



# Effects of the natural colloidal particles from one freshwater lake on the photochemistry reaction kinetics of ofloxacin and enrofloxacin<sup>☆</sup>

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## ABSTRACT

Understanding the effect of natural colloidal particles (NCPs) on the photochemistry of organic pollutants is crucial to predict the environmental persistence and fate of them in surface waters, and it is, yet, scarcely elucidated. In this study, the pre-filtered surface water (through a 1 μm capsule filter) from Baiyangdian Lake was further separated into four different size NCPs: F1 (0.65–1.0 μm), F2 (100 kD–0.65 μm), F3 (10–100 kD) and F4 (1–10 kD) by cross-flow ultrafiltration (CFUF), and the photochemical kinetics and mechanisms of ofloxacin (OFL) and enrofloxacin (ENR) were investigated in the presence of those particles under simulated sunlight. Results showed that OFL and ENR underwent both direct and indirect photolysis in F1–F4 solutions, and the observed pseudo first-order rate constants ( $k_{obs}$ ) for target compounds differed depending on the size of NCPs. Direct photolysis accounted for >50% of the degradation in all cases and was the dominant degradation pathway for the two target antibiotics with the exception of OFL in F1 solution. Except for ENR in both F3 and F4 solutions, nearly all NCPs enhanced the degradation of both target compounds by indirect photolytic pathways, especially in F1 solution that showed the largest reactivity for OFL and ENR, promoting the reactions by 63% and 41%, respectively. The excited state colloidal organic matter (<sup>3</sup>COM<sup>\*</sup>) plays a significant role in the indirect photolysis, and the adsorptions of OFL and ENR to NCPs were likely to have a pronounced effect in the photochemistry process. Pearson's correlations analysis showed that the  $k_{obs(OFL)}$  was significant positive correlated with binding of Fe ( $r = 0.963$ ,  $P < 0.05$ ), and the  $k_{obs(ENR)}$  was significant positive correlated with the adsorption percentage of OFL ( $r = 0.999$ ,  $P < 0.01$ ).

This paper has demonstrated that different size NCPs showed the different photochemical contribution to the reaction rate for OFL and ENR.

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## 1. Introduction

Since the discovery of penicillin (Fleming, 1929), humans have developed thousands of strong bactericidal antibiotics and been widely applied in treatment of disease (Kümmerer, 2009; Kümmerer, 2003) and production of livestock and aquaculture (Gaskins et al., 2002; Grave et al., 2008), which led to a large amount of those compounds and their metabolites introducing into the aquatic environment. There are hundreds of antibiotics now being detected in both sewage treatment plant discharges (Leung

et al., 2012; Wu et al., 2016; Zhou et al., 2013) and natural water bodies such as rivers, lakes, and reservoirs (Cheng et al., 2014; Cheng et al., 2016b; Yao et al., 2017). In aquatic ecosystems, the residues of antibiotics not only can cause adverse health effects in aquatic organisms (Jo et al., 2011; Mückter, 2006), but also accelerate the generation of antibiotic resistance genes (ARGs) (Kümmerer, 2009; Xu et al., 2016), which could eventually enter the human body through horizontal gene transfer, and produce unpredictable negative effects on human health (Martínez, 2008; Peng et al., 2008). Ubiquitous antibiotics have become the focus of environmental pollutants in the aquatic environment (Liu et al., 2017; Suzuki & Hoa, 2012; Zhang et al., 2012). Among them, fluoroquinolones (FQs) is a common kind of antibiotic drugs that are widely used in humans and animals due to their broad activity

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spectrum against gram-positive and negative bacteria and good oral intake properties. They are the most frequently detected antibiotics, and have relatively high concentrations ( $\text{ng L}^{-1}$  to several  $\mu\text{g L}^{-1}$ ) from wastewaters to natural waters (Hao et al., 2015; Xu et al., 2015; Zhang et al., 2017). FQs water body pollution has become gradually a priority for researchers in environmental science.

An indisputable fact is that, although large number of studies about antibiotics has been reported, there is little still known about the environmental occurrence, transport, and ultimate fate of antibiotics (Guan et al., 2016; Kümmerer, 2009). Generally, both biotic and abiotic processes determined the pharmaceuticals fate in the environment (Fatta-Kassinos et al., 2011; Halling-Sørensen et al., 1998). In surface water three primary mechanisms occurs via hydrolysis, photodegradation and biodegradation. For antibiotics resistant to biodegradation and hydrolysis (Huang et al., 2001; Kümmerer, 2009; Kimura et al., 2007), photochemical degradation becomes the most significant transformation in surface water (Boreen et al., 2003; Edhlund et al., 2006). Under sunlight irradiation, antibiotics can absorb light, undergo direct photolysis (Li et al., 2011), or/and by indirect photolysis with reactive oxygen species (ROS), such as hydroxyl radicals ( $\bullet\text{OH}$ ) and singlet oxygen ( $^1\text{O}_2$ ), in the presence of naturally occurring photosensitizers (Andreozzi et al., 2006; Chen et al., 2009; Ge et al., 2010; Guerard et al., 2009b; Zhang et al., 2012). Most studies have confirmed that dissolved organic matter (DOM) played a major role in antibiotics transformation processes by indirect photolysis in natural water (Chen et al., 2009; Xu et al., 2011), in which photoexcitation-generated triplet excited state DOM ( $^3\text{DOM}^*$ ) and the other ROS that may react directly with antibiotics and promote the indirect photolysis (Fisher et al., 2006; Hassett, 2006; Leresche et al., 2016). On the contrary, DOM may interfere with the indirect photolysis of antibiotics by screening sunlight and scavenging ROS (Chiron et al., 2006; Guerard et al., 2009a; Wenk et al., 2015; Wenk et al., 2013). However, these results are difficult to extrapolate to natural systems due to the “reality” of natural systems that contain heterogeneous mixtures of particles from many sources (Fanun, 2014), accompanied by the special features in the adsorption properties of antibiotics depending on their hydrophilic characteristics (Nam et al., 2014). Xu et al. (2011) found that adsorption capacity determined the photodegradation rate of amoxicillin. However, information about how the diffusing small particles (i.e. colloid and nanoparticle) in natural waters, which are dominated by surface properties, including surface area and electrical charge, and known to their complex, heterogeneous compositions, involving an intimate association between chemical, mineralogical, such as DOM that is often known as the fulvic and/or humic compounds, inorganic oxides of aluminium, iron and silicon, carbonate and clay minerals affect the photochemical reactions of antibiotics is unknown (Filella, 2007). The composition of natural colloidal particles (NCPs) is rather complicated with the inorganic or organic fractions, and the DOM is applicable to that specific isolate and may not be able to cover all circumstances. Therefore, the results cannot be used to interpret the overall photoreactivity of NCPs in natural waters. NCPs are in the size range between 1 nm and 1  $\mu\text{m}$  of natural aquatic environments, and may reach a maximum of  $10^8$  particles per liter (Gustafsson & Gschwend, 1997; Kim, 1994). Therefore, it is critical to expand the investigation of the photochemistry of antibiotics on specific aquatic NCPs. Many studies have shown that NCPs can interact strongly with many other organic pollutants such as polycyclic aromatic hydrocarbons, estrogenic chemicals, endocrine-disrupting chemicals and other pharmaceuticals (Cheng et al., 2016a; Maskaoui & Zhou, 2010; Yan et al., 2015a; Yan et al., 2015b). In addition, many other studies also reported that FQs often show high adsorption to soil and sediment

( $K_d = 260\text{--}16543 \text{ L kg}^{-1}$ ), which showed their high accumulation and low mobility in natural solid media (Cheng et al., 2014; Riaz et al., 2017). The adsorption of organic pollutants on NCPs may accelerate the photodegradation through energy transfer reactions, light adsorption and efficient light scattering or reduce via excited-state quenching and radiation shielding (Gustafsson & Gschwend, 1997). However, the effect of NCPs on the photochemistry of antibiotics is still poorly understood. Nowadays, thanks to the development in the isolation of colloidal particles by cross-flow ultrafiltration (CFUF), we can collect large amounts of NCPs in a relatively short time (Jarvie et al., 2012; Orlandini et al., 1990; Zhou et al., 2007) and better investigate the effect of them on the transformation regularity of organic pollutants in natural water bodies.

Motivated by our previous studies (Cheng et al., 2016a), this paper focused on the effects of NCPs on the photochemistry of two FQs (OFL and ENR) (Table S1) that were widely detected in aqueous environment (Li et al., 2012). Although, some information on the photodegradations of these pollutants is available (Sturini et al., 2015; Wammer et al., 2013), no special study has been performed on the photochemistry of the antibiotics in the presence of different size NCPs as far as we know. Therefore, the major objectives of this study were to investigate the photochemistry kinetics of OFL and ENR on the influence of different size NCPs, and to explore the photochemical types and mechanisms of those two compounds in natural colloidal particle (NCP) solutions.

## 2. Material and methods

### 2.1. Chemicals

Oflxacin (purity >99%, OFL) and enrofloxacin (>99%, ENR) were purchased from Dr Ehrenstorfer (Augsburg, Germany). Their physicochemical and spectral properties were shown in Table S1 and Fig. S1, respectively. Methanol and isopropanol (HPLC grade) were purchased from Fisher Science Co. Sodium azide and sorbic acid (99%) from TCI (Japan).  $\text{Fe}_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$  (97%) was purchased from Acros Organics (Geel, Belgium). The other reagents were of analytical grade. Ultrapure water was obtained with a Millipore-Milli Q system.

### 2.2. Separation and characterization of NCPs

Based on our earlier studies and other research (Cheng et al., 2014; Cheng et al., 2016a; Li et al., 2012), sampling was performed in a slightly antibiotic-contaminated area ( $38^\circ 50.854' \text{N}$ ,  $115^\circ 57.387' \text{E}$ ) that both OFL and ENR were just in the range from several  $\text{ng L}^{-1}$  to ten more in the surface water of Baiyangdian Lake in Xiongan New Area, North of China. Prior to sampling, the HDPE fluorinated plastic barrels were soaked with 10% nitric acid overnight and thoroughly rinsed first with deionized water then the sample before collecting. The top 0.5 m layer of surface water was collected. Once transported to the laboratory, water samples were filtered immediately through 1.0  $\mu\text{m}$  capsule filters (Millipore) to obtain pre-filtered water samples.

As showed in Fig. 1, the pre-filtered water samples were further processed by CFUF (0.5  $\text{m}^2$  surface area, Millipore Pellicon 2) to obtain different size colloidal particles (Cheng et al., 2016a). By using a series of different molecular weights or pore size of Millipore Pellicon 2 ultrafiltration membrane cassettes (1 kDa-PLAC, 10 kDa-Biomax, 100 kDa- Biomax and 0.65  $\mu\text{m}$ -DVPP), four fractions in the colloidal size range were separated, namely: (i) coarse colloidal fraction: F1 (1–0.65  $\mu\text{m}$ ); (ii) fine colloidal fraction: F2 (0.65  $\mu\text{m}$ –100 kDa); (iii) ultrafine colloidal fraction: F3 (100–10 kDa) and F4 (10–1 kDa). The CFUF operations were carried out in two

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