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Articles

Treatment of diclofenac in aqueous solution by electro-oxidation using BDD electrodes

Tratamiento del diclofenaco en solución acuosa mediante electro-oxidación utilizando electrodos de DDB

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Abstract

The consumption of pharmaceutical products such as non-steroidal anti-inflammatories, including 2- [2- (2,6-dichloroanilino) phenyl] acetic acid, better known as diclofenac, has been increasing due to its easy acquisition, as a consequence the environment has had repercussions since it is excreted through the urine, causing a potential risk to be discharged into water bodies and creating persistence in the environment and in the processes of wastewater treatment. Therefore, it is necessary to use alternative processes of advanced oxidation because they have proven to be efficient in the degradation of xenobiotic compounds. The objective of this research was to apply an electro-oxidation system and photoelectro-oxidation by boron-doped diamond (BDD) electrodes using a BDD-BDD configuration to determine the operation variables for the oxidation of diclofenac in aqueous solution. The optimal conditions of the study were: current intensity of 1 A (current density (J) = 25.29 A / m^2), the pH of the sample (5-6), NaCl as supporting electrolyte, in the absence of UV light and treatment time of 360 minutes. The removal efficiency of diclofenac was 97.8 %, the TOC, COD showed efficiencies of 64.4 % and 89.3 %, respectively, whereas the biochemical oxygen demand (BOD$_5$) decrease after of treatment. The degradation kinetic of diclofenac was adjusted to a pseudo first order model, with a half-life time of 63.89 minutes and a k = 1.08 x 10^{-2} min^{-1}. The removal percentages of diclofenac using liquid chromatography (HPLC) were 99.64, 98.76 and 95.15 % for the concentrations of 150, 50 and 10 mg/l, respectively.

Keywords: electrochemical oxidation; diclofenac; UV light; BDD anode, AOP.

Resumen

El consumo de productos farmacéuticos como los anti-inflamatorios no esteroideos, entre ellos el ácido 2-[2-(2,6-dicloroanilino)fenil]acético, mejor conocido como diclofenaco, se ha incrementado debido a su fácil adquisición, como consecuencia existen repercusiones al ambiente, pues es excretado a través de la orina, ocasionando un riesgo potencial al ser descargados en cuerpos de agua y creando persistencia en el ambiente y en los procesos de tratamiento de aguas residuales. Por tal razón es necesario utilizar procesos alternativos de oxidación avanzada, debido a que han demostrado ser eficientes en la degradación de compuestos xenobióticos. El objetivo de esta investigación fue aplicar un sistema de electro-oxidación y fotoelectro-oxidación, utilizando electrodos de diamante dopados con boro (DDB) mediante una configuración DDB-DDB con la finalidad de determinar las variables de operación para la oxidación de diclofenaco en solución acuosa. Las condiciones óptimas del estudio fueron las siguientes: intensidad de corriente de 1 A (densidad de corriente (J) = 25.29 A/m^2), el valor de pH de la muestra (5-6), NaCl como electrolito soporte, en ausencia de luz UV y tiempo de tratamiento de 360 minutos. La eficiencia de remoción de diclofenaco fue 97.8 %, el carbono orgánico total (COT) y la demanda química de oxígeno (DQO) presentaron eficiencias del 64.4 y 89.3 %, respectivamente, mientras que la demanda bioquímica de oxígeno (DBO$_5$) disminuyó después del tratamiento. La cinética de degradación del diclofenaco se ajustó a un modelo de pseudo primer orden, con un tiempo de vida media de 63.89 minutos y una $k = 1.08 \times 10^{-2}$ min^{-1}. Los porcentajes de remoción de diclofenaco empleando cromatografía de líquidos (HPLC) fueron 99.64, 98.76 y 95.15 para las concentraciones de 150, 50 y 10 mg/l, respectivamente.

Palabras clave: oxidación electroquímica, diclofenaco, luz UV, ánodo de DDB, POA.

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Introduction

The use of non-steroidal anti-inflammatory drugs such as 2-[2-(2,6-dichloroanilino)phenyl]acetic acid, commonly known as diclofenac (DCF), has increased in recent years. In Mexico, this drug is part of the basic health sector, and is used to reduce pain, inflammation, as well as pain associated with rheumatic conditions (McGettigan & Henry, 2013. Commercial diclofenac is the salt of a weak acid with a partition coefficient of 13.4 and pKa of 4.15, it has a low solubility and weak ionization capacity; however the presence of nitrogen, oxygen, chlorine and sodium atoms promotes polarity in the molecule; favoring its solubility in water (Žilnik, Jazbinšek, Hvala, Vrečer, & Klamtc, 2007), it also presents acid-base properties since it acts as a proton acceptor or donor due to the presence of the amino group (NH) (Žilnik et al., 2007). It is an emerging compound because its presence in an aqueous environment causes damage to human health and the environment in low concentrations (Liu & Wong, 2013; Archer, Petrie, Kasprzyk-Hordernb, & Wolfaardtac, 2017), in addition to the fact that conventional treatment systems are not very efficient in removing them from the water. According to the Water Advisory Council, by 2015, 70 % of Mexico's water bodies are contaminated because they receive untreated municipal and industrial wastewater discharges. Among the contaminants detected are emerging compounds, which are not regulated and have toxic or mutagenic activity (Barceló, & López-de-Alda, 2008). The concentrations of pharmaceutical compounds in urban wastewater and even in drinking water, have been reported in µg/l and mg/l scale; their toxicity in aquatic organisms has been evaluated in several studies, which show cytotoxic effects in liver and kidney cells even at low concentrations (Bolong, Ismail, Salim, & Matsuura, 2009; Daughton & Brooks, 2011); promoting the implementation of new technologies for their degradation and elimination, because by their incomplete mineralization can lead to the formation of toxic chemicals (Rodríguez, Márquez, León, & Alvarez, 2013). Different technologies have been applied for the removal and/or degradation of diclofenac: biological treatments (Fatehifar, Borghei, & Ekhlasi-Nia, 2018; Jewell, Falås, Wick, Joss, & Ternes, 2016); physicochemical (Lonappan, Rouissi, Yuxue, Kaur-Brar, & Surampalli, 2019); and tertiary treatments such as catalytic hydrodechlorination (Nieto-Sandoval, Munoz, De-Pedro, & Casas, 2018) and electron irradiation (Tominaga, Dos-Santos-Batista, Silva-Costa-Teixeira, & Borrely, 2018); the disadvantage of these technologies is that they form subproducts, and in the case of biological processes it is necessary to adapt the microorganisms and increase the retention time (Vieno & Sillanpää, 2014). Within the physicochemical processes chemical precipitation, membrane filtration, adsorption, disinfection have been applied, however the removal percentages are low and the disadvantage is that the contaminant only changes phase (Bolong *et al*., 2009; De-Franco, De-Carvalho, Bonetto, De-Pelegrini-Soares, &

Féris, 2018). The best treatments for the removal of persistent compounds are the Advanced Oxidation Processes (AOP), this processes can produce changes in the chemical structure of the contaminants, by the generation and use of species with a high oxidizing power such as the hydroxyl radical (•OH) (Pourzamani, Hajizadeh & Mengelizadeh, 2018). The most commonly AOPs for diclofenac degradation are heterogeneous photocatalysis (Casillas *et al*., 2017; Lu *et al*., 2017; Martínez, Canle, Fernández, Santaballa, & Faria, 2011), photo-Fenton and Fenton variants (Pérez-Estrada *et al*., 2005; Araujo *et al.*, 2011; Bae, Kim, & Lee, 2013; Venegas-Orozco, 2013; Lu *et al*., 2017). Among the POAs is electrochemical oxidation or electro-oxidation (EO), used for the treatment of wastewater with persistent organic pollutants (Cao, Wang, & Zhao, 2017; Tominaga *et al*., 2018). EO could remove contaminants to full mineralization, in this process, the oxidation capacity of the anode used depends on its nature along with operational variables such as pH, contaminant concentration, temperature and agitation. The electro-oxidation process is carried out in an electrochemical cell with a working electrode (anode) and a counter electrode that completes the circuit (cathode), which are immersed in a solution (electrolyte) that can allow the transfer of electrons, if this does not occur, ions known as "support electrolyte" are added (Barrera, 2014). Boron-doped diamond electrodes (BDD) have a high anodic stability, wide potential window, high conductivity; they are inert and are non-active electrodes since they have weak adsorption properties, promoting the oxidation of organic compounds by radical route, from the formation of hydroxyl radicals (García-Montoya *et al*., 2015).

On the other hand, in photo-electro-oxidation (PEO), the presence of UV radiation causes a synergistic effect that promotes a high rate of oxidation due to a higher generation of •OH radicals compared to individual processes to obtaining better efficiencies. For this reason, in the present research work, an electro-oxidation and photo-electro-oxidation process was proposed for the treatment of diclofenac aqueous solutions (C_0 = 150, 50 and 10 mg/l) using a BDD-BDD configuration. The process was carried out during 6 hours at room temperature, pH (5-6), studying the effect of the current intensity 0.5 A ($J = 12.64\ A/m^2$) and 1.0 A ($J = 25.29\ A/m^2$), the support electrolyte (NaCl and Na_2SO_4) and the presence or absence of UV radiation (λ = 254 nm). This system allowed increasing the electrochemical reduction of oxygen for the generation of hydrogen peroxide.

Methodology

Preparation of aqueous solutions

Aqueous solutions were prepared using the diclofenac salt (DCF) (Sigma Aldrich México, CAS: 15307-79-6) in deionized water. The initial concentrations of the solutions were: 150, 50 and 10 mg/l.

Characterization methods

UV-Vis Spectroscopy

The aqueous DFC solution was scanned at 150 mg/l in a UV-Vis Cary Varian spectrophotometer from 400 to 200 nm to determine the maximum absorbance (λ_{max}). The λ_{max} was observed at 276 nm, which is similar to that reported by Casillas-García, Tzompantzi-Morales, Carbajal-Arizaga, López-Ganoa and Barrera-Rodríguez (2017) (275 nm). A calibration curve was made to analyze the behavior of DCF during treatments.

Infrared Spectroscopy

The aqueous solutions were characterized by infrared spectroscopy using the Shimadzu Fourier Affinity15 equipment, with a wavelength range of 4000–400 cm^{-1} and with 45 scans using an ATR cell, to identify the characteristic functional groups.

Fluorescence

All fluorescence spectra were performed in a spectrofluorometer (Model LS-55, Perkin Elmer, USA) equipped with a 150 watts xenon lamp as the excitation source. The spectrofluorometer was controlled with WINLAB software (Perkin Elmer, USA, 2000) operated from a desktop computer. The 3D excitation/emission matrices (EEM-3D) were constructed by collecting 45 emission spectra with emission lengths (λ_{em}) between 250 and 600 nm, while the excitation length (λ_{exc}) varied between 200 and 420 nm every 5 nm. To avoid Rayleigh and Raman disturbance of the water, a filter at 290 nm was used and a deionized water target was subtracted.

Physicochemical analysis

The samples were characterized by evaluating the following parameters: Chemical Oxygen Demand (COD), Biochemical Oxygen Demand (BOD_5) and Total Organic Carbon (TOC). COD and BOD_5 were performed according to the Mexican Standards NMX-AA-030/1-SCFI-2012 and NMX-AA-028-SCFI-2001, respectively. TOC was determined using the Total Organic Carbon analyzer O. I. Analytical 1020A equipment.

Liquid chromatography (HPLC)

The process samples with the best oxidation conditions were analyzed in an Agilent 1260 Infinity LC with a diode detector (DAD), using a C_{18} Zorbax SB column (5 µm, 150 mm × 4.6 mm). The mobile phase used was 0.2 % (v/v) acetic acid and acetonitrile, the flow was 1 ml/min, the column temperature was 30 °C and the detector was 275 nm.

Electro-oxidation treatment

An electrolytic cell (Figure 1) Condias® with BDD electrodes (3 anodes / 2 cathodes) was used. The dimensions of each BDD electrode were 3.0 x 20.5 x 0.2 cm, a contact area of 0.011m^2 (115.32 cm^2), the distance between the electrodes was 0.3 cm, and the area/volume ratio was 28.83 m^2/m^3. 0.4 l of DCF solution at 150 mg/l were treated for 6 hours at room temperature, with continuous agitation (400 rpm) and pH between 5 and 6, NaCl (2.5 g/l) and Na_2SO_4 (1.25 g/l) were used as support electrolyte. Two current intensities were analyzed: 0.5 A (J = 12.64 A/m^2) and 1.0 A (J = 25.29 A/m^2) in the presence or absence of UV light, using a short-wave lamp (λ = 254nm). Direct current was supplied with an EXTECH 382213 power supply.

Figure 1. Electrochemical cell used for the electro-oxidation process

The experiments were carried out according to an experimental design 2^3, and the results were analyzed by the Yates Algorithm and ANOVA (Supplementary Material I and II) in order to obtain the best experimental conditions. The study variables were current intensity (0.5 ($J = 12.64\ A/m^2$) and 1.0 A ($J = 25.29\ A/m^2$)) support electrolyte (NaCl and Na_2SO_4) and presence and absence or UV light.

Once the best conditions were obtained evaluating a DFC concentration, diclofenac aqueous solutions at 10 and 50 mg/l were treated at a current intensity of 1 A ($J = 25.29\ A/m^2$), in absence of UV light and using NaCl as support electrolyte.

The BDD electrodes were cleaned with a Na_2SO_4 solution (5 g/l; pH = 2), and power was supplied for 20 minutes at working current intensity, after which they were rinsed with deionized water. This cleaning process was carried out at the end of each electro-oxidation experiment.

During the electro-oxidation process, aliquots were taken at different times to analyze the concentration of COD and DCF by UV-Vis at 275 nm; and at the best operating conditions TOC, fluorescence, IR and DCF concentration by HPLC were determined.

Results

Characterization of aqueous solutions.

Infrared Spectroscopy

As part of the initial characterization of DCF, the IR spectrum of sodium DCF in solid and aqueous form was obtained (Figure 2), in which the characteristic bands for both phases could be located, among which are, N-H elongation (3385.07 y 3 259.69 cm^{-1} (solid) and 3 354.16 cm^{-1} (aqueous solution)); aromatic C-H (3 076.46 cm^{-1} and 3 069.76 cm^{-1} for the solid and aqueous solution respectively); aromatic C=C (1 597.05 and 1589.40 cm^{-1} (solid) and 1 507.16 cm^{-1} (aqueous solution)); aliphatic C-H (1 460.11 and 1448.54 cm^{-1} (solid) and 1 414.78 cm^{-1} (aqueous solution)); Ar-N elongation (1 280.73, 1 236.37 and 1 232.51 cm^{-1} (solid) and 1 239.28 cm^{-1} (aqueous solution)); C=O carboxylic group (1 286.52 cm^{-1} (solid) and 1 241.07 cm^{-1} (aqueous solution)); C-Cl (6 34.58 and 607.57 cm^{-1} (solid), 631.69 and 635.55 cm^{-1} (aqueous solution)). Likewise, the characteristic signal of the salt in the spectrum of the solid compound corresponding to COO^{-} Na^{+} with a value of 1 354.93 cm^{-1} is detected (Krajišnik *et al*., 2013; Bhadra, Seo, & Jhung, 2016).

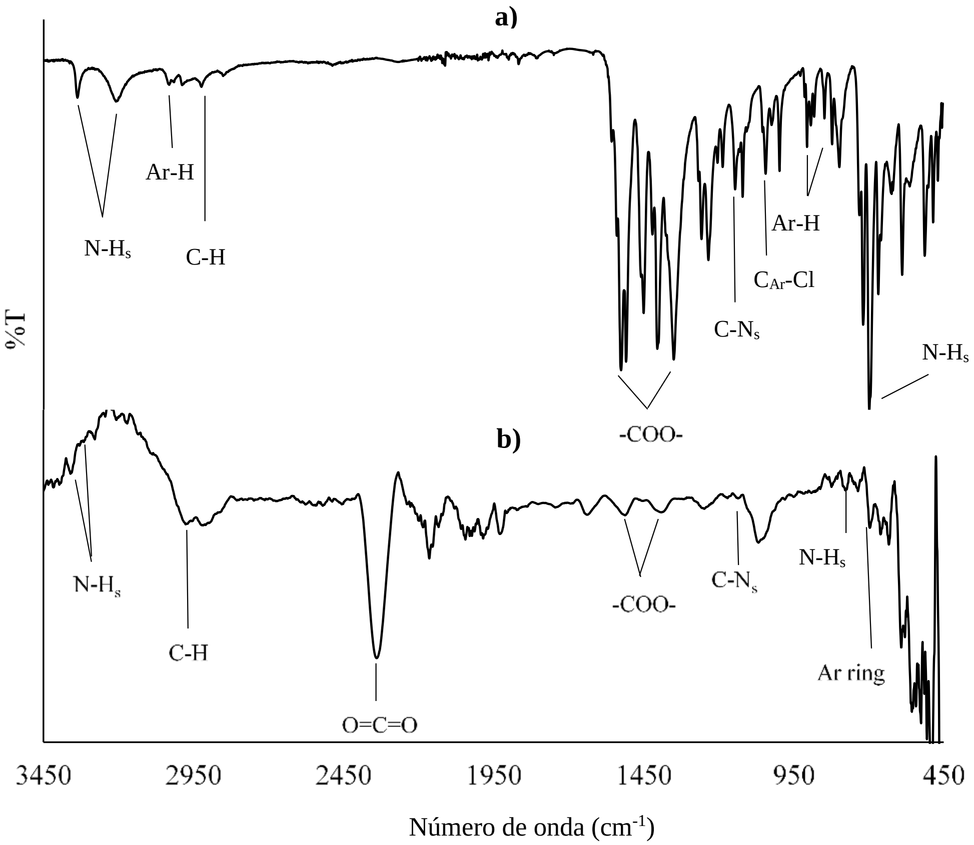


Figure 2. Infrared spectrum of sodium diclofenac (Sigma Aldrich, CAS: 15307-79-6) a) Solid; b) Aqueous solution.

In addition, the analysis of TOC, total carbon (TC), BOD_5, COD and the calculation of the biodegradability index (BDI) was carried out as shown in Table 1. According to Fajardo and Córdoba (2005), if the BDI (DBO_5/DQO) is < 0.2 the organic matter present in the water is a little biodegradable, while if the values are > 0.6 it is biodegradable. According to the above, Table 1 shows that the three analyzed concentrations have an BDI ≤0.2, as the concentration of DCF increases, the biodegradability index decreases.

Table 1. Initial characterization of Diclofenac aqueous solutions

Concentration (mg/l)	TOC (mg/l)	TC (mg/l)	COD (mg/l)	BOD$_5$ (mg/l)	BDI
10	4.87	6.02	15.25	4.34	0.21
50	26.55	31.94	60.43	2.59	0.04
150	70.70	93.50	180.36	1.96	0.01

Fluorescence

Figure 3 shows the excitation-emission matrix (EEM) of the DCF solution analysis, where two major fluorescence peaks (Peak A and B) and three minor peaks are observed. Peak A had a $\lambda_{exc}/\lambda_{em}$ of 240/362.5 nm and a fluorescence intensity (FI) of 299.64 Fluorescence Arbitrary Units (FAU). Peak B had a $\lambda_{exc}/\lambda_{em}$ of 285/364.5 nm and a FI of 355.54 UAF. The three smaller peaks were located at $\lambda_{exc}/\lambda_{em}$ of 245/420, 250/440 and 320/365 nm, respectively.

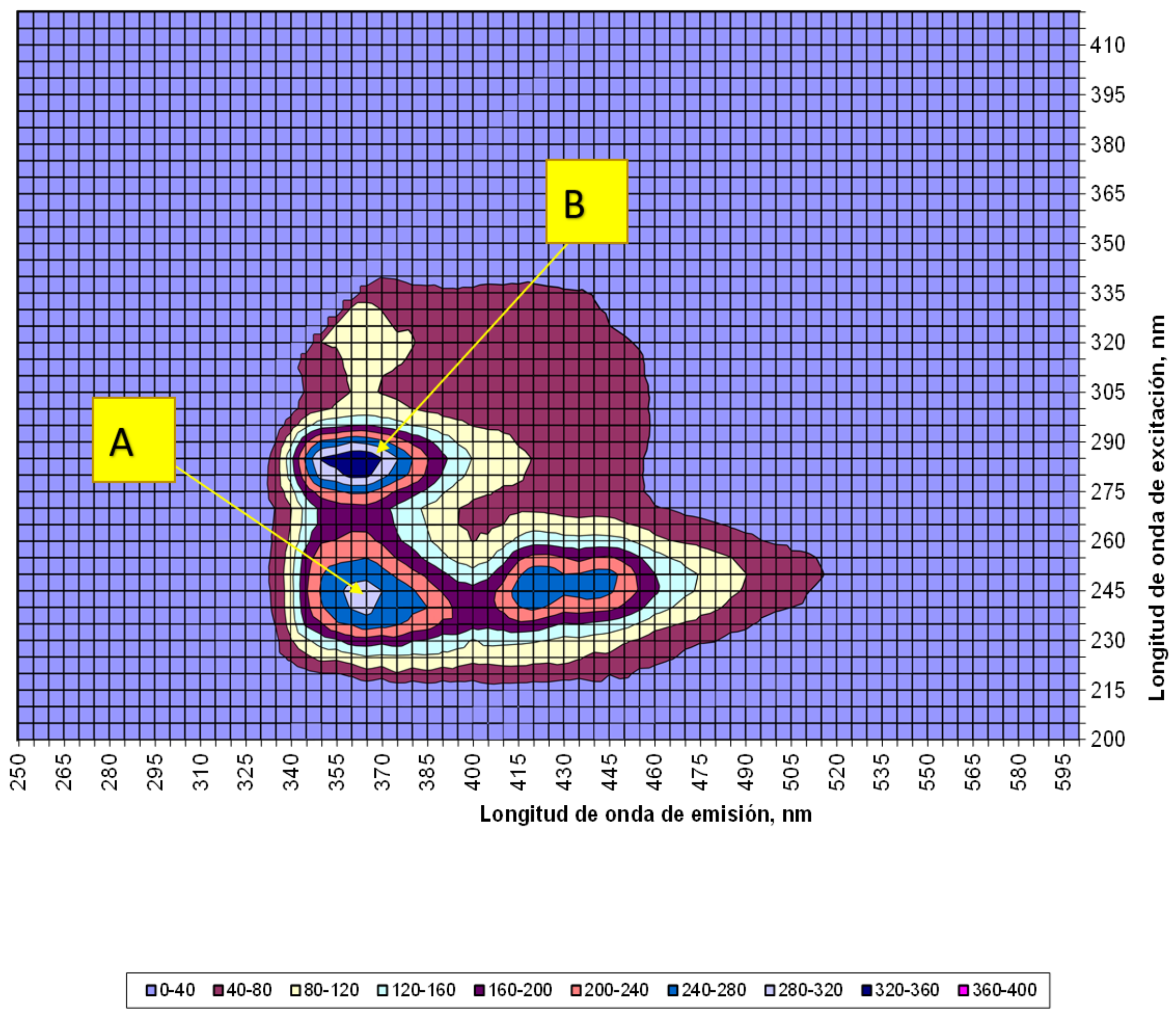


Figure 3. EEM of DCF at 150 mg/l.

Electro-oxidation (EO) process

The results of the OE process are shown in Table 2, applying different combinations of the study variables in the 8 experiments performed by triplicate at 150 mg/l of DCF and 360 min of treatment.

Table 2. Results of the diclofenac electro-oxidation process.

	A	B	C	Y	pH_0	pH_f	Time min	% of degradation	F_o	Probability
1	0.5	No	Na_2SO_4	13.2	6.36	4.18	360	90.5	5.25	0
2	1.0	No	Na_2SO_4	28.9	5.70	3.15	360	81	0.59	0.452
3	0.5	Si	Na_2SO_4	3.0	5.90	3.83	360	98	0.25	0.627
4	1.0	Si	Na_2SO_4	19.6	6.30	2.31	360	87.2	3.88	0.067
5	0.5	No	NaCl	32.8	5.29	6.71	360	77.7	1.99	0.178
6	1.0	No	NaCl	3.3	6.10	6.31	360	97.8	7.89	0.013
7	0.5	Si	NaCl	33.6	5.94	6.41	360	77.1	18.38	0.001
8	1.0	Si	NaCl	28.4	6.38	7.06	360	80.3	3.77	0.07

A = current intensity; B = UV light; C = support electrolyte; Y = DCF concentration measured by UV-Vis at 276 nm.

According to the results obtained in Table 2, it is observed that the best conditions were obtained when applying a current intensity of 0.5 A (J = 12.64 A/m^2) in presence of UV light and using Na_2SO_4 as support electrolyte, obtaining 98 % of mineralization. On the other hand, in experiment 6, where the process was carried out at 1.0 A (J = 25.29 A/m^2), NaCl and absence of UV light, a similar mineralization percentage of 97.8 % was obtained. For the analysis of the results, the effect of each one of the variables involved in the process was evaluated.

Effect of support electrolyte

The experiments were performed at an initial pH of 5.29-6.38, it was observed that by using Na_2SO_4 as a support electrolyte, the pH decreased to 2.31 (Table 2). According to Brillas, Garcia-Segura, Skoumal and Arias (2010), at pH = 2-3, it is possible that a precipitation-redissolution-degradation process of the drug occurs, because the pKa of DCF is 4.15, so when the experiments are carried out at a pH higher than pKa, the ionization of DCF is favored; at a pH lower than pKa, DCF is in its molecular form (Brillas et al., 2010). The ionized form of DCF is soluble and the electroactive species are susceptible to oxidation Pérez-Estrada *et al*., 2005; Brillas *et al*., 2010).

The decrease in pH when using Na_2SO_4 as a support electrolyte is explained by the formation of persulfate ion ($S_2O_8^{2-}$) (Equation (1)), which can be hydrolyzed to form peroxomonosulfate ion (HSO_5^-) and bisulfate ion (HSO_4^-), as shown in Equation (2) (Ross & Neta, 1982):

$$2SO_4^{2-} \rightarrow S_2O_8^{2-} + 2e^- \quad (1)$$

$$S_2O_8^{2-} + H_2O \rightarrow HSO_5^- + HSO_4^- \qquad (2)$$

HSO_5^- and HSO_4^- ions, are ampholytes that in balance with each other, form their conjugated acids (H_2SO_5 and H_2SO_4) through the dismutation reaction (equations (3) and (4)).

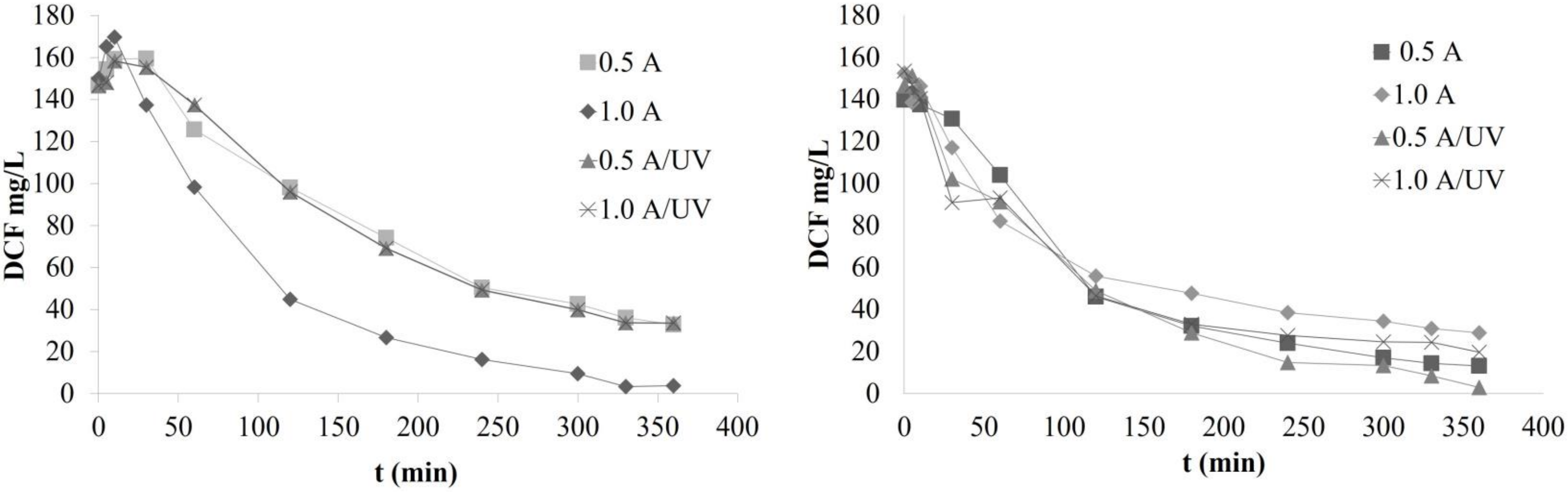
$$HSO_5^- + HSO_5^- \leftrightarrow H_2SO_5 + SO_5^{2-} \qquad (3)$$

$$HSO_4^- + HSO_4^- \leftrightarrow H_2SO_4 + SO_4^{2-} \qquad (4)$$

The peroxymonosulfuric acid (H_2SO_5) in small concentrations breaks down generating sulfuric acid and oxygen, which causes the decrease of the pH to values of 2-3 for being a strong acid, pKa = -3.0 (Equation 5):

$$H_2S\,O_5 \leftrightarrow H_2SO_4 + O_2 \qquad (5)$$

This decrease of pH can produce interference in the quantification, showing the apparent degradation of the same one, however, it is only precipitated, reason why it is necessary a good election of the support electrolyte or to have a control of the pH by an addition of a buffer. When Na_2SO_4 were used, the best removal percentage was 98 % at 0.5 A ($J = 12.64\ A/m^2$) and in presence of UV light (Figure 4), this result could be attributed to the formation of oxidants such as persulfate ($S_2O_8^{2-}$) however, the species that this radical forms when in aqueous solution propitiates an acid medium (H_2SO_4) which causes the precipitation-redissolution-degradation phenomenon of DCF mentioned before.



a) **b)**

Figure 4. Effect of support electrolyte a) NaCl and b) Na_2SO_4.

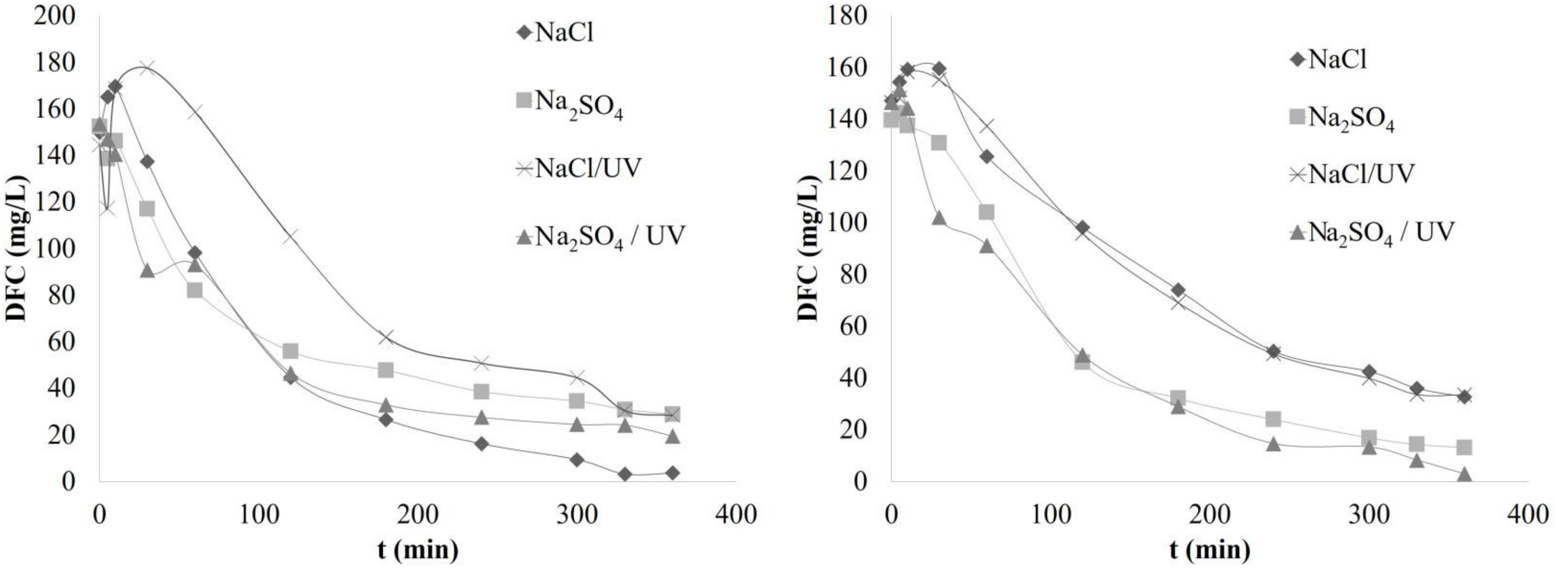
On the other hand, using NaCl maintains the pH value and generates the Cl^- ion, which is oxidized to $Cl_{2(g)}$ (Ec. 6) favoring indirect oxidation (Brillas & Sirés, 2015). The subsequent experiments were carried out according to the operating conditions established in experiment 6, to avoid interferences in its quantification:

$$2Cl^- \rightarrow Cl_{2(g)} + 2\ e^- \qquad (6)$$

According to research carried out by Brillas and Sirés (2015), active chlorine mediated oxidation becomes faster in acidic than in alkaline media due to the standard potential of Cl_2 (E° = 1.36 V/SHE). However, the major disadvantage of this procedure is that it is susceptible to generating toxic chloroderivatives, trihalomethanes and chloramines, which can increase the toxicity of the effluent. By using NaCl as a support electrolyte and a current intensity of 1.0 A ($J = 25.29$ A/m^2) a 97.8 % removal efficiency is obtained.

Effect of current intensity

The applied current intensity is one of the most important parameters in electrochemistry, because it controls the electrons transfer and the generation of oxidizing reagents, which directly influences the efficiency of contaminant removal (Gurung, Chaker-Ncibi, Shestakova, & Sillanpää, 2018). Figure 5 shows that when applying a current intensity of 1 A ($J =$ 25.29 A/m^2), NaCl and in the absence of UV light, 97.8 % of DCF removal is obtained; while at 0.5 A ($J = 12.64$ A/m^2) a 77.7 % degradation percentage is obtained, showing that the higher the current intensity, the higher the removal percentage. This is due to the fact that when increasing the applied current, there is a greater generation of H_2O_2, which induces a greater production of hydroxyl radicals (Jaafarzadeh, Ghanbari, & Moradi, 2015). On the other hand, when 0.5 A were applied, a remarkable difference was observed between the use of each of the support electrolytes: since with Na_2SO_4 better results were obtained (90.5 and 98 % in the absence and presence of UV light, respectively), this is related to the production of persulfate radicals that help DCF oxidation at lower current intensities than with NaCl. However, when the intensity is increased to 1 A ($J = 25.29$ A/m^2) the efficiency of the process decreases, reaching only 81 % for the experiments in the absence of UV light and 87.2 % in the presence of UV radiation. This phenomenon is due to the fact that when the current intensity increases, the hydrogen peroxide at the anode decomposes, which causes the appearance of parasitic reactions between the •OH radicals, generating O_2 gas or the dimerization of this radicals, which negatively affects the oxidative properties of the •OH radical (Jaafarzadeh *et al*., 2015; Yang *et al*., 2018).



a)

b)

Figure 5. Effect of current intensity. a) 1.0 A and b) 0.5 A

According to the ANOVA analysis it can be observed that the value of F_0 (0.25) for the current intensity variable is within the acceptance value (5.25) which indicates that it generates a significant effect on the electro-oxidation process.

In addition, the energy consumption of the system during electro-oxidation was calculated (Table 3). According to the Federal Electricity Commission (FEC) for Toluca city, the cost of each kWh is \$0.58, therefore the experiments conducted at 1.0 A ($J = 25.29$ A/m^2) have a cost of \$31.8 per m^3, while at 0.5 A ($J = 12.64$ A/m^2) of \$12.0 per m^3, these values were calculated at 180 min.

Table 3. Energy costs.

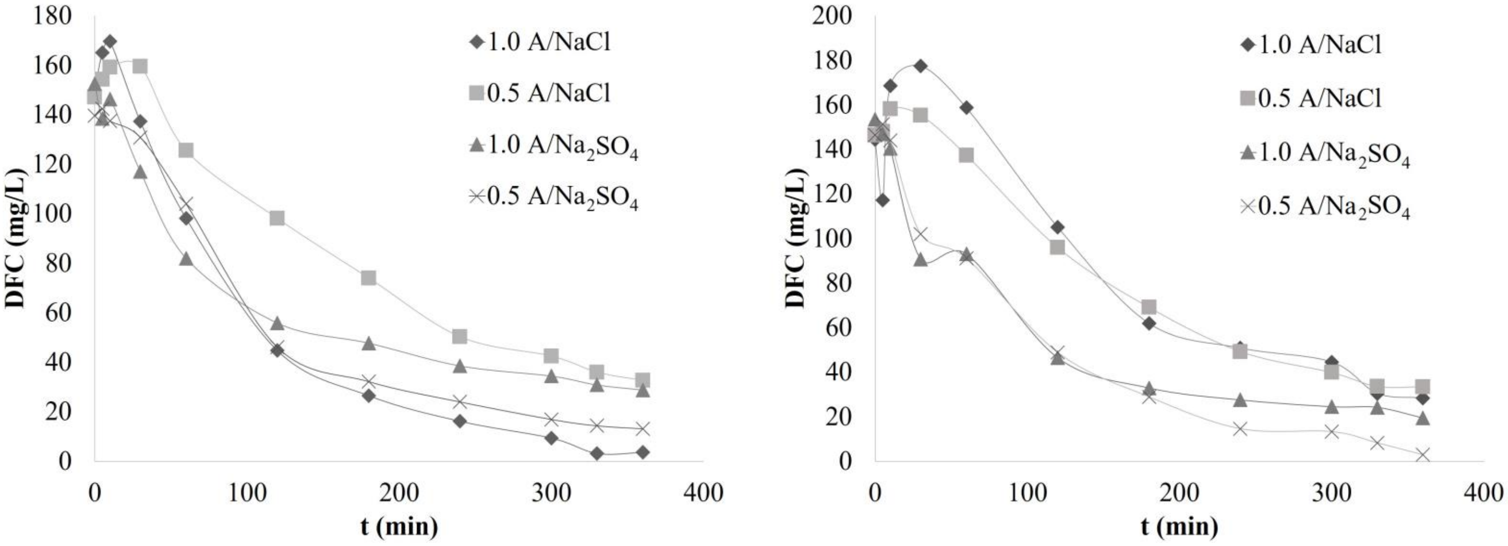
Current intensity (A)	Voltage (V)	Experiment time (min)	Power consumption (kW/m³)	Energy cost (MNX/m³)
0.5	5.5	180	20.63	12.0
1.0	7.3	180	54.75	31.8

Effect of UV light

The main function of UV irradiation is to break the chemical bonds when the absorbed photonic energy exceeds the bonding energy. When the bond is broken, a missing electron remains in each fragment resulting in the formation of radicals. In chlorinated compounds, such as diclofenac, under UV radiation they can break a relatively weak C-Cl bond (Bond dissociation energy = 330 kJ/mol) resulting in the formation of a chlorine radical (Cl•) and a disappearing electron in the carbon of the organic molecule, MO-C• (Keen, Thurman, Ferrer, Dotson, & Lindena, 201).

The percentage of degradation when using NaCl in the experiments performed at 0.5 A ($J = 12.64$ A/m^2) in the absence and presence of UV light are similar (77.7 and 77.1 %, respectively). On the other hand, in the experiments at 1 A ($J = 25.29$ A/m^2) in the presence of UV light, 80.3

% mineralization was obtained and 97.8 % in the absence of light (Figure 6). This phenomenon is attributed to the fact that in EO processes with electrolytes such as NaCl and BDD electrodes, high levels of electro-generated active chlorine are produced, a species that has oxidative properties. However, this phenomenon decreases when there is an incidence of UV light (Hurwitz, Pornwongthong, Mahendra, & Hoek, 2014; Sánchez-Montes *et al*., 2020.



a) **b)**

Figure 6. Effect of UV light on diclofenac electro-oxidation: a) Absence of UV light and b) Presence of UV light.

According to Sánchez-Montes *et al*. (2020) the process of EO in the presence of UV light —electrodes with a wide anodic electrochemical window, such as BDD and chlorinated support electrolytes— allows the formation of ClO_3^- y ClO_4^- species, where the concentration of ClO_3^- is an oxidizing species, its low redox potential (E° = 0. 35 V) in solutions with a pH of between 6 and 7 causes a decrease in the efficiency of the process (Hurwitz *et al*., 2014; Sánchez-Montes *et al*., 2020).

On the other hand, with Na_2SO_4 there is a higher percentage of degradation in the presence of UV light, because the radiation promotes the generation of the sulfate radical from the persulfate ion formed in the oxidation process (Eq. 7), which has a high redox potential (E° = 2.5-3.1 V). These sulfate radicals are usually more selective than •OH for the oxidation of organic contaminants (Lu *et al*., 2017):

$$S_2O_8^{2-} + hv \rightarrow 2SO_4^{\bullet} \qquad (7)$$

Based on the results obtained in the ANOVA, it is observed that the experiments performed had a value $p = 0.001$, which indicates that there is a statistically significant difference between them.

Effect of initial concentration

Figure 7 shows the UV-Vis scans obtained during the experiments carried out at different concentrations (150, 50 and 10 mg/l). A gradual decrease is observed in the experiment to 10 mg/l, having thus a 100 % efficiency at 330 min; while at 150 mg/l it is observed that the first hour of treatment is the most efficient obtaining more than 50 % of mineralization. According to the above, when the concentration of the drug increased, the treatment time is longer and the efficiency decreases.

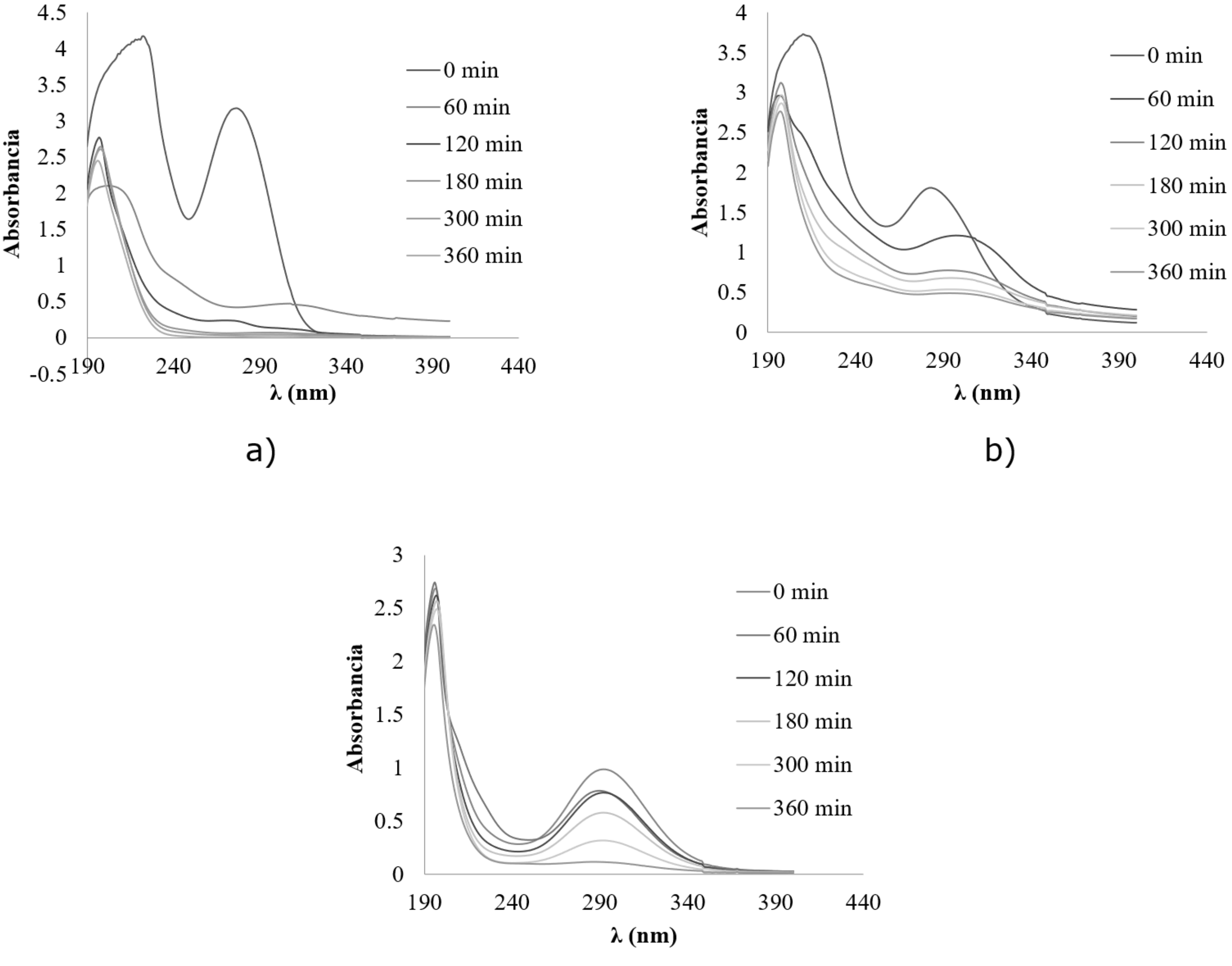


Figure 7. UV-Vis scanning of diclofenac at 1.0 A a) 150 mg/l, b) 50 mg/l and c) 10 mg/l.

According to the results, the best conditions for diclofenac oxidation were: NaCl as support electrolyte, 1.0 A (J = 25.29 A/m^2) and absence of UV light, which were used in concentrations of 10 and 50 mg/l of DCF. Table 4 shows the TOC, COD, BOD$_5$ and HPLC values obtained before and after the treatment, where it can be seen that in terms of COD and BOD$_5$ there is a 100 % efficiency, except for the concentration of 150 mg/l where in terms of COD an 89.3 % efficiency is obtained, indicating that there are still by-products susceptible to be oxidized by chemical means.

Table 4. Initial and final characterization of diclofenac.

SAMPLE (mg/l)		**UV-Vis (mg/l)**	**TOC (mg/l)**	**BOD$_5$ (mg/l)**	**COD (mg/l)**	**HPLC (mg/l)**	**% DFC UV-Vis**	**% DFC HPLC**	**% TOC**
10	Initial	10.7	4.34	4.87	15.25	10.7	99.98	99.64	63.7
	Final	0.108	0.00	1.77	0.00	0.48			
50	Initial	50.3	26.55	2.59	60.43	50.3	99.08	98.76	43.4
	Final	0.46	0.00	15.03	0.00	0.62			
150	Initial	150.7	70.70	1.96	180.36	150.7	99.99	95.15	64.4
	Final	0.010	0.00	12.15	13.13	0.54			

On the other hand, in terms of TOC, the following efficiencies were obtained: at an initial concentration of 150 mg/l, the efficiency achieved was 64.4 %, while for an initial concentration of 50 mg/l, 43.4 % was observed and for the lowest concentration of 10 mg/l, 63.7 % was obtained.

The results obtained by HPLC (Figure 8) showed a removal efficiency of 99.64, 98.76 and 95.15 % for the concentrations of 10, 50 and 150 mg/l respectively, at 330 minutes of treatment. These results indicate that the higher the concentration of DCF, the lower the percentage of removal. While in UV-Vis the removal percentages were 99.98, 99.08 and 99.99 % for the same concentrations, respectively.

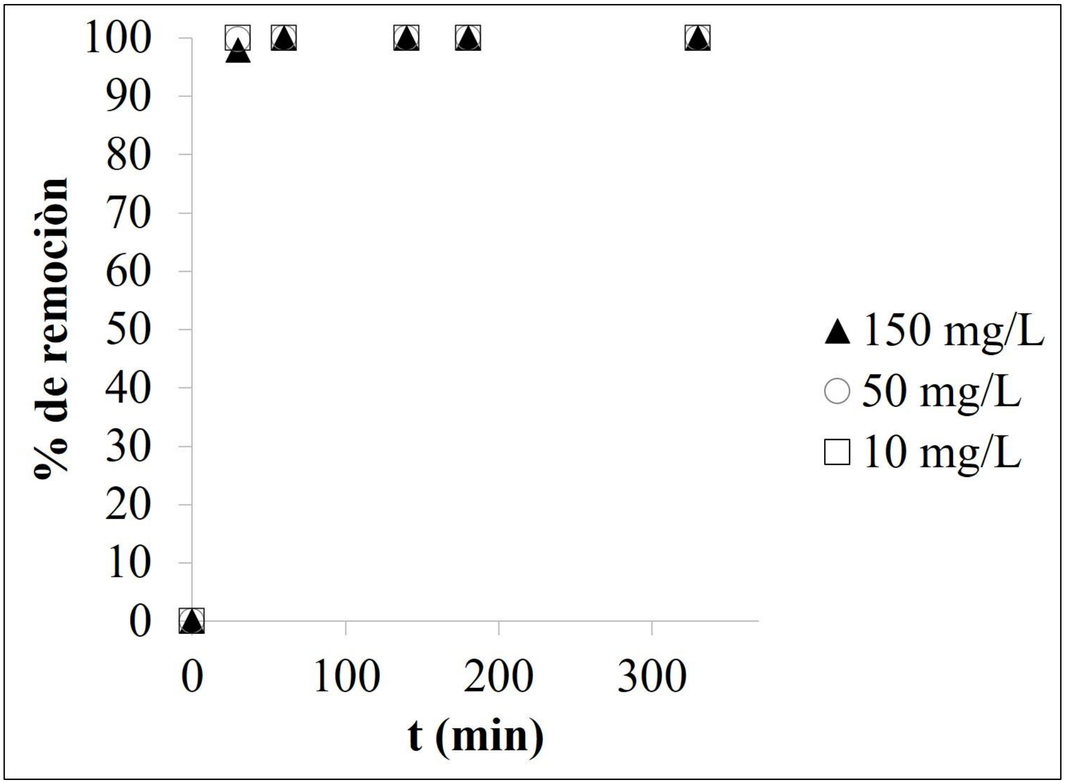


Figure 8. Electro-oxidation kinetics of diclofenac at different concentrations (analysis technique: HPLC).

After treatment the biodegradability index increased from 0.01 to 0.92 for the 150 mg/l concentration, indicating that the treatment improves the quality of the effluent.

After the electro-oxidation treatment, IR analyses were performed on the 10, 50 and 150 mg/l DCF solutions at the end of the treatment (Figure 9). The bands after 3000 cm^{-1} disappear, the signals corresponding to carboxylic acid C=O (1242.07 cm^{-1}), aliphatic C-H (2968 cm^{-1}), C-Cl (631.69 cm^{-1}) and Ar-Cl (1064.72 cm^{-1}) are not observed, which indicates the degradation of diclofenac. Can also be observed the presence of simpler metabolites with intense signals attributed to: CH_2 (3079.40 cm^{-1} elongation and 674.13 cm^{-1} deformation), C-Cl elongation (806.25, 811.08 and 794.68 cm^{-1}), and the presence of the trans isomer (1640.48 and 1652.05 cm^{-1}), which indicates the presence of an aliphatic halogenated compound.

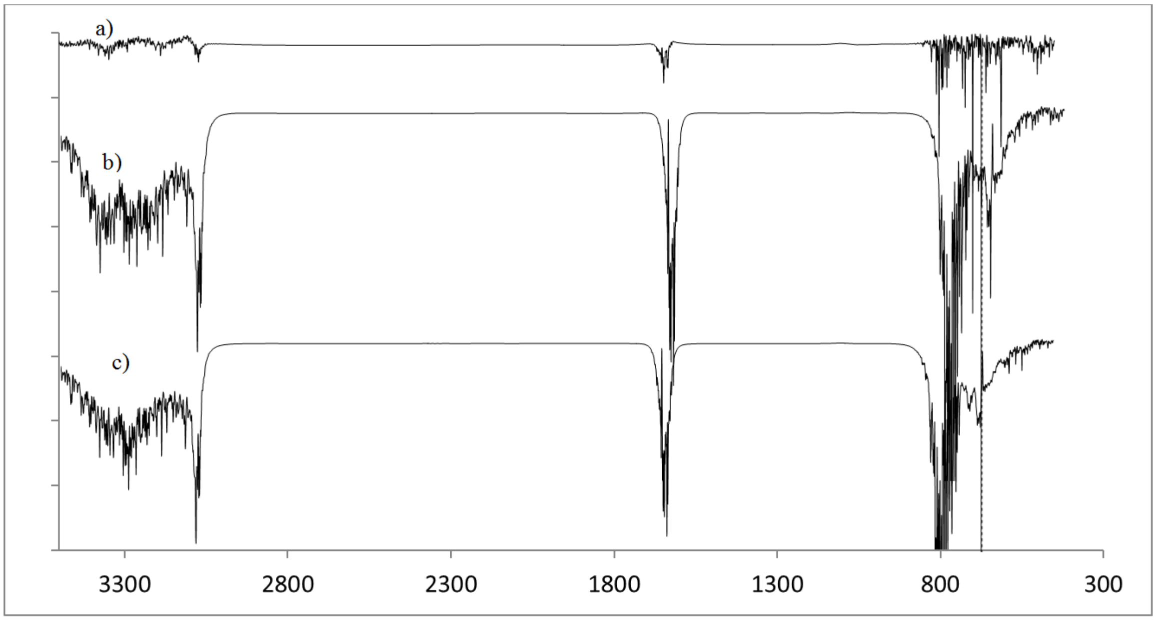


Figure 9. Infrared spectrum of diclofenac solutions after electro-oxidation treatment: a) 10 mg/l, b)50 mg/l, c)150 mg/l.

The fluorescence analysis performed after the electro-oxidation treatment shows a decrease in the wavelength values. The λ_{em} of the A and B peaks moved to longer wavelengths after the treatment (from 362.5 - 364.5 nm to 396.5 - 381.5 nm). On the other hand, the λ_{ex} moved to shorter wavelengths after treatment. The movement of peaks A and B could have been caused by the degradation of diclofenac during electro-oxidation. However, when the initial concentration was 150 mg/l, an increase in the sample IF was observed, this is due to the fact that the final sample is not completely oxidized (Figure 10).

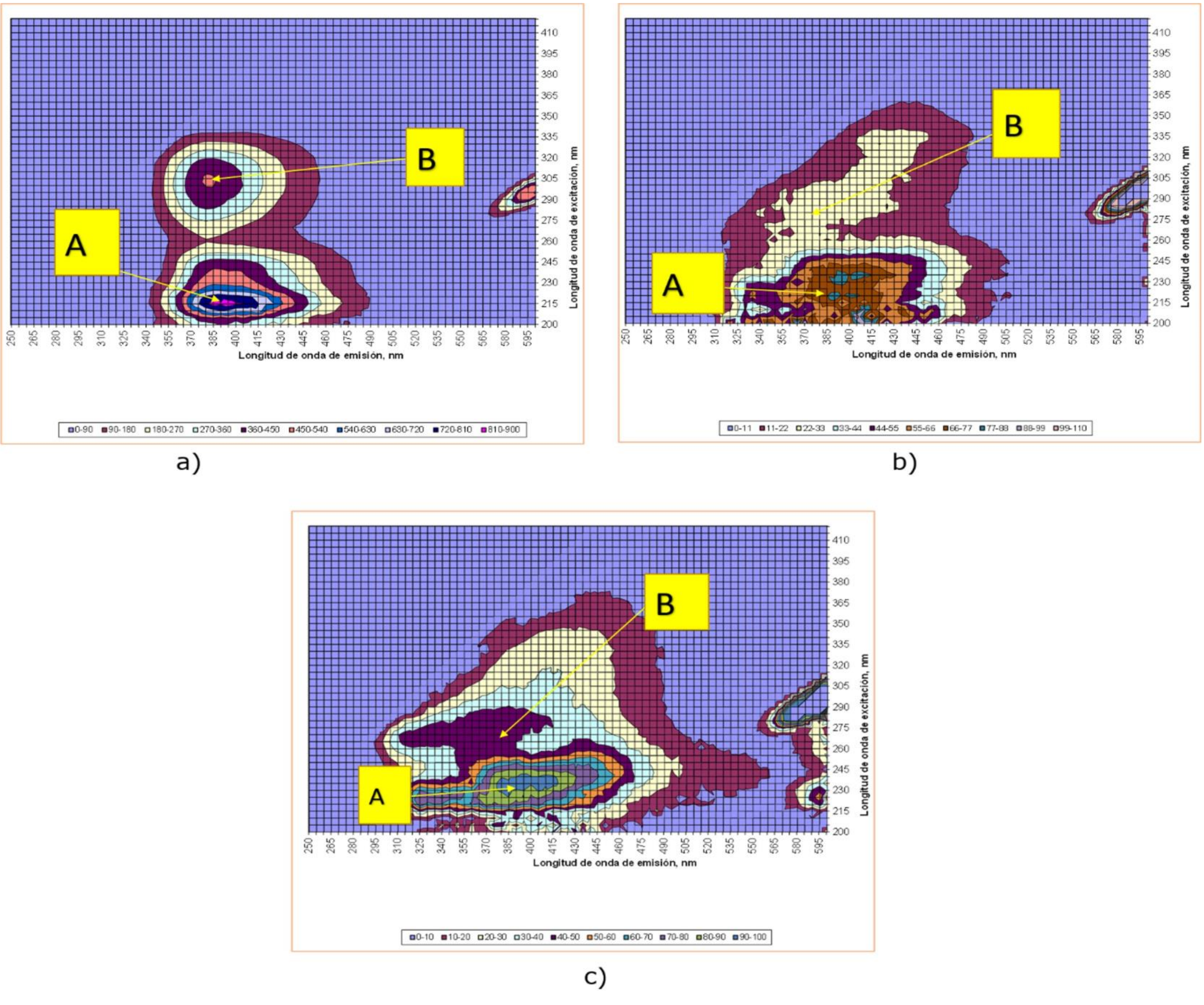


Figure 10. EEM of DFC after electro-oxidation treatment a) 10 mg/l, b) 50 mg/l and c) 150 mg/l.

Kinetics degradation of diclofenac

According to the literature, diclofenac has a first-order degradation kinetics (Brillas *et al*., 2010; Rivas, Gimeno, Borralho, & Beltrán, 2010; Lu *et al*., 2017)). The velocity constant is a constant of direct proportionality between the reaction rate and the concentration of the reagents; that is, the higher the concentration, the higher the velocity. The half-life is the time required to consume half the concentration of a compound.

The kinetic constants and half-life of diclofenac were obtained in each of the experiments, which are shown in Table 5, observing that in the experiment performed with NaCl, 1.0 A ($J = 25.29\ A/m^2$) and in the absence of UV light, the highest speed constant ($1.08 \times 10^{-2}\ min^{-1}$) and a half-life of 63.89 min was presented, which is similar to the one obtained by Brillas *et al*. (2010) of 1.02×10^{-2} and 1.32×10^{-2} at a current of 300 and 450 mA respectively. While applying a current intensity of 0.5 A ($J = 12.64\ A/m^2$) a lower speed constant ($4.5 \times 10^{-3}\ min^{-1}$) and a longer half-life of the drug (153.3 min) were obtained.

Table 5. Kinetic model of diclofenac degradation.

Sample		**Equation**	**K (min^{-1})**	**R^2**	**t$_{1/2}$ (min)**
NaCl	0.5 A	$\ln\left(\frac{C}{C_0}\right) = -0.0045t + 0.104$	4.5x10^{-3}	0.99	153.30
	1.0 A	$\ln\left(\frac{C}{C_0}\right) = -0.0108t + 0.1738$	1.08x10^{-2}	0.99	63.89
	0.5 A/UV	$\ln\left(\frac{C}{C_0}\right) = -0.0046t + 0.1034$	4.6x10^{-3}	0.99	150.00
	1.0 A/UV	$\ln\left(\frac{C}{C_0}\right) = -0.0048t + 0.1446$	4.8x10^{-3}	0.94	143.75
Na$_2$SO$_4$	0.5 A	$\ln\left(\frac{C}{C_0}\right) = -0.007t + 0.0087$	7x10^{-3}	0.98	98.57
	1.0 A	$\ln\left(\frac{C}{C_0}\right) = -0.0046t - 0.163$	4.6x10^{-3}	0.94	150.00
	0.5 A/UV	$\ln\left(\frac{C}{C_0}\right) = -0.0095t + 0.0523$	9.5x10^{-3}	0.97	72.63
	1.0 A/UV	$\ln\left(\frac{C}{C_0}\right) = -0.0056t - 0.1961$	5.6x10^{-3}	0.93	123.21

Statistical analysis

In order to know the effect that each one of the study variables has, the Yates algorithm (Supplementary Material I) and the analysis of variance were carried out. According to the results, the most significant effect is the support electrolyte since it has a very small P value. The interaction AB (Current intensity - UV light) is significant, having a level of approximately 19 %; therefore, there is a slight interaction between current intensity and UV light. While the interaction between the three effects also has a significant value of 10 % which again indicates that there is an interaction between current intensity, UV radiation and the supporting electrolyte.

Instantaneous current efficiency

Current efficiency is the ratio of the current consumed by the degradation of an organic pollutant. While the instantaneous current efficiency (ICE) is the current efficiency at the given time of electro-oxidation (Linares-Hernández *et al*., 2017). The ICEs were calculated using the following equation:

$$ICE = \frac{(C_i - C_f)}{8I\,\Delta t} FV \qquad (8)$$

Where C_i and C_f are the initial and final concentration of DCF at a Δt, both in g/l, F is Faraday´s constant (9 6487 C/mol), V is the volumen in liters, I is the apply current (1.0 A (J = 25.29 A/m^2)), Δt is the time difference in seconds.

According to Figure 11, the best instantaneous current efficiency for the 150 and 50 mg/l experiments occurs at 120 to 180 minutes of reaction, while at 10 mg/l it occurs at 10 minutes. This is because that is where the greatest presence of •OH radicals is found. On the other hand, the decrease in ICE can be explained by the depletion of free radicals near the electrode surface and the decrease in drug concentration.

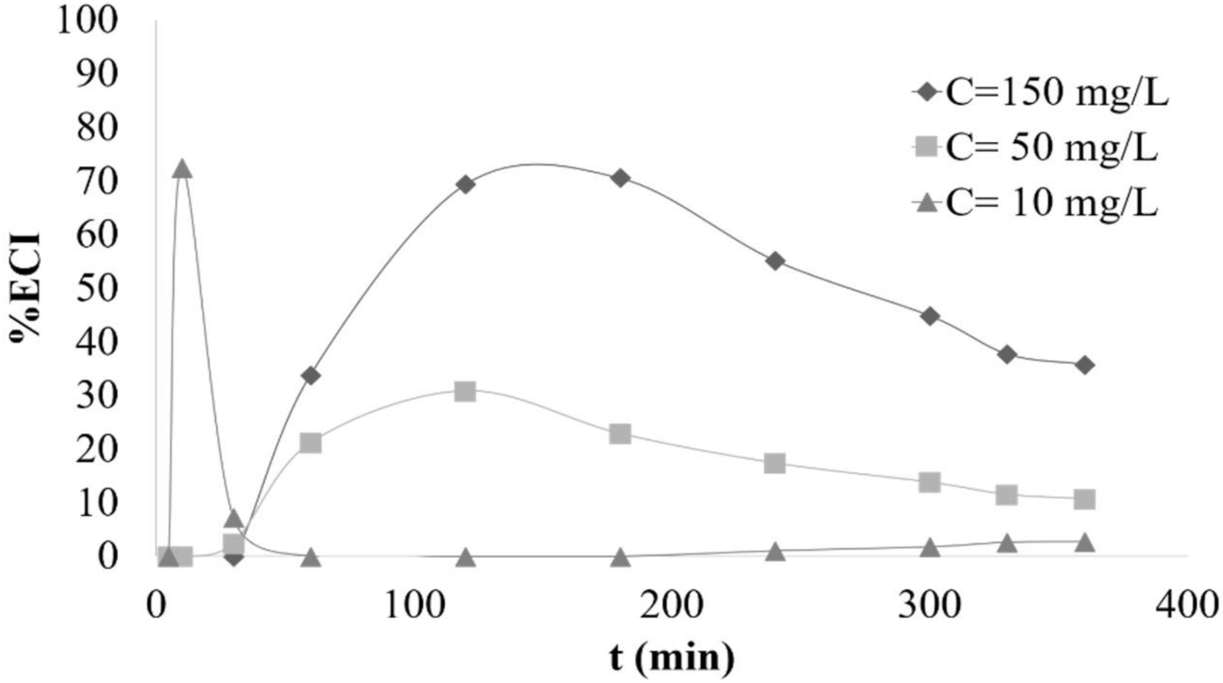


Figure 11. % of ICE during the DCF electro-oxidation reaction.

Conclusions

The electro-oxidation process with a BDD-BDD configuration, proved to be an efficient for the mineralization of diclofenac, the degradation was achieved due to the generation of hydroxyl radicals, which is one of the strongest oxidants.

The support electrolyte is the variable that has more effect within the oxidation process with a P value of 0.067, and it was determined that the process is favored by adding NaCl as support electrolyte.

The optimal conditions for a better efficiency in the mineralization of diclofenac were a current intensity of 1 A ($J = 25.29\ A/m^2$), the pH value of the sample (5-6.4), NaCl as a support electrolyte, in the absence of UV light, in a time of 360 minutes, with a removal efficiency of 97.8 %, while TOC, COD and BOD_5 showed efficiencies of 64.4, 89.3 and 100 %, respectively.

The degradation kinetics of diclofenac was of pseudo first order, with a mean life time of 63.89 minutes.

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