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Bisphenol A treatment by the hot persulfate process: Oxidation products and acute toxicity

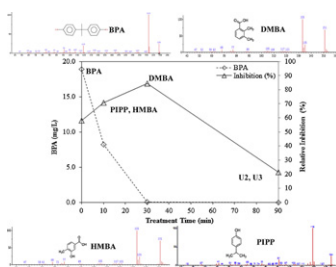
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HIGHLIGHTS

- ▶ The effect of varying operating parameters on hot persulfate treatment of BPA was investigated.
- ▶ Several aromatic and aliphatic oxidation products could be identified via GC-MS analyses.
- ▶ Products formed during the initial stages of treatment were found more toxic than BPA.
- ▶ A correlation existed between acute toxicity and 2,3-dimethyl benzoic acid evolution.

GRAPHICAL ABSTRACT



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ABSTRACT

In this study, a thermally activated persulfate oxidation process was investigated to treat aqueous Bisphenol A (BPA) solution. The effect of temperature (40–50–60–70 °C), initial pH (pH = 3.0, 6.5, 9.0 and 11.0) and persulfate concentration (0–20 mM) on bisphenol A (BPA) and TOC removals was examined. The activation energy for hot persulfate oxidation of BPA was calculated as 184 ± 12 kJ/mol. Acidic and neutral pH values were more favorable for BPA oxidation than basic pH values. TOC removals did not exhibit a specific pattern with varying initial pHs. Gas chromatography/mass spectrometry was employed to identify oxidation products. Several aromatic and a few aliphatic compounds could be detected including benzaldehyde, p-isopropenyl phenol, 2,3-dimethyl benzoic acid, 3-hydroxy-4-methyl-benzoic acid, ethylene glycol monoformate and succinic acid. Acute toxicity tests conducted with *Vibrio fischeri* indicated that the inhibitory effect of 88 µM BPA solution originally being 58%, increased to 84% after 30 min and decreased to 22% after 90 min hot persulfate treatment that could be attributed to the formation and subsequent disappearance of oxidation products.

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1. Introduction

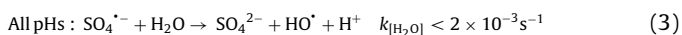
Bisphenol A (BPA, 4,4'-dihydroxy-2,2-diphenylpropane) is a high-volume production chemical primarily used as an intermediate and monomer in the production of epoxy resins and polycarbonates, which are additives to a number of consumer products [1]. BPA is released into the environment through a number of routes, including discharge of wastewater and wash water generated from BPA production facilities or consumer product

manufacturing facilities that utilize BPA, discharge from wastewater treatment plants, leaching from consumer products containing BPA at hazardous waste landfill sites, deposition of particulates or dust from BPA production, processing, or storage facilities, and accidental discharge [2]. The concentration of BPA found in water sources (generally in µg/L), is several orders of magnitude below the chronic toxicity level, with the exception of streams polluted by industrial effluents, i.e. 17.2 mg/L in leachates from hazardous waste landfills containing waste plastics [1,3]. Studies on humans and laboratory animals have demonstrated that BPA causes adverse health effects such as estrogenic potency, liver damage, pancreatic β-cell function disruption, thyroid hormone disruption, obesity-promoting effects and increases the prevalence of cardiovascular

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disease, diabetes, and liver-enzyme abnormalities [4,5]. BPA has been reported as the most commonly detected endocrine disrupting compound in natural waters [6]. Due to its widespread detection and serious health effects, BPA is one of the xenobiotic substances that have generated the greatest amount of interest and controversy during the past decade among scientific communities and public health agencies [7]. Such concerns have heightened the need for improved, advanced remediation techniques to effectively remove BPA from a variety of contaminated environmental media including water, wastewater, wastewater sludge, sediments and soils [8]. BPA degradation by aerobic processes requires very long time with reported half-lives of several days to weeks [9], making conventional treatment processes indispensable for BPA removal prior to the introduction of the waste stream into the aqueous environment. The inability of conventional treatment processes to remove BPA has stimulated the development and investigation of advanced oxidation processes (AOPs) based on the formation of highly active, oxidizing species such as HO• and other free radicals. In the last two decades, studies on chemical oxidation by ozone [2,10], H₂O₂/UV [11,12], Fenton's reaction [13,14], photo-Fenton process [15], ultrasonic irradiation [14,16,17] and TiO₂-mediated heterogeneous photocatalysis [18,19] postulated the effectiveness of AOPs for BPA removal.

Recently, sulfate radical (SO₄•⁻) based-AOPs have attracted great scientific interest due to its high efficiency in the degradation and mineralization of recalcitrant and/or toxic organic pollutants [20–25]. However, only very few studies investigated the toxicity of SO₄•⁻ based oxidation products [26,27]. The persulfate ion (S₂O₈²⁻) is often used as a chemical precursor that can generate SO₄•⁻ being capable of pollutant destruction with generally faster and more aggressive oxidation behavior as compared to the electron transfer process. SO₄•⁻ has a redox potential close to that of HO•, and is more stable in water [28]. Activation approaches of persulfate include thermal treatment, pH adjustment, or the addition of transition metals to produce SO₄•⁻. In the case of thermal activation (Eq. (1)), persulfate formation can be slowly initiated even at mild temperatures (30 °C). However, at higher temperatures (i.e. 90 °C) the activation energy of the “hot persulfate processes” is only 29 kJ/mol in neutral pH solutions. It has already been demonstrated that alkaline conditions can induce the mechanism of SO₄•⁻ interconversion to HO• (Eq. (2)) in the persulfate activation system. In addition, SO₄•⁻ may react with water at all pHs to produce HO•, in accordance with Eq. (3) [29]. However, Norman et al. [30] reported that the reaction rate constant of Eq. (3) is low in comparison to those of SO₄•⁻ reactions with organic compounds.



Although some works in the scientific literature deal with the removal of BPA by SO₄•⁻ based-AOPs [31,32] main efforts have focused only on the removal of the target pollutant, namely BPA and its total organic carbon content (TOC) as a measure of the effectiveness of the processes. However, the acute toxicity of the oxidation intermediates evolved by the reaction of BPA with SO₄•⁻ should be a critical point when establishing the benefits of SO₄•⁻ based-AOPs for BPA degradation.

In the present study, the treatment of BPA by the thermally activated hot persulfate process was investigated. The effect of increasing temperature on BPA degradation was examined and the activation energy (*E_a*) of the reaction was estimated. The influences of temperature (40–70 °C), initial pHs (pH = 3.0, 6.5, 9.0 and 11.0) and persulfate concentration (0–20 mM) on BPA and total organic carbon (TOC) removal rates were determined. In order to elucidate the reaction mechanism of BPA degradation by the hot persulfate

process, oxidation products were identified via gas chromatography/mass spectrometry (GC/MS). The changes in acute toxicity of aqueous BPA solution were also measured by employing the marine photobacteria *Vibrio fischeri*. To the best of our knowledge, this is the first study of its kind on the degradation of BPA by the hot persulfate process which also aimed at establishing the relationship between oxidation intermediates and acute toxicity.

2. Materials and methods

2.1. Materials

BPA (228 g/mol; C₁₅H₁₆O₂; CAS No: 80-05-7) was purchased from Sigma–Aldrich (USA) in 99.9% purity and used as received. Potassium persulfate (K₂S₂O₈, 99.0%) was supplied by Merck (Germany). Acetonitrile and dichloromethane were of liquid chromatography grade and purchased from Merck (Germany). All aqueous solutions were prepared with de-ionized water.

2.2. Experimental procedure

Hot persulfate oxidation experiments were performed for 120 min in 2 L-capacity glass beakers. The BPA concentration (total volume: 1 L) was fixed at 88 μM to facilitate analytical measurements. A magnetic stirrer equipped with an electronic contact thermometer (Yellowline MST Basic, IKA-WERKE) was used to ensure constant temperature and perfect mixing at a rate of 300 rpm during all experiments. The initial pH of the BPA solution was adjusted with concentrated (6 N) NaOH and H₂SO₄ solutions to the desired value before starting the experiment. In order to determine the treatment performance of hot persulfate oxidation, samples were withdrawn at regular time intervals and immediately placed in an ice bath (4 °C) to quench the reaction. Sample aliquots were analyzed for BPA, TOC and pH.

2.3. Analytical procedures

2.3.1. HPLC measurements

The quantification of the BPA was performed with an Agilent 1100 Series HPLC equipped with a Diode-Array Detector (DAD; G1315A, Agilent Series) set at 214 nm. A C18 Symmetry (Waters) column (3.9 mm × 150 mm, 5 μm particle size) was utilized as a stationary phase, while the mobile phase was a mixture of acetonitrile/water in 50/50 (v/v) ratio. The flow rate was set at 1.0 mL/min and the injection volume was 50 μL. The temperature of the column was set at 25 °C. Using this methodology, a detection limit of 0.14 mg/L of BPA was reached.

2.3.2. GC/MS measurements

The oxidation intermediates were extracted by means of solid-phase extraction (SPE). The SPE cartridges (Oasis HLB, 6 mL, 250 mg) were pre-conditioned with 5 mL of dichloromethane, 5 mL of methanol and 5 mL of ultrapure water. Then, the sample was passed through the SPE cartridges at a flow rate of 5 mL/min. The oxidation intermediates trapped in the SPE cartridges were eluted using 5 mL of dichloromethane. The oxidation intermediates were identified by GC/MS with an Agilent Technologies (USA) system composed of a 5975C model GC connected to an Agilent capillary column (HP5-MS, 30 m × 0.25 mm), coupled with a 7890A model MS. Helium was used as the carrier gas at a flow rate of 1.5 mL/min. 1 μL sample aliquots were injected from the injection port (220 °C) in splitless mode. For separation of the oxidation intermediates, the following temperature program was adopted; start at 40 °C; 40–200 °C (5 °C/min), 200–210 °C (1 °C/min), 210–280 °C (20 °C/min) and 280 °C (3 min). Qualitative analyses were performed in the electron impact (EI) mode at 70 eV using the full scan

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