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Oxidative removal of bisphenol A using zero valent aluminum–acid system

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ABSTRACT

Bisphenol A (BPA), a controversial endocrine disruptor, is ubiquitous in the aquatic environment. In this study, the oxidative degradation of BPA and its mechanism using zero valent aluminum (ZVAl)–acid system under air-equilibrated conditions was investigated. Under pH <3.5 acidic conditions, ZVAl demonstrated an excellent capacity to remove BPA. More than 75% of BPA was eliminated within 12 h in pH 1.5 reaction solutions initially containing 4.0 g/L aluminum and 2.0 mg/L BPA at $25 \pm 1\ ^{\circ}C$. The removal of BPA was further accelerated with increasing aluminum loadings. Higher temperature and lower initial pH also facilitated BPA removal. The addition of Fe^{2+} into the ZVAl–acid system significantly accelerated the reaction likely due to the enhancing transformation of H_2O_2 to $HO^{\bullet}$ via Fenton reaction. Furthermore, the primary products or intermediates including mono-hydroxylated BPA, hydroquinone, 2-(4-hydroxyphenyl)propane and 4-isopropenylphenol, were identified and a possible reaction scheme was proposed. The remarkable capacity of the ZVAl–acid system in removing BPA displays its potential application in the treatment of organic compound–contaminated water.

1. Introduction

As an important industrial chemical, bisphenol A [BPA; 2,2-bis(4-hydroxyphenyl)propane] is manufactured in large quantities for the production of polycarbonate plastic and epoxy resins (Tsai, 2006). In the United States, approximately 1.7 billion pounds of BPA are synthesized and used every year (Schwartz, 2005). The principal route of BPA's entrance into the aquatic environment is effluent from wastewater treatment plants (WWPTs) and landfill leachates (Kang et al., 2007). Bisphenol A is frequently found in effluents of domestic and industrial WWPTs because it is not completely eliminated during conventional biotic and abiotic treatments (Lee and Peart, 2000; Quinn et al., 2003; Rigol et al., 2002). The elimination rates of BPA in treatment plants ranged from 37 to 94% (Fuerhacker, 2003; Lee and Peart, 2000). High concentrations of BPA were frequently found in leachates at landfill sites (Asakura et al., 2004; do Nascimento et al., 2003; Yamamoto et al., 2001). For example, Yamamoto et al. (2001) reported that levels of BPA in leachate at a hazardous waste landfill site ranged from 1.3 to 17,200 μg/L (average 269 μg/L).

The ubiquity of BPA in the aquatic environment has greatly inspired the exploration of BPA removal methods, including physical (Pan et al., 2008), biological (Hirooka et al., 2005; Kadowaki et al., 2007; Kang et al., 2004), and chemical (Li et al., 2008; Lin et al., 2009; Ohko et al., 2001; Wang et al., 2010) techniques. For example, Lin et al. (2009) found that aqueous BPA could be efficiently removed by manganese dioxide. However, the authors demonstrated that the loss of BPA led to the formation of other organic intermediates

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instead of mineralization to CO_2. Advanced oxidation processes (AOPs) based on the formation and use of hydroxyl radical $HO^•$ were recently considered for more thorough removal of aqueous BPA. For example, 175 μM of BPA in water was completely mineralized to CO_2 by TiO_2-photocatalyzed reactions under UV irradiation of 10 mW/cm^2 for 20 h (Ohko et al., 2001). More recently, Wang et al. (2010) found that nearly 100% of BPA was removed by mesoporous Bi_2WO_6 under simulated solar light irradiation. Such a high efficiency of AOPs in treating BPA-containing water undoubtedly offers a promising alternative for the removal of aqueous organic contaminants.

Different AOPs use different mechanisms to generate $HO^•$ radicals. Like the widely known AOP zero valent iron (Joo et al., 2004, 2005; Kang and Choi, 2009; Lee et al., 2007; Noradoun and Cheng, 2005), zero valent aluminum (ZVAl)–acid system possesses high efficiency in producing reactive oxygen species because of its great thermodynamic driving force for electron transfer. The reduction potential of aluminum is −1.67 V (Al^{3+}/Al), much lower than that of iron (−0.44 V, Fe^{2+}/Fe). The electron transfer capacity of ZVAl has already been exploited for the degradation of other organic compounds. For example, Lien and Wilkin (2002) showed that ZVAl treated by surface modification with sulfate groups could easily eliminate methyl *tert*-butyl ether. In a recent study, Bokare and Choi (2009) demonstrated that commercially available ZVAl had the desirable capacity in oxidative degradation of 4-chlorophenol, sodium dichloroacetate, phenol and nitrobenzene.

The objective of the present work was to explore the degradation of BPA with ZVAl–acid system by investigating removal efficacy and influencing factors such as ZVAl loading, reaction temperature, pH, and Fe^{2+}. The principal reaction intermediates and products were also identified, and a reaction scheme was proposed.

2. Materials and methods

2.1. Chemicals

Bisphenol A standard (purity >99%), *N*,*O*-bis(trimethylsilyl) trifluoroacetamide with trimethylchlorosilane (BSTFA + TMCS, 99:1) and 2,9-dimethyl-1,10-phenanthroline (DMP) were purchased from Sigma–Aldrich (St. Louis, MO, USA). Aluminum powder (purity >99%, particle size 75–150 μm, surface covered with native aluminum oxide layer) was purchased from Sinopharm Chemical Reagent (Shanghai, China). Other chemicals and solvents used in this study were of analytical grade or high performance liquid chromatography (HPLC) grade. The concentration of the purchased hydrogen peroxide solution (30 wt%) was calibrated by titration with potassium permanganate (Bader et al., 1988). All chemicals were used as received. Ultrapure water (18.2 MΩ cm resistivity) was prepared using a Millipore purification system. Stock solution of 5.0 g/L BPA was prepared in acetone. The 1% (w/v) DMP solution was prepared in ethanol in a brown bottle. A copper (II) sulfate ($CuSO_4$) solution (0.01 M) was prepared by dissolving $CuSO_4 \cdot 5H_2O$ in ultrapure water. Phosphate buffer solutions (0.1 M) were prepared by mixing appropriate volumes of 0.5 M Na_2HPO_4 with 0.5 M NaH_2PO_4, with the final pH adjusted to pH 7.0 by NaOH (1 M). All solutions were stored at 4 °C prior to use.

2.2. Reaction setup

All reactions were carried out in 250-mL glass flasks with a total suspension volume of 100 mL under air-equilibrated conditions and in the absence of light. Unless otherwise noted, temperature was fixed at 25 ± 1 °C. The initial pH (pH_i) of the solutions was adjusted to the designated value with 1 M $HClO_4$ standard solution. A 40-μL aliquot of 5.0 g/L BPA stock solution was added to make a nominal initial concentration of 2.0 mg/L. Reaction mixtures were constantly shaken in a thermostatic mechanical shaker at 130 rpm. Reactions were initiated by adding a predetermined amount of ZVAl into the pre-equilibrated and constantly mixed solutions. Aliquots of 1.0 mL sample were periodically withdrawn and transferred to 2-mL centrifuge tubes containing 10 μL of methanol (as $HO^•$ scavenger). The samples were immediately vortexed for 10 s and centrifuged at 8000 rpm for 5 min. The supernatant was transferred to 2-mL vials and subjected to HPLC analysis to determine the remaining BPA concentration. All samples were stored at 4 °C and analyzed within 24 h. Except for the ZVAl-free control, all treatments were carried out in triplicates.

Specific treatments were included to evaluate the effect of Fe^{2+}, the presence of aluminum oxide and humic acid (HA). To determine the effect of Fe^{2+} and HA, a predetermined amount of $FeCl_2$ and HA were separately added into the reaction solutions. To evaluate the effect of the native aluminum oxide layer, the reaction rates were individually measured before and after the pretreatment of aluminum by mixing in a pH 1.5 acidic solution for 2 h.

To quantify the formation of H_2O_2 in the ZVAl–acid system, an additional reaction solution without BPA was also prepared. Aliquots of 1.0 mL samples were periodically transferred to 2-mL centrifuge tubes and immediately centrifuged at 8000 rpm for 5 min. One half mL subsample of the supernatant was collected and used for H_2O_2 measurement using a method according to Kasaka et al. (1998). The determination of H_2O_2 is based on a spectrophotometric method via the stoichiometric reaction of H_2O_2 with copper (II) ion and DMP. Briefly, 0.5 mL each of DMP, $CuSO_4$, phosphate buffer, and the sample supernatant was added to a 5-mL volumetric flask and the flask was filled up to 5 mL with water. After mixing, the solution was transferred to 1-cm cells and the absorbance was measured at 454 nm on a V-550 UV/Vis spectrophotometer (Jasco Technologies, Tokyo, Japan).

2.3. Chemical analysis

Bisphenol A concentrations in reaction samples were determined using a reverse-phase HPLC coupled with a variable-wavelength ultraviolet (UV) detector (Jasco). The detection wavelength was 196 nm. A Grace Alltima® C18 column (250 × 4.6 mm, 5 μm, Grace, Deerfield, IL, US) was employed for the separation. The isocratic mobile phase consisted of 55% acetonitrile and 45% 40 mM acetic acid solution with a flow rate of 1.0 mL/min. The injection volume was 25 μL. Under these conditions, the typical retention time for BPA was 6.2 min.