



Role of humic substances in the photodegradation of naproxen under simulated sunlight



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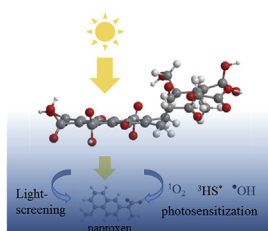
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HIGHLIGHTS

- HA inhibited the photodegradation of naproxen thoroughly.
- FA acted as dual roles in the photodegradation of naproxen (NP).
- $^3\text{NP}^*$ and $^1\text{O}_2$ account for direct photodegradation of naproxen.
- FA-mediated photodegradation was attributed to $^1\text{O}_2$ in aerated solution.

GRAPHICAL ABSTRACT



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ABSTRACT

Humic substances (HS) including humic acid (HA) and fulvic acid (FA) are ubiquitous in the natural waters. Although numerous studies documented their role in photodegradation of organic pollutants, the competitive effects of photosensitization and light-screening of HS on the photodegradation of pollutants are not yet clear. In this work, the role of HS in the photodegradation of the pharmaceutical naproxen (NP) was studied under simulated sunlight. The direct photodegradation quantum yield of NP in deionized water was 2.1×10^{-2} , and the apparent quantum yields for photosensitized degradation of NP in the presence of FA and HA were 2.3×10^{-4} and 2.6×10^{-5} , respectively. Both direct and photosensitized photodegradation decreased with increasing pH, consistent with the trend of singlet oxygen ($^1\text{O}_2$) reaction rate constants of NP. HA inhibited the photodegradation of naproxen thoroughly. In contrast, FA accelerated the photodegradation of NP at lower substrate concentration and light intensity, and vice versa. Direct photodegradation of NP declined sharply with spectral radiation attenuation of UV region, when HS-mediated photosensitization predominantly accounted for the photodegradation. The direct photodegradation was ascribed to decomposition of excited triplet state of naproxen ($^3\text{NP}^*$) and self-sensitization effect involving $^1\text{O}_2$. The FA-mediated photodegradation was mainly attributed to $^1\text{O}_2$ oxidation in aerated solution. These findings are important for assessing the competitive effects of humic substances on the photodegradation of pollutants under various conditions in natural waters.

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1. Introduction

The naturally occurring humic substances are ubiquitous in

surface waters (both fresh and marine waters), groundwaters, and soil porewaters where they play an essential role in numerous environmentally important processes (Zuo and Jones, 1997; Schmitt-Kopplin et al., 1998). Humic substances are yellowish-brown in color and have light absorption overlapped with the spectrum of terrestrial sunlight. It is well known that HS can

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undergo photochemical reactions to form hydroxyl radical ($\cdot\text{OH}$) (Vaughan and Blough, 1998), singlet oxygen ($^1\text{O}_2$) (Haag and Hoigné, 1986), superoxide radical anion and its conjugate acid ($\text{O}_2^{\cdot-}/\text{HO}_2^{\cdot}$) (Goldstone and Voelker, 2000), H_2O_2 (Draper and Crosby, 1983), hydrated electron (e_{aq}^-) and the excited triplet state of humic substances ($^3\text{HS}^*$) (Zepp et al., 1987). The formed $\cdot\text{OH}$ is readily quenched by HS itself (Hoigné et al., 1988), and e_{aq}^- is reactive to some electrophilic halogenated compounds (Burns et al., 1997). $\text{O}_2^{\cdot-}/\text{HO}_2^{\cdot}$ and H_2O_2 act indirectly as important precursors of reactive transients, but their oxidation capabilities are weak and they hardly induce appreciable transformation of organic contaminants (Richard and Canonica, 2005). Both $^1\text{O}_2$ and $^3\text{HS}^*$ play an important role in the indirect photodegradation of pollutants in natural waters (Vione et al., 2014).

The photosensitized degradation of pollutants in the presence of HS has already been reported (e.g. Boreen et al., 2003; Richard and Canonica, 2005; Chen et al., 2009; Yan and Song, 2014; Li et al., 2016). HS-mediated indirect photodegradation is considered a major attenuation pathway for pollutants that show little sunlight absorption (Oliveira et al., 2016; Silva et al., 2016a, 2016b). Mostly, HS act as inner filter and inhibit the direct photodegradation of organic pollutants (Vione et al., 2010). However, as mentioned above, HS are also capable to produce the reactive species such as $^1\text{O}_2$ and $^3\text{HS}^*$, which accelerate the photodegradation. Thus, HS could play dual roles in the degradation of pollutants that are susceptible to direct photolysis. The total effect depends on the competition between light-screening and photosensitization. Due to different reaction conditions, there are many studies reporting contrasting roles of HS in photodegradation even for the same compounds (e.g. Han et al., 2009; Leech et al., 2009; Chowdhury et al., 2010; Atkinson et al., 2011; Caupos et al., 2011; Bao and Niu, 2015). Therefore, it is essential to evaluate the dual roles of HS in the photodegradation to rationalize the paradoxical conclusions. Different sources of HS may result in different photoreactivity (Batista et al., 2016; Porras et al., 2016). Interestingly, we have found that the incident light intensity can also affect the dual roles of HS in the photodegradation of organic pollutant (Chen et al., 2013). However, the effect of other reaction parameters, including substrate concentration, solution pH, and spectral radiation attenuation is still unknown.

Naproxen is a synthetic non-steroidal anti-inflammatory drug (NSAID) and frequently prescribed as an analgesic, antiarthritic, and antirheumatic. It has been widely detected in the effluents of wastewater treatment plants (WWTPs), surface waters, and even drinking water with concentrations ranging from ng L^{-1} to $\mu\text{g L}^{-1}$ (Verenitch et al., 2006; Benotti et al., 2009; Lindholm-Lehto et al., 2016; Gumbi et al., 2017). Naproxen is photolabile and associated with a high incidence of both photoallergic and phototoxic reactions due to the production of reaction oxygen species and more toxic photoproducts (DellaGreca et al., 2004; Isidori et al., 2005; Bracchitta et al., 2013). Several studies on the photodegradation of naproxen have been published (Bosca et al., 2001; Arany et al., 2013; Durán-Álvarez et al., 2015; Avetta et al., 2016; Vulava et al., 2016). Although the role of singlet oxygen is discussed, the photodegradation mechanism especially in HS solutions is not fully understood.

The objective of this study is, therefore, to (i) determine quantum yields of direct and indirect photodegradation of naproxen, (ii) investigate the effect of naproxen concentration, incident light intensity, pH, and spectral radiation attenuation on the dual role of HS in the photodegradation of naproxen, (iii) probe into direct and indirect photodegradation mechanism of naproxen by quenching experiments.

2. Materials and methods

2.1. Chemicals

Naproxen (99%), pyridine (PYR, 99%) and sorbic acid (99%) were purchased from Sigma. *p*-nitroanisole (PNA, > 98%) was supplied by TCI. Humic acids (C, 35.06%; H, 3.77%; O, 60.11%; N, 1.06%) were obtained from Sigma. Fulvic acids (C, 51.04%; H, 5.22%; O, 39.13%; N, 4.62%) were extracted from weathered coal by acetone-sulfuric acid method and supplied by Henan ChangSheng Corporation. 2-propanol (99%) and NaN_3 (99%) were supplied by Wuhan chemicals corporation. All chemicals used were of at least analytical-reagent grade.

2.2. Photodegradation experiments

The photodegradation experiments were performed in a capped cylindrical Pyrex vessel (40 mm i.d., containing 50 mL of solution) with tubing in the cap to allow for bubbling solutions. The light source used was a 150-W Xenon Short Arc Lamp (Zolix Corporation, Beijing) and a cooling fan of the photochemical instrument controlled the temperature at 22 ± 1 °C. The light of wavelengths lower than 300 nm was filtered out with Pyrex glass to simulate sunlight. For the spectral radiation attenuation experiments, 320, 340, 360, 380, and 400 nm filters were used to cut off the light lower than the corresponding wavelengths. Light intensity was controlled by the input of constant electric current and monitored using the *p*-nitroanisole/pyridine (PNA/PYR) actinometer (Dulin and Mill, 1982). Deoxygenation was achieved by bubbling nitrogen gas into the solutions all the time. In general, 5.0 μM NP was irradiated in the presence of FA and HA (10 mg L^{-1}) at pH 7.0. Inhibition experiments were carried out with addition of 10 mM 2-propanol, NaN_3 , and sorbic acid in the reaction solutions. All photodegradation experiments were conducted in phosphate (10 mM) buffered solutions. Aliquots of samples (~300 μL) were withdrawn at various intervals and substrate decay was measured by HPLC. Three sequential replicates were included in all photodegradation experiments.

2.3. Determination of quantum yields of photodegradation

The quantum yield for direct photodegradation of NP was measured at pH 7.0 under simulated sunlight. The value was calculated according to Eq. (1) (Dulin and Mill, 1982).

$$\phi_s = \frac{k_s \sum L_\lambda \epsilon_\lambda^a}{k_a \sum L_\lambda \epsilon_\lambda^s} \phi_a \quad (1)$$

where *s* and *a* represent the substrate and actinometer, respectively. *k* is the rate constant for direct photodegradation (s^{-1}), L_λ values are lamp irradiance at a specific wavelength, obtained from the manufacturer, ϵ_λ values are the molar absorptivity of the substrate or actinometer ($\text{M}^{-1} \text{cm}^{-1}$) (Fig. 1 and Fig. A1), ϕ is the quantum yield of photodegradation. The quantum yield of *p*-nitroanisole/pyridine (PNA/PYR) actinometer was wavelength-independent and calculated according to Eq. (2) (Leifer, 1988).

$$\phi_s = 0.437[\text{PYR}] + 2.82 \times 10^{-4} \quad (2)$$

The apparent quantum yields (ϕ_i) of indirect photodegradation of NP in FA and HA solutions were determined using a filter to cut off the light with wavelength lower than 360 nm to exclude direct photodegradation of NP. The determination of apparent quantum yield has been described elsewhere as Eq. (3) (Chen et al., 2009).

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