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Bisphenol A degradation in aqueous solutions by electrogenerated ferrous ion activated ozone, hydrogen peroxide and persulfate: Applying low current density for oxidation mechanism

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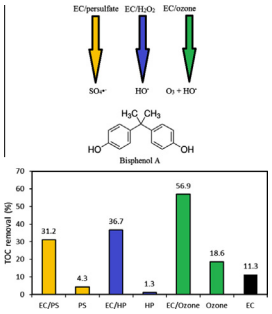
HIGHLIGHTS

- Three oxidants were activated by electrogenerated ferrous ion for BPA degradation.
- EC/ozone had the best performance in comparison with EC/PS and EC/HP.
- Reaction mechanisms of EC/oxidants systems were studied by quenching experiments.
- Reuse of electrochemical sludge was effective for activation of HP and PS.

GRAPHICAL ABSTRACT



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ABSTRACT

Bisphenol A (BPA) is an ubiquitous environmental contaminant which is categorized as an endocrine disruptor compound. In this study, BPA was removed using electrogenerated ferrous ion (EC) activated ozone, hydrogen peroxide (HP) and persulfate (PS). The effects of operating parameters such as pH, current density, oxidant dosage and time, were evaluated on three systems of EC/HP, EC/PS and EC/ozone. The acidic condition (pH = 3.0–5.0) was suitable for all the processes. The results showed that EC/ozone had the best performance in degradation of BPA compared to others. Moreover, the presence of chloride was investigated in three systems and the related results displayed a slight increase in removal efficiency. Electrochemical degradation of BPA in a divided cell proved that ozone was activated by both anode and cathode reactions while HP and PS were activated only in anode compartments endorsing HP and PS catalytic activation by ferrous ion. In addition, the reaction mechanism demonstrated that sulfate radical was the major oxidant in EC/PS while hydroxyl radical was the main agent in EC/HP and EC/ozone systems. However, the results indicated that ozone can solely degrade BPA significantly in comparison with other oxidants. The synergistic effects along with kinetic model were also assessed for all the processes. The mineralization was studied by total organic carbon (TOC) and the order of TOC removal was EC/ozone > EC/HP > EC/PS > ozone > EC > PS > HP. The electrochemical sludge generated was reused for activation of the oxidants as HP and PS were noticeably activated while no effect was observed on ozone application.

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1. Introduction

A large number of anthropogenic organic compounds have been detected in the water resources since during last decade the industries have produced bio-refractory compounds contributing to toxic pollutants that are released to the environment. These compounds can affect endocrine systems through an interface with synthesis, secretion, transport, binding, action or elimination of natural hormones in the body [1]. Bisphenol A (BPA) as an endocrine disrupting compound has attracted environmentalists' attention since it is frequently found in rivers, municipal wastewater, landfill leachate and so on [2,3]. BPA is generally utilized for producing polycarbonate plastics and epoxy resins. It is also applied for polyvinyl chloride (PVC) as a stabilizer or an antioxidant and annually several million tons are produced worldwide [4,5]. BPA may migrate from water and baby bottles to water which is a key issue as human exposure point of view [6]. BPA can induce feminization phenomena in various species of animals [6]. BPA is also considered to cause prostate cancer, cardiovascular disease, type 2 diabetes, birth defects, hormonal imbalance, and liver enzyme abnormalities [7,8].

BPA is highly resistant to biological and chemical degradations. Therefore, conventional processes are not efficient for complete BPA removal from aquatic environment. Nowadays, the use of the AOP technologies has been suggested as an effective alternative method for the degradation of recalcitrant pollutants since these technologies have high oxidation potential. Two main types of free radicals include sulfate radical ($SO_4^{\cdot-}$) and hydroxyl radical ($HO^{\cdot}$) which have oxidation potentials of $E^0 = 2.6–3.1$ V and $E^0 = 2.7$ V respectively, which are the main agents of oxidizing the organic compounds [8]. These free radicals are produced *in-situ* by various techniques. Amongst them, activation of chemical oxidants is the most common method. Frequent applications of chemical oxidants in water and wastewater treatment encompass ozone (O_3), hydrogen peroxide (H_2O_2) and persulfate ($S_2O_8^{2-}$) [9,10]. These oxidants can be activated by ferrous ion as a transitional metal for generation of free radicals [11,12]. Ferrous ion has been frequently used for activation of persulfate (PS) and hydrogen peroxide (HP) which in combination with the latter oxidant forms Fenton reagent [13]. Ozone also produces hydroxyl radical in presence of ferrous ion as a catalyst [14]. The production of free radicals based on Fe^{2+}/oxidant are presented by the following equations:

$$Fe^{2+} + H_2O_2 \rightarrow HO^{\cdot} + Fe^{3+} + OH^- \quad (1)$$

$$Fe^{2+} + S_2O_8^{2-} \rightarrow SO_4^{\cdot-} + Fe^{3+} + SO_4^{2-} \quad (2)$$

$$Fe^{2+} + O_3 \rightarrow FeO^{2+} + O_2 \quad (3)$$

$$FeO^{2+} + H_2O \rightarrow 2HO^{\cdot} + Fe^{3+} + OH^- \quad (4)$$

In recent decade, electrochemical processes have emerged as promising methods to remove a wide range of organic and inorganics pollutants [15]. In these processes, reaction mechanism is controlled by applied current to electrodes. Ferrous ion can be electrochemically generated in solution when iron electrode is used as an anode. In this way, ferrous ion is released to the solution through electrolytic oxidation of iron anode [16,17].

$$Fe_{(s)} \rightarrow Fe^{2+}_{(aq)} + 2e^- \quad (5)$$

On the other hand, electrogenerated ferrous ion reacts with generated hydroxide ion at cathode and produces metal hydroxide that is able to precipitate organic and inorganic pollutants. Indeed, coagulation mechanism occurs during electrolysis which is known as electrocoagulation (EC) process [18,19]. Not only does electrogenerated ferrous ion act as a catalyst in presence of oxidant but also it plays the role of coagulant agent. The combination of EC and chemical oxidant can dramatically increase the performance of the process for degrading the pollutant. It should be noted that low current density reduces the electrogenerated coagulant agents in electrochemical cell [17]. Hence, low electrical current diminishes the possibility of coagulation mechanism.

Various studies have focused on removal of BPA by chemical oxidation such as Fenton process [5], photocatalysis [20,21], ozonation, UV/oxidant [8,22] and so on. However, few works have fulfilled organic pollutant degradation based on EC/oxidant processes letting alone the comparison of three oxidants along with EC. In addition, no comparative study has been observed in literature for BPA degradation by EC/three oxidants so far.

In this study, the effects of operating parameters including initial pH, current density, oxidant dosage and reaction time were investigated and the optimization of each process was obtained. Moreover, the mineralization of BPA was studied based on TOC parameter. The effects of anodic and cathodic reactions were evaluated for the determination of contribution of each one. Quenching experiments were carried out by various alcohols in order to determine reaction mechanism. The electrochemical sludge was also reused as a source of ferrous ion for activation of the oxidants.

2. Materials and methods

2.1. Chemicals and reagents

All the chemicals were used as received without further purification. All solutions were prepared with deionized water. Sodium persulfate was purchased from Fluka Co. Hydrogen peroxide (30% w/w) was provided from Merck Chemicals. Sodium nitrite, ethanol and *tert*-butanol were purchased from Sigma–Aldrich Inc. Bisphenol A (CAS No. 80-05-7; purity grade >99%) was supplied from Sigma–Aldrich Company. Water, acetonitrile and methanol with chromatography grade were purchased from Samchun Chemicals (Southern Korea). Sodium hydroxide and potassium hydrogen phthalate were obtained from BDH Company.

2.2. Experimental setup

The treatability of BPA was evaluated using bench scale by EC/oxidant systems in an undivided electrochemical cell. The electrogenerated ferrous ion was kept in a Plexiglas cylinder with 600 mL volume (6 cm diameter and 21 cm height). The 500 mL solution containing 50 mg/L BPA was introduced to EC reactor. The concentration of BPA was prepared in sodium sulfate (Na_2SO_4) with concentration of 0.01 M and the BPA concentration (50 mg/L) was constant in all conditions. The solution pH was adjusted by H_2SO_4 (0.1 M) and NaOH (1%). The iron sheets were used as cathode and anode electrodes. In order to generate the ferrous ions, four iron electrodes with dimensions of 40 mm × 100 mm × 1 mm were placed in the reactor which 65 mm of each was immersed in the BPA solution. The current density was calculated by Eq. (6).

$$J = \frac{i}{A_e} \quad (6)$$

where J is the current density (mA/cm^2), i is applied current and A_e is total surface area of electrode which is immersed in solution.

The configuration of electrodes was monopolar arrangement. A digital DC power (3.0 A, 30 V) was used to apply various currents into the electrodes. After turning the DC power on, a certain amount of oxidant (PS and H_2O_2) was added to solution. In case of ozone, pure oxygen was used to generate ozone. Ozone generation was conducted by entering the oxygen into the ozone genera-