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Degradation of tetrabromobisphenol A by ferrate(VI) oxidation: Performance, inorganic and organic products, pathway and toxicity control

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HIGHLIGHTS

- Ferrate oxidation was an effective and green method for TBBPA removal.
- The second-order kinetics ranged from 4.5×10^4 to 0.9×10^3 $M^{-1}s^{-1}$ at pH 5.5–10.5.
- Ferrate oxidation of TBBPA had a relatively high level of bromine ion (about 30%).
- The relative inhibitory rate increased from 9% to 78% at initial reaction stage.
- Ferrate could effectively control the toxicity of the treated sample.

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ABSTRACT

This study systematically investigated the degradation of tetrabromobisphenol A (TBBPA) by ferrate (VI) oxidation. The reaction kinetics between ferrate (VI) with TBBPA were studied under pseudo-first-order conditions in the pH range 5.5–10.5. Then, a series of batch experiments were carried out to investigate other factors, including the ferrate (VI) dosage, temperature and interfering ions. Additionally, the generation of inorganic products (bromide ion and bromate) was evaluated. The organic intermediates were identified, and possible pathways were proposed. In addition, the toxicity variation was analyzed with marine luminous bacteria (*V. fischeri*). Degradation of TBBPA by ferrate (VI) oxidation was confirmed to be an effective and environmentally friendly technique. The reaction was fitted with a second-order rate model. With a ferrate (VI) dosage of 25.25 μmol/L, TBBPA concentration of 1.84 μmol/L, an initial pH of 7.0, and a temperature of 25 °C, a 99.06% TBBPA removal was achieved within 30 min. The evaluation of inorganic products showed that the capacity of ferrate (VI) oxidation to yield bromide ions was relatively strong and could prevent the formation of bromate compared to photocatalytic and mechanochemical techniques. Eleven intermediates were identified, and the proposed degradation pathway indicated that TBBPA might undergo debromination, beta scission, substitution, deprotonation and oxidation. The results of toxicity testing showed that ferrate (VI) could effectively control the toxicity of the treated samples, although the toxicity increased in the initial reaction stage due to the accumulation and destruction of more toxic intermediates.

1. Introduction

As one of the most important brominated flame retardants (BFRs), tetrabromobisphenol A (TBBPA) is widely used as a reactive BFR in the production of various materials, including electronic equipment, plastics, textiles and building materials, due to its moderate price and excellent flame-retardant property (Alaee and Wenning, 2002). It has been estimated that the market demand for TBBPA in China increased from 5.21×10^6 to 6.43×10^6 tons from 2014 to 2017 and is expected to increase significantly yearly. Because of its widespread use, high lipophilicity, and environmental persistence, TBBPA is ubiquitous in various environmental

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matrices, such as rivers, sediments, sewage sludge, landfill leachates and air near electronic waste treatment plants (Suzuki and Hasegawa, 2006; Choi et al., 2009; Y. Zhong et al., 2012a). Owing to its structural similarity to steroid hormones, TBBPA has been found to have estrogenic effects and can cause adverse effects on aquatic organisms, wildlife and even human health (Kitamura et al., 2002; Huang et al., 2013a). In recent years, TBBPA has received more and more attention and has been included as a hazardous substance in the OSPAR list (OSPAR, 2007). Therefore, it is necessary to develop effective techniques to remove TBBPA from contaminated environments.

In the last decade, a series of methods have been applied for the elimination of TBBPA from water, including biodegradation, physical adsorption, chemical oxidation (such as permanganate oxidation and ozonation) and photocatalytic degradation (Z.H. Sun et al., 2008; J. Zhang et al., 2009; J.R. Nyholm et al., 2010; J. Xu et al., 2011; Pang et al., 2014). However, the above treatment techniques have several inherent drawbacks. For instance, the biodegradation of TBBPA through anaerobic reductive debromination and aerobic mineralization (J.R. Nyholm et al., 2010) requires a long period to domesticate the microorganisms with a mean half-life of approximately 60 d for the whole metabolic process, which is difficult to achieve in conventional biological treatment plants (C.M. Potvin et al., 2012). The sorption behaviors of TBBPA in different soils are strongly pH dependent and are significantly affected by soil organic matter and the ionic strength, which further influence the transport, degradation, and bioavailability of TBBPA in the environment (Z.H. Sun et al., 2008). TBBPA can be efficiently mineralized through photocatalytic oxidation technology, but the high costs of the equipment and the difficulty in operation limit the practical application of this method (J. Eriksson et al., 2004). Due to their reasonable cost performance and facile operations, permanganate and ozone oxidation methods have been widely applied for the treatment of refractory wastewater (Kao et al., 2008; Qiang et al., 2013). However, there exist the risks of secondary heavy metal pollution in permanganate oxidation processes and bromate formation during ozonation treatments of brominated organic pollutants (Zhang et al., 2012a). Thus, it is important to develop an effective and environmentally friendly method to degrade TBBPA.

In recent years, ferrate (VI) oxidation has been considered as an environmentally friendly technique for pollution control and an efficient tool for degrading a large number of persistent organic compounds, such as pharmaceuticals (Anquandah et al., 2013; Jiang et al., 2013; Sharma et al., 2016b), personal care products (PCPs) (Yang and Ying, 2013), microcystins (Jiang et al., 2014; Sharma et al., 2016a) and endocrine disrupting chemicals (EDCs) (Yang et al., 2012; Zhang et al., 2012c; Machalová Šišková et al., 2016). The reduction products of ferrate (VI) and Fe(III) species are non-toxic and have the properties of flocculation, which further enhance the removal of metals, nutrients and organic matter (N. J. D. Graham et al., 2010; Prucek et al., 2015). In addition, ferrate (VI) can avoid the formation of chlorinated DBPs and bromate, which form during chlorination and ozonation processes (Y. Y. Eng et al., 2006; Sharma, 2010). All of the above advantageous properties make ferrate (VI) a promising, green, multi-functional oxidant capable of performing disinfection, oxidation, and coagulation in treatments of water and wastewater.

According to a literature survey, the degradation of TBBPA by ferrate (VI) has been reported by Yang et al. (2014), and they focused on a comparison with bisphenol A (BPA). Although the kinetics under the conditions of different pH values (7.0–10.0) were analyzed, systematic studies on other factors, such as the oxidant dosage, temperature and interfering ions, are still limited. The degradation pathway of TBBPA was proposed with two identified products, but the detection of more intermediates is important for further understanding ferrate (VI) oxidative degradation. In addition, the changes in hormonal activities using in vitro recombinant yeast bioassays were investigated; however, the results showed that no estrogenic and antiestrogenic activities were found throughout ferrate (VI) oxidation processes. Due to the properties of a high sensitivity and simple operation, luminescent bacteria detection methods have been widely used for testing the integrated and acute toxicity of reaction samples (T. Debenest et al., 2010; Molkenthin et al., 2013; Ding et al., 2015). Thus, in this study, the variation and control of toxicity during TBBPA degradation was investigated by using luminescent bacteria.

In addition, many of the previous studies regarding the elimination of TBBPA have focused on the determination of organic intermediates, which still contain a large fraction of bromine, such as tri-BBPA, di-BBPA, and mono-BBPA (C.C. Zhang and Zhang, 2012; Huang et al., 2013b). To date, the information on the change in the TBBPA toxicity and the generation of inorganic products (bromide ion and bromate), especially the generation level of bromide ions, is still lacking. The bromide ion can be generated through debromination, which has been confirmed as one of the major degradation mechanisms of TBBPA (J. Xu et al., 2011; Y.N. Guo et al., 2012b; An et al., 2013; Pang et al., 2014), and the further mineralization of TBBPA. Investigating the generation level of bromide ions can reflect the degradation of TBBPA and the variation of the toxicity. Hence, it is necessary to investigate the generation level of bromide ions and the variation of TBBPA toxicity as well as the removal efficiency.

Therefore, in the present study, the degradation of TBBPA through ferrate (VI) oxidation was systematically investigated. The reaction kinetics were studied as the function of the pH (5.5–10.5). Other factors influencing the TBBPA removal efficiency were also studied, including the oxidant dosage, initial pH, temperature and interfering ions. The generation of inorganic products (bromide ion and bromate) was evaluated at the same time. The organic intermediate products were identified, and possible degradation pathways were proposed. In addition, the variations and toxicity control during TBBPA degradation processes were analyzed. This study aims to develop the application of the environmental friendly oxidant ferrate (VI) for TBBPA degradation.

2. Materials and methods

2.1. Materials

Tetrabromobisphenol A (TBBPA, 98%) was purchased from Aladdin. The physio-chemical properties of TBBPA are shown in Table S1. Potassium ferrate (VI) (97%) was obtained from Sigma-Aldrich and used without further purification. The methanol, acetonitrile and dichloromethane (Merck, Germany) used in the experiments were of chromatographic grade. The freeze-dried bacteria *V. fischeri* used for the toxicity assessment was obtained from the manufacturer (DeltaTox, SDIX, USA) and stored at −20 °C. The other chemicals and reagents were of analytical grade and used as received.

All reaction solutions were prepared with deionized and ultrapure water (Milli-Q Direct 8, USA). A TBBPA solution with the desired concentration was prepared prior to experiments in a 0.5% methanol solution whose influence on the TBBPA removal could be ignored. The stock solution of ferrate (VI) was freshly prepared by dissolving 2.52 mol/L solid ferrate (VI) with a pH of 9.0 and used within 10 min to minimize the self-decomposition of ferrate (VI) (J. M. Schroyer and Ockerman, 1951).