement of the suspended particles and water in the mixed liquor (Giwa et al. 2015). In this study, a minute electric field was used to induce electrokinetic processes in the mixed liquor. When the power supply was turned on, the electric field force counteracts the permeation-induced deposition of negatively charged foulants away from the membrane surface and towards the anode (electrophoresis) (Chen et al. 2007). In addition, the positively charged bulk liquid is drifted towards the cathode then passed through the membrane in a process called electroosmosis (Ibeid et al. 2013). The simultaneous effects of electrophoresis and electroosmosis enhanced membrane filtration and, hence, reduced fouling.

The impact of applying a direct current field on the different fouling precursors was also investigated in this study to know its contribution to membrane fouling control. Studies

Table 1 Fouling parameters

Run	Current density (mA/cm^2)	Frequency of chemical cleaning (cleaning/day)	Fouling rate ΔTMP/dt (kPa/day)	Zeta potential (mV)
MBR	0	0.17	8.08	−16.87 ± 0.75
eMBR	0.5	0.14	4.52	−9.92 ± 0.29

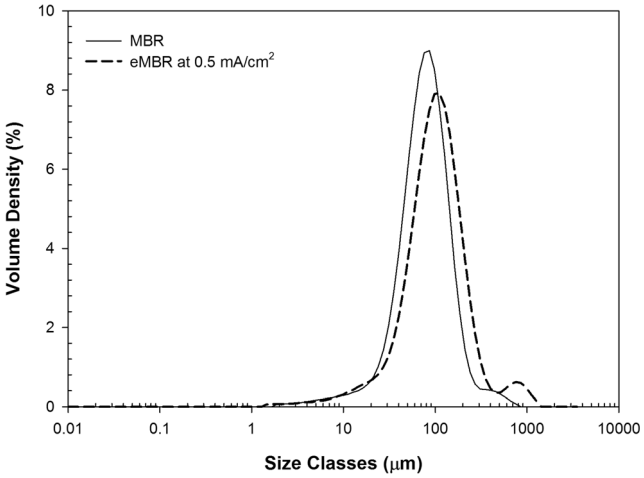

Fig. 2 Particle size distribution of sludge flocs in MBR and eMBR

have shown that the biological constituents of activated sludge such as EPS, SMP, and TEP are major foulant parameters in MBR (Drews et al. 2008; de la Torre et al. 2008; Lin et al. 2014). TEP can be considered as a new membrane fouling indicator more easily determinable with respect to EPS and SMP (de la Torre et al. 2008; Borea et al. 2017).

Figure 3 presents the normalized concentrations of the carbohydrate and protein components of SMP and EPS as well as the TEP in the mixed liquor of MBR and eMBR. As can be seen, there was a considerable reduction of all parameters measured after the application of the electric field in the eMBR. A decrease of the average normalized concentration by 80 and 52% was observed for SMPc and SMPp, respectively, and 70 and 58% for EPSc and EPSp, respectively. Similarly, substantial reduction equal to 97% was achieved for TEP. These results are consistent with other published studies (Giwa et al. 2015; Ibeid et al. 2015). The decrease of fouling precursors upon exposure of the sludge to direct current field was attributed to electrocoagulation and electrochemical oxidation. Microbial flocs have been reported to be negatively charged due to the ionization of EPS and SMP

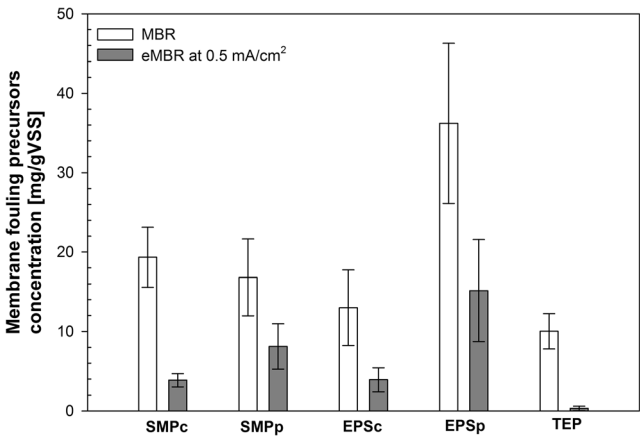

Fig. 3 Concentration of membrane fouling precursors in the mixed liquor of MBR and eMBR

functional groups such as carboxylic, sulfate, and phosphate (Lin et al. 2014), and thus, they can be destabilized, neutralized, and adsorbed by the aluminum hydroxide coagulants. Also, the electrochemical oxidation of water at the anode generates hydroxyl radicals (a powerful oxidant) which can mineralize polysaccharides and proteins making SMP, EPS, and TEP more biologically degradable (Wang et al. 2004). SMPs are generally adsorbed and reduced by electro-generated coagulants during electrocoagulation while EPS reduction is likely due to the coexistence of electrochemical oxidation (Hua et al. 2015). The different removal mechanisms could have entailed different percentages of removal between SMP and EPS. Since carbohydrates can be easily degraded by bacteria than proteins (Zhang and Bishop 2003), this has led to higher SMPc and EPSc removals than SMPp and EPSp.

Therefore, the integration of electrochemical processes (e.g., electrocoagulation, electrophoresis, and electroosmosis) with MBR caused a decrease of the foulant concentrations, improved sludge morphological properties, and controlled the movement of suspended particles and bulk liquid.

Effects of applied electric field on conventional pollutant removal

The influent and effluent characteristics were periodically monitored in this study to evaluate the bioreactor performance in terms of conventional pollutant treatment. Regarding organic matter removal, COD and DOC removal efficiencies were found almost similar in MBR and eMBR (Table 2).

Approximately 98% of COD and DOC were removed in both systems. It is noteworthy to mention that the influent wastewater used in this study was synthetic wastewater prepared by dissolving organic substances, such as glucose and sucrose, to simulate municipal wastewater. These substances are readily biodegradable which explains the high removal of COD and DOC in both systems (Borea et al. 2017).

The removal of humic substances was also calculated based on the UV_{254} absorbance (Table 2). The presence of electric field in the bioreactor enhanced the removal by almost 15% from 74.24% (MBR) to 90.68% (eMBR). Low concentration of humic substances is extremely important for the minimization of the formation of disinfection by-products in the effluents of the treatment plants which use chlorination (Ibeid et al. 2013; Ensano et al. 2017).

The enhanced removal in eMBR can be justified by the predominant effects of electrochemical processes in combination with the biological degradation and membrane filtration (Hosseinzadeh et al. 2015). In electrochemical systems involving sacrificial aluminium anode, as in the case of eMBR used in this study, metal complexes are formed which react with contaminants in wastewater forming flocs that can coagulate colloidal particles (Tafti et al. 2015; Chawaloesphosiya et al. 2015). These flocs are helpful for the fast adsorption of

Table 2 Comparison between MBR and eMBR for the removal of conventional pollutants

Parameters	Stage 1 (MBR)			Stage 2 (eMBR)		
	Influent	Effluent	% Removal	Influent	Effluent	% Removal
COD (mg/L)	411.23 ± 52.10	9.29 ± 4.21	97.70 ± 1.07	455.05 ± 16.55	6.34 ± 6.27	98.58 ± 1.43
DOC (mg/L)	158.79 ± 36.66	4.31 ± 1.28	97.18 ± 0.93	172.64 ± 35.83	2.48 ± 1.32	98.34 ± 1.26
UV_{254} (cm^{-1})	0.07 ± 0.05	0.01 ± 0.01	74.24 ± 7.36	0.08 ± 0.03	0.006 ± 0.002	90.68 ± 4.37
NH_4-N (mg/L)	33.69 ± 5.15	20.38 ± 1.89	38.05 ± 11.49	32.53 ± 7.37	11.12 ± 7.03	72.10 ± 13.06
PO_4-P (mg/L)	6.08 ± 0.99	4.36 ± 0.81	27.97 ± 10.67	6.61 ± 1.43	0	100

dissolved organic compounds (Elabbas et al. 2016). Giwa et al. (2016) added that oxidation and reduction of organic pollutants may as well be possible which led to its deposition at the anode and cathode, respectively.

Similarly, the treatment efficiency of ammonia nitrogen (NH_4-N) was significantly higher in eMBR (72.10%) than MBR (38.05%) (Table 2). This can be attributed to the electrocoagulation process (Giwa et al. 2016) and the oxidation of ammonia molecules at the anode to nitrate (Lin and Wu 1996) that improve the removal of NH_4-N in addition to the biological degradation of ammonia nitrogen by nitrification. This signifies that the minute electric field (0.5 mA/cm^2) applied in the eMBR system was not detrimental to nitrifying bacteria, the microorganisms responsible for the conversion of ammonia nitrogen (NH_4-N) to nitrate nitrogen (NO_3-N). Li et al. (2001) mentioned that direct exposure of nitrifying bacteria to applied DC greater than 2.5 A/m^2 has inhibitory effects on their metabolism. This result also indicates the negligible effects of accumulated metal ion complexes which can form a barrier that hinders the transfer of enzymes and nutrients through the microbial cell membrane (Bani-Melhem and Elektorowicz 2011). The intermittent application mode (5 min ON/20 min OFF) used in this study controls the excessive production of metal ion concentration over time. The total amount of Al^{3+} in the mixed liquor at the end of eMBR stage was 5.32 g.

Expectedly, the reduction of NH_4-N causes an increase in NO_3-N concentration. However, the amount of NO_3-N in MBR effluent (13.55 ± 5.63 mg/L) was seen to be extensively greater than eMBR (0.45 ± 0.47 mg/L). This is due to the further reduction of NO_3-N into N_2 by anaerobic microorganisms (denitrification) which is a favorable process (Borea et al. 2017). The intermittent application of electric field in this study causes alternating anoxic and aerobic conditions in the bioreactor. When the electricity is ON, the anoxic condition prevailed which favored the denitrification process, as shown by the decrease of ORP (OFF = 227.17 ± 57.15 mV, ON = 2.9 mV) and DO concentration (OFF = 5.4 ppm, ON = 1.2 ppm).

Furthermore, eMBR showed outstanding phosphorus treatment than conventional MBR. The results obtained in this study presented a 100% removal of PO_4-P in eMBR compared to only 27.97 ± 10.67% in MBR. This excellent performance can be ascribed to the electrocoagulation process which enables the adsorption of the soluble phosphorus in the mixed liquor by the generated Al coagulants and the precipitation of phosphate ions into $AlPO_4$(s) and $Al_6(OH_{15})PO_4$(s) according to Eqs. (4) and (5) (Kim et al. 2010; Bani-Melhem and Smith 2012). Our observations are in good agreement with previous results (Wei et al. 2009; Kim et al. 2010; Bani-Melhem and Smith 2012; Borea et al. 2017; Ensano et al. 2017).

$$Al^{3+} + {PO_4}^{3-} \rightarrow AlPO_{4(s)} \quad (4)$$

$${Al_6(OH)_{15}}^{3+} + {PO_4}^{3-} \rightarrow \left[Al_6(OH)_{15}\right]PO_{4(s)} \quad (5)$$

Effects of electric field on the removal of pharmaceutical compounds

The concentrations of DCF, CBZ, and AMX detected over time in the influent and effluent of MBR and eMBR are presented in Fig. 4. The average DCF, CBZ, and AMX concentrations in MBR effluent are 0.0054 ± 0.0007, 0.0052 ± 0.0006, and 0.0059 ± 0.0010 mg/L, respectively. The eMBR, on the other hand, exhibits enhanced permeate quality as can be seen by the more evident downward trend of the effluent pharmaceutical concentrations. After 35 days of continuous operation, the DCF, CBZ, and AMX concentrations in the eMBR effluent dropped down to 0.0021, 0.0016, and 0.0024 mg/L, respectively.

Figure 5 summarizes the average removal efficiencies of the selected emerging contaminants using MBR and eMBR. Notable differences between the two systems were found. DCF, CBZ, and AMX were removed in conventional MBR by 50.09 ± 11.02, 48.58 ± 6.58, and 44.54 ± 10.35%, respectively. For eMBR, higher removals were achieved for the three compounds (DCF = 75.25 ± 8.79%, CBZ = 73.84 ± 9.24%, and AMX = 72.12 ± 10.11%).

Since eMBR combines the action of electrochemical processes with biological degradation and membrane filtration, which are the main mechanisms of pollutant removal in MBR,

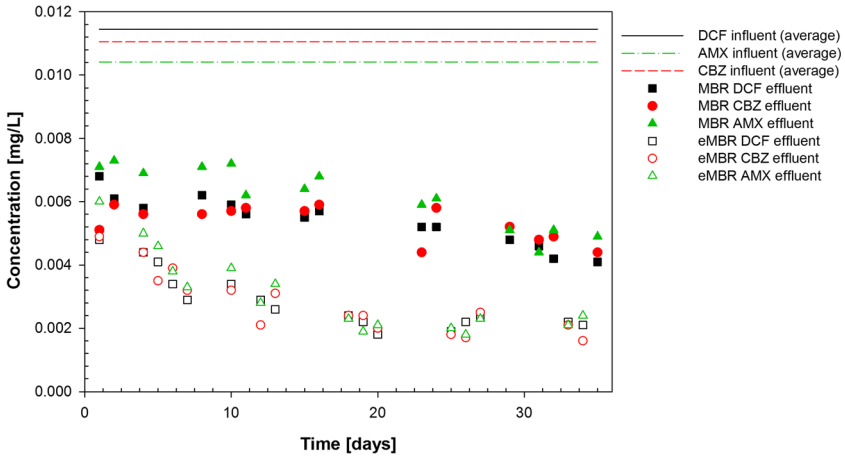

Fig. 4 Concentrations of DCF, CBZ, and AMX in the influent and effluent of MBR and eMBR

the differences on the removal efficiencies of pharmaceutical compounds are mainly attributed to the added effects of the electrochemical treatment. When the DC field is ON, the anode and the cathode are exposed to oxidative and reduced conditions, respectively, which generate in situ coagulants capable of absorbing dissolved organic pharmaceuticals (Yehya et al. 2015). Various charged monomeric and polymeric Al^{3+} complexes are also formed which neutralize the oppositely charged micropollutants allowing them to band together and form larger particles (Liu et al. 2015). Considering that PVDF ultrafiltration membrane (nominal pore size = 0.04 μm) used in this study has a molecular weight cut-off size of about 400 kDa and that the molecular masses of the three pharmaceuticals are DCF = 318.13 g/mol, CBZ = 236.27 g/mol, and AMX = 419.45 g/mol, the increase of their sizes as a result of electrocoagulation significantly improved the pharmaceutical retention at the membrane.

The physicochemical properties such as pKa and octanol partition constant (k_{ow}) values have known to affect the adsorption of pharmaceutical compounds on activated sludge as well as membrane filtration (Fan et al. 2014). Since the sludge flocs are negatively charged and DCF (pKa = 4.15) and AMX

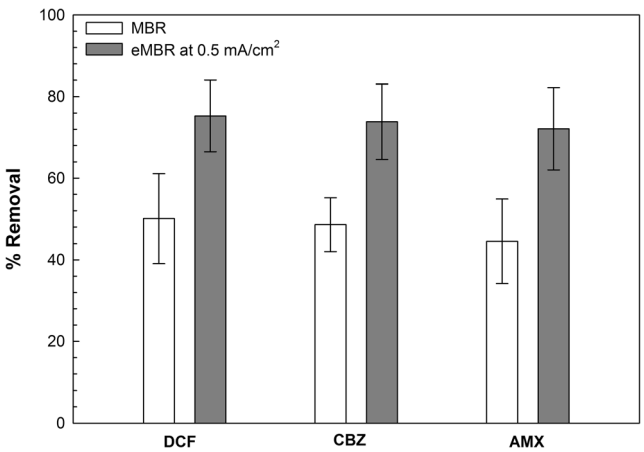

Fig. 5 Comparison of the removal of pharmaceuticals using MBR and eMBR for DCF, CBZ, and AMX

(pKa = 3.39) are also negatively charged at neutral pH (pH = 7–8) (Acero et al. 2016; Hu and Wang 2016), electrostatic repulsion may occur preventing its adsorption on the flocs. On the other hand, CBZ (pKa = 2.3) is relatively independent of the solution pH (Nghiem et al. 2006) and cannot be affected by electrostatic interaction which can promote the adsorption process. Additionally, the k_{ow} values of the selected pharmaceuticals (DCF = 0.70, CBZ = 2.45, AMX = 0.87) indicate that they have low hydrophobicity and hence they are less likely to be adsorbed on the hydrophobic sludge surface. Phan et al. (2015) mentioned that very hydrophobic compounds with $k_{ow} > 3.2$ are generally removed from the aqueous phase via sorption to biosolids. Nguyen et al. (2013) and Fan et al. (2014) supported these findings in their study.

The hydrophilic and anionic nature of pharmaceuticals are beneficial in their separation by membrane filtration. Nghiem et al. (2006) pointed out that negative species have higher charge density resulting in not only an increase in charge repulsion but also a larger molecule hydrated size. The application of electric field enhances this repulsion by promoting electrophoresis which drives the anionic compounds away from the membrane surface towards the oppositely charged electrode (Bani-Melhem and Elektorowicz 2010). These compounds move and deposit on the anode via electromigration. Attachment of the anionic compounds on the anode surface may promote direct oxidation leading to their decomposition (Yehya et al. 2015; Giwa et al. 2015). Water may also be electrooxidized at the anode surface leading to the formation of active species (hydroxyl radicals) which enhance the degradation of organic pharmaceuticals (Wang et al. 2004; Zhao et al. 2009).

Biodegradation gives minimal contribution to the removal of DCF and CBZ from MBR (Nguyen et al. 2013; Fan et al. 2014; Li et al. 2015; Phan et al. 2015). The recalcitrant behavior of these compounds may be due to the functional groups attached to their molecular structure (Tadkaew et al. 2011). Pharmaceuticals with strong electronic donating functional group (hydroxyl group) showed higher biodegradation removal efficiencies (Fan et al. 2014). However, DCF and

CBZ contain electronic withdrawing groups which impose restrictions on biodegradation (Phan et al. 2015). DCF has halogen, amine, and carboxylic groups while CBZ has amide. These functional groups are insusceptible to electronic attack by aerobic bacteria which is believed to be the rate limiting step in aerobic biodegradation in the MBR system (Fan et al. 2014). A lot of studies have proven the persistence of these compounds to biodegradation in MBR (Quintana et al. 2005; Kim et al. 2007; Reif et al. 2008; Tadkaew et al. 2011; Fan et al. 2014; Li et al. 2015; Phan et al. 2015). For AMX, the biological degradation may contribute to its removal in MBR. Andreozzi et al. (2004) proved that AMX can be biodegraded by activated sludge with a degradation constant, $k_{biol} = 4.43 \times 10^{-1}$/h.

From the results obtained in this study, it can be deduced that electrocoagulation and membrane filtration are the main removal mechanisms of pharmaceutical compounds inside an eMBR.

Conclusion

The integration of electrochemical processes with biological degradation and membrane filtration improves MBR performance in terms of pollutant removal and membrane fouling control. An enhancement of conventional pollutant removal along with a reduction of membrane fouling rate were obtained in the present study after the application of a CD equal to 0.5 mA/cm^2. An increase of DCF, CBZ, and AMX up to 25.16, 25.26, and 27.58%, respectively, was achieved in the eMBR with respect to the conventional MBR, due to the different electrochemical mechanisms developed inside the bioreactor. The possibility of enhancing the removal of emerging contaminants using eMBR will further add up to its attractiveness for wastewater treatment implementation. Thus, this eMBR system has shown a potential to replace the conventional activated sludge treatment system.

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