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# Electrochemical Degradation of Tetracycline on BDD in Aqueous Solutions

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This study focuses on the electrochemical oxidation of tetracycline hydrochloride (TC-HCl) on a boron-doped diamond (BDD) anode under different operating parameters (current density, temperature, TC initial concentration, and sample matrix). For comparison, a commercial Pt planar electrode and a self-prepared $PbO_2$ electrode were also tested. According to cyclic voltammetric analysis, the oxidation of TC on BDD was electrochemically irreversible. The degradation efficiency of TC increased with increasing current density or temperature, but decreased with increasing initial TC concentration. The BDD anode was superior to the $PbO_2$ and Pt electrodes for TC degradation and total organic carbon (TOC) removal. At 0.1 $A/cm^2$ and 25°C, the pseudo-first-order rate constants of TC electro-degradation on BDD were $1.26\times10^{-3}$ and $1.10\times10^{-3}$ $s^{-1}$ in 0.1 M $Na_2SO_4$ solution and municipal wastewater treatment plant secondary effluent, respectively. The sample matrix influenced more on TOC removal than on TC degradation.

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**Keywords:** boron-doped diamond electrode; tetracycline hydrochloride; electrochemical; degradation

## 1. INTRODUCTION

Over the past few years, pharmaceutical residues in the environment have received increasing attention due to their continuous input and persistence to the aquatic ecosystem, causing long term potential adverse impacts on the ecosystems and human health [1, 2]. Among various pharmaceuticals, antibiotics are one of the largest groups of pharmaceutical compounds widely used in human (domestic and hospital use) and veterinary medicines to treat diseases and promote growth [3]. The estimated amounts of annual antibiotics usage are between 100,000 and 200,000 t globally [4]. Among antibiotics, tetracyclines (TCs) are the second most common antibiotic group, in both production and usage [5]. Due to their antibacterial nature, traditional biological methods cannot destruct TC effectively [6]. Various TC removal efficiencies were reported for secondary wastewater treatment plants (WWTPs) in different areas. For example, TC was removed by 85% in an urban WWTP in Colorado [7], while the TC removals were 24–36% at two WWTPs in Hong Kong [8] and 66–90% at four WWTPs in Taiwan [9, 10]. Residues of TC have been frequently detected in the effluent of wastewater treatment plants [11], surface waters [12, 13] and sediments [11], which poses an increasing potential risk to human health and ecosystem safety. Therefore, it is greatly in need of new alternatives with better TC removal in WWTPs.

Recently, the removal of TC has been studied by some methods such as chlorine or chlorine dioxide oxidation [3], ozonation [14], and photo-catalytic degradation [15]. However, potential carcinogenic by-products may be formed during chlorination or ozonation [16]. Although ozonation and photo-catalysis processes can rapidly oxidize TC, incomplete mineralization probably occurs. It was reported that for TC degradation, the maximum removal efficiency of TOC was 40% after 2 h ozonation [17] and the 60% mineralization after 1 h photocatalysis [18]. Moreover, the use of photocatalysis to eliminate bio-recalcitrant organic compounds might produce intermediates more toxic than the parent compounds [19, 20]. Through the aid of electrochemically generated hydroxyl radicals (•OH) on anodes, electrochemical processes are also efficient for the treatment of wastewater containing refractory and toxic organic pollutants [21].

Pt, $PbO_2$, and BDD electrodes are commonly employed in the study for organic pollutant degradation. Among these anodes, BDD is a relatively new anode material and has received greater attention than the other two types of electrodes because it has several technologically important characteristics such as extremely high $O_2$ evolution overvoltage, inert surface for adsorption, strong oxidation power, and remarkable corrosion stability even in strongly acidic media [22, 23]. BDD anodes may achieve complete mineralization of organic pollutants (e.g., 17β-estradiol (E2) [24], bisphenol A (BPA) [25], acetaminophen [26], and estriol (E3) [27]). Therefore, in this work we explored the electrochemical degradation of TC under different temperatures, current densities, initial TC concentrations, and solution matrixes. The electro-degradation of TC on Pt and $PbO_2$ were also tested for comparison.

## 2. MATERIALS AND METHODS

### 2.1. Reagents

Figure 1 shows the chemical structure of tetracycline hydrochloride ($C_{22}H_{24}N_2O_8 \cdot HCl$) (TC-HCl) (Sigma-Aldrich) used in the experiments. Acetonitrile and oxalic acid (HPLC reagent grade) were purchased from ECHO Chemical Co. Ltd. (Taiwan). In each run, the stock solution of TC-HCl was freshly prepared with deionized water and then it was added into electrolyte (sodium sulfate, SHOWA Co. Ltd. (Japan)) to meet the required concentration for experiment.

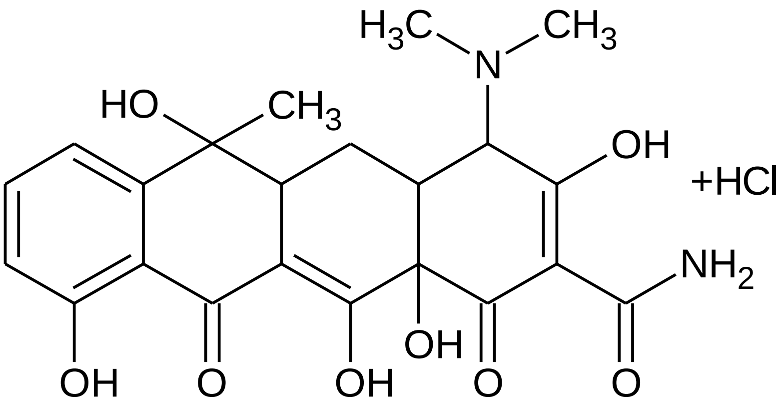

**Figure 1**. Molecular structure of tetracycline hydrochloride (TC-HCl).

### *2.2. Effluent from sewage treatment plant*

To evaluate the matrix effect on TC-HCl degradation, real samples of municipal wastewater treatment plant secondary effluent (MWTPSE) were collected. In the MWTP, the sewage from ~240,000 inhabitants is treated based on an activated sludge process. After collection, samples were kept refrigerated and then used in experiments as soon as possible. The composition of MWTPSE is provided in Table 1.

**Table 1.** Characteristics (total organic carbon (TOC), biological oxygen demand (BOD), conductivity, oxidation-reduction potential (ORP), and pH) of the municipal wastewater treatment plant secondary effluent (MWTPSE)

| Parameter | TOC (mg/L) | BOD (mg/L) | Conductivity (μs/cm) | ORP (mV) | pH |
|---|---|---|---|---|---|
| Value | 87 | 8 | 613 | 240 | 7.60 |

### *2.3. Electrochemical measurement*

The electrochemical behaviors of TC in prepared solutions were investigated using cyclic voltammetry (CV). The potential scan range was -0.6↔1.8 V (starting/ending at -0.6 V and scan rate = 100 mV/s) for the CV measurements. A CHI 660B electrochemical work station connected with a personal computer was used to conduct the voltammetric measurements. The working electrode was a BDD electrode with an area of 1 $cm^2$ and the counter electrode was a platinum wire. An Ag/AgCl electrode (3 M KCl, 0.207 V vs SHE (standard hydrogen electrode) at 25°C) was used as the reference electrode.

### *2.4. Electrolytic systems for the degradation of TC*

In this work, the electrolyses were performed in an open, and thermostatted divided cell, and each electrolyte was well stirred using a magnetic stirrer. The anode (area = 1 $cm^2$) was a planar Pt, boron-doped diamond (BDD, thin-film deposited on a niobium substrate (CONDIAS, Germany), or a self-prepared $PbO_2$ electrode. A Ti plate with a projected area of 1 $cm^2$ was used as the cathode. The anolyte (100 mL) was TC-HCl (25, 50, or 75 mg/L) in 0.1 M supporting electrolyte ($Na_2SO_4$) while the catholyte was only the 0.1 M $Na_2SO_4$. The anode and cathode compartments were separated by a Nafion-212 ion-exchange membrane separator. Prior to use, the Nafion-212 was heated at 65°C in 1 M (~3%) $H_2O_2$ for 1 h to remove organic impurities. Afterward, the membranes were washed three times with deionized distilled water (DDW) and stored in DDW. The electrochemical degradation of TC-HCl was conducted under constant current using a direct current (DC) power supply (Good Will Instrument Co. Ltd. GPS-2303). The cell voltage and current were monitored with time based on the readings of DC power supply.

### *2.5. Chemical analysis*

The samples of electrolysis were taken at intervals. The residual TC and total organic carbon (TOC) concentrations of samples were analyzed by a high-performance liquid chromatograph (HPLC) instrument (Hitachi Chromaster 5420) and a TOC analyzer (Shimadzu TOC-5000), respectively. The separations in the HPLC were performed on a RP-C18 column (250 mm×4.6 mm, particle size, 5μm). The mobile phase was acetonitrile/0.01 M oxalic acid (31:69, v/v), with a flow rate of 1 mL/min. The injection volume was 20 μL and the working wavelength for quantitative analysis was 365 nm. A personal computer equipped with a Hitachi chromaster system manager for HPLC systems was used to acquire and process chromatographic data. The retention time of TC was determined to be 6.7 min. The linear fitting of calibration curve yielded an $R^2$ value of 0.999. The specific energy consumption ($Ec$, in kWh/kg-TC) for TC degradation was calculated as follows [21],

$$Ec = IVt/\Delta m_{TC} \qquad (1)$$

where, $V$ is the average cell voltage (V), $I$ is the current (A), $t$ is the electrolysis time (h) and $\Delta m_{TC}$ is the mass of degraded TC (g).

According to TOC data, the mineralization current efficiency (MCE) for an electrolyzed solution at a given time (h) can be calculated by Eq. 2 [28].

$$MCE(\%) = \frac{nFV_s\Delta(TOC)_{\exp}}{4.32\times 10^7\, mIt}\times 100 \qquad (2)$$

where $n$ is the number of electrons consumed in the mineralization process, $F$ is the Faraday constant (96,487 C/mol), $Vs$ is the solution volume (L), $(TOC)_{exp}$ is the experimental TOC decay (mg/L), $4.32\times10^7$ is a conversion factor (= 3600 s/h × 12,000 mg of C/mol), and $m$ is the number of carbon atoms (22) in a TC molecule. The $n$ is 90 for the total mineralization of TC, assuming that the overall mineralization of the TC involves its conversion into $CO_2$, and mainly $NH_4^+$ from N degradation via the following reaction:

$$C_{22}H_{24}N_2O_8 + 36H_2O \rightarrow 22CO_2 + 2NH_4^+ + 88H^+ + 90e^- \qquad (3)$$

## 3. RESULTS AND DISCUSSION

### 3.1. Cyclic voltammetric analysis of TC on BDD electrode

Fig. 2 presents the cyclic voltammograms obtained for 0.1 M $Na_2SO_4$ solutions (supporting electrolyte) with and without 100 mg/L TC at a scan rate of 100 mV/s. In the absence of TC in 0.1 M $Na_2SO_4$, a small shoulder can be detected at about 1.5 V vs. Ag/AgCl. This is attributed to the oxidation of sulfate to persulfate [29]. When TC was present in the supporting electrolyte, a clear anodic peak at ~1.6 V vs. Ag/AgCl with a peak current remarkably higher than that of background solution (0.1 M $Na_2SO_4$) was mainly due to the contribution of TC oxidation. Possibly, aromatic intermediates might be formed in the oxidation process [21]; however, during the reverse scan from 1.8 to −0.6 V, no corresponding reduction peak could be identified, suggesting that the electrochemical oxidation of TC on BDD was totally irreversible.

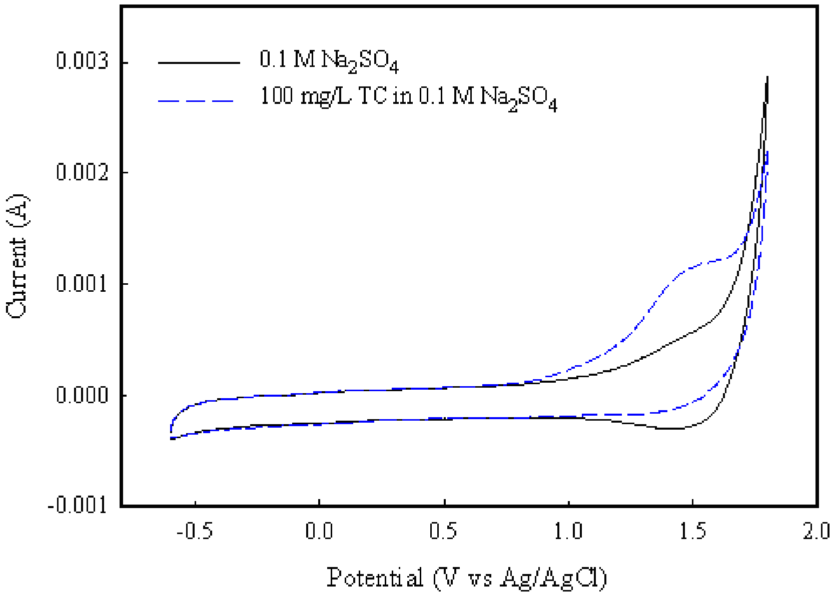

**Figure 2.** Cyclic voltammograms of 0.1 M $Na_2SO_4$ aqueous solutions with/without 100 mg/L TC on BDD at 25°C. Scan rate = 100 mV/s.

### 3.2. Effect of current density on TC degradation and TOC removal

Fig. 3 shows the effect of applied current density on TC decay. The degradation efficiency of TC ($(1 - C/C_o) \times 100\%$) (C: the residual concentration of TC at a given electrolytic time, and $C_o$: the initial concentration of TC) for the anodic oxidation of TC on BDD increased with the electrolysis time or current density ($I_{appl}$) (0.05–0.2 A/cm$^2$). For example, nearly 90% degradation could be accomplished at $I_{appl}$ =0.2 A/cm$^2$ for electrolysis time = 30 min, whereas it required more than 90 min of electrolysis time to achieve the same level of TC degradation at $I_{appl}$ = 0.05 A/cm$^2$. Moreover, the regressions of TC degradation data were all linear ($R^2$ = 0.944−0.998) for the three different $I_{appl}$ values (the inset in Fig. 3). Therefore, the degradation of TC is referred to as a bimolecular reaction between

TC and ·OH [30, 31]. Accordingly, if the concentration of ·OH does not change significantly, such reaction can be regarded as a pseudo-first order one and is written as follows.

$$\frac{-d[TC]}{dt} = k[TC][\cdot OH] = k_{app}[TC] \qquad (4)$$

The calculated apparent rate constants ($k_{app}$) were $4.68\times10^{-4}$, $1.26\times10^{-3}$, and $1.64\times10^{-3}$ $s^{-1}$ at 0.05, 0.1, and 0.2 A/cm$^2$, respectively.

The TOC abatement or removal efficiency ($(1 - TOC/TOC_o)\times100\%$) (TOC: the concentration of residual TOC at a given electrolytic time, and $C_o$: the initial concentration of TOC) also increased with increasing current density. For example, the TOC removal efficiency was ~75% at $I_{appl} = 0.2$ A/cm$^2$ for 150 min electrolysis time, whereas it was only 50% at $I_{appl} = 0.05$ A/cm$^2$ (Fig. 4). The greater degradation of TC and mineralization of TOC obtained at higher current density was attributed to the concomitant acceleration of water oxidation from Reaction 5, generating more amounts of reactive BDD(·OH) which promoted the degradation of TC and the removal of TOC. Note that increase of current density also resulted in the more production of other reactive oxygen species, like $S_2O_8^{2-}$ from Reaction 6 [32], which could also oxidize TC and intermediates.

$$BDD + H_2O \rightarrow BDD(\cdot OH) + H^+ + e^- \qquad (5)$$

$$2\ SO_4^{2-} \rightarrow S_2O_8^{2-} + 2e^- \qquad (6)$$

More specific energy consumption (*Ec*, in kWh/(kg TC)) was required when the applied current density increased. For example, to obtain an 80% TC degradation efficiency, the *Ec* value increased from ~$1.3\times10^2$ kWh/(kg TC) at 0.05 A/cm$^2$ to ~$3.9\times10^2$ kWh/(kg TC) at 0.2 A/cm$^2$.

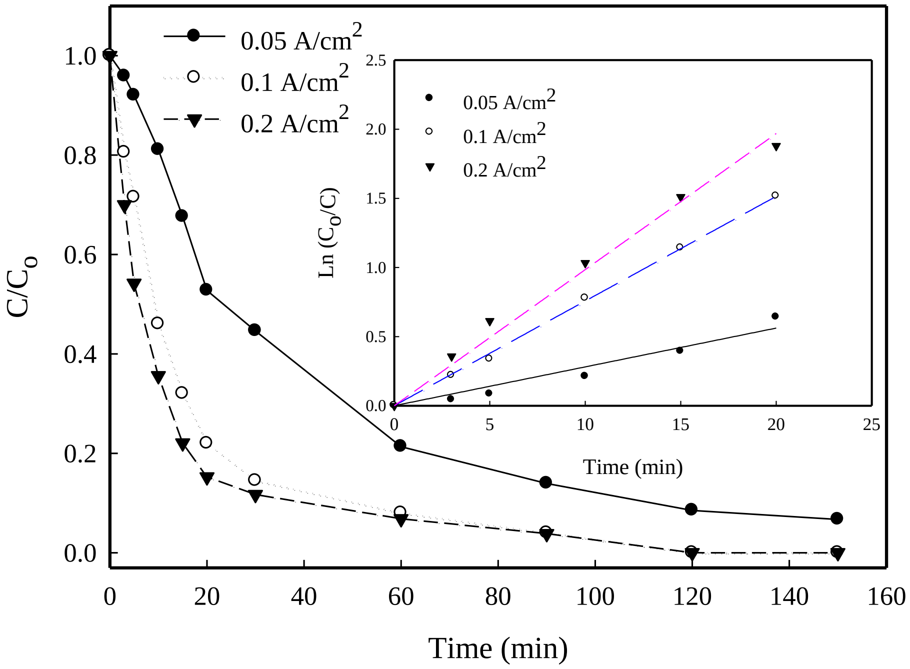

**Figure 3.** Effect of current density on TC degradation on BDD; inset: Ln($C_o$/C) against time (TC, 50 mg/L; electrolyte, 0.1 M $Na_2SO_4$; *T*, 25°C ; separator, Nafion 212).

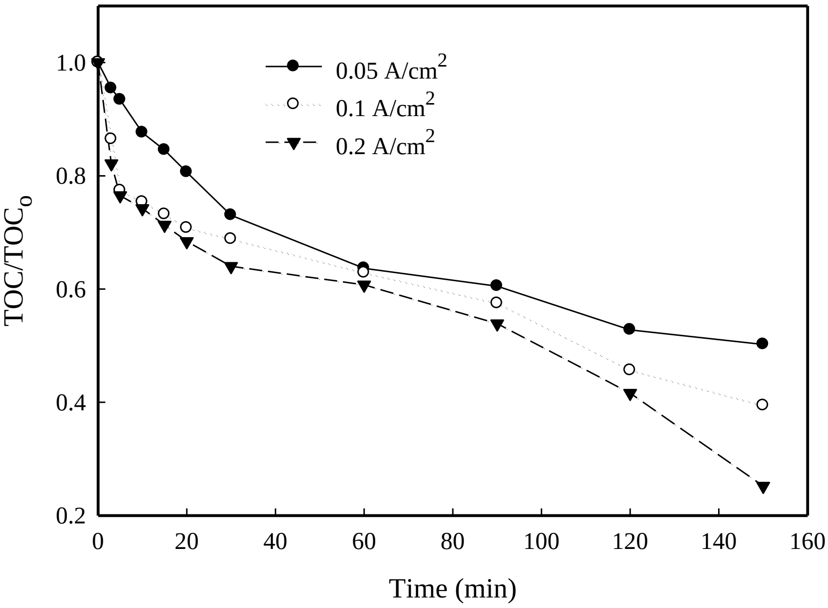

**Figure 4.** Effect of current density on TOC abatement on BDD (TC, 50 mg/L; electrolyte, 0.1 M $Na_2SO_4$; *T*, 25°C ; separator, Nafion 212).

### *3.3. Effect of TC initial concentration on TC degradation*

Three different initial TC concentrations (25, 50 and 100 mg/L) were tested to examine the effect of initial concentration on TC degradation at 0.1 A/cm$^2$ and 25°C. Fig. 5 shows the effect of the initial concentration of TC on the trend of $C/C_o$ during galvanostatic electrolysis. As can be seen, the removal efficiency of TC decreased with increasing initial TC concentration. When the initial TC concentration was 25 mg/L, the degradation efficiency ($[(1–(C/C_o)]\times100\%$) was close to 100% at 30 min electrolysis. Furthermore, it took 120 min to achieve ~100% TC degradation when the initial TC concentrations were 50 and 100 mg/L. In general, the increase of initial concentration of a compound increases its concentration gradient and mass transfer across the diffusion layer and thus its degradation on electrode. As a result, the total amount of degraded TC was greater when the initial TC concentration was higher. On the contrary, the apparent rate constant of TC degradation decreased ($2.84\times10^{-3}$–$8.77\times10^{-4}$ s$^{-1}$) with its initial concentration (25–100 mg/L) (the inset in Fig. 5). This can be interpreted in terms of an increase in flux of TC at the electrode surface may produce a higher surface concentration of degradation intermediates. Under galvanostatic conditions, the amounts of generated ·OH should be similar at the same operating conditions (except initial TC concentration) in electrolysis. However, the hydroxyl radicals have nonselective reactivity in relation to the adsorbed intermediates. Consequently, parts of hydroxyl radicals were used to oxidize the intermediate compounds generated from TC degradation. An earlier study suggested that the unspecific oxidation of many compounds (especially major intermediates) with ·OH might lead to the side reactions and parallel consumption of ·OH [24]. Thus, the apparent rate constants ($k_{app}$) of TC degradation were decreased with its initial concentration (25–100 mg/L).

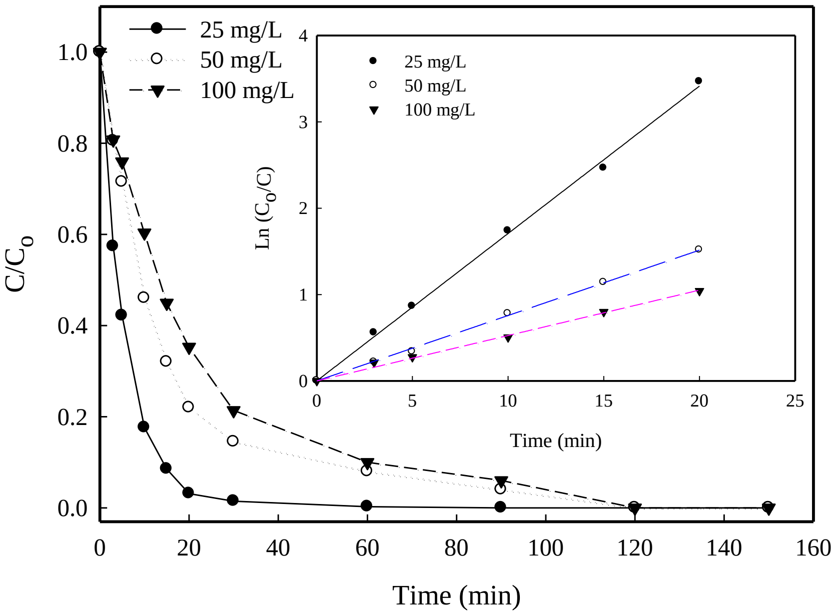

**Figure 5.** Effect of TC initial concentration on TC degradation on BDD; inset: Ln($C_0$/C) against time (current density, 0.1 A/$cm^2$; electrolyte, 0.1 M $Na_2SO_4$; *T*, 25°C ; separator, Nafion 212).

### *3.4. Effect of temperature on the degradation of TC*

As can be seen from Fig. 6, the TC degradation efficiency increased with the increase of temperature. For 20 min electrolysis, the degradation efficiency increased from 78% to 95% when the temperature increased from 25°C to 60°C. The TC degradation efficiency of 100% could be achieved at all three tested temperature. However, the time required for complete TC removal was shortened when the temperature rose due to the decrease of the solution viscosity and the increase of mass transfer rate of organics of interest from solution to the electrode surface [33]. The increase of TC removal efficiency with temperature could also be attributed to the electrogeneration of inorganic oxidizing agents (e.g., persulfate discussed in Section 3.3). Also, peroxodisulfates can be formed in solutions containing sulfates during the electrolysis using BDD electrodes [32]. These reagents are known to be very powerful oxidants and they can act as a mediator for the oxidation of organic pollutants; moreover, the reaction rate between peroxodisulfate ions and organic compounds increases with temperature. Therefore, the apparent rate constants ($k_{app}$), also increasing with increasing temperature, were $1.26\times10^{-3}$, $1.42\times10^{-3}$ and $2.39\times10^{-3}$ $s^{-1}$ at 25, 40 and 60°C, respectively. Accordingly, the activation energy for the electrochemical oxidation of TC at the BDD electrode was 15.6 kJ/mol.

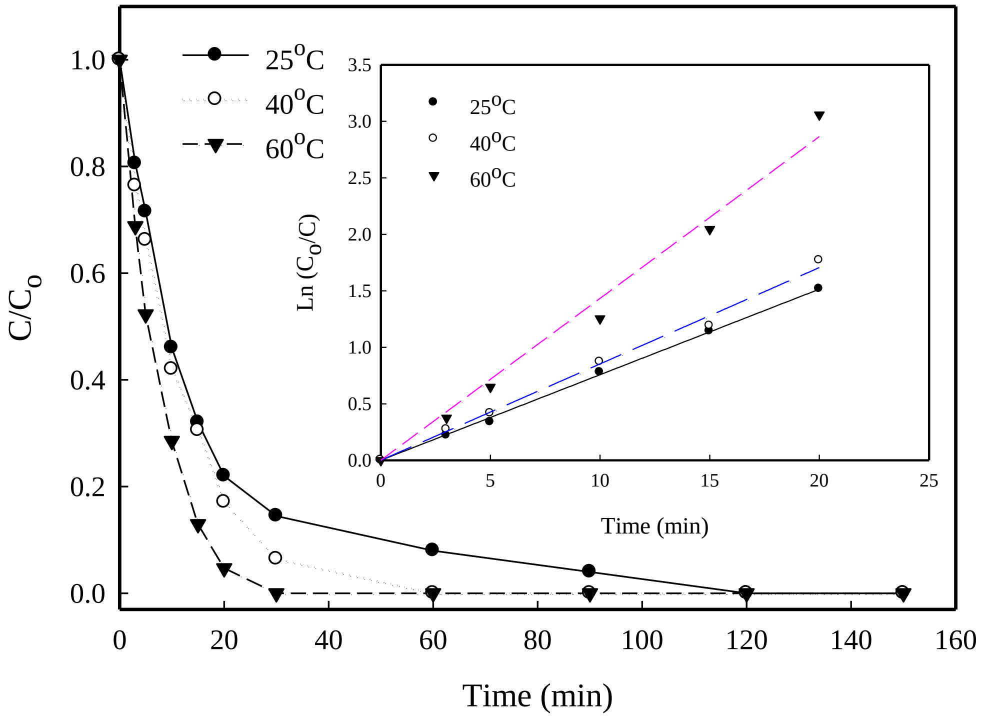

**Figure 6.** Effect of temperature on TC degradation on BDD; inset: Ln($C_o$/C) against time (current density, 0.1 A/cm$^2$; electrolyte, 0.1 M $Na_2SO_4$; TC, 50 mg/L; separator, Nafion 212).

### *3.5. Effect of anode materials on the degradation of TC*

It is well known that the anodic oxidation of organics is strongly dependent on anode material. Fig. 7a displays the trends of TC degradation on three different anodes (BDD, $PbO_2$, and Pt) at 0.1 A/cm$^2$ and 25°C. For 120 min electrolysis, the removal efficiency of TC reached nearly 100% on the BDD and $PbO_2$ anodes, whereas it was only about 50% on Pt. The calculated $k_{app}$ were $1.26\times10^{-3}$, $5.43\times10^{-4}$, and $1.93\times10^{-4}$ $s^{-1}$ on BDD, $PbO_2$, and Pt, respectively. Smaller than TC degradation efficiencies, the TOC removal efficiencies were only 60%, 38%, and 33% at 150 min on BDD, $PbO_2$, and Pt, respectively (Fig. 7b). The phenomenon is possibly due to the production of intermediates such as carboxylic acids which were more difficult to be degraded (by •OH) than their precursors. Furthermore, anode material may influence TC degradation and TOC abatement. Some earlier researches have proved that compared with $PbO_2$ and Pt, BDD exhibits weaker adsorption property, so hydroxyl radicals electrogenerated on BDD anode are very weakly adsorbed and consequently more reactive towards organics and intermediates oxidation reactions [24, 34]. Hence, the magnitude of TC degradation or TOC removal was in the order BDD > $PbO_2$ > Pt. This phenomenon was also observed for the degradation of some organic pollutants on BDD [25, 35].

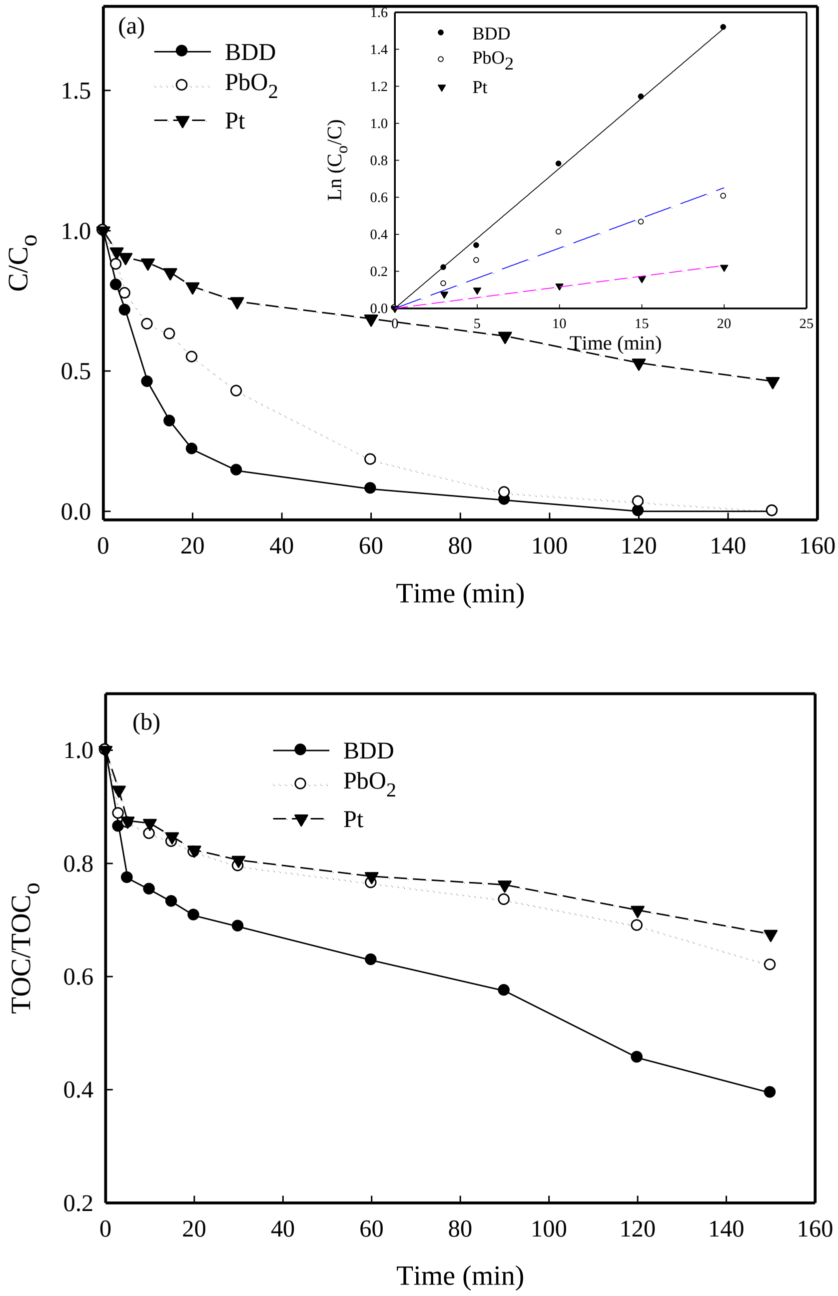

**Figure 7.** Effect of anode material on TC degradation (a) and TOC abatement (b); inset: ln($C_o$/C) against time (current density, 0.1 A/$cm^2$; electrolyte, 0.1 M $Na_2SO_4$; TC, 50 mg/L; *T*, 25°C ; separator, Nafion 212).

### *3.6. Effect of sample matrix on TC degradation and TOC removal*

To examine the effect of sample matrix on TC degradation, the electrochemical oxidation of TC was also tested on BDD in a real sample matrix - municipal wastewater treatment plant secondary effluent (MWTPSE) (spiked with 50 mg/L TC and 0.1 M $Na_2SO_4$). Fig. 8a shows that the degradation efficiency of TC in the MWTPSE was slightly lower than that in 0.1 M $Na_2SO_4$ solution for 120 min electrolysis. This result is attributed to the fact that the concentration of TOC was greater in the

MWTPSE than in the 0.1 M $Na_2SO_4$ solution. As a result, partial hydroxyl radicals generated from water electrolysis in anolyte were used to oxidize the organic compounds originally present in the MWTPSE. It is possible that dissolved organics present in the effluent competed with TC in the electrochemical and •OH-mediated degradation. The obtained $k_{app}$ were $1.26\times10^{-3}$ and $1.10\times10^{-3}$ $s^{-1}$ for the anodic TC oxidation at 0.1 A/$cm^2$ and 25°C in the 0.1 M $Na_2SO_4$ solution and MWTPSE matrix, respectively (the inset in Fig. 8a).

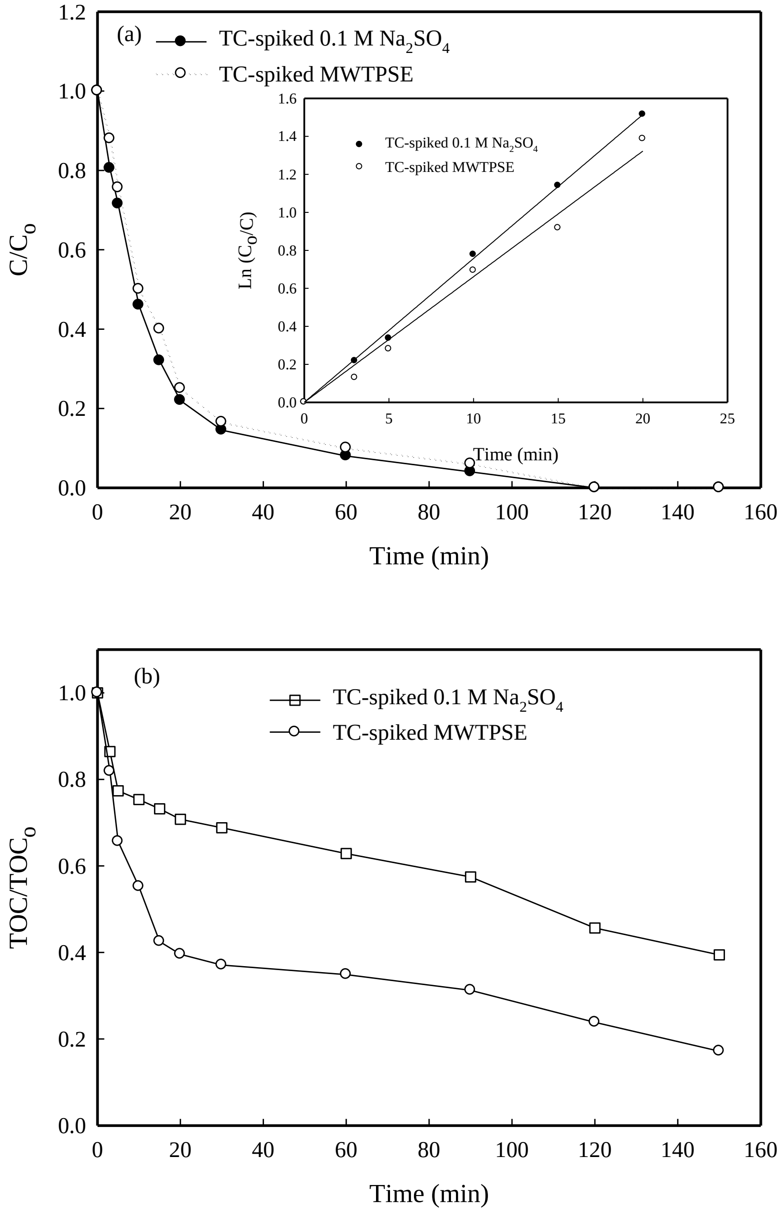

**Figure 8.** Effect of sample matrixes on TC degradation (a) and TOC abatement (b); inset: $Ln(C_0/C)$ against time (current density = 0.1 A $cm^{-2}$, TC = 50 mg/L, and $T$ = 25°C).

However, the TOC removal efficiency in the MWTPSE matrix was higher than that prepared in 0.1 M $Na_2SO_4$ solution (Fig. 8b). This phenomenon is associated with the aforementioned difference in TOC level of the two different matrixes and is likely related to the presence of organic compounds that could be rapidly degraded in the effluent. These dissolved organic compounds were easier to be degraded than TC in the MWTPSE. Hence, the influence of matrix on anodic TC degradation was more noticeable for TOC removal than for TC degradation.

## 4. CONCLUSIONS

The oxidation of TC on BDD was found to be electrochemically irreversible and followed an apparent pseudo-first-order reaction kinetics. The degradation efficiency of TC increased with increasing current density and temperature but noticeably decreased when the initial TC concentration increased. The performance of tested anodes for TC degradation was in the order BDD > $PbO_2$ > Pt.

At 0.1 A/cm$^2$ and 25°C, the $k_{app}$ values of TC degradation were $1.26\times10^{-3}$ s$^{-1}$ and $1.10\times10^{-3}$ s$^{-1}$ in the 0.1 M $Na_2SO_4$ solution and MWTPSE matrix, respectively. The activation energy for the TC degradation on BDD was 15.6 kJ/mol. Approximately 100% TC degradation and 75% TOC removal were achieved in the MWTPSE matrix within 150 min electrolysis. Therefore, the BDD electrode is promising to remove the TC and TOC in MWTPSE.

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## References

1. I. Sires and E. Brillas, *Environ. Int.* 40 (2012) 212.
2. R. Joaquín, T. Domínguez, P. González, J. Palo, Sánchez-Martín, *Chem. Eng. J.* 162 (2010) 1012.
3. P.H. Wang, P.S. Yap, T.T. Lim, *Appl. Cata. A* 399 (2011) 252.
4. K. Kuemmerer, *J. Antimicrob. Chemother.* 52 (2003) 5.
5. G. Gu, K.G. Karthikeyan, *Environ. Sci. Technol.* 39 (2005) 2660.
6. C. Reyes, J. Fernandez, J. Freer, M.A. Mondaca, C. Zaror, S. Malato, M.D. Mansilla, *J. Photochem. Photobiol. A* 184 (2006) 141.
7. S. Yang, J. Cha, K. Carlson, *J. Chromatogr. A* 1097 (2005) 40.
8. B. Li, T. Zhang, *Chemosphere* 83 (2011) 1284.
9. A.Y.C. Lin, T.H. Yu, S.K. Lateef, *J. Hazard. Mater.* 167 (2009) 1163.
10. A.Y.C. Lin, C. Lin, J. Chiou, P.K.A.Hong, *J. Hazard. Mater.* 171 (2009) 452.
11. A.L. Batt, S. Kim, D.S. Aga, *Chemosphere* 68 (2007) 428.
12. D.W. Kolpin, E.T. Furlong, M.T. Meyer, E.M. Thurman, S.D. Zaugg, L.B. Barber, H.T. Buxton, *Environ. Sci. Technol.* 36 (2002) 1202.
13. R.C. Wei, F. Ge, S.Y. Huang, M. Chen, R. Wang, *Chemosphere* 82 (2011) 1408.
14. M.M. Huber, A. Göbel, A. Joss, N. Hermann, D. Loffler, C.S. McArdell, A. Ried, H. Siegrist, T.A. Ternes, U. von Gunten, *Environ. Sci. Technol.* 39 (2005) 4290.
15. M. Addamo, V. Augugliaro, A. Di Paola, E. Garcia-López, V. Loddo, G. Marci, L. Palmisano, *J. Appl. Electrochem.* 35 (2005) 765.
16. A. Hebert, D. Forestier, D. Lenes, D. Benanou, S. Jacob, C. Arfi, L. Lambolez, Y. Levi, *Water Res.* 44 (2010) 3147.

17. M.H. Khan, H. Bae, J.Y. Jung, *J. Hazard. Mater.* 181 (2010) 659.
18. X.D. Zhu, Y.J. Wang, R.J. Sun, D.M. Zhou. *Chemosphere* 92 (2013) 925.
19. R. Andreozzi, I. Di Somma, R. Marotta, G. Pinto, A. Pollio, D. Spasiano, *Water Res.* 45 (2011) 2038.
20. M. Pérez-Moya, M. Graells, G. Castells, J. Amigó, E. Ortega, G. Buhigas, L.M. Pérez, H.D. Mansilla, *Water Res.* 44 (2010) 2533.
21. C.A. Martinez-Huitle and E. Brillas, *Appl. Catal. B* 87 (2009)105.
22. N. Oturan, J. Wu, H. Zhang, V.K. Sharma, M.A. Oturan, *Appli. Catal. B: Environ.* 140−141 (2013) 92.
23. M. Panizza, G. Cerisola, *Electrochim. Acta* 51 (2005) 191.
24. M. Murugananthan, S. Yoshihara, T. Rakuma, N. Uehara, T. Shirakashi, *Electrochim. Acta* 52 (2007) 3242.
25. M. Murugananthan, S.Yoshihara, T. Rakuma, T. Shirakashi, *J. Hazard. Mater.* 154(1−3) (2008) 213.
26. T.S. Chen, Y.M. Kuo, J.L. Chen, and K.L. Huang, *Int. J. Electrochem. Sci.* 8 (2013) 7625.
27. T.S. Chen and K.L. Huang, *Int. J. Electrochem. Sci.* 8 (2013) 6343.
28. M. Skoumal, C. Arias, P.L. Cabot, F. Centellas, J.A. Garrido, R.M. Rodríguez, and E. Brillas, *Chemosphere* 71 (2008) 1718.
29. C.I. Brinzila, M.J. Pacheco, L. Ciríaco, R.C. Ciobanu, A. Lopes, *Chem. Eng. J.* 209 (2012) 54.
30. X. Duan, F. Ma, Z. Yuan, L. Chang, X. Jin, *J. Taiwan Inst. Chem. Eng.* 44 (2013) 95.
31. E.B. Cavalcanti, S. Garcia-Segura, F. Centellas, E. Brillas, *Water Res*. 47 (2013) 1803.
32. M. Murugananthan, S.S. Latha, G.B. Raju, S. Yoshihara, *Sep. Purif. Technol.* 79 (2011) 56.
33. X. Chen and G. Chen, *Sep. Purif. Technol.* 48 (2006) 45.
34. M. Panizza and G. Cerisola, *Electrochim. Acta* 49 (2004) 3221.
35. T.S. Chen, P.H. Chen, K.L. Huang, *J. Taiwan Inst. Chem. Eng.* 45 (2014) 2615.