Int. J. Electrochem. Sci., 12 **(2017)** 12112 – 12124, doi: 10.20964/2017.12.700

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

Electrochemical Degradation of Lincomycin in Prepared and Environmental Aqueous Matrices

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Received: 23 September 2017 / *Accepted:* 27 October 2017 / *Published:* 12 November 2017

This study focuses on the performance of lincomycin (LC) electro-degradation in terms of LC degradation and total organic carbon (TOC) removal efficiencies. The LC degradation and TOC removal under several parameters, such as electrolytic cell (undivided vs. divided), current density, anode material (BDD, PbO_2, and Pt), and real environmental water matrix (municipal wastewater treatment plant secondary effluent (MWTPSE), groundwater (GW), and river water (RW)) were investigated and discussed. The results show that the electrochemical degradation of LC followed pseudo-first-order kinetics and the LC degradation efficiency and TOC removal increased with the increase in current density. The performance of LC degradation and TOC removal on the tested electrodes was in the order BDD > PbO_2 > Pt. The faster LC degradation occurred in the undivided cell, but the TOC removal was better in the divided cell. At 0.5 A/cm^2 and 25°C in 1 M Na_2SO_4, the apparent rate constants of LC degradation were 5.23×10^{-3} and 2.33×10^{-3} s^{-1} in the undivided and divided cells, respectively. Using this electrochemical oxidation process could completely mineralize the LC and TOC in the three different environmental matrices with the order GW > RW > MWTPSE.

Keywords: lincomycin; pharmaceuticals and personal care products (PPCPs); electro-degradation; boron-doped diamond electrode

1. INTRODUCTION

Over the past few decades, antibiotic residues in the environment have received great attention due to their occurrence in aquatic ecosystems having long-term adverse biological impacts and raising potential risks to the related ecosystems and public health [1, 2]. Some reports also show that residual antibiotics can promote the selection of genetic variants of microorganisms resulting in the occurrence of antibiotic resistant pathogens [3, 4]. Many antibiotics are difficult to degrade and thus appear to be quite persistent [5]. They are only partially eliminated in sewage treatment plants (STP), and are found in significant amounts in STP effluents and surface water [5–7]. Lincomycin (LC) is generally used in both human and veterinary medicine to act against gram-positive bacteria [8–10], and it is one of the antibiotics that is frequently found in surface waters and STP effluents [11, 12]. For instance, LC concentrations approaching 250 ng/L were found in the River Po (Italy) [11]. Moreover, in Taiwan, up to 70% detection frequency was found in six potential contamination sources, and the medium concentration was 56760 ng/L in animal husbandries [12]. This level of LC contamination noticeably exceeded the trigger value (10 ng/L) suggested by an environmental risk assessment of medicinal products in the EU [13].

The LC present in water may cause the spread of antibiotic resistant pathogens and antibiotic resistant genes in aquatic environments, and lead to public health problems. In the past few years, many researchers have studied the input, occurrence, fate, and effects of antibiotics in the environment, but only a few of them have addressed the control and removal of antibiotics from the aquatic environment.

The removal of LC from aqueous solution was performed previously by using photodegradation [14] or hydrogen peroxide [15]. Although LC could be completely removed by the photocatalytic method, the photocatalytic mineralization rate was slow; for instance, it took over 10 h to achieve complete mineralization of 50 mg/L LC [14]. Using hydrogen peroxide can make LC completely disappear, although it does not undergo complete oxidation [15].

In the past few years, electrochemical oxidation processes have received much attention because pollutants can be directly oxidized by an electron transfer reaction from organics to the electrode surface and/or indirectly oxidized by highly reactive hydroxyl radicals (•OH) electro-generated on the anode surface with a high O_2 evolution overpotential. •OH is the most oxidizing species that can effectively carry out the degradation and mineralization of persistent organic pollutants in water and wastewater [16, 17]. In this manner, a wide variety of anode materials, such as platinum (Pt) [18–20], PbO_2 [21, 22], dimensionally stable anodes (DSA) [18, 23], and boron-doped diamond (BDD) [24–26], have been employed for treating organic pollutants. Moreover, to the best of our knowledge, little attention has been paid to the electrochemical oxidation of LC in different environmental water media. Therefore, in this study, we examined the removal of LC from different environmental aqueous solutions by electrochemical oxidation. The effects of important operating parameters on the electrochemical degradation of LC, such as electrolytic cell, anode material, current density, and solution matrix were investigated. The obtained data are helpful to preliminarily evaluate the degradation and mineralization of LC in real aquatic environments with regard to using electrochemical processes.

2. MATERIALS AND METHODS

2.1. Reagents

Figure 1 displays the chemical structure of lincomycin (LC) hydrochloride ($C_{18}H_{34}N_2O_6 \cdot HCl$) used in the experiments. The LC was purchased from Sigma-Aldrich Co., Ltd. (USA) and used without further purification. Acetonitrile and methanol (HPLC grade solvent) and sodium tetraborate were purchased from ECHO Chemical Co. Ltd. (Taiwan) and J.T. Baker (USA), respectively. Lead(II) nitrate and sodium sulfate were purchased from Showa Co. Ltd. (Japan).

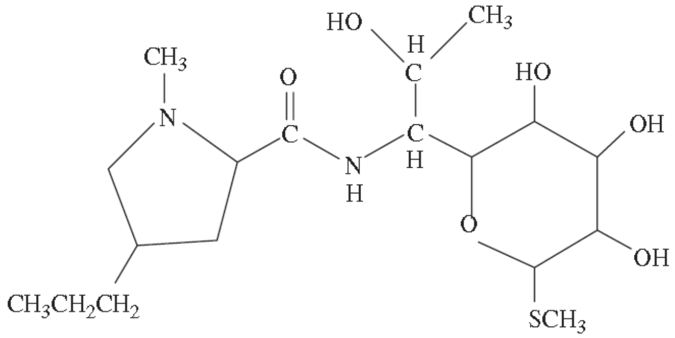


Figure 1. Molecular structure of lincomycin (LC) [27]

2.2. Characteristic of the real environmental aqueous matrices

The real environmental matrices were collected in Pingtung County, Taiwan (Table 1). After collection, samples were kept refrigerated before experiments.

Table 1. Characteristics (organic matter parameter concentration (mg/L), pH, and conductivity (EC, μs/cm)) of the tested environmental matrices municipal wastewater treatment plant secondary effluent (MWTPSE), groundwater (GW), and river water (RW)) without lincomycin (LC) addition.

Parameter	BOD	COD	TOC	pH	EC	Cl^-
MWTPSE	10.4	21	7.8	7.26	2030	495
RW	2.4	5.0	2.9	7.29	544	20
GW	0.3	2.0	1.3	6.69	193	2.2

2.3. Electrolytic systems for the degradation of LC

The electro-oxidation of LC in aqueous solutions was performed using an undivided or divided thermostatted electrochemical cell. When the undivided electrochemical cell (a glass beaker) was tested, the electrolyte was 1M Na_2SO_4 100 mL with 100 mg/L LC. For the divided cell H-type, the anode and cathode compartments were separated by an ion-exchange membrane separator (Nafion 212). The anolyte (100 mL) was LC (100 mg/L) in 1 M Na_2SO_4 or a LC-spiked real environmental matrix (Table 1), while the catholyte was only 1 M Na_2SO_4. The degradation of aqueous LC was carried out under various operating conditions (electrolytic cell, anode material, current density, and aqueous matrix). Three different electrodes (projected area = 2 cm^2) (Pt, boron-doped diamond (BDD/Nb (CONDIAS, Germany)), and a lab-prepared PbO_2 electrode [28]) were individually used as the anode, whereas a stainless-steel plate (SS 304) acted as the cathode for the electrolysis/degradation of LC. All the electrolytic experiments were performed using a DC power supply (Good Will Instrument CO., LTD, Taiwan, GPS-2303). The cell voltage and current were monitored over time based on the readings of the DC power supply.

2.4. Cyclic voltammetry (CV) of LC

Cyclic voltammetry (CV) was used to investigate if LC could be directly electro-oxidized on BDD in 1 M Na_2SO_4 solution. The CV measurements were conducted using a CHI 660B electrochemical workstation (CH Instruments, Inc., USA) connected to a personal computer. The BDD electrode tested in the electrolytic measurements was also used as the working electrode, while the counter electrode was a platinum wire, and the reference electrode was Ag/AgCl (3 mol KCl dm^{-3}, 0.207 V vs SHE (standard hydrogen electrode) at 25^oC). The potential scan (100 mV/s) of CV was conducted over the range of -0.2 to 2.0 V (vs Ag/AgCl).

2.5. Chemical analysis

The quantitative determination of LC was performed using an HPLC (Hitachi Chromaster 5420) equipped with a Mightysil RP-C18 column (250 mm × 4.6 mm, particle size, 5μm). A mixture of acetonitrile, methanol, and an aqueous solution (50 mM) of sodium tetraborate (20:20:60 v/v) was used as the eluent at the flow rate of 1.5 ml/min. The injection volume was 20 μL and the working wavelength for quantitative analysis was 214 nm. The retention time of LC was determined to be 4.7 min. The mineralization of the LC was monitored by determining the total organic carbon (TOC) (Shimadzu 5000 Model TOC analyzer).

3. RESULTS AND DISCUSSION

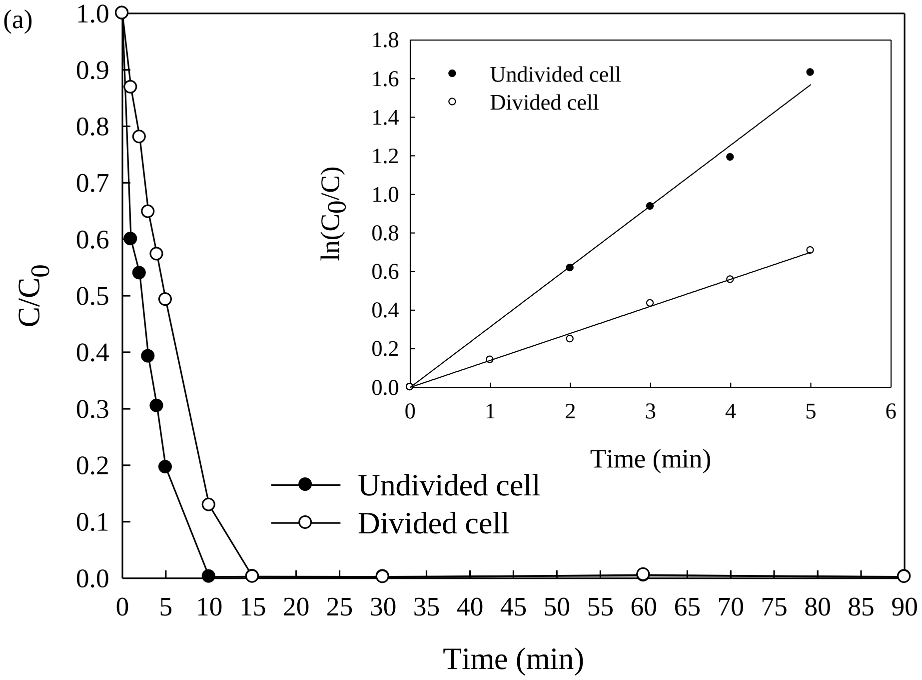
3.1. Effect of electrolytic cell on the degradation of LC

The type of electrolytic cell usually influences the electrochemical degradation of organic compounds. Hence, in this study, we tested two different electrolytic cells (divided and undivided) to investigate their performance with regard to LC degradation and TOC removal. Figure 2 shows the effects of the electrolytic cell on LC degradation and TOC abatement by using a PbO_2 anode. The LC degradation efficiency was lower in the divided cell than in the undivided one. During the electrolytic process, the reduction of LC also took place in the undivided cell by the nucleophilic addition reaction due to the nucleophile (OH^-) generated at the cathode electrode, which might attack the carbonyl group of LC to undergo a nucleophilic addition reaction (forming the alcohol group), making LC disappear rapidly. A faster LC degradation was thus obtained in the undivided cell than in the divided one. In both cases, the degradation of LC was completed within 15 min. According to earlier reports, the degradation of organics by electrochemical processes generally follows the pseudo-first-order reaction kinetics; for example, the degradation of 3,6-dichloro-2-methoxybenzoic acid (dicamba) using an electro-Fenton process [29], the electrochemical oxidation of salicylic acid [30], ofloxacin [31] or N,N-diethyl-m-toluamide (DEET) on BDD [32]. The obtained data were very well fitted to the corresponding straight lines (R^2 = 0.995−0.996) (Figure 2a inset). If the concentration of •OH does not change significantly, such a reaction can be regarded as a pseudo-first order one and written as follows [31,32].

$$\frac{-d[LC]}{dt} = k[LC][\bullet OH] = k_{app}[LC] \qquad (1)$$

Therefore, the pseudo-first-order kinetic equation was used to determine the apparent degradation rate constant (k_{app}) of LC. The calculated k_{app} were 5.23×10^{-3} and 2.33×10^{-3} s^{-1} at the undivided and divided cells, respectively. Di Paola et al. [33] also reported that the decomposition of lincomycin chiefly relied on •OH and followed a pseudo-first-order kinetics, although they used TiO_2 and UV light to oxidize LC. In contrast, Qiang et al. [34] concluded that the free amine group and sulfur group of LC were attacked by ozone with absolute second-order rate constants of 2.76×10^{6} and 3.26×10^{5} 1/M·s for neutral and monoprotonated forms, respectively. Moreover, Andreozzi et al. [35] indicated that the second-order kinetic constants for attacking lincomycin were 10^4 orders greater by •OH (4.37×10^{9} 1/M·s at pH = 5.5 and 4.59×10^{9} 1/M·s at pH = 7.5) than by ozone (1.53×10^{5} 1/M·s at pH = 3.0 and 4.93×10^{5} 1/M·s at pH = 6.7).

Figure 2b clearly shows that the TOC removal was better in the divided cell than in the undivided one, although the TOC removal efficiencies in these two cells were similar at initial stage of electrolysis time ($t \leq$ 15 min). After 60 min electrolysis, the LC mineralization efficiency of >80% was achieved in the divided cell; however, that in the undivided cell was less than 40% at the same experimental conditions.



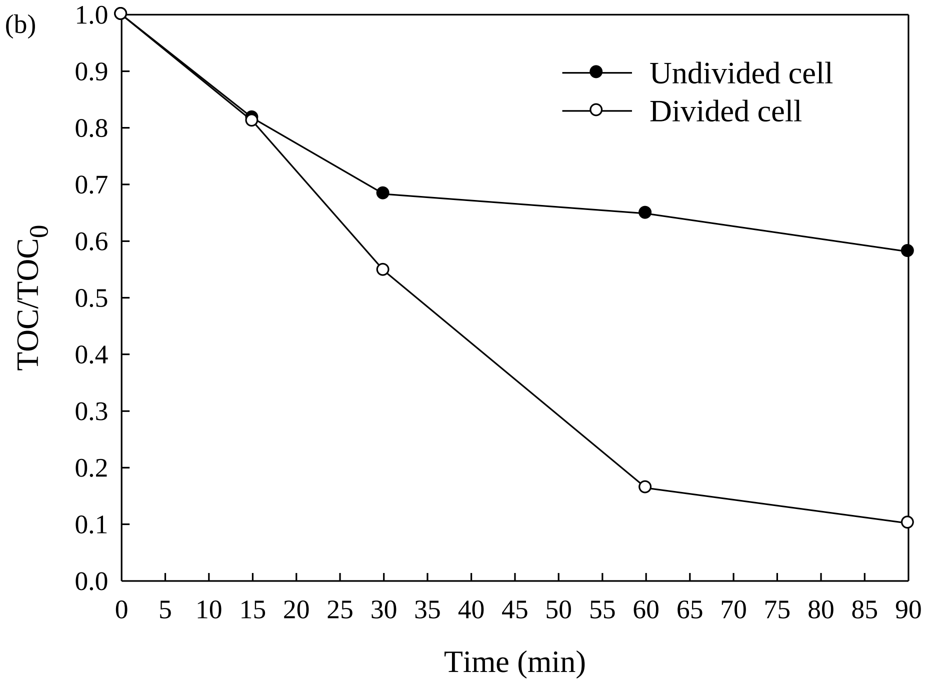


Figure 2. Effect of electrolytic cell on (a) lincomycin (LC) degradation (inset: ln(C_o/C) against time) and (b) TOC abatement (anode, PbO_2; current density, 0.5 A/cm^2; electrolyte, 1 M Na_2SO_4; $[LC]_o$ = 100 mg/L; *T*, 25°C; separator, Nafion 212).

This finding can be interpreted as showing that with the increase of electrolysis time, some oxidized LC and its electro-oxidation intermediates might be reduced at the cathode electrode to result in lower TOC removal in the undivided cell. Another possible reason is that solution pH might also influence the TOC removal, because the anolyte of the divided cell was more acidic than the electrolyte of the undivided cell during electrolysis. In terms of LC degradation and mineralization, the divided cell is more suitable than the undivided one. Accordingly, the former was used to carry out the subsequent tests in this study.

3.2. Effect of anode material on the degradation of LC

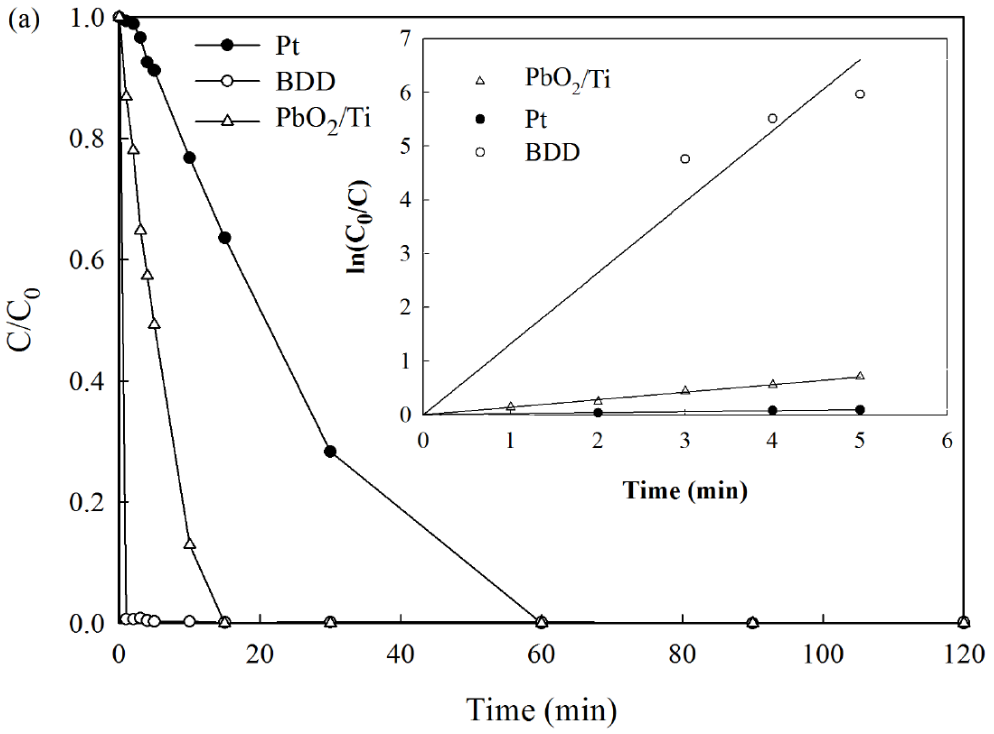
It is well known that the degradation and mineralization efficiency of organics is strongly dependent on anode material. Figure 3a presents a comparison of the trend of C/C_o ratio during the oxidation of 100 mg/L LC using three different anodes (BDD, PbO_2, and Pt) at 0.5 A/cm^2 and 25^{o}C. As can be seen from the figure, the complete degradation of LC occurred in a very short electrolysis period ($t < 5$ min) on BDD, whereas it needed 15 and 60 min for PbO_2 and Pt, respectively. The calculated apparent rate constants (k_{app}) were in the order BDD > PbO_2 > Pt (2.20×10^{-2}, 2.33×10^{-3}, and 3.10×10^{-4} s^{-1}, respectively) based on the plots shown in the inset of Figure 3a ($R^2 = 0.995-0.996$). This finding is associated with the nature of the electrode. The Pt is regarded as an active anode, while the BDD and PbO_2 are non-active anodes; in general, the organic oxidation is much more effective on a non-active anode than on an active one, because the generation of •OH is more efficient for the former than for the latter [29−32, 36−39]. The formation of •OH on BDD and its reaction with the organic compound (R) can be described as Reactions 2 and 3, respectively [36,37].

$$\mathrm{BDD} + \mathrm{H_2O} \rightarrow \mathrm{BDD}(\bullet\mathrm{OH}) + \mathrm{H}^+ + e^- \quad (2)$$

$$\mathrm{BDD}(\bullet\mathrm{OH}) + \mathrm{R} \rightarrow \mathrm{BDD} + m\mathrm{CO_2} + n\mathrm{H_2O} + \mathrm{H}^+ + e^- \quad (3)$$

The electro-oxidation of LC was also found to have first order kinetics at the anode surface of Ti/Pt, DSA, graphite, or three-dimensional (3D) GAC in 0.02 N Na_2SO_4, but these oxidation kinetics were slow, mainly due to difficult deprotonation which preceded the primary electron transfer of the oxidation process [40]. Note that the LC abatement was better on our Pt than on the aforementioned Ti/Pt. The deprotonation was easier on BDD via Reactions 2 and 3. It was reported that lincomycin was very difficult to oxidize, even at high electrode potential and in the presence of NaCl as an electrolyte on active anodes (e.g., Ti/Pt, DSA, and graphite), regardless of the Pt's high electrocatalytic activity towards organic oxidation due to the strong tendency of organic species (especially aromatic hydrocarbons) to adsorb on the platinum electrode surface [40].

Figure 3b shows a comparison of the trends of the TOC/TOC_0 ratio during the oxidation of 100 mg/L LC on the three anodes at the same operating conditions. It was observed that after 120 min electrolysis, a TOC removal efficiency ($(1 - TOC/TOC_0) \times 100\%$) of 100% was obtained on the BDD anode, whereas the TOC removal efficiencies were similar and low, at only about 18%, on the PbO_2 and Pt anodes. This should be related to the fact that compared with PbO_2 and Pt, the electro-generated hydroxyl radicals were more weakly adsorbed on BDD and consequently more reactive towards organic oxidation reactions, as stated in the discussion of LC electro-degradation [24,36].



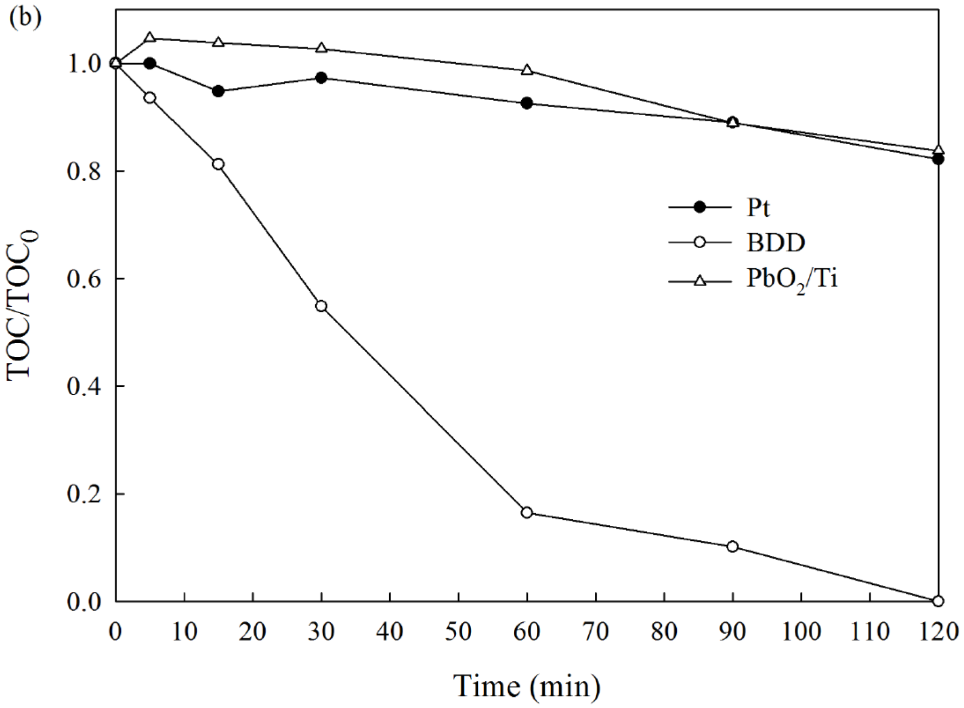


Figure 3. Effect of anode material on (a) LC degradation (inset: ln(C_o/C) against time) and (b) TOC abatement (current density, 0.5 A/cm^2; electrolyte, 1 M Na_2SO_4; $[LC]_o$ = 100 mg/L; *T*, 25°C; separator, Nafion 212).

Some earlier researchers also indicated that BDD electrodes were superior to Pt and PbO_2 anodes for the electro-oxidation of organic pollutants [32,38,39].

3.3. Cyclic voltammetry (CV) tests and effect of current density on the degradation of LC

The oxidation of organics by the electro-generated •OH is more efficient than the direct degradation of organics on the BDD anode [36]. However, in this study, no LC oxidation peak was detected in the cyclic voltammetry (CV) tests using the BDD electrode (Figure 4), so it is inferred that the oxidation of LC mostly relied on the •OH formed on the BDD anode surface. Carlesi Jara et al. also did not detect any clear oxidation peak on anodic materials (Ti/Pt, DSA, graphite, and 3D GAC electrodes) tested in acid solutions using the CV method, and they indicated that this was related to the effect of substituting nitrogen inside the aromatic framework, which made the lincomycin molecule more difficult to be oxidized [40]. The anodic peak at 1.56 V vs Ag/AgCl should be related to the oxidation of sulfate to persulfate [39,40], which is also useful for the degradation/oxidation of organic compounds, although persulfate is less powerful than •OH for organic oxidation because of the lower oxidation potential for persulfate (2.12 V vs. SHE) than for •OH (2.80 V vs. SHE) [41,42]. Despite the difference in material nature between active and non-active electrodes, hydrogen peroxide is another possible electro-generated oxidant in Na_2SO_4 electrolyte when using active [43] and non-active electrodes [44], but the consumption of H_2O_2 is very fast, likely due to its decomposition with formation of •OH radicals, so it can hardly affect the oxidation process [40].

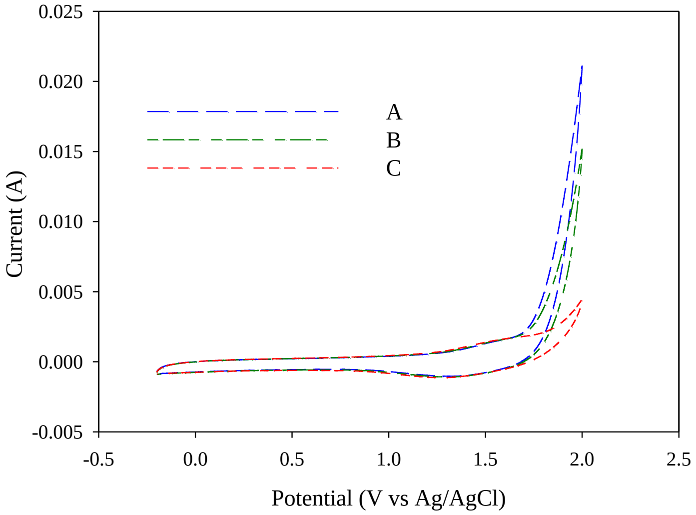


Figure 4. Cyclic voltammograms (scan rate = 100 mV) of (a) 1 M Na_2SO_4 (b) 1 M Na_2SO_4 + 25 ppm LC, and (c) 1 M Na_2SO_4 + 50 ppm LC for BDD at 25 °C.

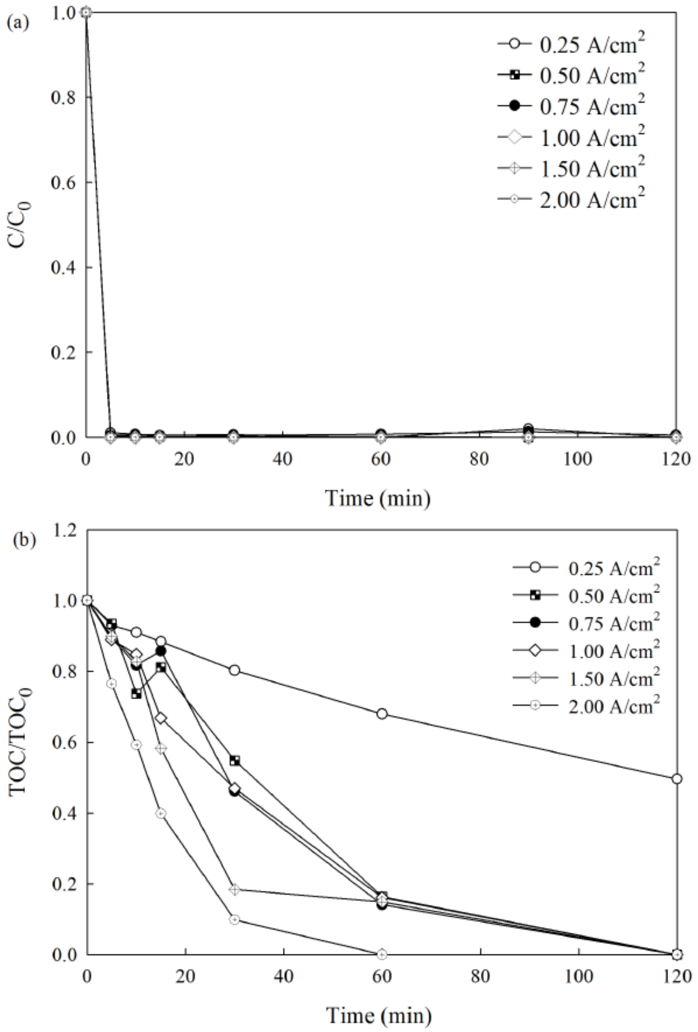


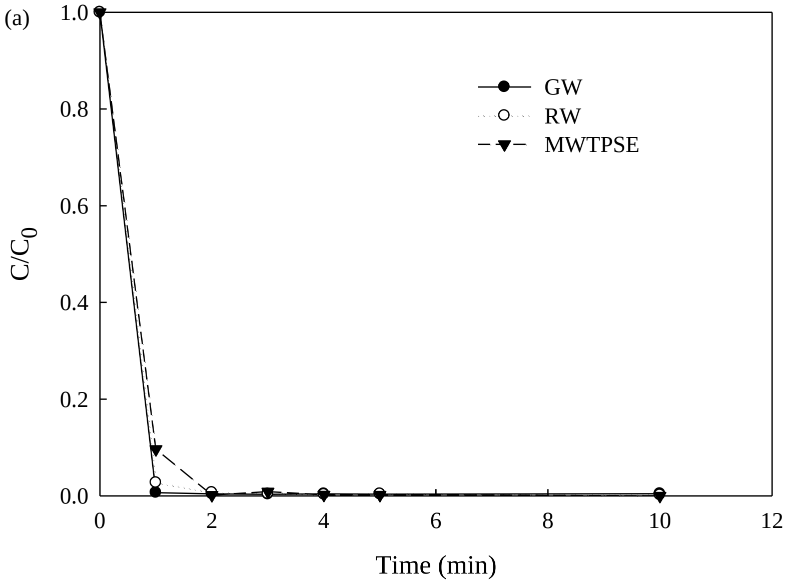
Figure 5. Effect of current density (0.25−2.0 A/cm^2) on (a) LC degradation and (b) TOC abatement at BDD anode ($[LC]_o$ = 100 mg/L; electrolyte, 1 M Na_2SO_4; *T*, 25°C; separator, Nafion 212).

The concentration of •OH on BDD is usually associated with the applied current density (I_{appl}). Figure 5a shows the effect of I_{appl} (0.25–2.0 A/cm^2) on the LC abatement for the oxidation of 100 mg/L of LC on the BDD anode. As can be seen from this figure, for all cases, the degradation of LC was rapid with 100% degradation efficiency at 5 min. Moreover, it is noted that the TOC abatement increased with increasing I_{appl}. For example, nearly 100% TOC removal could be accomplished at I_{appl} = 2.0 A/cm^2 for 60 min electrolysis time, whereas it only achieved 33% of TOC removal at 0.25 A/cm^2 (Figure 5b). This result is attributed to the greater generation of •OH with an increasing I_{appl}. In this context, the production of persulfate might also increase the degradation LC and its decomposition intermediates, and thus TOC removal.

3.4. Effect of environmental water matrix on LC degradation

In order to understand the effect of a real environmental water matrix on the electrochemical degradation of LC, three 1 M Na_2SO_4 and LC-spiked samples (municipal wastewater treatment plant secondary effluent (MWTPSE), groundwater (GW), and river water (RW)) were tested at the same operating conditions to evaluate degradation and mineralization efficiencies. Without LC addition, the original LC concentrations of the three matrices were all below the method detection limit.

Figure 6a shows that the degradation efficiency of LC was very fast for all cases, and the degradation efficiency of LC followed the order GW > RW > MWTPSE within 2 min at 1.5 A/cm^2 and 50°C. This result is related to the fact that the concentration of organic matter parameters in terms of biochemical oxygen demand (BOD), chemical oxygen demand (COD), or total organic carbon (TOC), was in the order MWTPSE > RW > GW (Table 1). As a consequence, some of the hydroxyl radicals generated from water electrolysis were used to oxidize the organic compounds originally present in the matrices. After 3 min electrolysis, LC was 100% removed in the tested environmental water matrices.



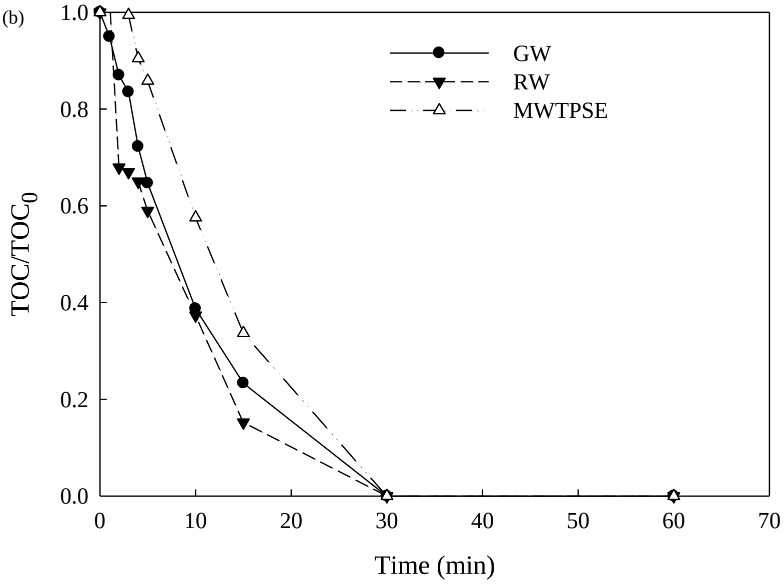


Figure 6. Effect of environmental water matrices on (a) LC degradation and (b) TOC abatement (anode, BDD; electrolyte, 1 M Na_2SO_4; current density, 1.5 A/cm^2; $[LC]_o$ = 100 mg/L; *T*, 50°C).

It is noted that the TOC was totally removed from each of tested environmental matrices after 30 min electrolysis. Therefore, the LC and other TOC originally present in the environmental aqueous matrices can be completely mineralized through the electrochemical oxidation process in a short time. The results indicate that the adopted electrochemical approach is a useful advanced oxidation process which can rapidly and effectively mineralize the organic pollutants (including LC) in different environmental aqueous matrices.

4. CONCLUSIONS

The electrochemical removal of LC conducted at different operating conditions suggests that the degradation and mineralization efficiency of LC increased with increasing current density, and the performance of the tested anodes for LC degradation and mineralization was in the order BDD > PbO_2 > Pt. The LC degradation was faster in the undivided cell than in the divided cell. In contrast, the higher TOC removal efficiency was observed in the divided cell. At 0.5 A/cm^2 and 25°C in 1 M Na_2SO_4 solution, the k_{app} of LC degradation were 5.23×10^{-3} and 2.33×10^{-3} s^{-1} in the undivided and divided cells, respectively.

A comparative study of LC-spiked different environmental water matrices (GW, RW, and MWTPSE) shows that the electrochemical oxidation process is effective for LC and inherent organic compound mineralization in the environmental water matrices, with the order GW > RW > MWTPSE. The complete mineralization of LC was achieved in the three different environmental matrices for 30 min electrolysis on BDD.

ACKNOWLEDGMENTS

The authors would like to thank the Ministry of Science and Technology, Taiwan for financially supporting this research under Grant Nos. MOST 102−2221−E−020−001−MY3 and 106-2221-E-020-003-MY3.

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