Effect of electrochemical processes applied to membrane bioreactors on the removal of antibiotics from wastewater

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Abstract

In the recent decades, the use of antibiotics is of great concern due to their continuous input and persistence in aquatic ecosystems even at low concentrations. The lack of appropriate treatment systems in conventional wastewater treatment plant, the unsuitable disposal of unused or expired antibiotics and their incomplete metabolization in humans severely affect the quality of surface and groundwater. The present work aims to study the combination of electrochemical processes with membrane bioreactors (electro MBR/eMBR) for the removal of antibiotics from synthetic municipal wastewater. Amoxicillin (AMX) was chosen and spiked, at a concentration of 10 □g/L into the influent wastewater, as representative of highly consumed antibiotic that is frequently detected in the aquatic environment. In order to reach the set objectives, an intermittent electric field of 0.5 and 1.15 mA/cm^2 was applied between two cylindrical perforated aluminum anode and stainless steel cathode, immersed around a membrane module in a laboratory scale eMBR. For comparison purposes, the reactor was also operated as a conventional membrane bioreactor. The results illustrate that the application of electrochemical processes to membrane bioreactors was able to increase the antibiotic removal with respect to the conventional MBR.

Keywords: amoxicillin (AMX); emerging contaminants (ECs); electrochemical processes; electro MBR; current density

1. Introduction

Increasing findings of pharmaceutical active compounds (PhACs) in wastewaters over the last decades have raised many concerns about the ecological and health hazards associated with these contaminants (Ba *et al.*, 2014). Antibiotics are the PhACs most widely used in medicine and agricultural settings (Sun *et al.*, 2016). However, only a small portion can be metabolized by humans and animals and the rest is excreted unchanged or as metabolites (Dorival-García *et al.*, 2013; Sun *et al.*, 2016). Effluents of wastewater treatment plants (WWTPs) are considered as the primary source of the release of these micropollutants into aquatic systems (Du *et al.*, 2014), since the elimination by WWTPs is often incomplete (Ba *et al.*, 2014). Although these compounds are detected at minute concentrations (from ng/L to μg/L), their adverse effects cannot be disregarded, given that pharmaceuticals cause biological effects at very low doses (Dorival-García *et al.*, 2013). The progressive spread and accumulation of antibiotic compounds in WWTP effluents lead to their presence in natural and artificial aquatic environments at sub-inhibitory concentrations, contributing to global proliferation of antibiotic resistant strains of bacteria and the diminished effectiveness of human therapeutic drugs (Dorival-García *et al.*, 2013; Karaolia *et al.*, 2017). Recently, along with super recalcitrant antibiotic resistant bacteria, related antibiotic resistance genes have been detected (Marti *et al.*, 2014; Sun *et al.*, 2016). Their presence together with the mutation of microbes represent an immeasurable risk to the ecological stability beyond a public health problem (Sun *et al.*, 2016). Different biological, physical and chemical treatment methods have been applied in order to remove these compounds from WWTPs effluents (Mukherjee *et al.*, 2013). Among these, MBR technology has emerged as an innovative technology with many advantages, compared to conventional activated sludge processes, such as high concentration of solids inside the reactor, reduction of excess sludge production, highly clarified wastewater effluent, considerable elimination of pathogens and viruses (Karaolia *et al.*, 2017; Melin *et al.*, 2006; Nguyen *et al.*, 2017). The removal efficiency of MBR for trace organic micropollutants is unclear and varies greatly due to the difference in their biodegradability (Tadkaew *et al.*, 2010). Therefore, MBR systems have been combined with different technologies in order to remove a larger variety of micropollutants than a single technology would do, while improving the quality of the final treated effluent compared to conventionally treated effluent (Karaolia *et al*., 2017). Recently, electrochemical processes have been applied to membrane bioreactors (electro MBR- eMBR) for improving MBR performance and, at the same time, reduce fouling rate (Borea *et al*., 2016; Ensano *et al*., 2016; Giwa *et al*., 2015; Hasan *et al*., 2012; Hasan *et al*., 2014). However, the antibiotic removal efficiency in an eMBR has not investigated yet. Thus, in the present study the performance of a laboratory scale eMBR, at different operating conditions, was investigated in terms of conventional pollutants and selected antibiotic removal from synthetic wastewater. Amoxicillin (AMX) was chosen as target compound since it is one of the most widely used antibiotic drugs to treat many different types of infections in both humans and animals (Meng *et al*., 2015; Moreira *et al*., 2015).

2. Materials and methods

The experimental activity was carried out at the Sanitary and Environmental Engineering Division (SEED) laboratory of the Department of Civil Engineering of the University of Salerno (Italy).

2.1 Experimental setup

A laboratory scale electro MBR, developed from the authors in a previous study (Borea *et al*., 2017), was used for the experimental activity (Figure 1).

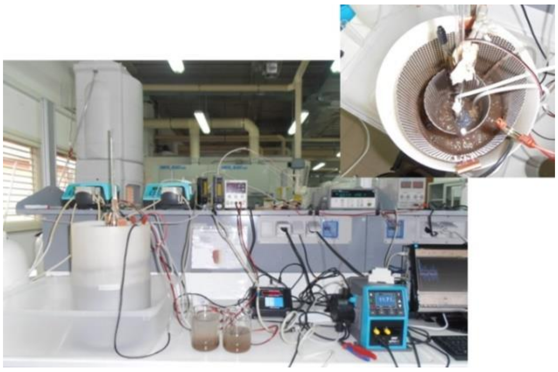

Figure 1. Picture of the eMBR used for the experimental activity

Perforated cylindrical aluminum anode and stainless steel mesh cathode were immersed inside a cylindrical bioreactor, with a working volume of 13 L, at a distance between them of 6 cm. The electrodes 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 (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, was placed vertically at the centre of the bioreactor. Air diffusers were placed at the bottom of the reactor. The reactor was continuously fed with a synthetic solution, simulating real municipal wastewater, characterized by the following composition (in mg/L), according to previous studies (Li *et al*., 2013; 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), $MgSO_47H_2O$ (21), $MnSO_4H_2O$ (2.68), $NaHCO_3$ (30), $CaCl_2$ $6H_2O$ (19.74) and $FeCl_36H_2O$ (0.14). The characteristics of synthetic wastewater are reported in a previous study (Borea *et al*., 2017). AMX ($C_{16}H_{19}N_3O_5S{\bullet}3H_2O$), produced by Sigma-Aldrich, was spiked in the synthetic wastewater at a concentration of 0.01 mg/L in order to simulate averaged detected concentrations of this compound. All solutions were prepared without pH adjustment using ultra-pure water obtained from a Millipore Milli-Q system with resistivity > 18 MO cm at room temperature.

2.2 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 flowrate of 15 LMH, extracting the effluent by a metering pump (qdos30; Watson-Marlow Pumps Group). The 15 min filtration cycle was composed of 14 min 30 s permeate production and 30 s backwashing. There were three runs involved: in run 1, the reactor was operated as a conventional MBR and in stage 2 and 3, a CD of 0.5 and 1.15 mA/cm^2, respectively, was applied intermittently (5 min ON/20min OFF) to electrodes inside the bioreactor according to a previous paper (Ensano *et al*., 2017). The selected intermittent operation mode was chosen according to the previous study conducted (Borea *et al*., 2017). Each stage lasted for around 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 an approximate value of 30 kPa. Each run was, therefore, characterized by different filtration cycles corresponding to the time span between two chemical cleanings.

2.3 Analysis

Influent, supernatant and effluent were characterized for their content of COD, ammonia nitrogen (NH_4-N), nitrate nitrogen (NO_3-N) and orthophosphate (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 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). AMX concentration was 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 %. 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, □TMP/dt.

3. Results and discussion

3.1 Conventional pollutants removal

The removal efficiencies of COD in the MBR and in the eMBR at 0.5 and 1.15 mA/cm^2 were equal to 97.7%, 98.6% and 97.8%, respectively (Figure 2). Therefore, the MBR and eMBR at 1.15 mA/cm^2 showed almost the same values while a slight increase was observed in the eMBR at 0.5 mA/cm^2. As reported in a previous paper (Borea *et al*., 2017), the high COD removals observed in all the three runs could be attributed to the characteristics of the synthetic wastewater used mainly constituted by glucose and sucrose and, thus, rapidly biodegradable. The application of the electric field also led to an improvement of nitrification process with an increase of NH_4-N removal efficiency from 38.1% to 65.1% in the eMBR at 0.5 mA/cm^2 and 50.2% in the eMBR at 1.15 mA/cm^2 (Figure 2). The reduction reactions at the cathode side, when the electric field was ON, consumed the DO inside the reactor, generating anoxic conditions (Borea *et al*., 2017). This was corroborated by the decrease of the ORP and the DO values observed in the eMBR when the electric field was applied.

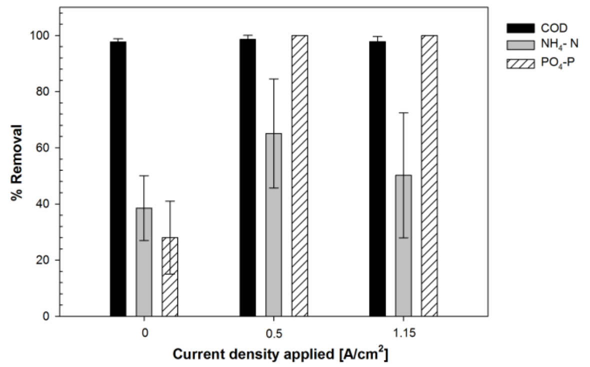

Figure 2. Removal of conventional pollutants in the MBR and in the eMBR at 0.5 and 1.15 mA/cm^2

Due to the anoxic conditions created, the denitrification process was allowed and, thus, a reduction of NO_3-N values was found from 13.2 mg/L in the MBR to 0.4 and 4.4 mg/L in the eMBR at 0.5 and 1.15 mA/cm^2, respectively. The better performance of the nitrification and denitrification process was observed at the lower values of the electric field applied. Thus, the increase of the electric field applied could have had an inhibitory effects on the metabolism of nitrifying bacteria (Li *et al*., 2001). Furthermore, eMBR at both the current densities applied showed a complete removal of PO_4-P compared with only 28% in MBR (Figure 2). The results found, in agreement with previous studies, are due to electrocoagulation and precipitation of $AlPO_4$ and $Al(OH)_3$ (Attour *et al*., 2014). The oxidation and reduction reactions at the anode and cathode side, 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 side with hydroxide ions OH^- formed at the cathode side. In addition, phosphorous $PO^{3-}{}_4$ ions can react with aluminium ions released from the aluminium electrode forming $AlPO_4$ compounds (Kim *et al*., 2010) that can float or precipitate in the membrane bioreactor.

3.2 Antibiotic removal

Figure 3 shows the removal efficiency of the selected antibiotic compound in the MBR and in the eMBR at the two current densities applied. AMX removals in the eMBR at 0.5 and 1.15 mA/cm^2 were 27.6% and 31.9%, respectively, higher than the control test (Figure 3). The increase of the removal efficiency can be mainly attributed to the additional effect of the electrochemical process.

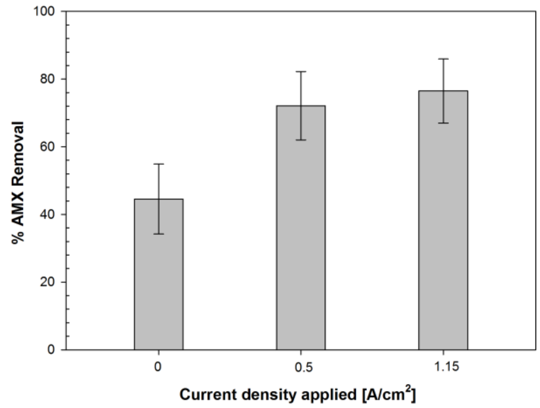

Figure 3. Removal of amoxicillin in the MBR and in the eMBR at 0.5 and 1.15 mA/cm^2

Charge neutralization between negatively charged micropollutants and positive electro-generated coagulants allow them to band together and form larger particles. Since the ultrafiltration membrane used in this study has a molecular weight cut-off size of about 400 kDa and the molecular mass of the AMX is equal to 419.45 g/mol, the increase of particle size during electrocoagulation significantly improved the pharmaceutical retention at the membrane. On the other hand, the anionic AMX compounds, due to electrophoresis and electromigration, were attracted towards the anode moving away from the membrane surface. This promoted the direct oxidation on the anode surface of AMX and its conversion to more biodegradable compounds. Therefore, the removal of AMX can be attributed to the coexistence of electro-coagulation and electro-chemical oxidation beyond to biodegradation. A slight increase of AMX removal was observed with the increase of the current density applied.

3.3 Membrane fouling

The application of electrochemical processes to the MBR led to a decrease of the fouling rate from 8.0 kPa/d for MBR to 4.5 kPa/d and 4.7 kPa/d for eMBR at 0.5 and 1.15 mA/cm^2, respectively. The decrease of membrane fouling could be attributed to the different electrochemical mechanisms developed inside the bioreactor such as electrocoagulation, electrosmosis and electrophoresis (Borea *et al*., 2017, Ensano *et al*. 2016). Therefore, the application of electrochemical processes to the MBR allowed to extend the time between chemical cleaning and the filtration cycles.

4. Conclusions

The application of electrochemical processes to the MBR enhanced the removal of conventional pollutants and decreased the membrane fouling rate. The application of current densities equal to 0.5 and 1.15 mA/cm^2 increased the percentages of AMX removal up to 27.6% and 31.9%, respectively, compared with the conventional MBR, due to the different electrochemical mechanisms developed inside the bioreactor. The increase of current density from 0.5 to 1.15 mA/cm^2 did not affect significantly the performance of the eMBR. Thus, the study reveals that the eMBR with a low value of current density can be effectively applied for improving the removal of emerging contaminants. Further studies should also focus on the evaluation of the system performance for the treatment of real wastewater and on the scale up of the system.

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