Impact of Anode Materials on Electrochemical Degradation of Carbamazepine: A Case Study of Producing the Main By-Product 10,11-Epoxycarbamazepine after Electrochemical Degradation of Carbamazepine

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Received: January 6, 2022
Accepted: May 17, 2022

DOI: 10.22146/ijc.71976

Abstract: *Copper (Cu), nickel (Ni), platinum (Pt), and graphite (G)" have been applied to the electrochemical degradation of carbamazepine (CBZ) from its aqueous solution. The optimum results were observed with graphite anode as follows: fully complete removal of CBZ, 0.0758 min^{-1} rates constant, and 0.59 Wh/mg consumption energy under these conditions: 5 V, 0.5 g NaCl, and a graphite anode. Kinetics was also considered in the present study, in which rate constants ranged between 0.0023 and 0.0886 min^{-1}. It was observed that applied voltage affects consumption energy giving 0.34, 0.59, and 1.08 Wh/mg using 3, 5, and 7 V, respectively. Field emission scanning electron microscope (FESEM) and energy dispersive X-ray spectroscope (EDS) were used to characterize the organo-metallic precipitates which were formed using Ni and Cu anodes. The main by-product of 10,11-epoxycarbamazepine (EPX-CBZ) was elucidated and monitored using liquid chromatography-time of flight/mass spectrometry (LC-ToF/MS). Therefore, graphite is a promising electrode in that it performs well compared to other electrodes in removal and energy consumption.*

Keywords: *electrochemical degradation; carbamazepine; 10,11-epoxycarbamazepine; anode materials; graphite anode*

■ INTRODUCTION

Highly utilization of pharmaceuticals and personal care products resulted in increasing their presence in aquatic samples, then affecting organism life in water [1-2]. One of these pharmaceuticals is carbamazepine (CBZ) which is frequently used in the treatment of trigeminal neuralgia and psychiatric diseases [3]. It has been recognized as an emerging contaminant because of its ecological risk potential and chronic and synergistic effects.

It was reported that carbamazepine was one of the top most utilized pharmaceuticals in Malaysia [4] and worldwide, reaching up to 1014 tons per year [5]. Carbamazepine has been frequently detected in water bodies, which may be attributed to its high degradation resistance towards oxidation and biological treatment [6-7]. According to previous studies, several treatment processes have been applied for the elimination of carbamazepine.

It could be removed by a very basic technique of membrane filtration or adsorption. However, these methods may not be suitable because of their low efficiency and high cost. It could also be not preferred because producing secondary pollution means carbamazepine is merely transferred to another medium and is not destroyed. Nezhadali et al. applied polypyrrole-chitosan-Fe_3O_4 magnetic nanocomposite as a magnetic nano sorbent to remove carbamazepine. It was removed in 94.5% after 25 min of electrolysis treatment [8].

Esquerdo et al. investigated the hybrid treatment and sequence of treatment processes, including ozone and activated carbon, on the removal of carbamazepine. He noticed that using ozone treatment first and then activated carbon is better than using activated carbon and then ozone to achieve 90% carbamazepine removal [9]. Some reports explained that CBZ had not degraded well using biological treatment as it takes a long time, and the removal efficiency is very low. Moya-Llamas et al. combined a sludge blanket reactor with a membrane bioreactor to remove carbamazepine from wastewater and observed a CBZ percent removal of 49.5% after 193 days [10].

He noticed that an enzymatic membrane bioreactor equipped with ultrafiltration or nanofiltration has a good advantage for removing CBZ, reaching up to 65%. This removal efficiency decreased with increasing initial concentration. Furthermore, the hydraulic retention time in most biological treatments is long, reaching up to 6 days [11]. As carbamazepine is highly resistant to biological treatment, combined gamma radiation and biological treatment were applied for the removal of CBZ from wastewater. It was observed the removal of CBZ was 99%, but total organic carbon (TOC) was 26.5% using only gamma radiation, but after combination with biological degradation, TOC removal was increased to 79.3% [12].

Based on the findings from the literature, it is necessary to look for alternative technology that participates in developing cost-effective treatment methods. It is very well known that advanced oxidation approaches are effective and promising methods to oxidize carbamazepine which is attributed to the high potential of hydroxyl radical (E° = 2.7 V vs. Standard Hydrogen Electrode (SHE)) [13-14]. Hydroxyl radicals can react non-selectively with organic pollutants at ambient temperature and pressure [15-17]. Photocatalysis [18-19], electro-Fenton [20], UV/chlorine [21], electrochemical oxidation [22], and other techniques [23], have been used as effective options for the degradation of CBZ. The electrochemical oxidation process is one of the advanced oxidation methods that have high efficiency for the degradation of pollutants and good environmental compatibility, so it encourages a promising technology for the elimination of organic pollutants from water bodies [14].

In the electrochemical oxidation process, anodic oxidation could occur on the anode's surface and/or at the bulk solution, producing a very active oxidizing agent, active chlorine "ClO^-/HOCl" [24]. Removal of organic pollutants such as pharmaceuticals, dyes, pesticides, and so on depends strongly on the active chlorine when NaCl is present [25]. As reported in previous studies, graphite exhibited good results due to its long lifetime at specifically applied voltages, not too high, eco-friendly, and low evolving oxygen, which means at low current achieve high removal with low consumption energy. Using graphite is accompanied by releasing a very active oxidizing agent, "ClO_4^-" instead of hydroxyl radical. However, graphite has been used to remove different pharmaceuticals, as reported by Mussa et al. [26].

The aim of the present study is: (i) to optimize different anode materials for the removal of carbamazepine; (ii) to evaluate the electrochemical efficiency process for the elimination of carbamazepine, (iii) to determine the energy consumption and kinetic studies during the electrochemical oxidation process, (iv) to identify the 10,11-epoxycarbamazepine (EPX-CBZ) as the main by-product after electrochemical degradation process of CBZ.

■ EXPERIMENTAL SECTION

Materials

Carbamazepine standard compound (CAS no. 298-46-4) and 10,11-epoxycarbamazepine were provided from sigma-Aldrich (USA). The supporting electrolyte NaCl with high purity (99%) was bought from Merck (Germany). Acetonitrile, methanol, and formic acid were purchased from Merck (Germany). Other chemical reagents, such as tetrahydrofuran (Cas no. 109-99-9) and polyvinyl chloride, were purchased from Sigma Aldrich (USA). The stock solution of carbamazepine (1000 mg/L) has been prepared as follows: 0.01 g of standard reagent was dissolved in 10 mL of methanol and then preserved at –18 °C to minimize the degradation of the standard. Further dilutions of CBZ standard solutions were provided in de-ionized water (DIW) and were kept at 4 °C.

Instrumentation

Analytical methods

A field emission scanning electron microscope (FESEM) instrument (brand: JEOL, model: JSM-7800F) was employed to characterize the precipitation after the electrochemical oxidation procedure at nickel and copper anodes.

Carbamazepine degradation was analyzed using an accurate instrument: LC-TOF/MS from a Dionex Ultimate 3000/LC 09115047 (USA). It is equipped with a vacuum degasser, a quaternary pump, and an auto-sampler. All separations were provided on a chromatographic column of Gemini 5 µm NX 110Å C18 column (2.1 mm × 250 mm, Phenomenex).

Carbamazepine degraded solution and its main by-product (EPX-CBZ) were analyzed in positive ionization mode. The binary mobile phase consisted of 0.1% formic acid in de-ionized water (DIW) (mobile phase A) and acetonitrile in methanol (3:1 v/v) (mobile phase B). The flow rate was 0.3 mL/min, and the elution program was carried out as follows: starting with 5% B at 0.0 min; 0–3 min, 60% B; 3–6 min, 97% B; 6–11 min, 97% B; 11–11.1 min, 5% B; 11.1–16.1 min, 5% B. Injection volume was 30 µL.

The structure of carbamazepine and 10,11-epoxycarbamazepine were elucidated after isolation of protonated molecular ions $[M+H]^+$ and $[M+Na]^+$, respectively, using ESI-TOF instrument (Bruker/Germany). Furthermore, retention time (t_R) was considered an extra factor to confirm the identity of the EPX-CBZ by-product. Optimization of MS was obtained with the following settings: MS capillary voltages, 4000 [ESI (+)]; drying gas flow rate, 8.0 L/min; drying gas temperature, 190 °C; and nebulizer pressure, 4.0 bar. All analytes were acquired using an independent reference spray via the LockSpray interference to ensure accuracy and reproducibility.

Extraction of 10,11-epoxycarbamazepine

The main by-product (EPX-CBZ) was identified after electrochemical degradation of 200 µg/L of CBZ under the optimum conditions: 0.5 g NaCl and 5 V. Samples were subjected to an electrochemical degradation process for two hours, then it was monitored after each 20 min. The samples after that were treated with solid phase extraction (SPE) cartridges (Oasis HLB, 3cc) and then injected into LC-TOF/MS for further analysis and elucidation. Solid-phase extraction can be explained as follow: (i) all samples after the degradation process were filtered using 0.45 µm (Whatman filter paper); (ii) samples were loaded at a flow rate of 3 mL/min on SPE cartridges after the preconditioning step with 1 mL of methanol and 1 mL of DIW; (iii) drying of cartridges under vacuum for 5 min then elution of the intended 10,11-epoxycarbamazepine in a test tube using 5 mL of methanol as the best eluent for this purpose; (iv) gentle stream of N_2 was used for dryness the extract of EPX-CBZ then it was reconstituted with 1 mL of methanol-water (10:90, v/v); (v) finally, the extract was injected into LC-TOF/MS for analysis.

Procedure

Electrochemical procedure

The degradation of carbamazepine was provided in the laboratory in 50 mL glass beaker, and it was placed on a magnetic stirrer then, the solution was subjected to the rotation force to ensure all contents were mixed well under 500 rpm at normal conditions. The experimental setup used for this study is shown in Fig. 1.

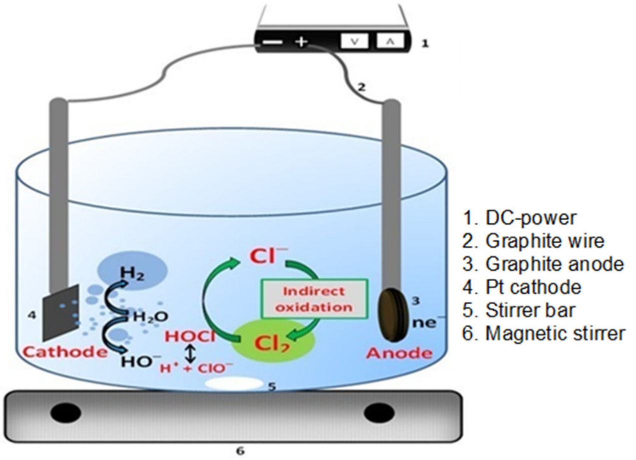


Fig 1. The schematic diagram of the real electrochemical process

Different anode materials have been used, namely: copper, nickel, platinum, and graphite. All have been applied and tested as anode electrodes, while the cathode electrode was fixed platinum in all experiments. The distance between anode and cathode was 4.0 cm to reduce the ohmic effect. Both electrodes assembly were connected to the DC power supply (CPX200 DUAL, 35 V 10 A PSU). All anode materials are plate sheets except for graphite powder. However, making graphite pellet was provided in steps, as explained in Fig. 2.

The influence of the electrochemical oxidation process factors such as applied voltage (3–7 V), processing time (0–80 min), and NaCl supporting electrolyte amount (0.1, 0.3, and 0.5 g) was examined at an initial concentration of carbamazepine 5 mg/L. During the electrochemical process, the electrode distance was maintained at 4 cm throughout the experiments.

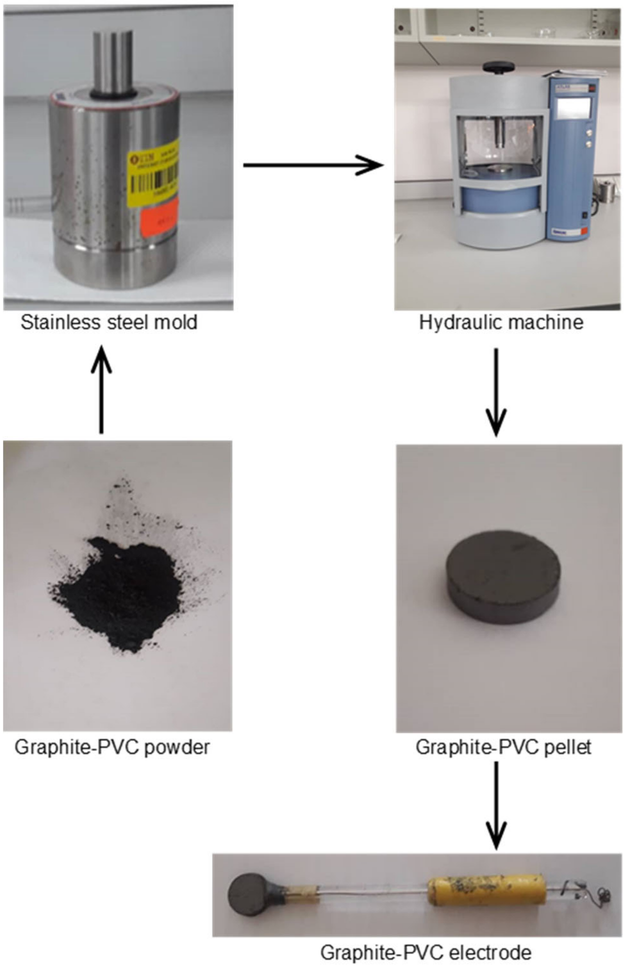


Fig 2. Steps of preparation of the graphite-PVC electrode

The consumption energy of electrochemical treatment of carbamazepine was also considered in the present study to confirm that the present study is preferred in terms of electric energy consumption.

■ RESULTS AND DISCUSSION

Effect of Anode Materials

In the electrochemical oxidation process, the anode is the electrode responsible for generating the electrons in solution to keep the oxidation-reduction process. The performance of the electrochemical oxidation process has been influenced by the type of anode material, as reported in previous studies [27-28]. In this study, four anode materials, namely: platinum (Pt), copper (Cu), nickel (Ni) plates, and graphite-PVC electrodes, were investigated for CBZ degradation. It is very well known that aluminum and iron anodes are common anodes used for this purpose, but they were not tested because these electrodes are only used for the electrocoagulation process, not the electrochemical oxidation process in which they produce a large volume of sludge, as reported by Nidheesh et al. [29].

Fig. 3(a) shows the effect of nature anode material on the degradation of carbamazepine at 0.5 g NaCl, 5 V, and 5 mg/L initial concentration of carbamazepine, and it was observed that graphite and platinum give the best percent removal of carbamazepine; contrarily for the two material anodes, Cu and Ni. This variation in percent removal depends on the mechanism of oxidation on the surface of the electrode. Nickel and copper prefer direct oxidation (i.e., producing hydroxyl radical as the main oxidizing agent) as the oxygen evolution potential is higher than Pt and graphite, while Pt and graphite prefer the indirect oxidation process, which means depending on the chlorine mediator in the solution. However, after 50 min, the removal was 96 and 93% of Pt and graphite, respectively, while it was 80 and 60% of Ni and Cu, respectively, under the same conditions of 5 V and 0.5 g NaCl. With increasing time, the removal was enhanced significantly in which it was complete at Pt, Ni and graphite except for copper, and it was 77%. It is well known that Pt as anode has good efficiency for removal of CBZ, but it is more expensive than graphite anode.

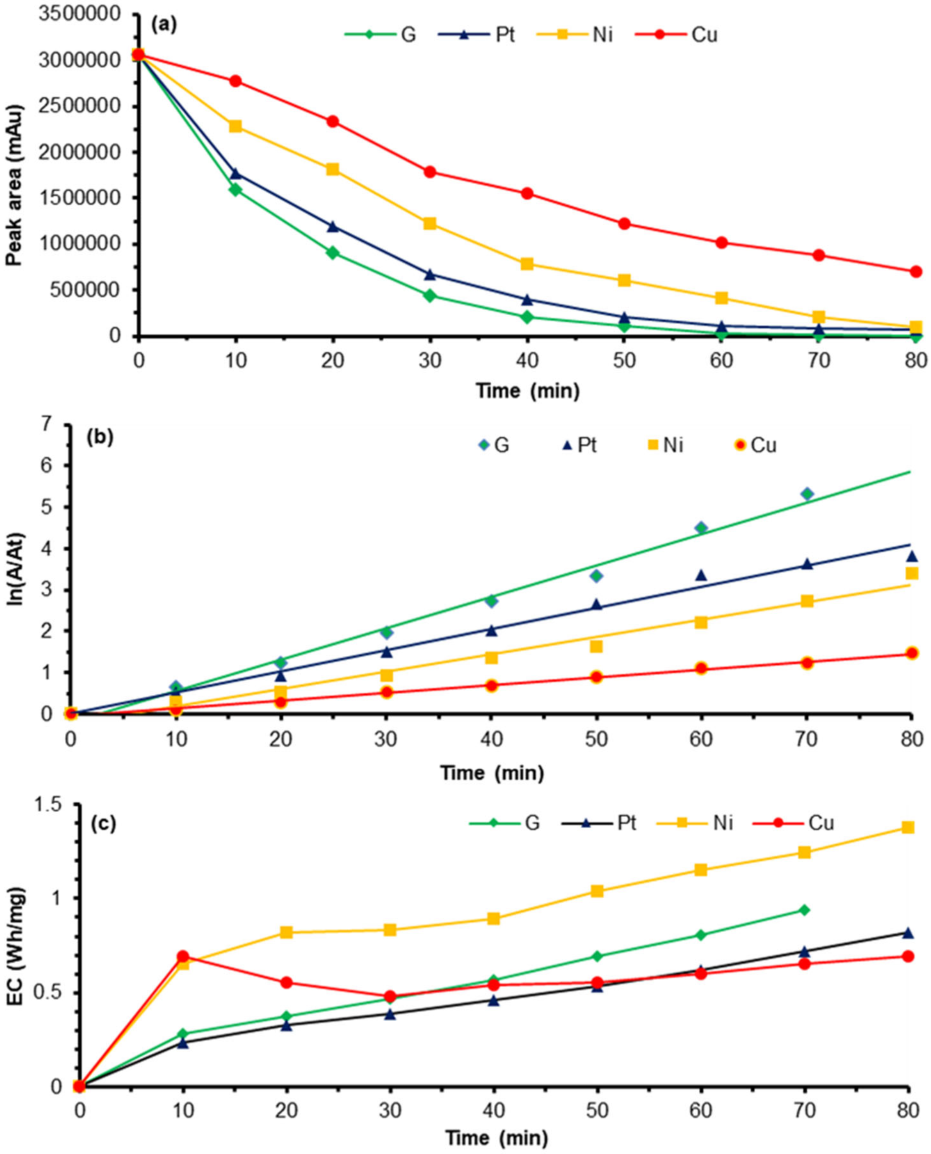


Fig 3. Effect of anode materials on (a) the removal of carbamazepine; (b) pseudo-first-order kinetic model; (c) consumption energy model during the electrochemical process under these conditions (5 mg/L CBZ; 0.5 g NaCl; 5 V)

In the present study, Ni and Cu electrodes were not suitable for the degradation of CBZ as their efficiency was insufficient. Both electrodes were corroded completely within one cycle of an electrochemical process, in agreement with that study reported by Nordin et al. He noticed that nickel and copper corroded after 120 and 95 min, respectively, after electrochemical degradation of dye [30].

Hypochlorite ions, as the main oxidizing agent, play an important role in the oxidation of carbamazepine. However, an excess concentration of ClO^- could not change more, so it remains constant through the electrochemical reaction. Based on this prospect, most of the indirect electrochemical oxidation reactions in the presence of chlorine obey the pseudo-first-order kinetics model [31-32]. The model could be presented in Eq. (1).

$$\frac{d[CBZ]_t}{dt} = -k_{obs}[CBZ]_t \quad (1)$$

where k_{obs} is the observed first-order rate coefficient; $[CBZ]_t$ is the total concentration of carbamazepine at the reaction time of t. After integrating Eq. (1) and rearranging it, Eq. (2) could be presented as follow:

$$\ln([CBZ]_t / [CBZ]_0) = -k_{obs}t \quad (2)$$

According to the equation, ln ($[CBZ]_t/[CBZ]_0$) was plotted versus electro-reaction time to generate a straight line, coefficient of determination (r2) ranged between 0.974 and 0.9958, with a slope of $-k_{obs}$ (Fig. 3(b)).

High-rate constants were observed with Pt and graphite of 0.0758 and 0.0513 min^{-1}. In contrast, the lowest rate constant was 0.019 min^{-1} for copper and nickel in the presence of 0.5 g NaCl and 5 V. These results may be attributed to the efficiency of anode materials in producing enough electrons in the solution.

According to the results reported in Table 1, it was observed that the degradation rate values were strongly influenced by the electrolytic anode materials. Based on the existing literature, nickel and copper are active electrodes that can be applied for direct electrochemical degradation because they produce hydroxyl radicals for the electrochemical degradation of organic pollutants [33]. It was found that the nickel electrode is inactive during the electrochemical process in the presence of supporting electrolytes such as Na_2SO_4 [34]. Graphite and Pt anode materials prefer an indirect electrochemical oxidation process, so supporting electrolytes' existence strongly enhances removal efficiency for carbamazepine [35]. The energy consumption was investigated and calculated according to Eq. (3) [36] during the electrochemical oxidation process of carbamazepine at all studied anode materials of Ni, Cu, Pt, and graphite.

$$EC = \frac{V.I.\Delta t}{\Delta[\text{reduced mass}]} \qquad (3)$$

where EC (Wh/mg of carbamazepine) is the energy consumption required to degrade carbamazepine under certain conditions; V is the applied voltage; I (A) is the passed current in an electric cell; t (h) is the electrolysis time; Δ[reduced mass] is the reduced amount (mg) of carbamazepine. The energy consumption of carbamazepine is presented in Fig. 3(c), and it was observed that the energy consumption was very high in the case of nickel, while it was the lowest regarding copper anode. However, the percent removal was very low at both anodes. The consumption of energy was slightly different at platinum and graphite, and at the same time, the removal was also high for both electrodes. Consequently, graphite has been chosen for its availability and low price.

Effect of Applied Voltage

The applied voltage is influential in eliminating organic pollutants using the electrochemical treatment process. Some reported papers indicated that the decomposition of electrode materials, especially anodes might be attributed to the high applied voltage or oxygen evolution in some occurred reactions [37].

Different values of applied voltage have been investigated on the degradation of carbamazepine, and it was varied at 3, 5, and 7 V under these conditions: initial concentration of carbamazepine at 5 mg/L and supporting electrolyte amount NaCl of 0.5 g for all experiments. The results obtained are shown in Fig. 4(a).

Table 1. Pseudo-first-order rate constants for carbamazepine at different affecting parameters such as anode materials, sodium chloride amount, and applied voltage

Parameters	Quantity	No. points	Rate constant (min^{-1})	Coefficient of determination (r2)
Anode materials	Graphite-PVC	7	0.0758	0.9908
	Platinum	8	0.0513	0.9982
	Nickel	8	0.0418	0.9784
	Copper	8	0.019	0.9958
Sodium chloride (g)	0.1	8	0.0023	0.8565
	0.3	8	0.0274	0.9921
	0.5	7	0.0758	0.9908
Applied voltage (V)	3	8	0.0199	0.9864
	5	7	0.0758	0.9908
	7	4	0.0886	0.9875

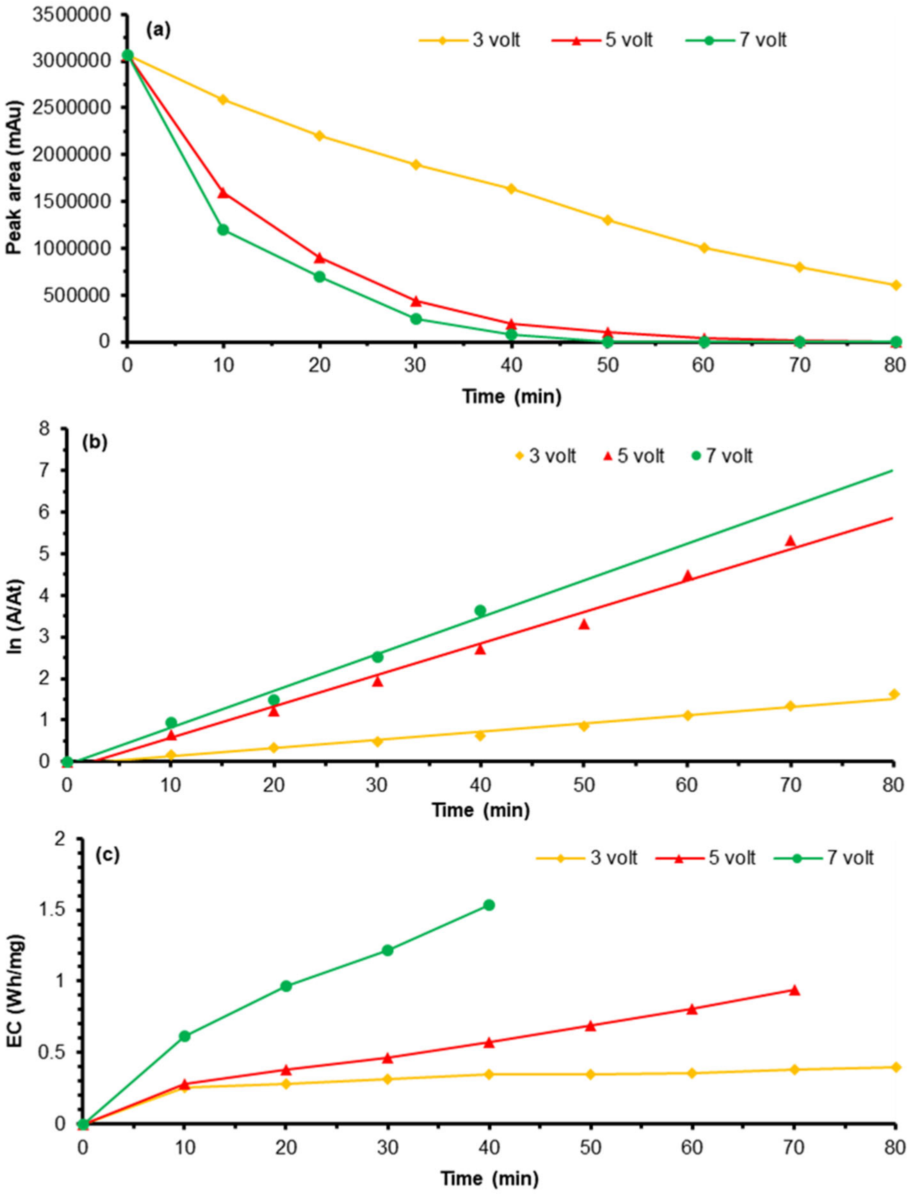


Fig 4. Effect of applied voltages on (a) the removal of carbamazepine; (b) pseudo-first-order kinetic model; (c) consumption energy model during the electrochemical process under these conditions (5 mg/L CBZ; 0.5 g NaCl; graphite as an anode)

It was observed that the removal of carbamazepine was 80.1% at 3 V after 80 min, while it was completely removed at 5 and 7 V after 80 and 50 min, respectively. This could be attributed to the high applied voltage producing more electrons that play an important role in forming active chlorine (Cl_2/HOCl) in bulk solution. However, high removal efficiency on the degradation of carbamazepine and high energy consumption was observed. It was noted that the removal rate was influenced highly by increasing applied voltage due to inducing oxygen evolution [38-39].

Electro-Fenton has been applied for the degradation of carbamazepine, and it was observed that increasing the current from 0.2 to 2 A resulted in decreasing the degradation process of carbamazepine from 68 to 53%. As the electro-Fenton requires ferrous ions, the current can be used for the oxidation-reduction process to form H_2O_2. High applied voltage resulted in more energy consumption and shortened the life of the electrode [40]. At the same time, low applied voltage leads to slow degradation and waiting a long time to achieve some removal of carbamazepine. However, from the above findings, 5 V was chosen as the optimum applied voltage for further experiments.

Increasing of applied voltage resulted in producing more ClO^- which contributes strongly to the acceleration of electrochemical removal of carbamazepine. High k_{obs} of 0.0886 min^{-1} was observed at 7 V, which is slightly greater than k_{obs} at 5 V and eight times greater than k_{obs} at 3 V. However, all models fit pseudo-first-order kinetics as the coefficient of determination greater than 0.98 value as presented in Fig. 4(b) and Table 1.

Energy consumption steadily increased with time during the electrochemical process (Fig. 4(c)). It seems that high energy consumption was accompanied by 7 V of 1.5332 Wh/mg compared to 5 V of 0.9371 Wh/mg. However, the lowest consumption of energy was 0.4 Wh/mg with 3 V, but the percent removal was 80% after 80 min. It could be concluded that 5 V was the best selection for further experiments.

Effect of Supporting Electrolyte

In the electrochemical treatment process, the amount of supporting electrolyte is very effective when the indirect process is dominant.

As a general rule, keeping a low ohmic drop between the electrodes across the electrochemical cell requires high conductivity in solution to enhance the electrochemical efficiency [41]. NaCl as a supporting electrolyte has been chosen to increase the efficiency of the electrochemical treatment process for caffeine, compared to other electrolytes such as Na_2SO_4, which lead to a low efficient treatment process [36]. This can be attributed to increasing the electron transfer resulting in high electrical conductivity. The generation of chlorine, then the main oxidizing agent of hypochlorite ion OCl^- could be presented in Eq. (4-7).

$$2Cl^- \rightarrow Cl_2 + 2e^- \quad (4)$$

$$Cl_2 + H_2O \rightarrow H^+ + Cl^- + HOCl \quad (5)$$

$$HOCl \leftrightarrow H^+ + ClO^- \quad (6)$$

$$ClO^- + \text{organic pollu tan t} \rightarrow CO_2 + H_2O + Cl^- \quad (7)$$

Different electrolyte amounts of 0.1, 0.3, and 0.5 g NaCl have been applied to the electrochemical degradation of carbamazepine using graphite anode and 5 V (Fig. 5(a)).

The carbamazepine degradation efficiency increased significantly with the 0.3 and 0.5 g NaCl. After 80 min, the removal was complete, 97.7% of 0.5 and 0.3 g NaCl, respectively, while it was 77% of 0.1 g NaCl.

From Fig. 5(b) and Table 1, it was observed that k_{obs} of 0.0758 min^{-1} was the greatest at 0.5 g NaCl compared to 0.1 g and 0.3 g NaCl which was 0.0274 and 0.0023 min^{-1}, respectively. Gracia-Espinoza et al. reported that increasing sodium chloride using Nb/BDD as anode increased the rate constant, reaching 0.189 min [3]. The highest consumption energy of 2.8798 Wh/mg was achieved using 0.1 g NaCl at 5 V and 5 mg/L initial concentration of carbamazepine (Fig. 5c). At the same time, the percent removal is very low, accompanied by 0.1 g NaCl. For 0.3 and 0.5 g NaCl, the consumption energy was too close to 0.8889 and 0.937 Wh/mg, respectively. Finally, 0.5 g NaCl was selected for further experiments.

Characterization of Anode Materials

As we know, the selection of anode material is not only accompanied by the high efficiency of degradation for organic pollutants, but also it is related to some considerations such as: (i) the anode material must not be influenced by corrosion during the electrochemical oxidation process; (ii) the anode must be cheap, highly conductive, and produce fewer metal ions. However, Anglada et al. reported that using metal anodes might result in metal ions in the solution; thus, this approach needs a separation step to recover the metallic species, as explained in Eq. (8-15) [42]. Graphite reaction has not been reported here because it does not release ions to the solution like Ni and Cu electrodes to form precipitates. These precipitates may refer to the formation of organometallic compounds in the presence of Ni and Cu ions, as represented here:

$$Ni^0 \rightarrow Ni^{2+} + 2e^- \quad (8)$$

$$2Cl^- \rightarrow Cl_2 + 2e^- \quad (9)$$

$$Cl_2 + H_2O \rightarrow OCl^- + H^+ + HCl \quad (10)$$

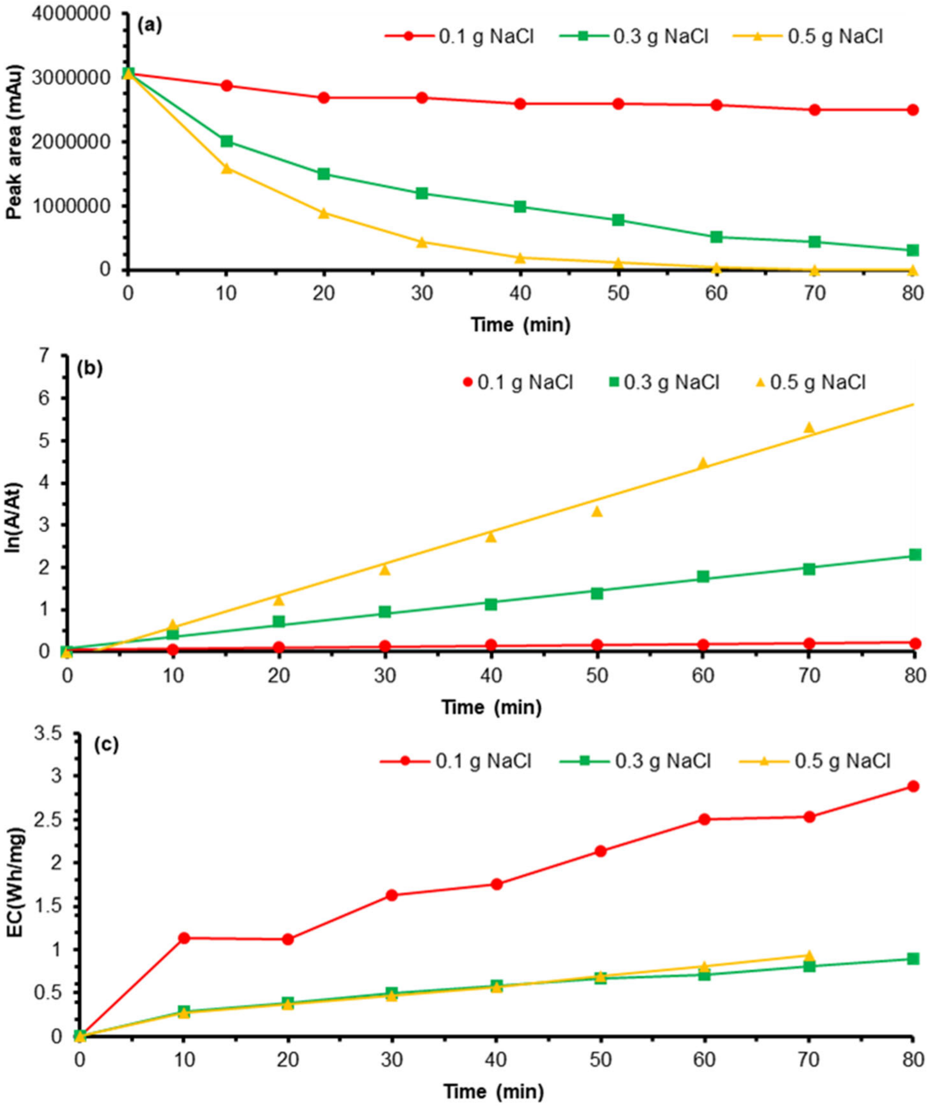


Fig 5. Effect of sodium chloride amounts on (a) the removal of carbamazepine; (b) pseudo-first-order kinetic model; (c) consumption energy model during the electrochemical process under these conditions (5 mg/L CBZ; 5 V; graphite as an anode)

$$Ni^{2+} + Cl_2/H_2O + O-C \rightarrow Ni[O-C]_{ppt} + CO_2 + H_2O + Cl^- \quad (11)$$

$$Cu^0 \rightarrow Cu^{2+} + 2e^- \quad (12)$$

$$2Cl^- \rightarrow Cl_2 + 2e^- \quad (13)$$

$$Cl_2 + H_2O \rightarrow OCl^- + H^+ + HCl \quad (14)$$

$$Cu^{2+} + Cl_2/H_2O + O-C \rightarrow Cu[O-C]_{ppt} + CO_2 + H_2O + Cl^- \quad (15)$$

where (O–C) is the organic compound.

It is well known that Ni^{2+} and Cu^{2+} ions were formed in the solution after the electrochemical oxidation process of nickel and copper anodes, respectively resulting in the generation of organometallic compounds. Graphite and platinum electrodes have not been discussed because they did not release ions in the solution. Therefore, the precipitates have not formed. The precipitates were only formed with nickel and copper electrodes and then washed in water. After that, they dried at room temperature for further characterization using EDX-FESEM. From Fig. 6, it could be observed that the intensities peaks for Ni and Cu (kα: 7.47 and kα: 8.04, respectively) are matched with energies listed in the energy table for EDX analysis. From EDX spectrum results, the elements on the surface of the precipitate were C, O, Cl, Na, Ni, and Cu, using Ni and Cu as anode electrodes. Of course, C and O are from organic content, while Cl and Na are from the electrolyte salt (NaCl). However, Ni and Cu were from material anodes. Consequently, graphite-PVC was selected as the best anode for further experiments for these considerations: (i) efficient conductivity material; (ii) inert to side chemical reactions; (iii) available; (iv) no elements released to the solution compared to Ni and Cu; (v) high removal efficiency.

Stability of Graphite Electrode

Graphite has been selected as the best anode material compared to other materials, including Ni, Cu, and Pt. However, as we know, graphite is carbonaceous, which means it suffers from corrosion when used for a long time. Hence, its stability has been tested after ten cycles of the electrochemical treatment process using SEM. It was clear from Fig. 7, that the morphology of graphite before and after electrochemical treatment is different. The surface becomes more scraped, and small holes are observed during the electrolysis period after electrochemical treatment. The electrochemical stability experiments were studied under these conditions: 0.5 g NaCl, 5 V, 5 mg/L of carbamazepine, and 60 min. The percent removal of carbamazepine ranged between 88% and 99% after ten cycles indicating that graphite is able to overcome all these challenges when used for a long time.

It could be concluded that CBZ can be easily degraded by the graphite even after ten cycles which means three hours of the electrochemical oxidation process. Graphite-PVC composite exhibited good stability and excellent results in terms of electrochemical efficiency as it acted as an electron transfer catalyst thanks to its excellent electrical conductivity [43].

EPX-CBZ Identification during the Electrochemical Degradation Process

As discussed previously, the percent removal of carbamazepine was more than 99% within 80-min electrolysis by applying different anode materials. To explore the degradation pathway of carbamazepine, the

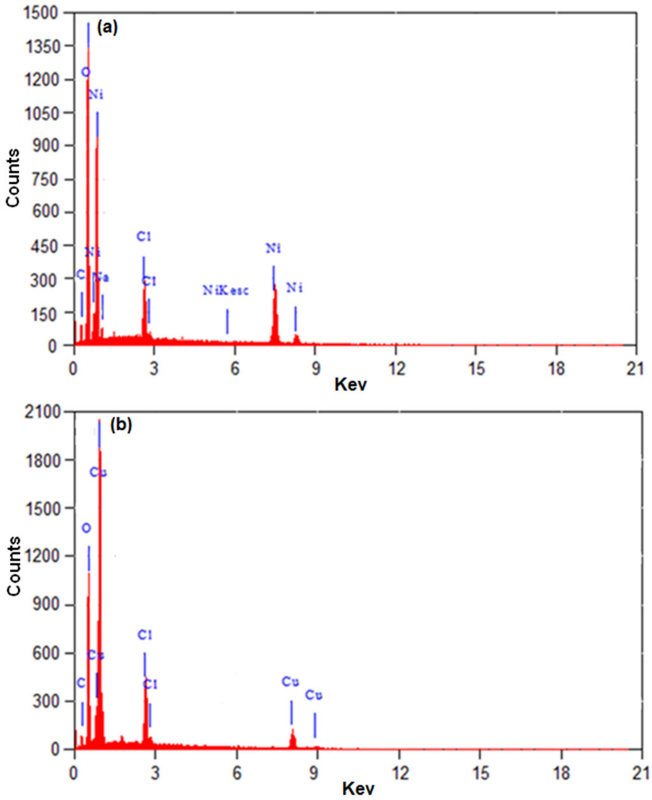


Fig 6. EDX-FESEM spectrums of (a) nickel and (b) copper after the electrochemical oxidation process of carbamazepine under these conditions: 5 mg/L CBZ; 5 V; 0.5 g NaCl

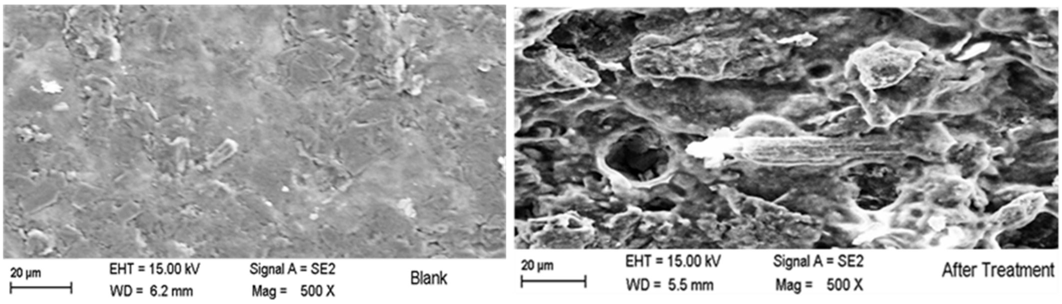


Fig 7. EDX mappings of graphite electrode before (left) and after ten cycles of electrolysis (right) under these conditions: 5 mg/L CBZ; 5 V; 0.5 g NaCl

formation of minor by-products during the synergetic process was detected by LC-TOF/MS analysis, and the results are shown in Table 2.

LC-TOF/MS is usually a crucial instrument in the electrochemical treatment process. This instrument was commonly used for qualitative and quantitative analysis after electrochemical degradation of the target compound. Further, it offers a rapid and accurate elucidation of the by-product structures in terms of the number of unsaturated bonds, number of rings, number of carbon, and so on. Due to the complexity of the detailed pathways, many intermediates, and the unavailability of standards, only the main by-product is illustrated and studied here. The determined EPX-CBZ and the proposed degradation process scheme of the electrochemical degradation of carbamazepine at 0.5 g NaCl, 5 V, and 200 µg/L spiked in 50 mL were provided.

To understand the oxidation behavior of carbamazepine on graphite and other material anodes, experiments were conducted in the presence of a standard compound of the main by-product EPX-CBZ.

It was observed that the intensity of EPX-CBZ is large enough using graphite and Pt anodes. In contracts, Cu and Ni anodes exhibited low intensity of EPX-CBZ. The main base peak was at *m/z* 275 and 7.621 min, which refers to $[M+Na]^+$ at all anode materials. It can be deduced that the main by-product 10,11-epoxycarbamazepine formed after hydroxylation of the olefinic double bond on the central heterocyclic ring of carbamazepine, generating an intermediate of carbocation that is responsible for forming the main by-product EPX-CBZ as shown in Scheme 1.

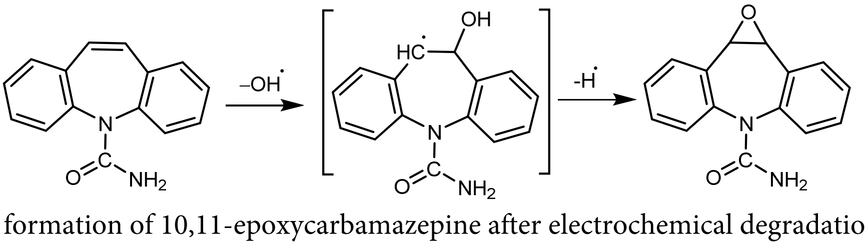
After identifying the optimized conditions for the formation of by-product EPX-CBZ through electrochemical degradation of carbamazepine and confirming no interference of EPX-CBZ, this method was validated using the external calibration curve standards of EPX-CBZ. Excellent linearity was obtained over the tested EPX-CBZ concentration ranges (10–1000 µg/L) of the linear equation "y = 481.5 × −4453". These results confirm the accuracy and reliability of using the oxidation products to quantify EPX-CBZ. The limit of quantification (LOQ, signal to noise (S/N) > 10) for the EPX-CBZ method was determined to be 0.109 µg/L.

In the electrochemical degradation process, 200 µg/L of carbamazepine was spiked in 50 mL of water and then electrochemically degraded. After that, every 10 min, the sample was withdrawn and then extracted using Oasis-HLB cartridges as described previously. Finally, all samples were injected into LC-TOF/MS for further analysis.

Table 2. Accurate mass measurements of the proposed by-products obtained by LC-TOF/MS after electrochemical of carbamazepine under these conditions: 5 V; 0.5 g NaCl; 200 µg/L of CBZ

Retention time (min)	Composition molecular ion	*m/z* ratio	Error (ppm)	S/N
7.621*	$C_{15}H_{12}N_2O_2$, $[M+Na]^+$	275.0821	1.1	340
8.216	$C_{15}H_{11}ClN_2O_2$, $[M+Na]^+$	309.0248	3.1	102
9.112	$C_{15}H_{14}N_2O$, $[M+Na]^+$	277.0700	1.7	114
10.485	$C_{15}H_{14}N_2O_3$, $[M+H]^+$	272.1480	0.4	84
11.012	$C_{15}H_{13}ClN_2O_3$, $[M+H]^+$	306.1082	−2.8	91

*EPX-CBZ is the main by-product



Scheme 1. proposed formation of 10,11-epoxycarbamazepine after electrochemical degradation of carbamazepine

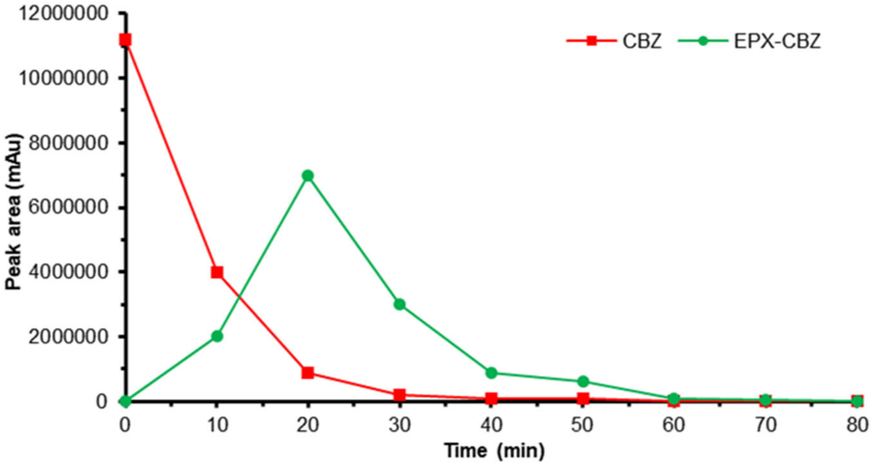


Fig 8. Monitoring 10,11-epoxycarbamazepine after electrochemical degradation of carbamazepine under these conditions: 5 volts; 0.5 g NaCl; 200 µg/L of CBZ

From Fig. 8, it could be observed that concentrations of EPX-BZ in the aqueous solution of treated carbamazepine differed from time to time due to appearance/disappearance reactions of EPX-CBZ in the solution. The lower EPX-CBZ concentration detected in the solution indicated a larger CBZ elimination. The varied detected concentrations of EPX-CBZ at different electrolysis times ranged from 13 to 142 µg/L. However, the highest concentration of EPX-CBZ was 142 µg/L at 20 min of electrolysis. The highest concentration of EPX-CBZ means the high consumption of CBZ at that time. It is important to note that at the far time of electrolysis, both EPX-CBZ and CBZ were almost eliminated and detected at the lowest concentration (below LOQ).

■ CONCLUSION

Electrochemical degradation of carbamazepine was carried out to optimize the influencing variables such as anode materials, applied voltage, and electrolyte amount was evaluated. The degradation efficiency of carbamazepine was achieved at more than 95% after 80 min electrolysis using graphite as anode under the optimal conditions with 0.5 g NaCl and 5 V. Copper and nickel as anode materials have shown minimum elimination of carbamazepine compared with graphite and platinum anodes. The supporting electrolyte sodium chloride was found to be effective for the elimination of carbamazepine, in which increasing of NaCl amount resulting high degradation rates from 0.0023 to 0.0758 min^{-1}. An increase in applied voltage resulted in increased degradation of carbamazepine accompanied by high consumption energy ranging from 0.4 to 1.5 Wh/mg. LC-TOF/MS analyzed and identified the main by-product 10,11-epoxycarbamazepine after different intervals using all selected anode materials. It was observed that the maximum yield was fooled by graphite anode compared to other anodes. EPX-CBZ was monitored for 80 min then after that, it was completely eliminated. The results obtained in this study show that electrochemical degradation is an efficient method for the degradation of carbamazepine and its main by-product 10,11-epoxycarbamazepine, in an aqueous medium. It could be concluded that graphite is the promising anode material electrode compared to copper, nickel, and platinum electrodes in terms of removal and consumption energy.

■ ACKNOWLEDGMENTS

The authors are very grateful for the financial support provided by Universiti of Al-Ameed (Karbala, Iraq). Many thanks to all staff at “Central Research for Instrumental Management, CRIM” for their continuous support.

■ AUTHOR CONTRIBUTIONS

Author (1) conducted full experimental work in terms of setting the electrochemical cell and collecting results. Author (2) has written the full paper and revised it well in terms of organization and presentation. Author (1) analyzed sharing with the author (2) the main by-product after electrochemical degradation using LC-TOF/MS.

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