



# Degradation of atenolol by UV/peroxymonosulfate: Kinetics, effect of operational parameters and mechanism



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## HIGHLIGHTS

- DO can influence  $\text{SO}_4^-$ -based AOPs remarkably.
- HA-induced absorption and indirect photolysis was vital at the early reaction stage.
- Four attacking ways were involved in the degradation mechanisms.

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## ABSTRACT

Photoactivation of peroxymonosulfate (PMS) with UV (254 nm) irradiation was used to generate the  $\text{SO}_4^-$ -based advanced oxidation process, which was adopted to degrade atenolol (ATL) in water. The second-order reaction rate constants of ATL with  $\text{HO}^\cdot$  and  $\text{SO}_4^-$  were determined, and the effects of operational parameters (dose of PMS, solution pH,  $\text{HCO}_3^-$ , humic acids (HA), and  $\text{N}_2$  bubbling) were evaluated as well. Finally the main transformation intermediates were identified and possible degradation pathways were proposed. The results showed that there was a linear positive correlation between the degradation rate of ATL and specific dose of PMS (1–16 M PMS/M ATL). Increasing solution pH from 3 to 9 promoted elimination of ATL due to the pH-dependent effect of PMS photodecomposition, while further pH increase from 9 to 11 caused slowing down of degradation because of apparent conversion of  $\text{HO}^\cdot$  to  $\text{SO}_4^-$ . 1–8 mM  $\text{HCO}_3^-$  exerted no more than 5.3% inhibition effect on ATL destruction, suggesting  $\text{HCO}_3^-$  was a weak inhibitor. Absorption (or complexation) and photosensitized oxidation induced by HA improved ATL degradation during the first minute of degradation process, whereas photon competition and radical scavenging effects became the leading role afterward. Bubbling with nitrogen enhanced the degradation rate due to the stripping of dissolved oxygen. Hydroxylation of aromatic ring, cleavage of ether bond, oxidation of primary and secondary amine moieties, and dimerization were involved in the degradation mechanism of ATL by UV/PMS.

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## 1. Introduction

Pharmaceuticals and Personal Care Products (PPCPs), as an emerging class of environmental pollutant, have attracted increasing concern due to their adverse effect on human health and ecosystems (Nassef et al., 2010). Among the PPCPs,  $\beta$ -blockers are an important subclass, extensively used for the treatment of disorders such as hypertension (high blood pressure), angina, and arrhythmias.  $\beta$ -Blockers were frequently detected in sewage treatment plant effluent and even surface water with a concentration ranging from  $\text{ng L}^{-1}$  to  $\mu\text{g L}^{-1}$  (Maurer et al., 2007), which means  $\beta$ -blockers cannot be totally removed in sewage treatment plant and finally are discharged into natural aquatic ecosystem. Among the

$\beta$ -blockers, the toxicity of atenolol (ATL) is the most serious to aquatic organisms and humans (Muruganathan et al., 2011). Therefore, it is important to develop treatment technologies for ensuring effective interception of ATL in drinking water before distribution to consumers.

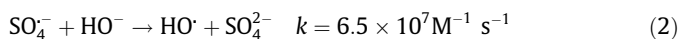
The conventional water treatment processes (coagulation/flocculation, filtration, chlorination) are the primary barrier to hinder ATL from entering drinking water. Unfortunately, there is no facilities specifically designed to remove ATL and other PPCPs in drinking water plants and thus elimination of these PPCPs is not satisfactory (Alder et al., 2010). Therefore, enhanced treatment technologies are in need. The hydrophilic properties of ATL cause them tend to stay in water phase rather than volatilize to air or partition to the sediments (Vieno et al., 2007), which makes adsorption of activated carbon inefficient (Liu et al., 2009). Biodegradation of ATL is limited as long treatment time is required and more resistant by-products are formed (Muruganathan et al.,

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2011). ATL can undergo direct or indirect photolysis under solar or UV light in aqueous solution but with long half lifetime (Ji et al., 2012; Zeng et al., 2012). Chemical oxidation such as ozonation and chlorination has been proved to be an efficient technology for the removal of ATL but with great quantities of transformation products (Liu and Williams, 2007), some of which show toxic activity. Previous researches have demonstrated that advanced oxidation processes (AOPs) based on the generation of HO<sup>•</sup> like TiO<sub>2</sub>-mediated photocatalysis, pulse and gamma radiolysis, and electro- or photoelectro-Fenton can mineralize ATL effectively (Song et al., 2008; Isarain-Chávez et al., 2010; Ji et al., 2013). However, due to the nonselectivity of HO<sup>•</sup>, HO<sup>•</sup>-based AOPs are limited when HO<sup>•</sup> reacts with the coexisting water constituents with similar rate constants to that of the target pollutant. SO<sub>4</sub><sup>•-</sup>, more selective and oxidative than HO<sup>•</sup> in general, has been therefore proposed and evaluated for pollutant destruction recently (Fang and Shang, 2012).

SO<sub>4</sub><sup>•-</sup> is usually generated by activation of peroxodisulfate (S<sub>2</sub>O<sub>8</sub><sup>2-</sup>, PDS) or peroxymonosulfate (HSO<sub>5</sub><sup>-</sup>, PMS) ion using heat, base, UV or transition metals (Anipsitakis and Dionysiou, 2004). Recent studies related to the activation of PDS or PMS mainly have focused on metal ion-mediated processes, among which cobalt ion was found to be the best activator. Although heterogeneous metal ion/oxide-mediated activators were used to reduce the concentration of hazardous metal ion in the treated water (Anipsitakis et al., 2005; Yang et al., 2009), the negative effects of residual metal ion on human health need to be evaluated. By contrast, UV irradiation was considered as an environmentally friendly and applicable way to activate PDS or PMS to form active oxidative species (Fang and Shang, 2012), as summarized in the following reactions:



Considering the frequent detection of  $\beta$ -blockers in the aquatic environment and the limited data available on the treatment of ATL contaminated water by SO<sub>4</sub><sup>•-</sup>-based AOPs, the main purpose of present work is to investigate the degradation of  $\beta$ -blockers by UV/PMS process under different operational conditions, i.e., dose of PMS, solution pH, bicarbonate ion, humic acid, and nitrogen stripping. ATL, as a typical  $\beta$ -blocker, was selected as target compound to conduct the experiments. The destruction kinetics and mechanisms of ATL by HO<sup>•</sup> and SO<sub>4</sub><sup>•-</sup> were also discussed through competitive kinetics and analysis of liquid chromatography–electrospray ionization–mass spectrometry (LC–ESI–MS).

## 2. Material and methods

### 2.1. Materials and reagents

ATL, HA, potassium peroxymonosulfate (OXONE, 2KHSO<sub>5</sub>·KHSO<sub>4</sub>·K<sub>2</sub>SO<sub>4</sub>), benzoic acid (BA), *Tert*-butyl alcohol (TBA), phosphoric acid were of ACS reagent grade and purchased from Sigma–Aldrich. HPLC-grade methanol (for HPLC mobile phase) and 99.8% anhydrous methanol (used as radical quencher) were also purchased from Sigma–Aldrich. Other reagents such as NaNO<sub>2</sub>, NaNO<sub>3</sub>, NaCl and H<sub>2</sub>SO<sub>4</sub> with reported purities >98% were obtained from reagent company of Sinopharm Chemical Reagent (Shanghai, China). 0.45 and 0.7  $\mu\text{m}$  glass fiber filters were ordered from Millipore (London, UK). HA stock solution was prepared by adding 0.3 g of dry HA powder to 1 L of deionized water, and stirring overnight. The solution was then filtered through 0.7  $\mu\text{m}$  glass fiber filters. The TOC of the HA stock solution was found to be 103.7 mg L<sup>-1</sup>

through a TOC–VCPH analyzer (Shimadzu, Japan). All other reagents were used as received without further purification, and solutions were prepared in 18.2 M $\Omega$  cm Milli-Q water. High purity (99.99%) compressed N<sub>2</sub> or O<sub>2</sub> was purchased from Jingong (Hangzhou, China).

### 2.2. Experimental procedures

The experiments were performed in a sealed 1.8 L cylindrical glass reactor (1.5 L samples, inner diameter of 4.0 cm). A low-pressure mercury UV lamp (Heraeus, GPH212T5L/4, 10 W, ozone-free, lamp centered at 253.7 nm) was placed in the center of the reactor (Fig. SM-1 in Supplementary Material (SM)). The incident radiation intensity of UV lamp was about  $3.7 \times 10^{-6}$  Einstein L<sup>-1</sup> s<sup>-1</sup> measured by the method of iodide–iodate chemical actinometer (Rivas et al., 2010). The optical path length was determined to be 3.5 cm by measuring the photolysis rate of H<sub>2</sub>O<sub>2</sub> (Rahn et al., 2003). The pH of solution was adjusted with 0.1M H<sub>2</sub>SO<sub>4</sub> for pH < 6 and buffered with phosphate or borate salts (2 mM) for 6 < pH < 12. Samples were withdrawn at predetermined time intervals and quenched using excessive NaNO<sub>2</sub>. Controlled experiments on the effects of phosphate, sulfate, and borate were carried out and negligible effects of the three anions were observed (Fig. SM-2). The results are consistent with the conclusion of Guan et al. (2011). All experiments, done in an air-conditioned room at 23  $\pm$  2 °C, were conducted in triplicate and error bars represent 95% confidence interval. ATL at initial concentration of 20  $\mu\text{M}$  was placed in the reactor and well mixed with a magnetic stirrer. A thin glass tube with a diffuser immersed in the solution was used to purge target gas. The reactor was surrounded by aluminum foil and covered with black UV blocking cloth. The reaction was considered to start once the PMS was added into the reactor and UV lamp was turned on.

### 2.3. Analysis methods

Concentrations of PMS were determined using the method described by Huang et al. (2002). ATL and BA were tested by HPLC (Agilent 1200, USA) equipped with a UV–Vis detector and a 4.6 mm  $\times$  250 mm (5  $\mu\text{m}$ ) SB–C18 column. The analysis was carried out isocratically with a 87/13 (v/v) pH 2.5 phosphate buffer/methanol mobile phase and the flow rate was set at 1.0 mL min<sup>-1</sup>. The injection volume was 40  $\mu\text{L}$ . A Dionex ICS-2000 ion chromatograph equipped with a 25  $\mu\text{L}$  sample loop was used to determine the concentration of the NO<sub>2</sub><sup>-</sup> and NO<sub>3</sub><sup>-</sup> in the solution. UV–Vis spectra of ATL and PMS in distilled water were determined with a UV-2550 UV–Vis spectrophotometer (Shimadzu, Japan) in the wavelength range of 200–800 nm.

To determine the second-order rate constant of ATL with HO<sup>•</sup> and SO<sub>4</sub><sup>•-</sup>, the competitive kinetic methods were applied (Guan et al., 2011).  $k_{\text{HO}^\bullet/\text{ATL}}$  was determined from degradation of mixtures of ATL (20  $\mu\text{M}$ ) and BA (20  $\mu\text{M}$ ) by the typical HO<sup>•</sup>-based AOPs (UV/H<sub>2</sub>O<sub>2</sub>), while  $k_{\text{SO}_4^{\bullet-}/\text{ATL}}$  was obtained from oxidation of mixtures containing 20  $\mu\text{M}$  ATL and 20  $\mu\text{M}$  BA in the presence of 20 mM HO<sup>•</sup> quencher (TBA).

### 2.4. Intermediates identification

In order to obtain sufficient amounts of all possible intermediates for analysis, the oxidation process was investigated at initial concentrations of ATL of 200  $\mu\text{M}$  and PMS dosage of 320  $\mu\text{M}$ . The reaction intermediates and products were analyzed by using an Agilent 6460 triple quadrupole HPLC–MS. The mass spectrometric measurements were carried out using an ESI in positive ion mode. A Zorbax SB C18 column (2.1 mm  $\times$  150 mm, 5  $\mu\text{m}$ ) was used to separate ATL and the intermediates. The analysis was carried out

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