



# Role of humic substances in the degradation pathways and residual antibacterial activity during the photodecomposition of the antibiotic ciprofloxacin in water



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## ABSTRACT

This study focuses on the photo-transformation, in presence of humic substances (HSs), of ciprofloxacin (CIP), a commonly-used fluoroquinolone antibiotic whose presence in aquatic ecosystems is a health hazard for humans and other living organisms. HSs from the International Humic Substances Society (Elliott humic acid and fulvic acid, Pahokee peat humic acid and Nordic lake) and a humic acid extracted from modified coal (HA<sub>CM</sub>) were tested for their ability to photodegrade CIP. Based on kinetic and analytical studies, it was possible to establish an accelerating effect on the rate of CIP decomposition caused by the humic substances. This effect was associated with the photosensitized capacity of the HSs to facilitate energy transfer from an excited humic state to the ground state of ciprofloxacin. Except for Nordic lake, which experienced a lower positive effect, no significant differences in the CIP transformation were found among the different humic acids examined. The photochemistry of CIP can be modified by parameters such as pH, CIP or oxygen concentration. The irradiation of this antibiotic in the presence of HA<sub>CM</sub> showed that antimicrobial activity was negligible after 14 h for *E. coli* and 24 h for *S. aureus*. In contrast, the antimicrobial activity was only slightly decreased after 24 h of irradiation by direct photolysis. Although mineralization of CIP irradiation in the presence of a HA<sub>CM</sub> solution was not achieved, biodegradability was achieved after 12 h of irradiation, indicating that microorganisms within the environment can easily degrade CIP photochemical by-products.

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## 1. Introduction

The presence of drugs in the environment and their fate are matters of increasing concern in recent years (Knapp et al., 2005; Petrie et al., 2015; Senta et al., 2013). Specifically, antibiotics constitute the most prevalent group of persistent drugs. These micro-pollutants are closely related to the proliferation of bacterial resistance to antibiotics and have a direct relationship with adverse ecological and human health effects (Korzeniewska et al., 2013; Rivera-Utrilla et al., 2013).

Fluoroquinolones (FQs) are an important group of antibiotics that are widely used in human and veterinary medicine. Among this group, ciprofloxacin (CIP) is one of the most frequently prescribed compounds because of their broad activity spectrum against gram-positive and gram-negative bacteria and good oral intake properties. After administration, CIP is only partially metabolized in the body and largely excreted in its pharmacologically active form (Babić et al., 2013; Schaeffer, 2002). Previous research has demonstrated the presence of CIP in environmental matrices and the inefficiency of wastewater treatment plants to completely remove CIP from wastewaters (Gros et al., 2006; Senta et al., 2013; Watkinson et al., 2007).

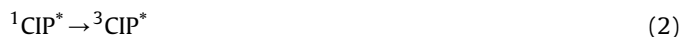
Additionally, it has been demonstrated that CIP is sensitive to UV-visible light (Albini and Monti, 2003). In fact, direct photolysis is an important removal pathway for this contaminant (Sturini

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et al., 2012a). Albin and Monti (2003) showed that the photoexcitation of CIP generates the triplet excited state  $^3\text{CIP}^*$  (Reactions 1 and 2). This state can produce photoproducts (Reaction 3), or react with molecular oxygen, which is an energy transfer process that leads to the formation of singlet oxygen (Reaction 4), or participate in an electron transfer process to form the superoxide anion and the CIP cation radical (Reaction 5).



However, some experimental conditions such as pH, irradiation wavelength and water matrix components can affect the photochemical pathways of certain pollutants in aquatic system. This is particularly the case for dissolved organic matter (DOM), which is mostly composed of humic substances (HSs) and can be viewed as a natural constituent in aquatic systems. It has been suggested that HSs may have some impact as a photosensitizer on the photodegradation kinetics of CIP because of their known reactivity under sunlight on the surface of water (Ge and Chen, 2010; Knapp et al., 2005).

Indirect photodegradation studies have evaluated different substrates and found that HSs can absorb light and produce triplet excited states ( $^3\text{HS}^*$ ), which can react via an energy transfer process with dissolved molecular oxygen or with other water constituents (Richard and Canonica, 2005). Humic excited states can also directly react with substrates in photoredox reactions (Cannonica et al., 1995; Golanoski et al., 2012; Wenk et al., 2011).

Despite the fact that the photodegradation reaction of CIP has been extensively investigated in different aquatic systems (Babić et al., 2013; Carlos et al., 2012; Ge and Chen, 2010), the mechanism by which HSs, as DOM models, participate in the process has not been investigated, at least to the best of our knowledge. Additionally, and in spite of CIP being a strong antibiotic, the roles of HSs in the reduction of antimicrobial activity and the enhancement of the biodegradability of the resulting solutions have been poorly evaluated.

Therefore, in this study the phototransformation of CIP in the presence of HSs was systematically investigated to elucidate the reaction pathways and contribute to the understanding of the matrix conditions that determine whether or not HSs are able to enhance the photochemical remediation of waters contaminated with this antibiotic. The reaction pathways were investigated by identifying both the main reactive species formed and the initial organic by-products generated. Further, the matrix composition was evaluated by examining the pH, type and concentration of the DOMs and the concentration of CIP. Finally, to provide further insight to the beneficial effects of HSs, the elimination of the antimicrobial activity of CIP and the improvement of the biodegradability of the treated solutions in the presence and absence of HSs were also investigated.

## 2. Experimental section

### 2.1. Reagents and materials

Sodium dihydrogen phosphate dihydrate, di-potassium hydrogen phosphate anhydrous, potassium hydrogen phthalate, hydrochloric acid fuming 37%, sodium hydroxide and acetonitrile gradient grade for liquid chromatography were purchased from Merck. Elliott humic acid ( $\text{HA}_E$ , 1S102H) and fulvic acid ( $\text{FA}_E$ , 2S102F), Pahokee peat humic acid ( $\text{HA}_{PEAT}$ , 1S103H) and the aquatic natural organic matter known as Nordic lake ( $\text{NOM}_{NORDIC}$ , 1R108N) were purchased from the International Humic Substances Society (IHSS). The humic acid sample known as  $\text{HA}_{CM}$ , as reported previously (Porras et al., 2014), was extracted in the laboratory from an air-modified low-rank coal from the Amaga region in Colombia. Ciprofloxacin (CIP, 99.3%) used as a target molecule was supplied by Sigma–Aldrich. Furfuryl alcohol (FFA, Sigma–Aldrich, 98%) was used as a scavenger of singlet oxygen and 2,4,6-trimethylphenol (TMP, Alfa-Aesar, 98%) was used as a scavenger of the triplet excited state. Water was purified using a Millipore Milli-Q device.

### 2.2. Solution preparation

HSs stock solutions of  $40 \text{ mg L}^{-1}$  were prepared in phosphate buffered solution ( $1 \times 10^{-3} \text{ M}$ ) at pH 8 and filtered through  $0.45 \mu\text{m}$  sterile cellulose acetate filters prior to use. A CIP stock solution ( $1.5 \times 10^{-4} \text{ M}$ ) was prepared in Milli-Q water and stored at  $4^\circ\text{C}$ . Finally, samples solutions of CIP-HSs mixtures were prepared from the stock solutions using Milli-Q water. Through HPLC it was verified that the aqueous CIP solutions are stable at room temperature for several days in the dark in the absence or presence of HSs. To evaluate the pH effect, CIP solutions were adjusted as required using sodium hydroxide (0.1 M) or hydrochloric acid (0.1 M).

### 2.3. Photochemical experiments

Polychromatic irradiations were conducted in a device equipped with five fluorescent tubes (TLAD 30W05 Philips) emitting wavelengths between 300 and 450 nm with a maximum at 365 nm. The reactor consisted of a Pyrex bottle, illuminated from the top, containing 20 mL of air-saturated CIP solution under magnetic stirring. The reactor was equipped with two fans, which kept the solution at  $25 \pm 1^\circ\text{C}$  (Supporting Information S1). Aliquots (1 mL) were withdrawn after selected irradiation times. Experiments under deoxygenated or oxygenated conditions were performed by purging argon or oxygen, respectively, into the prepared solutions prior to (20 min) and during the irradiation experiments. The aliquots were immediately analyzed by HPLC.

### 2.4. Analytical determination of CIP and the photoproducts

Quantitative analysis of CIP was performed in an HPLC Agilent series 1200 system using a C-18 column (Zorbax eclipse XDD-C18,  $4.6 \times 150 \text{ mm}$ ,  $5 \mu\text{m}$ ) with a phosphate buffer ( $1 \times 10^{-5} \text{ M}$ ; pH 3)/acetonitrile (87/13) solution as the mobile phase operated in isocratic mode. The injection volume was  $25 \mu\text{L}$  and CIP quantification was performed with a UV detector (278 nm). HPLC–MS analysis was carried out using an Agilent Chromatograph equipped with a UV–visible photodiode array detector and atmospheric-pressure ionization (API) chamber working in positive mode using a reverse phase column (Zorbax eclipse XDD-C18,  $4.6 \times 150 \text{ mm}$ ,  $5 \mu\text{m}$ ).

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