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Anodic Degradation of Ofloxacin on a Boron-Doped Diamond Electrode

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This study investigates the electrochemical oxidation of ofloxacin mainly on a boron-doped diamond (BDD) anode under galvanostatic electrolysis. The influence of operating parameters such as current density, initial concentration of ofloxacin, and temperature was investigated. For comparison, a Pt planar electrode and a dimensional stable anode (DSA) were also tested. According to cyclic voltammetric analysis, the oxidation of ofloxacin on BDD was found to be electrochemically irreversible. The electro-degradation of ofloxacin was a pseudo-first-order reaction, and the apparent rate constant was 1.2×10^{-3} s^{-1} for the anodic ofloxacin oxidation on BDD at 100 mA/cm^2 and 30°C in 0.1M Na_2SO_4 electrolyte. The degradation efficiency of ofloxacin increased with increasing current density and temperature, but noticeably decreased as initial ofloxacin concentration increased. Furthermore, the BDD anode was superior to the Pt and DSA electrodes for ofloxacin degradation in terms of degradation efficiency and oxidation rate. The activation energy for the ofloxacin degradation on BDD was 4.79 kJ/mol.

Keywords: Boron-doped diamond; Ofloxacin; Degradation; Electrochemical

1. INTRODUCTION

The presence of pharmaceutical compounds in surface and ground water bodies is an emerging environmental issue and has received considerable attention during the last two decades. Many pharmaceuticals are lipophilic and resistant to biodegradation, so municipal wastewater treatment plants (MWTPs) usually have poor removal efficiencies of lipophilic pharmaceuticals which then are discharged into the environment [1−5]. The presence of pharmaceuticals in the effluent of MWTPs

may cause serious effects (e.g., endocrine disrupting and critical side effects) on the aquatic ecosystem. Thus, it is necessary to develop reliable wastewater treatment processes for the removal of emerging environmental pollutants—lipophilic pharmaceuticals.

The ofloxacin (7-fluoro-2-methyl-6-(4-methylpiperazin-1-yl)-10-oxo-4-oxa-1-azatricyclo[7.3.1.$0^{5,13}$]trideca-5(13),6,8,11-tetraene-11-carboxylic acid) antibiotic belongs to a class of drugs called fluoroquinolones (fluorinated carboxyquinolone). It is used to treat bacterial infections that cause bronchitis, pneumonia, chlamydia, gonorrhea, skin infections, urinary tract infections, and infections of the prostates. The annual consumption of ofloxacin was equal to 7,025,000 doses in 2005 in Taiwan (population = 22.77 million) [4]. The detection frequencies of ofloxacin in several potential pharmaceutical contamination sources in Taiwan were over 90 %, and the highest detected concentration of ofloxacin was up to 13,633 ng/L [4]. Moreover, the removal efficiencies of ofloxacin ranged 0% to 88% in second wastewater treatment processes [6]. Hence, it is quite urgent to develop approaches for removing ofloxacin to minimize its contamination in the environment. However, little information is available on the destruction of ofloxacin in aqueous solutions based on anodic oxidation.

Recently, many studies have been carried out to investigate the destruction of toxic organic contaminants on synthetic BDD thin film anodes [7−9]; in addition, the BDD electrodes have exhibited several unique advantages including high mineralization of toxic organic contaminants in wastewater. However, to the best of our knowledge, the electro-degradation of ofloxacin on BDD has not been addressed yet in literature. Thus, in this study we aim to investigate the electrochemical degradation of ofloxacin at a BDD electrode. Cyclic voltammetry was carried out to characterize the electrochemical behavior of ofloxacin on BDD. Then, galvanostatic electrolyses were performed to explore the kinetics and efficiencies of ofloxacin degradation under different operating parameters such as applied current, initial concentration of ofloxacin, electrolyte temperature, and anode materials.

2. MATERIALS AND METHODS

In this study, the ofloxacin was purchased from Sigma (USA) and it was used without further purification. Fig. 1 shows the molecular structure of ofloxacin (an aromatic compound) [10]. Na_2SO_4 (SHOWA Co. Ltd. (Japan)) was employed to prepare the supporting electrolyte. HPLC analytical grade acetonitrile was purchased from ECHO Chemical Co. Ltd. (Taiwan). The electrochemical behaviors of ofloxacin in the prepared solutions were investigated with cyclic voltammetry (CV). The potential scan range was 0.6↔1.5 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 disk electrode (WINDSOR SCIENTIFIC Co. Ltd. (UK)) with an area of 0.07 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. In the electro-oxidation test, The BDD electrode was purchased from CONDIAS GmbH (Germany) (substrate: Niobium; BDD coating thickness: 2.0 mm), while the dimensional stable anode (DSA) (Ti/IrO_2) and Pt electrode were supplied from SPEMET Co.

Ltd. (Taiwan). The anolyte (100 mL) was ofloxacin (25, 50, or 100 mg/L) in 0.1 M Na_2SO_4 while the catholyte was only 0.1 M Na_2SO_4. The electro-oxidation of the ofloxacin aqueous solution was galvanostatically performed in a thermostatted divided cell, and each electrolyte was well stirred using a magnetic stirrer.

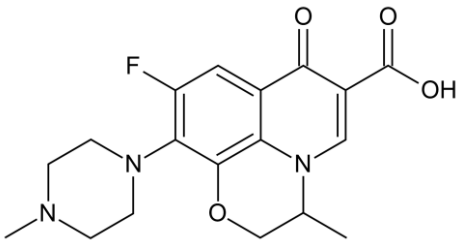

Figure 1. Molecular structure of ofloxacin [10].

The anode and cathode compartments were separated by an AMI-7001 ion-exchange membrane separator. Prior to use, the AMI-7001 was heated at 65°C in 1 M (~3%) H_2O_2 for 1 h to remove organic impurities. Then, the membranes were washed three times with deionized distilled water (DDW) and stored in DDW. All the electrolytic experiments were performed using a 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. Samples were taken at intervals during the electrolysis. The concentrations of residual ofloxacin in samples were analyzed by a HPLC instrument (Hitachi chromaster 5420). The separations were performed on a RP-C18 column (250 mm×4.6 mm, particle size, 5μm). The mobile phase was acetonitrile/0.075 M H_3PO_4 (30:70, v/v), with a flow rate of 1mL/min. The injection volume was 20 μL and the working wavelength for quantitative analysis was 308 nm. A personal computer equipped with a Hitachi chromaster system manager for the HPLC system was used to acquire and process chromatographic data. The retention time of ofloxacin was determined to be 3.2 min (Fig. 2). The linear fitting of calibration curve yielded an R^2 value of 0.9995 (the inset in Fig. 2).

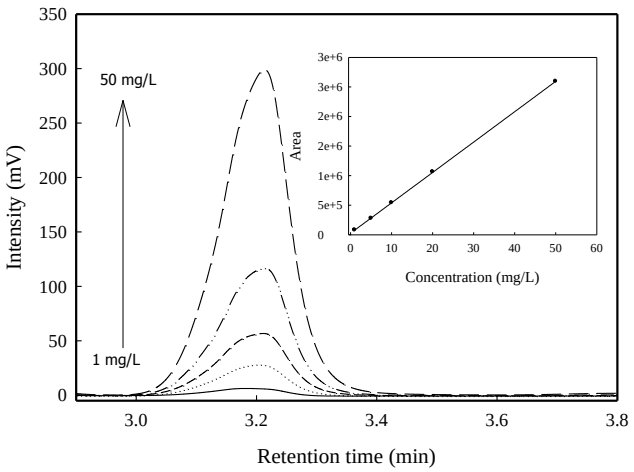

Figure 2. HPLC chromatograms for different ofloxacin concentrations; inset: peak area against concentration.

3. RESULTS AND DISCUSSION

3.1. Cyclic voltammetric analysis of ofloxacin on BDD electrode

Cyclic voltammetric experiments were performed to examine the electrochemical behavior of ofloxacin at BDD in sodium sulfate solution (supporting electrolyte, 0.1 M). Fig. 3 shows the cyclic voltammograms of 100 mg/L ofloxacin in 0.1 M Na_2SO_4. During the first anodic sweep from 0.6 to 1.5 V, a well-shaped oxidation peak was observed at about 1.22 V versus Ag/AgCl, but the reverse scan from 1.5 to 0.6 V, no corresponding reduction peak could be identified, suggesting that the electrochemical oxidation of ofloxacin (an aromatic compound (Fig. 1)) at BDD was totally irreversible. Additionally, as the number of scanning cycle increased, the anodic peak current decreased until it reached stable. This phenomenon has also been observed in the anodic oxidation of other aromatic compounds such as phenol [11], nitrophenols [12, 13], chlorophenols [14], polyhydroxybenzene [15], and 17β-estradiol (E2) [16] on BDD electrodes. This phenomenon can be attributed to the deposition of organic films on BDD surface, which then deactivated the electrode. According to some earlier investigations [11, 15, 16], this fouling layer can be removed by anodic polarization in the potential region of water decomposition (>2.3 V).

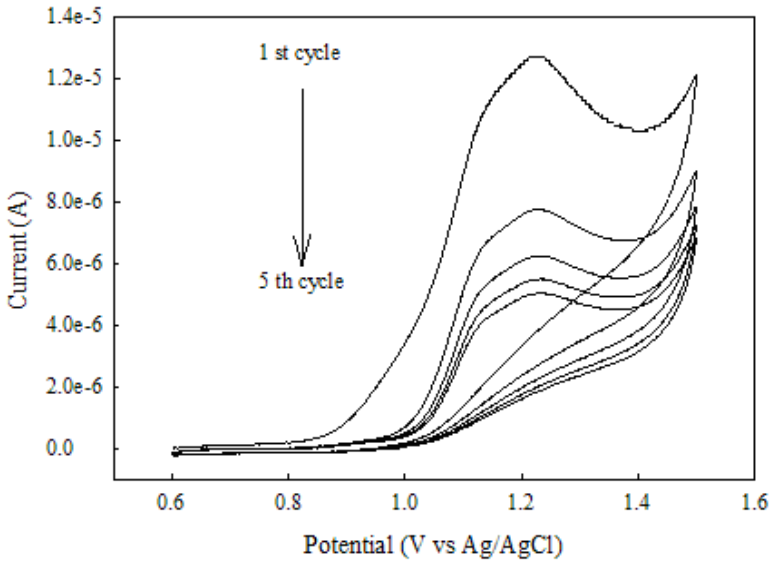

Figure 3. Cyclic voltammograms of ofloxacin solution (100 mg/L) in 0.1 M Na_2SO_4 on BDD electrode at 25°C. Scan rate = 100 mV/s.

3.2. Effect of current density on ofloxacin degradation

Fig. 4 shows the trend of C/C_o ratios (C: the residual concentration of ofloxacin at a given electrolytic time, and C_o: the initial concentration of ofloxacin) for the anodic oxidation of ofloxacin on the BDD electrode at different applied current densities (I_{appl}) (20−100 mA/cm^2). As can be seen from Fig. 4, the rate of ofloxacin degradation was greatly dependent on the I_{appl} and became faster with increasing current density. For example, nearly 100% degradation could be accomplished at I_{appl} =100

mA/cm^2 for electrolysis time = 60 min, whereas it required more than 150 min of electrolysis time to achieve the same level of ofloxacin degradation at I_{appl} = 20 mA/cm^2. This phenomenon is related to the fact that increasing current density led to the increase of overpotential and hydroxyl radical (·OH) that was associated with the direct and indirect degradation of ofloxacin, respectively.

The regressions of ofloxacin degradation data were all linear (R^2 = 0.945−0.995) for the three different I_{appl} values (initial ofloxacin concentration = 50 mg/L) (the inset in Fig. 4). Therefore, the degradation of ofloxacin is referred to as a bimolecular reaction between ofloxacin and ·OH. Accordingly, if the concentration of ·OH does not change significantly, such reaction can be regarded as a pseudo-first order reaction and written as follows.

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

The calculated apparent rate constants (k_{app}) were 2.2×10^{-4}, 5.9×10^{-4}, and 1.2×10^{-3} s^{-1} at 20, 50, and 100 mA/cm^2, respectively. The rate constants almost linearly increased with increasing I_{appl} at a constant initial concentration of ofloxacin, revealing that the degradation process of ofloxacin was controlled more by electrode kinetics than by mass transfer in the tested current density range.

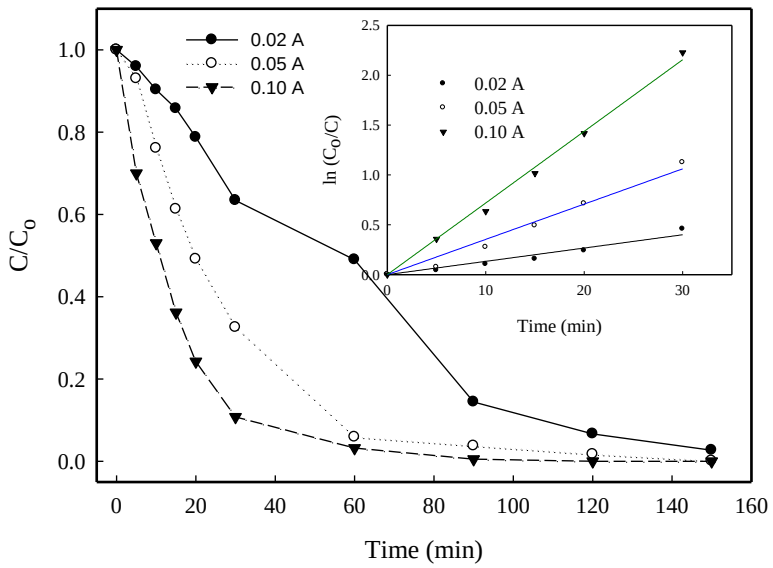

Figure 4. Effect of current density (20−100 mA/cm^2) on ofloxacin degradation at BDD anode. (projected anode surface area, 1 cm^2; ofloxacin, 50 mg/L; electrolyte, 0.1M Na_2SO_4; *T*, 30°C ; separator, AMI-7001).

3.3. Effect of initial ofloxacin concentration on ofloxacin degradation

Three different initial ofloxacin concentrations (25, 50 and 100 mg/L) were tested to examine the effect of initial ofloxacin concentration on ofloxacin degradation on the BDD electrode surface at 100 mA/cm^2 and 30°C. Fig. 5 shows that the degradation efficiency of ofloxacin decreased with

increasing initial ofloxacin concentration. When the initial ofloxacin concentration was 25 mg/L, the degradation efficiency ($[(1–(C/C_o)]\times100\%$) of ofloxacin was close to 100% at 60 min electrolysis. Furthermore, it took 90 and 120 min to achieve ~100% ofloxacin degradation when the initial ofloxacin concentrations were 50 and 100 mg/L, respectively. 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 ofloxacin was greater when the initial ofloxacin concentration was higher. On the contrary, the apparent rate constant of ofloxacin oxidation decreased (2.3×10^{-3}–0.9×10^{-3} s^{-1}) with its initial concentration (25–100 mg/L). This can be interpreted in terms of an increase in flux of ofloxacin at the electrode surface may produce a higher surface concentration of oxidation intermediates. Under galvanostatic conditions, the amounts of generated ·OH should be similar at the same operating conditions (except initial ofloxacin 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 ofloxacin 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 [17].

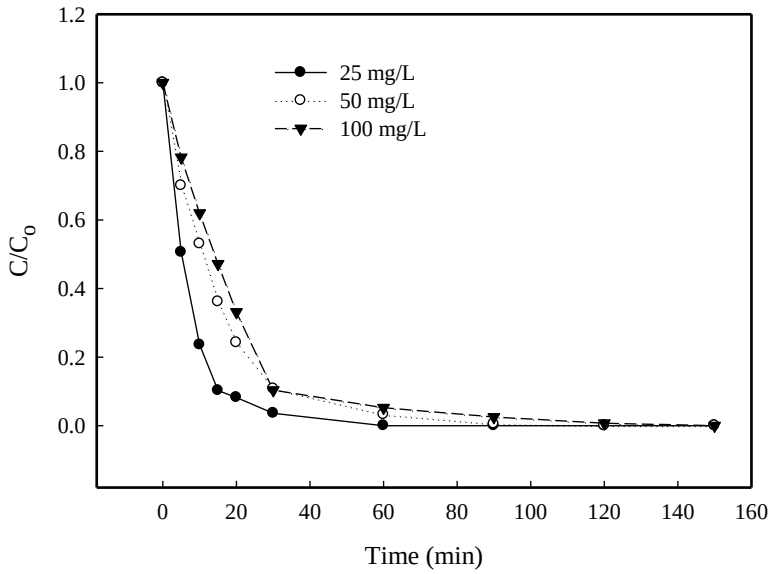

Figure 5. Effect of initial ofloxacin concentration (25−100 mg/L) on ofloxacin degradation (current density, 100 mA/cm^2; electrolyte, 0.1M Na_2SO_4; *T*, 30°C; separator, AMI-7001).

3.4. Effect of temperature on ofloxacin degradation

The increase of temperature (30–70°C) increased the degradation of ofloxacin (electrolysis time = 60 min) (Fig. 6). Brillas et al. [18] also found that the percentage of TOC removal gradually rose with increasing temperature for the mineralization of paracetamol on a BDD electrode. This phenomenon is related to the fact that the increase of temperature enhances both the mass transfer of active species to the anode surface and the kinetics of ofloxacin degradation on anode and by ·OH.

Near 100% ofloxacin degradation was accomplished within 90 min electrolysis for all the three tested temperatures (30–70°C). Furthermore, the regressions of ofloxacin degradation data were all linear (R^2 = 0.992−0.996) for the three different temperatures (the inset in Fig. 6). The obtained pseudo-first-order rate constants (k_{app}) are 1.2×10^{-3}, 1.3×10^{-3}, and 1.5×10^{-3} s^{-1} at 30, 50, and 70°C, respectively. Accordingly, the activation energy *E*a value calculated using the Arrhenius's law was 4.79 kJ/mol for the ofloxacin degradation.

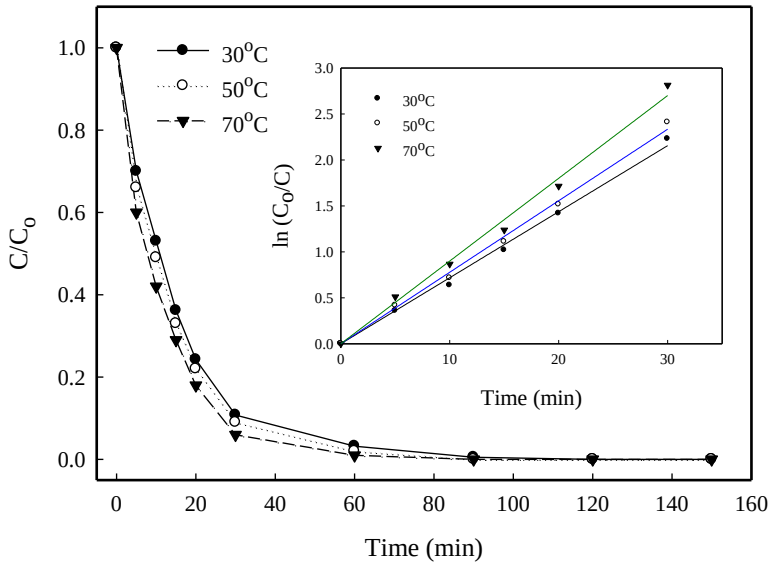

Figure 6. Effect of temperature on ofloxacin degradation at BDD; inset: ln (C_o/C) against time (ofloxacin, 50 mg/L; current density, 100 mA/cm^2; electrolyte, 0.1M Na_2SO_4; separator, AMI-7001).

3.5. Effect of anode material on ofloxacin degradation

It is well known that the anodic oxidation of organics is strongly dependent on anode material. In this study, three anodes (BDD, Pt, and DSA) were compared for their performance of ofloxacin oxidation at 100 mA/cm^2 (ofloxacin initial concentration = 50 mg/L). Fig. 7 presents that for ofloxacin degradation, BDD anode was clearly superior to Pt and DSA. It was noted that after 90 min constant current electrolysis, no residual ofloxacin was detected when BDD was used as the anode. At the same electrolysis time, however, the degradation efficiency of ofloxacin was only about 50.5% and 13.3% on the Pt and DSA anodes, respectively. The result is in accordance with the magnitude of anode potentials of tested electrodes that followed the order BDD > Pt > DSA (3.31, 2.91, and 2.30 V vs Ag/AgCl, respectively) during electrolysis. The electrochemical oxidation of organic pollutants may be resulted from physically adsorbed active oxygen (·OH) or chemisorbed active oxygen (oxygen in the oxide lattice, MO_{x+1} (M: metal)); in general, ·OH is more effective than O in MO_{x+1} for organic pollutant oxidation. A higher anodic potential may generate a greater electron trapping activity, favorable to the direct oxidation of organic pollutants on the anode surface [19] and the production of ·OH from water electrolysis for ·OH-mediated reactions [20]. The more free or adsorbed ·OH

produced on the BDD than on the MO_{x+1} might cause electrophilic attack of ofloxacin (with an aromatic ring) and its derivatives. Consequently, the magnitude of ofloxacin degradation efficiency was in order BDD > Pt > DSA. Jara et al. [21] also reported that the abatement of ofloxacin (50 mg/L) at a fixed current density (20 mA/cm^2) was better on Ti/Pt than on DSA. The ofloxacin degradation efficiency on BDD in this study was noticeably better than that on Pt or DSA observed by Jara et al. [21]. Some researchers also indicated that BDD electrodes were superior to Pt and GC anodes for the electro-oxidation of organic pollutants (e.g., bisphenol A) [22, 23].

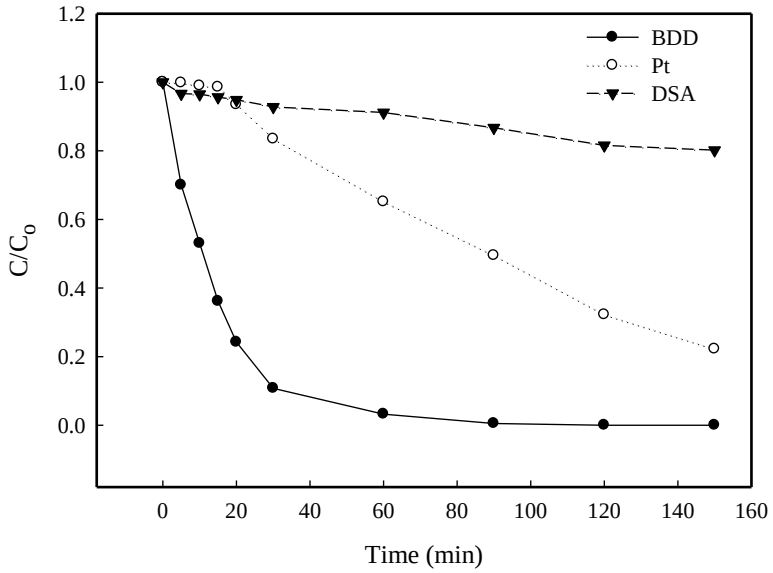

Figure 7. Effect of anode material on ofloxacin degradation (current density, 100 mA/cm^2; electrolyte, 0.1M Na_2SO_4; *T*, 30°C; separator, AMI-7001).

4. CONCLUSIONS

In this study, the electrochemical characteristic of ofloxacin on a BDD electrode and the oxidation of ofloxacin at different current densities, initial ofloxacin concentrations, electrolyte temperatures, and anodes were explored. It was found that ofloxacin oxidation appeared without the occurrence of corresponding reduction in CV analysis, so the electrochemical behavior of ofloxacin was irreversible on the BDD electrode.

The degradation of ofloxacin was a pseudo-first-order (kinetic) reaction, which yielded an apparent rate constant of 1.2×10^{-3} s^{-1} for the ofloxacin anodic oxidation on BDD at 100 mA/cm^2 and 30°C in 0.1M Na_2SO_4 electrolyte. The degradation efficiency and apparent rate constant increased with increasing current density (20−100 mA/cm^2) and temperature (30−70°C). The activation energy was 4.79 kJ/mol for ofloxacin degradation on BDD. Additionally, the degradation efficiency of ofloxacin decreased as the initial ofloxacin concentration increased.

The performance of tested anodes for ofloxacin degradation in terms of ofloxacin degradation efficiency was in order BDD > Pt > DSA. When the BDD electrode was used, no residual ofloxacin was detected at 90 min constant current electrolysis; at the same electrolysis time, however, the

degradation efficiency of ofloxacin was only about 50.5% and 13.3% on the Pt and DSA anodes, respectively. Therefore, the BDD electrode is superior to the Pt and DSA anodes for the degradation of ofloxacin in aqueous solutions.

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