

Removal of pharmaceutical compounds by electrochemical processes in real wastewater

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Abstract.

This study investigated the viability of treating pharmaceuticals from real municipal wastewater using electrochemical process i.e. intermittent electrocoagulation. Batch experiments were performed using a laboratory scale electrochemical reactor with aluminum and stainless steel as anode and cathode, respectively. Diclofenac (DCF), carbamazepine (CBZ) and amoxicillin (AMX) were selected as representative of highly consumed pharmaceuticals under different drug categories (anti-inflammatory, antiepileptic and antibiotic) that are frequently detected in water resources. The effects of continuous and intermittent (5 min ON/ 20 min OFF) application of direct current (DC) field on the abatement of pharmaceutical compounds were determined and found to favor the latter in terms of treatment efficiency at varying current densities (CD = 0.3, 0.5 and 1.15 mA/cm²). The removal efficiencies of conventional pollutants namely chemical oxygen demand (COD), dissolved organic carbon (DOC), aromatic and humic substances (in terms of UV₂₅₄), ammonia nitrogen (NH₄-N) and orthophosphate (PO₄-P) were also obtained and found to be directly proportional to current density and reaction time.

Keywords: diclofenac (DCF); carbamazepine (CBZ); amoxicillin (AMX); emerging contaminants (ECs); electrocoagulation

1. Introduction

Pharmaceutical compounds are emerging contaminants whose occurrence in the aquatic ecosystems has elicited serious concerns due to their adverse chronic toxicological effects on living organisms including human beings (Houtman *et al.*, 2014). Since conventional biological treatment methods remain inadequate to completely degrade recalcitrant pharmaceuticals from contaminated wastewater (Inyang *et al.*, 2015), advanced wastewater treatment technologies should therefore be explored. It has been demonstrated that electrochemical processes offer an attractive approach for treating refractory pollutants from wastewater due to their distinct advantages such as simple, highly effective and lesser footprint (Ensano *et al.*, 2017).

In addition, the significant improvement of the electrode materials and their coupling with low-cost renewable energy resources make electrochemical processes a more appealing method. In an electrochemical system using a sacrificial anode, electrocoagulation is the main mechanism of pollutant removal (Ensano *et al.*, 2016). The electrochemical dissolution of the anode generates various monomeric and polymeric metal ion complexes which react with contaminants in the wastewater forming flocs that can both destabilize and aggregate colloidal particles or precipitate and adsorb dissolved compounds (Elabbas *et al.*, 2016; Ganzenko *et al.*, 2014). In the case of aluminum anode, Al³⁺ ions, formed from the electro-oxidation of the anode, react with OH⁻ ions, generated from water reduction at the cathode, producing amorphous Al(OH)₃(s) flocs. The application of electricity in the system also generates bubbles due to the evolution of oxygen gas and hydrogen gas at the anode and cathode, respectively. These bubbles contribute to the collection of generated flocs by electro-flotation process (Liu *et al.*, 2015). Heavier flocs settle at the bottom thru sedimentation. Electrocoagulation has been used as cheap alternative to chemical coagulation for wastewater treatment. Aside from its low operating costs, electrocoagulation has compact treatment facility, faster rate of pollutant removal and lower production of sludge (Koby and Demirbas 2015). Additionally, electrocoagulation has better treatment efficiency than chemical coagulation since the latter produces unwanted anions, such as chloride and sulfide ions, that may compete with cations in the solution and therefore affect the removal of contaminants (Pérez *et al.*, 2015). Flocs produced from electrocoagulation are more stable and contain less bound water which can be removed from the aqueous medium either by sedimentation, flotation or filtration (Elabbas *et al.*, 2016). Electrocoagulation has been successfully applied to various types of wastewater. In this study, the performance of electrochemical system in the elimination of pharmaceuticals from real municipal wastewater was examined. DCF, CBZ, and AMX were selected as representatives of therapeutic groups most frequently found in waters. The effect of varying experimental conditions such as initial concentration, reaction time and current density on the removal of these

compounds was studied. Intermittent application of minute electric field was also employed to reduce energy consumption and operational cost. To the best of the authors knowledge, this is the first paper which applies intermittent electrocoagulation on the removal of recalcitrant pharmaceuticals from raw wastewater.

2. Materials and Methods

2.1. Chemicals and Reagents

Analytical grade (purity > 99 %) 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 manufactured by Sigma-Aldrich and were used in this study without any further purification. A specified amount (0.01 mg/L) of each pharmaceutical was spiked into 1.8 L raw wastewater that was obtained from the effluent of primary clarifier in the municipal wastewater treatment plant of Salerno, Italy. The feed wastewater has the following composition: COD (1.7 mg/L), UV_{254} (0.207), NH_4-N (286.55 mg/L), NO_3-N (3.27 mg/L), PO_4-P (2.18 mg/L), pH (7.4), T (19 °C), redox potential (205) and conductivity (1780 $\mu S/cm$).

2.2. Experimental Set-up

All the experiments were carried out in a 2 L electrochemical reactor that contains aluminum anode (5 cm x 16.5 cm x 0.2 cm) and stainless steel cathode (6 cm x 16.5 cm x 0.2 cm) set 5 cm apart. A direct current was supplied by a DC regulated power source (TTi CPX400S 420W DC Power Supply). A mixing speed of 300 rpm was maintained using magnetic stirrer to ensure uniform concentration within the reactor. Before the start of each experiment, the electrodes were cleaned using sodium hypochlorite and was air-dried.

2.3. Laboratory Analyses

Dissolved oxygen concentration (DO), pH, temperature, conductivity and redox potential were measured using a multiparametric probe (Hanna Instruments, HI769828) before, during and after each run to understand the behavior of the process. Samples were collected from the influent and effluent and were analysed in terms of COD, DOC, UV_{254} , NH_4-N and PO_4-P according to standard methods (APAT, 2003). The amount of pharmaceutical compounds present in the samples were then analyzed 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%.

3. Results and Discussion

3.1 Removal of conventional pollutants

The removal efficiencies of conventional pollutants (COD, DOC, UV_{254} , NH_4-N and PO_4-P) are reported in Table 1. A total of 9 runs were performed at varying current densities (0.3, 0.5 and 1.15 mA/cm²) and HRT (3, 6 and 19h). From

the results observed, it can be generally construed that the treatment of the conventional pollutants is directly proportional to that of current density and HRT. The largest removal was obtained using 1.15 mA/cm² current density and 19 h reaction time. The removal of organic pollutants namely COD and DOC are largely attributed to the action of coagulants in the system. Aluminum metal complexes, that are formed from the dissolution of the sacrificial anode, reacts with the contaminants in the wastewater forming flocs which are helpful for the fast adsorption of dissolved organic compounds (Tafti *et al.*, 2015). UV_{254} is a parameter used to estimate the dissolved aromatic fraction of natural organic matter (NOM) as well as the humic substances in water samples (Weishaar *et al.*, 2003). During electrocoagulation, high molecular weight fraction of NOM is degraded into low molecular weight and more hydrophilic compounds (Mohora *et al.* 2014). Also, the functional groups of humic acid are attracted to positive Al species which facilitates their removal (Ulu *et al.* 2015). The decrease of NH_4-N concentration after the electrochemical treatment is due to the oxidation of ammonia molecules at the anode to nitrate (Lin and Wu 1996). Moreover, 100% of PO_4-P concentration was removed regardless of the current density applied. This can be ascribed to 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 $Al_6(OH_{15})PO_4(s)$ (Ensano *et al.*, 2016)

3.2 Removal of pharmaceutical compounds

Figure 1 shows the effects of continuous and intermittent application of electricity on the removal of selected pharmaceuticals from municipal wastewater. Using 0.01 mg/L initial concentration of each compound and HRT of 3 hours, it can be seen from the figure that, at lower current density (0.3 mA/cm²), the system with continuously applied DC field obtained higher abatement of the recalcitrant micropollutants than the intermittent system. However, as current density increases, the removal of the compounds favors the intermittent system. While both the continuous and intermittent applications generally obtained an increasing trend as CD increases, the difference between their treatment efficiencies also improves favoring the latter system. As discussed previously, the mechanisms involved during conventional electrocoagulation include the dissolution of the sacrificial anode, the formation of coagulants and the removal of pollutants by adsorption onto $Al(OH)_3$ flocs, charge neutralization and electro-flotation. These processes occur simultaneously in a system with continuously applied electric field. Nevertheless, in an intermittent application, these processes are initiated when the power is ON (5 min) and then the power gap (20 min OFF) allows further removal of the micropollutants hence maximizing the adsorption and neutralization potential of generated coagulants. As electricity intensifies, the amount of coagulants also increases, therefore, the higher removal. These results are in accordance with previously published literatures (Ensano *et al.*, 2017, Borea *et al.*, 2017). To better understand which removal mechanism works better in each pharmaceutical compound, the knowledge on their

Table 1. Removal of conventional pollutants at varying current density and HRT.

Current Density (mA/cm ²)	HRT (h)	% Removal				
		COD	DOC	UV ₂₅₄	NH ₄ -N	PO ₄ -P
0.3	3	17%	7%	28%	18%	100%
	6	9%	18%	45%	12%	100%
	19	14%	35%	42%	26%	100%
0.5	3	17%	11%	31%	21%	100%
	6	13%	23%	40%	25%	100%
	19	27%	31%	50%	19%	100%
1.15	3	9%	10%	44%	12%	100%
	6	14%	21%	59%	19%	100%
	19	25%	30%	73%	17%	100%

physicochemical properties is important. The low hydrophobicity of the selected pharmaceuticals ($K_{ow_DCF} = 0.70$, $K_{ow_AMX} = 0.87$, $K_{ow_CBZ} = 2.45$) suggests that they are more likely to be removed via charge neutralization rather than the adsorption on coagulants (Phan *et al.*, 2015). In this study, the pH of the solution ($pH_{ave}=7.4$) was not adjusted in order to simulate the typical pH of municipal wastewater. Since the acid dissociation constant (pKa) of DCF is 4.2 (Acero *et al.*, 2016), it is anionic at neutral pH. The uptake of this compound via electrocoagulation is attributed to the electrostatic attraction between DCF and the positive aluminum complexes. CBZ has two pKas: $pKa_1=2.3$ is related to the protonation of the NH₂ group; and $pKa_2=13.9$ is related to the deprotonation of the amino group (Rao *et al.*, 2016). At neutral pH, CBZ is in the molecular state and shows hydrophobic property (Nghiem *et al.*, 2006). Hence, among the three pharmaceuticals, CBZ has the highest tendency to be adsorbed on the Aluminum coagulants rather than charge neutralization. AMX, on the other hand, has three pKa values namely $pKa_1=2.68$, $pKa_2=7.49$ and $pKa_3=9.63$ which are attributed to the ionization of its carboxyl, amine and phenolic hydroxyl groups, respectively (Hu *et al.*, 2016). At pH~7, the carboxyl groups are transformed into COO⁻ while amine and phenol groups remains neutral (Putra *et al.*, 2009). This further suggests that AMX can also be removed by charge neutralization.

4. Conclusions

This study proves that intermittent electrocoagulation is effective in the treatment of municipal wastewater contaminated with recalcitrant pharmaceuticals. Conventional pollutants namely organic compounds (COD and DOC), aromatic and humic substances (UV₂₅₄) and nutrients (NH₄-N and PO₄-P) were removed via adsorption onto aluminum coagulants, oxidation on the anode surface and precipitation. The treatment efficiencies of these pollutants improved with the current density and reaction

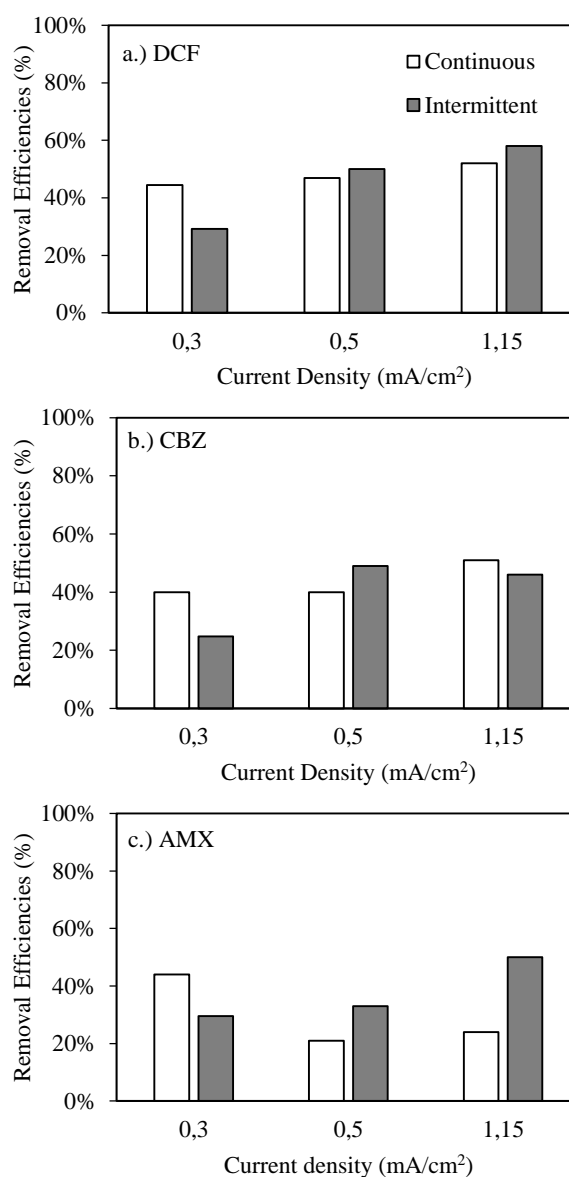


Figure 1. Removal efficiencies of a.) DCF, b.) CBZ and c.) AMX using continuous and intermittent (5 min ON/ 20 min OFF) electrocoagulation at varying current densities (Initial concentration of each pharmaceutical = 0.01 mg/L, HRT=3 hours)

time. Meanwhile, the removal of selected pharmaceuticals DCF, CBZ and AMX depends on their physicochemical characteristics. Hydrophobic CBZ has higher tendency to be adsorbed by the generated coagulants while AMX and DCF are more likely to be removed by charged neutralization and electro-flotation. Both continuous and intermittent DC application showed increasing removal as the current density increases. However, for practical reasons, intermittent electrocoagulation is more favorable as it minimizes energy consumption as well as the anode passivation phenomenon.

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