



Degradation kinetics and mechanism of oxytetracycline by hydroxyl radical-based advanced oxidation processes



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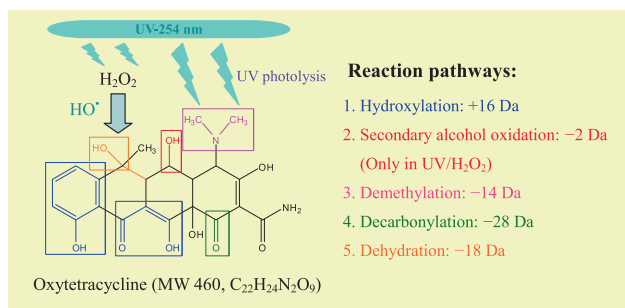
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HIGHLIGHTS

- HO[•] played a much more significant role than UV in degrading OTC by UV/H₂O₂.
- Ca²⁺ and Mg²⁺ had no effects on OTC degradation though they can bind with OTC.
- The presence of Cu²⁺ slightly increased the OTC removal in UV/H₂O₂ process.
- Limited TOC elimination was obtained during the mineralization studies of OTC.
- Five reaction pathways were proposed based on identified byproducts by LC-QTOF/MS.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 30 June 2015

Received in revised form 9 September 2015

Accepted 10 September 2015

Available online 28 September 2015

Keywords:

Oxytetracycline

Advanced oxidation processes (AOPs)

Hydroxyl radical

UV-254 nm/H₂O₂

Mechanism

ABSTRACT

In this study, the degradation kinetics and transformation mechanism of oxytetracycline (OTC) by UV-254 nm and UV-254 nm/H₂O₂ were investigated. The removal of OTC increased with increasing initial H₂O₂ dosage while excess H₂O₂ acted as an inhibitor of HO[•]. The observed UV fluence based pseudo first-order rate constant of OTC (k_{obs} , cm² mJ⁻¹) decreased while the degradation rate at the initial 13 min (μ M min⁻¹) increased with increasing initial OTC concentrations. Presence of different water constituents in the reaction system had a different degree of influence on the degradation efficiency of OTC. Though after 10 h irradiation, there was only a limited elimination of total organic carbon (TOC), successful transformation of OTC was demonstrated by the detection of thirty-one degradation byproducts in the UV/H₂O₂ system. Potential degradation mechanisms for OTC were proposed exhibiting five main pathways, including hydroxylation (+16 Da), secondary alcohol oxidation (-2 Da), demethylation (-14 Da), decarbonylation (-28 Da) and dehydration (-18 Da). This study indicates that UV-254 nm/H₂O₂ is an effective technology for the removal of OTC from an aquatic environment.

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1. Introduction

Antibiotics, one of the largest groups of pharmaceuticals and personal care products (PPCPs), have received increasing attention

and scientific interest in recent years [1–6]. Oxytetracycline (OTC), for example, is an important broad spectrum antibiotic and has been used in livestock for the disease prevention and growth promotion worldwide [5,6]. In the United States, it is one of the ten approved antibiotic growth promoters [7]. Most OTC is excreted without undergoing metabolism leading to its frequent detection in surface water, sewage water, groundwater, drinking water,

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seawater and sediment throughout the world [1,4,5,8,9]. Up to $0.34 \mu\text{g L}^{-1}$ of OTC has been detected in surface water in the United States [10], while 20–800 mg L^{-1} of OTC has been reported in the effluent from the wastewater treatment plant (WWTP) of one of the biggest OTC producers in China [11]. OTC occurrence in natural environment can affect the selection of genetic variants of microorganisms resulting in the development of drug resistant bacteria or pathogens, which may subsequently induce a risk to the ecosystem and human health [2,4,5,12,13]. It is thus important to remove such a compound from contaminated water. Conventional water treatment methods, such as biodegradation and chlorination, cannot remove OTC efficiently due to its bio-resistant property and chemical stability (Fig. 1) [14,15]. Therefore, it is necessary to develop more efficient and environmentally friendly technologies for the removal of this microcontaminant.

Advanced oxidation processes (AOPs) via the generation of highly reactive free radicals, such as hydroxyl radical ($\text{HO}\cdot$) and sulfate radical ($\text{SO}_4\cdot^-$), have been considered as a promising alternative for the destruction of recalcitrant organic pollutants [16–19]. Hydroxyl radical-based AOPs (HR-AOPs) are a traditional and highly efficient process, because $\text{HO}\cdot$ is a non-selective oxidant ($E_0 = 2.72 \text{ V}$, depending on the experimental conditions [18]) having high second-order rate constants with organic compounds in the range of $10^8\text{--}10^{10} \text{ M}^{-1} \text{ s}^{-1}$ [20]. A number of technologies have been applied to generate $\text{HO}\cdot$ including Fenton process, photo-Fenton process, UV-254 nm/ H_2O_2 and photocatalysis. Due to the high $\text{HO}\cdot$ quantum yield from the direct dissociation of H_2O_2 ($\Phi = 1.0$, i.e., 1.0 mol of $\text{HO}\cdot$ being generated with the absorption of 1.0 mol UV photons at 254 nm), as shown in Eq. (1) [21], and a potential complete mineralization of contaminants, UV-254 nm/ H_2O_2 has been widely studied and used for the degradation of various organic contaminants [22–25]. The feasibility of UV/ H_2O_2 in removing OTC has been investigated by several researchers [24–27]. However, the systematic degradation of OTC by UV/ H_2O_2 has not been evaluated so far, including the effects of oxidant dosage, contaminant concentration, common water quality parameters and mineralization.



In addition to kinetics, information on the transformation mechanism of OTC by UV/ H_2O_2 is also very limited. In the study by Yuan et al. [27], UV direct photolysis resulted in the detection of three main byproducts as identified by LC–MS/MS while UV/ H_2O_2 led to six main byproducts as identified by GC–MS. Four main byproducts were reported by Jeong et al. [28] from γ -irradiation of OTC in water where $\text{HO}\cdot$ and e_{aq}^- acted as the reactive species. Reaction byproducts and pathways were also studied by photocatalysis using TiO_2 under simulated solar irradiation [29]. Nevertheless, the number of reported byproducts was very limited and the reaction pathways were still unclear, especially for the degradation of OTC by UV/ H_2O_2 .

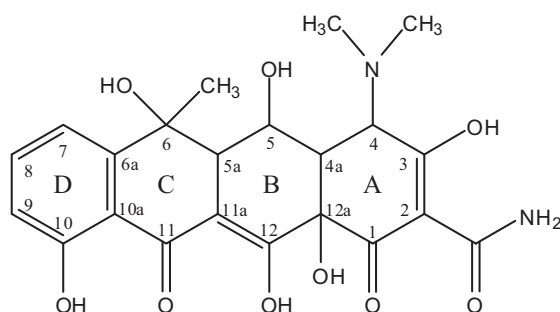


Fig. 1. Structure of OTC.

The objective of this work was to systematically investigate the photochemical degradation of OTC by UV/ H_2O_2 . In our previous study [30], the influence of pH and bicarbonate/carbonate on the removal of OTC was extensively evaluated. In this work, the role of $\text{HO}\cdot$ and the effect of H_2O_2 dosage, OTC concentration and background water matrix such as inorganic anions, metal cations, and natural organic matter (NOM) were studied. The consumption of H_2O_2 and mineralization efficiency in terms of total organic carbon (TOC) elimination were also assessed. Finally, the degradation mechanism was proposed based on the identified reaction byproducts.

2. Materials and methods

2.1. Materials

Oxytetracycline hydrochloride (>95%) was purchased from Sigma–Aldrich (St. Louis, MO, USA). Hydrogen peroxide (50%, w/w) was purchased from Fisher Scientific (Pittsburgh, PA, USA). Suwannee River humic acid standard I (HA) and fulvic acid standard II (FA) were obtained from International Humic Substances Society (IHSS, University of Minnesota, St. Paul, MN, USA) and used as representatives of NOM. Other chemicals, such as sodium chloride (NaCl), sodium sulfate (Na_2SO_4), sodium nitrate (NaNO_3), calcium nitrate tetrahydrate ($\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$), magnesium nitrate hexahydrate ($\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), ferric nitrate nonahydrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$), and cupric sulfate pentahydrate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) were all ACS grade and used as received. Milli-Q water (Milli-pore Corp., Billerica, MA) was used to prepare all aqueous solutions.

2.2. Analysis

The quantification of OTC was carried out by a high performance liquid chromatography (HPLC, Agilent 1100 Series). The detailed measurement information can be found elsewhere [30]. An Agilent 6540 ultra-high definition accurate-mass quadrupole time-of-flight tandem mass spectrometer (QTOF/MS) coupled with an Agilent 1290 infinity HPLC system (LC-QTOF/MS) was used for the detection and identification of degradation byproducts. An Agilent ZORBAX Eclipse XDB-C18 narrow-bore rapid resolution column ($2.1 \times 50 \text{ mm}$, $3.5 \mu\text{m}$) was utilized as a stationary phase. The mobile phase consisted of A: 0.1% formic acid in H_2O and B: 0.1% formic acid in acetonitrile, with a gradient elution of 5% B linearly increased to 90% in the initial 5 min, kept for 1 min, and back to 5% B in the next 0.1 min. The flow rate was 0.2 mL min^{-1} , with the sample injection volume of $5 \mu\text{L}$ and column temperature of $30 \text{ }^\circ\text{C}$. The mass spectrum (m/z 30–500) was analyzed in positive ion mode by electrospray ionization (ESI) with the drying gas temperature of $350 \text{ }^\circ\text{C}$, drying gas flow of 7 L min^{-1} and collision energy of 25 eV. Data were analyzed through Agilent MassHunter B.04.00 workstation software.

TOC was measured by a Shimadzu VCSH-ASI TOC Analyzer. The concentration of H_2O_2 was analyzed by a spectrophotometric method using a Hewlett Packard UV–vis spectrophotometer [31].

2.3. Photochemical experiments

A bench scale photochemical apparatus equipped with two 15 W low-pressure Hg UV lamps with monochromatic emission at $\lambda_{\text{max}} = 254 \text{ nm}$ was utilized for photochemical experiments. The average UV fluence rate through the reaction volume was determined to be 0.1 mW cm^{-2} by three different methods [32]. For OTC degradation experiments, the initial concentrations of OTC, H_2O_2 and phosphate buffer were $10 \mu\text{M}$, 0.5 mM and 5 mM , respectively, unless stated otherwise. At each UV fluence interval,

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