

Article

Removal of Pharmaceuticals from Wastewater by Intermittent Electrocoagulation

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Abstract: The continuous release of emerging contaminants (ECs) in the aquatic environment, as a result of the inadequate removal by conventional treatment methods, has prompted research to explore viable solutions to this rising global problem. One promising alternative is the use of electrochemical processes since they represent a simple and highly efficient technology with less footprint. In this paper, the feasibility of treating ECs (i.e., pharmaceuticals) using an intermittent electrocoagulation process, a known electrochemical technology, has been investigated. Diclofenac (DCF), carbamazepine (CBZ) and amoxicillin (AMX) were chosen as being representative of highly consumed drugs that are frequently detected in our water resources and were added in synthetic municipal wastewater. The removal efficiencies of both individual and combined pharmaceuticals were determined under different experimental conditions: hydraulic retention time (HRT) (6, 19 and 38 h), initial concentration (0.01, 4 and 10 mg/L) and intermittent application (5 min ON/20 min OFF) of current density (0.5, 1.15 and 1.8 mA/cm²). Results have shown that these parameters have significant effects on pharmaceutical degradation. Maximum removals (DCF = 90%, CBZ = 70% and AMX = 77%) were obtained at a current density of 0.5 mA/cm², an initial concentration of 10 mg/L and HRT of 38 h.

Keywords: diclofenac (DCF); carbamazepine (CBZ); amoxicillin (AMX); emerging contaminants (ECs); electrochemical processes; current density; electric field

1. Introduction

The presence of ECs, such as pharmaceuticals, in our water resources has raised great concern among scientists worldwide due to their persistence in nature and ecotoxicological effects on terrestrial and aquatic organisms. Among these pharmaceuticals, diclofenac (DCF), carbamazepine (CBZ) and amoxicillin (AMX) are three of the most frequently detected in the aquatic environment [1,2]. DCF is a nonsteroidal anti-inflammatory drug (NSAID) usually administered to alleviate degenerative joint diseases such as rheumatoid arthritis, osteoarthritis, non-articular rheumatism and sport injuries [3]. It is also used to reduce menstrual pain and as veterinary medicine. CBZ is an antiepileptic drug used to control seizures and for the treatment of trigeminal neuralgia and some psychiatric diseases (e.g., bipolar disorders) [4]. AMX, on the other hand, is a broad spectrum antibiotic used to treat bacterial infections caused by susceptible microorganisms [5]. Due to their low biodegradability, they are incompletely removed in conventional wastewater treatment plants, thereby, posing a high risk

of contamination into the receiving water bodies [6–8]. A maximum concentration of 1.2 µg/L of DCF was detected by Ternes [9] in German Rivers receiving sewage effluents, and 290 ng/L was measured in the groundwater of Barcelona, Spain [10]. CBZ has the highest concentration (6.3 µg/L) detected among the 32 drug residues investigated in German sewage treatment plant (STP) effluents [9]. In another study [6], it has the second highest average mass load (364 mg/1000 inh/d), out of the 73 pharmaceuticals studied, in the secondary effluent of municipal wastewater treatment plants (WWTPs); DCF ranked eighth while AMX was 26th. AMX has average values of 0.24 and 0.01 µg/L in the WWTP influent and effluent, respectively, as reviewed by Verlicchi et al. [6]. AMX was also found in the surface water of Victoria Harbor, Hong Kong at a maximum concentration of 76 ng/L [11].

At relatively low concentrations, these three compounds are proven to cause cytological damages on terrestrial and aquatic ecosystems. Triebkorn et al. [12] reported that 1 µg/L of DCF changes the liver ultrastructure, liver glycogen and kidney protein of a rainbow trout (*Oncorhynchus mykiss*). At lower concentration (10 ng/L), DCF can impair osmoregulatory ability of a green shore crab *Carcinus maenas* [13]. Almeida et al. [14] proved that beyond the threshold concentration of 3 µg/L, CBZ causes an impairment of antioxidant enzymes of the clam *Ruditapes philippinarum*. It can also affect the mortality, emergence and fertility of the non-biting midge *Chironomus riparius* at a concentration equal to 1.1 mg/kg [15]. AMX is also toxic toward the algae *Cyanophyta Synechococcus leopoldensis* at concentrations ranging from 50 ng/L to 50 mg/L [16] and inhibits the photosynthesis of *Synechocystis* sp. [17]. It is, therefore, necessary to remove these emerging contaminants from wastewater prior to discharge in receiving waters.

Over the past decades, several technologies have been developed for the treatment of these pharmaceutical compounds from wastewater [18,19]. Among these methods, electrocoagulation is currently gaining attention from the scientific community due to the many advantages it offers over the conventional biological treatment. It is referred to as an environmental technology owing to the fact that it uses a clean reagent (electron) for the abatement of organic and recalcitrant pollutants [20]. It produces less sludge, has compact treatment facility (less footprint) and the possibility of complete automation can be expected [21,22]. A 62% removal of 12.5 mg/L CBZ was obtained by the electrocoagulation process under slightly acidic conditions (pH 4) with a $j = 44 \text{ mA/cm}^2$ using Al electrode in the study of Yehya et al. [23]. Liu et al. [24] investigated the electrocoagulation-flotation of DCF in the presence of other NSAIDs, i.e., ibuprofen and ketoprofen, and the results suggested that the addition of a cationic surfactant (cetyl trimethyl ammonium bromide, CTAB) significantly increased the elimination of 100 µM DCF (29.6 mg/L) from synthetic (from 12% to 97% DCF removal) and real hospital wastewater (from 27% to 95% DCF removal) by applying a current of 0.5 A. About 80% of 30 mg/L AMX was eliminated from aqueous solution after 4 h in a non-optimized electrochemical cell at 2.45 V potential using an iron anode and titanium plates as the anode and cathode, respectively [25]. In another study [26], the reduction of the concentration of sulfamethoxazole by the electrocoagulation-flotation process with aluminum electrodes was over 80%.

Intermittent electrocoagulation was studied in recent years in order to contrast the high energy consumption and anode passivation phenomenon [27,28]. Ren et al. [29] applied a pulse electrocoagulation technology to the treatment of refractory berberine hydrochloride (BH) wastewater and found a removal of BH and chemical oxygen demand (COD) equal to 90.1% and 62.6%, respectively.

As discussed above, there are already studies conducted for the removal of these pharmaceuticals from wastewater or synthetic solutions through electrocoagulation, however, only some of them applied intermittent electrocoagulation. Therefore, this is the first study that utilizes a synthetic municipal wastewater contaminated with a mixture of three pharmaceuticals using initial concentrations as low as 0.01 mg/L per compound along with an intermittent application of low values of current density. The main objective of this research is to investigate the removal from synthetic wastewater of three pharmaceutical compounds (i.e., DCF, CBZ and AMX) through the applications of intermittent electrocoagulation using an aluminium anode. DCF, CBZ and AMX were selected as representative of highly consumed pharmaceuticals under different drug categories (anti-inflammatory,

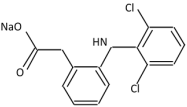
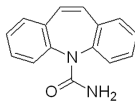
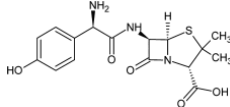
antiepileptic and antibiotic) that are currently detected in all sorts of water. The effects of varying experimental conditions such as initial concentration, reaction time and current density on the removal of these compounds were also examined.

2. Materials and Methods

2.1. Chemicals

All pharmaceuticals under study, i.e., diclofenac sodium salt (DCF), carbamazepine (CBZ), and amoxicillin trihydrate (AMX), were of analytical grade (purity > 99 %) obtained from Sigma-Aldrich and were used without any further purification. The physicochemical characteristics of these compounds are summarized in Table 1.

Table 1. Physicochemical properties of diclofenac, carbamazepine and amoxicillin.

	Diclofenac (DCF) (Sodium Salt) [30]	Carbamazepine (CBZ) [31]	Amoxicillin (AMX) [32]
Structure			
Molecular Formula	C ₁₄ H ₁₀ Cl ₂ NNaO ₂	C ₁₅ H ₁₂ N ₂ O	C ₁₆ H ₁₉ N ₃ O ₅ S·3H ₂ O
CAS No.	15,307-79-6	298-46-4	61336-70-7
Usage	Analgesic, Anti-inflammatory	Analgesic, Antiepileptic	Antibiotic
Molecular weight (gmol ⁻¹)	318.13	236.27	419.45
pKa	4.3	2.3, 13.9 [33]	2.4, 7.4, 9.6
Water Solubility (gL ⁻¹) (at 25 °C)	2.37	0.018	1–3

A specified amount of each pharmaceutical was added to 1.8 L of synthetic municipal wastewater having the following composition (in mg/L) which is in accordance to previous studies [34–37]: C₆H₁₂O₆ (200), C₁₂H₂₂O₁₁ (200), protein (68.33), (NH₄)₂SO₄ (66.73), NH₄Cl (10.91), KH₂PO₄ (4.43), K₂HPO₄ (9.0), MgSO₄·7H₂O (21), MnSO₄·H₂O (2.68), NaHCO₃ (30), CaCl₂·6H₂O (19.74) and FeCl₃·6H₂O (0.14). 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. The main physical–chemical characteristics of synthetic wastewater used in this study are COD [mg/L] 555.12 ± 33.53, UV₂₅₄ [cm⁻¹] 0.12 ± 0.02, NH₄-N [mg/L] 26.54 ± 2.58, NO₃-N [mg/L] Not detected, PO₄-P [mg/L] 9.24 ± 2.23, pH 7.15 ± 0.32, temperature [°C] 19.51 ± 1.32, redox potential (ORP) [mV] 182.22 ± 45.22, Conductivity [μS/cm] 283.61 ± 26.11. Characteristics of the synthetic wastewater are similar to a previous study [37].

2.2. Experimental Setup

The experimental setup is shown in Figure 1. Batch experiments were carried out in a 1.8 L electrochemical reactor with aluminium (5 cm × 16.5 cm × 0.2 cm) and stainless steel (6 cm × 16.5 cm × 0.2 cm) plates as the anode and cathode, respectively. The electrode distance was maintained at 5 cm during electrolysis. A direct current was supplied by a DC regulated power source (TTi CPX400S 420W DC Power Supply) at an intermittent application of 5 min ON/20 min OFF. A mixing speed of 300 rpm was performed using a magnetic stirrer to ensure good mixing in the reactor, minimize regional differences and break up flocs. It is comparable to the different stirring speed used in other studies [38–40]. Sodium hypochlorite was used to clean the electrodes before starting the experiment.

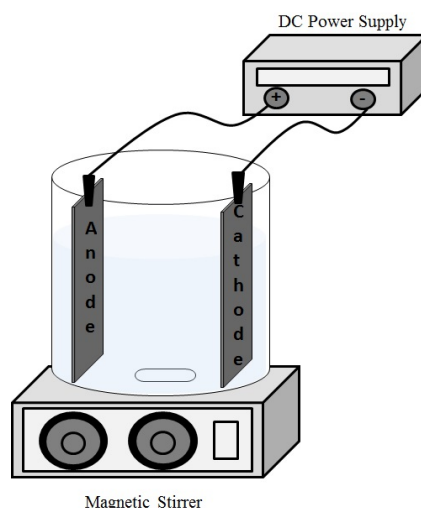


Figure 1. Experimental setup of the electro-chemical reactor.

A total of 21 experimental runs were performed to investigate the influence of different parameters (i.e., initial pharmaceutical concentration, reaction time and current density) on the removal rate of studied pharmaceuticals (Table 2). Synthetic solutions of simulated municipal wastewater (SWW) with or without added pharmaceuticals (DCF, CBZ, AMX and mixture of the three compounds, MIX) were prepared and the removal efficiencies were determined at varying initial concentrations (0, 0.01, 4 and 10 mg/L), treatment time (6, 19 and 38 h) and current density (0.5, 1.15 and 1.8 mA/cm²). The values of the initial concentrations were selected mainly for research interest in order to understand the effects of varying the initial concentration on the removal of the selected pharmaceuticals. They were chosen from the range of levels used in other studies [18,41]. In addition, several studies have detected such concentrations in the influent and effluent of WWTPs [42,43].

Table 2. Experimental runs.

Run		Pharmaceutical Initial Concentration (mg/L)			Hydraulic Retention Time (HRT) (h)	Current Density (mA/cm ²)
Group	No.	Diclofenac (DCF)	Carbamazepine (CBZ)	Amoxicillin (AMX)		
Synthetic wastewater SWW	1	0	0	0	19	0.5
	2	0	0	0	19	1.15
	3	0	0	0	19	1.8
DCF	4	4	0	0	19	0.5
	5	4	0	0	19	1.15
	6	4	0	0	19	1.8
CBZ	7	0	4	0	19	0.5
	8	0	4	0	19	1.15
	9	0	4	0	19	1.8
AMX	10	0	0	4	19	0.5
	11	0	0	4	19	1.15
	12	0	0	4	19	1.8
Mixture of three pharmaceuticals MIX	13	4	4	4	19	0.5
	14	4	4	4	19	1.15
	15	4	4	4	19	1.8
	16	0.01	0.01	0.01	6	0.5
	17	0.01	0.01	0.01	19	0.5
	18	0.01	0.01	0.01	38	0.5
	19	10	10	10	6	0.5
	20	10	10	10	19	0.5
	21	10	10	10	38	0.5

2.3. Analytical Methods

Influent and effluent samples were collected and filtered using 1.2- μm glass fiber filters (Whatman, Maidstone, UK). They were then analysed in terms of chemical oxygen demand (COD), ammonia nitrogen ($\text{NH}_4\text{-N}$) and orthophosphate ($\text{PO}_4\text{-P}$) according to standard methods [44]. Dissolved oxygen concentration (DO), pH, temperature, conductivity and ORP were obtained using a multiparametric probe (Hanna Instruments, HI769828). Two samples were taken from the reactor after each run for the analysis of dissolved aluminium and iron concentrations. One is filtered using 0.45 μm filter paper and the other is not filtered. Then, they are digested with 67% HNO_3 prior to measurement in the inductively coupled plasma-optical emission spectrometer (ICP-OES Spectrometer, Thermo Electron Corp., iCAP 6000 Series) according to standard methods [44]. Dissolved organic carbon (DOC) was measured using total organic carbon (TOC) Analyser (Thermo Scientific, HIPERTO). Samples were also analysed for UV_{254} (a measure of ultraviolet absorption at wavelength of 254 nm) using a Lambda 12 UV-Vis spectrometer (Perkin Elmer, USA). The ratio between UV_{254} and DOC is known as SUVA_{254} which is a useful parameter in estimating the dissolved aromatic carbon content in water samples [45]. Meanwhile, the pharmaceutical compounds were analysed using a 4000Q Trap liquid chromatography–mass spectrometry (LC–MS/MS) System (Applied Biosystems, Foster City, CA, USA) in electrospray ionization (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

COD, $\text{NH}_4\text{-N}$ and $\text{PO}_4\text{-P}$ were monitored in this study as they are good indicators of wastewater quality. To evaluate the removal of these conventional pollutants, experiments were carried out for synthetic wastewater contaminated with a mixture of the three compounds (MIX) at varying current densities ($j = 0.5, 1.15$ and 1.8 mA/cm^2). The initial concentration of each pharmaceutical in the solution was 4 mg/L and the HRT was 19 h (Table 2). From the results obtained in the experiments (Figure 2), current density affects both the removal of COD and $\text{NH}_4\text{-N}$ from MIX wastewater. As j is increased, COD and $\text{NH}_4\text{-N}$ removals are also improved.

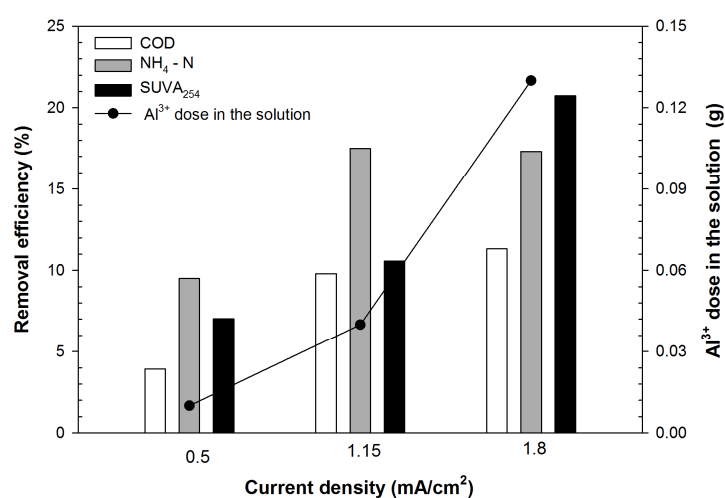


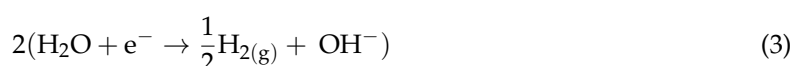
Figure 2. Removal efficiencies of COD, $\text{NH}_4\text{-N}$ and SUVA_{254} at varying current densities (conditions: initial concentration = 4 mg/L, HRT = 19 h) and concentration of Al^{3+} dissolved in the solution at increasing current density.

In an electrochemical system utilizing a sacrificial anode, which in this case is aluminum, the main mechanisms for the contaminant removal are adsorption, precipitation, electro-flotation and charge neutralization [24,29,38]. Upon application of an electric current, Al^{3+} ions produced by dissolution of the aluminium anode (Equation (1)) immediately undergo spontaneous hydrolysis reactions with OH^- ions, generated through the electro-reduction of water at the cathode (Equation (3)), forming various monomeric species such as $\text{Al}(\text{OH})^{2+}$, $\text{Al}(\text{OH})_2^+$, $\text{Al}_2(\text{OH})_2^{4+}$, $\text{Al}(\text{OH})_4^-$, and polymeric species such as $\text{Al}_6(\text{OH})_{15}^{3+}$, $\text{Al}_7(\text{OH})_{17}^{4+}$, $\text{Al}_8(\text{OH})_{20}^{4+}$, $\text{Al}_{13}\text{O}_4(\text{OH})_{24}^{7+}$, $\text{Al}_{13}(\text{OH})_{34}^{5+}$, which then transform finally into $\text{Al}(\text{OH})_{3(s)}$ according to complex precipitation kinetics [46,47]. At pH 7–8, the prevailing Al species are the insoluble $\text{Al}(\text{OH})_{3(s)}$ (Equation (4)) hydroxides with traces of positive charge complexes [46]. These precipitates act as “swift flocs” and have large surface areas which are helpful for the fast adsorption of contaminants from wastewater [48].

At the Anode:



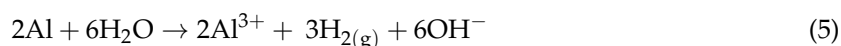
At the Cathode:



In the solution:



In addition, upon the application of electricity, water electrolysis occurs producing oxygen gas and protons (H^+) at the anode (Equation (2)) and hydrogen gas and hydroxyl anion (OH^-) (Equation (3)) at the cathode. According to Cañizares et al. [47], chemical dissolution of the aluminum anode should also be considered in the electrocoagulation process. It is the result of the oxidation of the aluminum plate with simultaneous reduction of water, forming hydrogen gas (Equation (5)):



The iron concentration was also measured in the solution and showed negligible results which means that the stainless steel cathode did not undergo any appreciable change during the electrocoagulation treatment other than hydrogen evolution as a result of the electro reduction of water. Based on a previous study conducted by Picard et al. [49], the total H_2 evolved during electrocoagulation using a stainless steel cathode conforms with the theoretical value calculated using Faraday's law and that no chemical dissolution of the cathode has occurred.

In the present case, for $\text{pH} > 7$, the primary mechanism for the removal of organic compounds is sweep coagulation with adsorption of organic substances on amorphous aluminium hydroxide precipitates [50,51]. Consequently, the increasing current density led to an increase of COD removal efficiency because of the increased production of the coagulant (Al^{3+} ions) on the anode (Figure 2).

Electro-flotation is another mechanism for the removal of organic matter [24,29,38]. The production of bubbles, due to hydrogen evolution at the electrodes, contributed to the collection of generated flocs by H_2 flotation. Upon increasing the current intensity, the bubble generation rate increases and the bubble size decreases, thus increasing its total surface area and improving pollutants removal efficiency [24] as reported in Figure 2. It should be taken into account that flotation depends on the nature of the organic matter. Anionic compounds are difficult to remove by hydrophobic bubbles [24].

Though the treatment efficiencies increased as the current density increases, low removal of COD (<15%) was still observed. This can be attributed to the insufficient amount of coagulants generated which could have improved the removal of organic compounds from the wastewater. According to Faraday's law (Equation (6)), the theoretical Al^{3+} dissolved in the solution at current densities 0.5, 1.15 and 1.8 mA/cm^2 are 6.31 g, 14.52 g and 22.95 g, respectively. However, as per the actual measurement,

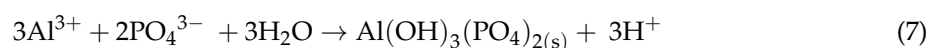
only 0.01, 0.04 and 0.13 g of Al^{3+} were detected in the solution, hence superfaradaic efficiencies can be neglected in this study. This could be attributed to the passivation of the anode surface, found at the end of the batch test due to either the dissolution of aluminum or the directly oxidized film formed on the electrode. Passivation affects the polarization resistance causing lower cell potential than the theoretical value [52]. The passive film, indeed, increases the resistance and reduces the release of the coagulant and bubbles, decreasing the current and removal efficiency [53].

$$m = \frac{ItM}{zF} \quad (6)$$

where I corresponds to electric current (A), t is the applied electrocoagulation time (s), M is the molecular mass of aluminum, z is the valence of metal ions and F is the Faraday's constant (96,487 C/mol).

Another important consideration in the determination of the quality of treated water is the concentration of natural organic matter (NOM). NOMs are potential precursors for the formation of disinfection byproducts (DBPs), which are suspected human carcinogens, during tertiary water treatment (i.e., chlorination) [54]. More specifically, humic substances comprise the aromatic fraction of NOMs and were generally perceived to be the primary precursors for DBP formation [45,50]. SUVA_{254} is a useful parameter in estimating the dissolved aromatic carbon content in water samples and hence the aquatic humic substances [51]. In the study conducted by Weishaar et al. [45], SUVA_{254} has been proven to strongly correlated with the percent of aromaticity of the 13 organic matter isolates obtained from a variety of aquatic environments. From Figure 2, it can be seen that SUVA_{254} removal efficiencies increase at increasing current density. This means that the presence of an electric current improves the removal of aromatic and humic compounds from wastewater. Ulu et al. [55] suggested that during electrocoagulation, the functional groups of humic acid are attracted to positive Al species which facilitates their removal. Mohora et al. [56] also added that due to electrocoagulation, high molecular weight fraction of NOMs was degraded into low molecular weight and more hydrophilic compounds which are less prone to coagulate.

On the other hand, complete removal of phosphorus was achieved regardless of the composition of the wastewater and the current density applied. This can be explained by the interactions between aluminium and phosphate ions inside the reactor which resulted in the significant removal of the latter from the solution [57]. Aside from adsorption onto $\text{Al}(\text{OH})_3$ coagulants, excess aluminium ions (Al^{3+}) react with phosphorous ions to form $(\text{AlOH})_3(\text{PO}_4)_2(\text{s})$ and $\text{AlPO}_4(\text{s})$ that precipitate out in the bioreactor according to the following reactions (Equations (7) and (8)) [58]:



Several studies have reached the same conclusion on the phosphorus removal capability of the electrochemical process using aluminum as the anode [37]. Wei et al. [59] integrated the electrocoagulation system with a membrane bioreactor and observed an increase in Ortho-P removal from 18.9% to 86.6% after direct current was applied to the bioreactor [60]. The $\text{PO}_4\text{-P}$ and total P removal efficiencies of the MBR system with the electrocoagulation unit were 77.2% and 79.9%, respectively, which were significantly higher than that of the MBR system without the coagulation process ($\text{PO}_4\text{-P}$ = 59.0% and total P = 41.0%) [61].

3.2. Effects of Parameters on Pharmaceutical Removal

3.2.1. Current Density

To understand the effects of current density (j) on the removal of pharmaceuticals from simulated municipal wastewater, varying current densities (0.5, 1.15 and 1.8 mA/cm^2) were applied intermittently

(5 min ON and 20 min OFF) to both individual and mixture component systems at an initial concentration of 4 mg/L and HRT of 19 h (Table 2, Run 4–15). The term “removal” is used here for the conversion of the target pharmaceutical to compounds other than the parent compound. As it can be seen in Figure 3, pharmaceutical removal increases at increasing current density. The results are consistent for both systems with the maximum removal obtained at 1.8 mA/cm².

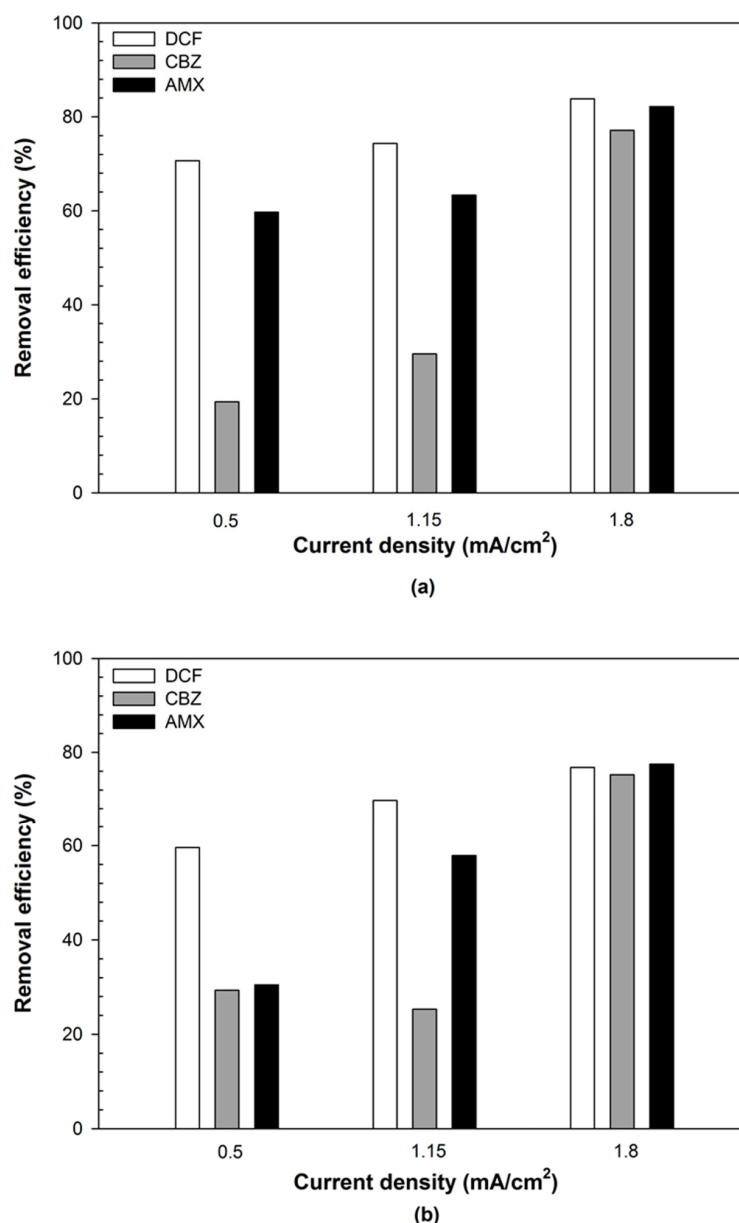


Figure 3. Effects of current density on the removal of pharmaceuticals by electrochemical processes: (a) Individual pharmaceuticals; (b) Mixture of pharmaceuticals (conditions: initial concentration = 4 mg/L, HRT = 19 h).

In the electrocoagulation process as previously reported, the removal mechanisms are adsorption onto Al(OH)₃ flocs, charge neutralization and electro-flotation [62]. The pH of the solution is considered to be a key parameter affecting the elimination of pharmaceuticals, however, in this study, the initial pH (pH = 7–8) of the solution was not adjusted to simulate the typical pH of municipal wastewater. The generated Al³⁺ ions formed via electrodisolution of anodes (Equation (1)) react with OH[−] ions produced through the electro-reduction of water at the cathode (Equation (3)) which

are then hydrolysed to various metal hydroxide complexes depending on the solution pH and turn into amorphous $\text{Al}(\text{OH})_{3(s)}$ (Equation (4)) [47]. Phan et al. [63] mentioned that very hydrophobic compounds with $k_{ow} > 3$ are generally removed from the aqueous phase via sorption to biosolids. The k_{ow} values of the selected pharmaceuticals (DCF = 0.70, AMX = 0.87, CBZ = 2.45) indicate that they have low hydrophobicity and, hence, they are less likely to be removed by adsorption on coagulants or hydrogen bubbles but more likely to be removed by charge neutralization. Indeed, since DCF has an acid dissociation constant value (pK_a) of 4.2, it implies that it carries negative charge at neutral pH. Therefore, high uptake of DCF can be observed due to the strong electrostatic attraction between DCF and these complexes. CBZ has a pK_{a1} of 2.3 related to the protonation of the NH_2 group and pK_{a2} of 13.9 related to the deprotonation of the amino group [33]. The structure of CBZ is in the molecular state at neutral pH and CBZ shows a hydrophobic property when it retains a molecular structure. Nghiem et al. [64] added that CBZ was relatively independent of the solution chemistry and is uncharged at common pH conditions typical of natural water or wastewater. This is probably the reason why CBZ obtains the lowest removal among the three compounds although it has the higher hydrophobicity. AMX, meanwhile, has three pK_a values due to the ionization of its functional groups, identified as carboxyl ($\text{pK}_{a1} = 2.68$), amine ($\text{pK}_{a2} = 7.49$) and phenolic hydroxyl ($\text{pK}_{a3} = 9.63$) [65]. At pH 7–8, carboxyl groups of AMX are transformed into COO^- (Equation (9)) while amine remains neutral and phenol groups are not protonated or deprotonated within the above pH range studied [66]. Hence, the removal of AMX in the solution is also due to adsorption onto the flocs as well as charge neutralization by electrostatic attraction between the functional groups and the complexes in the solution.



With increasing current density, the concentration of generated coagulants also increases, hence more pharmaceuticals are adsorbed onto the flocs or neutralized. Consequently, the bubble density increased with current density; the higher the j values, the smaller the bubble size. Liu et al. [24] cited that, at lower current density, the cathode generated larger and fewer bubbles, and the reaction mechanism was based on coagulation, while at higher current density, the cathode generated bubbles with much higher density and smaller sizes, so the removal mechanism was based on flotation. As it can be seen in Figure 3, generally, there was no significant difference between the removal rates of individual pharmaceutical solution and mixture component—except for AMX at $0.5 \text{ mA}/\text{cm}^2$ —due to the minimal contribution of their concentration ($4 \text{ mg}/\text{L}$) on the total amount of organic compounds in the mixture. The COD and DOC concentrations in the mixture with or without added pharmaceuticals were almost the same (COD~515 mg/L , DOC~200 mg/L). The presence of different organic compounds in the solution promotes competitive adsorption between the different species leading to the reduction of adsorption of some organics in the mixture. The effects of this competitive adsorption can be much more highlighted using aqueous solution containing pharmaceuticals only, as observed by Liu et al. [24].

3.2.2. Initial Pharmaceutical Concentrations

The effects of varying initial concentration (0.01, 4 and 10 mg/L) on pharmaceutical removal were investigated using a mixture component system at a current density of $0.5 \text{ mA}/\text{cm}^2$ and HRT of 19 h (Table 2, Run 14, 17 and 20). For CBZ and AMX, degradation efficiencies increase at an increasing initial concentration (Figure 4). This can be attributed to the increase of concentration gradient which means a stronger driving force to overcome all mass transfer resistances of solutes between the aqueous and the solid phase [67,68]. As a result, there is better adsorption to electrocoagulants. The initial concentration has little or no effect on DCF removal which ranged from 59.57% to 62.73%. Among the three compounds, DCF is the most soluble (Table 1), hence, as DCF is adsorbed on the aluminum hydroxide precipitates, it becomes more stable in the solution. As a result, it became more difficult to remove the pharmaceutical, possibly due to an increase in the interaction between the DCF and the adsorbent.

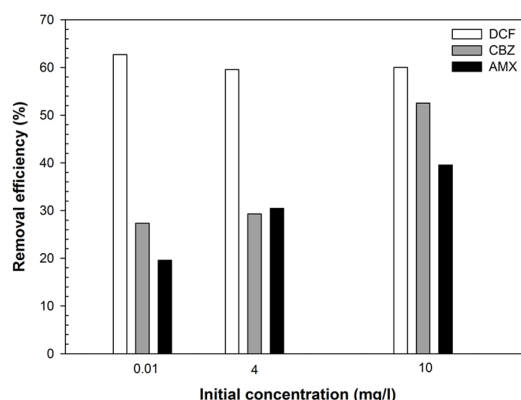


Figure 4. Effects of initial concentration on the removal of pharmaceuticals by electrochemical processes (conditions: $j = 0.5 \text{ mA/cm}^2$, $\text{HRT} = 19 \text{ h}$).

3.2.3. HRT

Figure 5 shows the removal efficiencies of each pharmaceutical as the HRT is varied at 6, 19 and 38 h under initial concentrations of 0.01 mg/L and 10 mg/L at a current density of 0.5 mA/cm^2 (Table 2, Run 16–21). As it can be seen from Figure 5, the removal efficiencies of three pharmaceuticals are directly proportional to the treatment time. Increasing the electrolysis time was known to have a major role in the performance of the electrochemical processes. The longer the treatment time, the more complex the ions are that are generated on the aluminum electrodes and are released into the solution [69]. This, in turn, increases the hydroxide flocs which are responsible for the precipitation and adsorption of the emerging contaminants. For all pharmaceuticals under investigation, the highest removal was obtained after 38 h of treatment.

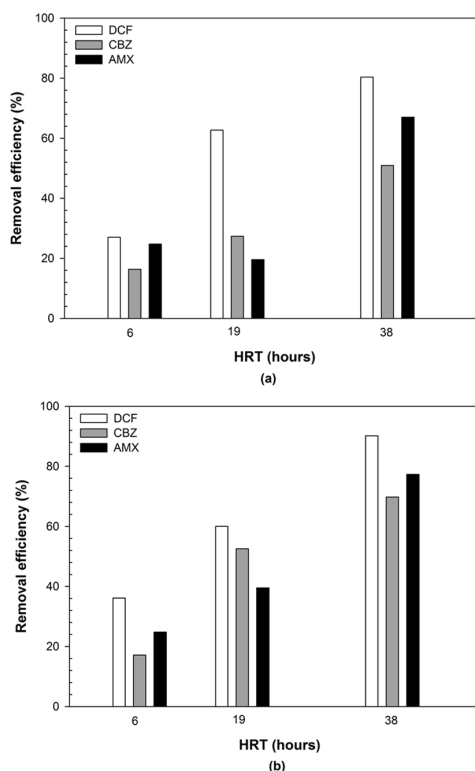


Figure 5. Effects of HRT on the removal of pharmaceuticals by the electrochemical process at an initial concentration of 0.01 mg/L (a) and 10 mg/L (b) ($j = 0.5 \text{ mA/cm}^2$).

3.3. Effects of the Intermittent Electric Field on Energy Consumption

Compared with the conventional electrocoagulation process, the application of an intermittent electric field reduces the consumption of the energy as well as of the anode material since the dissolution of the aluminium stops during the power gap. According to energy consumption law (Equation (10)) [29], energy consumption was a function of the θ^2 :

$$Q = VIt\theta^2 \quad (10)$$

where Q (W h) was the energy consumption; V (V) was the peak voltage; I (A) was the peak current; t (s) was the reaction time and θ was the intermittent cycle (in the conventional electrocoagulation process θ was equal to 1).

Considering that in the present case, θ is equal to 0.2 and t is the HRT applied, the energy consumptions for the different runs are reported in Table 3.

Table 3. Applied voltages, current intensities and energy consumptions of the different experimental runs.

N° Run	HRT (t) (h)	Current Density (j) (mA/cm ²)	Peak Voltage (V)	Peak Current (A)	Energy Consumption (W h)
1-4-7-10-13-17-20	19	0.5	19.65	0.08	1.19
2-5-8-11-14	19	1.15	46.07	0.19	6.65
3-6-9-12-15	19	1.8	60.59	0.3	13.81
16	6	0.5	19.65	0.08	0.38
18	38	0.5	19.65	0.08	2.39
19	6	0.5	19.65	0.08	0.38
21	38	0.5	19.65	0.08	2.39

Compared with the continuous electrocoagulation process, the reduction of the energy consumption is equal to 96% for all the experimental runs.

4. Conclusions

This study proves the viability of the intermittent electrocoagulation process in the treatment of conventional pollutants (COD, NOM, NH₄-N and PO₄-P) and emerging contaminants (DCF, CBZ and AMX) from wastewater using a sacrificial aluminum anode. All the three studied parameters, namely current density, initial concentration and treatment time, have been shown to significantly affect the degradation of these pollutants. The interaction between generated Al(OH)₃ coagulants and pollutants results to the destabilization and aggregation of suspended particles and the precipitation and adsorption of dissolved contaminants. H₂ flotation was also responsible for the collection of micropollutants from wastewater. Higher current density and longer treatment time, therefore, lead to higher pollutant removal due to the increase of coagulant concentration and smaller bubble generation in the solution. Consequently, degradation efficiency increased at the increasing initial concentration of pharmaceuticals due to the stronger driving force which overcomes all mass transfer resistances of solutes between the aqueous and the solid phase. Moreover, the removal of pharmaceuticals from synthetic municipal wastewater contaminated with single pharmaceuticals has been shown to have no significant difference as compared with mixture systems due to the competition between the organic compounds present in the solution. Future studies should be focused on the investigation of the role that pH plays in the removal of DCF, CBZ and AMX from real municipal wastewater. Isotherm and kinetic studies could also be explored to know the mechanism of adsorption of these micropollutants on the aluminum hydroxide precipitates. Furthermore, the impedance of the anode could also be determined to characterize the passive film across the electrode.

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