



Oxidation of the antibacterial agent norfloxacin during sodium hypochlorite disinfection of marine culture water



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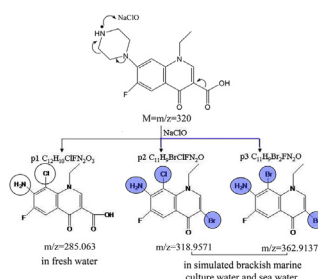
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HIGHLIGHTS

- Norfloxacin was oxidized to two new Br-DBPs during sodium hypochlorite disinfection of marine culture water.
- The addition of bromide ions accelerates the reaction rate of norfloxacin with sodium hypochlorite.
- The carboxyl of NOR was oxidized by sodium hypochlorite when bromide ions were present or it was stable.
- The bio-accumulative properties of Br-DBPs were found to be more substantial than those of norfloxacin.

GRAPHICAL ABSTRACT



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ABSTRACT

Chlorination disinfection and antibiotic addition are two universal processes of marine culture. The generation of disinfection byproducts (DBPs) is unavoidable. Antibiotic residue not only pollutes water but also acts as a precursor to the production of new DBPs. The fate of antibiotic norfloxacin (NOR) in chlorination disinfection was investigated. It was observed that NOR could be oxidized by disinfection agent sodium hypochlorite, but the oxidation rate varied considerably with the type of disinfected water. For fresh water, marine culture water and sea water, the reaction rate constant was 0.066 min^{-1} , 0.466 min^{-1} and 1.241 min^{-1} , respectively. The difference was primarily attributed to the promotion role of bromide ions in seawater and marine culture water. Moreover, the bromide ions could result in the generation of brominated DBPs (Br-DBPs). The kinetics, products, reaction centers and mechanisms were investigated. The active site of NOR was found to be the N4 atom on piperazinyl in fresh water. During marine culture water and sea water disinfection, the carboxyl on NOR was oxidized and two Br-DBPs were formed. This was attributed to the lowering of the reaction's required activation energy when performed in the presence of bromide ions. The Br-DBPs were also confirmed in real shrimp pond brackish water. Quantitative structure activity relationships and the total organic halogen analysis showed that the DBPs in marine culture water possessed stronger toxicological properties than the DBPs in fresh water. The toxicity increase was attributed to the production of Br-DBPs in the disinfection process of marine culture water.

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1. Introduction

Recirculating aquaculture systems have been widely used in marine culture in order to reduce the consumption of seawater and fresh water resources (Hambly et al., 2015; Krom et al., 2014; Kenneth et al., 2011). In the recirculating system, disinfection processes are essential in preventing epidemic diseases (Gong et al., 2016; Chu et al., 2013; Lyon et al., 2014). The chemical disinfectants used in this process are usually chlorine containing compounds (Park et al., 2016; Liu et al., 2016a,b; Kahler et al., 2016). Chlorine disinfection eliminates pathogens, however chlorine also reacts with other organic substances in water to generate halogenated disinfection byproducts (DBPs) (Liu et al., 2016a,b; Jeong et al., 2015). Halogenated DBPs such as trihalomethanes (THMs) (Han et al., 2015; Pan et al., 2014) and haloacetic acids (HAAs) (Cardador and Mercedes, 2016; Smith et al., 2016) have attracted much concern due to their potential health risks.

Antibacterial agents are frequently added to fish feeds in order to promote their growth (Ellsworth et al., 2006; Robert et al., 2008; Sun et al., 2012; Carvalho et al., 2014). These antibiotics, however, cannot be completely absorbed by the animals. As a result, many of them entered into the aquaculture water (Zhang et al., 2013a). Indeed, various antibiotics, such as ciprofloxacin, enrofloxacin, ofloxacin, flumequine, lomefloxacin, and norfloxacin (NOR) have been repeatedly detected at concentrations ranging from 142 to 10,000 $\mu\text{g/L}$ in farm wastewater in China (Zhang et al., 2012). Antibiotic residue in water not only causes marine culture pollution, but also acts as a special precursor that reacts with disinfectants to produce new DBPs (Huber et al., 2005; Navalon et al., 2008). For example, Dodd et al. (2005) reported that several DBPs were originated from the reactions of ciprofloxacin and enrofloxacin with chlorine from the disinfection process. Wang et al. (2010a) reported the oxidation of fluoroquinolone antibiotics by chlorine dioxide, in this process, fluoroquinolone's piperazinyl N4 atom was attacked by chlorine dioxide leading to dealkylation, hydroxylation and intramolecular ring closure at the piperazine moiety. This was then followed by the production of new DBPs through the reaction of fluoroquinolone antibiotics with chlorine dioxide.

These investigations were conducted using freshwater samples, and only chlorinated DBPs (Cl-DBPs) have been observed to date. Considering that there are high concentrations of bromide ions (65 mg L^{-1}) in seawater, residual antibiotics actually coexist with bromide ions in brackish marine culture water (a mixture of seawater and fresh water at a ratio of approximately 1:2). Hypochlorite with strong oxidation properties can oxidize bromide ions to hypobromite which can react more rapidly with many organic pollutants than hypochlorite (Ichihashi et al., 1999). Moreover, bromine substitution processes are faster than those of chlorine. Therefore, the chlorine disinfection process of marine culture wastewater may possibly generate brominated DBPs (Br-DBPs). It has been reported that the toxicity of Br-DBPs is much higher than that of Cl-DBPs (Liu and Zhang, 2014; Yang and Zhang, 2013). For example, Plewa et al. (2002) reported that bromoacetic acid was 18.4 and 89.8 times more cytotoxic than chloroacetic acid in *Salmonella typhimurium* and Chinese hamster ovary cells, respectively. Through studies of chronic cytotoxicity and DNA damage (SCGE assay) in CHO cells, including an analysis of the structure–activity relationships of DBPs, Richardson et al. (2007) revealed that bromoacetic acid was the most genotoxic on mammalian cells of the regulated DBPs. The toxic nature of Br-DBPs encouraged us to investigate the reactions of sodium hypochlorite (NaClO) with antibacterial agents in the presence of bromide ions.

As an initial investigation, this paper will be primarily focused on the kinetics and pathways of the reaction between NaClO and

antibacterial agents. Special attention will be paid to the identification of the reaction products. As shown in Fig. 1, NOR is a typical fluoroquinolone antibiotic agent with piperazine ring, nalidixic ring and lateral chain. It is widely used in aquaculture and frequently detected at concentrations of $2.5\text{--}35000 \mu\text{g L}^{-1}$ in shrimp ponds located along the coast of Guangxi, China. Therefore, NOR was selected as the target antibiotic in the initial investigation. The aim of this paper is to evaluate the activity and the health risk of Br-DBPs in the chlorine disinfection process of marine culture water.

2. Materials and methods

2.1. Chemicals

Analytical grade NOR was obtained from the Dalian Meilun biological technology company and was used without further purification. Norfloxacin stocks were prepared in pure water. NaClO, NaCl, NaBr and $\text{Na}_2\text{S}_2\text{O}_3$ were obtained from the Guangzhou Chemical Reagent Company, China. The available chlorine content of NaClO amounted to 10% of the total chlorine content. All reagent solutions were prepared using water from a Millipore Milli-Q Ultrapure Gradient A10 purification system. Real brackish water samples of shrimp ponds were obtained from Qinzhou, Guangxi province, China.

2.2. Analytical methods

An Agilent 1050 high performance liquid chromatography (HPLC) system equipped with a Zorbax RX-C18 column ($4.6 \text{ mm} \times 250 \text{ mm}$, $5 \mu\text{m}$), fluorescence detector, and single-wavelength UV detector was used to monitor NOR in NaClO disinfection process experiments. The mobile phase used was trifluoroacetic acid and acetonitrile at a flow rate of 0.30 ml min^{-1} . The detection wavelength was set to 278 nm for NOR. The residual NaClO after the reaction was determined by way of iodometry.

2.3. Batch kinetic experiments

To avoid missing some of the transformed products, the initial concentration of NOR was set to 0.1 mM. Excess NaClO was added to initiate the reaction. In the kinetics studies, the pH value of the reaction solution was maintained by 10 mM phosphate ($\text{pH} = 6\text{--}8$) and borate buffer ($\text{pH} = 9$). Samples were collected at specified time intervals during the reaction period by adding Na_2SO_3 to terminate the reaction. Concentrations of residual NOR were analyzed by HPLC. All of the kinetic experiments were conducted at room temperature (298.15 K) and duplicate at least twice. Pseudo-first-order rate constants for losses of NOR were obtained from the slopes of fitted linear plots of $\text{Ln}([\text{NOR}])$ vs. time ($0.97 > r^2 > 1$).

2.4. Product identification

Reaction products were analyzed based on the accurate mass,

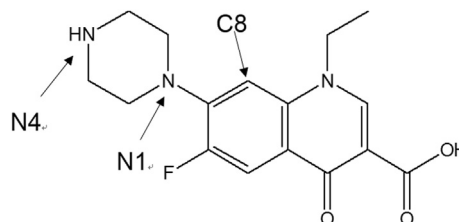


Fig. 1. Structure of NOR.

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