Experimental design methodology applied to electrochemical oxidation of carbamazepine using Ti/PbO2 and Ti/BDD electrodes

C. García-Gómez a, P. Drogui b, F. Zaviska b, B. Seyhi b, P. Gortáres-Moroyoqui a,*, G. Buelna c, C. Neira-Sáenz a, M. Estrada-alvarado a, R.G. Ulloa-Mercado a

a Instituto Tecnológico de Sonora (ITSON), Departamento de Biotecnología y Ciencias Alimentarias, 5 de Febrero 818 Sur CP. 85000 Ciudad Obregon, Sonora, Mexico
b Instituto nacional de la recherche scientifique (INRS-Eau Terre et Environnement), Université du Québec, 490 rue de la Couronne, Quebec QC G1K 9A9, Canada

Keywords: Carbamazepine; Electrooxidation; Removal; Ti/PbO2; Ti/BDD

1. Introduction

The degradation of pharmaceuticals and their residues is of particular interest due to its presence in the environment and their capacity of affecting aquatic organisms even if they exist at trace concentrations (µg L−1 or ng L−1) [1]. Carbamazepine is one of the most detected pharmaceutical active compounds (PhACs) in water bodies. Its removal has become an issue from the human health and environmental risks point of view, due to its latent recalcitrance and toxicity properties. The oxidative removal of carbamazepine in aqueous medium has been investigated by electrooxidation processes using Ti/PbO2 and Ti/BDD circular anode electrodes in the presence of Na2SO4 as electrolyte in a batch electrochemical reactor. The effect of different parameters such as current intensity (from 1 to 2 A), electrolysis time (from 60 to 120 min), recirculation flow rate (from 167 to 333 ml min−1), and anode material (PbO2 and BDD) were investigated by an experimental design methodology. A Factorial Design 23 was firstly used to determine the effect of parameters mentioned above on CBZ removal. The electrolysis time and current intensity were the main parameters affecting CBZ removal rate. Then, the optimal experimental parameters for carbamazepine removal were investigated using a Central Composite Design. The optimal conditions determined turned out to be Ti/PbO2 anode, current intensity 1.37 A, electrolysis time 101 min, and recirculation flow rate 232 ml min−1. Under these conditions the removal of 88 ± 1.2% of CBZ and 3.159 mg L−1 min−1 of p-nitrosodimethylaniline were achieved. The decay kinetics was fitted a first-order reaction.

Carbamazepine (CBZ), a widely consumed psychotropic pharmaceutical, is one of the most frequently detected pharmaceutical active compounds (PhACs) in water bodies. Its removal has become an issue from the human health and environmental risks point of view, due to its latent recalcitrance and toxicity properties. The oxidative removal of carbamazepine in aqueous medium has been investigated by electrooxidation processes using Ti/PbO2 and Ti/BDD circular anode electrodes in the presence of Na2SO4 as electrolyte in a batch electrochemical reactor. The effect of different parameters such as current intensity (from 1 to 2 A), electrolysis time (from 60 to 120 min), recirculation flow rate (from 167 to 333 ml min−1), and anode material (PbO2 and BDD) were investigated by an experimental design methodology. A Factorial Design 23 was firstly used to determine the effect of parameters mentioned above on CBZ removal. The electrolysis time and current intensity were the main parameters affecting CBZ removal rate. Then, the optimal experimental parameters for carbamazepine removal were investigated using a Central Composite Design. The optimal conditions determined turned out to be Ti/PbO2 anode, current intensity 1.37 A, electrolysis time 101 min, and recirculation flow rate 232 ml min−1. Under these conditions the removal of 88 ± 1.2% of CBZ and 3.159 mg L−1 min−1 of p-nitrosodimethylaniline were achieved. The decay kinetics was fitted a first-order reaction.

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Hydroxyl radical is by far one of the most powerful oxidants that can be used in water treatment. It is highly reactive and characterized by a half-life of approximately $10^{-9}$ s [10,11].

The electrochemical oxidation of aqueous solutions, which contain organic pollutants, by the use of Ti/catalyzer anode, proceeds in two steps [12]. The first step is the anodic discharge of the water, forming hydroxyl radicals which are absorbed on the active sites of the electrode (M).

$$\text{H}_2\text{O} \rightarrow \text{M(OH)}^+ + \text{H}^- + e^-$$

(1)

After this the absorbed hydroxyl radical oxidizes the pollutant (R):

$$\text{M(OH)}^+ + R \rightarrow \text{M} + \text{RO} + \text{H}^+ + e^-$$

(2)

where RO represents the oxidized pollutant which can be produced continuously by the hydroxyl radicals which are also constantly formed, since the anodic discharge of the water goes on.

However, the short lifetime and the high reactivity of the hydroxyl radical, make its detection very difficult. Methods to detect hydroxyl radicals include electron paramagnetic resonance (EPR) spectroscopy [13], fluorometric assay [11] and high performance liquid chromatography [14]. Nevertheless, the application of these methods demands expensive reagents and complex operation procedures [15–17]. UV-visible absorption spectroscopy method is applied to investigate the hydroxyl radical [9,10,18,19]. P-Nitrosodimethylaniline (RNO) is an organic dye molecule having a strong yellow color in aqueous solution and is easy to detect. Methods to detect hydroxyl radical, make its detection very difficult. Methods to detect hydroxyl radicals include electron paramagnetic resonance (EPR) spectroscopy [13], fluorometric assay [11] and high performance liquid chromatography [14]. Nevertheless, the application of these methods demands expensive reagents and complex operation procedures [15–17].

The novelty of the current research lies in the investigation of the major factors influencing on electrooxidation process and their ability to remove CBZ. The current research is of high importance due to extensive presence of pharmaceuticals compounds in wastewaters. The performance of this system in continuous mode electrochemical oxidation of CBZ simulated wastewater were soundly investigated by the response surface methodology (RSM), because RSM is a powerful tool to describe and optimize complex systems [21–24].

The aim of this study is to evaluate carbamazepine removal in an electrooxidation process using Ti/PbO$_2$ and Ti/BDD anode. Also RNO was used as a probe molecule to assess the production of reactive oxygen species.

2. Materials and methods

2.1. Preparation of the synthetic solution

CBZ analytical grade reagent (99%) was obtained from Acros Organics BVBA (Belgium). Synthetic stock solution of CBZ was prepared in glass beakers containing 30 mg of CBZ in 2 L of Milli-Q water (Milli-Q/Milli-RO Millipore System), which was solubilized using magnetic stirrer (500 rpm) at environmental temperature (25 °C) during 24 h. This solution was kept in refrigeration (4 °C). Afterward, a volume of 667 ml of CBZ stock solution was mixed with distilled water to a final volume of 1 L. The conditioning step was performed at a high speed of 750 rpm for 20 min. The mixing was achieved by using a Teflon-covered stirrer bar deposited at the bottom of the beaker. The resulting mixture constituted the synthetic CBZ with final concentration of 10 mg L$^{-1}$. Even though sodium chloride (NaCl) is the most common supporting electrolyte used for electrocoagulation process, its use remains controversial due to possible formation of organic chlorine by-products. On recent studies [25,26], it was shown that sodium sulfate (Na$_2$SO$_4$) is the best supporting electrolyte for the electrochemical process, considering economical, effective, and environmental point of view. Therefore, Na$_2$SO$_4$ was used as supporting electrolyte, which was added at a concentration of 400 mg L$^{-1}$ to increase the conductivity. Na$_2$SO$_4$ was an analytical grade reagent supplied by Mat laboratory (Quebec, QC, Canada). All CBZ degradation experiments were performed with a volume of 1 L.

2.2. Experimental unit

The electrolytic reactor unit used was built in acrylic material with dimensions of 13.5 cm of length, 3.5 cm of width, and 14.0 cm of height. The total volume was 1000 ml including the electrolytic reactor (650 ml) and a coupled reservoir (350 ml). Circular mesh (12 cm diameter and 0.1 cm thick) of titanium (Ti) electrode was used as cathode. Also, circular mesh electrodes of titanium coated with lead oxide (Ti/PbO$_2$) and titanium coated with bored doped diamond (Ti/BDD) were used as anode. The inter-electrode gap was 1 cm. The electrodes were supplied by Electrolytica Inc. (Amherst, NY, USA). All experiments were carried out at room temperature (25 °C).

2.3. Experimental design

Experimental design of the electrooxidation process for CBZ removal was carried out by using successively factorial design (FD) and central composite design (CCD) methodology. Both FD and CCD are widely used for the response surface methodology (RSM) [27]. RSM is a collection of mathematical and statistical methods for modeling and analysis of a process in which a response of interest can be influenced by several variables. It is used to determine the optimum operating conditions or to determine a region for the factors in which certain speciation is met [28]. In our study, the FD was employed to firstly investigate the main and interaction effects of the factors on the CBZ removal. Subsequently, the CCD was used to describe the process in the experimental domain and also for the optimization of this process to achieve the best CBZ removal at the lowest energy consumption.

The optimization is the way of adjusting control variables in any process to find out the suitable factors levels that return the best possible outcome (response). The traditional “trial-and-error” or one-factor-at-a-time (OFAT) approach for optimization has lots of drawbacks in relation to the absence of interactions effect as well as the efficiency to predict the true optimum. Generally, there are two different strategies for optimization: (a) simplex optimization and (b) response surface methodology (RSM). Simplex optimization is a stepwise strategy of the experiments, which are performed one by one. The exception is the starting simplex, in which all experiments can be run in parallel. An exact optimum can only be determined by RSM, while the simplex method will encircle the optimum [29]. As our objective is to optimize process parameters using RSM, we will probe into this optimization methodology. The RSM is mainly based on second-order models; so it illustrates quadratic surfaces such as minimum, maximum, ridge and saddle. If the second-order model is found to be adequate (Eq. (1)), then canonical analysis is performed to determine the location and the nature of the stationary point of the second-order model. The stationary point is the combination of design variables, where the surface is at either maximum or minimum in all directions. If the stationary point is maximum in some direction and mini- mum in another one, then the stationary point is a saddle point. When the surface is curved in one direction but is fairly constant in another one, then this type of surface is called ridge system [30]. The visualization optimization of the predicted model equation can be obtained by the 3D surface response plot and by contour plots through determination of coordinate axes.
Desirability function is a popular and established technique to concurrently determine these settings of input variables that can give the optimum performance levels for one or more responses. Harrington [31] first developed the desirability function which was later modified by Derringer and Suich [32] for specifying the relationship between predicted responses on a dependent variable and the desirability of the responses. The desirability is an objective function (D) that ranges from zero (low) outside of the limits to one (maximum) at the goal. The numerical optimization finds a point that maximizes the desirability function. The characteristics of a goal may be altered by adjusting the weight or importance of the factors based on experimenter’s desire.

CCD is formed by uniformly distributed points within the space of the coded variables (Xi). One of the advantages of CCD is the possibility to explore the whole experimental region and the usefulness of interpolating the response. The CCD matrix allows the description of a region around an optimal response. It is comprised of factorial matrix (above described) and 12 additional experiments. Six of which were at the center of the experimental region and six were at the axial position of each variable investigated.

The experimental response associated to a CCD matrix is represented by a quadratic polynomial model (Eq. (1)) [33–35]:

\[
Y = b_0 + \sum_{i=1}^{k} b_i X_i + \sum_{i=1}^{k} b_{ij} X_i^2 + \sum_{j=2}^{k} \sum_{i=1}^{k} b_{ij} X_i X_j
\]  

(3)

where \(Y\) = experimental response; \(b_0\) = average of the experimental response; \(b_i\) = estimation of the principal effect of the factor \(i\) for the response \(Y\); \(b_{ij}\) = estimation of the second effect of the factor \(i\) for the response \(Y\); \(b_{ij}\) = estimation of the interaction effect between factors \(i\) and \(j\) for the response \(Y\).

A four-factorial (a two-level) and central composite design, with six replicate at the center point led to a total number of forty experiments employed for response surface modeling. The independent process variables used in this study were: the current intensity (\(X_1\)), the electrolysis time (\(X_2\)), recycling flow rate (\(X_3\)), and type of anode (categoric factor) (\(X_4\)). CBZ removal efficiency (\(Y_1\)) and energy consumption (\(Y_2\)) were considered dependent factors (responses). The experiment region investigated for carbamazepine removal and the code values are shown in Table 1. Experimental data were analyzed by using the design Expert Software version 9 (Stat-Ease Inc., USA) including ANOVA in order to obtain the interactions between the process variables.

### 2.4. Oxidation potential of the electrooxidation cell

RNO was an analytical grade reagent supplied by Sigma Aldrich (purity 97%). An RNO stock solution (4 × 10⁻³ mol L⁻¹) was prepared in a glass tank containing 1 L of buffer in which 600.72 mg of RNO was added. A mixture constituted by the synthetic RNO solution with final concentration of 45 ppm was used in which 400 mg L⁻¹ of NaSO₄ was added to increase the electrical conductivity. Buffer solutions were prepared using anhydrous dibasic sodium phosphate (99% purity) and crystalline monobasic potassium phosphate (98% purity). The pH value of the buffer solution was 7. Anhydrous dibasic sodium phosphate and crystalline monobasic potassium phosphate were analytical grade reagents and supplied by EMD Chemicals (Darmstadt, Germany).

### 2.5. Analysis

The concentration of CBZ in the solution was determined by the absorption spectral measurements. The maximum absorption of CBZ measured at 286 nm was chosen to evaluate the residual CBZ concentration. A calibration curve of known CBZ concentration (0–15 mg L⁻¹) versus relative absorbance was used to calculate the residual CBZ concentration and to define the efficiency of removal. Once appropriate values of the optimal parameters were determined, the optimal conditions were repeated in triplicate to verify the reproducibility. The bleaching rate was monitored by absorbance measurements of RNO at 440 nm. The RNO calibration curve was obtained by plotting the RNO absorbance at 440 nm as a function of RNO concentration (from 0 mg L⁻¹ to 50 mg L⁻¹). ROS (reactive oxygen species), like O₂ and OH, produced in situ have been shown to bleach RNO by chemical oxidation [24]. The amount of RNO removed corresponds to the amount of ROS formed in the system.

The peroxodisulfuric acid (H₂S₂O₄) production was estimated using Wessler reaction, which consists in the iodide ions oxidation into iodine. When oxidant agents are present in solution, iodide ions are oxidized to give iodine. When excess I⁻ ions are present in solution, I₂ reacts with the excess of I⁻ to form I₃⁻ ion according to Eq. (2) [36].

\[
I_2 + I^- \rightarrow I_3^-
\]  

(4)

Tri-iodide is analyzed by absorbance measurements \((a^2 = 26303 Lmol^{-1} cm^{-1})\) [37] using a spectrophotometer Carry UV 50 (Varian Canada) at 352 nm.

### 2.6. Operating parameters

The pH was determined using a pH-meter (Fisher Acumet model 915) equipped with a double junction Cole-Palmer electrode with Ag/AgCl reference cell. Total organic carbon (TOC) was measured using a Shimadzu TOC 5000A analyzer (Shimadzu Scientific Instruments, Kyoto, Japan). The conductivity was monitored using a Conductimeter (Oakton model 915) equipped with a conductivity probe. Concentrations of initial and residual CBZ and RNO were established by spectrophotometric method using a spectrophotometer Carry UV 50 (Varian Canada Inc.).

### 3. Results and discussion

#### 3.1. Preliminary investigations

It is well known that the type of anode material used can greatly influence electrochemical oxidation processes [38,39]. This can be attributed to the different crystalline natures of electrodes that catalyze electrochemical oxidation [40]. Thus, experiments were conducted to determine the oxidation behavior of CBZ on Ti/SnO₂, Ti/BDD and Ti/PbO₂ anodes, under controlled conditions: current

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### Table 1
Experimental range and levels of independent process variables.

<table>
<thead>
<tr>
<th>Coded variables (X_i)</th>
<th>Factor (U_i)</th>
<th>Description</th>
<th>Experimental field</th>
<th>U_i</th>
<th>ΔU_i</th>
</tr>
</thead>
<tbody>
<tr>
<td>X_1</td>
<td>U_1</td>
<td>Current intensity (A)</td>
<td>Min. value (-1)</td>
<td>1</td>
<td>1.5</td>
</tr>
<tr>
<td>X_2</td>
<td>U_2</td>
<td>Electrolysis time (min)</td>
<td>Max. value (+1)</td>
<td>2</td>
<td>0.5</td>
</tr>
<tr>
<td>X_3</td>
<td>U_3</td>
<td>Recycling flow rate (ml min⁻¹)</td>
<td>167</td>
<td>120</td>
<td>60</td>
</tr>
<tr>
<td>X_4</td>
<td>U_4</td>
<td>Type of anode</td>
<td>Ti/PbO₂</td>
<td>250</td>
<td>83</td>
</tr>
</tbody>
</table>

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intensity (2 A), recycling flow rate (333 ml min\(^{-1}\)), NaSO\(_4\) concentration (400 mg L\(^{-1}\)), and initial CBZ concentration (10 mg L\(^{-1}\)).

When Ti/SnO\(_2\) was used the electrical resistance increased rapidly, indicating that the electrodes were most likely covered with organic substances causing a passivation, and this was demonstrated by Scanning Electron Microscope (SEM), which showed the presence of C (11.4%) on the surface of the electrode after the experiment.

A similar behavior has been observed by Nagata et al. [41] in treating different effluents containing endocrine-disrupting chemicals (e.g., 7b-estradiol, bisphenol, pentachlorophenol, and dichlorophenol) using an electro-oxidation process with a threedimensional electrode system. Nagata et al. [41] analyzed the electrode surface (Ti/Pt anode electrode) before and after the continuous electrochemical process by using X-ray photoelectron spectrometry (XPS). After the treatment, a large carbon peak was observed instead of the Pt peak, suggesting that the electrode surface was covered with organic substances that were formed during the treatment of the organic-containing effluent. This situation may affect the treatment performance in a long term experiment. That is why the Ti/SnO\(_2\) was not selected for the next step of the experimentation.

Ti/BDD and Ti/PbO\(_2\) are more effective than Ti/SnO\(_2\) for CBZ removal (Fig. 1). The high percentages of CBZ removal (around 90%) were recorded with Ti/PbO\(_2\) and Ti/BDD after 100 minutes of treatment. Therefore these two electrodes were chosen for the next step of this study. In fact, the nature of the electrode material strongly influences both the selectivity and the efficiency of the direct oxidation process.

Oxidation with OH\(^{-}\) radicals is not only the oxidation mechanism occurring on such a BDD anode. When sulfate ions are present, they are oxidized on Ti/BDD anode and peroxodisulfuric acid (H\(_2\)S\(_2\)O\(_8\)) is generated. H\(_2\)S\(_2\)O\(_8\) is powerful oxidant (S\(_2\)O\(_8^{2-}\)/SO\(_4^{2-}\), \(E^\circ = 2.08 \text{ V}\)) capable of oxidizing and modifying the structure of organic molecules [42] and leading to more oxidized and less toxic compounds [43–47,41].

The S\(_2\)O\(_8^{2-}\) ions are formed from the oxidation of SO\(_4^{2-}\) species at very high potentials [44]:

\[
2\text{SO}_4^{2-} \rightarrow \text{S}_2\text{O}_8^{2-} + 2e^- \quad E = 2.01 \text{ V} \tag{5}
\]

Because of Na\(_2\)SO\(_4\) was used as electrolytic support, sulfate ions are present, therefore it is possible to assume that hydroxyl radicals (OH\(^{-}\) and peroxodisulfates (S\(_2\)O\(_8^{2-}\)) were produced. To observe the interaction between the presence of S\(_2\)O\(_8^{2-}\) and CBZ both concentrations were monitored after an experiment using BDD anode. Final solution was maintained in standby for analysis; samples of 10 ml of the effluent at different times (0 through 140 h) were taken and mixed with an excess of potassium iodide (500 mg). This method is based on the direct titration of iodine produced by oxidation of iodide [46]:

\[
\text{S}_2\text{O}_8^{2-} + 2F^- \rightarrow 2\text{SO}_4^{2-} + I_2 \tag{6}
\]

\[
I_2 + 2\text{S}_2\text{O}_8^{2-} \rightarrow 2I^- + \text{S}_4\text{O}_6^{2-} \tag{7}
\]

The mixture was allowed to react for 15 min while stirring. Then was analyzed by spectrophotometric method at a wavelength of 353 nm, the results are shown in Fig. 2. It can be observed that the presence S\(_2\)O\(_8^{2-}\) does not influence the degradation of CBZ, which is evidenced because CBZ concentration is constant after 140 h, and the concentration of S\(_2\)O\(_8^{2-}\) decreased until <0.05 mg L\(^{-1}\) (Fig. 2b), indicating that the removal is carried out only by the radical hydroxyl.

The persulfuric acid is unstable in aqueous solution, it is decomposing in dilute sulfuric acid solutions with liberation of oxygen according to reaction (5):

\[
\text{S}_2\text{O}_8^{2-} + \text{H}_2\text{O} \rightarrow 2\text{HSO}_4^- + \frac{1}{2} \text{O}_2 \tag{8}
\]

This is the reason why the concentration of persulfuric acid decrease with the time.

3.2. Experimental design for the electrooxidation of CBZ

The influence of four main factors has been investigated: current intensity (\(U_1\)), electrolysis time (\(U_2\)), recirculation flow rate (\(U_3\), ml min\(^{-1}\)) and type of anode (\(U_4\)). CBZ removal (\(Y_1\)) and energy consumption (\(Y_2\)) were considered as dependents factors (response). A two-level full factorial design was used (2\(^k\), k being the number of factors; k = 4). The factors levels were coded as −1 (low), 0 (central point) and +1 (high). A total of eight experiments were carried out for both Ti/PbO\(_2\) and Ti/BDD electrodes (anodes).

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**Fig. 1.** Preliminary electro-oxidation tests for CBZ removal on three different anodes: Ti/SnO\(_2\), Ti/PbO\(_2\) and Ti/BDD (current intensity: 2 A; recycling flow rate: 333.33 ml min\(^{-1}\); NaSO\(_4\) concentration: 0.4 g L\(^{-1}\); initial CBZ concentration: 10 mg L\(^{-1}\)).

**Fig. 2.** Monitoring interaction between concentration of persulfate (S\(_2\)O\(_8^{2-}\)) and CBZ: (a) electrooxidation process (current intensity: 1.5 A; recycling flow rate: 250 ml min\(^{-1}\); NaSO\(_4\) concentration: 0.4 g L\(^{-1}\); initial CBZ concentration: 10 mg L\(^{-1}\)) and (b) after electrooxidation process.
The conditions in each experiment were modified using different combinations of the two selected levels. The experimental response associated to a 2^4 factorial design (four variables) is represented by a linear polynomial model with interaction:

\[
Y = b_0 + b_1X_1 + b_2X_2 + b_3X_3 + b_4X_4 + b_{12}X_1X_2 + b_{13}X_1X_3 + b_{14}X_1X_4 + b_{23}X_2X_3 + b_{24}X_2X_4 + b_{34}X_3X_4
\]

where \(Y\) represents the experimental response, \(X_i\) the coded variable \((-1 \text{ or } +1)\), \(b_i\) represents the estimation of the principal effect of the factor \(i\) for the response \(Y\), whereas \(b_{ij}\) represents the estimation of interaction effect between factor \(i\) and \(j\) for the response.

The response \((Y)\) investigated is the carbamazepine removal efficacy. The coefficients of the equation model were calculated using the half-difference between the arithmetic average of the values of the response when the associated coded variable is at a level \((-1)\) and the arithmetic average of the values of the response while the associated coded variable is at a level \((-1)\). The levels of the four variables studied for each experimental system and results are shown in Table 2. The coefficients of the polynomial model were calculated by means of Design-Expert® Program Software (Design Expert 7, 2007, Stat-Ease Inc., Minneapolis):

\[
Y = 76.14 + 7.01X_1 + 9.63X_2 + 0.091X_3 - 5.30X_4 - 0.84X_1X_2 + 0.41X_1X_3 + 1.45X_1X_4 + 0.056X_2X_3 + 2.87X_2X_4 - 0.47X_3X_4
\]

It is worth noting that the recorded responses are well fitted to the polynomial model with a regression coefficient \(R^2\) of 0.963. Besides, the low relative deviation values recorded (between the actual and predicted values) indicated that the linear polynomial model described by Eq. (2) is satisfactory (see Table 2). The coefficient \(b_0 = 76.14\) represents the average value of the response of the 16 assays. Eq. (8) shows that the removal of carbamazepine is very influenced by the electrolysis time \((b_2 = +9.63)\) which has positive effect on the studied response. The percentage of CBZ removal increases on average 19.26\% \((2 \times 9.63)\) when the electrolysis time goes from 60 to 120 min. The second most important factor on the removal of CBZ is the current density with a positive effect \((b_1 = +7.01)\). The increase of current intensity contributes to improve the removal rate of the CBZ. The percentage of CBZ removal increases on average 14.02\% \((2 \times 7.01)\) when the current density goes from 1 to 2 A. The effect of recirculation flow \((b_3 = +0.091)\) was relatively weak. However, the type of anode had a negative effect and higher \((b_4 = -5.3)\) on CBZ oxidation. The use of BDD anode contributed to a decreased rate of CBZ removal. The average rate of CBZ oxidation decreased 10.60\% \((2 \times 5.30)\) when the BDD anode was used. Among the interaction terms, \(X_1X_4\) (current intensity and the anode material) and \(X_2X_4\) (electrolysis time and anode material) have the most important coefficient \((b_{14} = +1.45\text{and } b_{24} = +2.87\text{, respectively})\), both effects are positive.

The importance of the factors and interactions has been put into evidence using graphical Pareto analysis. Pareto analysis gives more significant information to interpret the results [48,49]. Indeed, this analysis calculates the percentage effect of each factor on the response, according to the following relation (Fig. 3):

\[
P_i = \left( \frac{b_i^2}{\sum b_i^2} \right) \times 100 \ (i\neq0)
\]

\(b_i\) represents the estimation of the principal effect of the factor. The contributions of the principal effects \((X_1, X_2, X_3\text{ and }X_4)\) on the percentage of CBZ removal are 26.09\%, 49.24\%, 0.004\% and 14.92\%, respectively. The contribution of the interaction effects \((X_1X_2, X_1X_3, X_1X_4, X_2X_3\text{ and }X_2X_4)\) on the percentage of CBZ removal were 0.37\%, 0.002\%, 1.12\%, 0.09\%, 4.37\% and 0.12\% respectively. Thus, \(X_1X_2, X_1X_3, X_1X_4\text{ and }X_2X_4\) have a negligible effect (equal or less than 0.12\% on the response) in comparison with the others \((X_1X_2\text{ and }X_2X_4)\). The interpretation of the interactions \(X_1X_2\text{ and }X_2X_4\) is shown in Figs. 4 and 5 respectively. These figures were obtained as follows: each summit of the square represents a combination between the levels \((-1\text{ or }+1)\) and of two factors: current intensity and anode material (Fig. 4) and electrolysis time and anode material (Fig. 5). For example, in Fig. 4, the corner at the top (at the left) of this figure corresponds to Ti/PbO\(_2\) anode and current intensity of 2 A imposed. The value of 87% represented in the rounded-cartridge is obtained by calculating the average of the experimental results from the assays carried out with Ti/PbO\(_2\) anode operated at a current intensity of 2 A (assays 5–8). When the anode material (variable \(X_4\)) is fixed at the lowest level (i.e., Ti/PbO\(_2\) is imposed), the current intensity had always an influence on the response, but it more important than the first case while imposing Ti/PbO\(_2\) anode material. The average rate of CBZ removal passed from 62.37\% to 79.25\% (a degradation gain of 16.92 units). Consequently, it can be noticed that the effect of current intensity is not constant, it depends on another factor, which is the anode material type.

Considering now \(X_1X_2\) the same approach can be used to interpret this interaction (Fig. 5). When the anode material (variable \(X_2\)) is fixed at the lowest level (i.e., Ti/PbO\(_2\) is imposed), the electrolysis time \((X_1)\) has a significant influence on the response, the average rate of carbamazepine removal increased from 74.67\% to 88.2\% (a degradation gain of 13.53 units). However, if the anode material is fixed at the highest level (i.e., Ti/BDD is imposed), the electrolysis time has a notable effect on the response. The average rate of CBZ removal passed from 58.33\% to 88.33\% (a degradation gain of 30.0 units). Consequently, the effect of the electrolysis time is not constant and is a major factor that influenced the rate of CBZ oxidation, but it directly depends on the type of anode material used.

A factorial design is a powerful tool to determine the interactions affecting the response and indicates if the lowest or the highest levels of the factors are favorable or not. The results are reliable based on the tendency of the response, which are greatly influenced by the factors having a significant effect. However, this type of model cannot be used to predict or to determine the optimization conditions. In a second step, a surface response methodology was used to determine the optimal operating condition for CBZ removal.

### 3.3. Optimization of CBZ removal

Central composite matrix [49] was used to represent the response of the three numeric factors in the all experimental field. Indeed, the central composite matrix presents a number of advantages such as: (i) the ability to explore the whole experimental region; (ii) the possibility to determine the coefficient of a mathematical model fitting with a second-order polynomial equation; (iii) the usefulness of interpolating the response. There are three quantitative factors \((U_1, U_2\text{ and }U_3)\) and one categorical factor \((U_4)\) that might potentially affect the removal efficiency of CBZ. The CCD matrix is comprised of three sets: factorial matrix (assays 1–16), a set of point at the center of the experimental domain (assays 23–28 and 35–40) and star matrix (assays 17–22 and 29–34). A total of forty experiments were required for response surface modeling. The response can be described by a second order model for predicting the response in all experimental regions from the following equation:
Table 2
Experimental factorial matrix in the 2^4 design for calculation of effects for different anode materials (Ti/PbO_2 and Ti/BDD) and experimental results.

<table>
<thead>
<tr>
<th>Experiment number</th>
<th>Experiment design</th>
<th>Experiment plan</th>
<th>Y_1: Actual removal efficiency (%)</th>
<th>Y_2: Predicted removal efficiency (%)</th>
<th>Relative deviation (Y_2 - Y_1)</th>
<th>Y_3 Energy consumption (kW h m^{-3})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-1 -1 -1 -1</td>
<td>1 60 167 Ti/PbO_2</td>
<td>70.71</td>
<td>68.18</td>
<td>2.52</td>
<td>14.5</td>
</tr>
<tr>
<td>2</td>
<td>-1 +1 -1 -1</td>
<td>1 120 167 Ti/PbO_2</td>
<td>79.80</td>
<td>83.27</td>
<td>-3.48</td>
<td>29.6</td>
</tr>
<tr>
<td>3</td>
<td>-1 -1 +1 -1</td>
<td>1 60 334 Ti/PbO_2</td>
<td>71.00</td>
<td>68.37</td>
<td>2.63</td>
<td>15.2</td>
</tr>
<tr>
<td>4</td>
<td>-1 +1 +1 -1</td>
<td>1 120 334 Ti/PbO_2</td>
<td>82.00</td>
<td>83.68</td>
<td>-1.69</td>
<td>30.2</td>
</tr>
<tr>
<td>5</td>
<td>+1 -1 -1 -1</td>
<td>2 60 167 Ti/PbO_2</td>
<td>78.00</td>
<td>80.16</td>
<td>-2.17</td>
<td>43.2</td>
</tr>
<tr>
<td>6</td>
<td>+1 +1 -1 -1</td>
<td>2 120 167 Ti/PbO_2</td>
<td>95.00</td>
<td>91.89</td>
<td>3.11</td>
<td>81.2</td>
</tr>
<tr>
<td>7</td>
<td>+1 -1 +1 -1</td>
<td>2 60 334 Ti/PbO_2</td>
<td>79.00</td>
<td>81.99</td>
<td>-2.00</td>
<td>46.8</td>
</tr>
<tr>
<td>8</td>
<td>+1 +1 +1 -1</td>
<td>2 120 334 Ti/PbO_2</td>
<td>96.00</td>
<td>93.94</td>
<td>2.05</td>
<td>89.6</td>
</tr>
<tr>
<td>9</td>
<td>-1 -1 -1 +1</td>
<td>1 60 167 Ti/BDD</td>
<td>47.47</td>
<td>49.885</td>
<td>-2.41</td>
<td>15.8</td>
</tr>
<tr>
<td>10</td>
<td>-1 +1 -1 +1</td>
<td>1 120 167 Ti/BDD</td>
<td>79.80</td>
<td>76.45</td>
<td>3.34</td>
<td>31.2</td>
</tr>
<tr>
<td>11</td>
<td>-1 -1 +1 +1</td>
<td>1 60 334 Ti/BDD</td>
<td>45.45</td>
<td>48.195</td>
<td>-2.74</td>
<td>16.4</td>
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<tr>
<td>12</td>
<td>-1 +1 +1 +1</td>
<td>1 120 334 Ti/BDD</td>
<td>76.77</td>
<td>74.987</td>
<td>1.78</td>
<td>31.8</td>
</tr>
<tr>
<td>13</td>
<td>+1 -1 -1 +1</td>
<td>2 60 167 Ti/BDD</td>
<td>69.70</td>
<td>67.665</td>
<td>2.03</td>
<td>45.2</td>
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<tr>
<td>14</td>
<td>+1 +1 -1 +1</td>
<td>2 120 167 Ti/BDD</td>
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<td>90.873</td>
<td>-2.99</td>
<td>86.8</td>
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<tr>
<td>15</td>
<td>+1 -1 +1 +1</td>
<td>2 60 334 Ti/BDD</td>
<td>70.71</td>
<td>67.615</td>
<td>3.09</td>
<td>46.8</td>
</tr>
<tr>
<td>16</td>
<td>+1 +1 +1 +1</td>
<td>2 120 334 Ti/BDD</td>
<td>88.89</td>
<td>91.047</td>
<td>-2.16</td>
<td>92.8</td>
</tr>
</tbody>
</table>

Fig. 3. Graphical Pareto analysis of the effect of electrolysis time, current intensity, type of anode and recirculation flow rate on CBZ removal.

Fig. 4. Interaction b_{14} between current intensity and type of anode material.

Y = b_0 + \sum_{i=1}^{k} b_i X_i + \sum_{j=1}^{k} b_{ij} X_i X_j + e_i \quad (12)

where Y, experimental response; b_0, average of the experimental response; b_{ij}, estimation of the principal effect of the factor j for

For BDD: Y_1 = -73.977 + 71.707X_1 + 1.545X_2 - 2.901X_1 10^{-3}X_3 - 0.055X_1X_2 + 9.850X_1 10^{-3}X_1X_3 + 2.245 10^{-3}X_1X_3 - 17.166X_1^2 - 6.022 10^{-3}X_2^2 - 3.147 10^{-3}X_3^2 \quad (14)

From these Eqs. ((12) and (13)), it can be seen that, current intensity and electrolysis time are very significant for the CBZ removal using either PbO_2 or BDD anode material. They are
positive effect on the response. Thus, an increase of both current intensity and time increased the electrochemical removal of the CBZ. However, the flow had a low effect on the electrooxidation of CBZ in the investigated experimental region. Considering the interaction among the factors, it is worth noting that the interaction \( X_1X_2 \) is the most important when either PbO2 or BDD anodes were used.

Table 4 shows the analysis of variance (ANOVA) of regression parameters of the predicted response surface quadratic model for CBZ removal. As it can be seen from this table, the model \( F \)-value of 41.47 and a low probability value (Pr > \( F \) = 0.0001) indicate that the model is very significant. The value of the correlation coefficient \( R^2 = 0.9605 \) means that only 3.6% of the total variation could not be explained by the empirical model and indicates that the regression model explained the electrooxidation process well. According to Joglekar and May [50], \( R^2 \) should be at least 0.80 for a good fit of a model. Furthermore, the lack of fit F-value of 16.76 and the probability value (Pr > \( R \) = 0.0034) indicate that the lack of fit of the model is not significant. Fig. 6 shows that the percentage of the CBZ removal increases with current intensity and electrolysis time. The CBZ removal is maximum in the region from 1.25 to 2 A (for current intensity) and for 90–120 min (for electrolysis time). The comparison of actual (measured) and predicted values of CBZ removal are presented in Fig 7. The agreement between the actual and predicted values of CBZ removal is satisfactory and in accordance with the statistical significance of the quadratic model presented in Table 4.

The energy consumption is calculated from the followed equation:

\[
E = \frac{1 \times U \times t}{V}
\]

where “\( E \)” is the energy consumption in kW h m\(^{-3}\), “\( U \)” the current intensity (A), “\( t \)” the treatment time (h) and “\( V \)” the volume of treated water (m\(^{3}\)).

Table 3
Central composite matrix and experimental results.

<table>
<thead>
<tr>
<th>Experiment number</th>
<th>Experimental design</th>
<th>Experimental plan</th>
<th>Removal efficiency (%)</th>
<th>Energy consumption (kW h m(^{-3}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>( PbO_2 ) anode (( U_4 ))</td>
<td>( X_1 ) ( X_2 ) ( X_3 )</td>
<td>( U_1 ) (A) ( U_2 ) (min) ( U_3 ) (ml min(^{-1}))</td>
<td></td>
<td></td>
</tr>
<tr>
<td>17</td>
<td>–1.32 0 0</td>
<td>0.66 90</td>
<td>250.5</td>
<td>53.47</td>
</tr>
<tr>
<td>18</td>
<td>1.32 0 0</td>
<td>2.34 90</td>
<td>250.5</td>
<td>87.00</td>
</tr>
<tr>
<td>19</td>
<td>0 –1.32 0</td>
<td>1.5 39.55</td>
<td>250.5</td>
<td>70.71</td>
</tr>
<tr>
<td>20</td>
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<td>1.5 140.45</td>
<td>250.5</td>
<td>97.98</td>
</tr>
<tr>
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<td>79.00</td>
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<tr>
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</tr>
<tr>
<td>23</td>
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<td>89.90</td>
</tr>
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<td>24</td>
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<td>89.80</td>
</tr>
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<td>250.5</td>
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<td>250.5</td>
<td>87.63</td>
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<tr>
<td>27</td>
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<td>1.5 90</td>
<td>250.5</td>
<td>89.10</td>
</tr>
<tr>
<td>28</td>
<td>0 0 0</td>
<td>1.5 90</td>
<td>250.5</td>
<td>89.90</td>
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<td>29</td>
<td>0 0 0</td>
<td>1.5 90</td>
<td>250.5</td>
<td>89.80</td>
</tr>
<tr>
<td>30</td>
<td>0 0 0</td>
<td>1.5 90</td>
<td>250.5</td>
<td>89.90</td>
</tr>
</tbody>
</table>

Table 4
ANOVA results for the response surface quadratic model for CBZ removal and energy consumption.

<table>
<thead>
<tr>
<th>Source</th>
<th>Analysis of variance</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>d.f.</td>
</tr>
<tr>
<td>CBZ removal</td>
<td>Model</td>
</tr>
<tr>
<td></td>
<td>Residual</td>
</tr>
<tr>
<td></td>
<td>Lack of fit</td>
</tr>
<tr>
<td></td>
<td>Pure error</td>
</tr>
<tr>
<td>Energy consumption</td>
<td>Model</td>
</tr>
<tr>
<td></td>
<td>Residual</td>
</tr>
<tr>
<td></td>
<td>Lack of fit</td>
</tr>
<tr>
<td></td>
<td>Pure error</td>
</tr>
</tbody>
</table>

\( R^2 = 0.9605 \) for CBZ removal. 
\( R^2 = 0.9991 \) for Energy consumption.

\( ^{a} \) Degree of freedom.
The analysis of variance (ANOVA) of regression parameters of the predicted response surface quadratic model for energy consumption shows that the model is significant ($F$-value of 3090.01 and a low probability value $Pr > F = 0.0001$). The value of the correlation coefficient ($R^2 = 0.999$) indicate that only 1% of the total variation could not be explained by the empirical model.

To rigorously determine the optimal condition for CBZ removal in terms of cost/effectiveness, the energy consumption during electrolysis has to be taken into account. The criteria selected for the optimization condition for this electrooxidation process are the removal of CBZ has to be maximized with the highest importance (5/5 weighting factor) and the energy consumption has to be minimized with less importance (3/5 weighting factor) in order to reduce the treatment cost related to energy consumption. Based on these criteria imposed, the Design-Expert® Program Software proposed interesting solutions, one for each anode material classified per order of desirability (Table 5). PbO2 was found to be the best anode material in term of CBZ removal efficacy (near 8% higher as compared to the BDD anode).

On one hand, the desirability is a value varying from zero to one and it gives information about the adequacy between the solution and the criteria imposed. If the value is closer to one, it means that the solution is very close from what we want and the software has done few compromises to satisfy the imposed criteria. On the other hand, if the desirability is closer from zero, it means that it is very difficult to satisfy the criteria without making a lot of compromise. The best solution for CBZ removal in terms of energy consumption/effectiveness has been found using PbO2 anode with at time of 101 min of treatment using a 232 ml min$^{-1}$ of recirculation flow rate and 1.37 A. In this condition, the CBZ removal should be nearly 89% with an energy consumption of 40 kW h m$^{-3}$. Once the appropriate values of the optimal parameters were determined, the optimal conditions using PbO2 anode (the best optimal solution proposed in terms of CBZ removal and energy consumption) were triplicate to verify the reproducibility (Fig. 8). During the series of experiments, the maximal value of the CBZ removal obtained under optimal process conditions has been confirmed experimentally, the residual concentration of CBZ was analyzed, the experimental response was $88 \pm 1.2\%$ and recorded at the end of these experiments, a value that was very near to that proposed by the model ($89.33\%$ of CBZ degradation). Apparent rate constant for oxidative removal of CBZ, obtained from the slop of straight lines of the inset in Fig. 8 was $0.021$ min$^{-1}$, the exponential decrease of CBZ concentration indicates a first order reaction kinetic with a correlation coefficient ($R^2$) of 0.965. In order to complete the information, other index has been used for evaluating model adaptation to measured data: the root mean square error (RMSE) representing the scatter of errors between simulated and measured data, evaluated by the means of Eq. (15).

$$RMSE = \sqrt{\frac{1}{n}\sum (Y_{meas} - Y_{pred})^2}$$ (16)

where $Y_{meas}$ is the measured variable, $Y_{pred}$ is the simulated variable and $n$ is the number of available observations. The first order reaction kinetic provides the best-fit model, having the lowest RMSE of 0.231.

It is interesting to compare the kinetic constant recorded in our study ($0.021$ min$^{-1}$) with values obtained in other experimental conditions where the removal rate of CBZ (10 mg L$^{-1}$) by photocatalytic process (UV/TiO2) is well described by the first order kinetic model ($0.017$ min$^{-1}$) [51]. The type of oxidant species produced could influence the kinetic rate of pollutant degradation.

Likewise, residual TOC concentrations were measured. The residual concentration recorded at the end of the electrooxidation process was $7.42 \pm 0.8$ mg TOC L$^{-1}$ ($30.43 \pm 0.8\%$ of removal). By comparison, $10.64 \pm 0.8$ mg TOC L$^{-1}$ was measured in the initial solution. These results indicated that the CBZ was only transformed into smaller molecules, such as anthranilic acid and acridine; CBZ was not completely oxidized into water and carbon dioxide. Therefore, the pollutant was transformed into by-products. However, additional experiments should be carried out to rigorously put in evidence the formation of products during electrooxidation of the CBZ.

#### Table 5

<table>
<thead>
<tr>
<th>Current intensity (A)</th>
<th>Electrolysis time (min)</th>
<th>Recycling flow rate (ml min$^{-1}$)</th>
<th>Anode material degradation</th>
<th>Degradation yield (%)</th>
<th>Energy consumption (kW h m$^{-3}$)</th>
<th>Desirability</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.37</td>
<td>101</td>
<td>232</td>
<td>PbO2</td>
<td>89.33</td>
<td>40</td>
<td>0.723</td>
</tr>
<tr>
<td>1.242</td>
<td>120</td>
<td>162</td>
<td>BDD</td>
<td>81.52</td>
<td>44</td>
<td>0.737</td>
</tr>
</tbody>
</table>
The electro-oxidation process using optimal conditions was applied to the RNO solution with the PbO2 anode. The results of RNO degradation are shown in Fig. 9. The experiments were carried out by triplicate to verify the effectiveness and reproducibility of the electro-oxidation process performance of bleaching rate of RNO. As it is observed from this results, the bleaching rate of RNO increased with treatment time.

The removal rate of RNO recorded over 101 min of treatment was 3.159 mg L⁻¹ min⁻¹. The ROS (i.e., OH, O₂⁻, etc.) production rate is equal to the RNO disappearance rate according to Eq. (16).

\[ V_{ROS} = \frac{d[RNO]}{dt} = -k[RNO] \]  

where “[RNO]” is the concentration of RNO, “k” is the first order reaction rate constant (t⁻¹) and “\(V_{ROS}\)” is the production rate of ROS. Integration of Eq. (16) gives:

\[ \ln \left( \frac{C_0}{C} \right) = kt \]  

where “C₀” is the initial concentration of RNO, “C” is the concentration of RNO at time “t,” and “t” is the reaction time, and “k” is the reaction rate constant. “k” could be calculated from the slope of a plot of \(\ln (C_0/C)\) from Eq. (8). The insert panel of Fig. 9 shows that the RNO disappearance rate follows a first-order kinetic model. The first-order kinetic reaction rate constant in the electro-oxidation process was 0.07 min⁻¹ and RMSE of 1.953. The high removal rate of CBZ was mainly attributed to ROS continuously produced over time. In our experimental conditions (optimal conditions process), the ROS production rate was estimated to be 37.75 × 10⁻³ mM h⁻¹, in which the value can be compared to that recorded (22.6 × 10⁻³ mM h⁻¹) by Daghrir et al. [52] while treating a p-nitrosodimethylaniline solution using a photo-electro catalytic oxidation process.

4. Conclusions

The electro-oxidation of carbamazepine was tested using three different anode materials: Ti/SnO₂, Ti/PbO₂ and Ti/BDD cylindrical mesh electrode systems. The first part of this study was performed in synthetic medium of CBZ using sodium sulfate as an electrolyte; thus, the contribution of the direct effect of electrolys was taken as evidence. The best results for CBZ removal were obtained with the Ti/PbO₂ and Ti/BDD anode. An experimental design methodology has been applied to determine the optimal experimental conditions. The factorial design (FD) demonstrated that the electrolysis time and current intensity are the most influencing parameters on the electrochemical oxidation of CBZ. The effect of these two main factors is around 75% on the investigated response, whereas the effect of anode material, recycling flow rate and the other interaction effects represent 25% on the investigated response. Moreover, a central composite design (CCD) was employed to define the optimal operating conditions for CBZ removal. Current intensity and electrolysis time were found to be very meaningful for CBZ removal using either Ti/PbO₂ or Ti/BDD anode material. They are positive effect on the response. Ti/PbO₂ operated at a current intensity of 1.37 A during 101 min of treatment time and recycling flow rate of 232 ml min⁻¹ was found to be the optimal conditions in terms of effectiveness/energy consumption. Under these conditions, the system was able to oxidize 88 ± 1.2% of CBZ and for removing large amounts of RNO at a rate of 3.159 mg L⁻¹ min⁻¹. This process appears to be a promising technology that can be used as tertiary treatment to remove emerging pollutants from wastewaters.

Conflict of interest

All authors of this research work disclose there is not any financial institution and personal relationship with other people or organization that could inappropriately influence this work.

References