Applicability of the electrocoagulation process in treating real municipal wastewater containing pharmaceutical active compounds

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HIGHLIGHTS

- Electrocoagulation was applied to municipal wastewater containing pharmaceuticals

- High diclofenac, carbamazepine and amoxicillin removals were obtained

- Higher current density and electrolysis duration improved pharmaceuticals removal

Graphical Abstract
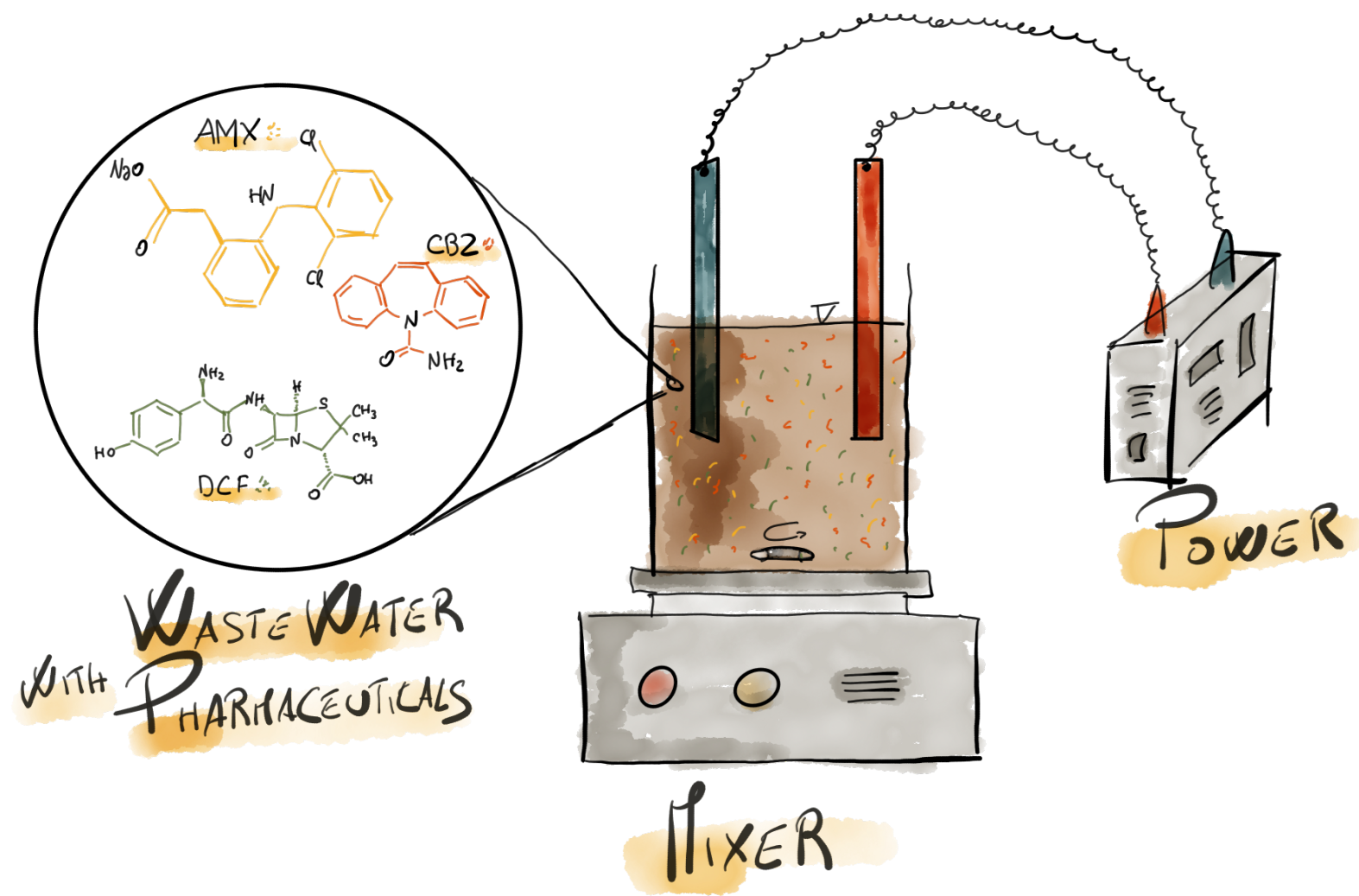
Abstract

In this study, the viability of using electrocoagulation process as a method for pharmaceuticals removal from real municipal wastewater was demonstrated. Batch experimental runs were performed using a simple laboratory scale electrochemical reactor with aluminium and stainless steel as anode and cathode, respectively. Diclofenac (DCF), carbamazepine (CBZ) and amoxicillin (AMX) were selected as representative of pharmaceuticals frequently detected in the aquatic environment. The effects of varying experimental parameters namely current density (0.3, 0.5 1.15 and 1.8 mA cm^{-2}), initial pharmaceutical concentration (0.01, 4 and 10 mg L^{-1}), electrolysis duration (3, 6 and 19 h) and application mode (continuous vs. intermittent) on pharmaceutical removal efficiencies were evaluated. High pharmaceutical abatement was recorded at elevated current density and prolonged electrolysis duration due to additional electro-generated coagulant species in solution.
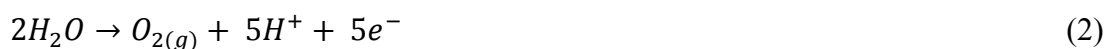
1. Introduction

Electrocoagulation is a relatively inexpensive alternative to chemical coagulation. Aside from low operating costs, electrocoagulation boasts of a compact treatment, rapid pollutant removal and low sludge production [1–3]. Flocs produced from electrocoagulation are more stable, contain less bound water, and thus can be removed from the aqueous medium either by sedimentation, flotation or filtration [4,5]. The higher treatment efficiency of electrocoagulation compared to chemical coagulation is attributed to the absence of additional anions i.e. chloride and sulfide ions that may compete with cations in solution and impede contaminant removal [1,6].

The electrocoagulation process relies on a sacrificial anode [7] which undergoes electrochemical dissolution to generate various monomeric and polymeric metal ion complexes. The generated metal species in solution destabilize colloidal contaminants in the wastewater, form flocs and aggregated particles and adsorb dissolved compounds [8]. For example, Al^{3+} ions, generated by the electro-oxidation of aluminium anode, react with OH⁻ ions produced from water reduction reaction at the cathode to form amorphous Al(OH)$_3$(s) flocs (Eq. 1-4). The application of electricity in the system causes the evolution of gaseous oxygen and hydrogen at the anode and cathode, respectively (Eqs. 2 and 4). These gases facilitate the collection of flocs at the liquid surface via flotation [9] while the heavier flocs settle at the reactor bottom by sedimentation.

At the anode:

$$(Al)_{(s)} \rightarrow Al^{3+}{}_{(aq)} + 3e^-$$
(1)

$$2H_2O \rightarrow O_{2(g)} + 5H^+ + 5e^-$$
(2)

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At the cathode:

$$2(H_2O + e^- \rightarrow \frac{1}{2}H_{2(g)} + OH^-) \tag{3}$$

In solution:

$$Al^{3+} + 3OH^- \rightarrow Al(OH)_{3(s)} \tag{4}$$

Electrocoagulation has been successfully applied to decontaminate various types of wastewaters. Chromium was successfully removed from tannery wastewater [4]; total petroleum hydrocarbon (TPH) from oil refinery wastewater [1]; Al, Zr and PO_4-P from can manufacturing wastewater [2]; colour from sugar beet molasses [10] and textile wastewaters [11]; Mn, Cu and Zn from oil refinery wastewater [5], phosphate from mining wastewater [12] and arsenic from groundwater [13] by electrocoagulation.

Recently, electrocoagulation was found effective in removing refractory pharmaceutical active compounds from synthetic wastewater [14]. Pharmaceutical compounds are biologically active and their presence in the aquatic environment pose serious concerns due to their adverse chronic toxicological effects on living organisms including human beings [15–17]. These compounds can persist and bioaccumulate in the environment [18]. Moreover, conventional biological treatment methods are inadequate in completely removing recalcitrant pharmaceuticals from wastewater [19].

In this study, the performance of the electrocoagulation process for the elimination of select pharmaceuticals from real municipal wastewater was investigated. Diclofenac (DCF), carbamazepine (CBZ) and amoxicillin (AMX) were chosen as representative therapeutic drugs most frequently detected in waters and were used to spike the real wastewater. Based

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on the extensive literature review of the authors, the study is the first to present detailed findings on the removal of DCF, CBZ and AMX from real municipal wastewater by intermittent electrocoagulation. The effect of varying experimental conditions such as initial pharmaceutical concentration, current density and electrolysis duration on pharmaceuticals removal was examined. Intermittent application of minute electric field was also employed to reduce energy consumption and operational cost.

2. Experimental

2.1 Chemicals and materials

The pharmaceutical compounds used namely DCF ($C_{14}H_{10}Cl_2NNaO_2$), CBZ ($C_{15}H_{12}N_2O$) and AMX ($C_{16}H_{19}N_3O_5S.3H_2O$), were all analytical grade (purity > 99%, Sigma Aldrich) and were used without any purification. The raw wastewater was obtained from the effluent of the primary clarifier in the municipal wastewater treatment plant of Salerno, Italy. The feed composition is presented in **Table 1**.

Table 1 Composition of real wastewater used for the experiment

Parameter	Average value	Unit of measurement
COD	107 ± 25.46	$mg\ L^{-1}$
DOC	18 ± 6.52	$mg\ L^{-1}$
UV_{254}	0.23 ± 0.08	cm^{-1}
NH_4-N	291 ± 124.49	$mg\ L^{-1}$
NO_3-N	2.67 ± 2.99	$mg\ L^{-1}$
PO_4-P	1.36 ± 1.59	$mg\ L^{-1}$
DFC	0.0020 ± 0.0011	$mg\ L^{-1}$

CBZ	0.0010 ± 0.00097	**mg L^{-1}**
AMX	0.0016 ± 0.0018	**mg L^{-1}**
pH	7.24 ± 0.32	
T	19.08 ± 2.12	**°C**
Conductivity	1705.58 ± 453.79	**(μS cm^{-1})**

2.2 Experimental set-up

A series of batch experimental runs were conducted using a 2 L electrochemical reactor containing an aluminium anode (5 cm x 16.5 cm x 0.2 cm) and a stainless-steel cathode (6 cm x 16.5 cm x 0.2 cm) set 5 cm apart (see **Fig. 1**). Before the start of each run, the electrodes were cleaned using sodium hypochlorite solution, then they were washed thoroughly with water and left overnight to air-dry. A direct current was applied by a DC regulated power source (TTi CPX400S 420W DC Power Supply) and a 300-rpm mixing speed was maintained by a magnetic stirrer to ensure homogeneity within the reactor and to minimize break up of flocs. The intermittent application of electricity (5 min ON/20 min OFF) was based on a previous studies [14,20].

2.3 Experimental conditions

A total of 31 experimental runs were conducted to investigate the influence of different parameters, namely initial pharmaceutical concentration, reaction time, current density and its application mode, on the removal efficiency of DCF, CBZ and AMX using electrocoagulation process. Initial concentrations of each compound were varied from 0.01, 4

and 10 mg L^{-1} and current density was applied intermittently (5 min ON/ 20 min OFF) at 0.3, 0.5, 1.15 and 1.8 mA cm^{-2} according to a previous study [14,20]. Meanwhile, intermittent and continuous application of electric field using current density equal to 0.3 mA cm^{-2} were also conducted in order to know their significance in their removal efficiencies. Lastly, electrolysis time was set at 3, 6 and 19 h using intermittent mode of electricity application. The different combinations of parameters for each run are summarized in **Table 2**.

Table 2. Batch experimental runs.

Batch run	Initial concentration [mg L^{-1}]			Current density [mA cm^{-2}]	Electrolysis time [h]	Mode of application
	DCF	CBZ	AMX			
1	0.01	0.01	0.01	0.3	3	Continuous
2	0.01	0.01	0.01	0.3	3	Intermittent
3	0.01	0.01	0.01	0.3	6	Intermittent
4	0.01	0.01	0.01	0.3	19	Intermittent
5	0.01	0.01	0.01	0.5	3	Intermittent
6	0.01	0.01	0.01	0.5	6	Intermittent
7	0.01	0.01	0.01	0.5	19	Intermittent
8	0.01	0.01	0.01	1.15	3	Intermittent
9	0.01	0.01	0.01	1.15	6	Intermittent
10	0.01	0.01	0.01	1.15	19	Intermittent
11	0.01	0.01	0.01	1.8	3	Intermittent
12	0.01	0.01	0.01	1.8	6	Intermittent
13	0.01	0.01	0.01	1.8	19	Intermittent
14	4	4	4	0.3	3	Intermittent
15	4	4	4	0.3	6	Intermittent
16	4	4	4	0.3	19	Intermittent
17	4	4	4	0.5	3	Intermittent

18	4	4	4	0.5	6	Intermittent
19	4	4	4	0.5	19	Intermittent
20	4	4	4	1.15	3	Intermittent
21	4	4	4	1.15	6	Intermittent
22	4	4	4	1.15	19	Intermittent
23	4	4	4	1.8	3	Intermittent
24	4	4	4	1.8	6	Intermittent
25	4	4	4	1.8	19	Intermittent
26	10	10	10	0.3	3	Intermittent
27	10	10	10	0.3	6	Intermittent
28	10	10	10	0.3	19	Intermittent
29	10	10	10	0.5	3	Intermittent
30	10	10	10	0.5	6	Intermittent
31	10	10	10	0.5	19	Intermittent

2.4 Analytical methods

Samples were collected before (influent) and after (effluent) each run and were filtered using 1.2 µm glass fibre filters (Whatman, Maidstone, UK). These were analyzed for chemical oxygen demand (COD), dissolved organic compounds (DOC), ultraviolet absorbance at 254 nm (UV_{254}), ammonia nitrogen (NH_4-N) and orthophosphate (PO_4-P) following standard methods [21]. 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 [22]. Dissolved oxygen concentration (DO), pH, temperature, conductivity and redox potential were measured using a multiparametric probe (Hanna Instruments, HI769828). The concentrations of pharmaceutical compounds in the influent and effluent samples were both measured using 4000Q Trap LC–MS/MS System (Applied Biosystems, Foster City, USA) in

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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^{-1}). The method detection limit (MDL) was between 0.9 and 8 ng L^{-1} in the spiked water samples. The precision of the method, calculated as relative standard deviation, ranged from 0.9 to 3.0%.

3   Results and discussions

3.1 Effect of mode of electricity application and initial pharmaceutical concentration

Fig. 2 shows the removal efficiencies of DCF, CBZ and AMX under continuous and intermittent supply of electricity at initial pharmaceutical concentration of 0.01 mg L^{-1}, current density of 0.3 mA cm^{-2} and electrolysis time of 3 h. As shown, the removal efficiencies operated with continuous supply of electricity were higher than the intermittent mode (5 min ON/20 min OFF) for all selected pharmaceuticals. This is expected because the continuous operation provided uninterrupted supply of Al^{3+} species, which are responsible for the charge neutralization and subsequent precipitation of suspended micropollutants as well as the simultaneous adsorption of dissolved organic matter and other chemical species. However, the difference in % removal between the continuous and the intermittent modes of electricity application was not very large (~15% difference) considering that the 5 min ON/20 min OFF interval consumes 96% less energy (according to the Energy Consumption Law) and produces only 20% Al^{3+} species (Faraday's law) compared to that of continuous operation [14]. This indicates that the electrocoagulation process was maximized and production of excess $Al(OH)_3$ was controlled with intermittent application of electricity since the dissolution of the aluminium anode stops during the power gap. Thus, the anode

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passivation is limited by intermittent electrical supply. For this reason, intermittent application of 5 min ON/ 20 min OFF was used in the succeeding experiments.

As shown in **Fig. 3**, a 1,000-fold increase in initial pharmaceutical concentration caused reduction in removal efficiencies by 22%, 23%, and 40% for DCF, CBZ and AMX, respectively for a 3 h (intermittent) reaction time. At constant current density and electrolysis duration, the anode generated the same amount of Al^{3+} species for all runs. Hence, the reduction in removal efficiencies for DCF, CBZ and AMX is attributed to the inadequate adsorption sites on the aluminium hydroxides at higher pharmaceutical concentrations [9]. Liu et al. [9] also explained that competition for active sites on the coagulant surface is increased by the presence of organic impurities and other chemical species in real wastewater. In addition, the low hydrophobicity of each of the selected pharmaceuticals (K_{ow} values of 0.70, 0.87 and 2.45 for DCF, AMX and CBZ, respectively) suggests that these species are more likely to be removed by charge neutralization rather than by adsorption on coagulants [23]. In this study, however, the pH of the municipal wastewater ($pH_{ave} = 7.4$) was not adjusted. Since the acid dissociation constant (pKa) of DCF is 4.2 [24], DCF is anionic at neutral pH. Therefore, the removal of DCF by electrocoagulation is attributed to the electrostatic attraction between DCF and the positive aluminium complexes. Meanwhile, CBZ has two pKas: $pKa_1 = 2.3$ is related to the protonation of the NH_2 group; and $pKa_2 = 13.9$ is related to the deprotonation of the amino group [25]. At neutral pH, CBZ is in its molecular state and shows hydrophobic property [26]. Hence, among the three pharmaceuticals, CBZ has the highest tendency to be adsorbed on the aluminium species. 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

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groups, respectively [27]. At pH~7, the carboxyl groups are transformed into COO- while amine and phenol groups remain neutral [28]. This further suggests that AMX can also be removed by charge neutralization.

3.2 Effect of current density and electrolysis duration

In **Fig. 4**., the highest pharmaceutical removal was achieved when the current density was set to 1.8 mA cm^{-2} while the lowest was obtained at current density = 0.3 mA cm^{-2}. Higher current density enables faster release rate of aluminium ions compared to lower current density. In addition, more but smaller bubbles are released at high current density and this can favour flotation [9]. As shown in **Fig. 4**, removal efficiencies are directly proportional to the electrolysis duration regardless of the current density applied. Prolonging the electrolysis time denotes increased generation of complex aluminium ions and hydrogen bubbles via the electro-dissolution of the anode and reduction of the cathode, respectively. These promote both electrocoagulation and electroflotation processes leading to higher contaminant removal. However, at high current density (1.15 and 1.8 mA cm^{-2}), no significant difference in pharmaceutical removal was observed between electrolysis duration of 6 and 19 and the removal trends are similar for both these current densities. This phenomenon can be ascribed to electrode passivation wherein the surface of the anode becomes coated by an oxidized film which increases the anode's polarization resistance and reduces the release of both coagulant species and bubbles, thereby reducing pharmaceutical removal efficiencies.

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The kinetic mechanism that controls the adsorption of the selected pharmaceuticals onto aluminum hydroxides was evaluated by fitting experimental data to the linearized form of the pseudo-second order kinetic model shown in Eq. (8) [34].

$$\frac{t}{q_t} = \frac{1}{kq_e^2} + \frac{t}{q_e} \tag{8}$$

where q_e (mg g^{-1}) and q_t (mg g^{-1}) are the amounts of pharmaceutical adsorbed on the aluminum hydroxides at equilibrium and at any time t, respectively, and k (g mg^{-1} min^{-1}) is the rate constant of the pseudo-second order equation.

The plots of t/q_t vs. t (**Fig. 5**) for all pharmaceuticals at varying current densities have high coefficients of determination ($R^2 > 0.95$). This indicates that the rate-limiting step which governs the uptake of DCF, CBZ and AMX onto the metal hydroxides is chemisorption. Chemisorption involves valency forces through sharing or exchange of electrons between the adsorbate molecules and adsorbent's active sites [29]. **Table 3** lists the kinetic parameters (i.e., equilibrium adsorption capacity, rate constant k and coefficient of determination R^2) obtained from this model at varying current densities.

Table 3. Pseudo second-order kinetic model parameters at varying current densities

Pharmaceutical	Current density (mA cm^{-2})	Model parameter		
		q_e mg g^{-1}	k (g mg^{-1} min^{-1})	R^2
DCF	0.3	3333.3	2.14 E-06	0.9943
	0.5	2500.0	2.43 E-06	0.9968
	1.15	1000.0	9.07 E-06	0.9892
	1.8	625.0	3.29 E-05	0.9997
CBZ	0.3	3333.3	2.33 E-06	0.9975

	0.5	3333.3	9.22 E-07	0.9918
	1.15	1000.0	9.99 E-06	0.9986
	1.8	666.7	2.14 E-05	0.9994
AMX	0.3	3333.3	7.47 E-07	0.9999
	0.5	2000.0	1.27 E-06	0.9579
	1.15	555.6	2.67 E-05	0.9650
	1.8	500.0	5.13 E-05	0.9992

3.3 Removal of conventional pollutants

The removal efficiencies for conventional pollutants (COD, DOC, UV_{254}, NH_4-N and PO_4-P) are presented in **Fig. 6**. As shown, the removal of conventional pollutants is generally directly proportional to current density and electrolysis time. The largest removal in terms of organic matter was obtained at current density = 1.8 mA cm^{-2} and electrolysis duration = 19 h. The removal of organic pollutants namely COD, DOC and UV_{254} is largely attributed to the action of coagulants in the system. Aluminium metal complexes react with the contaminants in the wastewater forming flocs which are helpful for the fast adsorption of dissolved organic compounds [30]. During electrocoagulation, high molecular weight fraction of the organic matter is degraded into low molecular weight and more hydrophilic compounds [31]. Also, the functional groups of humic acids become attracted to the positive Al species which facilitate their removal [32]. The decrease of NH_4-N concentration after the electrochemical treatment is due to the oxidation of ammonia molecules at the anode to nitrate [33]. The better performance was observed at current density of 1.8 mA/cm^2 and 6 h electrolysis time. 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) (Eq. (5)) and $Al_6(OH_{15})PO_4$(s) (Eq. (6)) [34].

$$Al^{3+} + PO_4{}^{3-} \rightarrow AlPO_{4(s)} \tag{5}$$

$$Al_6(OH)_{15}{}^{3+} + PO_4{}^{3-} \rightarrow [Al_6(OH)_{15}]PO_{4(s)} \tag{6}$$
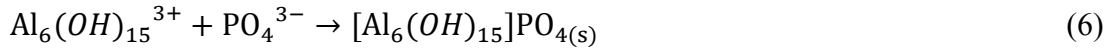
3.4 Operating cost analysis

The three major components used in the calculation of the operating cost of an electrochemical system are the costs of energy, sacrificial electrodes and chemicals [35-39]. In this study, no adjustments were done in the pH and the conductivity of the system. Hence, no chemicals were used and the cost for chemicals was excluded in the calculation for operating cost as shown in Eq. (7). Moreover, other direct and indirect cost items such as sludge transportation and disposal costs as well as the labor and maintenance costs were regarded as constants and were also excluded [35]:

$$\text{Operating cost} = aC_{energy} + bC_{electrode} \tag{7}$$

where C_{energy} pertains to the electrical consumption in kWh per m^3 of wastewater treated while $C_{electrode}$ to the electrode consumption in kg aluminum per m^3 wastewater treated. The coefficients a and b pertain to the unit prices of electrical energy (0.176 € kWh^{-1}) and the electrode material (Al) (1.85 € kg^{-1}), respectively, obtained from Italian Market (2016). C_{energy} and $C_{electrode}$ can then be calculated using Eq. (8) and Eq. (9):

$$C_{energy} = \frac{VIt\theta^2}{v} \tag{8}$$

$$C_{electrode} = \frac{ItM}{zFv} \tag{9}$$

where *V* corresponds to the peak voltage (V), *I* is the current (A), *t* is the operating time (s), θ is the intermittent cycle, *v* is the volume of the wastewater (m^3), *M* is the molecular weight of

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Al, z is the number of electrons involved in the redox reaction ($z = 3$) and F is the Faraday's

constant (96,487 c mol^{-1}). Intermittent cycle or pulse duty cycle (θ) is defined as the power-

on time divided by the whole cycle time. Since the intermittent cycle used in this study is 5

min ON and 20 min OFF, it follows that the intermittent works 20% or 0.2 of the total

reaction time (cycle time = 25 min).

Table 4 summarizes the calculations for operating cost at varying current density with

electrolysis time of 19 h and intermittent supply of electricity at 5 min ON/ 20 min OFF. The

computed operating costs were 0.1, 0.2, 0.81 and 1.57 € m^{-3} when current densities of 0.3,

0.5, 1.15 and 1.8 mA cm^{-2}, respectively were applied. The operating cost increased almost

linearly ($R^2 = 0.9914$) with current density.

Table 4. Operation cost per cubic meter of wastewater treated.

Current density (mA cm^{-2})	Contact time (h)	Peak voltage (V)	Peak current (A)	C_{energy} (kWh m^3)	$C_{electrode}$ (g m^{-3})	aC_{energy} (€ m^{-3})	$C_{electrode}$ (€ m^{-3})	Operation cost (€ m^{-3})
0.3	19	11.23	0.05	0.21	31.88	0.04	0.06	0.10
0.5	19	19.65	0.08	0.60	51.00	0.11	0.09	0.20
1.15	19	46.07	0.19	3.33	121.13	0.58	0.22	0.81
1.8	19	60.59	0.3	6.91	191.26	1.21	0.35	1.57

4 Conclusions

The present study demonstrated the applicability of the electrocoagulation process for

the treatment of municipal wastewater contaminated with pharmaceuticals specifically DCF,

CBZ and AMX. The removal of DCF, CBZ and AMX by electrocoagulation is attributed to

the physicochemical characteristics of each pharmaceutical. Hydrophobic CBZ has the

greater tendency to be adsorbed on the coagulants while AMX and DCF are more likely to be removed by charge neutralization and electro-flotation. Continuous application of electric field caused higher pharmaceutical removals than intermittent application. However, for practical reasons, intermittent electrocoagulation is usually implemented as this reduces energy consumption and anode passivation. Moreover, conventional pollutants namely organic compounds, aromatic and humic substances and nutrients can be removed by adsorption onto the aluminium coagulants, precipitation and oxidation on the anode surface. The treatment efficiencies for these pollutants improved with higher current density and prolonged electrolysis duration.

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List of Figure captions

Fig. 1. Schematic of the batch electrochemical reactor

Fig. 2. DCF, CBZ and AMX removal efficiencies under continuous and intermittent supply of electricity. (Experimental conditions: Initial pharmaceutical concentration = 0.01 mg L^{-1} current density = 0.3 mA cm^{-2} and electrolysis time = 3 h)

Fig. 3. DCF, CBZ and AMX removal efficiencies at varying initial pharmaceutical concentration (Experimental conditions: current density = 0.5 mA cm^{-2}, electrolysis time = 3 h; intermittent supply of electricity)

Fig. 4. DCF, CBZ and AMX removal efficiencies at varying current density and electrolysis time (Experimental conditions: initial pharmaceutical concentration = 4 mg L^{-1}; intermittent supply of electricity)

Fig. 5. Pseudo second-order kinetic model plots for adsorption of DCF, CBZ and AMX at different current densities a) 0.3 mA/cm^2, b) 0.5 mA/cm^2, c) 1.15 mA/cm^2 and d) 1.8 mA/cm^2 (initial concentration: 4 mg L^{-1})

Fig. 6. Removal of conventional pollutants at varying current density and electrolysis time (Experimental conditions: initial pharmaceutical concentration = 0.01 mg L^{-1}; intermittent supply of electricity)

Figure 1

1 - Magnetic plate
2 - Magnetic stirrer
3 - Anode
4 - Cathode
5 - Power Supply
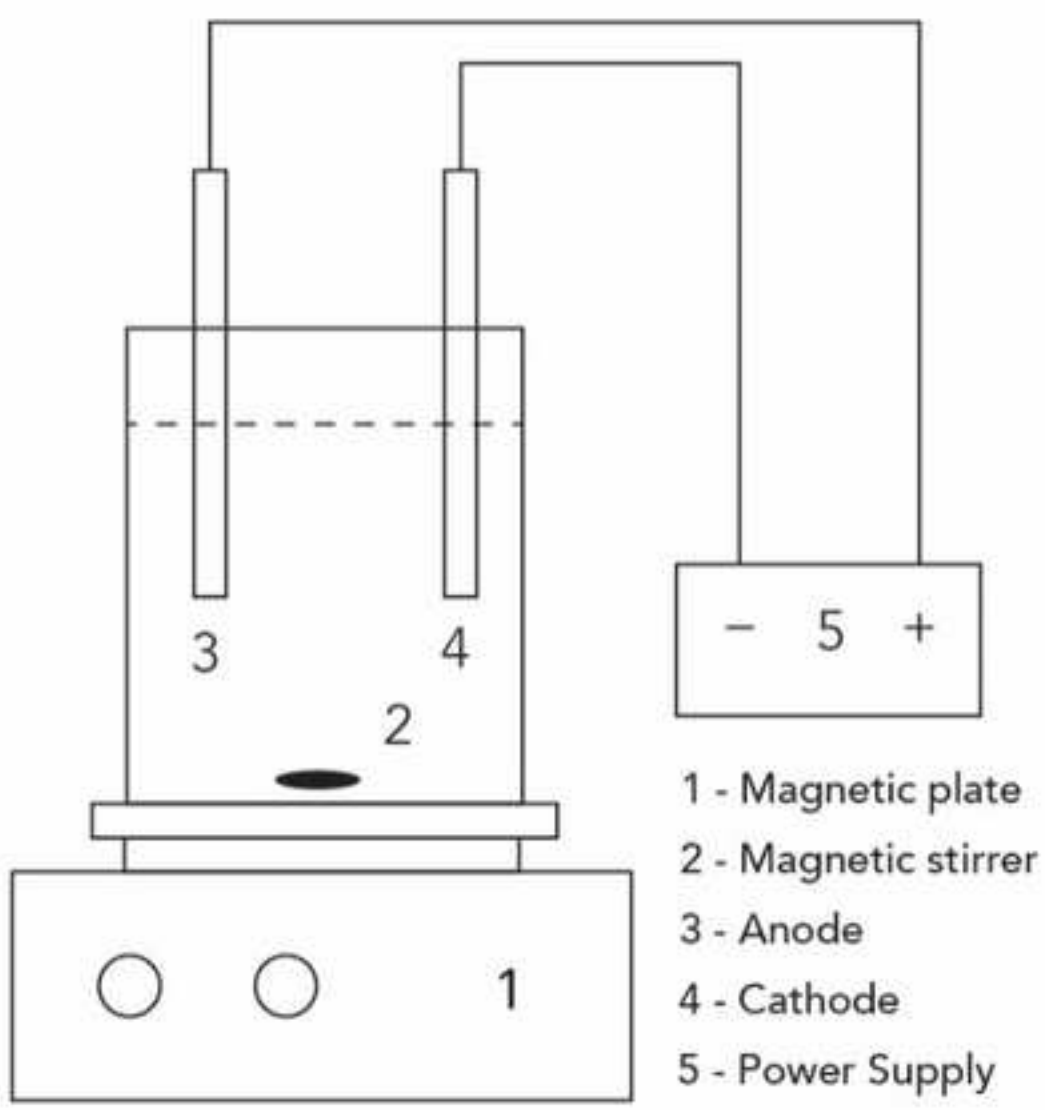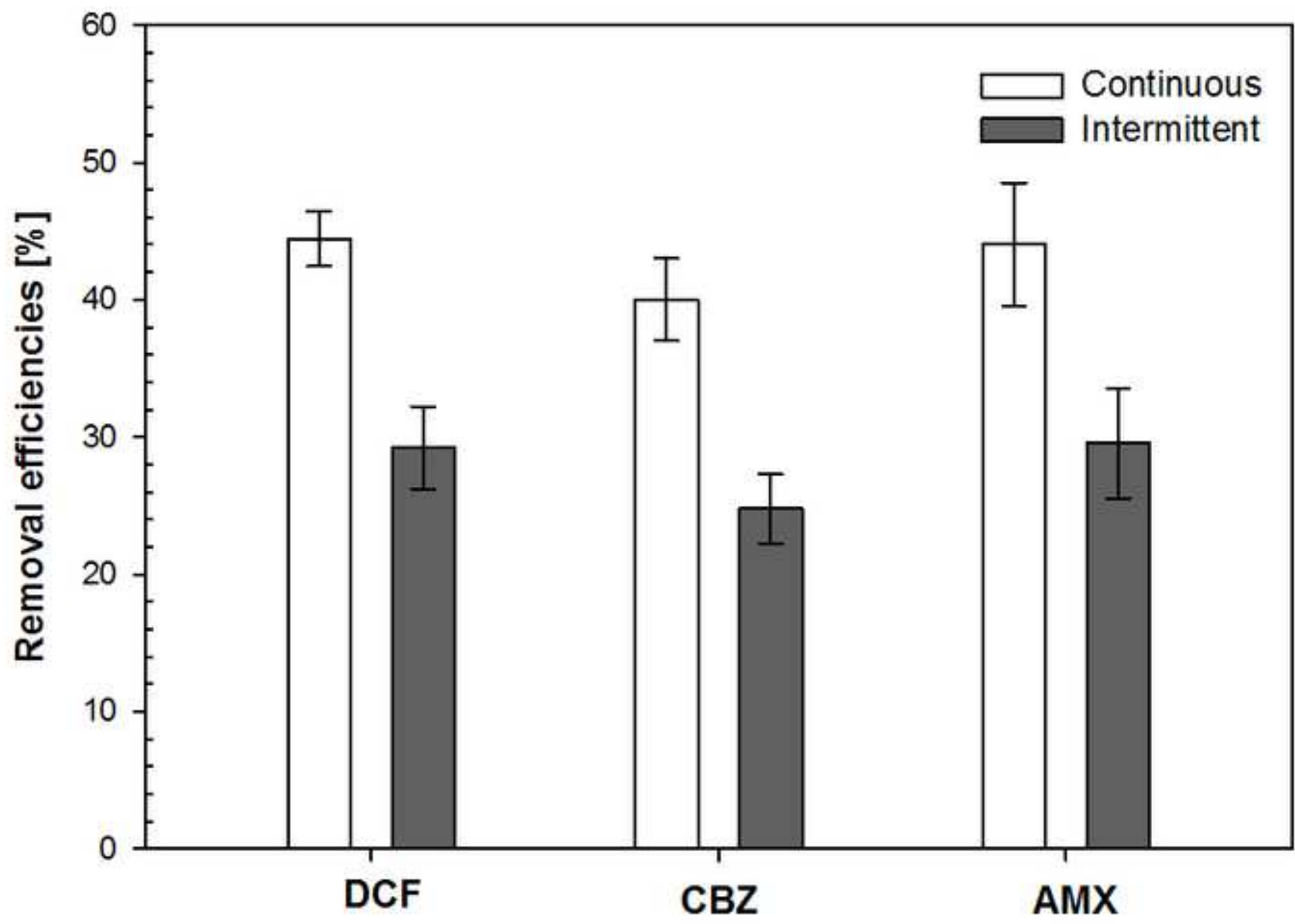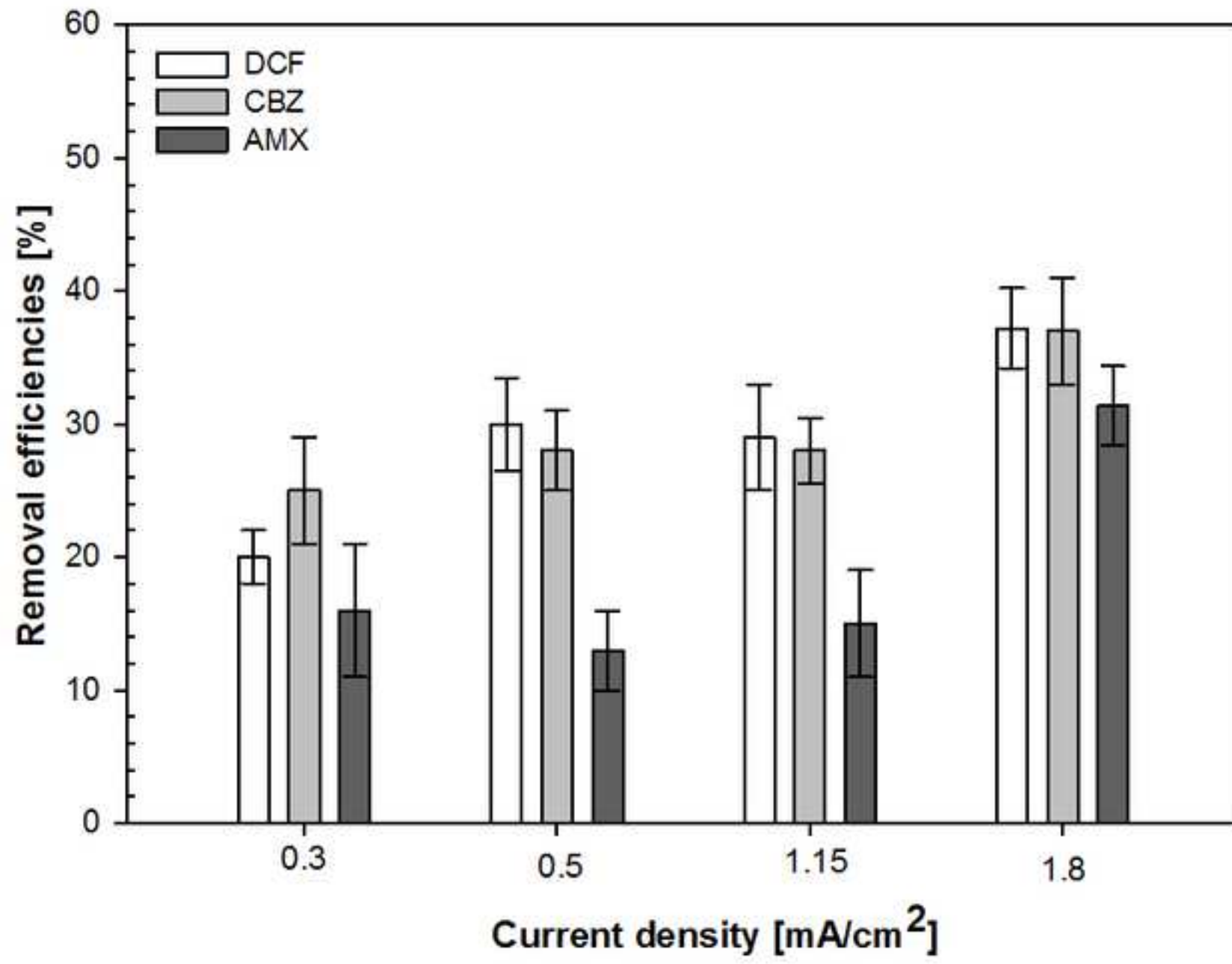
Figure 2

Figure 3

Figure 4

Figure 5

Figure 6