



Continuous treatments of estrogens through polymerization and regeneration of electrolytic cells



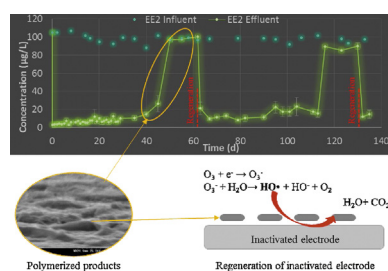
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HIGHLIGHTS

- Trace natural and synthetic estrogens were removed effectively by electrochemical oxidation process.
- Removal efficiency of 93–98% was achieved through electrochemical polymerization.
- Passivated electrodes were completely recovered to their initial conditions in continuous operation.
- Removal performance could be controlled and enhanced by a mathematical model.

GRAPHICAL ABSTRACT



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ABSTRACT

This study proposes a novel electrolytic method for simultaneous removal of trace estrogens and regeneration of electrolytic cells for long-term wastewater treatment. Continuous treatments of estrogens estrone (E1), 17 β -estradiol (E2) and 17 α -ethinyl estradiol (EE2) were theoretically and experimentally studied using an electrolytic reactor equipped with a multi-packed granular glassy carbon electrode reactor. Experimental results demonstrated that E1, E2 and EE2 were effectively removed through electro-polymerization on the granular glassy carbon (and Pt/Ti) anode counter. Polymer formed during continuous treatment was quickly decomposed and electrodes were regenerated completely by \cdot OH radicals produced through the reduction of ozone. Calculated overall energy consumptions were less than 10 Wh/m³, demonstrating extremely low energy consumptions. In addition, a mathematical model developed based on the limiting mass transfer rate and post-regeneration could represent general trends in time series data observed in experiments.

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1. Introduction

Removal of estrogenic compounds has drawn much attention due to their toxicity to aquatic life forms at trace levels. It was reported that ecological effect of estrogenic compounds 17 β -estradiol (E2) and 17 α -ethinyl estradiol (EE2) on medaka (*Oryzias*

latipes), zebrafish (*Danio rerio*) and fathead minnow (*Pimephales promelas*) lies in the range of 0.2–10 ng/L [1–3]. However, residues were detected higher than the threshold in surface water in many countries. E1, E2 and EE2 were reported in the range of 10–100 ng/L in Tama river, Japan [4], Taiwan, China [5], Thailand and Vietnam [6]. The occurrence of estrogens in receiving water was reported due to incomplete removal from wastewater treatment plants [7]. Therefore, elimination of these compounds in effluents of sewage treatment plants (STP) before discharge into environment is important to preserve the ecosystem.

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The application of membrane bioreactor, biofilm, activated sludge, adsorption, filtration and enzymatic treatments have been reported as highly efficient methods to remove estrogens [8–15]. However, several drawbacks were noted that did not enable these applications to be practical for STPs, including transformation of E2 to E1 [8], a high level of E1 remaining in the treated STPs [9] and a long treatment time [13,14]. The electrochemical oxidation process is expected to overcome the above drawbacks due to its ability to decompose organic pollutants without the further addition of chemicals, rapid degradation, and easy maintenance [16]. In our former studies, the electrochemical removals of endocrine disrupting chemicals (EDCs), natural and synthesis estrogens were conducted using a three dimensional Pt/Ti electrode reactor [17–20]. The study proposed a direct oxidation of trace phenolic EDCs and estrogens at extremely low energy consumption. In the study, the possibility and fundamental characterization of removing natural and synthetic estrogen (E1, E2 and EE2) by direct electrochemical oxidation process was examined and it has pointed out that further removal of estrogens was inhibited due to polymer formation on electrode surface [18]. In this study, an emphasis is placed on continuous removals of E1, E2 and EE2 through regeneration of inactivated electrodes.

Recently, studies on electro-polymerization of organic compounds have been initiated. Not only phenol, a conventional chemical used in polymerization, treatment of phenolic endocrine disrupting chemicals (EDCs) bisphenol-A (BPA) and its derivatives [21], nonylphenol (NP), 4-t-octylephenol (OP), 2,4-dichlorophenol (DCP), pentachlorophenol (PCP), and 17 β -estradiol (E2) was investigated [20]. Kuramitz et al. [21] reported a complete removal of 228 $\mu\text{g/L}$ BPA, BPS and DPA was achieved in 10 min. The dissolved BPA in aqueous solution was immobilized on the carbon fiber anode surface at a low potential. Tahar and Savall [22] suggested the possibility to form permeable polymeric film by electrochemical oxidation of phenol on condition that the working electrode potential is situated at the onset of oxygen evolution. The first comparative reaction mechanism of E2 in a redox environment indicated that a dimer or a quinone was formed and resulted in a semi-conducting polymer [23]. This paper intends to fill a gap in the literature as there are no reports that focus on continuous removal of estrogens through electro-polymerization and regeneration of the inactivated electrodes by $\cdot\text{OH}$ radical production.

The objective of this work is to evaluate continuous removal performance of E1, E2 and EE2 by granular glassy carbon electrolytic reactor. The removal of trace estrogens depends on the mass transfer onto the electrodes, therefore, a mathematical model constructed based on limiting mass transfer rate, diffusivities, and related physical properties of the electrolytic cells was constructed to predict the removal performance. In addition, several important

operating conditions such as electric current, hydraulic retention time (HRT), anode materials were evaluated. Furthermore, as maintenance of the electrolytic system is very important for practical reasons, the electrode regeneration and continuous removals of estrogens were evaluated.

2. Materials and methods

2.1. Chemicals and reagents

Estrone (CAS number: 58-05023) of 98% purity, 17 β -estradiol (CAS number: 58-04043) of 97% purity and 17 α -ethinyl estradiol (CAS number: 57-63-6) of 98% purity were selected as targeted estrogens referred to their high toxicity and occurrence in water environments. N,O-Bis(trimethylsilyl) trifluoroacetamide (BSTFA) containing trimethylsilane (TMS) (99:1) and Pyridine were used as derivative and catalyst to enhance detection of each estrogen. Bisphenol A- deuterated 14 (BPA-d14) was used as a surrogate to enhance the measurement accuracy. Chemicals were purchased from Wako Chemical Company in Japan. A stock solution containing 1 mg/mL of E1, E2, EE2 and BPA-d14 was prepared in acetone (99.5%) and kept in refrigerator at 0 °C. A desired concentration of feeding solution was prepared by diluting the stock solution into deionized water (conductivity 0.06 $\mu\text{S/cm}$, Auto still WG222S, Yamato Scientific Co., Ltd., Japan).

2.2. Experimental apparatus

Fig. 1 shows the interior of the reactor and its configurations in continuous treatments of estrogens. The reactor consists of two compartments filled up with glassy carbon (or Pt/Ti) granular anodes and a Pt/Ti mesh cathode. The average size of GCE was 3 mm. The surface area of the mesh-type electrode was about 20 cm². To prevent adsorption the reactors were made of stainless steel equipped with a Teflon sheet. Total liquid volume and surface area of anodes were about 500 mL and 2000 cm², respectively. A portion of the liquid inside the anode compartments was recycled to ensure completely mixed conditions. The cathode and anode chambers were separated by a porous Teflon sheet and glass beads. Multi-anodes were connected with a direct current (DC) supply at a constant current mode. The feed solution containing estrogens was fed continuously to the reactor using a peristaltic pump.

2.3. Operating conditions

The removal performances were evaluated under different operating conditions such as electric current (Run 1), hydraulic retention time (Run 2–1, 2–2), electrode materials (Run 3), water

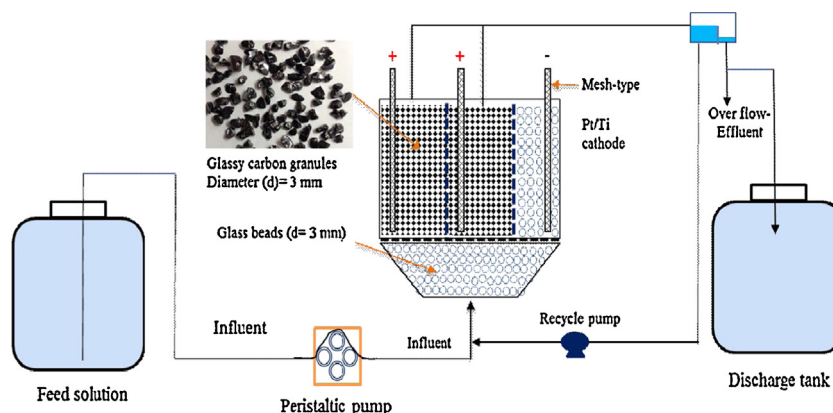


Fig. 1. Experimental apparatus in continuous experiment.

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