



Sulfate radical-based oxidation of fluoroquinolone antibiotics: Kinetics, mechanisms and effects of natural water matrices



Canlan Jiang, Yuefei Ji, Yuanyuan Shi, Jifei Chen, Tianming Cai*

College of Resources and Environmental Sciences, Nanjing Agricultural University, Nanjing 210095, China

ARTICLE INFO

Article history:

Received 12 July 2016

Received in revised form

7 October 2016

Accepted 9 October 2016

Available online 12 October 2016

Keywords:

Ciprofloxacin

Fluoroquinolone antibiotics

Sulfate radical

Transformation mechanisms

Water matrix

ABSTRACT

Widespread occurrence of fluoroquinolone antibiotics (FQs) in surface water, groundwater, soil and sediment has been reported and their remediation is essentially needed. Sulfate radical ($\text{SO}_4^{\bullet-}$) based advanced oxidation processes (SR-AOPs) are promising technologies for soil and groundwater remediation. In this study, the degradation kinetics, mechanisms, and effects of natural water matrices on heat-activated persulfate (PS) oxidation of FQs were systematically investigated. Experimental results clearly demonstrated that 92% of CIP was removed within 180 min (pH = 7, 60 °C). Higher temperature and lower pH facilitated the degradation of ciprofloxacin (CIP). The piperazine moiety of CIP was identified as the reactive site for $\text{SO}_4^{\bullet-}$ attack by comparison with substructural analogs, flumequine (FLU) and 1-(2-fluorophenyl) piperazine (FPP). A comparison of the degradation of CIP, norfloxacin (NOR), enrofloxacin (ENR) and ofloxacin (OFL) confirmed that the presence of cyclopropane ring also influence the degradation of FQs. Water matrix significantly influenced the degradation of CIP and ENR, and the degradation rate followed the order of Milli-Q water (pH = 7) > groundwater > artificial seawater > artificial surface water > lake water. Degradation products of CIP in different water matrix were enriched by solid phase extraction (SPE) and then analyzed by liquid chromatography-electrospray ionization-triple quadrupole mass spectrometry (LC-ESI-MS/MS). Detailed transformation pathways of CIP were proposed and were compared with respect to different water matrices. Four transformation pathways including stepwise piperazine ring oxidation, OH/F substitution, hydroxylation, and cyclopropane ring cleavage were proposed for CIP degradation. Results clearly show that the water matrix influenced the degradation of FQs appreciably, a phenomenon that should be taken into consideration when applying SR-AOPs for remediation of soil and groundwater contaminated by FQs.

© 2016 Elsevier Ltd. All rights reserved.

1. Introduction

Fluoroquinolone antibiotics (FQs) such as ciprofloxacin (CIP) are widely used to treat infections caused by a broad spectrum of bacteria species (Hooper and Wolfson, 1991; Oliphant and Green, 2002). FQs have been frequently prescribed worldwide for both clinical and veterinary purposes (Kümmerer, 2009). The extensive usage and wide application of FQs result in their occurrence in the environment through various routes including municipal sewage treatment plant (STP) effluent, agricultural runoff, and landfill leachates (Golet et al., 2003; Kümmerer, 2009). For example, CIP is frequently detected in the environment with relatively high concentrations, e.g., concentration of $0.6 \mu\text{g L}^{-1}$ in Olona River and

$1.7\text{--}0.63 \mu\text{g L}^{-1}$ in sewage treatment plant effluent in Italy (Castiglioni et al., 2008). Higher concentration up to $16 \mu\text{g L}^{-1}$ was reported in treated hospital wastewater effluents (Kovalova et al., 2012; Michael et al., 2013). FQs can be microbially degraded by active sludge during wastewater treatment processes (Li and Zhang, 2010; Lindberg et al., 2006). Unfortunately, the removal of FQs in conventional STPs is inefficient and, consequently, they are introduced into the aquatic environment (Michael et al., 2013). Natural abiotic attenuation processes, such as photolysis and oxidative transformation by minerals, play an important role in determining the fate of FQs as well as eliminating their ecotoxicological effects (Ge et al., 2010; Sturini et al., 2010; Zhang and Huang, 2005); however, such processes generally proceed at slow rates. The widespread occurrence of FQs in the environment has led to an increase in bacterial resistance to antibiotics and made human and animals more susceptible to these microbes (Baquero et al., 2008; Kümmerer, 2009). Thus, removal of FQs from the aquatic

* Corresponding author.

E-mail address: ctm@njau.edu.cn (T. Cai).

environment is of great importance for reducing their ecologic risks.

Various techniques have been extensively studied for removing FQs from aqueous solution, such as adsorption (Gu and Karthikeyan, 2005; Li et al., 2014), permanganate oxidation (Hu et al., 2010); chlorination (Dodd et al., 2005), ozonation (DeWitte et al., 2008; Liu et al., 2012), and photocatalysis using TiO_2 as catalyst (Paul et al., 2007, 2010). Among studied techniques, advanced oxidation processes (AOPs) are promising remediation alternatives for destruction of many contaminants in soil and groundwater (Klavarioti et al., 2009; Oturan and Aaron, 2014). Traditional AOPs based on the generation of highly oxidizing hydroxyl radicals ($\text{HO}\cdot$, $E^0 = 2.7\text{ V}$) such as $\text{Fe}^{2+}/\text{H}_2\text{O}_2$, $\text{UV}/\text{H}_2\text{O}_2$, and $\text{O}_3/\text{H}_2\text{O}_2$ have been widely applied in wastewater treatment and pollution control (Buxton et al., 1988; Pignatello et al., 2006). However, the unselective nature of $\text{HO}\cdot$ and the requirement of acidic conditions largely limit practical applications (Pignatello et al., 2006).

Activated persulfate oxidation processes generating highly reactive sulfate radicals ($\text{SO}_4^{\bullet-}$, $E^0 = 2.5\text{--}3.1\text{ V}$) are promising *in-situ* chemical oxidation technologies (ISCO) for the remediation of groundwater and soil (Tsitonaki et al., 2010). $\text{SO}_4^{\bullet-}$ is an electrophilic species that can react with a wide range of contaminants primarily through electron transfer with *second-order-rate* constants ranging from 10^6 to $10^9\text{ M}^{-1}\text{s}^{-1}$ (Neta et al., 1977, 1988). $\text{SO}_4^{\bullet-}$ can be generated from persulfate (PS) or peroxymonosulfate (PMS) when these precursors are subjected to activations including heat, UV radiation, chelated or unchelated transition metals, and strongly alkaline pH (Neta et al., 1977; Tsitonaki et al., 2010). Degradation of CIP and other FQs by Fe^{2+}/PS and UV/PMS were reported (Epold et al., 2015; Mahdi-Ahmed and Chiron, 2014; Ji et al., 2014), and results demonstrated that $\text{SO}_4^{\bullet-}$ could effectively destruct FQs and even mineralize them to CO_2 and H_2O . Transformation pathways including piperazine ring cleavage, defluorination (substitution of fluorine by a hydroxyl group) as well as hydroxylation were observed during $\text{SO}_4^{\bullet-}$ -based oxidation of FQs (Feng et al., 2015; Guo et al., 2016; Ji et al., 2014; Mahdi-Ahmed and Chiron, 2014). Nevertheless, the underlying mechanisms governing the transformation pathways of FQs are largely unknown, which are essential for better understanding the formation of reaction intermediates/products.

In practical application, $\text{SO}_4^{\bullet-}$ -based oxidation of contaminants can be significantly influenced by natural water constituents ubiquitously present in waters because the formation and consumption rate of $\text{SO}_4^{\bullet-}$ can both be affected by water chemistry (Guan et al., 2011; Ji et al., 2015a; Nie et al., 2014; Yang et al., 2014; Wu et al., 2015). Previous studies have shown that the presence of different inorganic species and natural organic matter (NOM) may appreciably influence the degradation efficiencies of activated persulfate oxidation processes (Yang et al., 2014; Lutze et al., 2014; Wu et al., 2015). Moreover, the degradation intermediates and products may also be closely related to the natural water constituents (Fang and Shang, 2012; Lu et al., 2016). While most studies were conducted under well laboratory-controlled conditions for investigating the effects of water constituents like bicarbonate and NOM (Mahdi Ahmed et al., 2012; Fan et al., 2015; Ji et al., 2015b), degradation of FQs in different water media, such as groundwater, fresh water and seawater, is not well understood (Homem and Santos, 2011). For successful environmental remediation, identifying the natural water matrix effect on activated PS oxidation is crucial and warrants further study which comprises the main purpose of this study.

In the present study, we assessed the feasibility of employing a heat-activated PS oxidation process to degrade FQs in Milli-Q water as well as in different natural water matrices. Heat activation was

employed here due to its catalyst-free and high efficiency nature (Kolthoff and Miller, 1951b; Tsitonaki et al., 2010). Degradation kinetics of CIP and influence factors including pH and temperature were systematically studied. Structurally related compounds containing either piperazine ring (i.e., 1-(2-fluorophenyl) piperazine, FPP) or oxo-quinolinecarboxylic acid moiety (i.e., flumequine, FLU) were used to probe the reactive site of CIP towards $\text{SO}_4^{\bullet-}$ attack. Degradation of CIP was further compared with other FQs widely used, including enrofloxacin (ENR), norfloxacin (NOR), and ofloxacin (OFL), to evaluate whether the results of CIP could be extrapolated to other FQs. Particularly, degradation of CIP and ENR were investigated in natural and artificial waters with different pH, inorganic species, and total organic carbon contents (TOC) to gain insights into how degradation may be affected by natural water constituents. Additionally, solid phase extraction followed by liquid chromatography-tandem mass spectrometry (SPE-LC-MS/MS) was used to identify reaction intermediates/products of CIP generated in various water matrices. Based on the structural elucidation of the intermediates/products, detailed mechanisms and transformation pathways for CIP oxidation in different water matrices were proposed.

2. Materials and methods

2.1. Chemicals and materials

Potassium persulfate (PS, $\text{K}_2\text{S}_2\text{O}_8$, >99.5%) was purchased from Aladdin Chemistry Co. Ltd (Shanghai, China). Ciprofloxacin (CIP, >98%), enrofloxacin (ENR, >98%), norfloxacin (NOR, >98%) and ofloxacin (OFL, >98%) were obtained from Sigma-Adrich (St. Louis, MO). Flumequine (FLU, >99.5%) and 1-(2-fluorophenyl) piperazine (FPP, >99.5%) were purchased from TCI (Tokyo, Japan). Molecular structures of FQs and substructural analogs are provided in Table 1. Acetonitrile (ACN), methanol (MeOH), and formic acid were of HPLC grade and were purchased from Tedia (Fairfield, OH). Milli-Q water (18 $\text{M}\Omega\text{ cm}$) prepared from a Millipore Milli-Q system (Millipore, Milford, MA) was used for preparing stock solution. Oasis hydrophilic-lipophilic balance (HLB) SPE cartridges (6 cc/200 mg, WAT106202) were purchased from Water Corporation (Milford, MA).

2.2. Water samples

Natural fresh water was collected from Tai Lake, a typical shallow lake with water eutrophication problem in Jiangsu province (Dokulil et al., 2000; Liu et al., 2013). Natural shallow groundwater was collected from a household well in Quanjiaohe village in Hunan province. Artificial seawater was synthesized following ASTM international standard (Manasfi et al., 2015). Artificial surface water was prepared according to Tong et al. (2011) which resembled hard surface water. Detailed information for preparing the two artificial waters is provided in Supporting Information (SI, Text S1). All natural and artificial waters were 0.2 μm membrane-filtered and stored at 4 °C before usage. Selected properties of natural and artificial waters are listed in Table 2 and all experiments were carried out within two months after sampling.

2.3. Experimental setup

Prior to heat activation, 4 mL FQs stock solution (150 μM) and 0.4 mL PS stock solution (100 mM) were transferred into 33 mL screw-cap cylindrical glass vials with Teflon septa and mixed to achieve a total 20 mL reaction solution by adding 15.6 mL Milli-Q water or natural/artificial water samples. Controls with FQs alone showed no loss of target compounds, indicating FQs are hydrolysis-

Download English Version:

<https://daneshyari.com/en/article/6364266>

Download Persian Version:

<https://daneshyari.com/article/6364266>

[Daneshyari.com](https://daneshyari.com)