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Effect of Operating Parameters on Electrochemical Degradation of Estriol (E3)

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This study investigates the effect of operating parameters on the electrochemical (anodic) degradation of estriol (E3) in aqueous solutions. We mainly focused on the use of a boron-doped diamond (BDD) electrode for the E3 degradation at various current densities, initial E3 concentrations, and temperatures. The performance of BDD for E3 degradation was compared with that of Ti/Pt and a dimensional stable anode (DSA). The oxidation of E3 on BDD was found to be electrochemically irreversible according to cyclic voltammetric analysis. In electrolysis, the degradation (anodic oxidation) of E3 was a pseudo-first-order (kinetic) reaction, which yielded an apparent rate constant of 8.9×10^{-3} s^{-1} on BDD at 20 mA/cm^2 and 30°C in 0.1M Na_2SO_4 electrolyte. The degradation of E3 along with chemical oxygen demand (COD) removal was better on the BDD than on the Ti/Pt and DSA. Approximately 5 min was needed to achieve ~100% E3 (500 μg/L) degradation at 50–100 mA/cm^2, whereas the required electrolysis time was double at 20 mA/cm^2. The degradation efficiency of E3 noticeably decreased as initial E3 concentration increased, while the effect of temperature (30–70°C) was relatively slight on E3 degradation. The activation energy was 3.56 kJ/mol for the E3 degradation on BDD.

Keywords: Boron-doped diamond; Endocrine disrupting chemicals; Estriol; Degradation; Electrochemical

1. INTRODUCTION

Over the past few decades, many endocrine disrupting chemicals (EDCs) have shown adverse effects on aquatic organisms [1]. These adverse effects include cancer, vitellogenin induction, feminized reproductive organs, reduced fecundity, changes in sex ratio, and developmental degeneration [2−5]. Among EDCs, estrogens are known to have high potential for endocrine disruption of organisms in the aquatic ecosystem [6−8]. Numbers of studies have indicated that 17αethynylestradiol (EE2) and 17β-estradiol (E2) two of most potent estrogenic compounds, followed by estrone (E1) and estriol (E3) [9]. These natural and synthetic estrogens are primarily of concern because they can adversely affect a number of aquatic species at very low concentration (ng/L level) [10, 11].

Sewage treatment plants (STPs) and livestock wastewaters are both of the major sources of estrogens released to the aquatic environment [12−14]. For instance, Sim et al. [14] measured estrogens in the wastewater samples collected from several municipal wastewater treatment plants (M-WWTPs), livestock wastewater treatment plants (L-WWTPs), hospital WWTPs (H-WWTPs), and pharmaceutical manufacture WWTPs (P-WWTPs) in Korea. They found that the concentrations of estrogens in the WWTP influents were 0.011 to 8.15 μg/L for E1, ND to 0.634 μg/L for βE2, ND to 0.766 μg/L for αE2, ND for EE2, and 0.046 to 2.28 μg/L for E3. In general, STPs can not completely or effectively remove trace levels of steroid estrogens in wastewater [15, 16]. Therefore, estrogens are often found in surface waters. According to a US national survey between 1999 and 2000 of 139 polluted streams and rivers, estrogens ranged from <5 to 112 ng/L for E1, <5 to 93 ng/L for E2, <5 to 51 ng/L for E3, and <5 to 831 ng/L for EE2; moreover, the detection frequencies were 7.1%, 10%, 21.4%, and 15.7%, for E1, E2, E3, and EE2, respectively [17]. With a higher water solubility of the estrogens, E3 is the metabolite and breakdown product of E1 and E2, and it is often detected at higher levels than E1, E2, and EE2 in M-WWTP influent [14, 18]. When considering the serious adverse impacts of E3 on our environment and health, it is quite urgent to develop approaches for removing E3 to minimize its contamination in the environment. However, little information is available on the destruction of E3 in aquatic environment.

Electro-oxidation can be regarded as a simple, rapid, and clean approach for the destruct of emerging environmental pollutants in water and wastewater [19]. Recently, many studies have been carried out to investigate the destruction of toxic organic contaminants on synthetic BDD thin film anodes [20−22]; in addition, the BDD electrode material exhibited several unique advantages and could achieve total mineralization of the toxic organic contaminants in wastewater. Nevertheless, to the best of our knowledge, the electro-degradation of E3 on BDD has not been addressed yet in literature. Thus, this study aims to investigate the electrochemical degradation of E3 at a BDD electrode in aqueous solutions under galvanostatic control. The effects of current density, initial concentration of E3, electrolyte temperature, and anode materials on E3 electro-degradation were evaluated.

2. MATERIALS AND METHODS

2.1. Chemicals and Materials

Fig. 1 shows the chemical structure of estriol (E3) which has three OH groups (one on the leftmost ring and the other two on the rightmost ring). In this study, the E3 chemical (Wako Pure Chemical Industries, Ltd.) was analytical grade and it was used without further purification. The E3 stock solution was prepared by adding excess E3 into deionized distilled water (DDW) up to its maximum solubility (441 mg/L, 25°C) and then the prepared solution was filtered to make it free from non-soluble substances. The exact concentration of this stock solution was measured through a high performance liquid chromatography (HPLC) technique which used the standard solutions of E3 (in CH_3CN solvent) (see section 2.4 below). The working solution with required concentration was obtained by diluting the stock solution using 0.1 M Na_2SO_4. 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 Ti/Pt (Pt coating thickness: 25 μm) electrode were supplied from SPEMET Co. Ltd. (Taiwan). The ion exchange separator (AMI-7001, Membranes International Inc.) is a type of strong base anion exchange membrane with quaternary ammonium functional groups [23]. Besides, 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).

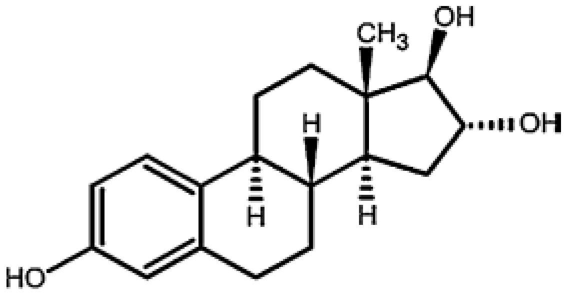

Figure 1. Molecular structure of estriol (E3) [24].

2.2. Electrochemical Measurement

The electrochemical behaviors of E3 in the prepared solutions were investigated with cyclic voltammetry (CV). The potential scan range was 0↔1.2 V (starting/ending at 0 V and scan rate 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.

2.3. E3 Electrolysis

In this work, the tested concentrations of E3 were slightly higher than those found in STPs and natural water systems to assure good E3 quantification in the electro-oxidation process. The anolyte (100 mL) was E3 (250, 500, or 750 μg/L) in 0.1 M Na_2SO_4 while the catholyte was only 0.1 M Na_2SO_4. The electro-oxidation of the E3 aqueous solution was galvanostatically performed in a thermostatted divided cell, and each electrolyte was well stirred using a magnetic stirrer. 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 E3 in samples were analyzed by a HPLC instrument (see below).

2.4. Analysis

The concentrations of E3 were measured by HPLC (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/water (45:55, v/v), with a flow rate of 1mL/min. The injection volume was 20 μL and the working wavelength for quantitative analysis was 205 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 E3 was determined to be 3.65 min (Fig. 2). Triplicate measurements were conducted for a series of prepared E3 standard solutions to determine the measurement errors of the HPLC method. The relative standard deviations (RSDs) were 1.2−2.9% in a range of low E3 concentrations (10−1000 μg/L). The linear fitting of calibration curve yielded an R^2 value of 0.999 (the inset in Fig. 2). Chemical oxygen demand (COD) measurements were performed to evaluate the abatement of organic compounds during the degradation of E3 and intermediates. For the determination of COD (consistent with the closed reflux colorimetric method), 2 mL of sample was introduced into a commercially available digestion tube and the mixture was then heated for 120 min at 150°C. The reduced amount of oxidizing agent was subsequently determined colorimetrically using a colorimeter (Hach DR/890) and expressed as the COD.

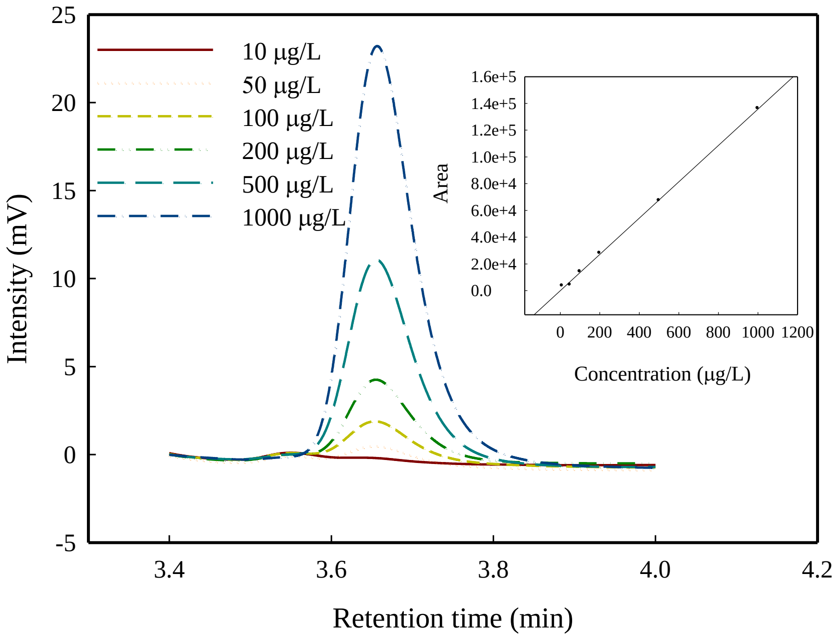

Figure 2. HPLC chromatograms for different E3 concentrations; inset: peak area against concentration.

3. RESULTS AND DISCUSSION

3.1. Cyclic voltammetry

Cyclic voltammetric experiments were performed to examine the electrochemical behavior of E3 at BDD in sodium sulfate solution (supporting electrolyte, 0.1 M). Fig. 3 shows the cyclic voltammograms of 10 mg/L E3 in 0.1 M Na_2SO_4. As can be seen from Fig. 3, during the first anodic sweep from 0 to 1.2 V, a well-shaped oxidation peak is observed at about 0.78 V versus Ag/AgCl. In the reverse scan from 1.2 to 0 V, no corresponding reduction peak is observed, suggesting that the electrochemical oxidation of E3 at BDD is totally irreversible. Additionally, as the number of cycle increased, the anodic peak current decreased until a steady state is reached. This phenomenon has also been observed in the anodic oxidation of other phenolic compounds such as phenol [25], nitrophenols [26, 27], chlorophenols [28], polyhydroxybenzene [29], and 17β-estradiol (E2) [30] on BDD electrodes. This phenomenon can be attributed to the deposition of organic films on BDD surface that deactivate the electrode. According to some earlier investigations [25, 29, 30], this fouling layer can be removed by anodic polarization in the potential region of water decomposition (>2.3 V).

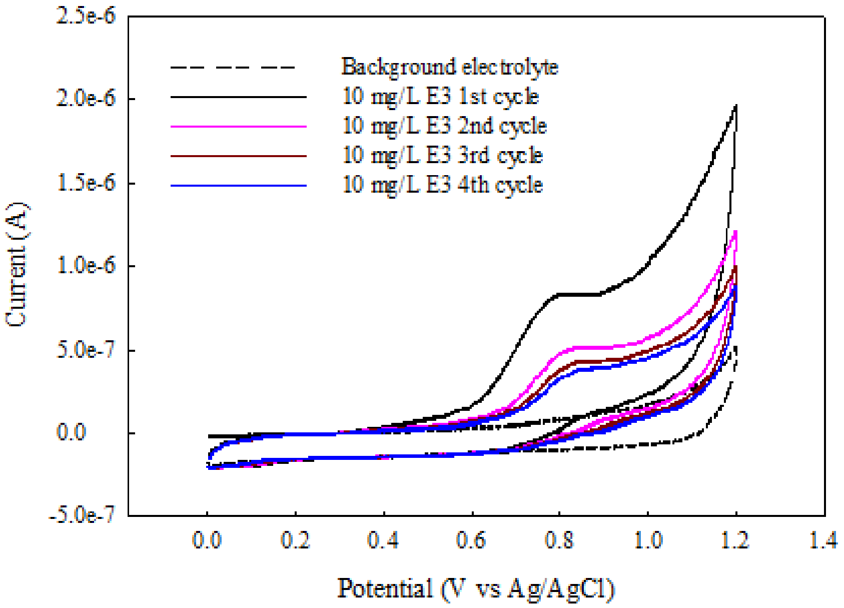

Figure 3. Cyclic voltammograms of E3 solution (10 mg/L) and background electrolyte (0.1 M Na_2SO_4) on BDD electrode at 25°C. Scan rate = 100 mV/s.

3.2. Effect of current density

Current density is an important parameter that may influence electrochemical oxidation of EDCs. Fig. 4 shows the ratios of C/C_o (C: the residual concentration of E3 at a given electrolytic time, and C_o: the initial concentration of E3) for the anodic oxidation of E3 on the BDD electrode at different applied current densities (I_{appl}) (20−100 mA/cm^2). As expected, the degradation efficiency (= $(1-(C/C_o))\times100\%$) of E3 increased with increasing I_{appl}. The increase of current density from 20 mA/cm^2 to 50 mA/cm^2 markedly increased the degradation efficiency of E3. The degradation efficiencies of E3 were similar at 50 and 100 mA/cm^2; nevertheless, most of E3 could be degraded in a very short time (<2 min) in the electrolysis. Near 100% E3 degradation could be accomplished within 10 min electrolysis at 20 mA/cm^2, and only one half (5 min) was required at 50–100 mA/cm^2. Because the E3 degradation reaction was too fast at high I_{appl} (50 and 100 mA/cm^2), the low current density (20 mA/cm^2) was used to carry out the subsequent tests in this study based on sampling consideration.

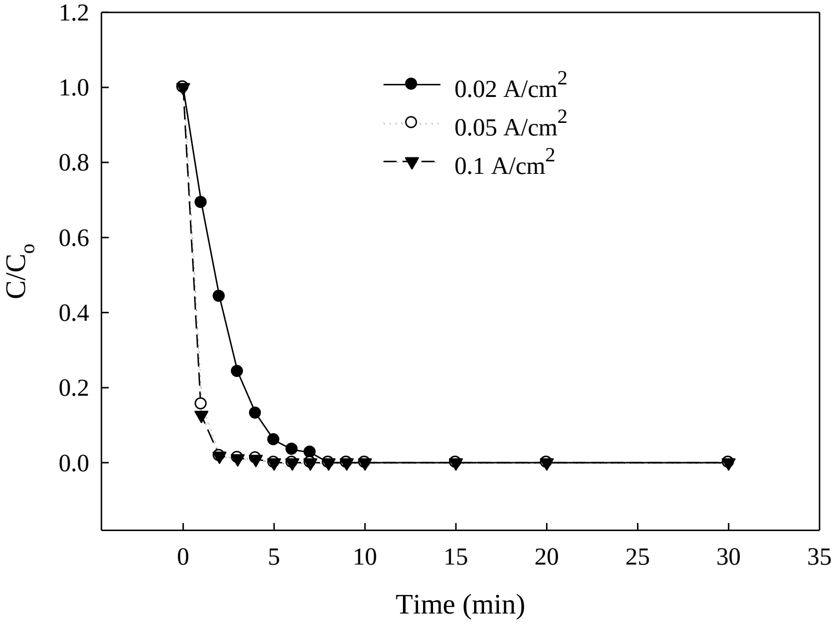

Figure 4. Effect of current density on E3 degradation at BDD anode. (E3, 500 μg/L; electrolyte, 0.1M Na_2SO_4; *T*, 30°C ; separator, AMI-7001).

3.3. Effect of initial E3 concentration

Three different initial E3 concentrations (250, 500 and 750μg/L) were tested to examine the effect of initial E3 concentration on E3 degradation on the BDD electrode surface at 20 mA/cm^2 and 30°C. Fig. 5 shows that the degradation of E3 decreased with increasing initial E3 concentration. When the initial E3 concentration was 250 μg/L, the degradation of E3 was nearly 100% at 3 min electrolysis. Only 66.2% E3 was degraded at 3 min electrolysis for triple initial E3 concentration (750 μg/L); furthermore, it took 8 min to achieve ~100% E3 degradation when the initial E3 concentrations were 500 and 750 μg/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. This condition is favored for a diffusion-control reaction (e.g., the one on BDD at 20 mA/cm^2 and 30°C) (see more discussion in Section 3.5 below). Therefore, it is inferred that the electro-generated hydroxyl radicals (·OH) should play an important role for the degradation of E3. Additionally, the amounts of generated ·OH should be similar at the same operating conditions (except initial E3 concentration) in electrolysis. However, the higher the initial E3 concentration, the more the ·OH was needed for rapid E3 degradation. It is also possible that competitive consumption of ·OH was present and parts of hydroxyl radicals were used to oxidize the intermediate compounds generated from E3 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 [31]. Nevertheless, the difference in degradation efficiency due to various initial E3 concentrations was negligible after the electrolysis for 8 min because of the depletion of E3.

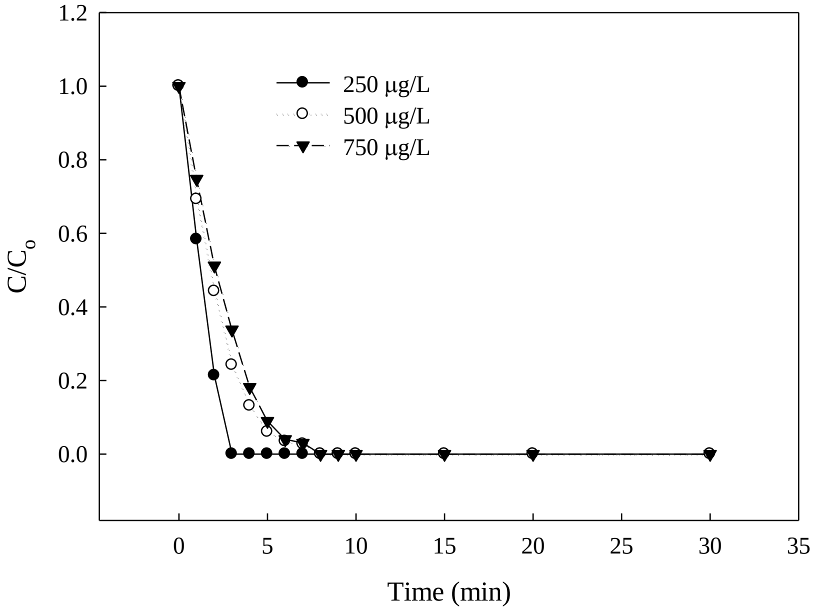

Figure 5. Effect of different initial concentration on E3 degradation with BDD anode; inset: ln (C/C$_o$) against time (current density, 20 mA/cm^2; electrolyte, 0.1M Na_2SO_4; *T*, 30°C; separator, AMI-7001).

3.4. Effect of anode material

It is well known that the anodic oxidation of organics is strongly dependent on anode material. In this study, three anodes (BDD, Ti/Pt, and DSA) were compared for their performance of E3 oxidation at 20 mA/cm^2 (E3 initial concentration = 500 μg/L). Fig. 6 shows that for E3 degradation, BDD anode was clearly superior to Ti/Pt and DSA, although the DSA was slightly better than the Ti/Pt. It was noted that after 8 min constant current electrolysis, no residual E3 was detected when BDD was used as the anode. At the same electrolysis time, however, the degradation efficiency of E3 was only about 19.3% and 27.1% on the Ti/Pt and DSA anodes, respectively. To achieve 100% E3 degradation, the Ti/Pt and DSA anodes needed more than 30 min, which was almost four-fold longer that BDD did. Likewise, the trend of COD removal was similar to that of E3 on the three anodes. For 120 min electrolysis of E3, BDD achieved an 100% COD removal (complete mineralization of E3) whereas the COD removal on DSA was less than 40% and that on Ti/Pt was even lower (Fig. 7).

The result is in accordance with the tendency of oxygen evolution potentials of tested electrodes (BDD > DSA ≥ Ti/Pt) [19]. Also, the magnitude of anode potentials of tested electrodes followed the order BDD > DSA > Ti/Pt (3.01, 1.68, and 1.54 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 [32] and the production of ·OH from water electrolysis for ·OH-mediated reactions [33]. The more free or adsorbed ·OH produced on the BDD than on the MO_{x+1} might cause electrophilic attack of E3 (with an aromatic ring) and its derivatives. As a result, the magnitude of E3 degradation efficiency or its mineralization rate was in order BDD > DSA > Ti/Pt. 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) [34, 35].

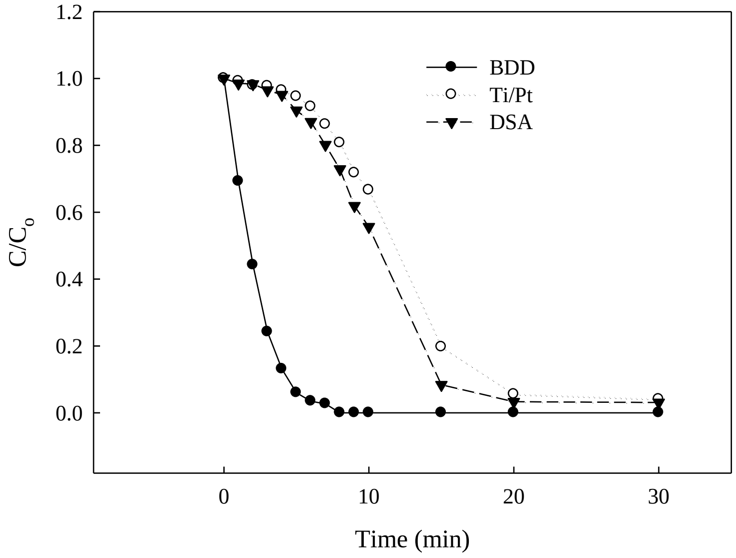

Figure 6. Comparative study of different electrodes on E3 degradation with equal surface area of 1 cm^2. (E3, 500 µg/L; current density, 20 mA/cm^2; electrolyte, 0.1M Na_2SO_4; *T*, 30°C; separator, AMI-7001).

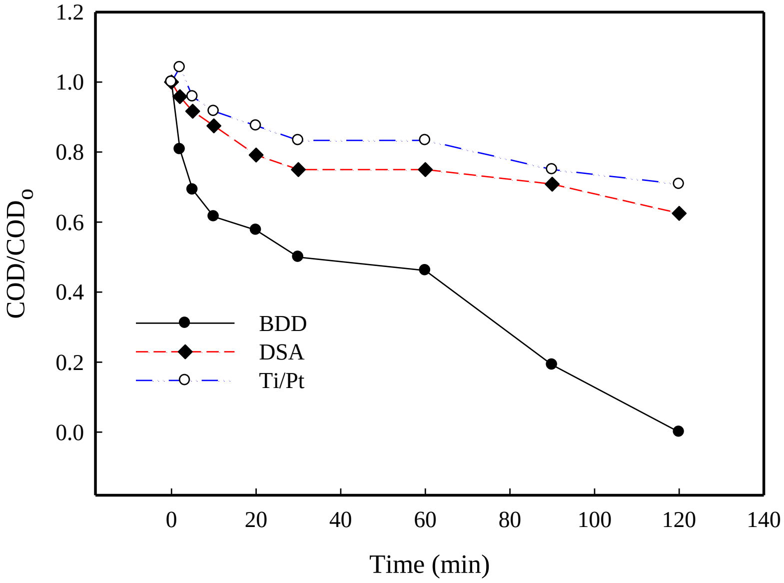

Figure 7. Variation of COD/COD_o with time at different anode materials for E3 electro-oxidation (E3, 10 mg/L; current density, 20 mA/cm^2; electrolyte, 0.1M Na_2SO_4; *T*, 30°C; separator, AMI-7001).

3.5. Effect of temperature

The increase of temperature (30–70°C) slightly increased the degradation of E3 at 20 mA/cm^2 (Fig. 8). Similarly, Mahmoud and Ahmed [36] observed that phenol degradation was nearly complete as the solution temperature reached 25°C and further phenol removal was negligible at >25°C on Ni-Al_2O_3 composite-coating electrodes. Furthermore, the regressions of E3 degradation data were all linear (R^2 = 0.97−0.98) for the three different concentrations (the inset in Fig. 8). Accordingly, the degradation of E3, is simplified to a bimolecular reaction between E3 and ·OH, and can be regarded as a pseudo-first-order reaction, if the concentration of ·OH does not change significantly.

$$\frac{-d[E3]}{dt} = k[E3][\cdot OH] = k_{app}[E3] \qquad (1)$$

where the k and k_{app} in Eq. 1 are the rate constant and apparent (pseudo-first-order) rate constant of reaction, respectively.

The obtained pseudo-first-order rate constants (k_{app}) are 8.9×10^{-3}, 9.6×10^{-3}, and 1.05×10^{-2} s^{-1} at 30, 50, and 70°C, respectively. The activation energy *E*a value calculated using Arrhenius's law was 3.56 kJ/mol for the E3 degradation. For a diffusion-controlled homogeneous reaction, the *E*a value is typically less than 40 kJ/mol [37]. It is inferred that the E3 oxidation was probably a diffusion-controlled reaction.

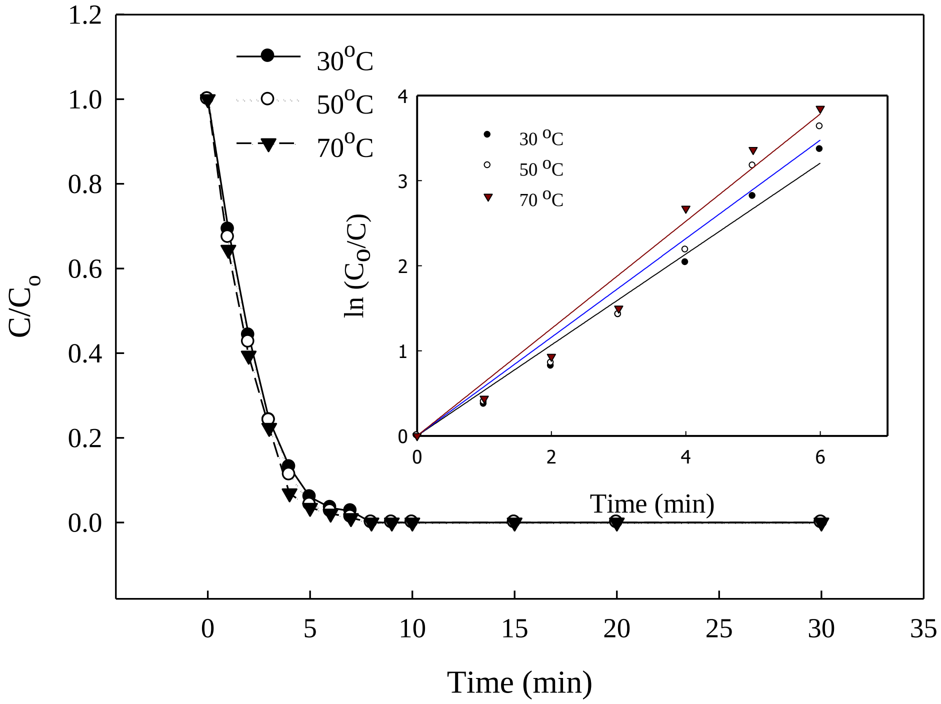

Figure 8. Effect of temperature on E3 degradation with BDD anode; inset: ln (C_o/C) against time (E3, 500 µg/L; current density, 20 mA/cm^2; electrolyte, 0.1M Na_2SO_4; separator, AMI-7001).

4. CONCLUSIONS

In this study, well-defined irreversible cyclic voltammograms were obtained for the oxidation of E3, indicating that the E3 oxidation was irreversible on the BDD electrode. E3 can be completely degraded using the BDD anode in short-time electrolysis and the degradation of E3 was a pseudo-first-order reaction.

The degradation of E3 increased with increasing applied current density (20−100 mA/cm^2) at 30°C. Although the degradation efficiencies of E3 were similar at 50 and 100 mA/cm^2, most of E3 could be electrochemically degraded in a very short time (<2 min). The performance of tested anodes for E3 degradation in terms of E3 degradation and COD removal efficiencies was in order BDD > DSA > Ti/Pt. When the BDD electrode was used, after 8-min constant current electrolysis, no residual E3 was detected; at the same electrolysis time, the degradation efficiencies of E3 were only approximately 19.3% and 27.1% on the Ti/Pt and DSA anodes, respectively. Additionally, the degradation efficiency of E3 decreased as the initial E3 concentration increased. The apparent rate constant of E3 degradation on the BDD anode slightly increased (8.9×10^{-3} to 1.05×10^{-2} s^{-1}) with the increase of temperature (30−70°C) at 20 mA/cm^2 in 0.1M Na_2SO_4 electrolyte. Furthermore, the activation energy was 3.56 kJ/mol for E3, revealing that the E3 electro-oxidation is a diffusion-controlled. The use of the BDD electrode is very promising for the degradation of E3 in aqueous solutions at room temperature.

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