A STUDY ON DIRECT ELECTROLYSIS OF ESTROGENS BY GRANULAR GLASSY CARBON ELECTRODES

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1. INTRODUCTION

Natural and synthesis hormones, estrogens, are characterized as strong endocrine disrupting chemicals (EDC). The effect of estrogens on the aquatic life form has investigated at very low concentration 0.2-64 (ng/l). Concentration range has been reported from ND-100 ng/l in Asian countries [1], [2]. Trace concentration of estrogens have posed many challenges for treatment of EDCs. Conventional treatments have been reported whether low kinetics or incomplete removal. In electrochemical process, organic pollutants could be degraded through electron exchange directly on the surface of electrode (direct oxidation) or other mediates (indirect oxidation). In this research, cyclic voltammetric techniques in combination with batch experiments were employed to examine the direct electrolysis of estrogens at low electric current. The results were further used to evaluate the removal of estrogen and mass transfer based on a mathematical model.

2. MATERIALS AND METHODS

2.1 Materials

Estrogens including E1, E2, EE2 (analytical grade), BSTFA (1% TMS) and Pyridine, were purchased from Wako Chemical Company, Japan. A Glassy Carbon electrode (Cat.No. 002012; 3.0 mm diameter, BAS), Platinum wire and Ag/AgCl (Cat.No. 012167) used as working electrodes, counter electrode, and reference electrode, respectively, were purchased from BAS Inc. The PK-3 consisted of a coarse diamond polish 1µm (Cat.No. 012621) and a polishing alumina 0.05 µm (Cat.No. 012620) cleaning kit was used to clean the electrode. Sep-pack Plus C18 Cartridges 55-105µm were used in solid phase extraction.

2.2 Cyclic Voltammetric Measurement

Voltammetric measuments were carried out by a HZ-5000 Hokotu Analyzer. The cyclic voltametric was conducted for E1, E2 and EE2 at the concentration of 5ppm each in the range of 0-1.3V, scan rate 100mV/s with 10mM Na_2SO_4.

The batch experimental apparatus of this study (Fig.1) includes two compartments consisting of 3-dimensional granular electrodes (anode) and a Pt/Ti counter cathode. Total volume and surface area of the working electrode (anode) were 500 cm^3 and 2,000 cm^2, respectively [6].

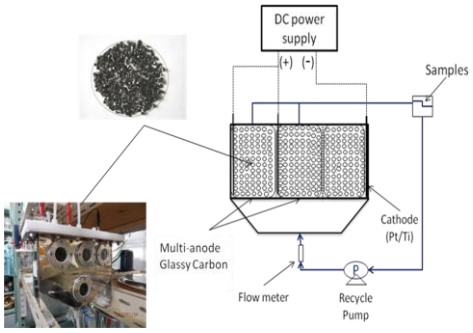

Fig.1: experimental apparatus

2.3 Mathematical Model

In the batch experiment, if the reaction is sufficiently rapid and the whole electrolysis is controlled by the mass transfer rate, the organic degradation would follow the first-order kinetics. The electrolysis removal of estrogen is simplified following equation (1):

$$C = C_0 \, Exp^{\left(-k\frac{A}{V}t\right)} \quad (1)$$

Where, C is concentration, C_0 is initial concentration, k is mass transfer coefficient, A is total working area, V is the volume of reactor and t is time. The mass transfer coefficient was calculated from the Wilson-Geankoplis equation [5].

3. RESULTS AND DISCUSSION

3.1 Electrochemical Behavior of Estrogens

Fig. 2 demonstrates the progressive cyclic voltamograms of E1, E2, and EE2 at 5 ppm in the range of 0-1.3V with 10mM Na_2SO_4. The result shows that only oxidation process was occurred in this experiment. The oxidation peaks of E1, E2, and EE2 occurred at 0.74V, 0.76V and 0.69V vs Ag/AgCl at 3.2 µA, 1.3 µA, and 2.6µA, respectively. The oxidation peaks were reduced in subsequent cycles. This result may imply that electro-polymerization of organic compounds have taken place on the surface of electrode. The same phenomena were reported elsewhere [3], [4].

Keywords: Electrochemical, estrogen, wastewater treatment, direct oxidation process, environmental hormone
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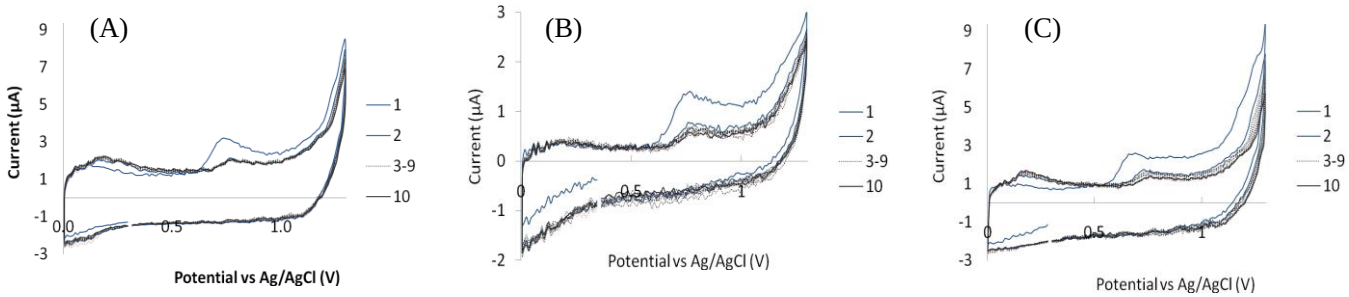

Fig.2: Progressive cyclic votammograms of estrogens (concentration: 5ppm, potentials 0-1.3V, scan rate 100mV/s)
A) E1; B) E2; C) EE2

3.2 Electrochemical Removals of Estrogens

Electrochemical removals of E1, E2 and EE2 in batch experiments were applied at zero (0), 0.1mA and 1 mA. The results were compared with the mathematical model. As showed in Fig 3A, the removal of E1 and E2 at 1mA achieved within 1 hour. Fig. 3-B shows the removal of E1, E2, and EE2 at 0.1 and 1mA in comparison with equation (1). The result showed that EE2 were removed down to 17.6 and 20.6 μg/L at 1mA and 0.1mA, respectively, after 4 hours. Within 1hour of treatment, the removals of E1, E2, and EE2 achieved quite fit with the calculation result by Eq. (1). In general, this study shows a possible treatment of trace estrogens at low current 5-50 x 10^{-4} A/m^2 which is 2-3 orders lower compared to other, 125-250 A/m^2 [7]. This may indicate that the glassy carbon electrode enhanced the total working area and mass transfer due to its large specific area and absorption capacity.

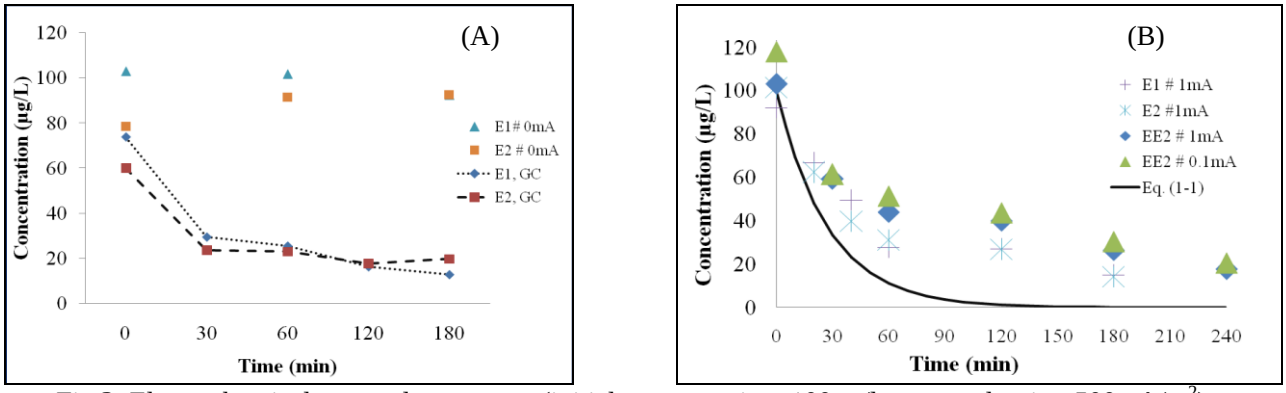

Fig.3: Electrochemical removals estrogens (initial concentration: 100μg/l; current density: 500mA/m^2)
A) E1 and E2 at 0A and 1mA; B) E1, E2 and EE2 at 1mA and EE2 at 0.1mA

8. CONCLUSIONS

The voltammetric technique showed that oxidation of estrogen is occurred at low current density 1.8-4.5 A/m^2 in the range of 0.6-0.8V vs. Ag/AgCl. In batch experiment, there was no significant different removal of estrogens between the current densities of 5x10^{-4} and 50x10^{-4} A/m^2. In the early stage of electrochemical oxidation of estrogen, the removal of estrogens were relatively governed by the mass transfer but estrogens were not completely removed after several hours, therefore, more research on removal of estrogen should be conducted.

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