Photoelectrocatalytic degradation of pharmaceutical carbamazepine using Sb-doped $Sn_{80\%}$-$W_{20\%}$-Oxide Electrodes

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Abstract

The continuous release of pharmaceutical compounds in the environment is of concern due to their potential toxicological effects on living organisms, even at low concentrations. The insufficient removal of bioactive contaminants such as pharmaceuticals by conventional wastewater treatment processes has led scientists to investigate and develop efficient technologies such as advanced oxidation processes (AOPs) to address the issue. The objective of the present work was to study the applicability of thermally-prepared Sb-doped $Sn_{80\%}$-$W_{20\%}$-oxide thin film coated electrodes for the photoelectrocatalytic degradation of a recalcitrant pharmaceutical compound, carbamazepine (CBZ). The efficiency of photolytic and photocatalytic processes for removal of CBZ were also evaluated for comparison. The formation of transformation products was investigated and the results showed lower levels of transformation products in the water treated by the photoelectrocatalytic method compared to the photolytic and photocatalytic methods, by the end of 60-min treatment. This suggests a potentially lower overall toxicity of the final solution treated by the photoelectrocatalytic method. An estimation of the energy consumption to reach an order of magnitude reduction in the concentration of CBZ for each type of process indicated a lower energy requirement for the photoelectrocatalytic method, with the highest energy efficiency observed at the applied current density of 6 mA/cm^2.

Keywords: Pharmaceuticals; Carbamazepine; Photoelectrocatalysis; Tin-tungsten-oxide; Wastewater treatment

1. Introduction

Over recent decades, increased awareness of impact of organic contaminants on the environment have stimulated research on wastewater treatment. The extensive production, consumption, and resulting discharge of organic products such as pharmaceuticals into the environment continuously deteriorate the quality of natural waters impacting the quality of drinking water supplies. Most of the pharmaceutically-active compounds (PhACs) and/or their bioactive metabolites enter water bodies via direct or indirect sources such as the indiscriminate discharge of pharmaceutical industry and hospital effluents or the urban and agricultural runoff [1]. These compounds are not fully eliminated during wastewater treatment and are consequently discharged into receiving water bodies [2, 3]. Detection of pharmaceuticals in groundwater [4, 5] and surface waters [6, 7], has been reported worldwide, in concentrations ranging from ng/L to μg/L. The low concentration of pharmaceuticals in aquatic environment is due to dilution effects, bio- and photodegradation, or sorption to sediments. Studies have shown that certain pharmaceuticals may pose various risks for aquatic organisms at such low concentrations [8, 9]. Biological treatment is commonly used for the removal of organic contaminants but this approach is not always suitable for the treatment of industrial wastewaters containing recalcitrant and toxic compounds that are resistant to biodegradation or negatively impact biological treatments [10]. The major concerns related to presence of pharmaceutical compounds in the environment include aquatic toxicity, development of antibiotic resistance in pathogenic bacteria, genotoxicity, and endocrine disruption [11]. To prevent the potential harmful effects of these pollutants and protect our drinking water resources, research efforts are being conducted to develop effective treatment technologies for their elimination and the minimization of their residual biological activity.

In particular, carbamazepine (CBZ) is one of the most frequently detected pharmaceuticals in wastewater treatment plant (WWTP) effluents [12, 13], surface water [14, 15], groundwater [16], and even in drinking water [2]. Carbamazepine is a widely prescribed antiepileptic drug with an estimated global consumption of 1,014 tons per year in 2008 [17]. The frequent occurrence of CBZ in aquatic environment (often found at 1 to 2 μg/L [14]) is also linked to the high persistence of the drug (practically non-biodegradable [18]) and inadequacy of the treatment methods applied in WWTPs, with removal efficiency usually below 10% [17]. In a classification scheme proposed by Joss et al. (2006) [19] for biological degradation of pharmaceuticals, CBZ was classified in the category "no removal". Because of potential adverse effects of CBZ on aquatic life [12] and the higher toxicity of some of its transformation products such as acridine [20], numerous efforts have been made in recent years to prevent the release of CBZ and its transformation products in the aquatic environment [17, 21]; however, there is still a need for the development of efficient treatment technologies for the removal of CBZ and its potentially hazardous transformation products.

Advanced oxidation processes (AOPs) have shown to be promising methods to remove many toxic and bio-recalcitrant organic compounds from water [10, 22, 23]. AOPs are chemical oxidation processes based on the *in situ* generation of highly reactive and non-selective oxidizing species such as hydroxyl radicals ($^{\bullet}OH$) with half-life of approximately 10^{-9} s [24]. These reactive species react efficiently with refractory organic compounds such as CBZ [22], leading to the destruction of the organic molecule. AOPs for water and wastewater treatment include electrochemical oxidation, ozonation, photocatalysis, ultrasonic radiation, Fenton and photo-Fenton processes, among which ozone-based techniques are the most commonly investigated methods followed by ultraviolet (UV) radiation-based techniques [25]. Combined AOPs such as

photoelectrocatalysis, which combines electrochemical oxidation and UV irradiation, provide higher efficiency for degradation of organic contaminants in aqueous solution [10, 26]. Photoelectrocatalysis offers several advantages such as modularity, portability, easy automation, low specific footprint, and the possibility of treating highly concentrated and bio-refractory wastes. Since the generation of oxidizing species such •OH radicals takes place at the anode surface, the nature of electrode materials is a key element in the photoelectrocatalytic treatment, governing the efficiency, stability, cost, catalytic activity and selectivity of the system [27].

Semiconductors can be used as promising electrode materials due to their ability to efficiently produce charge carriers (electron/hole pairs) by absorbing light [28, 29]. However, the main limitation in the use of semiconductors in photocatalytic processes is the recombination of photogenerated charge carriers (i. e. electrons/holes). To address this issue, many efforts have been made to minimize the recombination of electron/holes by applying techniques such as coupling semiconductors with the possibility of tuning their electronic band structures, or incorporating noble metals into their matrix [29]. Previous studies have investigated the applications of TiO_2 [30], RuO_2-IrO_2 [31], ZnO [32], SnO_2-Sb_2O_3/PbO_2 [33], Ti/PbO_2 [34] , SnO_2 [35], WO_3 [36], TiO_2-SnO_2 and TiO_2-WO_3 [37], and boron-doped diamond (BDD) [23, 34] as anode materials for the removal of organic contaminants through catalytic advanced oxidation processes.

To our knowledge, antimony-doped tin-tungsten oxide anode material has not yet been investigated for the elimination of organic pollutants from wastewaters. The aim of the present study was to evaluate the effectiveness of Sb-doped $Sn_{80\%}$-$W_{20\%}$-oxide electrode coatings synthesized *via* a thermal deposition method, as a photoelectrocatalyst for the removal of aqueous CBZ. A range of Sn/W-oxide compositions had previously been produced and characterized by our laboratory and evaluated for their capability for degradation of a model organic dye. Our results

showed that the Sb-doped $Sn_{80\%}$-$W_{20\%}$-oxide composition exhibited the highest intrinsic photoelectrocatalytic activity [38] and this composition was thus selected as the anode composition in the current study. For comparison purposes, the photolytic, photocatalytic and photoelectrocatalytic experiments were conducted to evaluate differences in the level of CBZ removal, apparent degradation kinetics and formation of transformation products (TPs). The effect of current density on photoelectrocatalytic degradation efficiency was investigated, and the energy consumption of each treatment strategy was also estimated.

2. Experimental

2.1. Electrode preparation

Sb-doped $Sn_{80\%}$-$W_{20\%}$-oxide anode coatings were fabricated on 50 mm × 100 mm × 2 mm flat titanium substrates *via* a thermal deposition method. The titanium substrates, which were used as the support for metal-oxide films, were pretreated before the deposition of the coatings in the following order: polishing using 600-grit SiC sandpaper, rinsing with acetone and sonicating in deionized water, and then etching in a boiling solution of HCl (37wt.%, Fisher) and water (1:1, v/v) for 45 min. For each coating, a coating precursor solution was prepared by adding metal salt solutions of $SnCl_2 \times 2H_2O$ (ACS reagent, ≥ 98.0%, Sigma Aldrich), $Na_2WO_4 \times 2H_2O$ (Certified ACS, 100.0%, Fisher), and $SbCl_3$ (ACS reagent, ≥ 99.0%, Sigma Aldrich) in proper amounts to yield a coating with a relative Sn/W molar composition of 80% Sn and 20% W. A small amount of Sb (~3 mol%) was always present in the coating solution, however this amount is not reflected in the coating abbreviation further in the text. All solutions in this work were prepared using Milli-Q water (resistivity: 18.2 MΩ.cm). To form a metal-oxide coating, the coating solution was painted onto the pretreated side of the Ti substrate, dried in an oven at 100°C for 10 min to evaporate the solvent, and then baked in an air furnace at 500°C for 10 min. This process was repeated ten times

to form a proper thickness of the coating. After the last application, the electrodes were annealed at 500°C for 2 hours to complete the formation of metal oxides.

2.2. Photoelectrochemical reactor

The photoelectrochemical reactor consisted of a 900-mL cylindrical beaker made of Pyrex glass with a Teflon lid to hold the cell components. The reactor was placed in a water bath to keep the temperature constant at 25°C during experiments. The Ti substrate coated with Sb-doped $Sn_{80\%}$-$W_{20\%}$-oxide thin film served as the working electrode (anode). Only one side of the anode was coated with the oxide, while the other side was covered by an electrochemically insulating tape. A 93 mm × 100 mm × 2 mm curved stainless steel plate (316L) served as the counter electrode (cathode). The electrodes were placed vertically in the cell facing each and 5.5 cm apart. Saturated calomel electrode (SCE) was used as the reference electrode. The electrodes were connected to a power source operated in the constant current mode during experiments. UV light irradiation was supplied by a 10W UV lamp (GPH212T5L, Atlantic Ultraviolet Corp.) with the maximum emission at 254 nm. The lamp was placed in the middle of the cell between the working and counter electrodes. 0.1 M potassium phosphate buffer solution at pH 7, prepared from KH_2PO_4 salt (ACS Certified, Fisher), was used as the supporting electrolyte. A thermometer was used to monitor the temperature of the solution in the reactor during experiments. Filtered air was blown into the reactor medium through a Pyrex gas dispersion tube (Fisher) to provide oxygen as an electron scavenger (to promote the redox reactions) as well as for mixing. The reactor was fully covered by aluminum foil to avoid exposure of the operator to UV light.

2.3. Degradation experiments

A stock solution of 10 mg/L carbamazepine (Powder, Sigma Aldrich) in 0.1 M potassium phosphate buffer (pH 7) was prepared. The solution was stirred for 24 hours and stored at 4°C to be used within 1-2 days. For each experiment, a certain volume of the stock solution was mixed with the supporting electrolyte to yield a 550-mL solution of 0.2 mg/L CBZ in 0.1 M potassium phosphate buffer. A freshly coated electrode was sonicated in deionized water for 20 min before each experiment to remove residual contamination from the surface of the electrode. Photolysis experiments were performed under UV irradiation. Photocatalysis experiments were performed under UV light irradiation while the electrodes were placed inside the cell without being connected to a power source. Furthermore, photoelectrocatalytic degradation experiments were performed under UV light irradiation and by applying different constant current densities of 1, 2, 4, 6 and 10 mA/cm^2. In each experiment, one sample was taken from the working solution before inserting the electrodes into the solution (namely, at $t < 0$) and one sample was taken after placing the electrodes inside the cell and before starting the experiment (at $t = 0$), to investigate the possible adsorption of dissolved organic molecules onto the electrode surfaces. Aliquots of 500 μL were taken from the solution at pre-determined intervals during the experiments over a 60-min period. The aliquots were then diluted with a water-methanol mixture (90:10, v/v) by a factor of 2 and then analyzed by Liquid Chromatography-High Resolution Mass Spectrometry (LC-HRMS) to determine the concentration of CBZ in the solution. Each experiment was performed in duplicates or triplicates.

2.4. Analysis of carbamazepine and transformation products (TPs)

The analysis was performed on an Accela 600 LC System (Thermo Scientific, Waltham MA, USA) in tandem with an LTQ XL Orbitrap mass spectrometer. Both the LC and the MS

systems were controlled by the ThermoXcalibur 2.0 software (Thermo Scientific, San Jose CA, USA). A 0.2 µm in-line filter unit followed by a guard column (5 mm × 2.1 mm ID; 1.8 µm) was used prior to the analytical column (50 mm × 2.1 mm ID; 1.8 µm C18 Zorbax Eclipse Plus) (Agilent Technologies, Santa Clara CA, USA). Separation of a 25 µL injection was conducted at 30°C with a binary buffer system composed of 2 mM ammonium formate and 0.1% formic acid in Mili-Q water (Solvent A) and methanol 0.1% formic acid (Solvent B). A gradient elution at 0.25 mL/min of A:B was conducted as follows; initial 90:10 (0-1 min), 65:35 (1-2 min), ramp to 60:40 (2-5 min), 0:100 (5-9 min) and hold at 100% B (9-12 min).

Detection of carbamazepine and its transformation products was performed using an electrospray ionization source (ESI) in positive mode. Optimization of the instrument parameters for quantification of carbamazepine was performed by direct infusion of a standard solution at 10 µL/min, while source optimization conditions were determined using infusion flow analysis. Nitrogen was used as sheath, auxiliary and sweep gas, while helium was used as the collision gas. Analysis was done on full scan mode at 30000 resolution for the FT-MS Orbitrap detector (*m/z* 50-500) while the ion trap was used to generate the MS2 spectra for confirmation of carbamazepine. Post-acquisition data processing was carried out for the detection of carbamazepine transformation products (TP) previously reported in the literature [20, 39-42]. The mass accuracy windows was set at ±10 ppm monoisotopic mass tolerance for molecular ion exact mass (M)+ or (M+H)+. Due to the absence of internal standards to identify the TPs based on their retention time, isomeric compounds could not be discriminated using a post-acquisition analysis and these TPs were grouped together.

3. Results and discussion

3.1. Photolytic vs. photocatalytic treatment: degradation efficiency and reaction kinetics

The photolysis experiments were performed under UV light irradiation in the absence of electrodes in the electrolyte, whereas the photocatalysis experiments were performed under UV irradiation in the presence of electrodes in the cell. In both cases, there was no current applied to the cell. Comparison of the CBZ concentration in the electrolyte before and after inserting the electrode into the solution revealed that the change in CBZ concentration in the solution due to a possible adsorption of dissolved molecules onto the electrode surfaces was negligible (< 5%). Fig. 1 shows decay of carbamazepine concentration as a function of irradiation time. After 60 min of UV treatment, 75% and 83% of initial carbamazepine (0.2 mg/L) was removed by photolysis and photocatalysis, respectively. However, the difference between the removal percentage of the two processes was not statistically significant (Student's t-test, $p > 0.05$). For both processes, the degradation was well-described by the pseudo-first-order reaction kinetics ($R^2 \geq 0.98$) over the whole 60-min treatment time. The corresponding apparent kinetic rate constants, k_{app}, were equal to 0.022 min^{-1} and 0.029 min^{-1} for photolytic and photocatalytic degradation, respectively (not significantly different, as per Student's t-test, $p > 0.05$).

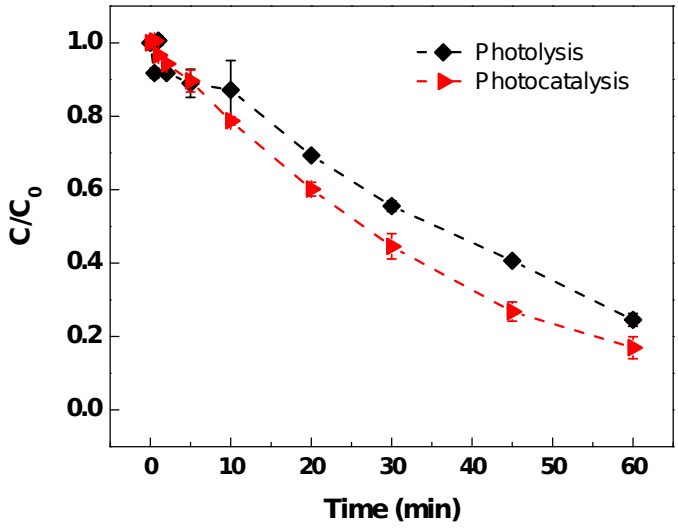


Fig. 1. Carbamazepine concentration as a function of treatment time during photolytic and photocatalytic carbamazepine oxidation; $[CBZ]_0$ = 0.2 mg/L. Error bars represent the difference between the mean value and upper/lower values of the range (n = 2).

3.2. Photoelectrocatalytic degradation

Photoelectrocatalytic degradation experiments were carried on a 0.2 mg/L carbamazepine solution in a three-electrode configuration at different current densities of 1, 2, 4, 6 and 10 mA/cm^2 and constant light intensity. The dependence of the CBZ removal kinetics on the applied current density is shown in Fig. 2a. The kinetics of CBZ degradation increased with an increase in applied current density up to 6 mA/cm^2 and then the degradation rate levelled off in the range of 6 to 10 mA/cm^2. The initial increase in kinetics might be due to an increasing number of oxidative species (*e. g.* hydroxyl radicals) formed at the electrode-electrolyte interface. However, after a threshold value is reached, the extra energy provided by the increased current will unfavorably serve to produce oxygen rather than additional oxidizing species [43]. In addition, mass transport of CBZ to the electrode surface at high current densities might become a rate-determining-step, leading to

a constant CBZ oxidation rate. It also worth noting that the apparent kinetics of CBZ degradation depends not only on the current density, but also on the electrolyte volume to electrode surface area ratio, which is the case for heterogeneous catalytic reactions. Thus, the time needed to fully oxidize CBZ can conveniently be shortened by increasing the anode surface area.

The kinetic analysis revealed the pseudo-first-order kinetic ($R^2 \geq 0.98$) for the initial photoelectrocatalytic degradation of CBZ (within the first 5 min of degradation reaction) at different current densities. The apparent photoelectrocatalytic degradation initial rate constants, k_{app}, are summarized in

Table **1**. The positive effect of current density on k_{app} was pronounced, indicating the beneficial impact of the increased current density on the degradation kinetics. However, when the rate constant is normalized with respect to the current density, a decrease in normalized initial apparent rate constant is obtained (Fig. 2b). This indicates that with an increase in current density, there is also an increased portion of current that is used for some parallel processes. Given that only the CBZ concentration was monitored in these experiments, it is possible that formation of CBZ transformation products were part of these parallel processes as well as oxygen evolution.

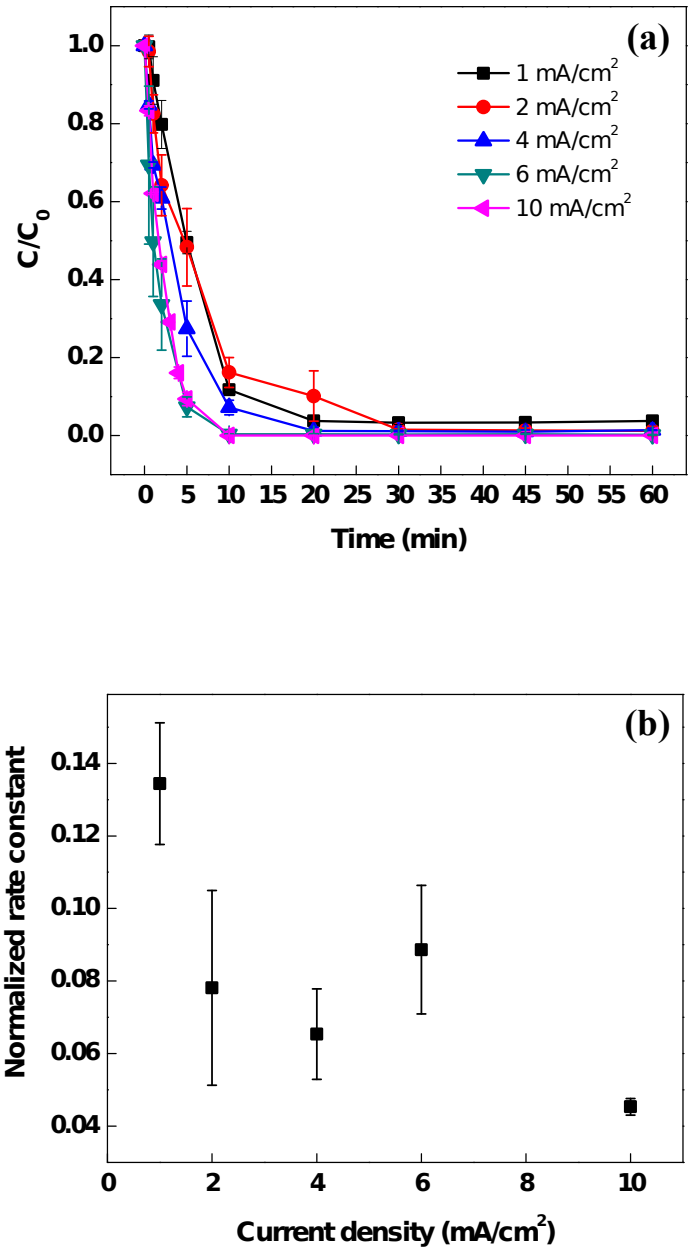


Fig. 2. (a) Concentration decay over 60 min and (b) normalized apparent initial rate constant with respect to the current density, for the photoelectrocatalytic degradation of carbamazepine at different current densities using Sb-doped $Sn_{80\%}$-$W_{20\%}$-oxide coated anodes; $[CBZ]_0$ = 0.2 mg/L. Error bars represent the difference between the mean value and upper/lower values of the range (n = 3).

Table 1

Apparent initial kinetic rate constants, k_{app}, for photoelectrocatalytic degradation of carbamazepine in potassium phosphate buffer (pH 7) at different current densities using Sb-doped $Sn_{80\%}$-$W_{20\%}$-oxide coated anodes; $[CBZ]_0$ = 0.2 mg/L. Data represent mean values ± the difference between the mean and upper/lower values of the range (n = 3).

Current density (mA/cm^2)	Apparent rate constant, k_{app} (min^{-1})
1	0.13 ± 0.02
2	0.16 ± 0.05
4	0.26 ± 0.05
6	0.53 ± 0.11
10	0.45 ± 0.02

3.3. Identification of transformation by-products (TBPs)

To evaluate the applicability of the photoelectrocatalytic treatment method for the removal of CBZ, the analysis of transformation products is necessary as they can be found at higher concentrations and/or exhibit ecotoxicological activity than the parent compound [44]. Several studies have demonstrated that some compounds produced from photodegradation of carbamazepine may pose important risks to human health and the environment [45, 46]. Samples collected for the different treatments investigated (photolysis, photocatalysis and photoelectrocatalysis) were analyzed for the detection of transformation products of CBZ. In the case of photoelectrocatalysis, only samples from experiments performed at the lowest and highest current densities (1 and 10 mA/cm^2) were analyzed. The CBZ transformation detected are summarized in Table 2. None of the TPs were detected in the stock solution or at time 0.

Table 2

List of carbamazepine transformation products detected.

Analyte	Formula	Ions	Exact mass	Reference(s)
10,11-dihydro-10,11-epoxycarbamazepine	$C_{15}H_{12}N_2O_2$	[M+H]+	253.0977	[39]
2-hydroxycarbamazepine	$C_{15}H_{12}N_2O_2$	[M+H]+		[39, 41]
3-hydroxycarbamazepine	$C_{15}H_{12}N_2O_2$	[M+H]+		[39, 41]
TP266	$C_{15}H_{10}N_2O_3$	[M+H]+	267.0770	[41]
1-(2-benzadehyde)-(1H,3H)-quinazoline-2,4-dione	$C_{15}H_{10}N_2O_3$	[M+H]+		[20, 40]
TP223	$C_{14}H_9NO_2$	[M+H]+	224.0712	[41]
acridone-N-carbaldehyde	$C_{14}H_9NO_2$	[M+H]+		[20]
9-carboxylic acid-acridine	$C_{14}H_9NO_2$	[M+H]+		[42]
9(10H)-acridone	$C_{13}H_9NO$	[M+H]+	196.0765	[20, 42]
9-hydroxy-acridine	$C_{13}H_9NO$	[M+H]+		[20]
acridine	$C_{13}H_9N$	[M+H]+	180.0814	[20]
acridine 9-carbaldehyde	$C_{14}H_9NO$	[M+H]+	208.0757	[20]
TP251	$C_{15}H_{11}N_2O_2$	[M]+	251.0821	[41]
TP268	$C_{15}H_{12}N_2O_3$	[M+H]+	269.0926	[41]

For the treatment of CBZ solution by UV radiation (photolysis only), the TPs *m/z* 251.1 and *m/z* 253.1 were detected in addition to carbamazepine (*m/z* 237.1) (Fig. 3a). The detected TP *m/z* 251.1 was reported as 1-(2-benzaldehyde)-4-hydro-(1H,3H)-quinazoline-2-one (BQM) [40] and may be a mono-keto derivative of a hydroxylated compound [47]. The *m/z* 253.1 response corresponds to 10,11-dihydro-10,11-epoxycarbamazepine [48]. In Fig. 3. Carbamazepine transformation products for various treatment conditions (a) photolysis, (b) photocatalysis, (c) photoelectrocatalysis at 1 mA/cm2, and (d) photoelectrocatalysis at 10 mA/cm^2. Anode: Sb-doped $Sn_{80\%}$-$W_{20\%}$-oxide coated electrodes; $[CBZ]_0$ = 0.2 mg/L; pH 7.

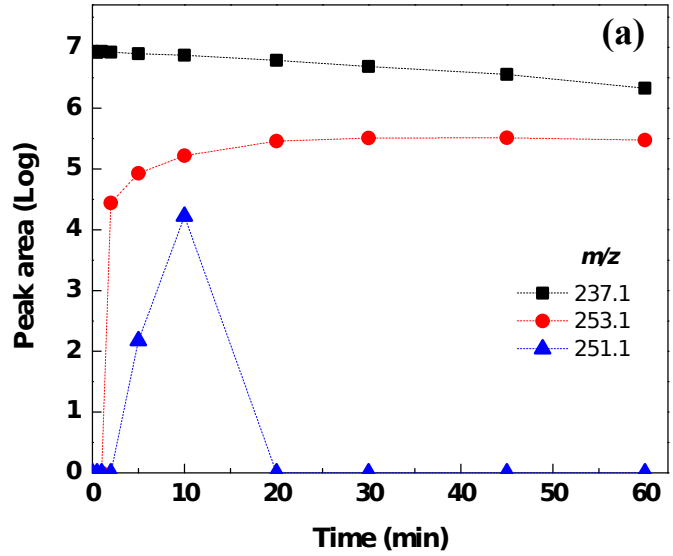
a, the fact that the TP *m/z* 253.1 remains unchanged after 30 min while carbamazepine (*m/z* 237.1) concentration continue to decrease and the TP *m/z* 251.1 has already been degraded

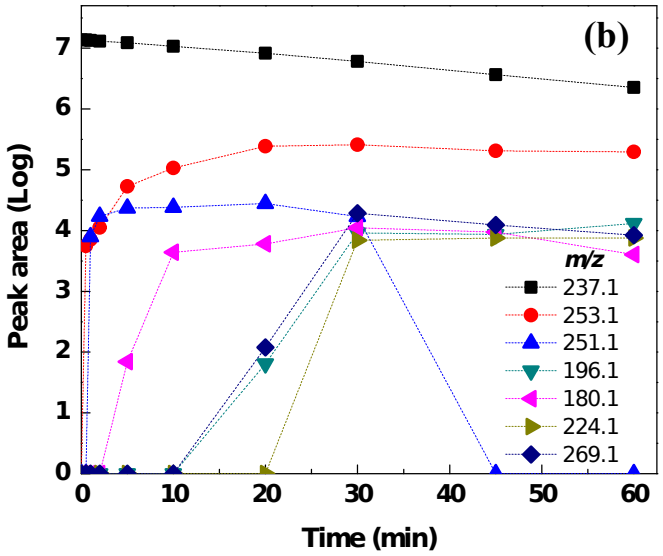
suggests that carbamazepine is oxidized into other transformation products that were not investigated in this study.

Fig. 3b shows the transformation products formed during photocatalysis. In addition to the products detected for photolysis, TPs *m/z* 196.1, *m/z* 180.1, *m/z* 224.1, and *m/z* 269.1 were detected. The molecular ion identified at *m/z* 224.1 was considered to be 4-aldehyde-9-acridone, according to Li et al. (2013) [49] and Hübner et al. (2014) [50]. This compound was characterized by two fragment ions of *m/z* 196.1 (loss of CO) and *m/z* 180.1 (loss of CO_2) [51], well-known as 9(10H)-acridone and acridine, respectively. Acridine, a stable azaarene compound, is a highly toxic compound with known mutagenic and carcinogenic activity [45]. Donner et al. (2013) [52] demonstrated that the carbamazepine transformation products acridine and acridone were shown to be significantly more toxic than the parent compound across three standardized ecotoxicity assays using bacteria *Vibrio fischeri*, algae *Pseudokirchneriella subcapitata*, and cladoceran *Daphnia magna*, with acridone reported to be less toxic than acridine across all three assays. The molecular weights of some transformation products being greater than CBZ imply the addition of oxygen into the molecular structure [47]. As can be seen in Fig. 3b, the photocatalytic degradation of CBZ led to the formation of transformation products, including acridine and acridone which remain in solution even after 60 min of treatment. This observation indicates that the photocatalytically-treated solution is potentially more toxic than the initial solution as it contains compounds more toxic than CBZ. However, concentrations of these toxic TPs were not determined.

The analysis of aliquots from photoelectrocatalytic degradation of carbamazepine at a current density of 1 mA/cm^2 (Fig. 3c), led to detection of the same TPs as those formed during photolysis (Fig. 3a). However, both *m/z* 251.1 and *m/z* 253.1 compounds first increased and then

decreased until disappearance after 20 min of photoelectrocatalysis. As shown in Fig. 3d, relatively more transformation products were detected during photoelectrocatalytic process carried out at a higher current density, 10 mA/cm^2. The TP *m/z* 267.1 was identified as 1-(2-benzaldehyde)-(1H,3H)-quinazoline-2,4-dione (BQD) [40] and formed as a result of oxidation of hydroxy-groups of di-hydroxylated compound (CBZ + 2OH, *m/z* 271.1) [36]. The TP *m/z* 208 was identified as acridine 9-carbaldehyde [20], which is considered to have higher cytotoxicity than carbamazepine. Furst et al. (1995) [53] demonstrated that this compound caused 40% death in lymphocytes while carbamazepine had no effect on the viability of cells. As can be seen in Fig. 3d, the transformation products were detectable in samples taken from the solution within 30 s to 5 min of treatment, as carbamazepine concentration was constantly decreasing, confirming their formation as the combined effects of UV-irradiation and the electrical current. However, acridine and acridone as well as other products disappeared after 10 min of photoelectrocatalysis, implying that they had higher transformation rates than production rates afterwards. The results showed that the photoelectrocatalytic process at a current density of 10 mA/cm^2 led to an appreciable reduction in the amount of detectable transformation products concurrently with reduction in carbamazepine concentration when compared to photolytic and photocatalytic processes alone. It is therefore probable to expect a lower toxic response for this case; however, cell or whole organism based bioassays should be performed to verify this hypothesis.


(a)
Peak area (Log)
Time (min)
m/z
237.1
253.1
251.1


(b)
Peak area (Log)
Time (min)
m/z
237.1
253.1
251.1
196.1
180.1
224.1
269.1

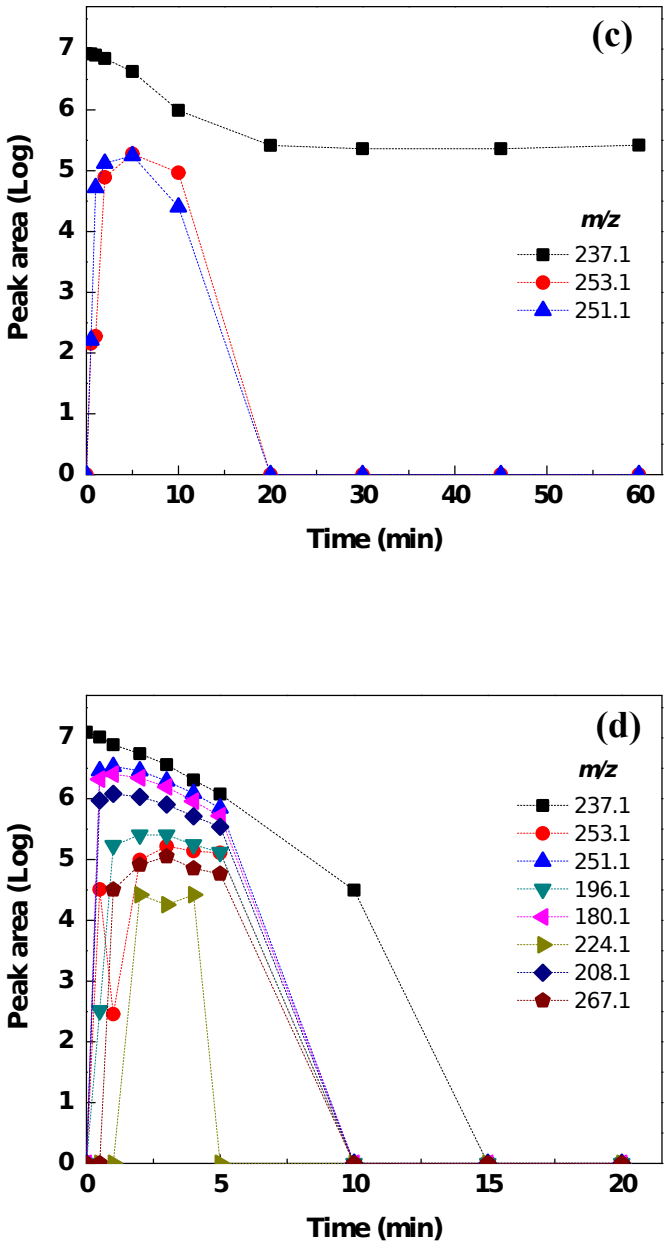


Fig. 3. Carbamazepine transformation products for various treatment conditions (a) photolysis, (b) photocatalysis, (c) photoelectrocatalysis at 1 mA/cm2, and (d) photoelectrocatalysis at 10 mA/cm^2. Anode: Sb-doped $Sn_{80\%}$-$W_{20\%}$-oxide coated electrodes; $[CBZ]_0$ = 0.2 mg/L; pH 7.

4. Energy consumption

To assess the cost-effectiveness and overall performance of an alternative treatment technology, evaluation of the energy requirement of the process is necessary. In general, the energy consumption of AOPs depends on experimental parameters including the nature and concentration of the target contaminant, configuration of the reactor, and the type of the light source (if any) [54]. In this work, only for comparison purposes, the total energy consumption during a process was estimated as the sum of the electrical energy used and the input power of the UV lamp. An estimate of the electrical energy consumption per volume of treated solution (kWh/m^3) was calculated using the following equation [55]:

$$E_{Electrical} = \frac{Current\ (A)\ \times\ Time\ (h)\ \times\ Cell\ Voltage\ (V)}{1000\ \times\ Treated\ Volume\ (m^3)} \quad (1)$$

Assuming the first-order CBZ degradation kinetics, the UV input energy (kWh/m^3) was calculated for all three processes using the following equation [54]:

$$E_{UV} = \frac{Lamp\ Power\ (W)\ \times\ Time\ (h)}{1000\ \times\ Treated\ Volume\ (m^3)} \quad (2)$$

The $E_{Electrical}$ and E_{UV} have been defined as the energy required to reach 90% removal or, in other words, one order of magnitude reduction in the concentration of the pollutant. The treatment time required to reach the desired level of degradation was obtained from the plot of log C/C_0 versus time (for photolysis and photocatalysis, the values were estimated by extrapolation). Fig. 4 presents the total energy consumption for photolytic, photocatalytic, and photoelectrocatalytic degradation of 0.2 mg/L carbamazepine to reach 90% removal. Results revealed that photolytic and photocatalytic processes required much greater treatment time and energy input (32 and 24 kWh/m^3, respectively) than the photoelectrocatalytic process to reach a certain degree of CBZ

removal. These results are similar to those obtained in another study to remove 90% of 0.01 mg/L carbamazepine by photochemical treatment employing UV light (22.7 kWh/m^3) [56]. This observation implies that the electrochemical oxidation played a more important role in removal of the organic pollutant than the photochemical oxidation. The electrochemical oxidation is mainly controlled by the transfer of electrons and the consequent production of charge carriers at the electrode surface, whereas the photochemical oxidation is mainly controlled by the mass transport of generated oxidants to the bulk solution. Since at high current densities the degradation reactions become diffusion-limited, the contribution of photochemical energy (E_{UV}) to the oxidation of CBZ decreases relative to the electrochemical energy ($E_{Electrical}$) (Fig. 4). In photoelectrocatalytic processes, the total energy consumption decreased with increasing applied current density up to 6 mA/cm^2 as the required treatment time decreased. In other words, the photoelectrocatalytic process with the current density of 6 mA/cm^2 had the lowest energy requirement and, thus, the highest degradation efficiency for the removal of carbamazepine under the conditions of this work. These results confirm the findings of the above-mentioned degradation kinetic analysis, and are comparable with the energy requirement of UV/H_2O_2 processes for 90% removal of 0.01 mg/L carbamazepine as reported in the literature [56, 57]

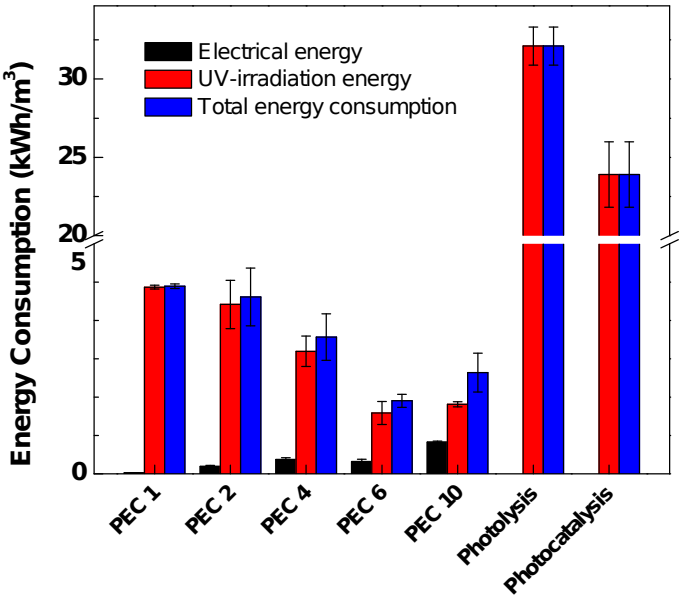


Fig. 4. Estimation of the energy consumption to reach 90% removal of carbamazepine by different treatment processes; $[CBZ]_0$ = 0.2 mg/L. PEC 1 to 10 refer to photoelectrocatalytic processes at current density of 1 to 10 mA/cm^2. Error bars represent the difference between the mean value and upper/lower values of the range (n = 3).

5. Conclusions

The Sb-doped $Sn_{80\%}$-$W_{20\%}$-oxide coated anode was found to be a good candidate for the photoelectrocatalytic oxidation (removal) of carbamazepine (CBZ) present in an aqueous electrolyte. The CBZ degradation rate increased with increasing applied current density, but then levelled off after reaching a threshold value. Acridine and acridone, two transformation products of CBZ with known ecotoxicological effects, were identified as TPs in water subjected to photocatalytic and photoelectrocatalytic (at 10 mA/cm^2) treatments but these compounds were further oxidized (removed) in the photoelectrocatalytic process at longer treatment times, before complete removal of CBZ was achieved, and within the 60-min treatment time. The UV-based

treatment processes in the absence of applied current, exhibited much lower efficiency for the removal of CBZ compared to the simultaneous use of UV irradiation and electrical current (the photoelectrocatalytic process). During photoelectrocatalysis, the contribution of the electrochemical oxidation to the removal of CBZ was found to be more significant than that of the photochemical oxidation. Results demonstrated that the Sb-doped $Sn_{80\%}$-$W_{20\%}$-oxide anode is a promising photoelectrocatalyst for effective and energy-efficient degradation of CBZ in neutral aqueous environment. The findings of this study also further demonstrate the importance of a careful consideration of the formation of transformation products and residual toxicity while assessing the potential of new treatment technologies for the removal of recalcitrant contaminants.

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