Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2015.1103309

57 (2016) 19981–19987
September

Photodegradation of tetracycline antibiotics in aqueous solution by UV/ZnO

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Received 15 April 2015; Accepted 29 September 2015

ABSTRACT

Photodegradation of three tetracycline antibiotics (TCs), tetracycline (TTC), oxytetracycline (OTC), and chlorotetracycline (CTC), by UV/ZnO were studied. The effects of ZnO concentration (0.5–2.0 g L^{-1}) and solution pH (5–11) were evaluated. Results revealed that the photodegradation of TCs were enhanced by increasing ZnO dosage and solution pH. The TOC rose first and then fell during the photodegradation of TTC and CTC, which could be explained by the reaction sequences, i.e. adsorption, degradation, and then mineralization. Acute toxicity assessment indicated an obvious inhibitory effect and the increased toxicity of TCs photodegradation products on the growth of *Photosbacterium phosphoreum* T3 once the photodegradation reaction started. This research firstly investigated the photodegradation of TCs under UV/ZnO process, which would have a potential significance for the practical treatment of TCs wastewater.

Keywords: Tetracycline antibiotics; Photodegradation; UV/ZnO; TOC; Toxicity

1. Introduction

Tetracycline antibiotics (TCs) are one group of the most widely used antibiotics for preventing and treating diseases and used as medicine, feed additives for livestock [1,2], and antibacterial agents in aquaculture [3]. Tetracycline (TTC), oxytetracycline (OTC), and chlorotetracycline (CTC) are 3 commonly used TCs. More and more attention has been drawn into TCs not only due to the large quantity of usage and sales, but also the residual concentration level in both aquatic and soil environment [4–7]. TCs used as veterinary antibiotics may enter the aquatic environment after animal manure is applied as fertilizer, leading to potential adverse impacts on aquatic and terrestrial organisms [4].

TCs can be easily degraded in aqueous solution by photocatalytic processes in short time periods [8–10]. Series of photocatalytic processes are conducted by employing semiconductors, such as zinc oxide (ZnO) and titanium dioxide (TiO_2). When the semiconductors adsorb photons with an equal or higher energy to the band gap, the valence band electrons (e^-) will be promoted to the conduction band energy level with the generation of holes (h^+) in valence band (reaction (1)). The holes could react with water (H_2O) and hydroxyl ions (OH^-) trapped on the catalyst surface and produce hydroxyl radicals (reactions (2) and (3)). Meanwhile, the promoted electrons can further react with oxygen to generate superoxide ions ($^{\cdot}O_2^-$) which can subsequently produce hydrogen peroxide (H_2O_2) and hydroxyl ions (reactions (4) and (5)). Then, reaction between hydrogen peroxide and the conduction

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band electrons yields far more hydroxyl radicals and hydroxyl ions (reaction (6)). In the whole photocatalytic process, the formed hydroxyl radicals considered as strong oxidant and the holes can both directly oxidize the adsorbed organic matter (OM) leading to the degradation reaction (reactions (7) and (8)) [10–12].

$$\text{Semiconductor} + h\nu \rightarrow e^- + h^+ \tag{1}$$

$$h^+ + H_2O \rightarrow H^+ + {}^{\bullet}OH \tag{2}$$

$$h^+ + OH^- \rightarrow {}^{\bullet}OH \tag{3}$$

$$e^- + O_2 \rightarrow {}^{\bullet}O_2^- \tag{4}$$

$$^{\bullet}O_2^- + H_2O + H^+ \rightarrow H_2O_2 + OH^- \tag{5}$$

$$H_2O_2 + e^- \rightarrow {}^{\bullet}OH + OH^- \tag{6}$$

$$^{\bullet}OH + \text{organic matter (OM)} \rightarrow \text{degradation of OM} \tag{7}$$

$$h^+ + OM \rightarrow OM^{\bullet +} \rightarrow \text{oxidation of OM} \tag{8}$$

It was reported that about 70% of TTC would be removed after 5 h UV irradiation in absence of catalysts, but only 10% of TOC was mineralized [13]. In contrast, close to 50% of TTC was eliminated after 10 min and 90% of TOC was removed after 120 min in the presence of 0.5 g L^{-1} TiO_2 under UV irradiation [9]. With 1.0 g L^{-1} TiO_2 addition, more than 95% of TTC was removed but only approximate 40% of TOC was detected after 60 min irradiation [8]. Comparing to UV/TiO_2 processes, TCs photodegradation under UV/ZnO processes was less studied. The photocatalytic oxidation of TTC under simulated solar light in the presence of ZnO was also investigated. With the optimal condition of 1.0 g L^{-1} ZnO dosage and pH 11, TTC would be completely removed after 10 min irradiation, accompanied with a low mineralization [10]. There are also some researches on the degradation of amoxicillin, ampicillin, and cloxacillin by UV/ZnO photocatalytic processes, with the conclusion that the photocatalytic reactions under optimal conditions (ZnO 0.5 g L^{-1} and pH 11) followed a pseudo-first-order kinetics with the rate constants 0.018, 0.015, and 0.029 min^{-1}, respectively [12].

In this study, the photodegradation of TCs (TTC, OTC, and CTC) in aqueous solution under UV/ZnO processes were investigated by evaluating the effects of ZnO dose and solution pH. The total organic carbon (TOC) and luminous bacteria inhibition rate were determined to evaluate the mineralization and products' toxicity. To the best of our knowledge, this is the first study on photodegradation of TCs under UV/ZnO processes which may have a potential significance for the treatment of TCs in the aqueous environment.

2. Materials and methods

2.1. Materials and chemicals

TTC and OTC from Dr. Ehrenstorfer at GmbH (Augsburg, GER) and CTC from Sigma-Aldrich Co. (St. Louis, MO) were at 95–97% purity. Acetonitrile and methanol at HPLC grade were obtained from Fisher Scientific (Geel, BEL). All other reagents (e.g. ZnO, H_2SO_4, NaOH, etc.) were supplied by Sinopharm Chemical Reagent Co. Ltd (Shanghai, CN) at analytical grade purity. All chemicals were used directly without further purification. Reagent water was produced from a Milli-Q Reference Ultrapure Water Purification System (Millipore, Billerica, MA, US). TCs stock solutions were prepared in water at 1.6 mM stored at 4˚C protected from light and used within 1–2 d after preparation. The bacteria *Photosbacterium phosphoreum* (T3) was provided as freeze-dried powder (0.5 g each bottle) by the Institute of Soil Science, Chinese Academy of Sciences, Nanjing, PR China.

2.2. Photodegradation experiment

The photodegradation experiments were conducted in a 250-mL reactor with 200 mL of tetracycline antibiotics solution at initial concentration of 0.16 mM. UV irradiations were carried out in a low-pressure Hg lamp (G4T5 TUV 32 W, 450 μW cm^{-2}). Reactions were initiated by adding ZnO into the solution mixed by magnetic stirring at room temperature (20˚C). Before irradiation, the system should be maintained in the dark for at least 30 min to reach the adsorption equilibrium. The initial solution pH was adjusted by 1 N H_2SO_4 or NaOH. Aliquots were taken by a syringe periodically from the reaction solution and filtered through 0.45 μm membranes for HPLC and TOC analysis. Immediately upon sampling, the reaction was quenched by adding 0.1 N H_2SO_4 to reach pH ~2. Samples were stored in 2-mL amber vials at 4˚C and analyzed within 2–3 d.

2.3. Analytical determination

TCs were analyzed by a Dionex P680 high-performance liquid chromatography (HPLC) system (Dionex, Sunnyvale, US) with a C18 reverse phase column (250 mm × 4.6 mm, 5 μm, Dikma, Beijing, CN) at 20˚C. The mobile phase was a mixture of 75% 0.01 M oxalic acid and 25% acetonitrile with a flow rate of 1 mL min^{-1}. TCs were detected at 369 nm by a diode array UV/vis detector. The spectra of TCs photodegradation products were scanned by a UV-1800 spectrophotometer (Mapada, Shanghai, CN). Total organic carbon (TOC in mg L^{-1}) was measured by an Elementar (Hanau, Germany) Vario TOC analyzer system.

2.4. Acute toxicity assay

The products' acute toxicity of UV/ZnO photocatalysis was assessed by a bioluminescent assay with marine photobacteria, *Photosbacterium phosphoreum* T3. Prior to toxicity assessment, the bacteria were reactivated in 1 mL 2% NaCl solution and kept in an ice water bath. The amount of 0.144 mL of each sample and 20 μL of reactivated bacteria suspension were added to 36 μL 15% NaCl solution. The bioluminescence of bacteria was measured by a multi-detection microplate reader (Synergy TM2, Bio-Tek Instruments, Inc. Vermont, US) after 15 min exposure at room temperature. Luminescence inhibition percentage was used to express the toxic effect of TCs photodegradation products on *P. phosphoreum* T3. The inhibition rate was calculated by Eq. (9) (L = luminescence). All samples were performed in triplicates in this study.

$$\text{Inhibition rate } = \frac{L_{\text{blank}} - L_{\text{sample}}}{L_{\text{blank}}} \times 100\% \qquad (9)$$

3. Results and discussion

3.1. Effect of ZnO concentration

There was no significant TCs degradation under UV irradiation in the absence of ZnO addition. In this study, different dosages of ZnO (0.5, 1.0, 1.5, and 2.0 g L^{-1}) were conducted in the photocatalysis reactions at pH 3.8 ± 0.2. Experiments showed the photodegradation of TCs followed pseudo-first-order reaction kinetics and the kinetic rate constants were increased at higher ZnO concentrations within 180 min irradiation (Fig. 1). More ZnO dosage provided more adsorption positions for TCs and produced more ·OH radicals, but with further increase of ZnO concentration, the increase in the turbidity of the suspension would lead to a decrease in UV light penetration, while the degradation rate constants reached the

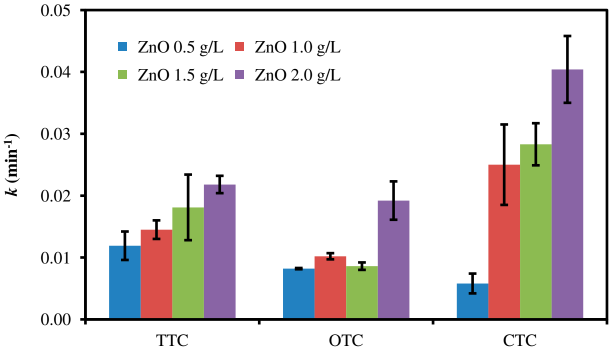

Fig. 1. TCs photodegradation pseudo-first-order rate constants at different ZnO concentration under UV/ZnO process.
Note: $[TCs]_0$ = 0.16 mM, pH 3.8 ± 0.2, and T = 20℃.

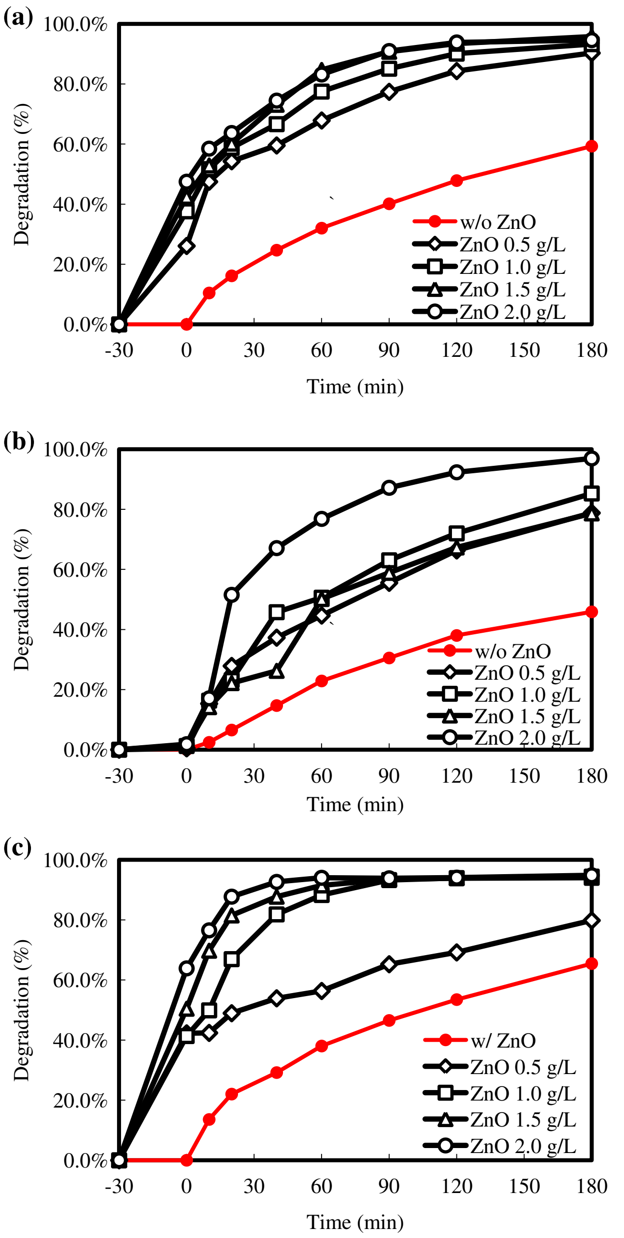

Fig. 2. Effect of ZnO concentration on the degradation efficiency of TTC (a), OTC (b), and CTC (c) under UV/ZnO process.
Note: $[TCs]_0$ = 0.16 mM, pH 3.8 ± 0.2, and T = 20℃.

maximum value [12]. To determine the optimal ZnO concentration, the degradation efficiency was considered (Fig. 2). It was obvious that the photodegradation of TCs were all enhanced by adding ZnO to the solution under UV irradiation. But further increase of ZnO dosage from 1.0 to 2.0 g L^{-1} did not bring significant enhancement on the removal percentage of TTC and CTC after 180 min reaction, which slightly increased from 93.3 to 94.6% for TTC, and from 94.4 to 94.9% for CTC. However, the removal of OTC showed a notable increase from 85.2 to 96.9%. This might be explained by the different adsorption property among different TCs. For further comparing other factors' impact to the three TCs photodegradation, the optimal ZnO concentration was chosen to be 1.0 g L^{-1}.

3.2. *Effects of pH*

To evaluate the effects of initial pH, solutions were adjusted to pH 5.0, 7.0, 9.0, and 11.0 by NaOH and H_2SO_4, and photodegradation reactions were carried out with 1.0 g L^{-1} ZnO dosage at room temperature (20℃). The photodegradation of TCs at different pH also followed pseudo-first-order reaction kinetics and

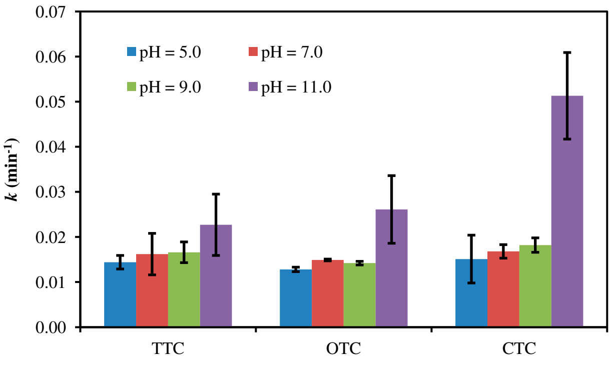

Fig. 3. TCs photodegradation pseudo-first-order rate constants at different pH under UV/ZnO process.
Note: $[TCs]_0 = 0.16$ mM, $[ZnO] = 1.0$ g L^{-1}, and $T = 20$℃.

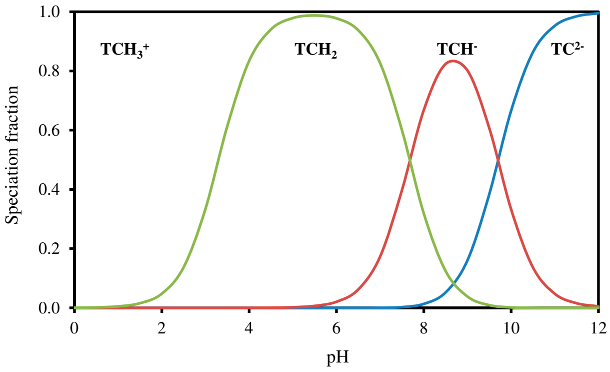

Fig. 4. Speciation fraction of TCs at different pH.

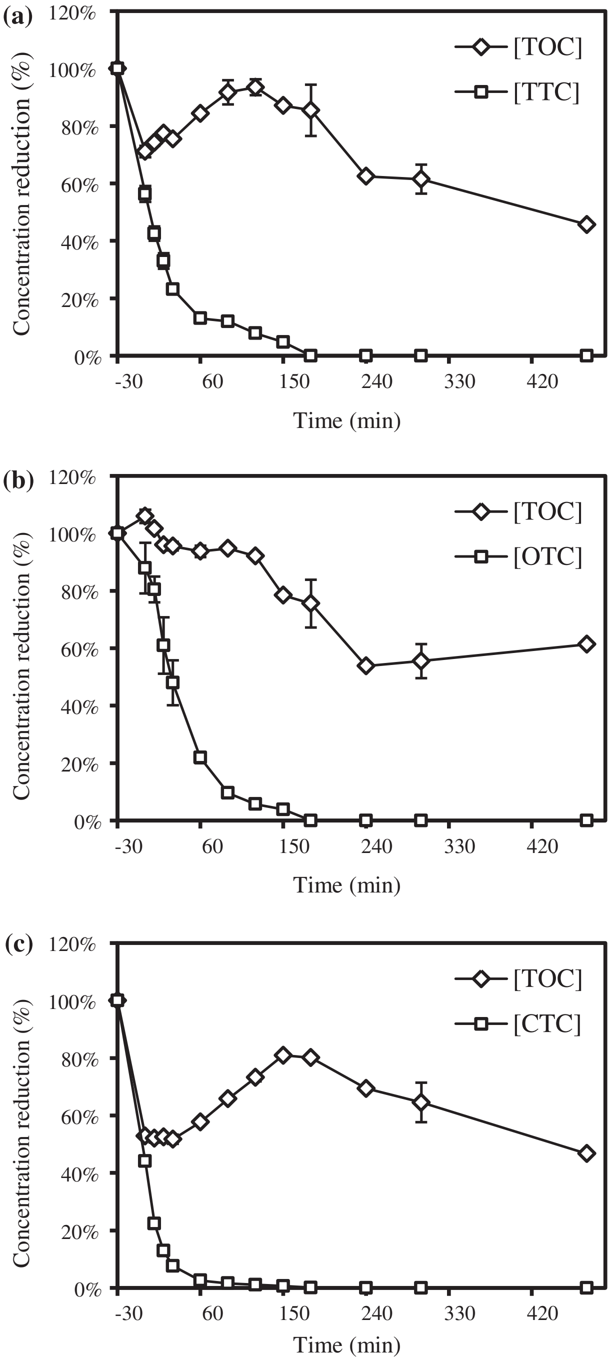

Fig. 5. The TCs concentration and solutions TOC during UV/ZnO photodegradation: (a) TTC, (b) OTC, and (c) CTC.
Note: $[TCs]_0 = 0.16$ mM, $[ZnO] = 1.0$ g L^{-1}, pH 7.0, and $T = 20$℃.

the rate constants increased at higher pH (Fig. 3). This could be explained by the different properties of TCs and ZnO at different pH. The zero point charge of ZnO is 9.0 ± 0.3 [14], so the surface of ZnO is positively charged at $\mathrm{pH} < 9$ and negatively charged at $\mathrm{pH} > 9$. Likewise, TCs presented different species at different pH [15,16] (Fig. 4). It was obvious that more negative TCH^- species would be formed instead of zwitterion $TCH_2^{\pm}$ when pH varied from 5.0 to 9.0, meanwhile, positively charged ZnO surface would attract more TCH^- molecules which led to a faster trend of TCs photodegradation rate. Both TC species (TC^{2-}) and ZnO were negative charged when pH was increased to 11.0 and there would be a declined degradation rate due to the repulsive force between TC^{2-} and ZnO. However, the reason for the maximum rate at this pH was likely due to the large quantities of OH^- ions on ZnO surface, which favored the

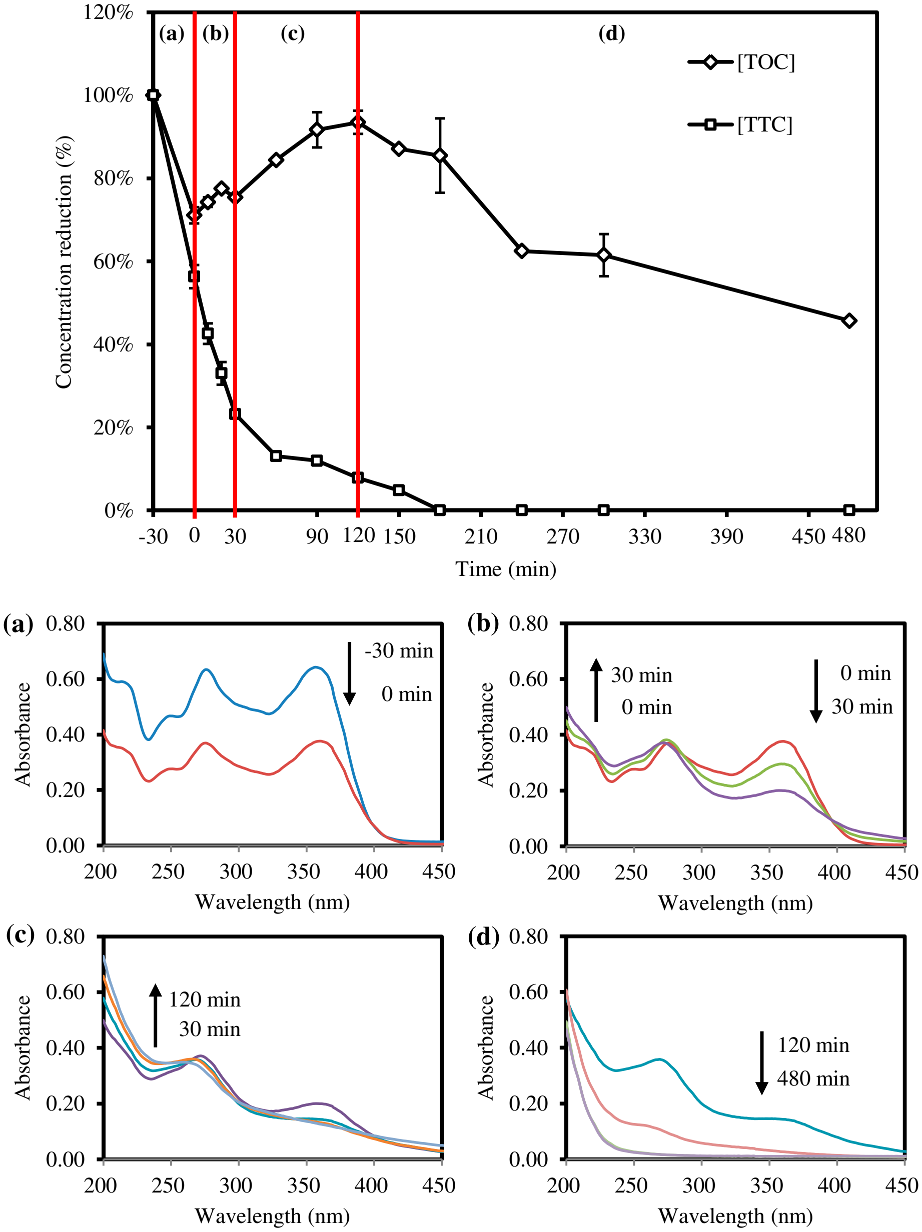

Fig. 6. Spectra of TCs photodegradation solution at different reaction time: (a) −30 to 0 min, (b) 0–30 min, (c) 30–120 min, and (d) 120–480 min.
Note: $[TCs]_0 = 0.16$ mM, $[ZnO] = 1.0\ \mathrm{g\ L^{-1}}$, pH 7.0, and $T = 20$°C.

formation of ·OH radicals [12,17], and subsequently the hydrolysis of TCs [18].

The removal for TTC, OTC, and CTC reached 96.7, 98.2, and 100% at pH 11.0 after 150 min irradiation. But for pH 7.0, the TCs removal could also reached 94.6, 91.7, and 95.2%. Considering little efficiency distinction and the amount of alkali dosage, 7.0 was chosen to be the appropriate pH.

3.3. TOC determination

Approximate 54.4 and 53.2% of TOC were removed for TTC and CTC after 480 min irradiation (Fig. 5) with a trend of rising first and then falling. To explain this trend, the spectra of TTC solution during photodegradation were scanned (Fig. 6).

In the first 30-min dark period (a), TTC concentration and solution TOC decreased 43.7 and 28.9%, respectively, which was caused by the ZnO adsorption. The same result was obtained by the spectrum (a) from the time −30 to 0 min. The adsorption was also reported in the photodegradation of OTC under UV/TiO_2 [19]. More than 85% of OTC was removed from aqueous solution by the adsorption of TiO_2 after 210 min in the absence of light.

In the following 30 min (b), TOC did not change much (from 71.1 to 75.4%), while TTC concentration decreased from 56.3 to 23.2%. It was found that the absorbance of the solution increased at the wavelength 200–275 nm and decreased at 300–400 nm (spectrum (b)). It is known that TCs' A ring chromophore contributes to the absorption band at 250–300 nm, whereas the BCD ring chromophore contributes to both 250–300 nm and 340–380 nm [20]. Therefore, the decreased absorption at 300–400 nm was due to the breakdown of TTC's BCD ring and the products contributed to the increased absorption bands at 200–275 nm. There might be equilibrium between TTC's photodegradation and adsorption by ZnO which led to the stabilization of TOC.

After that, TOC showed a rising trend from 30 to 120 min. According to spectrum (c), observable increase appeared at 200–275 nm but little absorption changed at 300–400 nm. Most of TTC had been degraded into small molecules which led to less adsorption of TTC on ZnO, and the degradation products entered into the solution, resulting in an increased TOC. However, the mineralization in fact may not be enhanced.

In the last period from 120 to 480 min, TTC was completely degraded at 180 min but the mineralization was still in progress with a TOC loss of 38.6% at the end of period. It could be observed that the absorbance of the solution decreased sharply from 120 to 300 min and then remained stable until the end of the reaction (spectrum (d)), which meant that this period was dominated by the mineralization of TTC products.

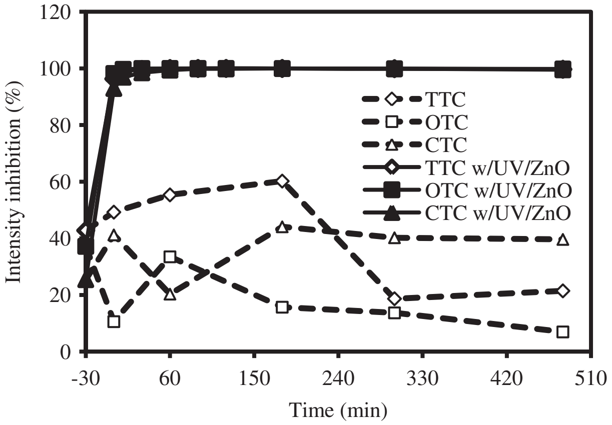

Fig. 7. Toxicity during the photodegradation of TCs.
Note: $[TCs]_0 = 0.16$ mM, $[ZnO] = 1.0$ g L^{-1}, pH 7.0, $T = 20$℃.

OTC showed a different degradation pattern compared with TTC and CTC. This might be due to the less adsorption of OTC on ZnO, which was proved by the little removal of OTC concentration during the mixture time in the darkness (Figs. 2(b) and 6(b)).

3.4. Toxicity assessment

An obvious inhibitory effect of TCs photodegradation products on the growth of *P. phosphoreum* T3 was observed when the photodegradation reaction started (Fig. 7), which was much higher than that of TCs solution without UV/ZnO. Previous study showed that ZnO was very toxic to *Vibrio fischeri* and the 30-min EC_{50} value was 1.8 ± 0.1 mg L^{-1} [21], and the total inhibition of algae *Pseudokirchneriella subcapitata* growth was observed at 0.16 mg Zn L^{-1} [22]. In addition, TCs photodegradation products under UV showed a decreased toxicity than the original TCs after 60 min irradiation [23]. Prior to the acute toxicity measurement, the samples had been filtered by 0.45 μm membranes. Therefore, the high toxicity of TCs photodegradation products might be due to the dissolved Zn ions and ZnO from high level of ZnO dosage.

4. Conclusions

The photodegradation of tetracycline antibiotics in aqueous solution under UV/ZnO process was investigated, and the degradation of TCs was increased at higher ZnO dosage and pH. Both TCs concentration and TOC were reduced under UV/ZnO process but the acute toxicity of products was higher than the original solution due to the high toxicity of ZnO. Overall, UV/ZnO process could be used as an efficient way for the treatment of TCs wastewater if coupled with a better method to recover ZnO, and centrifugation, washing, and vacuum drying might be feasible choices.

Acknowledgement

This work was supported by the Fundamental Research Funds for the Central Universities (2015YJS127).

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