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Effects of the natural colloidal particles from one freshwater lake on the photochemistry reaction kinetics of ofloxacin and enrofloxacin[☆]

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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 ($^3COM^*$) 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 $k_{\mathrm{obs(OFL)}}$ was significant positive correlated with binding of Fe ($r = 0.963$, $P < 0.05$), and the $k_{\mathrm{obs(ENR)}}$ 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.

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 (ng L^{-1} to several μg 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 biodegradaton. For antibiotics resistant to biodegradaton 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 (•OH) and singlet oxygen ($^1O_2$), 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 ($^3DOM^*$) 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 μm 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 additon, many other studies also reported that FQs often show high adsorption to soil and sediment ($K_d = 260–16543$ 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

Ofloxacin (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). $Fe_2(SO_4)_3•5H_2O$ (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°50.854′N, 115°57.387′E) that both OFL and ENR were just in the range from several 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 μm 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 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 μm-DVPP), four fractions in the colloidal size range were separated, namely: (i) coarse colloidal fraction: F1 (1–0.65 μm); (ii) fine colloidal fraction: F2 (0.65 μm-100 kDa); (iii) ultrafine colloidal fraction: F3 (100-10 kDa) and F4 (10-1 kDa). The CFUF operations were carried out in two

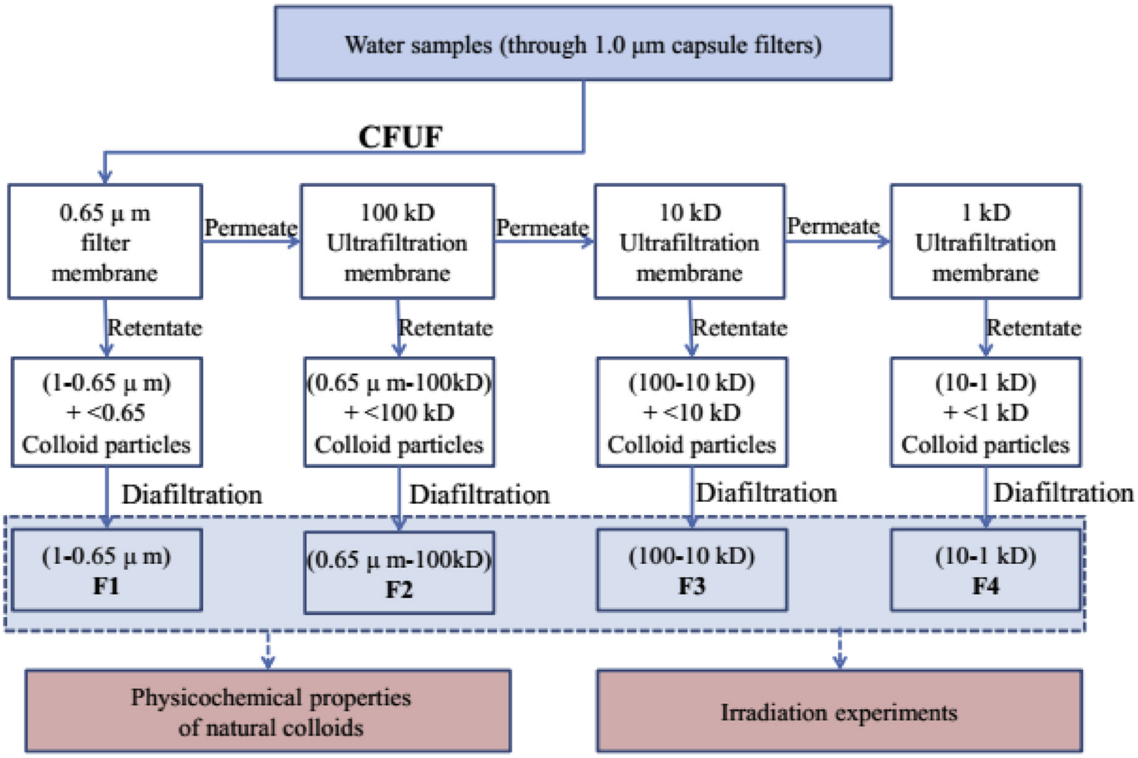

Fig. 1. Procedure used for the different size NCPs separation (F1-F4).

modes, concentration and diafiltration (Kilduff & Weber, 1992). In the concentration mode, the retentate (colloidal particles) cyclically flowed back into the feed tank, while the permeate (sub-colloidal particles and soluble phase) was leaked into a separate tank. A volumetric concentration factor (VCF) of 10 was executed after finishing the operation (Wilding et al., 2004). Followed by diafiltration mode, the retentate volume is maintained constant by replacing the volume lost as permeate with ultrapure water. The total volume of water added was 10 times the retentate volume (Guo et al., 1994). At the end of isolation, all four fractions (F1-F4) were preserved at −18 °C until the following experiments.

The above-obtained aquatic NCPs (F1-F4) were evaporated in a vacuum rotary evaporator (IKA RV05) below 50 °C, and then the concentrated solution were collected in a glass beakers for dry colloidal particles preparation by using a freeze dryer (Christ ALPHA2-4). Colloidal organic carbon (COC) contents were determined with a Shimadzu Total Organic Carbon Analyzer (model TOC-5000A) equipped with a Solid Sample Module (SSM-5000A). Main elements (K, Ca, Na and Mg) and trace metals (Fe) were observed by Axial Inductively Coupled Plasma Atomic Emission Spectrophotometer (ICP-AES, Jobin Yvon ULTIMA). The physicochemical properties of NCPs were summarized in Table S2. In addition, the concentrations of OFL and ENR in the original NCPs were below the limit of detections (LODs) according to the following 2.5 antibiotic detection method.

2.3. Irradiation experiments

An XPA-1 merry-go-round photochemical reactor (Xujiang Electromechanical Plant, Nanjing, China) and a simulated solar light source (500 W xenon lamp with 290 nm filter, $\lambda > 290$ nm) were used to perform the photochemistry experiments in a dark fume cupboard. The light intensity (290–420 nm) at the reaction systems was 0.96 mW cm^{-2}, which was measured using a radiometer (PMA 2100 Solar Light Co.). The water bath was circulated cooling to maintain the reaction temperature at (25 ± 1) °C. The photochemical experiments were done in a quartz glass vials containing 50 mL reaction solution under continuous stirring.

Photochemistry experiments were performed by irradiating each antibiotic separately (single-compound experiments) and all two antibiotics in the same solution (mixture experiments). The initial concentration of each compound was 5 μg L^{-1}. Eventually, F1-F4 (10 mg L^{-1}) were added. The reaction solutions were irradiated in triplicate using 50 mL quartz tubes with an internal diameter of 3.0 cm, and thoroughly mixed and stored in dark for 24 h. Dark controls were performed under the same conditions. The pH values of the irradiated solutions were not adjusted in order to avoid the influences of buffering agent or other pH regulators in the photochemical process, for the pH varied very little and ranged from 6.24 to 6.74.

In the quenching experiments, the roles of $^1O_2$ and •OH were assessed in experiments containing 1.0 mM sodium azide and 20 mM 2-propanol into the colloidal particle solutions, respectively. The role of excited state colloidal organic matter (COM), presumably, $^3\text{COM}^*$ was conducted with the addition of sorbic acid (0.50 mM) into the NCP solutions.

Inner-filter corrections were applied to evaluate the contributions of both the direct and indirect photolysis in the different size of NCP solutions (F1-F4) (Leifer, 1988). A light-screening factor ($S_{\sum\lambda}$) was used according to the method presented in Guerard et al. (2009a) to quantify the effect of light absorbed by those NCPs on the direct photolysis rate. The wavelength-specific light-screening factor (S_λ) was calculated from the equation,

$$S_\lambda = \frac{1 - 10^{-\alpha_\lambda l}}{2.303\alpha_\lambda l} \quad (1)$$

where α_λ (cm^{-1}) is the wavelength specific attenuation coefficient, l

(cm) is the pathlength of the tubes used in photochemical experiments. $S_{\sum\lambda}$ was determined by taking the ratio of the integrated area of a plot of S_λ versus wavelength (nm) and dividing by theoretical area of the plot if no inner filtering occurred (i.e., $S_\lambda = 1.0$ for all wavelengths). The direct photolysis rate coefficients in NCP solutions (k_{dp}) were predicted from the equation, $k_{dp} = S_{\sum\lambda} \times k_{con\circ}$, where $k_{con\circ}$ is the direct photolysis rate coefficient experimentally determined in ultrapure water controls. S_λ was calculated for OFL and ENR for the region of 290–350 nm.

2.4. Adsorption experiments

Experiments were conducted to study the adsorption of OFL and ENR on different size NCPs. Solutions of single and mix of OFL and ENR ($5\ \mu g\ L^{-1}$) containing $10\ mg\ L^{-1}$ of F1-F4 were thoroughly mixed and stored in dark for 24 h. The samples were transferred to centrifuge tubes fitted with a 1kDa cut off filter (Pall, USA) and centrifuged at 4000 rpm (15 min) using an Anke (TDL-40B, Shanghai, China) centrifuge (Xu et al., 2011). The samples were analyzed by UPLC-MS/MS and the adsorption percentage (AP) of OFL or ENR to different size NCPs was determined according to the following equation:

$$AP\ (\%) = \frac{C_0 - C}{C_0} \times 100 \qquad (2)$$

Where C_0 is the initial concentration of target antibiotic, C is the residual concentration of target antibiotic after adsorption.

2.5. Antibiotic analysis

The concentrations of OFL and ENR were analyzed by UPLC-MS/MS, which were performed on a Waters ACQUITY ultrahigh performance liquid chromatograph (UPLC) system hyphenated with a TQD triple quadruple mass spectrometer fitted with a Z-spray electrospray ionization source (Waters). The column used for separation was BEH C18 column (1.7 μm, 50 mm × 2.1 mm) supplied by Waters.

The analysis was performed using 0.1% formic acid in Milli-Q water as eluent A and methanol as eluent B in gradient elution mode at flow rate of $0.3\ mL\ min^{-1}$. The elution gradient started with 80% of eluent A and linearly decreasing to 10% A over the first 2 min. Mobile phase composition was the same within following 1.8 min. In 0.2 min percentage of eluent A was increased to the initial mobile phase composition and these conditions were held for 2 min. After gradient elution, the column was equilibrated for 2 min before next injection. An injection volume of 5 μL was used in all analysis. The column temperature was kept at 40 °C. The mass spectrometer was operated in positive ionization mode. The optimized parameters were capillary voltage, 2 kV; cone voltage, 30 V; source and desolvation temperatures were 120 °C and 400 °C, respectively. Nitrogen gas was used as the desolvation gas ($700\ L\ h^{-1}$) and cone gas ($50\ L\ h^{-1}$). Argon gas was used for collision-induced dissociation. Multiple reaction monitoring (MRM) was used for quantification of targeted antibiotics. The precursor mass, product ion, and optimized tandem mass spectrometry parameters for the analysis are also provided in the Supporting Information (Table S1). The limit of detections (LODs), estimated as S/N = 3, were $8.2\ ng\ L^{-1}$ for OFL and $18.6\ ng\ L^{-1}$ for ENR. The limit of quantifications (LOQs), estimated as S/N = 10, were $27.5\ ng\ L^{-1}$ and $61.9\ ng\ L^{-1}$ for OFL and ENR, respectively.

All the samples were analyzed in triplicate, and the relative standard deviation was less than 10%. Photodegradation kinetics of the two antibiotics was calculated using the first-order kinetic model:

$$\frac{dC}{dt} = -kC \qquad (3)$$

where C represents the concentration of target antibiotic at the time t, and k represents the rate constant. The half-life ($t_{1/2}$) of the antibiotics was calculated using $t_{1/2} = \ln 2/k$.

2.6. Statistical analysis

Pearson's correlation (SPSS software, Windows version 16.0, SPSS Inc.) was performed in order to determine relationships between photochemistry of antibiotics and the physicochemical properties of NCPs (F1-F4).

3. Results and discussion

3.1. OFL and ENR reaction kinetics in NCP solutions

Photochemistry reaction kinetics of OFL and ENR were investigated in pure water (PW) and in different size of NCP (F1-F4) solutions. Moreover, their reaction kinetics was also investigated with both individual solutions of each analyte and their mixture. Initial concentration of each compound in the single and mixture solutions was $5\ \mu g\ L^{-1}$, and NCPs (F1-F4) were $10\ mg\ L^{-1}$ that were close to those in natural waters (Cheng et al., 2016a). During all photochemistry experiments, no obvious loss of OFL and ENR was observed in the dark controls, indicating the decay by microbiological or hydrolytic means was negligible during the photochemistry experiments.

The UV-Vis absorbance spectrums of OFL, ENR and F1-F4 indicated the possibility that direct photolysis of OFL and ENR in pure water and indirect photolysis of OFL and ENR in the presence of F1-F4 can perform due to the overlap of the UV-Vis absorbance spectrum of targeted compounds and NCPs and the emission spectrum of the simulated solar ($\lambda > 290$ nm, Fig. S1) (Ge et al., 2010). Photochemistry reaction kinetics of the mixture of OFL and ENR ($5\ \mu g\ L^{-1}$) in pure water (PW) and different NCP solutions (F1-F4, $10\ mg\ L^{-1}$) were presented in Fig. 2, and the different profiles were obtained for OFL and ENR.

As shown in Fig. 2, the photochemistry reactions of target antibiotics in PW and F1-F4 solutions followed the pseudo-first-order kinetics. The strong linear regression ($R^2 > 0.95$) indicates that the photodegradation data of each antibiotic in NCP solutions fitted the first-order kinetic model Eq. (2) well. The observed pseudo first-order rate constants (k_{obs}) for solar degradation of FQs were shown in Fig. 3, and the half-lives ($t_{1/2}$) ranged from 0.37 h for ENR in F1 solution for single-component experiment to 6.86 h for OFL in F4 solution for mixture experiment. Under the same light sources (500 W, Xenon lamp), the obtained k_{obs} and $t_{1/2}$ values of ENR were comparable with previous studies (Li et al., 2011). However compared to other pharmaceuticals, such as ormetoprim with $t_{1/2} = 5.9–68.6$ h (500 W, Xenon lamp) (Guerard & Chin, 2012), or phenicol antibiotics with $t_{1/2} = 143–500$ h (1000 W, Xenon lamp) (Ge et al., 2009), the shorter half-lives in this study implied that photodegradation is a central factor in determining environmental fate of FQs in aquatic environment. The k_{obs} values obtained in single-component and mixture irradiation experiments were compared and no significant impacts ($P < 0.01$) were observed in the case of antibiotics mixture irradiation (Fig. 3). This result may be contributed to the similar adsorption capacity of targeted antibiotics in single-component and mixture additions sorption experiments (Table S2). Many studies have shown that hydrophobic organic contaminants (HOCs, e.g. polycyclic aromatic hydrocarbons) and ionic organic contaminants (IOCs, e.g. antibiotics) can be

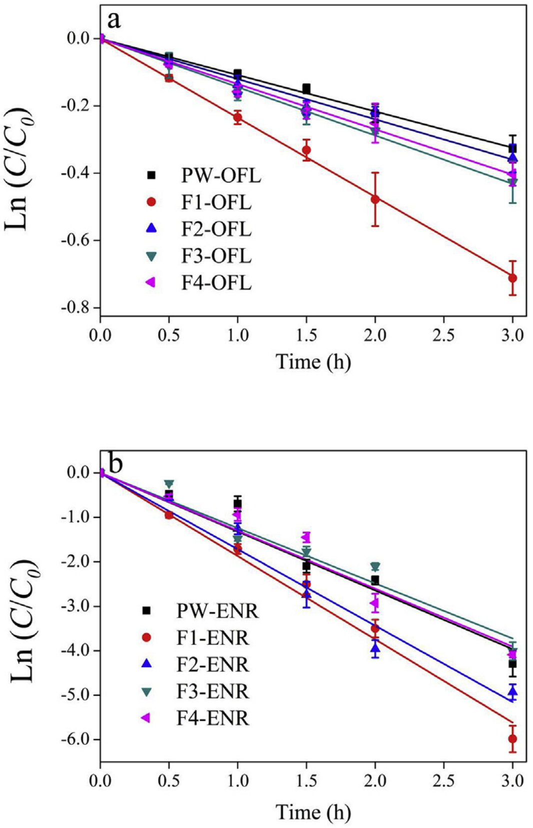

Fig. 2. Photochemical reaction kinetics of the mixture of FQs ($5\ \mu g\ L^{-1}$): ofloxacin (a) and enrofloxacin (b) obtained in pure water (PW) and in different size of NCP solutions (F1-F4, $10\ mg\ L^{-1}$).

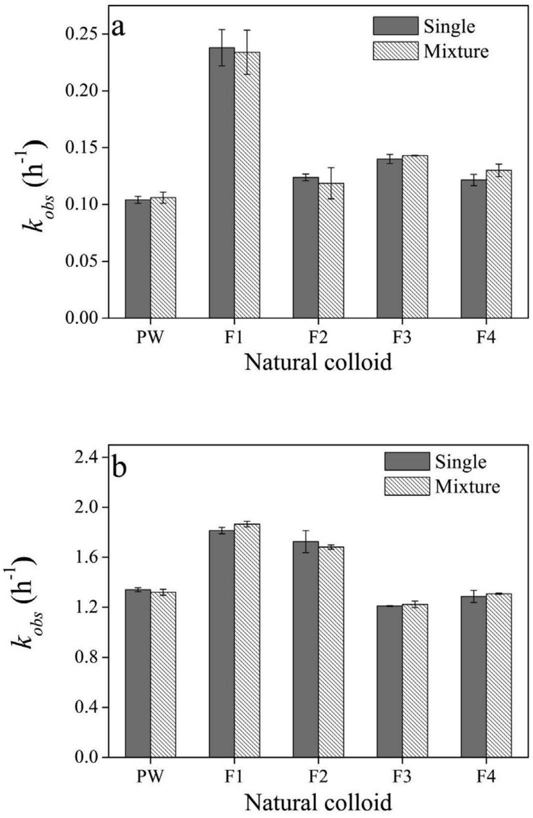

Fig. 3. Observed pseudo first-order rate constants (k_{obs}) for ofloxacin (a) and enrofloxacin (b) ($5\ \mu g\ L^{-1}$) with single compound and their mixture experiments in pure water and in different size of NCP solutions (F1-F4, $10\ mg\ L^{-1}$).

adsorbed onto natural organic matter (NOM), seriously affecting the transport, transformation and biological uptake ability in water environment system (Mccarthy & Jimenez, 1985; Rui et al., 2016). Consequently, the photosensitized degradation process can be altered through interactions with COM. Previous studies have revealed that the sorption-enhanced indirect phototransformation of β-lactam and sminoglycoside antibiotics in NOM-enriched solutions due to the facilitate energy transfer (Rui et al., 2016; Xu et al., 2011). It was speculated that the like adsorption capacity of the sensitizer with antibiotics in single and mixture additions had the similar energy transfer, but additional studies were required to assess the nature of the interaction between antibiotics and NCPs. So the subsequent photochemistry experiments were conducted in the mixture solutions of both OFL and ENR in the following experiments to save large amounts of time and money.

As shown in Table 1, OFL and ENR underwent both direct and indirect photolysis in the different size of NCP solutions (F1-F4). Direct photolysis accounted for >50% of the degradation in all cases and was the dominant degradation pathway for both target antibiotics with the exception of OFL in F1 solution. In addition, except ENR in both F3 and F4 solutions, nearly all NCPs used in this study enhanced the degradation of both target compounds by indirect photolytic pathways, especially in F1 solutions that showed the largest reactivity for OFL and ENR, promoting the reactions by 63% and 41%, respectively (Table 1). The differences in NCP (F1-F4) photoreactivity might attribute to a combined effect of multiple causes. One might attribute to inner-filter effects, and it was compensated for the indirect photolysis rate coefficients for by dividing k_{ip} by the screening factor ($S_{\sum\lambda(290\text{-}340)}$). The result unequivocally showed that the direct photolysis of OFL and ENR were inhibited by light screening in NCP solutions, and the small NCPs had the stronger inner-filter effects than large ones (Table 1). This result was major contributed to the strong overlapping absorption spectra of small particles with OFL or ENR (Fig. S1). Thus, the small particles have the stronger competitive absorption of actinic photons than large NCPs. Moreover, the compositions of NCPs, especially COM, could scavenge the ROS (e.g., •OH and $^1O_2$) and inhibited the possible photo-sensitized photolysis of FQs (Ge et al., 2010; Lam et al., 2003). In NCPs, the contents of colloidal organic carbon (COC) were much higher in the small ones, such as the F3 ($462.89\ g\ kg^{-1}$) and F4 ($277.12\ g\ kg^{-1}$), than in the F1 ($103.31\ g\ kg^{-1}$) (Table S2). This also resulted in a slow photodegradation rate in the smaller size of NCPs.

3.2. OFL and ENR reaction types in NCP solutions

As shown in Table 1, except for direct photolysis, the photochemistry of OFL and ENR also had experienced indirect photolysis by photosensitization for the different size NCPs (F1-F4), and the contributions of indirect photolysis to the overall degradation for OFL and ENR ranged from 28% to 63% and 15%–41%, respectively. Many studies have confirmed that sunlight mediated indirect photolysis in (simulated) natural waters was mainly caused by the reactive species, e.g. $^1O_2$, •OH and $^3COM^*$, that were derived from NCPs (Ge et al., 2010; Xu et al., 2011; Yan et al., 2015a). To assess the role of the different reactive species formed by NCPs under xenon lamp irradiation, it was performed adding to solutions of FQs in the presence of different size NCPs: (1) 2-propanol, an •OH scavenger (Ge et al., 2010), (2) sodium azide, both •OH and $^1O_2$ quencher (Ge et al., 2010) and (3) sorbic acid, a $^3COM^*$ quencher (Xu et al., 2011).

Table 1
Observed pseudo first-order rate constants (k_{obs}), half-lives ($t_{1/2}$) and predicted contributions from the direct and indirect photolysis of OFL and ENR in presence of different size NCPs (F1-F4).

Sampling sites	$S_{\sum\lambda(290-350)}$[a]	k_{obs} (h^{-1})	$t_{1/2}$ (h)	k_{dp}[b] (h^{-1})	k_{ip}[c] (h^{-1})	DP[d] (%)	IP[d] (%)
OFL							
PW[e]	NA	0.106 ± 0.005	6.54	0.106	NA	100	0
F1	0.821	0.234 ± 0.019	2.96	0.087	0.147	37	63
F2	0.809	0.119 ± 0.014	5.82	0.086	0.033	72	28
F3	0.773	0.143 ± 0.033	4.85	0.082	0.061	57	43
F4	0.784	0.130 ± 0.006	5.33	0.083	0.047	64	36
ENR							
PW	NA	1.320 ± 0.024	0.53	1.320	NA	100	0
F1	0.834	1.866 ± 0.023	0.37	1.101	0.765	59	41
F2	0.813	1.682 ± 0.017	0.41	1.073	0.609	64	36
F3	0.785	1.223 ± 0.026	0.57	1.036	0.187	85	15
F4	0.797	1.308 ± 0.005	0.53	1.052	0.256	80	20

[a] Light screening factor for wavelengths 290–350 nm.
[b] k_{dp} represents the rate constant predicted for contribution of direct photolysis to the overall degradation of the target antibiotic in natural colloidal particle solution.
[c] k_{ip} represents the rate constant predicted for contribution of indirect photolysis to the overall degradation of the target antibiotic.
[d] The percentage contribution of direct photolysis (DP) and indirect photolysis (IP) to the overall observed degradation.
[e] Pure water.

Generally, lower values of k_{obs} were measured in the presence of all three scavengers (Table 2). The addition of isopropanol induced a certain retardation of the photochemistry reaction of two FQs, indicating that their photoreactions involved photo-oxidation via •OH. The addition of sodium azide inhibited the photochemistry reaction both of OFL and ENR, and the inhibitive effects of sodium azide were slightly more significant than that of isopropanol, suggesting that two FQs also underwent $^1O_2$-mediated photolysis.

It is undisputed that the quenching effects were clearly more pronounced with sorbic acid. However, this compound can behave as a scavenger of either $^3COM^*$ or the triplet-excited states of the antibiotic itself. To prove this point, the photochemistry of the mixture with sorbic acid but without NCPs was investigated. Although some inhibitions in the removal of the antibiotics were observed (data not shown), those effects were very lower than in the addition of NCPs. This suggests that the main effect of sorbic acid involves the contribution of COM to the photooxidation of the antibiotics under the emulated conditions, although the contributions of other reactions types cannot be ruled out, they are of lesser importance. This is in agreement with the results reported form other organic pollutants (Carlos et al., 2012; Xu et al., 2011).

It was also known that the efficiency for the reaction of OFL or ENR with reactive species (e.g. •OH, $^1O_2$ and $^3COM^*$) might be relevant with the proximity between antibiotic and reactive specie (Xu et al., 2011). NCPs bound antibiotic is closer to those particles than unbound molecules in the bulk solution, thereby enhancing the energy transfer and thus the degradation. To support this proposal, the adsorption of target antibiotics on NCPs was studied. The result of adsorption of target antibiotic by NCPs indicated that NCPs bound antibiotics were likely to have a pronounced effect on its photodegradation (Table S2). For example, as AP of ENR increased form 87.45% (F3) to 95.10% (F1) in mixture-components irradiation experiments, the percentage contribution of indirect photolysis to the overall observed degradation changed from 15% (F3) to 41% (F1), due to the enhancement of the energy transfer compared to the unbound molecules by NCPs in the bulk solution.

Table 2
Observed pseudo first-order rate constants (k_{obs}) obtained for the photodegradations of the mixture of antibiotics (5 μg L^{-1} of each antibiotic) in the presence of different size NCPs (F1-F4, 10 mg L^{-1}).

	F1	F2	F3	F4
OFL				
None	0.234 ± 0.019	0.119 ± 0.014	0.143 ± 0.033	0.130 ± 0.006
2-propanol[a]	0.194 ± 0.003	0.098 ± 0.001	0.121 ± 0.012	0.109 ± 0.008
Sodium azide[b]	0.181 ± 0.001	0.079 ± 0.005	0.117 ± 0.002	0.103 ± 0.006
Sorbic acid[c]	0.102 ± 0.006	0.057 ± 0.005	0.078 ± 0.005	0.072 ± 0.003
Fe (III)[d]	0.258 ± 0.016	0.129 ± 0.014	0.344 ± 0.013	0.177 ± 0.013
ENR				
None	1.866 ± 0.023	1.682 ± 0.017	1.223 ± 0.026	1.308 ± 0.005
2-propanol	1.656 ± 0.065	1.469 ± 0.008	1.184 ± 0.043	1.208 ± 0.160
Sodium azide	1.631 ± 0.087	1.383 ± 0.155	1.179 ± 0.055	1.194 ± 0.028
Sorbic acid	1.249 ± 0.122	1.019 ± 0.059	1.339 ± 0.068	1.042 ± 0.061
Fe (III)	1.706 ± 0.016	1.683 ± 0.015	2.261 ± 0.105	1.876 ± 0.023

[a] 2-propanol (20 mM).
[b] Sodium azide (1.0 mM).
[c] Sorbic acid (0.5 mM).
[d] Fe (III) (5 μg L^{-1}).

3.3. *Relationship between photochemistry of antibiotics and NCP properties*

To further investigate the photochemistry reaction mechanisms of antibiotics in NCP solutions, the physicochemical properties of NCPs were determined (Table S2). The colloidal organic carbon (COC) content varied from 103.310 g kg^{-1} to 462.892 g kg^{-1}. The element concentrations for Ca, Mg, Na and K in the NCPs ranged from 7.644 g kg^{-1} to 214.606 g kg^{-1}, while the Fe content varied from 159 mg kg^{-1} to 492 mg kg^{-1}. This result was consistent with our previous study (Cheng et al., 2016a). The colloidal fractions contain significant concentrations of elements, especially Ca, Mg, Na and K, which may be ascribed to the high surface area, organic C content and cation-exchange capacity (CEC) of colloidal particles (Ran et al., 2000). Therefore, it is not surprising that NCPs has a strong ability to fix dissolved cations and organic pollutants, such as antibiotics (Table S2) (Pan et al., 2012; Yan et al., 2015b).

Pearson correlation analysis showed that the values of k_{obs} were mainly negatively correlated with binding of Ca, Mg, Na and K (Table 3). This result may be attributed to the competitive adsorption between the antibiotics and cations in NCPs (Chen et al., 2011; Wang et al., 2011). Pan et al. (2012) have demonstrated that Mg (II) decreased DOM-OFL binding and OFL decreased DOM-Mg binding due to the competitive effect between Mg (II) and OFL. The enhanced association of antibiotics with NCPs is likely to have a pronounced effect on its photochemistry reaction. This conclusion could be confirmed by the relationship between the values of k_{obs} and AP of antibiotics, which they had positive correlations, especially of $k_{obs(ENR)}$ with AP_{ENR} that are significant relationships ($r = 0.999$, $P < 0.01$) (Table 3). The energy transfer from excited state COM to antibiotics, possibly facilitated by the binding, might play a

Table 3
Pearson correlation coefficients (r) between the $k_{obs.}$ of antibiotics and the physicochemical properties of NCPs.

	pH	COC [a]	Ca	K	Mg	Na	Fe	AP_{OFL} [b]	AP_{ENR}	$k_{obs(OFL)}$	$k_{obs(ENR)}$
pH	1										
COC	0.254	1									
Ca	−0.481	0.482	1								
K	0.641	0.833	0.327	1							
Mg	0.153	0.976*	0.652	0.833	1						
Na	0.189	−0.375	−0.905	−0.472	−0.567	1					
Fe	−0.221	−0.734	0.086	−0.403	−0.579	−0.332	1				
AP_{OFL}	0.736	0.185	0.061	0.694	0.242	−0.455	0.299	1			
AP_{ENR}	0.068	−0947	−0.679	−0.659	**−0.963***	0.482	0.658	0.028	1		
$k_{obs(OFL)}$	0.021	−0.603	0.075	−0.165	−0.454	−0.404	**0.963***	0.488	0.609	1	
$k_{obs(ENR)}$	0.179	−0.906	−0.685	−0.558	−0.921	0.442	0.667	−0.083	**0.999****	0.642	1

**. Significant correlation at $p < 0.01$.
*. Significant correlation at $p < 0.05$.
[a] Colloidal organic carbon.
[b] The adsorption percentage of FQs.

key role in the photooxidation of antibiotics (Song et al., 2007; Xu et al., 2011). In addition, correlation analysis also showed that the k_{obs} were positive correlated with binding of Fe, especially for OFL that are significant relationships ($r = 0.963$, $P < 0.05$) (Table 3). This result was proposed for the photo-oxidation of FQs by NCPs which involves formation of a surface complex between FQs and surface-bound Fe, especially Fe(III), through adsorption, and initial oxidation at the piperazinyl N_1 atom to form radical intermediates that ultimately lead to the final products (Zhang & Huang, 2007). In addition, Fe (III) in natural waters is commonly complexed by DOM or colloids through carboxylic acid functional groups (Faust & Zepp, 1993; Weller et al., 2013). The Fe(III)-carboxylate Fenton-like system without additional H_2O_2 to photodegrade organic pollutants in surface waters is also considered an effective way, because of its high efficiency generation of •OH, which can highly oxidate the organic pollutants (Mangiante et al., 2017; Wang et al., 2010). In order to validate this mechanism, the role of Fe (III) on the photochemistry reaction of FQs in the different size of NCP solutions was investigated (Table 2). The addition of Fe (III) well promoted the photodegradations of antibiotics in NCP solutions. This study indicates that Fe in NCPs may well play an important role in the photochemistry of fluoroquinolone antibiotics.

Unexpectedly, pH was not found to be significantly correlated with the k_{obs}. This result may be due to the narrow ranges of pH (6.24–6.74) in our NCP solutions. However, depending on the solvent pH, two antibiotics exhibit complex ionization patterns because of multiple ionizing groups with different pK_a values (Table S1). With increasing pHs from acidity to alkalinity, the predominant species of OFL and ENR changed from $(OFL/ENR)^+$ and $(OFL/ENR)^{\pm}$ to $(OFL/ENR)^-$ (Fig. S2), where the zwitterion and then anion dominate would have dramatic effects (Ge et al., 2018; Salma et al., 2016). In addition, it's worth mentioning that the correlation between COC and the k_{obs} was not statistically significant ($P > 0.05$). The most likely reason was NCPs are rarely found in purified forms but most often are components of complex heteroaggregates in natural systems, even a ‘homogeneous’ colloid class such as the humic substances are better described as a complex mixture that includes recognizable biomolecules (Wilkinson, 2007). This is also the focus to make clear the compositions of different size of NCPs, including organic and inorganic fractions, and even the quantification of roles they play in the photochemistry of pollutants in our further works.

4. Conclusions

This work provides the first photochemical data on the degradations of low concentrations of FQs in different size natural colloidal particles solutions under simulated sunlight irradiation. The results proved that different size NCPs were shown to be distinctly different efficient to photoactivate the degradation of antibiotics. Under the influence of NCPs, OFL and ENR underwent both direct and indirect photolysis. On one hand, the direct photolysis of OFL and ENR were inhibited by light screening in the NCP solutions, especially for the ultrafine NCPs that had the stronger inner-filter effects than larger ones. On the other hand, the photochemistry of OFL and ENR also had experienced indirect photolysis by photosensitization for the different size NCPs, which was consistent with a predominantly $^3COM^*$ mediated pathway. The adsorption of antibiotics on NCPs plays a very significant role in the photodecomposition of antibiotics. Our results demonstrate the need to conduct more systematic studies that investigate the role of the compositions of different size of NCPs in the photosensitized degradation of organic pollutants.

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Appendix B. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.envpol.2018.06.017.

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