



Degradation kinetics and mechanism of β -lactam antibiotics by the activation of H_2O_2 and $\text{Na}_2\text{S}_2\text{O}_8$ under UV-254 nm irradiation



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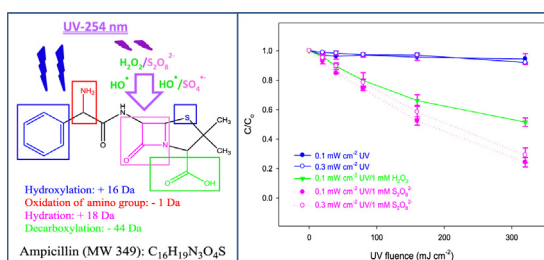
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HIGHLIGHTS

- Removal efficiency was comparable at different UV fluence rates but same fluence.
- Reducing pH to 3 or 2 did not inhibit the removal of nitrobenzene by UV/ $\text{S}_2\text{O}_8^{2-}$.
- 1.84×10^{-14} M $[\text{HO}^\bullet]_{\text{ss}}$ and 3.10×10^{-13} M $[\text{SO}_4^{\bullet-}]_{\text{ss}}$ in UV/ $\text{S}_2\text{O}_8^{2-}$ were estimated.
- HO^\bullet reacted faster with the β -lactams than $\text{SO}_4^{\bullet-}$ but sharing similar byproducts.
- Transformation pathways included hydroxylation, hydrolysis and decarboxylation.

GRAPHICAL ABSTRACT



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ABSTRACT

The extensive production and usage of antibiotics have led to an increasing occurrence of antibiotic residuals in various aquatic compartments, presenting a significant threat to both ecosystem and human health. This study investigated the degradation of selected β -lactam antibiotics (penicillins: ampicillin, penicillin V, and piperacillin; cephalosporin: cephalothin) by UV-254 nm activated H_2O_2 and $\text{S}_2\text{O}_8^{2-}$ photochemical processes. The UV irradiation alone resulted in various degrees of direct photolysis of the antibiotics; while the addition of the oxidants improved significantly the removal efficiency. The steady-state radical concentrations were estimated, revealing a non-negligible contribution of hydroxyl radicals in the UV/ $\text{S}_2\text{O}_8^{2-}$ system. Mineralization of the β -lactams could be achieved at high UV fluence, with a slow formation of SO_4^{2-} and a much lower elimination of total organic carbon (TOC). The transformation mechanisms were also investigated showing the main reaction pathways of hydroxylation (+16 Da) at the aromatic ring and/or the sulfur atom, hydrolysis (+18 Da) at the β -lactam ring and decarboxylation (-44 Da) for the three penicillins. Oxidation of amine group was also observed for ampicillin. This study suggests that UV/ H_2O_2 and UV/ $\text{S}_2\text{O}_8^{2-}$ advanced oxidation processes (AOPs) are capable of degrading β -lactam antibiotics decreasing consequently the antibiotic activity of treated waters.

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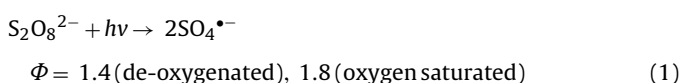
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1. Introduction

Antibiotics, one of the most widely used and frequently prescribed categories of pharmaceuticals, are applied not only for the inactivation or killing of microbes [1], but also for various animal husbandry and agricultural purposes [2]. The estimated annual use of antibiotics for human in Germany was 300 tons and for animals was 1700 t [3]. The annual consumption in the United States was estimated to be 3290 t for humans, 13,540 t for livestock, 150 t for aquaculture, 150 t for pets and 70 t for crops [2]. The Food and Drug Administration (FDA) reported that in 2011, more than 880 t of penicillin class of antibiotics and 26 t of cephalosporin class of antibiotics were approved for use in food-producing animals alone in the US [4]. Besides, up to 90% of human prescription antibiotic consumption can be excreted without undergoing metabolism [5]. The lack of an effective treatment before wastewater discharge can subsequently lead to their wide occurrence in natural environments [6–8]. The full impacts of the antibiotic residuals in the natural waters on the ecosystem and ultimately humans have yet to be fully evaluated [5,9]. Although acute toxicity may not be significant, a number of studies have gradually revealed the severe chronic toxicity of certain antibiotic species [10]. Their existence in the aquatic environment, even at very low concentration levels, can promote the growth of antibiotic resistant bacteria or pathogens [1,5,6,9–11].

A number of technologies have been developed for the removal of such microcontaminants in wastewater treatment plants [10]. Advanced oxidation processes (AOPs) are considered as promising alternatives to conventional wastewater treatment processes for water decontamination [10,12,13]. The main mechanism of AOPs is through the generation of highly reactive free radicals. Traditional AOPs mainly function by hydroxyl radicals (HO^\bullet , HR-AOPs) [14]; however, sulfate radical-based AOPs (SR-AOPs) have also been attracting significant scientific interest for the destruction of micropollutants such as pharmaceuticals and cyanotoxins [15–18].

The combination of UV-254 nm light, which has been extensively applied in water treatment facilities for disinfection purposes, with hydrogen peroxide, i.e., UV-254 nm/ H_2O_2 , is one of the most common ways to generate hydroxyl radicals [14]. UV/ H_2O_2 has been demonstrated to be very effective in degrading various organic contaminants, including endocrine disrupting compounds, pharmaceuticals, pesticides, and cyanotoxins [14,16,18,19]. The single step dissociation of H_2O_2 to form hydroxyl radicals, with no sludge formation and potentially complete contaminant mineralization, has made it the most frequently applied oxidant in AOPs [20,21]. Persulfate ($\text{S}_2\text{O}_8^{2-}$, PS), on the other hand, has a high redox potential and is quite stable at room temperature. After activation, by UV, transition metals, and/or elevated temperature or pH, sulfate radicals ($\text{SO}_4^{\bullet-}$) can be generated [15]. Both UV/ H_2O_2 and UV/PS processes could be influenced by natural water quality as suggested by the comparable reaction of HO^\bullet and $\text{SO}_4^{\bullet-}$ at 8.5×10^6 and $9.1 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$, respectively, with natural alkalinity, i.e., HCO_3^- [22,23]. Limited information is available on the reaction rate constant of natural organic matter (NOM) with $\text{SO}_4^{\bullet-}$. However, its reactivity is expected to be at least one order of magnitude lower than $k_{\text{HO}^\bullet/\text{NOM}}$ [24,25]. Besides, under UV-254 nm irradiation, $\text{S}_2\text{O}_8^{2-}$ has a much higher radical quantum yield than H_2O_2 , as shown in Eqs. (1) and (2) [26,27]. In fact, a better performance of UV/PS than UV/ H_2O_2 in the degradation of cyanotoxin cylindrospermopsin in various natural water samples has been reported [28].



The purpose of this study was to investigate the removal of selected β -lactam antibiotics (penicillins: ampicillin, penicillin V, and piperacillin; and cephalosporin: cephalothin) by UV-254 nm/ H_2O_2 and UV-254 nm/ $\text{S}_2\text{O}_8^{2-}$ AOPs. Since HO^\bullet is non-selective and can react effectively through hydrogen atom abstraction (H-abstraction) and hydroxyl addition at the double bond [23], a modification of the β -lactam ring can thus be expected. On the other hand, $\text{SO}_4^{\bullet-}$ reaction occurs mainly by electron abstraction or to a lesser extent through H-abstraction [22]. Therefore, the elimination of a carboxylate, hydroxylation at the aromatic ring or the double bond of the β -lactams is more likely for sulfate radical reaction [29]. This study can thus provide valuable information on the elimination of the antibiotic reactivity by UV-AOPs through kinetic evaluation and transformation mechanism assessment. A high initial concentration of 50 μM of the pollutant was used in this study with the aim of quantitatively evaluating mineralization potential (e.g., in terms of sulfate anion formation and total organic carbon (TOC) elimination). The contribution of hydroxyl and sulfate radicals in UV/ $\text{S}_2\text{O}_8^{2-}$ was examined. The reaction pathways were accessed through the identification of transformation products (TPs) by mass spectrometry.

2. Materials and methods

2.1. Materials

The antibiotics, ampicillin (AMP, sodium salt, Fisher), penicillin V (PEN, potassium salt, Fisher), piperacillin (PIP, sodium salt, Sigma Aldrich) and cephalothin (CEP, sodium salt, Sigma Aldrich), and the oxidants, H_2O_2 (50%, v:v, Fisher) and $\text{Na}_2\text{S}_2\text{O}_8$ (98%, Sigma Aldrich), as well as other chemicals were all ACS (American Chemical Society) grade and used as received. Table 1 shows the structure of the examined antibiotics.

2.2. Analysis

The concentration of organic compounds was determined by HPLC with a photodiode array detector. Three different methods were applied. Both methods no. 1 and 2 used an Agilent 1100 Series quaternary LC and a Nova-Pak C_{18} Waters ($3.9 \times 150 \text{ mm}$, $5 \mu\text{m}$) column with a mobile phase of 0.1% acetic acid in Milli-Q water (A) and 100% acetonitrile (B). Method no. 1 used an isocratic mode with 80% A and 20% B. Method no. 2 used a gradient analysis mode, starting with 95% A, and gradually changing to 65% A in 12 min, then back to 85% A in the next four minutes, and returning to 95% A in the last two minutes. Both methods had an identical injection volume of 20 μL , a flow rate of 0.5 mL min^{-1} and a column temperature of 25°C . Method no. 3 used a C_{18} Discovery HS (Supelco) column ($2.1 \times 150 \text{ mm}$, $5 \mu\text{m}$) with a mobile phase of 0.05% (v/v) trifluoroacetic acid (TFA) in acetonitrile solution and 0.05% TFA in Milli-Q water in a 40:60 (v:v) ratio. A flow rate of 0.2 mL min^{-1} , an injection volume of 20 μL and a column temperature of 40°C were applied. The competitors for determining second-order rate constant, i.e., para-chlorobenzoic acid (pCBA) and m-toluic acid (m-methylbenzoic acid, TA), were analyzed by either method no. 1 or 2 dependent on the other compound in the competing reaction solution. For example, at the determination of $k_{\text{HO}^\bullet/\text{AMP}}$, pCBA was analyzed by method no. 1; while at the determination of $k_{\text{HO}^\bullet/\text{CEP}}$, pCBA was analyzed by method no. 2. The limit of detection and quantification for each compound are listed in Table 2 [30].

The concentration of H_2O_2 and $\text{Na}_2\text{S}_2\text{O}_8$ was measured based on the spectrometric determination of triiodide complex at 352 nm resulting from the oxidation of iodide anion [31,32]. Sulfate anions were quantified by a Dionex Ion Chromatography equipped with

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