



Light-source-dependent role of nitrate and humic acid in tetracycline photolysis: Kinetics and mechanism



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HIGHLIGHTS

- Tetracycline (TC) photolysis followed pseudo-first-order kinetics.
- Light-source-dependent TC photolysis was promoted or inhibited by NO_3^- or HA.
- TC photolysis involved O_2^- -mediated self-sensitized photolysis.
- TC photolysis pathways involved hydroxylation and loss of some groups.

ARTICLE INFO

Article history:

Received 7 October 2012
Received in revised form 11 March 2013
Accepted 25 March 2013
Available online 22 April 2013

Keywords:

Photolysis
Tetracycline
Humic acid
Nitrate
Light conditions

ABSTRACT

To elucidate the environmental fate of tetracycline (TC), we reported the light-source-dependent dual effects of humic acid (HA) and NO_3^- on TC photolysis. TC photolysis rate was highly pH- and concentration-dependent, and was especially enhanced at higher pH and lower initial TC concentrations. Under UV-254 and UV-365 irradiation, HA inhibited TC photolysis through competitive photoabsorption or reactive oxygen species (ROS) quenching with TC; under solar and xenon lamp irradiation, TC photolysis was enhanced at low HA concentration due to its photosensitization, whereas was suppressed at high HA concentration due to competitive photoabsorption or ROS quenching with TC. Similarly, the effect of NO_3^- on TC photolysis varied with light irradiation conditions. Even under the same light irradiation conditions, the effects of HA or NO_3^- on TC photolysis varied with their concentrations. The electron spin resonance spectrometer and ROS scavenger experiments demonstrated that TC photolysis was involved in O_2^- -mediated self-sensitized photolysis. The photolysis pathways were involved in hydroxylation and loss of some groups. More toxic intermediates than TC were generated under different light irradiation conditions. These results can provide insight into the potential fate and transformation of TC in surficial waters.

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1. Introduction

Recently, tetracycline (TC) has received great attention due to its booming application in husbandry, aquaculture, and medical treatment (Khetan and Collins, 2007). When released into aqueous environment, TC can destruct the ecosystem balance, develop the resistant genes, and harm human health (Gu and Karthikeyan, 2005; Barkovskii and Bridges, 2012). Therefore, it is highly urgent to investigate the environmental behaviors of TC in aqueous systems.

Photolysis is an important transformation pathway for TC in natural aqueous environments (Wammer et al., 2011). TC can undergo direct photolysis (Jiao et al., 2008) and indirect photolysis initiated by natural aquatic constituents, such as humic acid (HA) and nitrate (NO_3^-) (Bautitz and Nogueira, 2007; Chen et al., 2008;

Jiao et al., 2008; Wammer et al., 2011; Gómez-Pacheco et al., 2012). We did a comprehensive literature research on the role of HA and NO_3^- in TC photolysis, which was summarized in Table S1 of the Supplementary Information (SI). HA can either promote or suppress TC photolysis under different light irradiation conditions (Chen et al., 2008; Jiao et al., 2008; López-Peñalver et al., 2012). For example, TC photolysis was promoted by HA under UV-365 irradiation (Jiao et al., 2008), whereas was attenuated by HA under gamma irradiation (López-Peñalver et al., 2012). Similarly, NO_3^- promoted, suppressed or had little effect on TC photolysis under different light irradiation conditions (Bautitz and Nogueira, 2007; Chen et al., 2008; Jiao et al., 2008; López-Peñalver et al., 2012). Obviously, differences in experimental conditions (e.g., HA and NO_3^- concentration) and solution chemistry (e.g. pH and ionic strength) largely hamper comparisons among different studies on the role of HA and NO_3^- in TC photolysis. Therefore, it is imperative to investigate the light-source-dependent effects of HA and NO_3^- on TC photolysis kinetics under the same experimental conditions.

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In addition to direct or indirect photolysis, TC can also undergo self-sensitized photolysis (Chen et al., 2008). TC concentration in surface water and groundwater around the world is at the $\mu\text{g L}^{-1}$ levels (Jiang et al., 2011; Wei et al., 2011). As the generated reactive oxygen species (ROS) was too low to be detectable for TC at the $\mu\text{g L}^{-1}$ levels, it is difficult for us to investigate the self-sensitization of TC at the $\mu\text{g L}^{-1}$ levels. In some cases, the concentration is high (up to a few mg L^{-1}), such as sewage treatment plant and hospital wastewater (de Godos et al., 2012). Therefore the high levels of TC could be of substantial environmental concern and the self-sensitization of TC should be considered at the mg L^{-1} levels. Some studies have demonstrated that ROS was generated during TC photolysis (Hasan and Khan, 1986; Miskoski et al., 1998; Khan and Musarrat, 2002; Chen et al., 2008). Nevertheless, the type of ROS responsible for TC self-sensitized photolysis is still highly contentious. For example, several studies have demonstrated that singlet oxygen ($^1\text{O}_2$) was responsible for the self-sensitized TC photolysis (Hasan and Khan, 1986; Miskoski et al., 1998; Chen et al., 2008, 2011). Other study found that superoxide radical ($\text{O}_2^{\cdot-}$) was responsible for the self-sensitized TC photolysis (Khan and Musarrat, 2002).

Many previous reports mainly focused on one light irradiation condition when investigating the toxicity of TC and its intermediates (Jiao et al., 2008; Wammer et al., 2011; López-Peñalver et al., 2012). The toxicity of TC and its photoproducts varied with light irradiation conditions. Some works demonstrated that the photoproducts are more toxic than TC under UV-254 and UV-365 irradiation (Jiao et al., 2008; López-Peñalver et al., 2010). In comparison, Wammer et al. (2011) found that the toxicity of TC and its photoproducts decreased under simulated sunlight irradiation. Therefore, it is interesting to compare the toxicity of TC and its intermediates under different light irradiation conditions and make sure which light irradiation condition is more environmentally compatible for TC photolysis.

In this work, we investigated the light-source-dependent effects of environmental factors (i.e., initial TC concentration and pH) and primary water constituents (i.e., HA and NO_3^-) on TC photolysis. The light irradiation conditions included sunlight (natural or simulated), which was relevant in natural water, and UV light (UV-254 and UV-365), which was relevant in water treatment plants. The ROS and photoproducts were investigated to elucidate the TC photolysis mechanism. Furthermore, the light-source-dependent toxicity evolution during the TC photolysis was also discussed.

2. Experimental section

2.1. Photolysis experiments

The materials and chemicals used in our experiments are shown in Section S1. Four light sources were used to investigate the light-source-dependent TC photolysis: solar light in Peking ($116^\circ 17' \text{ N}$, $39^\circ 56' \text{ E}$, March, 11:00 am–1:00 pm, 2012) (Chen et al., 2006), a xenon lamp (CHF-XM-500W; Trusttech, China) with wavelength of 300–800 nm to simulate sunlight, and a UV lamp (Cnlight Co., Ltd.) with prominent emission bands at approximately 365 nm (UV-365) and 254 nm (UV-254). The light intensities of the solar and the xenon lamp in the center of the TC solution were $6.0\text{--}8.0 \text{ mW cm}^{-2}$ and 12.0 mW cm^{-2} , respectively, as measured by a radiometer (Spectra Evolution, SR-1100). The light intensity of the UV lamp in the center of the reactive solution was 14.0 and 19.2 mW cm^{-2} for UV-365 and UV-254, respectively, as measured by a UVX radiometer (Model UVX-25, UVP Co.). Fig. S2 of the SI shows the schematic of the photolysis experiments.

2.2. Determination of reactive oxygen species

Electron spin resonance (ESR; Bruker ESP-300E, Germany) signals for ROS were obtained on a Bruker model ESP300E electron

paramagnetic resonance spectrometer. DMPO (0.2 M) was used as the spin trap for hydroxyl radical ($\cdot\text{OH}$) and $\text{O}_2^{\cdot-}$. TEMP (0.2 M) was used as the spin trap for $^1\text{O}_2$. ESR measurements were conducted at room temperature as reported previously (Li et al., 2011a).

2.3. Instrument analysis

High performance liquid chromatography (HPLC; Waters 2830, USA) was employed to measure TC concentration. The photoproducts of TC were analyzed by HPLC-MS-MS using an Applied Biosystems triple-quadrupole mass spectrometer (Applied Biosystems; API3200, USA) coupled to the same HPLC system. Section S2 of the SI summarizes the detailed HPLC and HPLC-MS-MS methods.

2.4. Toxicity assessment of TC and its photoproducts

The toxicity of TC and its photoproducts was indicated by its bioluminescence inhibition assay toward *Photobacterium phosphoreum* (*P. phosphoreum*). The bacteria were reactivated according to the reported method (Li et al., 2011a). The bioluminescence was measured and the luminescence inhibition percentage (%) was calculated according to the published method (Li et al., 2011a).

3. Results and discussion

3.1. Light-source-dependent photolysis kinetics of TC

In the dark condition, TC biodegradation and hydrolysis is below 5.0% and thus can be neglected during photolysis as shown in Fig. S3 of the SI. The light-source-dependent TC photolysis is shown in Fig. 1a. The plot of $\ln(C_0/C_t)$ versus reaction time (t) yielded straight lines with the correlation coefficient (R^2) higher than 0.94 (Table S2), indicating that TC photolysis followed pseudo-first-order kinetics. The photolysis rate constants under four types of light irradiation conditions followed the order of UV-254 > UV-365 > solar > xenon lamp with TC concentration of 10 mg L^{-1} (see Table S2 of the SI). The photolysis rate constants varied with light wavelength and intensity, demonstrating that TC photolysis was light-source-dependent. Ge et al. (2009) observed similar phenomenon for the photolysis of phenicols that quickly disappeared under UV-Vis irradiation but was stable under sunlight irradiation. The absorption spectrum of TC contains two bonds in the regions of 230–320 and 320–370 nm, with peak wavelengths of ca. 275 nm and 360 nm (Fig. 1b). The photoabsorption in these regions contributes to TC photolysis under UV irradiation. Solar and xenon lamp radiation contains a small fraction (<5%) of UV light (Hong et al., 2005), which contributes to TC photolysis. The relative light intensity of each type of light source was normalized by that of solar irradiation. The photolysis rate constants were then divided by the relative light intensities to obtain the light-intensity-normalized TC photolysis rate constants, which were 0.020, 0.016, 0.005, and 0.003 min^{-1} under UV-254, UV-365, solar, and xenon lamp irradiation with TC concentration of 10 mg L^{-1} , respectively. Based on the photolysis parameters, including light intensity, wavelength, irradiation area of the photolysis reactor (Yin et al., 2010), the calculated quantum yields were approximately 0.18%, 0.16%, 0.07%, and 0.04% under UV-254, UV-365, solar, and xenon lamp irradiation, respectively. Both the light-intensity-normalized TC photolysis rate constants and the quantum yields followed the order of UV-254 > UV-365 > solar > xenon lamp, explaining the light-source-dependent TC photolysis rate order.

The light-source-dependent TC photolysis with the initial concentrations varying from 10 to 40 mg L^{-1} is shown in Fig. 1c and d. Similarly, the fitting results showed that TC photolysis followed first-order kinetics at different initial TC concentrations under varying light irradiation conditions. Taking xenon lamp for exam-

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