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Spectroscopic study of degradation products of ciprofloxacin, norfloxacin and lomefloxacin formed in ozonated wastewater

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ABSTRACT

This study addressed the formation and properties of degradation products of ciprofloxacin, norfloxacin and lomefloxacin formed during ozonation of secondary wastewater effluent containing these fluoroquinolone antibiotics. The generation of the degradation products was interpreted in the context of transformations of effluent organic matter (EfOM) tracked via absorbance measurements. The structures of 20 degradation products were elucidated for ciprofloxacin and norfloxacin, respectively. 27 degradation products were identified for lomefloxacin. The prevalent oxidation pathways were suggested based on the structures of the identified products formed in the absence and presence of the hydroxyl radical scavenger t-butanol. These pathways were largely similar for all studied fluoroquinolones and involved attacks on the piperazine ring and the quinolone structure. The quinolone ring remained intact in the presence of t-butanol thus indicating that this functional group could only be oxidized by OH radicals while the piperazine ring was readily oxidized by molecular ozone. The cleavage of the quinolone moiety that resulted in several identified degradation products occurred via the attack by hydroxyl radicals on the carbon-carbon double bond adjacent to the carboxylic acid group. Lomefloxacin had more diverse oxidation products due to the presence of a methyl group on its piperazinyl ring. The concentrations of the identified degradation products behaved non-monotonically as a function of ozone dose or treatment time, yet exhibited interpretable correlations versus changes of EfOM absorbance. Examination of these correlations allowed developing a novel approach for elucidating the transformations of fluoroquinolone antibiotics during ozonation.

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1. Introduction

The occurrence and environmental behavior of antibiotics, notably fluoroquinolones, sulfonamides, tetracyclines and macrolides have become an increasingly important issue due to the promotion by these compounds of the antibiotic resistance within the native bacterial populations in the impacted environments (Huber et al., 2005; Diwan et al., 2010; Moore et al., 2010). The increased resistance can then be transferred by plasmids to other bacterial populations, including human pathogens, as has been reported for tetracycline (Chee-Sanford et al., 2001; Rysz and Alvarez, 2004).

Fluoroquinolone compounds, which are the most widelyused antibiotics in the treatment of respiratory and bacterial

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infections (Tesar et al., 2004) can be expected to cause similar effects (Martinez-Martinez et al., 1998; Werner et al., 2010; Mackiw et al., 2012). Several studies have confirmed the occurrence of a variety of fluoroquinolone compounds in effluents of municipal wastewater treatment plants (WWTP) and showed that these compounds are only partially eliminated by conventional wastewater treatment. For instance, concentrations of ciprofloxacin in WWTP effluents have been reported to be as high as 5.6 μ g L⁻¹ (Batt et al., 2007) while in hospital effluents they were 3–87 μ g L⁻¹ (Carmosini and Lee, 2009). Up to 31 mg L^{-1} of ciprofloxacin was found in discharges from pharmaceutical manufacturers (Larsson et al., 2007). Another fluoroquinolone norfloxacin is also one of the most frequently detected antibiotics in wastewater effluents; its concentrations range from 27 to 489 ng L⁻¹ levels (Golet et al., 2003; Castiglioni et al., 2005; Xu et al., 2007).

The insufficient removal of these compounds by conventional wastewater treatment operations necessitates an examination of their removals by alternative methods. Ozonation and advanced oxidation processes (AOPs) have generated considerable interest due to their ability to efficiently oxidize a wide range of pharmaceuticals (Radjenovic et al., 2009). Extensive studies examining the oxidation of antibiotics by ozone or AOPs have focused on the optimization of operational conditions, the degradation kinetics of the target compounds and residual bioactivity (Balcioglu and Otker, 2003; Dodd et al., 2006, 2009; Siminiceanu and Bobu, 2006; De Bel et al., 2009; De Witte et al., 2009a; An et al., 2010; De Witte et al., 2010; Heynderickx et al., 2011). These studies have established that in some cases the products generated via the oxidation of the antibiotics appear to have a higher toxicity than the parent compounds (De Bel et al., 2009). The identification of relevant degradation products and determination of mechanisms governing their generation have also been addressed in prior research. For instance, several studies have examined the formation of degradation products upon the oxidation of fluoroquinolone antibiotics by AOPs (Paul et al., 2007, 2010; De Witte et al., 2008; De Witte et al., 2009b) and oxidants including MnO₂ (Zhang and Huang, 2005), Cl₂ (Dodd et al., 2005) and ClO₂ (Wang et al., 2010). De Witte et al. (2008, 2009b) identified twelve degradation products formed in the case of the oxidation of ciprofloxacin by ozone while eleven species were observed for levofloxacin. However, the degradation products identified in these studies do not necessarily exhaust the range of species formed in these processes, and more information also needs to be obtained about their yields and formation kinetics. On the other hand, these studies have been carried out in the absence of effluent organic matter (EfOM) that is present in all wastewaters. Prior research has shown that the degradation of trace-level contaminants including pharmaceuticals and personal care products (PPCPs) and antibiotics by AOPs and the formation of their degradation products take place simultaneously with the decay of EfOM or natural organic matter (NOM) (Shon et al., 2006; Wert et al., 2007; Rosario-Ortiz et al., 2008). Interactions of EfOM or NOM with O3 or other oxidants have been reported to cause consistent changes of their absorbance and fluorescence (Rosario-Ortiz et al., 2010; Ben Abdelmelek et al., 2011). The existence of strong relationships between the degradation of these contaminants and

the evolution of spectroscopic parameters of AOP-treated wastewater have been addressed in considerable detail in recent publications (Wert et al., 2009; Nanaboina and Korshin, 2010; Liu et al., 2012).

In the light of these findings, there is a need to examine how the formation of the oxidation products of antibiotics and other trace-level organic contaminants is associated with ozone dose or relevant AOP conditions, and whether changes of EfOM properties caused by these processes are related to and indicative of the kinetics, yields and speciation of these degradation processes. To our knowledge, prior research has not addressed the issue of the formation and breakdown of the degradation products of fluoroquinolones in the presence of EfOM. In this study, we examined the degradation pathways of three representative fluoroquinolones, ciprofloxacin, norfloxacin and lomefloxacin (Fig. 1) by ozone applied to municipal wastewater effluent. We also examined relationships between the generation and breakdown of the degradation products of these antibiotics and, on the other hand, changes of wastewater absorbance. The observed correlations were interpreted based on a consistent numerical model reflecting the mechanisms of the oxidation of these species.

2. Materials and methods

2.1. Reagents and wastewater

Sources of LC/MS-grade water, acetonitrile, formic acid, mass spectrometric grade ammonium acetate, KH₂PO₄, NaOH, Na₂SO₃ and selected antibiotics are provided in the Supplementary material (SM).

A grab sample of wastewater secondary effluent before disinfection was collected in Seattle area and transported to the laboratory within hours of sampling. The sample was filtered with a 0.45 μm filter and stored at 4 °C.

For the identification of degradation products, 1 mg of each fluoroquinolone was dissolved in 100 mL Milli Q water to make an initial concentration of 10 mg L⁻¹ for the ozonation experiments. To study the evolutions of these degradation products in real wastewater, parent antibiotic species were spiked from prepared stock solutions into wastewater samples to make an initial concentration of 100 μ g L⁻¹. Because the background levels of the studied antibiotics in the wastewater were at least two or more orders of magnitude lower than the amount spiked, the behavior of the entire amount of the antibiotics present in the samples was determined.

2.2. Ozonation experiments

A 2000 series ozone generator with Mini Hicon ozone analyzer (IN USA Incorporated, Norwood, MA, USA) was used to produce a 50–60 mg L⁻¹ O₃ stock solution. O₃ concentration was determined by the standard 4500-O₃ indigo colorimetric method (APHA, 1995). To study the fate of degradation products in wastewater, ozonation was conducted by injecting a series of volumes of O₃ stock solution into each wastewater sample flask to achieve desired O₃ concentrations in the range of 0–5.0 mg L⁻¹. Another experiment was carried out by Download English Version:

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