



Fast removal of the antibiotic flumequine from aqueous solution by ozonation: Influencing factors, reaction pathways, and toxicity evaluation



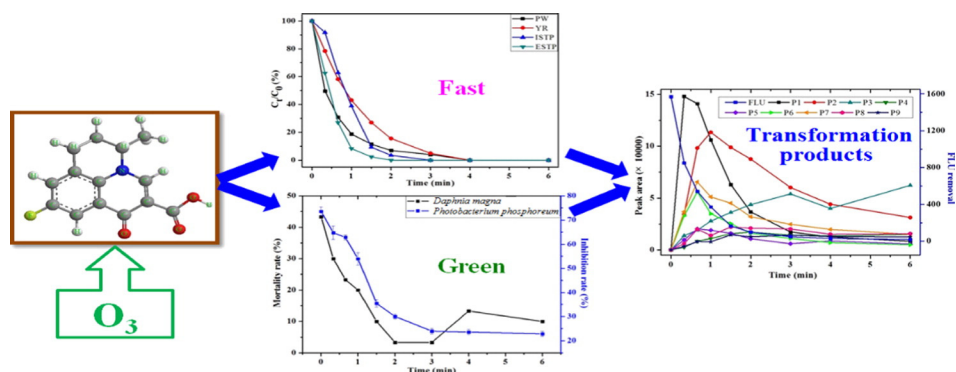
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HIGHLIGHTS

- 100% removal of FLU (20 µg/L–20 mg/L) was achieved by ozonation in 4–6 min.
- The effects of different matrices on FLU ozonation were tested.
- The transformation products and pathways were proposed.
- FLU ozonation showed less acute toxicity to water organisms.

GRAPHICAL ABSTRACT



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ABSTRACT

As one of the first generation of fluoroquinolone antibiotics, flumequine (FLU) has been detected ubiquitously in surface waters and municipal wastewaters. In light of FLU's possible adverse effects on aquatic species, the removal of this antibiotic has received worldwide attention. In this study, the kinetics, transformation products, mechanisms and toxicity variations of the ozonation process for FLU were systematically determined. The possible effects of solution pH, addition of inorganic ions, dissolved organic matter, and *tert*-butyl-alcohol (a radical scavenger), as well as the type of water matrices on FLU removal by ozonation, were studied from the perspective of the degradation kinetics. The data obtained suggested that ozone can be used as an effective oxidant for the fast removal of FLU from natural waters. Using liquid chromatography-mass spectrometry, a total of thirteen transformation products of FLU during ozonation were identified, and their specific reaction mechanisms were also proposed. The degradation pathways involving the hydroxylation, decarboxylation and defluorination were tentatively proposed. Meanwhile, the generation of three low-molecular-weight carboxylic acids was also observed. In addition, the potential toxicity of the transformation mixtures of FLU by ozone was evaluated. Overall, this paper can be a unique contribution to the systematic elucidation of the ozonation process of this antibiotic in water.

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1. Introduction

As a broad-spectrum antimicrobial agent of the fluoroquinolone family, flumequine (FLU) has been widely used in hospitals, households and veterinary applications for treating bacterial infections (Adachi et al., 2013; Van Doorslaer et al., 2014). In particular, FLU is directly administrated to the water as a feed additive in aquaculture, often in large quantities owing to its poor bioavailability to aquatic species (Čvančarová et al., 2013; Van Doorslaer et al., 2014). Due to its continuous introduction into the aqueous environment and its resistance to degradation, FLU has been ubiquitously detected in surface waters at concentrations ranging from ng L^{-1} to $\mu\text{g L}^{-1}$ (Bu et al., 2013; Van Doorslaer et al., 2014; Lin et al., 2015). Previous reports have indicated that FLU in aquatic ecosystems could trigger specific transcriptional alterations in microbial communities and thus contribute to the development of resistant bacteria (Cabello et al., 2013; Labella et al., 2013). Indeed, antibiotic resistant bacteria and related resistance genes induced by this antibiotic have been widely found in different natural waters (Naviner et al., 2011; Rutgersson et al., 2014). Additionally, FLU can cause certain adverse biological effects on aquatic organisms by inhibiting their growth and reproduction or exhibiting its genotoxic and carcinogenic properties (Zouneková et al., 2011; Ma et al., 2012). Thus, the occurrence of this antibiotic in natural waters has become a major environmental concern worldwide.

As conventional processes in wastewater treatment plants (WWTPs) are unable to act as a reliable barrier and eliminator toward this antibiotic, many treatment methods, such as advanced oxidation processes (AOPs) (Miranda-García et al., 2011; Garcia-Segura et al., 2012; Rodrigues-Silva et al., 2013a, 2013b), direct photolysis (Sirtori et al., 2012) and biotransformation by different ligninolytic fungi (Čvančarová et al., 2013) have recently been investigated for the degradation and removal of FLU from the aqueous phase. Among these treatment methods, AOPs, characterized by the generation of hydroxyl radicals ($\text{OH}\cdot$) under ambient conditions, have been suggested as cost-effective mechanisms for the elimination of persistent micropollutants from aqueous systems. Ozone in particular is a strong oxidizing agent and has been widely used in water treatment for disinfection, increasing biodegradability and efficient removal of a variety of residual pharmaceuticals, such as antibiotics (Gómez-Ramos et al., 2011; Liu et al., 2012; Carbajo et al., 2015; Tay and Madehi, 2015). Ozone can react with organic pollutants through direct reaction (known as ozonolysis) and/or indirect reactions with $\text{OH}\cdot$, which are produced by O_3 decomposition (Mawhinney et al., 2012; Chang et al., 2014). During aqueous ozonation, $\text{OH}\cdot$ reacts non-selectively with most of the organic compounds, whereas O_3 , being electrophilic, reacts selectively with the electron-rich reaction sites of organic compounds, such as unsaturated double bonds and aromatic rings (Miao et al., 2015). Therefore, organic compounds in water may be decomposed by both O_3 and $\text{OH}\cdot$ through a series of oxidation and radical reactions involving a variety of mechanisms, such as the Criegee mechanism, electrophilic substitution, hydrogen abstraction and electron abstraction (Mawhinney et al., 2012; Miao et al., 2015; Tay and Madehi, 2015). Furthermore, ozonation is advantageous in treatment of both wastewater and drinking water for several reasons: (1) the effective destructive process with the reduced formation of harmful byproducts compared to chlorine; (2) the rapid removal of odorific compounds and organic contaminants in a shorter contact time compared to UV; and (3) the lack of secondary pollution compared to permanganate (Miao et al., 2015). Notably, ozonation could also disinfect various pathogenic microorganisms, such as antibiotic resistant bacteria, preventing the dissemination of antibiotic resistance (Carbajo et al., 2015).

Previous studies have indicated that the ozonation process could not totally mineralize the target chemicals but only break down or rearrange the molecular structure (Prasse et al., 2012; Carbajo et al., 2015). Therefore, the transformation products with unknown ecotoxicological

potential (especially some enhanced or undesired biological effects) might inevitably be formed. Although aqueous ozonation of certain fluoroquinolone antibiotics and degradation of FLU by a number of other techniques have recently been investigated, most studies are inadequate and partially focused on the degradation kinetics (Miranda-García et al., 2011; Garcia-Segura et al., 2012; Ho et al., 2013), simple proposals of some transformation products or pathways (Sirtori et al., 2012; Rodrigues-Silva et al., 2013a, 2013b), and the decomposition processes without toxicity determinations by standardized bioassays (De Witte et al., 2009; Tay and Madehi, 2015). Additionally, the effects of different environmental water matrices on removal of organic micropollutants, which are crucial for the practical applications of these techniques in water treatments, have seldom been reported in these studies. In this sense, very little is currently known regarding the transformation processes, the specific reaction mechanisms and pathways of FLU, and the first generation of fluoroquinolones by the widely used ozonation, as well as the potential influences of water matrices on FLU removal and toxicity assessments of the transformation mixtures. These systematical evaluations are of vital importance for the purposes of environmental protection and wastewater treatment.

Therefore, the present study investigated the transformation of FLU during aqueous ozonation. A wide range of operating parameters influencing the treatments, including solution pH, the addition of inorganic anions and cations, dissolved organic matter, and *tert*-butyl-alcohol (TBA, a typical $\text{OH}\cdot$ scavenger), as well as the type of water matrices, were studied from the perspective of the degradation kinetics. The possible ozonation pathways of FLU were first proposed by characterizing certain major transformation products using liquid chromatography-mass spectrometry, and the specific reaction mechanisms for their formation by the attack of O_3 and/or $\text{OH}\cdot$ were also proposed. Meanwhile, the generation of several low-molecular-weight carboxylic acids was determined. Notably, the influences of different water matrices on FLU removal and the toxicity of partially oxidized mixtures for *Daphnia magna* and *Photobacterium phosphoreum* were assessed for the practical application of this technique in water treatment. In this sense, this paper provided a number of unique contributions to the systematic elucidation of the ozonation process of this widely used antibiotic in water.

2. Materials and methods

2.1. Chemicals

FLU (CAS NO. 42835-25-6, purity 98%) was purchased from Tokyo Chemical Industry Co., Ltd. (Tokyo, Japan), and used without further purification. The molecular formula and molecular weight of FLU are $\text{C}_{14}\text{H}_{12}\text{FNO}_3$ and $261.25 \text{ g mol}^{-1}$, respectively. Acetonitrile and formic acid used in the HPLC and LC-MS measurements were of HPLC grade and supplied from Merck (Darmstadt, Germany). The other reagents used in this study, such as NaCl, NaNO_3 , Na_2SO_4 , KCl, CaCl_2 , MgCl_2 , humic acid (HA) and TBA, were of analytical grade and obtained from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Ultrapure water ($>18.2 \text{ M}\Omega \text{ cm}$) was prepared with a Milli-Q Plus system (Millipore, Bedford, USA) and employed throughout the studies.

2.2. Ozonation experiments

20 mg L^{-1} of FLU solution (50 mL) was introduced into a 100 mL semi-batch glass reactor. Ozone was produced from pure water by a DJ-Q2020A electrolysis-type ozone generator (Yichang, China). The ozone gas generated was continuously bubbled into the reactor bottom at a constant flow rate (36 mL min^{-1}) through a glass tube (0.5 m) with a sintered end. The inlet ozone concentration in the gas phase was set by changing the electric current of the generator and measured as 140.6 mg L^{-1} by an iodometric method (APHA, 2012). The reacted solution was perfectly mixed by a magnetic stirrer (IKA RCT® Basic,

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