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Research article

Oxidation of bisphenol A in water by heat-activated persulfate

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ABSTRACT

The heat-activated persulfate oxidation of bisphenol A (BPA), a representative endocrine disrupting compound, was investigated with respect to the effect of several process variables on degradation rates. The activation temperature appears to be the single most important parameter, i.e. a temperature increase from 40 to 70 °C results in an 80-fold rate increase. Regarding initial BPA concentration, the reaction follows a pseudo-first order rate expression, where the kinetic constant decreases from $11.5 \cdot 10^{-2}$ to $3.5 \cdot 10^{-2} \text{ min}^{-1}$ when BPA concentration increases from 110 to 440 µg/L. Reactions in actual water matrices, such as bottled water and secondary treated wastewater, are slower than in pure water since various organic/inorganic water constituents compete with BPA for being oxidized by the reactive oxidizing species; this was confirmed with experiments in pure water spiked with humic acid or bicarbonate. Interestingly though, the presence of chloride seems to promote BPA degradation. Furthermore, degradation is favored at near-neutral pH and increased sodium persulfate (SPS) concentrations.

Experiments at an increased BPA concentration of 20 mg/L were performed to identify transformation by-products (TBPs), as well as assess the mineralization and toxicity of the treated samples. Liquid chromatography time-of-flight mass spectrometry (LC-TOF-MS) revealed the formation of eleven TBPs of BPA and plausible pathways including hydroxylation, oxidation, cleavage and oligomerization reactions are proposed. Mineralization occurs slower than BPA degradation, while the toxicity to marine bacteria *Vibrio fischeri* increases during the early stages of the reaction but it progressively decreases thereafter.

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1. Introduction

In recent years, a new generation of environmental pollutants has arisen due to the increased use of synthetic chemicals. Unlike conventional pollutants, the concentrations of the so-called “emerging micro-pollutants” found at surface water and wastewater typically range from ng/L to µg/L (Lintelmann et al., 2003). The unique property of these compounds is that they have a significant toxicological effect even at very low concentrations. Within the family of micro-pollutants, a major group are the so-called “endocrine disrupting chemicals” (EDCs). EDCs can interfere with hormone action and major physiological systems, and in doing so they can have adverse effects on human and wildlife health (Lintelmann et al., 2003; Valitalo et al., 2016).

Bisphenol A (BPA) is perhaps the most representative member

of the EDCs family mainly due to its excessive use. It is predominantly used in plastics manufacturing (epoxy and polycarbonate resins) as plasticizer and hardener, as well as an additive in flame retardants, brake fluids and thermal papers (Oehlmann et al., 2008). BPA is known to have weak estrogenic activity at concentrations as low as few ng/L-µg/L (Vandenberg et al., 2007), while it is resistant to biodegradation. A study conducted by the US Center for Disease Control and Prevention detected BPA in 95% of urine samples from a reference population of 394 American adults at an average concentration of 1.63 and 1.12 ng/mL in male and female urine, respectively (Calafat et al., 2004; Vandenberg et al., 2007). In addition, several studies have correlated the exposure to BPA with sperm count reduction and increased cancer cells (Salian et al., 2009). Therefore, there is a need for alternative processes in order to reduce the release and accumulation of EDCs in the environment.

Advanced oxidation processes (AOPs), a family of technologies based on the in situ production of very reactive species, offer a

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promising alternative for wastewater treatment (Comninellis et al., 2008; Michael et al., 2013). Among others processes, the sulfate radical-AOP has been discussed in the literature as an efficient and affordable process. Sodium persulfate (SPS) ($\text{Na}_2\text{S}_2\text{O}_8$) has recently attracted the attention of the scientific community as a promising source of sulfate radicals because of its moderate cost, high stability and aqueous solubility, as well as the fact that it is solid at ambient temperature, which facilitates its transport and storage (Frontistis et al., 2016; Lin et al., 2011). Nonetheless, persulfate itself is a moderate oxidizing agent and it must be activated to generate highly reactive sulfate radicals (2.1–3 V), which react typically 103–105 times faster than the anion persulfate (Tsitonaki et al., 2010).

Several studies have demonstrated that SPS can be activated by elevated temperatures (30–99 °C) (Frontistis et al., 2016), the presence of transition metals, mainly iron, (Hussain et al., 2012), ultraviolet (UV) irradiation (Frontistis et al., 2014; Gao et al., 2012), ultrasounds (Darsinou et al., 2015) and microwaves (Yang et al., 2009). Among them, Olmez-Hanci et al. studied the degradation of BPA using heat-activated (2013) or UV-activated (2015) persulfate. Our group (Darsinou et al., 2015) have recently shown that persulfate can indirectly be activated by low frequency ultrasound. The activation is possibly due to the creation of several hot spots of elevated temperature induced by ultrasound irradiation, as well as the increase of liquid bulk temperature associated with heat dissipation.

In this work, the heat-activated persulfate oxidation of BPA is investigated with emphasis on issues that have not been dealt with before; these include working at environmentally realistic BPA concentrations, assessing the effect of water matrix on degradation, and elucidating plausible reaction pathways based on the identified transformation by-products (TBPs).

2. Materials and methods

2.1. Materials

BPA ($\text{C}_{15}\text{H}_{16}\text{O}_2$) and SPS ($\text{Na}_2\text{S}_2\text{O}_8$, 99+%) were purchased from Sigma-Aldrich and used as received.

The water matrices used in this work were: (i) ultrapure water (UPW, pH = 6) taken from a water purification system (EASY-pureRF-Barnstead/Thermolyne, USA), (ii) commercially available bottled water (BW, pH = 7.5, 0.4 mS/cm conductivity containing 211 mg/L bicarbonate, 10 mg/L chloride, 15 mg/L sulfate, 5 mg/L nitrate and 78 mg/L of various metal ions), and (iii) secondary treated wastewater (WW) taken from the university campus treatment plant. Mean values of the WW physicochemical parameters were as follows: pH = 7.85, conductivity = 311 $\mu\text{S}/\text{cm}$, total suspended solids = 1.2 mg/L, chemical oxygen demand = 19 mg/L; total organic carbon = 6.2 mg/L, bicarbonate = 220 mg/L, chloride = 0.44 mg/L, phosphate = 1.9 mg/L; sulfate = 30 mg/L, nitrate = 21 mg/L.

In addition to the actual matrices, UPW was added humic acid (HA, Sigma-Aldrich), sodium bicarbonate (BIC, Sigma-Aldrich) or sodium chloride (Sigma-Aldrich) to evaluate the effect of major organic or inorganic constituents of water/wastewater on degradation.

2.2. Heat-activated persulfate experiments

In a typical experiment, 120 mL of an aqueous solution containing the desired concentration of BPA were loaded in a glass, double walled cylindrical reaction vessel. The appropriate amount of SPS was then added and the reaction took place under magnetic stirring in open air equilibrium. The solution temperature was

controlled using a thermostatic bath (Grant LfV6). Samples of 1.2 mL were periodically taken from the reactor, quenched with methanol, cooled down at 4 °C in an ice bath for about 5 min and then analyzed as follows.

2.3. Analytical methods

2.3.1. Measurement of BPA and TBPs

High performance liquid chromatography was employed to monitor the concentration of BPA. The analytical protocol (columns, mobile phase, detector) is described in detail elsewhere (Darsinou et al., 2015).

Liquid chromatography time-of-flight mass spectrometry (LC-TOF-MS) operated in negative ionization mode was used for the identification of TBPs as described in detail in our previous work (Darsinou et al., 2015). LC analyses was run with water (LC-MS grade) with 0.01% formic acid (solvent A) and acetonitrile (solvent B) as mobile phase with a flow-rate of 0.3 mL/min. A linear gradient was run as follows: 1% B (initial conditions) to 99% B in 15 min and then returned to 1% B after 3 min. The total chromatographic run time was 18 min.

2.3.2. Ion chromatography and total organic carbon

SO_4^{2-} ions were quantified by a Dionex ICS-1500 ion chromatography system equipped with ASRS Ultra II suppressor and an IonPac AS9-HC. The mobile phase was an aqueous sodium carbonate (9 mM) solution at a flow rate of 1 mL/min. Total organic carbon (TOC) was measured using an Aurora 1030W analyzer (OI Analytical).

2.3.3. Ecotoxicity

The luminescent marine bacteria *Vibrio fischeri* were used to assess the acute ecotoxicity of BPA prior to and after the decomposition by activated persulfate. The inhibition of bioluminescence of *V. fischeri* exposed to undiluted BPA solutions for 15 min was measured using a LUMISTox analyzer (Dr Lange, Germany) and the results were compared to an aqueous control.

3. Results and discussion

3.1. Effect of temperature

The effect of temperature in the range 40–70 °C on the degradation of 220 $\mu\text{g}/\text{L}$ BPA in UPW in the presence of 625 mg/L SPS was investigated and the results are shown in Fig. 1. Considering that

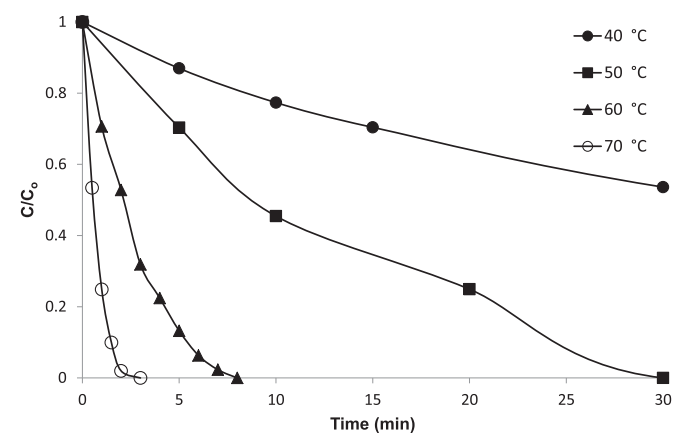


Fig. 1. Effect of temperature on BPA degradation. Experimental conditions: $[\text{BPA}]_0 = 220 \mu\text{g}/\text{L}$, $[\text{SPS}] = 625 \text{ mg}/\text{L}$, $\text{pH}_0 = 6.5$, UPW.

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