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REMOVAL OF ENDOCRINE DISRUPTERS BY A CARBON ELECTROLYTIC REACTOR

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ABSTRACT

Water demand for agricultural production has become a crucial factor for sustainable development. With regard to reducing the risk posed by water supplied from irrigation or natural water sources, water reuse and recycling have been initiated in many parts of the world, especially where water scarcity is becoming serious due to the impact of climate change. One of the challenges in water reuse is how to eliminate toxic compounds from agricultural wastewater. This paper demonstrates a method to remove estradiol (E2), an environmental hormone excreted mainly from animal husbandry farms and 2,4 dichlorophenol (DCP), a weed control chemical. The operating conditions for electro-chemical oxidation of estrogens (estrone (E1), E2 and ethynylestradiol (EE2) and 2,4 dichlorophenol (2,4D) were evaluated using synthetic wastewater. The results showed that although estrogens and DCP oxidized in the range of 0.5-0.8V, the optimal condition for electropolimerization was achieved in alkaline conditions. In addition, the continuous treatments show that more than 80% of removal efficiency was achieved with energy consumption around 1-10 Wh/m^3. It is recommended that further studies using available materials at local sites should be conducted to make this process possible in practice.

Keywords: Activated carbon, advance oxidation process, endocrine disrupter, environmental hormone, wastewater.

Xử lý chất rối loạn nội tiết bằng hệ thống điện phân sử dụng điện cực carbon

TÓM TẮT

Nhu cầu nước cho sản xuất nông nghiệp trở thành một yếu tố cần thiết cho sự phát triển bền vững. Để giảm thiểu các rủi ro đến từ nguồn nước tưới tiêu hoặc nguồn nước tự nhiên, tái sử dụng hoặc quay vòng sử dụng nước được thực hiện ở một số nơi trên thế giới, đặc biệtt những nơi bị ảnh hưởng bởi biến đối khí hậu. Thách thức lớn trong tái sử dụng nước là loại bỏ các độc chất trong nước thải cho các hoạt dộng nông nghiệp. Nghiên cứu này thử nghiệm một phương pháp mới nhằm loại bỏ estradiol (E2), một dạng hormon môi trường có nguồn gốc từ các trang trại chăn nuôi và DCP, thành phần của thuốc diệt cỏ. Các thí nghiệm được thực hiện trên đối tượng nước thải nhân tạo nhằm đánh giá một số điều kiện cơ bản ảnh hưởng tới hiệu quả xử lý. Kết quả cho thấy quá trình oxi hoá của E1, E2, EE2 và DCP xảy ra trong khoảng hiệu điện thế từ 0.5-0.8V, điều kiện tối ưu cho việc xử lý tốt nhất ở pH kiềm tính. Hiệu quả xử lý đạt trên 80% tại điện thế 1.0V với điện năng tiêu thụ khoảng 1-10 Wh/m^3. Để có thể áp dụng công nghệ này vào thực tiễn, cần thực hiện thêm các nghiên cứu sử dụng vật liệu carbon hoạt tính chế tạo từ phế phụ phẩm sẵn có trong nông nghiệp nhằm giảm chi phí đầu vào.

Từ khoá: Carbon hoạt tính, chất rối loạn nội tiết, điện hoá, hormone môi trường, nước thải.

1. INTRODUCTION

Endocrine disrupters (EDs) such as estrogens and chlorinated phenolic compounds have become emerging contaminants due to their adverse impacts on aquatic life at extremely low levels. Highlighting the toxicity of the EDCs, several definitions on how EDs pose serious problems to humans and wildlife have been proposed. One definition states that an EDC is “an exogenous agent that interferes with the synthesis, secretion, transport, binding, action, or elimination of natural hormones in the body which are responsible for maintenance or homeostasis, reproduction, development and or behavior" (Kavlock *et al.*, 1996). However, Hester and Harrison (1999) simplified EDCs as any chemicals that can mimic endogenous hormones, interfere with pharmacokinetics, or act by other mechanisms to cause the disruption of human or animal endocrine systems. It has recently been reported that 17β-estradiol (E2) causes sex reversal in Medaka (*Oryziaslatipes*) at a concentration of 1 ng/L (Lei *et al.*, 2013) or its reproductive potential at 8.66 ng/L (Seki *et al.*, 2005). The U.S. EPA has recommended E2 as the first watch among the candidate contaminants (Richardson and Ternes, 2014). While E2 is mostly released from animal and livestock wastewater, 2,4 dichlorophenol, which contains E2, is a main component of pesticides used in weed control. Due to its persistence in the environment, bio-accumulative properties and potential to generate unintentional by-products, an appropriate treatment of these compounds should be evaluated.

In Vietnam, Duong *et al.* (2010) reported the occurrence of nonyl phenol (NP), octyl phenol (OP), bisphenol A (BPA), estrone (E1), 17β-estradiol (E2) and 17α-ethynyl estradiol (EE2) at significant values in river water. Especially, the concentrations of E1, E2, and EE2 were found at 62.4, 10.2, and 28.7 ng/L, respectively, which are much higher than the thresholds for aquatic life forms. Recently, Duong *et al.* (2014) reported 940 micro-pollutants found in river sediment. Surprisingly, many organochloride pesticide compounds had concentrations exceeding sediment quality guidelines. Therefore, an appropriate approach in the treatment of organic pollutants should be developed to reduce the residue of contaminants before being discharged to receiving waters.

The treatments of EDs were conducted by physical and chemisorption processes using nylon microfiltration membranes (Han *et al.*, 2012), by biological processes using a membrane bioreactor (Trinh *et al.*, 2011; Zhou *et al.*, 2011; Meang *et al.*, 2013), activated sludge (Li *et al.*, 2010), and enzymatic treatments (Tanaka *et al.*, 2009; Reis and Sakakibara, 2012). These processes showed advantages in the treatment of high loading rate pollutants. However, they require several operating conditions for optimal treatment performance such as temperature, pH, and contact time. The electrochemical process could overcome these drawbacks based on its potential to produce strong oxidative species (·OH radicals). The OH radical is considered to be able to destruct the binding of organic contaminants (Chen, 2004). Cong and Sakakibara (2015) demonstrated an effective and enhanced continuous removal of estrogens through electro-polymerization and regeneration of electrolytic cells using granular Pt/Ti and glassy carbon electrodes at practical conditions (pH 7.0 and 24°C). It was reported that 92-97% of the estrogens were continuously removed without inhibition of the reactor within a month. However, using such a commercial electrode material is very costly and may limit its application in the treatment of wastewater.

In the electrochemical process, cyclic voltammetry (CV) is a highly sensitive technique to detect the oxidation and reduction reactions of contaminants on the surface of electrodes. To examine the reaction of endocrine disruptors, several types of electrodes were used. Gatrell and Kirk (1993) initially investigated the oxidation of phenol on platinum and peroxidized platinum surfaces. Recently, carbon nanotubes have been employed to evaluate the electrochemical response of EDCs (Gan *et al.*, 2013). However, the use of commercial products like platinum or nanotube carbon may limit their application in practice due to their high costs and availability. In this study, we seek for low cost carbon materials, such as carbon fiber or modified activated carbon, as alternative materials for electrochemical oxidation of ECs. The removal efficiency of a mixture of DCP and E2 was evaluated using a novel electrolytic reactor composed of carbon fiber electrodes.

Electrochemical behaviors, batch removal efficiency, and continuous removal performance were evaluated.

2. METHODOLOGY

2.1. Reagents

Estrogens (E1, E2, EE2), and DCP were purchased from Wako Chemical Company, Japan. The purity of the chemicals and solvents used in this experiment were of a grade for gas chromatography analysis. Stock solutions of each E1, E2, EE2, and DCP were made at 1000 ppm (1 mg/mL) in acetone 5000 (acetone for PCB analysis). This stock was prepared because estrogens have a very low solubility and also allowed the same bulk conditions for every experiment.

2.2. Experimental design

The cyclic voltammetry analysis was conducted using a conventional three-electrode system, which consisted of a working electrode, a reference electrode, and a counter electrode. In this study, two types of apparatuses were used to examine the electrochemical reactions of estrogens and DCP. To verify the performance of the system, a modified reactor was made to have similar conditions as the reactor for electrolysis. The modified CV system was made of a glassy carbon working electrode (10 cm^2) connected to a Pt wire counter electrode and an Ag/AgCl reference electrode. The dimensions of the working electrodes were 50 mm × 10 mm × 1 mm (*length* × *width* × *thickness*). Electrochemical oxidation responses were examined in 150 mL of 10 mmol/LNa_2SO_4 solution containing 0.01 mmol/L E1, 0.01 mmol/LE2, or 0.01 mmol/L EE2. The potential is hereafter represented in volts (V) versus Ag/AgCl. All CV analyses were carried out using a HZ-5000 analyzer (Hokuto Electronic Inc.). In batch experiments, an initial concentration of 200 μg/L E2 was prepared in 10 mM Na_2SO_4 as the electrolyte. The residue of E2 in the reactor was measured at 0, 30, and 60 minutes while the total organic carbon (TOC) was measured at 0, 20, 40, and 60 minutes after the operation.

The apparatus (Fig. 1) included two compartments consisting of compressed carbon fibers (anodes) and a Pt/Ti rod (cathode). Total liquid volume and surface area of the carbon fiber anodes were about 50 mL and 4,000 cm^2, respectively. The reactor was connected to a direct current (DC) supply with current and potential control modes. In the continuous experiment, the potential was operated in run 1 to run 3 with potentials of 1.0, 0.5, and 1.0 V. The hydraulic retention time (HRT) was controlled at 15 minutes using a peristaltic pump. The influent and effluent samples were taken every 24 hours.

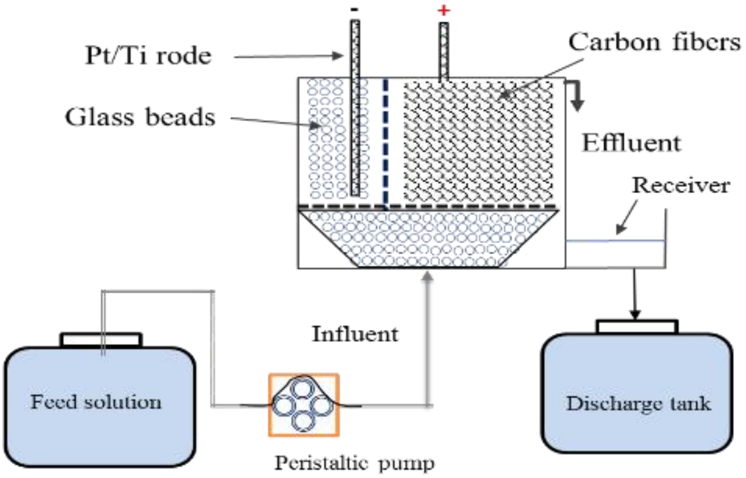

Figure 1. Experimental apparatus in continuous experiment

2.3. Data analysis

Samples were processed right after being taken from the reactor. The detailed procedure for the measurement of influent and effluent is described in Cong and Sakakibara (2015). Samples were pretreated with surrogates and internal standards to enhance the accuracy of concentrations. BPA-*d14* was introduced into the water samples as the surrogate. All samples were filtered through a 0.65 μm membrane filter to remove any suspended solids. Samples of 100 mL of influent or effluent were extracted with 20 mL of ethyl acetate (99.7% purity) after adding 10 g NaCl and 0.2 mL of 1M HCl. Extracted samples were dehydrated using Na_2SO_4 (*anhydrous*). After concentration via a rotary evaporator, extracted estrogen samples were dried under a gentle nitrogen stream and controlled to 0.5 mL. Derivatizations of E1, E2, EE2, and DCP were obtained using BSTFA (1% TMS) catalyzed by pyridine. An internal standard method was applied to calibrate the concentrations of E1, E2, EE2, and DCP. All samples were analyzed using GC/MS QP5050 (Shimadzu, Japan). The measurement of total organic carbon (TOC) in the batch experiment was conducted using a TOC-5000A (Shimadzu, Japan).

3. RESULTS AND DISCUSSIONS

3.1. Influence of operating conditions

3.1.1. Initial concentrations

Electrochemical responses of 0.27, 2.7, 13.6, and 27.2 mg/L E2 were evaluated using glassy carbon electrodes at pH 6.5-7.0 and a scan rate of 100mV/s. Figure 2 shows the influences of E2 concentrations on the oxidation process. As shown, oxidation occurred at potentials ranging from 0.5 to 0.8 V (vs. Ag/AgCl). The current peaks increased relatively twice when the concentration increased by one order. The same phenomena were observed in the case of E1, EE2, and DCP. In the electrolysis of the phenolic compounds using the cyclic voltammetry mode, the compounds exchange electrons directly on the surface of the electrode and oxidize. The result indicates that direct oxidation of phenolic compounds through electrochemical polymerization could be applied to a wide loading range of phenolic contaminants.

3.1.2. Bulk pH

Influence of pH on oxidation of estrogens was experimentally investigated for 0.01 mM E1, 0.01 mM E2, and 0.01 mM EE2 at different pH conditions in phosphate buffer solution (PBS). Figure 3 shows the electrochemical response of EE2 in acidic (pH 3.0 - 5.5), neutral (pH 6.9 - 7.0), and alkaline (pH 10) conditions. As shown, EE2 was oxidized at a wide range of pH values from acidic to alkaline conditions (3 to 10). It was noted that the oxidation peaks occurred at a lower potential (0.35 V) when the pH was around 10. Around pH 10, EE2 (and E2) was dissociated due to its *pKa* around 10.4. The same results were observed in the case of E1 and E2. It is hypothesized that E1, E2, and EE2 can be oxidized easily because the molecules are represented in negative forms. The influence of pH on DCP oxidation was not conducted because the *pKa* of DCP is 7.89 which is suitable for treatment at a neutral pH. It was reported that the electrochemical polymerization of phenol is more favored in alkaline than in acidic solutions. At neutral conditions (pH 7), the oxidation peak situates around 0.65 V. This result suggests that direct a oxidation process could be an alternative choice for treatment of various wastewater containing endocrine disrupters.

3.1.3. Scan rates

Scan rate is an important parameter in cyclic voltammetry analysis. Theoretically, the oxidation current peak is linearly proportional with the square root of the scan rate following the Randles-Sevcik equation. We assumed that the oxidation of estrogen was governed by 2-electron electro-polymerization processes. The

Randles-Sevcik equation describes the effect of scan rate on the peak current i_{pf} represented in (1) (Bard and Faulkner, 2001):

$$i_{pf} = (2.69 \times 10^5)\, n^{3/2} A D^{1/2} C^* v^{1/2} \qquad (1)$$

Where, n is the number of electrons exchanged during electro-polymerization; A (cm^2) is the active area of working electrode; D (cm^2/s) is the diffusion coefficient; C^* (mol/cm^3) is the bulk concentration of E1, E2, and EE2; and v is the voltage scan rate (V/s). In this study, n=2; A = 10 cm^2, D_{E1} = 0.54 x 10^{-5}cm^2/s; D_{E2} = 0.52 x 10^{-5}cm^2/s; D_{EE2} = 0.51 x 10^{-5}cm^2/s; C^* = 10^{-5}mol/cm^3, v = 0.01 to 1.0 V/s.

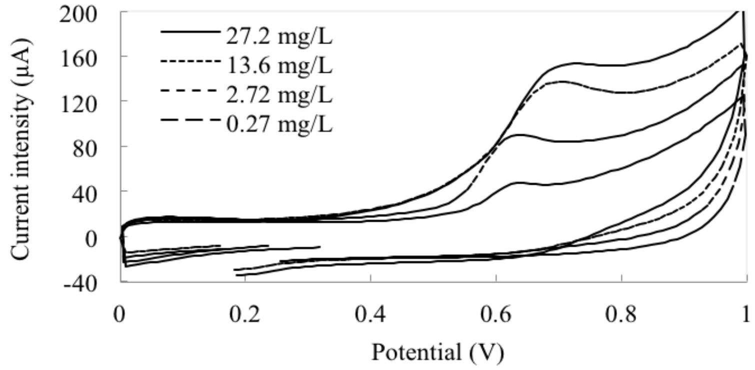

Figure 2. Oxidation of E2 at different concentrations

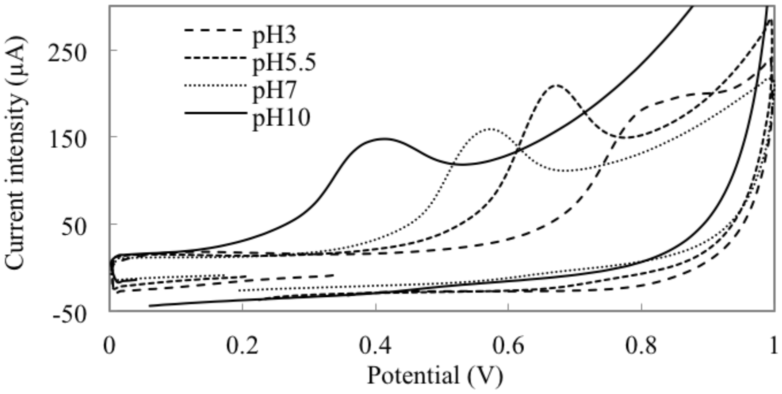

Figure 3. Electrochemical responses of EE2 at different pH values

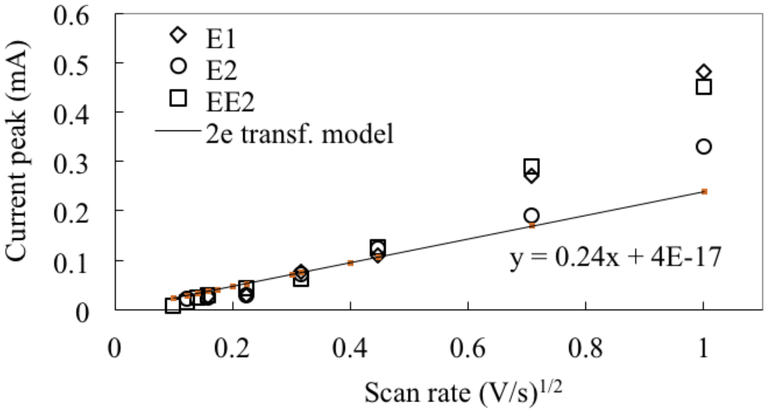

Figure 4. Influence of scan rates on the oxidation current peak.

Note: Experimental conditions: electrolyte: 10 mmol/L Na_2SO_4*; E1, E2, EE2 concentration: 0.01mmol/L*

Figure 4 shows the electrochemical oxidation responses of E1, E2, and EE2 against scan rates on glassy carbon electrodes. The data represent oxidation peaks of 0.01 mM for E1, E2, and EE2 at different scan rates. The observed data show that oxidation current peaks were linearly proportional to the square root of the scan rates. The observed data are in good agreement with the model based on the 2-electron transfer process at a scan rate between 10 and 30 mV/s. However, when the scan rate was set at 1.0 V/s, the oxidation peaks exhibited a higher response in current intensity. This can be attributed to the transformation of electrolytes or water electrolysis, rather than direct oxidation of the estrogens.

3.2. Electrolytic removal of estradiol

3.2.1. Batch treatment of E2

A batch treatment of E2 was conducted using carbon fiber electrodes in a 200 mL beaker under the potential control mode at 1.0V. Figure 5 demonstrates a complete removal of 200 µg/L E2 within 60 min. To confirm the complete removal of E2, total organic carbon (TOC) was measured at 20, 40, and 60 minutes after the operation. As shown, at the point of complete removal of E2, a removal efficiency of TOC was achieved around 0.9. This result indicates that the effective removal of E2 could be obtained at a potential around 1.0 V. This experiment shows the preliminary performance of E2 using simple electrolytic equipment. Therefore, further studies on reactor configurations should be carried out to enhance removal performance.

3.2.2. Continuous removal of E2 and DCP

From the obtained results in the previous sections, a continuous treatment of a mixture of E2 and DCP was conducted under different electric potentials (Fig. 6). At 1.0 V, removal of DCP and E2 was about 60% within 20 hours. The removal of E2 and DCP may attribute to the electrochemical polymerization process. To verify the system sensitivity, the potential was reduced to 0.5 V. The effluent concentration of residuals increased dramatically. However, when the potential was set back to 1.0V, the removal efficiency of E2 and DCP increased to above 80%. In general, the removal efficiency of DCP was higher than that of E2 which may be due to the higher mass transfer rate of DCP. Indeed, a good removal efficiency of E2 and DCP was obtained at 1.0 V but there were still some fluctuations due to not reaching a steady state. Therefore, a further optimization of the reactor should be developed to enhance the removal performance.

Energy consumption (EC) is always the greatest concern in the electrochemical process. The energy consumption was obtained from the continuous treatment of 100 µg/L E2 and DCP (Fig. 7). The EC was compared with other well-known advanced oxidation processes for the treatment of E1, E2, and EE2 (Muriganathan *et al.*, 2007; Sakar *et al.,* 2014). The data show that the oxidation of E2 and DCP achieved about 87 - 91% removal efficiency at 0.001-0.01 kWh/m^3 of synthetic solutions while other processes consumed up to 10 - 100 kWh/m^3.

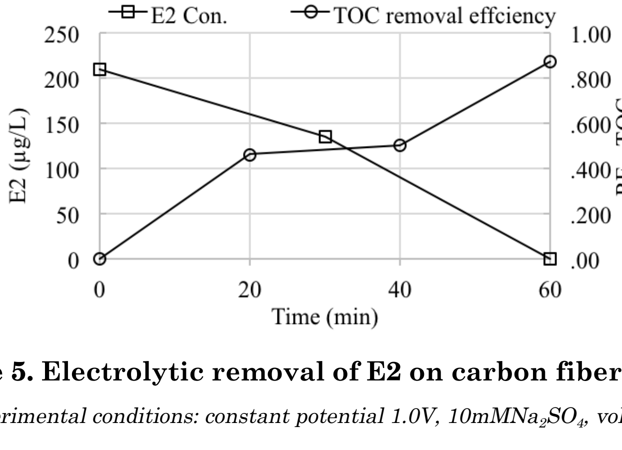

Figure 5. Electrolytic removal of E2 on carbon fiber anodes

Note: Experimental conditions: constant potential 1.0V, 10mMNa$_2$SO$_4$, volume 100 mL

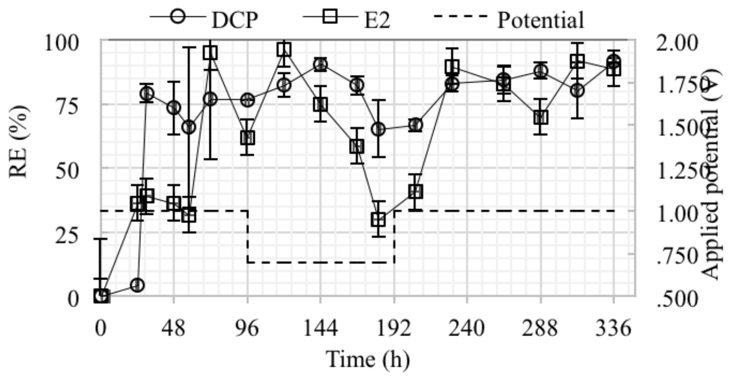

Figure 6. Continuous removal of a mixture DCP and E2 by a carbon fiber electrolytic reactor at different applied potentials

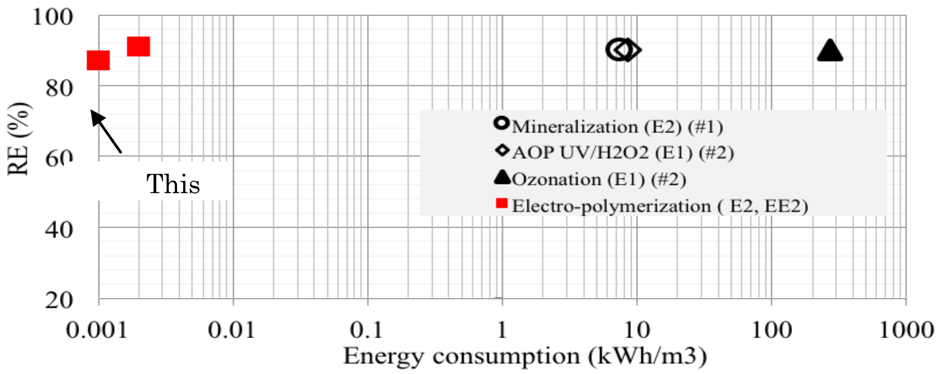

Figure 7. Removal performance of this study compared with published literature

Source: (#1) Murugananthan et al., (2007), (#2) Sakar et al., (2014).

4. CONCLUSIONS

The electrochemical oxidations of E1, E2, EE2, and DCP were investigated on glassy carbon and carbon fiber electrodes with different operating conditions such as the concentration of estrogens in bulk solution, the pH of the media, and scan rates. The following findings were drawn from the experimental studies: 1) E1, E2, EE2, and DCP were oxidized in the range of 0.5 to 0.8 V on glassy carbon and carbon fiber electrodes. This result indicated that the direct oxidation process occurred during the treatment of these compounds. 2) Initial concentrations of estrogens in bulk liquid influenced the oxidation rate. An increase by one order of magnitude in the initial concentration resulted in twice the oxidation current peaks. This result indicated that the mass transfer rate was a limiting step that governed the electron transfer between bulk liquid and electrodes. 3) The potential of oxidation was lowered in alkaline conditions. This condition was reported to favor the electro-polymerization of phenolic compounds. 4) High rate removal of E2 and DCP was achieved around 87% - 91% at very short hydraulic retention times which is suitable for the treatment of contaminated water for reuse and recycling purposes.

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