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Feasibility of a two-stage reduction/subsequent oxidation for treating Tetrabromobisphenol A in aqueous solutions

Si Luo, Shao-gui Yang*, Cheng Sun*, Xiao-dong Wang

State Key Laboratory of Pollution Control and Resource Reuse, School of the Environment, Nanjing University, Nanjing 210093, PR China

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ABSTRACT

A “two-stage reduction/subsequent oxidation” (T-SRO) process consists of Fe–Ag reduction and Fenton-like oxidation under ultrasound (US) radiation. Due to the refractory oxidation of brominated flame retardant, T-SRO was employed to remove Tetrabromobisphenol A (TBBPA) by the combination of first debromination and succeeding oxidation. It indicated that the T-SRO process resulted in a complete decrease in TBBPA concentration and a 99.2% decrease in BPA concentration. The T-SRO process for the removal of TBBPA is much effective than Fenton-like oxidation of TBBPA alone. The result showed that US radiation improved the Fenton-like oxidation rate of BPA solutions. The addition of dissolved iron into the Fenton-like oxidation system could accelerate the first 2 min reaction, but had little effect on the following process. The main intermediate products resulting from TBBPA reduction and BPA oxidation were identified by GC–MS and LC-MS/MS. On the basis of this analysis, reactions with •OH radical were identified as the major chemical pathways during BPA oxidation.

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1. Introduction

Tetrabromobisphenol A (TBBPA) is one of the most widely used brominated flame retardant around the world. It can be covalently bound to the polymer in the manufacturing process (de Wit, 2002). TBBPA and its dimethylated derivative have been detected in various environmental matrices, and they negatively affect various aspects of mammalian and human physiology (Sellström and Jansson, 1995; Helleday et al., 1999; Meerts et al., 2000; Öberg et al., 2002). Consequently, removal of TBBPA in the contaminated environment is necessary and significant. The reported treatment mainly includes biotransformation, photochemical transformations and thermal decomposition (Mackenzie and Kopinke, 1996; Barontini et al., 2004; Eriksson et al., 2004). In addition, it also indicated that removal of the halogen substituent is a key step in the degradation of halogenated aromatic compounds.

This may occur as an initial step via reductive, hydrolytic, or oxygenolytic mechanisms or may occur after ring cleavage at a later stage of degradation (Monserate and Haggblom, 1997).

Zero valent iron (ZVI) and bimetallic particles have been used for degradation of halogen-containing organic substance (Orth and Gillham, 1996; Cwiertny et al., 2006). In our previous work (Luo et al., 2010), we reported that TBBPA was reductively debrominated to bisphenol A (BPA) over Fe–Ag bimetallic nanoparticles under US radiation. However, it is well known that BPA exhibits estrogenic activity, which increases the proliferation rate of breast cancer cells and induces the acute toxicity to freshwater and marine species (Pulgar et al., 1998; Kaiser, 2000). Therefore, the debromination of TBBPA in Fe–Ag/US system is incomplete, BPA must be further degraded. An effective method for BPA mineralizing is the application of Fenton (Fenton-like) oxidation technologies (Gözmen et al., 2003; Ioan et al., 2007). On the other hand,

* Corresponding authors. Tel./fax: +86 25 89680580.

E-mail addresses: yangdlut@126.com (S.-g. Yang), envidean@nju.edu.cn (C. Sun).

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ZVI can be used to substitute ferrous salts in the Fenton-like oxidation, and it seems to have similar degradation rates to homogeneous ferrous catalyst. It has confirmed that phenol (Bremner et al., 2006) and 4-chlorophenol (Zhou et al., 2008) could be rapidly degraded in ZVI/H₂O₂ system.

Since iron can reductively transform the electron-withdrawing moieties and render recalcitrant compounds more amenable to subsequent oxidation processes, several researchers presented the ZVI reduction for the pretreatment of wastewater (Mantha et al., 2001, 2002; Oh et al., 2005). Oh et al. (2003) reported the enhanced Fenton oxidation of TNT and RDX through pretreatment with ZVI. Thus, in consideration of the complete treatment of TBBPA, ZVI-based reductive debromination followed by Fenton-like oxidation is proposed, where Fe–Ag bimetallic nanoparticles are used to debrominate TBBPA because of its higher catalytic activity relative to ZVI.

This paper evaluates the effectiveness and feasibility of a T-SRO treatment of TBBPA. Experiments are conducted to examine separately the performance of the Fe–Ag nanoparticles reductive and Fenton-like oxidative systems. The effect of US radiation in Fenton-like oxidation process is discussed; the influence of dissolved iron (ferrous and ferric ions) on the oxidation kinetics of ZVI/H₂O₂ system is also investigated. On the basis of identifying intermediate and final products, the reaction pathways are proposed.

2. Experimental section

2.1. Materials

Tetrabromobisphenol A, bisphenol A and *tert*-butanol were obtained from Sigma–Aldrich Company. H₂O₂ (30%, v/v) was purchased from Fisher Company. AgCl, FeSO₄·7H₂O, Fe₂(SO₄)₃, H₂SO₄, NaOH, Na₂SO₃, 1,10-phenanthroline and ferrous ammonium sulfate were provided by Nanjing Chemical Company. HPLC-grade methanol and dichloromethane were purchased from Tedia Company and used without further purification. Milli-Q water was used throughout this study. The zero valent iron used was iron powder (Shenzhen Junye Nano Material Co., Ltd, >99.9%, <60 nm).

2.2. Synthesis and characterization of Fe–Ag bimetallic nanoparticles

Fe–Ag bimetallic nanoparticles with core-shell structure were synthesized by reductive deposition of Ag on ZVI nanoparticles as described in the literature (Luo et al., 2010).

Various analytical techniques including XRD, XPS and XRF were used to characterize the fresh and reacted (after reduction process) Fe–Ag bimetallic samples. X-ray diffraction (XRD) analyses of the samples were performed using Switzerland ARL X'TRA X-ray diffractometer ($\lambda = 1.5418 \text{ \AA}$). The metal oxidation states and surface atomic composition of Fe–Ag samples was examined via X-ray photoelectron spectroscopy (XPS, Thermo VG Scientific ESCALAB 250). X-ray fluorescence (XRF, Switzerland ARL Corporation) was used to measure the mass of Ag deposited on the surface of nanoiron.

2.3. Reduction experiment of TBBPA

The reduction of TBBPA (5 mg L⁻¹) was conducted by Fe–Ag nanoparticles (0.8 g L⁻¹) under US radiation (40 kHz and 100 W). Debromination experiments were performed in a chamber as shown in Fig. SM-1 (a) attached in Supplemental Material (SM). The detailed procedure of reduction experiment was reported in the literature (Luo et al., 2010).

2.4. Fenton-like oxidation experiment

To keep a constant temperature (25 ± 1 °C), the Fenton-like process was conducted in a chamber as presented in Fig. SM-1 (b). The reduction and oxidation experiments were carried out in the same vessel. In each bottle, the solution contained BPA and Fe–Ag nanoparticles after reduction. Its initial pH was adjusted to 3.0 ± 0.1 with 0.1 M H₂SO₄ and 0.1 M NaOH solutions. The oxidation experiments were started by dropping H₂O₂ solutions into the mixture by a separatory funnel. The flow rate was controlled at 2 mg L⁻¹ min⁻¹ and lasted 10 min in the whole oxidation process. At the given reaction time intervals, 1 mL sample was withdrawn. 10 μL 1 M *tert*-butanol was immediately added into the sample as reaction inhibitor. Then the samples were filtered by a syringe filled with a little silanized glass wool. The concentrations of BPA and intermediates in the filtrate were measured by high-performance liquid chromatography (HPLC). If no specific instructions are given, initial pH of Fenton-like oxidation is 3.0 ± 0.1, nanoparticles loading is 0.8 g L⁻¹ and Ag content in Fe–Ag composite material is 1 wt.%.

2.5. Analytical methods

The concentrations of TBBPA were analyzed via HPLC (Agilent 1200, USA), with a C18 reversed-phase column (150 mm × 4.6 mm, 5 μm particles, Agilent, USA). Identification of reductive debromination products was performed by LC-ESI-MS/MS (Thermo LCQ Advantages, QuestLCQ Duo, USA) equipped with electrospray ionization with Beta Basic-C18 HPLC column (150 mm × 2.1 mm id, 5 μm Thermo, USA). The specific operation conditions of HPLC and LC-ESI-MS/MS were provided in the literature (Luo et al., 2010).

The HPLC operation conditions of BPA were as follows: the mobile phase was 30% water in methanol. At the detection wavelength of 226 nm and flow rate of 1.0 mL min⁻¹, the BPA retention time was 3.4 min. Since the oxidation products were so complex, a Thermo Finnigan Trace gas chromatography interfaced with a Polaris Q ion trap mass spectrometer (GC/MS, Thermo, Finnigan, USA) equipped with DB-5 fused-silica capillary column (30 m × 0.32 mm i.d., 0.25 μm film thickness) was used for analyzing the samples. Prior to GC–MS analysis, the samples were extracted with dichloromethane for three times. The extracted solution was dehydrated using anhydrous sodium sulfate and concentrated to 1 mL by rotary evaporation. After the solvent was blown away by the gentle nitrogen, trimethylsilylation was carried out at 50 °C for 30 min using 0.2 mL of bis(trimethylsilyl)trifluoroacetamide (BSTFA). The initial temperature of the column oven was 40 °C and following 1 min hold at this temperature, and then increased up to 300 °C with a heating rate of 6 °C min⁻¹.

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