

CONTINUOUS TREATMENTS OF ESTROGENS BY GLASSY CARBON GRANULAR REACTOR

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1. INTRODUCTION

Presence of estrogens in water has been identified to have adverse impact on aquatic life form at trace concentration (ng/L) [1]. The main sources of estrogens are from human and animals. Among estrogens and its derivatives, a large quantity of E1, E2, and E3 are excreted daily via urine (95%) [2]. However, conventional treatments of such kind of strong trace pollutants have not achieved below a safe level for aquatic ecosystem. Our former studies have shown that estrogens (E1, E2 and EE2) were removed by electrochemical oxidation process using a granular reactor and electrochemical responses of oxidation process were verified by cyclic voltammetry technique. In this research, continuous treatments of two most strong natural estrogens (Estrone - E1, and Estradiol - E2) as target pollutant were conducted using a granular electrode reactor under different influent concentration and electric currents.

2. MATERIALS AND METHODS

2.1 Materials

Estrogens including E1, E2 (analytical grade), BSTFA (1% TMS) and Pyridine, surrogates (E2-d3 and BPA-d14) and internal standard (Naphthalene-d8) were purchased from Wako Chemical Company, Japan. Granular glassy carbon electrodes were purchased from HTW, Germany.

2.2 Experimental apparatus and methods

The experimental apparatus in this study (Fig.1) includes two compartments consisting of granular electrodes with average size of 2-3mm as anode and a Pt/Ti mesh-type cathode. Total volume and surface area of the working electrode (anode) were 500 cm³ and 2,000 cm², respectively.

Synthetic estrogen wastewater was prepared at 100μg/L and 1μg/L (Table 1) with 10mM Na₂SO₄ supporting electrolyte. Influent rate of feeding estrogens was controlled by peristaltic pump. The recirculation rate within the system was set at 500ml/min. Hydraulic Retention Time (HRT) was set at 180min. Influent and effluent sampling points were taken at the point entering the reactor (1) and overflow (2) (Fig 1). In run 1, sample was daily taken while 3-day sampling was applied for run 2. Extraction of estrogen was carried out by liquid-liquid phase extraction following by GCMS analysis.

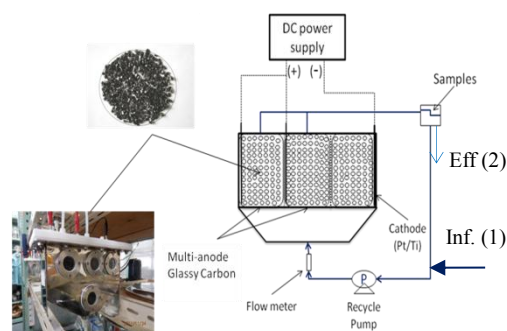


Fig.1 Experimental apparatus

Table 1: Operating conditions of continuous experiments

Run No.	Feed solution	Influent Concentration (μg/L)	Supporting electrolyte (mg/L Na ₂ SO ₄)	Recycling (ml/min)	HRT (min)	Current (mA)
Run 1	E1, E2	100	10mM	500	180	1.0
Run 2 (after regeneration)	E1					

3. RESULTS AND DISCUSSION

3.1 Electrode Responses

Fig 2 shows electrode responses observed by cyclic voltammetry technique. The short dashed-line shows a clear oxidation current peak of 0.01mM E2 for new electrode. The dotted and long dashed lines represent the first and second consecutive runs of the same electrode with a significant decrease of current peaks. However, the current peak was recovered to its original (solid line) after an application of 3.6 mg/l dissolved ozone by cycles of CV scan in the range of 0~1.5V. This result suggests that an application of ozone could be adapted to avoid electrode passivation. In our former studies, we found that the polymer formed during direct electrochemical oxidation process can be easily decomposed to regenerate anodes through the generation of OH radicals by Fenton reaction (3) or by advanced electrochemical oxidation process (4).

Keywords: Electrochemical, direct oxidation process, estrogen, continuous treatment, electrode regeneration

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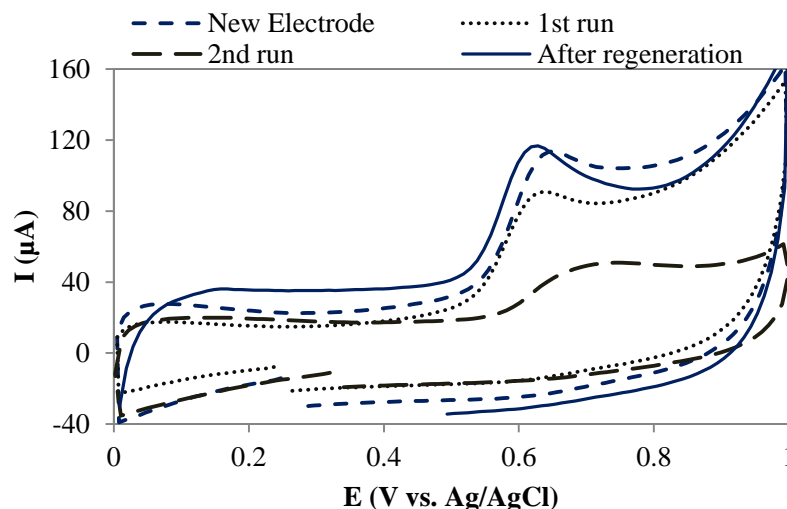


Fig. 2 Electrode regeneration

3.2 Electrochemical Removals of Estrogens

Fig. 3 demonstrates the removal of estrogen by glassy carbon granular electrode reactor at 1mA with 10mM Na₂SO₄. It is clearly to see that 87% of E1 and 94% of E2 were removed within two days of operation. Noticeably, removal of E2 achieved 97.8% then kept stable for almost of the operation time. Simultaneously, the observed influent concentration remaining around 100 μg/L (initial concentration) suggests that the removal of E1 and E2 were occurred by electrochemical process.

In comparison with the case of E2, the removals of E1 were not stable, varied in the range of 70-90%. This may be due to the complex conversion among estrogens during oxidation process. However, the concentration of E1 in the effluent increased gradually from around day 21 and approached to influent concentration. The phenomena may be explained due to electrode passivation through electro-polymerization process. The same phenomena were reported elsewhere [3,5]. In this research, electrode regeneration was conducted on day 28 by injection and electrolytic reduction of dissolved ozone for 30 minutes. The result showed that removal of E1 was similar to its original state. Given the fact that the influent concentration in this experiment is about 3 orders higher than that of estrogen in STP effluents, this process is expected to as an alternative option for treatment of trace pollutant in sewage water treatment plants.

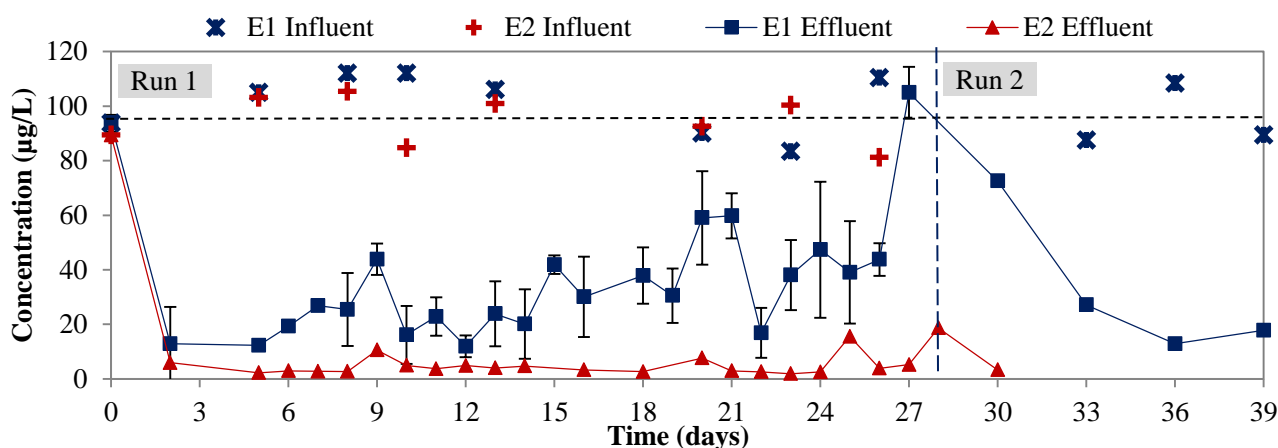


Fig. 3 Continuous treatment of E1 and E2 at 1mA

4. CONCLUSION

Removals of E1 and E2 were achieved up to 87% and 94% by a continuous electrochemical oxidation. Electric energy consumption was in the range of 0.5-1.0 Wh/m³. Electrode regeneration was possible with an application and concurrent reduction of ozone.

REFERENCES

- [1] Tilton, S. C.; Foran, C. M.; Benson, W. H., Relationship between ethinylestradiol-mediated changes in endocrine function and reproductive impairment in Japanese medaka (*Oryzias latipes*). *Environmental Toxicology and Chemistry* 2005, 24, 352-359.
- [2] Combalbert S. and Hernandez-Raquet G., Occurrence, fate, and biodegradation of estrogens in sewage and manure, *Appl Microbiol Biotechnol* 86, 2010, 1671-1692
- [3] Sakakibara Y., Kounoike T., Kashimura H., Enhanced Treatment of Estrogen and Endocrine Disrupting Chemicals (EDCs) by A Granular Bed Electrochemical Reactor, *Water Science & Technology* 62, 2010, 2218-2224.
- [4] Shimura, M.; Uddin, M. H.; Sakakibara Y.; Tanaka T. *JSCE, Ser. G (Environmental Research), Ref. Data*, **2011**, 67 (7), 697-703.
- [5] Kuramitz H., Matsushita M., and Tanaka S.: Electrochemical removal of bisphenol A based on the anodic polymerization using a column type carbon fiber electrode, *Water Research* 38, 2001, pp. 2331-2338.