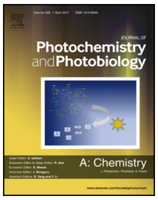
Journal of Photochemistry and Photobiology A: Chemistry 356 (2018) 239–247

Contents lists available at ScienceDirect

Journal of Photochemistry and Photobiology A: Chemistry

journal homepage: www.elsevier.com/locate/jphotochem



The effect of pH, nitrate, iron (III) and bicarbonate on photodegradation of oxytetracycline in aqueous solution

Chanjuan Li[a], Dahai Zhang[a], Jialin Peng[b], Xianguo Li[a,*]

[a] *Key Laboratory of Marine Chemistry Theory and Technology (Ocean University of China), Ministry of Education, Qingdao 266100, China*
[b] *Qingdao Institute of Bioenergy and Bioprocess Technology, Chinese Academy of Sciences, Qingdao 266101, China*

ARTICLE INFO

Article history:
Received 13 October 2017
Received in revised form 2 January 2018
Accepted 3 January 2018
Available online 3 January 2018

Keywords:
Oxytetracycline
Photodegradation
pH
Comprehensive effect
Simulated sunlight

ABSTRACT

Photodegradation is a very important elimination pathway of Oxytetracycline (OTC) in aquatic environments. The photochemical behavior of OTC in absence/presence of nitrate, iron (III) and bicarbonate, especially their combinations, was systematically studied in aqueous solution by employing a Suntest-CPS+ sunlight simulator in this work. Meanwhile, the effect of solution pH (4.8–9.1) and irradiation intensity (250–500 W/m^2) on the removal efficiency of OTC have also been assessed. The results showed that OTC degradation followed a pseudo-first-order kinetics in most conditions except for irradiation in neutral/alkaline solutions and in presence of NO_3^-, where a two-step pseudo-first-order kinetics was obeyed. OTC degradation was highly pH-dependent and increased significantly with increasing pH. The presence of NO_3^- and HCO_3^- promoted the photochemical loss of OTC in aqueous solution by generating hydroxyl radicals and adjusting solution pH, respectively; whereas iron (III) was found to play a negative role under the conditions studied. The influence of NO_3^- coupled with Fe^{3+} was not a simple additive effect and the overall performance was to inhibit OTC degradation. In addition, combination of HCO_3^- and NO_3^- exhibited an antagonistic effect. Results from irradiation in co-presence of NO_3^-, Fe^{3+} and HCO_3^- suggested that direct photolysis of OTC was much more efficient than its indirect photolysis. These results provide a meaningful reference for understanding the fate and transformation of OTC in natural water systems.

1. Introduction

Antibiotics, a class of pharmaceutical and personal care products(PPCPs), are produced and consumed in great quantities worldwide, and are becoming the focus of attention because of the issue of antibiotics-resistant bacteria and genes. China, as the largest producer and user of antibiotics all around the world, consumed 92,700 tons of 36 frequently used antibiotics, with about 53,800 tons released into the general environment in 2013 [1,2]. Among those antibiotics, oxytetracycline (OTC) is an important member of tetracyclines (TCs) that is extensively used for treating human and animal diseases and applied as a feed additive for promoting animal growth in a variety of aquacultures [3]. The applied TCs are poorly ingested by organisms, and the majority is excreted in faeces and urine without metabolism. TCs are therefore widely detected in various environmental components, such as surface waters and sewage water [4,5]. Zou et al. reported that the concentration of OTC in Bohai Bay was up to 0.27 μg/L [6]; while OTC has been detected in very high concentrations ranging from 20 to 800 mg/L in one of the biggest OTC producer's wastewater treatment plant in China [7]. Conventional water treatment methods, such as filtration, coagulation, flocculation and biodegradation showed very poor efficiencies to remove OTC due to its chemical stability and bio-resistance [8]. The extensive usage and frequent detection of antibiotics poses a great threat to the general ecosystem and human health through the development of antibiotics-resistant bacteria and pathogens [9]. For example, OTC has been involved in the aetiology of several diseases, such as hypouricemia and hypokalemia [10]. It can also exhibit significantly toxic effects to algae, which as primary producers play a key role in the whole aquatic ecosystem [11]. Aquatic environment is vital to the survival of humans, animals and plants, and waters are important media for the occurrence of OTC. Therefore, it is meaningful to assess the behavior and fate of OTC in aquatic environments.

Photochemical degradation is an important pathway of OTC elimination in surface waters [3,12,13]. In recent years, photodegradation of OTC using advanced oxidation processes (AOPs),

---

* Corresponding author.
E-mail addresses: 1576522502@qq.com (C. Li), lixg@ouc.edu.cn (X. Li).

https://doi.org/10.1016/j.jphotochem.2018.01.004
1010-6030/

such as Photo-Fenton oxidation, UV/TiO_2, UV/MgAl calcined hydrotalcites, UV/H_2O_2, UV/Persulfate (PS), has been extensively studied by several groups due to the efficient formation of strongly oxidative radicals to highly effectively remove OTC [9,14–18]; whereas researches related to the environmental fate and transformation of OTC were quite sparse. Psoralen and Riboflavin, used as phototherapy drugs, have been reported that they could act as photosensitizers themselves [19,20]. Upon UV or visible light irradiation, their triplet excited state can react with oxygen to generate reactive oxygen species (ROSs, such as $^1O_2$), which is a central intermediate for cytotoxic action in potential photodynamic therapy. The common pathways involved in the phototransformation of OTC in surface waters were direct photolysis [13,21], indirect photolysis with ROSs (such as $HO^•$, $^1O_2$, $O_2^{-•}$)[10] and even self-sensitized degradation[22]. These photochemical processes can be substantially impacted by complex aquatic constituents, such as humic acids (HA), Fe^{3+}, NO_3^-, HCO_3^-, Cl^- and SO_4^{2-} etc., which can act as either sensitizers to enhance the indirect photodegradation or as irradiation filters and/or $HO^•$ scavengers to inhibit photolysis of organic compounds. Among these common constituents, Fe^{3+}, NO_3^- and HCO_3^- are ubiquitous in natural aquatic environments and previous studies have shown that they play an important role in the photodegradation of organic pollutants [23–26]. However, most of these studies were focused on the individual effect of each component on photolysis, and their interaction on photodegradation of OTC is poorly understood. Therefore, the underlying mechanism for the comprehensive effects of nitrate, ferric ion and bicarbonate needs to be further clarified.

OTC is an amphoteric molecule which consists of a 4-ring system with multiple function groups such as tertiary amino- and hydroxyl- groups (**SI, Fig.S1**). Solution pH, as one of the important factors for photodegradation of organic pollutants [27,28], could simultaneously affect the speciation and structure as well as degradation mechanism of OTC. pH may have different effects on OTC photodegradation under different operating conditions, such as light source, temperature, presence/absence of oxygen. For example, Liu et al. suggested that OTC photodegradation followed a pseudo-first-order kinetics at various pH values from 3.0 to 11.0 in UV-C system and UV/H_2O_2 system [29]; Jin et al. reported that OTC photolysis followed a second-order kinetics in oxygen-free condition and pointed out that thermodynamic collision process occurred in alkaline condition [13]. Recently, diverse researches focused on the photocatalytic degradation of OTC have showed that the degradation rate of OTC in aqueous solution was greatly affected by pH, and OTC degradation was optimal at the zero-point charge (pH_{zpc}) due to its higher adsorption onto the surface of catalyst, leading to increased rate of OTC degradation [30–32]. The effect of pH on degradation of OTC under simulated sunlight was rather scarce. Thus, as one of the key factors of aquatic systems, pH deserves extensive attention for studies on photodegradation of OTC.

With this background in our mind, the objective of the present study was to investigate the behavior and kinetics of OTC photodegradation in simulated natural water system. The main scope of this work was to investigate direct and indirect photolysis of OTC in presence/absence of nitrate, iron (III) and bicarbonate in aqueous solution under simulated sunlight irradiation, with particular emphasis on the interaction of these three ions on photochemical degradation of OTC. The influences of pH as well as irradiation intensity were also evaluated. We believe the study is of significance for understanding the environmental fate of OTC in surface waters and helps to better evaluate the environmental fate and persistence of other antibiotics in natural waters.

2. Materials and methods

2.1. Chemicals

Oxytetracycline hydrochloride (purity: 96.5%, CAS: 2058-46-0) was purchased from Dr. Ehrenstorfer-Gmbh (Germany). High performance liquid chromatography (HPLC)-graded solvents (acetonitrile, formic acid) were obtained from J&K Chemical Co. Ltd. (Beijing, China). Other chemicals, such as $NaNO_3$, $NaHCO_3$, $FeCl_3 \cdot 6H_2O$, NaCl and isopropanol are all of analytical grade and were used directly without further purification. HCl (0.1 M) and NaOH (0.2 M) were used for pH adjustment. All the experiments have been performed at pH 7.0 (±0.1) except for those designed for studying the effects of initial pH.

Individual stock solution of OTC was prepared by dissolving Oxytetracycline hydrochloride in Millie-Q water from a Millipore Gradient A10 system (USA) to achieve a final concentration of 250 mg/L. This solution was freshly prepared before experiments and stored in dark at 4 °C. OTC solution for photolysis was prepared by adding an appropriate volume of stock solution into Millie-Q water to obtain a concentration of 20 mg/L, and filled into quartz cuvettes (φ28 mm × 60 mm) for irradiation.

2.2. Photo-degradation experiments

Irradiation was provided by a Suntest CPS+ sunlight simulator (Atlas, Germany) equipped with a 1.1 kW xenon lamp which simulates natural sunlight. Special UV filters are provided to yield desired irradiation spectra. The wavelength of excitation source for all degradation reactions is in a range of 300–800 nm. Schematic and radiation intensity at different wavelengths of the sunlight simulator are given in Supporting information (**Fig.S2**). Irradiance was maintained constant at 765 W/m^2 during all the experiments except for the study that considers the effects of light intensity. Capped quartz tubes with 25 mL OTC solution were soaked in a water bath and secured in the groove of the device, directly under the irradiance. The temperature of the water bath was kept constant at 20 °C, controlled by a cooling water circulator. As dark controls, some of the reaction tubes were wrapped with aluminum foil and set aside separately at the same temperature of 20 °C. At each designated time interval, one of the reaction tubes was removed periodically. Then 1.5 mL reaction mixture was taken out from the tube using a syringe and filtered through a 0.22 μm membrane before the OTC concentration was quantified by using a high-performance liquid chromatography (HPLC).

2.3. Analytical method

The concentration of OTC was analyzed by using a Hitachi L-2000 series HPLC system, equipped with a L-2130 binary pump, a L-2200 auto sampler, a L-2300 column compartment and a L-2455 diode-array detector. The analytical column was a Venusil MP C18 reverse-phase column (250 mm × 4.6 mm, 5 μm, Agela Technologies, China) in a thermostatic oven at 30 °C. The mobile phase A was acetonitrile and B was ultrapure water with 0.15% formic acid (20:80, v/v). The injection volume was 20 μL with a constant flow rate of 1.0 mL/min for mobile phase. The analytical wavelength of the diode-array detector was set at 267 nm.

pH values were measured with a pH meter (pH-220, Qiwei, China). UV–vis spectra of OTC and ions selected for study (nitrate, iron (III), bicarbonate) were analyzed by an ultraviolet spectrophotometer (UV2550, Shimaduz, Japan)