Evaluation of the Removal of Diclofenac Sodium from Aqueous Solution by Electrocoagulation

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Abstract- Researches regarding the treatment of effluents containing drugs are important, since conventional methods are not always enough to remove a particular component. The objective of this work was to evaluate the efficiency of the electrocoagulation process using aluminum electrodes in the treatment of water containing the anti-inflammatory diclofenac sodium, and to study the effect of variation of some parameters. In the experiments performed in different combinations of pH values, current density and sodium chloride and diclofenac sodium concentrations, the removal varied between 27.83% and 56.50%, with the best result being obtained with the experimental conditions of initial pH of 3, 1.0 g/L sodium chloride concentration, initially containing 0.05 g L of diclofenac and with current density of 12 A/m².

Keywords- Diclofenac Sodium, Electrocoagulation, Effluent Treatment

I. INTRODUCTION

Emerging pollutants are potentially toxic substances with little knowledge about the effects on the environment, which are indispensable for today's society, such as pharmaceuticals, cosmetics and pesticides. Nevertheless, these substances are introduced and distributed on a large scale to the environment and, in general, have significant potential to generate environmental impacts [1, 2]. Pharmaceutical compounds affect biochemical and physiological functions of living beings. Meanwhile, these substances can also induce unwanted changes in soil, water, and aquatic fauna and flora [3]. Even when present in low concentrations in the environment, emerging pollutants can have adverse effects on aquatic organisms. The extent of effects depends on exposure, susceptibility to the compound in question, and degradability [4].

An emerging contaminant, diclofenac sodium (DS) (Fig. 1) is a non-steroidal anti-inflammatory drug, prescribed for the treatment of inflammatory conditions and for pain relief. Its solubility in aqueous medium is insufficient to dissolve the entire dose in the gastrointestinal tract, with about 65% being excreted through the urine and taken by sanitary sewage into the environment. However, this drug presents great resistance to biological and chemical treatments, in addition to being bio accumulative [5]. According to Letzel, Metzner and Letzel (2008), DS is one of the most significant pharmaceutical active compounds present in the water medium [6].

A variety of methods can be used to promote the removal of drugs from the aqueous medium, such as activated carbon filtration, activated sludge system, ozonation, advanced oxidation processes, biodegradation, among others [7,8]. In relation to DS removal, recent studies have used different techniques, such as water/transcutol/ethylene glycol/capryol-90 green nanoemulsions (Shakeel et al.,2014 [9]); Adsorptive removal with Zr-based metal–organic frameworks (Hasan, Khan, Jhung, 2015 [10]); Use of aluminum pillared HDTMA/or AMBA modified sericite hybrid materials (Tiwari, Lalhriatpuia, Lee, 2015 [11]); Combined processes based on hydrodynamic cavitation and heterogeneous photocatalysis (Bagal, Gogate, 2013 [12]); Adsorption using oxidized activated carbon (Bhadra, Seo, Jhung, 2016 [13]); Ce@TiO2 nanocomposites (Thiruppathi et al., 2017 [14]); Coprecipitation at micrometric and nanometric range by supercritical antisolvent processing (Franco, Reverchon, de Marco, 2018 [15]) and photocatalytic degradation using TiO2- WO3 mixed oxide catalysts (Mugunthan, Saidutta, Jagadeeshbabu, 2018 [16]).

The present study aimed to evaluate the removal of diclofenac sodium by the electrocoagulation process using a reactor in parallel with aluminum plates. The influence of important parameters such as initial pH, current density and concentrations of diclofenac sodium and sodium chloride were studied in order to determine the treatment potential in different experimental conditions, besides finding the optimum conditions of operation.
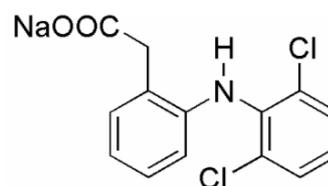

Figure 1. Molecular structure of diclofenac sodium.

II. METHODOLOGY

A. Materials

The experiment was carried out in a 15x15x11cm acrylic vat containing 1.6L of solution, placed on a stirring plate (THELGA) under medium agitation without heating. For the assembly of the monopolar reactor in parallel, 8 aluminum plates of 10x10cm were placed in the tank, 1.0cm apart, with a total surface area of contact with the effluent of 0.880m². At the end of each experiment, the electrodes were cleaned with 0.3M hydrochloric acid (HCl) solution and running water in order to avoid passivation. The aluminum electrodes were connected to a power supply model 3205S (HIKARI) and the pH was monitored using a pH meter model pH 21(HANNA) (Fig. 2).

B. Parameters evaluated

Initially, it was evaluated which initial pH of the solution provides a more efficient removal of diclofenac. The initial pH was adjusted using 0.3M sodium hydroxide (NaOH) solution or 0.3M HCl solution. The initial pH values of 3, 5, 7, 9 and 11 were evaluated, with fixed parameters: experimental time of 45 minutes, sodium chloride (NaCl) concentration of 1.0 g/L, initial DS concentration of 0.05 g / L and current density of 12 A / m².

Then, by adjusting the pH that provided greater removal of DS, the effect of varying the current density and initial NaCl concentration for different initial concentrations of DS was evaluated over time. Table I shows the parameters evaluated in each experiment. Each test was performed for 75 minutes, with samples being collected every 10 minutes (starting at 15 minutes) for analysis of the remaining diclofenac sodium concentration.

C. Analysis of diclofenac sodium concentration

The concentration of DS was monitored by measuring the absorbance of the solution in the Biochrom Libra S50 spectrophotometer, at the wavelength of 275 nm. Initially, an analytical curve was constructed using standard solutions. Subsequently, the absorbance values measured throughout the experimental tests were converted to g/L concentration of diclofenac sodium from the constructed analytical curve. The data obtained from the electrocoagulation experiments were processed using Excel® software.
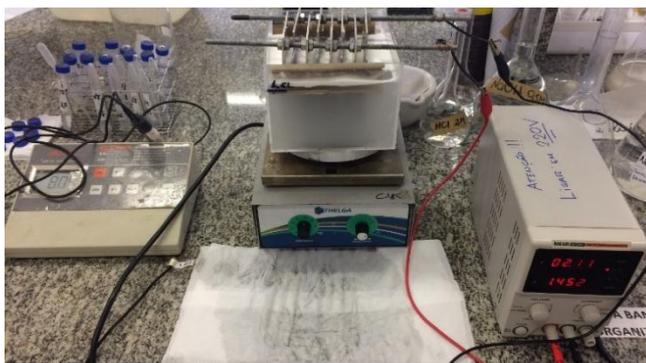

Figure 2.   System assembled to carry out the electrocoagulation process.

TABLE I.   EXPERIMENTAL CONDITIONS OF EACH EXPERIMENT IN ORDER TO EVALUATE THE EFFECT OF VARYING THE INITIAL CONCENTRATION OF SODIUM DICLOFENAC, THE NaCl CONCENTRATION AND THE CURRENT DENSITY WHILE KEEPING CONSTANT THE OPTIMAL pH.

Experiment	Diclofenac sodium initial concentration (g/L)	NaCl concentration (g/L)	Current density (A/m²)
1		2,0	12
2	0,03	1,0	12
3		1,0	36
4		1,0	70
5	0,04	1,0	12
6		2,0	12
7	0,05	1,0	12
8		1,0	36
9		1,0	70
10	0,06	1,0	12
11	0,07	2,0	12
12		1,0	12
13	0,07	1,0	36
14		1,0	70

III. RESULTS AND DISCUSSION

A. Analytical curve

An analytical curve using standards at different concentrations was constructed for conversion of the absorbance values of the experiments to g/L concentration of diclofenac sodium (Fig. 3). Equations 1 and 2 represent, respectively, the equation of the calibration curve and the determination coefficient (R²).

$$y = 3,0677x + 0,0253 \tag{1}$$
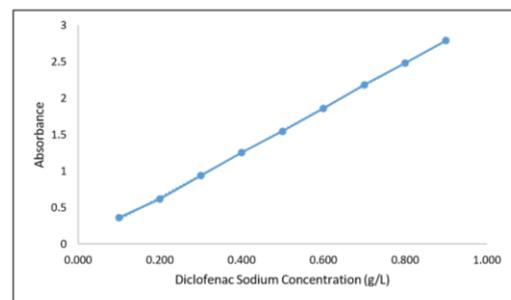
$$R^2 = 0,9997 \tag{2}$$

Figure 3.   Analytical curve of concentration (in grams per liter) vs absorbance for diclofenac sodium aqueous solutions.

B. Initial pH

Five experiments were carried out with different initial pH values, remaining the other conditions fixed. It was observed that the pH of the medium gradually increased over time of the electrocoagulation, due to the formation of hydrogen at the cathode, and that from approximately 25 to 35 minutes the pH stabilized at 8 (Fig. 4).

It can be seen that with the initial pH of the solution equal to 3, the DS removal is higher than with the other pH values evaluated. In the pH range close to 4, the concentration of the ionic species of interest, $Al(OH)_3$, which leads to the formation of more flakes, is predominant. Hence, with the rapid increase in pH of the medium with the passage of the current, the initial pH of 3 favored for a longer time the predominance of the species of interest.

C. Initial diclofenac sodium concentration

The other experiments were carried out with the initial pH adjusted for 3. Tests with different initial concentrations of diclofenac sodium (0.03, 0.04, 0.05, 0.06 and 0.07 g / L) were performed. The fixed parameters were: NaCl concentration of 1.0 g / L, current density of 12 A / m².

Under the set conditions, when the initial concentration of diclofenac is 0.05 g/L, the remaining concentration after 75 minutes of the electrocoagulation procedure is lower, stabilizing after 35 minutes. In general, the initial DS concentration did not influence the percentage removal (Fig. 5).
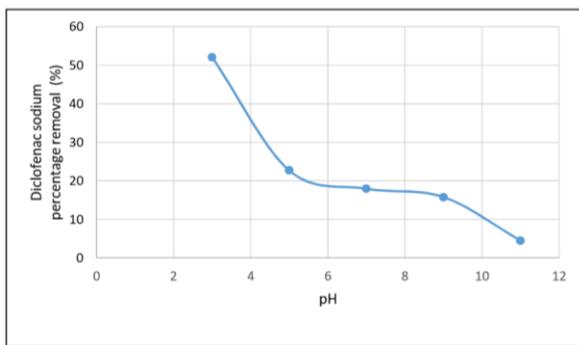

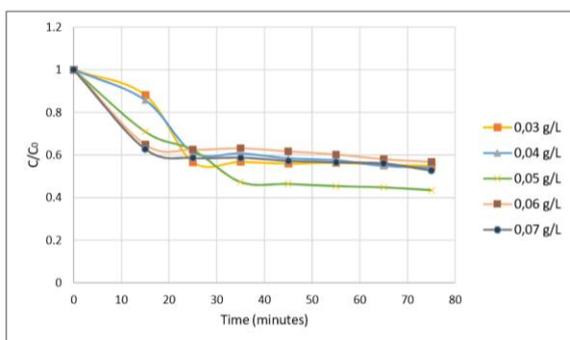Figure 4. Initial pH of the solution vs. removal of diclofenac sodium (%).

Figure 5. Final concentration by initial concentration of DS (C/C₀) vs time (minutes). Fixed parameters: NaCl concentration = 1.0 grams per liter, current density = 12 amperes per meter squared, initial pH = 3.

D. Sodium chloride concentration

The effect of the variation in NaCl concentration in solution was evaluated in three different initial concentrations of diclofenac sodium. From the data (Fig. 6), the removal does not vary significantly with NaCl variation when initial concentrations of diclofenac sodium of 0.03 g/L and 0.07 g/L are used. Therefore, in these cases the use of the lowest concentration of NaCl is justified, since the removal is similar, it is better the situation where the reagent consumption is lower. In the experiments of initial concentration of diclofenac of 0,05 g / L, the dosage of 1.0 g/L of NaCl is more advantageous, as it promotes a significantly greater removal.

E. Current density

The effect of variation of current density used during electrocoagulation was evaluated at initial concentrations of diclofenac sodium of 0.03, 0.05 and 0.07 g / L. For a higher initial concentration of diclofenac, 0.07 g/L, the higher current density, 70 A/m², promoted greater removal. When the reagent concentration is high and the current low, activation polarization may occur. Therefore, with the increase in current density, it was easier to break the activation energy barrier, promoting a higher percentage removal.

However, in experiments of initial concentrations of 0.03 g/L and 0.05 g/L diclofenac sodium, the greatest removal occurred when performing electrocoagulation at a current density of 12 A/m². When the reagent concentration is small, and the current is high, polarization occurs by mass transport, as the current flow can lead to a depletion of the reagent species on the surface of the electrode. Therefore, the lower current density favored removal at such DS concentrations (Fig. 7).

IV. CONCLUSIONS

The removal of diclofenac sodium from aqueous solution was performed by the electrocoagulation process using aluminum electrodes and evaluated under various conditions of initial pH of the medium, current density and concentrations of diclofenac sodium and sodium chloride.

The removal of diclofenac sodium by electrocoagulation was efficient, reaching in certain experimental conditions about 50% of removal. The initial pH of the solution significantly altered the removal of diclofenac sodium, and it was found that the highest removal occurred with the initial pH of 3. The experimental condition that provided the greatest removal was using 1.0 g/L sodium chloride in solution containing 0.05 g/L of the drug at a current density of 12 A/m², with an initial pH of 3.

It was evaluated that the increase in NaCl concentration in solution from 1.0 g/L to 2.0 g/L did not significantly alter the efficiency of the electrocoagulation process. Therefore, although the removal is greater, the difference does not justify a greater expense with reagent.
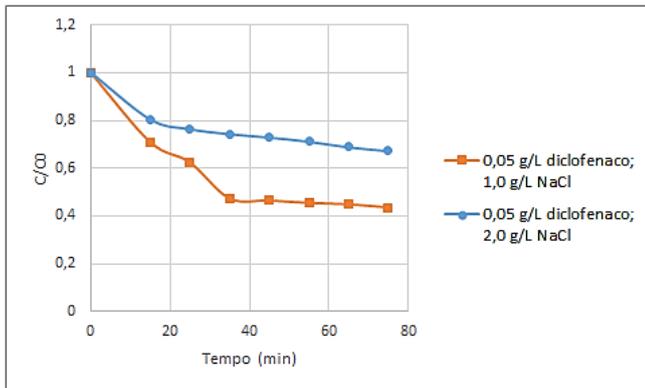
In general, removal of diclofenac sodium remained constant from 25 to 35 minutes after initiation of the procedure. Therefore, it is not justified to continue the treatment for longer, generating higher costs with energy consumption and wear of the plates.
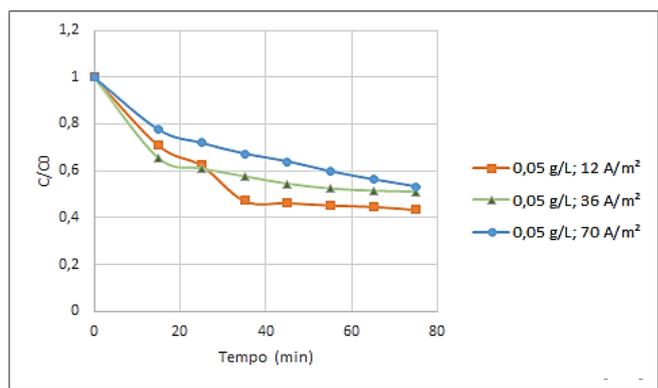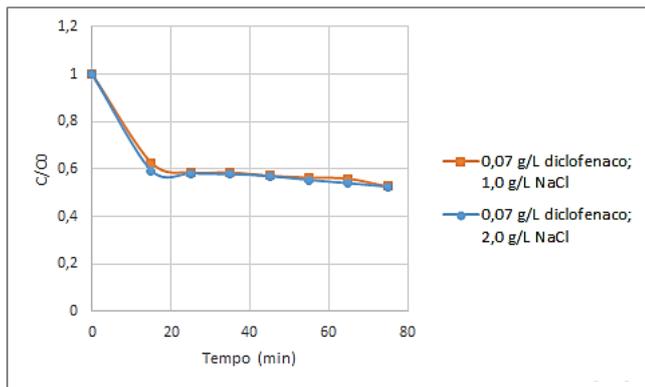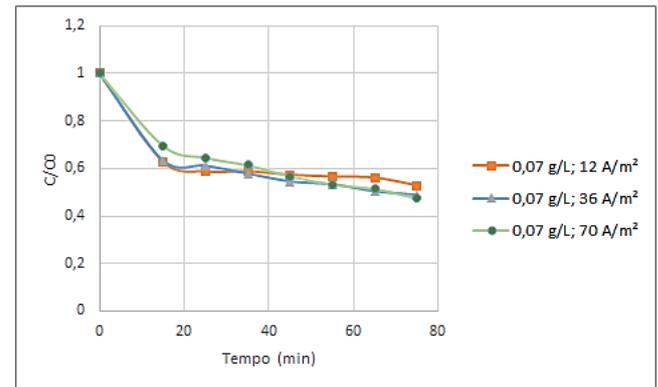
(a)

(b)
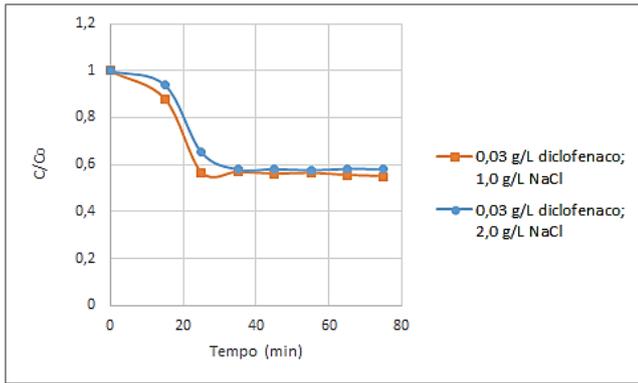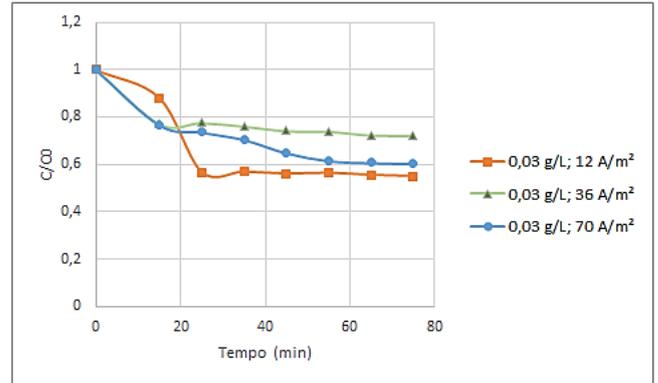
(c)

Figure 6.   Final concentration by initial diclofenac sodium concentration (C/C₀) vs time (minutes). Fixed parameters: Current density = 12 amperes per meter squared, initial pH = 3. (a) C₀ of DS = 0.03 grams per liter, NaCl concentration = 1.0 grams per liter and 2.0 grams per liter. (b) C₀ of DS = 0.05 grams per liter, NaCl concentration = 1.0 grams per liter and 2.0 grams per liter. (c) C₀ of DS = 0.07 grams per liter, NaCl concentration = 1.0 grams per liter and 2.0 grams per liter.

(a)

(b)

(c)

Figure 7.   Final concentration by initial diclofenac sodium concentration (C/C₀) vs time (minutes). Fixed parameters: NaCl concentration = 1.0 grams per liter, initial pH = 3. (a) C₀ of DS = 0.03 grams per liter, current density = 12, 36 e 70 amperes per meter squared. (b) C₀ of DS = 0.05 grams per liter, current density = 12, 36 e 70 amperes per meter squared. (c) C₀ of DS = 0.07 grams per liter, current density = 12, 36 e 70 amperes per meter squared.

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