



Oxidative degradation of atenolol by heat-activated persulfate: Kinetics, degradation pathways and distribution of transformation intermediates



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HIGHLIGHTS

- Effective removal of ATL from water was achieved by heat/PS.
- HCO₃⁻ and SRFA had inhibitory effects on ATL oxidation.
- Degradation products were identified and degradation pathways were proposed.
- Intermediate distribution was influenced by temperature.

ARTICLE INFO

Article history:

Received 25 December 2017

Received in revised form

4 May 2018

Accepted 12 May 2018

Available online 17 May 2018

Handling Editor: Chang-Ping Yu

Keywords:

Atenolol

Heat/PS

Degradation pathways

Distribution

ABSTRACT

Atenolol (ATL) has been widely detected in wastewater and aquatic environment. Although satisfactory removal of ATL from wastewater could be achieved, the mineralization ratio is usually low, which may result in the accumulation of its transformation products in the effluent and cause additional ecological risk to the environment. The aim of this study is to explore the effectiveness of heat activated persulfate (PS) in the removal of ATL from wastewater. Influencing factors including temperature, PS dosage, solution pH, existence of NO₃⁻, Cl⁻, HCO₃⁻ and Suwannee river fulvic acid (SRFA) were examined. Complete removal of ATL was achieved within 40 min at pH 7.0 and 70 °C by using 0.5 mM PS. Inhibitive effects of HCO₃⁻ and FA had been observed on ATL oxidation, which was increased with the increase of their concentration. Sulfate radical (SO₄^{•-}) was determined as the main reactive species by quenching experiment. Eight intermediates produced in ATL degradation were identified, and four degradation pathways were proposed based on the analysis of mass spectrum and frontier electron densities. The distribution of major intermediates was influenced by reaction temperature. Hydroxylation intermediates and deamidation intermediate were the most prominent at 50 °C and 60 °C, respectively. All intermediates were completely degraded in 40 min except P134 at 70 °C. Effective removal of TOC (74.12%) was achieved with 0.5 mM PS, pH 7.0 and 70 °C after 240 min. The results proved that heat activation of PS is a promising method to remove organic pollutants in wastewater.

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1. Introduction

β-blockers are widely used to treat arrhythmias and high blood pressure, by selective binding to β-adrenergic receptors to block the action of epinephrine, which can shrink blood vessels lead to high

blood pressure (Bhatia et al., 2017; Hinojosa-Reyes et al., 2017; Huggett et al., 2003). The currently marketed β-blockers include atenolol (ATL), bisoprolol, metoprolol, sotalol and propranolol (Alder et al., 2010; Ghauch and Tuqan, 2012; Tay and Ismail, 2016), among which ATL is the most consumed one (Xu et al., 2017). Furthermore, ATL has been frequently detected in wastewater treatment plants (WWTPs) because it cannot be completely metabolized by human body (Haro et al., 2017; Hinojosa-Reyes

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et al., 2017; Rastogi et al., 2015). Papageorgiou et al. reported that the maximum concentrations of ATL in the influent and effluent samples collected from a WWTPs located in Greece were 2.346 and 1.707 $\mu\text{g L}^{-1}$, respectively (Papageorgiou et al., 2016). The maximum concentrations of ATL at different stages of the WWTPs located in Albany area of New York, USA were 2.0 $\mu\text{g L}^{-1}$, 1.390 $\mu\text{g L}^{-1}$, 0.754 $\mu\text{g L}^{-1}$ and 40.8 ng g^{-1} dry wt in wastewater influent, primary effluent, final effluent and treated sludge, respectively (Subedi and Kannan, 2015), which indicated that the removal efficiency of ATL in wastewater was low and most of it was transferred to the sludge.

Some reports have shown that ATL has certain threat to aquatic organisms. The patterns of gene expression was altered in the brain of Atlantic salmon exposed to 11 $\mu\text{g L}^{-1}$ ATL for 5 days (Hampel et al., 2010). When the trout hepatocytes were exposed to 0.01 nM ATL, the abundance of glucose transporter 2 (GLUT2) mRNA regulating the glucose production, was reduced by complete abortion of epinephrine (Ings et al., 2012). Therefore, it is imperative to develop an effective treatment technique for the effective removal of ATL and its transformation intermediates in wastewater.

Previous study had shown that ATL could be removed by photolysis and biodegradation in aquatic environment, but both had very long half lifetime with 77–730 h and 340–2900 h, respectively (Yamamoto et al., 2009). In recent years, sulfate radicals ($\text{SO}_4^{\bullet-}$)-based AOPs have been widely used to destroy recalcitrant organic contaminants in wastewater because $\text{SO}_4^{\bullet-}$ had stronger oxidizing capacity and higher mineralization ability compared with hydroxyl radicals ($\bullet\text{OH}$) (Deng et al., 2013; Hu and Long, 2016; Jiang et al., 2016). $\text{SO}_4^{\bullet-}$ could be generated from persulfate (PS) or peroxymonosulfate (PMS) by dissolved metals (Xie et al., 2016), metal oxides (Zhang et al., 2016), ultraviolet light (Liu et al., 2013), heat (Ghauch et al., 2012b), ultrasound (Wei et al., 2017) and alkaline solution (Furman et al., 2010). Of various activation methods, heat-activation of PS was considered as an effective and simple way to generate $\text{SO}_4^{\bullet-}$ to remove numerous pollutants. Ghauch et al. investigated the degradation of bisoprolol (Ghauch and Tuqan, 2012), ibuprofen (Ghauch et al., 2012a) and naproxen (Ghauch et al., 2015) in a heat-activated system. They found that the removal rates of bisoprolol, ibuprofen and naproxen were 100%, 100% and 85%, respectively after 20 min when the molar ratios of bisoprolol, ibuprofen and naproxen to PS were 1:50, 1:50, and 1:20.36, respectively and 70 °C. In addition, in situ heat activation of PS could be achieved by the electrokinetically thermally activate persulfate (EK-TAP) system, which can not only improve the migration capacity of PS but also activate PS by alternating current in the subsurface (Zrinyi and Pham, 2017). Therefore, heat/PS was used to degrade ATL in this study.

The main purpose of this study is to systematically investigate the oxidative degradation process of ATL by heat/PS. Firstly, key factors influencing the degradation of ATL were evaluated including temperature, PS dosage, solution pH, and concentrations of NO_3^- , Cl^- , HCO_3^- and Suwannee river fulvic acid (SRFA). Secondly, major reactive species were identified by radical quenching experiment. Thirdly, the identification of transformation intermediates was studied using high resolution liquid chromatograph - time of flight - mass spectrometry (LC-TOF-MS). Fourthly, the degradation pathways of ATL were proposed, which was verified by the Gaussian theoretical calculations. Then, the distribution of transformation intermediates was analyzed. Finally, the TOC removal rate and PS consumption rate were investigated.

2. Materials and methods

2.1. Chemicals and reagents

Atenolol (ATL, $\text{C}_{14}\text{H}_{22}\text{N}_2\text{O}_3$, purity $\geq 99.0\%$) and sodium

persulfate ($\text{Na}_2\text{S}_2\text{O}_8$, purity $\geq 99.0\%$) were purchased from Sigma-Aldrich. Suwannee river fulvic acid (SRFA) was supplied by International Humic Substance Society (IHSS). HPLC grade methanol was obtained from Tedia Company (Fairfield, USA). Methanol for LC-TOF-MS analysis was obtained from Merck Company (Darmstadt, Germany). All of the other reagents were at least of analytical grade or higher. All the stock solutions were prepared by dissolving the chemicals into ultrapure water (18.2 M Ω cm) prepared from a Milli-Q system (Bedford, USA).

2.2. Experimental procedures

The degradation of ATL were carried out in a series of 40 mL EPA vials with polytetrafluoroethylene caps at desired temperatures (40–70 °C), which were controlled by a water bath shaker with constant temperature. Solutions containing ATL were pre-heated to the operating temperature, and subsequently appropriate volume of PS stock solution was spiked to achieve a total of 20 mL reaction volume with predetermined molar ratios of ATL and PS. The initial pH of reaction solution was adjusted to predetermined value by H_2SO_4 (0.1 mM) or NaOH (0.1 mM). At pre-specified time intervals, 0.5 mL reaction solution was withdrawn from the reactor, which was immediately quenched by 0.5 mL methanol for high-performance liquid chromatography (HPLC) analysis to determine the residual ATL concentration.

The transformation intermediates of ATL were performed in a 250 mL conical flask containing 100 mL reaction solution, which were collected from three different reaction temperature (50, 60 and 70 °C) at different reaction time to understand the effect of temperature on the distribution of ATL transformation intermediates. The solutions were concentrated by solid phase extraction (SPE) with CNW LC-C18 cartridges pre-conditioned with 10 mL methanol and 10 mL deionized water. Reaction solutions were percolated through the SPE cartridges at 0.5 mL min^{-1} . After that, the inner wall of the conical flasks was washed with 10 mL deionized water. The excess water remaining on the cartridge was removed by evacuation. Then, the transformation products were eluted with 2 \times 1 mL methanol for analysis by LC-TOF-MS.

2.3. Analytical methods

The residual concentration of ATL was monitored by HPLC (Agilent 1200, USA) equipped with a XDB C18 column and an UV-Vis detector using 30% methanol and 70% ultrapure water (0.01 mM ammonium acetate) as the mobile phase with a 0.8 mL min^{-1} of flow rate at 30 °C. The injection volume was 20 μL and detection wavelength was 254 nm.

The transformation intermediates generated from ATL were identified by LC-TOF-MS, equipped with a duo-spray ion source and an Agilent HPLC system. The separation was performed on an Agilent Eclipse Plus C18 column (5 μm , 150 mm \times 2.1 mm, i.d.) using 30% methanol and 70% ultrapure water as the mobile phase with a 0.2 mL min^{-1} of flow rate at 30 °C and the injection volume was 5 μL . Mass spectrometric analysis was carried out in a positive ion mode with the following experimental parameters: nebulizer gas 55 psi, auxiliary gas 55 psi, curtain gas 35 psi; temperature 550 °C; ion spray voltage 5500 V and scan range $m/z = 50$ –1200 amu.

The total organic carbon (TOC) of the reaction solutions was measured on a Shimadzu TOC-5000 total organic carbon analyzer (Shimadzu, Kyoto, Japan). The concentration of PS was determined by the previous method with modification (Liang et al., 2008).

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