



## Chemical and toxicological evaluation of an emerging pollutant (enrofloxacin) by catalytic wet air oxidation and ozonation in aqueous solution

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### HIGHLIGHTS

- ▶ CWAO was applied for the first time to degrade high concentration of a widely used antibiotic.
- ▶ The comparison of CWAO and ozonation to test their efficiency to degrade pharmaceutical is unique.
- ▶ The degradation products were identified by LC–MS/MS, GC–MS and IC.
- ▶ The degradation efficiency of enrofloxacin was determined by COD, TOC, BOD<sub>5</sub>/COD and toxicity.

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### ABSTRACT

This study evaluates the degradation efficiency of enrofloxacin (ENR) by catalytic wet air oxidation (CWAO) and ozonation. Results obtained by CWAO experiments show that 99.5% degradation, 37.0% chemical oxidation demand (COD) removal and 51.0% total organic carbon (TOC) conversion were obtained when 100 mol% FeCl<sub>3</sub> and 25 mol% NaNO<sub>2</sub> at 150 °C under 0.5 MPa oxygen pressure after 120 min are used. The degradation products are identified by liquid chromatography–tandem mass spectrometry (LC–MS/MS), gas chromatography–mass spectrometry (GC–MS) and ion chromatography (IC). The oxidation end products, F<sup>-</sup>, NO<sub>3</sub><sup>-</sup> and NH<sub>4</sub><sup>+</sup> were determined by IC. The BOD<sub>5</sub>/COD ratio as a measure of the biodegradability of the parent compound increased from 0.01 to 0.12 after 120 min of reaction time, indicating an improved biodegradability of the parent compound. The inhibition of bioluminescence of the marine bacteria *V. fischeri* decreased from 43% to 12% demonstrating a loss in toxicity of ENR during CWAO. Ozonation of 0.2 mM ENR was carried out with an ozone concentration of 7.3 g m<sup>-3</sup> at pH 7. ENR decomposition with a degradation rate of 87% was obtained corresponding to the reaction time. Moderate changes in COD (18%) and TOC (17%) removal has been observed. The bioluminescence inhibition increased from 8% to 50%, due to the generation of toxic degradation products during ozonation. In comparison to the widely use of well developed method of ozonation CWAO exhibits better performance in terms of COD, TOC removals and generates less toxic products.

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### 1. Introduction

Antibiotic formulation effluents are well known for their difficult elimination by traditional biological treatment methods and their contribution to environmental pollution due to their fluctuating and recalcitrant nature (Kümmerer, 2009a,b; Tomasz et al., 2012). Typical examples of antibiotics are fluoroquinolones (FQs), which are generally incompletely metabolized and enter the environment in their active forms (Speltini et al., 2010; Prieto et al.,

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2011). Due to the insufficient transformation or removal of FQs in the effluent of wastewater treatment plants (WWTPs), high concentrations of fluoroquinolones have been repeatedly detected worldwide at concentrations of 0.7–125 µg g<sup>-1</sup> in untreated hospital sewage (Chang et al., 2010; Zhang and Li, 2011), 40–500 ng L<sup>-1</sup> in secondary wastewater effluents (Li and Zhang, 2011; Tong et al., 2011), 10–120 ng L<sup>-1</sup> in surface waters (Giger et al., 2003; Chen et al., 2010), and up to 679.7 ng L<sup>-1</sup> in tap water detected in South China (Yiruhan et al., 2010). The presence of FQs in the environment affects aquatic ecology and human health (Rosanova et al., 2010; Zouneková et al., 2011), and also induces an increased antibiotic resistance among microorganisms (Zouneková et al., 2011).

Presently many waterways in China are contaminated by industrial effluent discharges due to the lack of proper wastewater

treatment. The pollution load makes it difficult to treat water to the levels suitable for drinking, other potable use or even irrigation. Nowadays China has also become a top producer and consumer of numerous antibiotic classes with an annual production of drugs representing about 30% of the world's production source (Xu et al., 2007). The occurrence of antibiotics, like tetracyclines, sulfonamides and fluoroquinolones has been reported in many environmental samples such as municipal wastewater, surface and groundwater, sludge and sediments (Jiang et al., 2011; Peng et al., 2011; Wei et al., 2011; Zhou et al., 2011). The immediate concern is the potential harmful effect of these compounds to aquatic organisms and humans by drinking water or the consumption of vegetables and crops irrigated by polluted effluents, which are very common in developing countries. The need for effective water recycling requires intensive research on low cost pollution abatement technologies since the existing solutions are not adequate. Therefore, it is necessary to develop efficient methods to eliminate antibiotics either directly in the discharge of the production lines of pharmaceutical industry or in effluents from WWTPs prior to their discharge into the aquatic environment (Li et al., 2008; Laera et al., 2012).

Among the emergent alternative processes, CWAO has been described by numerous authors as an efficient and promising method to treat pollutants like phenols, substituted phenols, carboxylic acids, ammonia and industrial effluents (Kolaczowski et al., 1999; Kumar et al., 2006; Kim and Ihm, 2011). CWAO exhibits reasonable performance for decomposition of refractory and toxic compounds either by degrading into biodegradable intermediates or into innocuous inorganic compounds by mineralization to carbon dioxide, water and inorganic salts under elevated process temperatures (100–320 °C) and pressures (0.1–20 MPa) as reported by many authors (Kayan et al., 2004; Eftaxias et al., 2006; Levec and Pintar, 2007; Kim and Ihm, 2011). At present the application of CWAO for degradation of antibiotics in wastewater effluents is very limited. Yang et al. (2005) investigated the degradation of initial wastewater from a pharmaceutical plant producing apramycin in Henan, China by CWAO and by traditional wastewater treatment consisting of coagulation and acidic hydrolysis. The authors described, for an initial apramycin concentration of 5000 mg L<sup>-1</sup>, an apramycin removal of 50.2% to 55.0%, a COD decay up to 46% and a BOD<sub>5</sub>/COD ratio of 0.49–0.54 by applying RuO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> and RuO<sub>2</sub>-CeO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> as catalysts, respectively. Ozonation, by decomposition of ozone, has a high potential for oxidation of harmful chemicals. Guinea et al. (2009) reported the efficiency of ozonation for the decomposition of ENR molecules with over 90% COD removal but not on the removal of final carboxylic acids.

The present study focuses on the development and application of a catalytic system (CWAO) which uses inexpensive and readily available oxidants and catalysts, NaNO<sub>2</sub> and FeCl<sub>3</sub>, respectively (Liang et al., 2005; Wang et al., 2007). In addition, ozonation is also being applied to degrade the chosen antibiotic in order to evaluate its suitability for industrial application by comparing the obtained results by CWAO. ENR, the most used FQs in veterinary medicine, has been selected as a target compound and the experiments were conducted to investigate the efficiency of ENR degradation in terms of ENR removal, COD removal, TOC abatement and BOD<sub>5</sub>/COD ratio. The degradation products occurring during the application of CWAO process have been identified by LC-MS/MS, GC-MS and IC techniques and the possible pathways have been proposed. Furthermore, the toxic potential of ENR and its degradation products have been determined by the bioluminescence of the marine bacteria *Vibrio fischeri*. Specific emphasis was put on the development of methods with low oxidation time and concentration of ozone or NaNO<sub>2</sub>/FeCl<sub>3</sub> to reduce wastewater treatment costs and to make the methods suitable for industrial application.

## 2. Materials and methods

### 2.1. Materials

Enrofloxacin (≥98%) was purchased from Fluka (Buchs, Switzerland), sodium hydroxide (>98%) and hydrochloric acid (32%) were obtained from Merck (Darmstadt, Germany). Ferric chloride (98%) was supplied by Sigma-Aldrich Chemie GmbH (Steinheim, Germany) and sodium nitrite (≥99%) by Fluka (Buchs, Switzerland). N,O-bis (trimethylsilyl) trifluoroacetamide (BSTFA, 98%) was purchased from Alfa Aesar (Alfa Aesar, China). Formic acid, methanol, acetonitrile and other chemicals were of HPLC grade and utilized without further purification. Millipore ultrapure water (Millipore, Watford, UK) was used to prepare all aqueous solutions throughout.

### 2.2. Catalytic wet air oxidation of ENR

Synthetic ENR stock solution of 0.2 mM was prepared in darkness in 500 mL Milli-Q water to which 2 mL of 0.1 M HCl was added to dissolve the antibiotic. Rather high concentration of ENR was chosen, aiming to investigate the suitability of the methods for degradation of contaminants in wastewater effluents or of heavily loaded production lines of antibiotic producing industry (Yang et al., 2005; Li et al., 2008). CWAO of ENR was carried out in a 50 mL Teflon-lined stainless steel autoclave. After adding the antibiotic solution (25 mL of 0.2 mM ENR) and the catalysts (FeCl<sub>3</sub> or NaNO<sub>2</sub> alone or both) to the autoclave, the container was sealed off and charged with pure oxygen up to a pressure of 0.5 MPa. Subsequently, it was heated to 150 °C in an oil bath. The stirring speed was set at 300 rps. After a given reaction time, the autoclave was removed from the oil bath and cooled down to room temperature before decompressed. The samples were then collected for further analysis.

### 2.3. Ozonation of ENR

The degradation experiments were carried out in a Pyrex glass tubular photoreactor of 1.4 L capacity, capable of providing good contact between the liquid and gas reactants. As described by Li et al. (2008), ozone was generated from dried air by an ozone generator (Ozon Erzeuger 24 g of Erwin Sander Elektroapparatebau, Uetzen, Germany), and its concentration was determined by an ozone measuring device. Ozonation was performed by bubbling an ozone/air mixture at a flow rate of 7.3 L h<sup>-1</sup> through a sintered glass filter (pore size 50–80 μm) into the antibiotic solution. The unreacted ozone in the flow gas was first measured by means of an ozone-meter, and then destroyed with an OGV-500 catalyst (Fischer Labor und Verfahrenstechnik, GmbH, Bonn, Germany). Samples (20 mL) were withdrawn at defined time intervals and nitrogen gas was used to remove the residual ozone.

### 2.4. Sample analysis

The ENR solutions were analyzed by a reversed-phase HPLC with an Agilent 1100 series (Agilent Technologies, Germany) on a Zorbax C18 column (4.6 mm × 150 mm long, 5 μm) at 30 °C. The wavelength was 278 nm. Aliquots of 20 μL were injected automatically followed by isocratic elution with mobile phase of 12.5/12.5/75 methanol/acetonitrile/0.01 M oxalic acid (v/v/v) at the flow rate of 1.0 mL min<sup>-1</sup>.

Primary degradation products were identified by LC-MS/MS. The analysis of the degradation products were performed on a Waters Acquity UPLC/2996 PDA/Quattro Micromass equipped with a Waters X-Terra MS C18 (2.1 mm i.d. × 150 mm long, 4.6 μm) col-

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