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Photodegradation of Norfloxacin in aqueous solution containing algae

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Abstract

Photodegradation of Norfloxacin in aqueous solution containing algae under a medium pressure mercury lamp (15 W, λ_{max} = 365 nm) was investigated. Results indicated that the photodegradation of Norfloxacin could be induced by the algae in the heterogeneous algae-water systems. The photodegradation rate of Norfloxacin increased with increasing algae concentration, and was greatly influenced by the temperature and pH of solution. Meanwhile, the cooperation action of algae and Fe(III), and the ultrasound were beneficial to photodegradation of Norfloxacin. The degradation kinetics of Norfloxacin was found to follow the pseudo zero-order reaction in the suspension of algae. In addition, we discussed the photodegradation mechanism of Norfloxacin in the suspension of algae. This work will be helpful for understanding the photochemical degradation of antibiotics in aqueous environment in the presence of algae, for providing a new method to deal with antibiotics pollution.

Key words: photodegradation; Norfloxacin; algae; kinetic analysis; mechanism

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Introduction

Pharmaceuticals and personal care products (PPCPs) have attracted attention in recent years because of their presence in the aquatic environment (Ellis, 2006; Loraine and Pettigrove, 2006; McClellan and Halden, 2010; Yoon et al., 2010; Sui et al., 2011). Detection of antibiotics is of particular concern due to its adverse effect on the aquatic microorganism, and the problem that may be created by the existence of antibiotics in the aquatic environment (Esplugas et al., 2007; Mompelat et al., 2008; Benotti et al., 2009; Zhang et al., 2010).

Norfloxacin is a synthetic antibacterial agent of fluoroquinolone, which is widely used in human and veterinary medicine (Crdoba-Díaz et al., 1998; Rahman et al., 2004; Zhang et al., 2009). However, it is persistent against the biological degradation due to the pharmaceutical activity of Norfloxacin (Haque and Muneer, 2007; Yu and Bao, 2009; Dhaneshwar et al., 2011), which results in the long time existence in the aquatic environment. Therefore, there is a need of developing an effective technology system, including pre- or advanced treatment system in integrated with advanced oxidation process (AOP). Recent studies show that AOP can be successfully applied for the removal of pharmaceuticals in water (Beltrn et al., 2009; Hapeshi et al., 2010; Paul et al., 2010).

The degradation of antibiotics, individually or in combination with other organic compound, induced by the AOP have been investigated, including the photocatalysis of different catalysts (Li and Haneda, 2003; Ren et al., 2009; Zhang et al., 2010), the analysis of degradation mechanism (Son et al., 2004; Hu et al., 2007), the enhancement of photocatalytic efficiency (Krishna et al., 2006; Wang et al., 2006). The catalysts used in the photocatalytic reaction are TiO_2 (Hu et al., 2007), Fe_2O_3 (Karunakaran and Senthilvelan, 2006), WO_3 (Martínez et al., 2011) and ZnO (Xie et al., 2011) etc. The antibiotics can be tailored to the lower molecular weight of organic compound by the hydroxyl radical which is one the most powerful oxidation agents (Paul et al., 2010; Zhang et al., 2010). However, the degradation of antibiotics catalyzed by the catalysts need the subsequent treatment in order to reduce the impact of catalysts on the aqueous environment. Thus, it is necessary to develop the new photocatalytic system to degrade the hazardous compounds.

The degradation of organic compound by the photoinitiation of some microorganisms has attracted interest in recent years (Zuo and Jones, 1996; Liu et al., 2004; Li et al., 2008). The microorganisms may adsorb the certain wavelength of light to produce the photoactive compounds which can result in the transformation of organic compound in the aquatic environment (Liu et al., 2003; Peng et al., 2006). Algae are an important type of microorganism in the sea water and the fresh water, it can induce the generation of H_2O_2, hydrated electron and singlet oxygen ($^1O_2$) under irradiation, and the organic compound may be degraded by the participation of photoactive compounds (Sandvik et al., 2000). Therefore, algae photocatalysis may be a possible alternative/complementary technology for

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destruction of antibiotics in the aquatic environment. Liu et al. (2003, 2004) reported that the degradation rate of 17 α-ethynylestradiol could be enhanced by the addition of algae in solution containing Fe(III). Peng et al. (2006) studied the photodegradation of bishphenol A in simulated lake water containing algae, humic acid and ferric ions, finding that algae could enhance the photodegradation of bishphenol A under a near UV light, and the reason of rapid degradation could arise from the hydroxyl radical produced by the algae. Zepp and Schlotzhauer (1983) studied the influence of algae on the photolysis rates of chemicals in water. Moreover, Deng et al. (2006, 2008, 2010) investigated the photoreduction of heavy metal by the presence of algae in aqueous solution. It is applicable to the degradation of antibiotics with the oxidative radicals photoproduced from the algae, and to the best of our knowledge, there are few studies on the degradation of antibiotics by algae photocatalysis.

In this study, the photodegradation of Norfloxacin and its kinetics were investigated in aqueous containing algae, and the effects of key parameters were examined in details. A possible mechanism was proposed. Norfloxacin was selected as the model pollutant in this article since it had been widely detected in aqueous environment. This research not only provides information for effects of key factors of algae photocatalysis, but also can provide a new alternative to deal with the antibiotics pollution.

1 Materials and methods

1.1 Materials

Norfloxacin was purchased from Sigma-Aldrich Co. (USA) and used as received. Alga used in the experiments was *Chlorella vulgaris* obtained from the Wuhan Hydrobilology Institute of Chinese Academy of Sciences (China). Algae were grown in the axenic culture medium at 25°C using a 24-hr light cycle in the culturing room. Under condition of logarithmic growth phase, algae were taken for use in experiments after being washed. The cell counting was carried out under inverted microscope at 400× (XSP-8, Batuo Co., China) and the density of algae (cell/L) was calculated. Different concentrations of algae were gained by diluting washed algae with double-distilled water.

1.2 Photochemical experiments

The degradation experiments were carried out in a cylindrical reactor (XPA, Xujiang Co, China, 1000 mL capacity) with a 15-W medium pressure mercury lamp (Xujiang Co, China) at the wavelength of 365 nm (λ_{max}). The incident of photo flux, measured by the potassium ferrioxalate actinometry (Braun and Maurette, 1991), was 1.32×10^{-4} Einstein/(L·min). The temperatures of reaction solutions were maintained at (25 ± 0.5)°C by a cooling water circulation. pH of solution was adjusted by adding dilute hydrochloric acid solution or sodium hydroxide solution.

The photolysis of Norfloxacin was carried out without algae. The Norfloxacin solutions with desired concentrations were transferred into the reactor, and the samples were taken out at different intervals under the irradiation. Furthermore, the degradation of Norfloxacin catalyzed by the algae was performed. The solutions with desired concentrations of Norfloxacin and the harvested algae were added into the reactor. The solutions containing algae inside the cylindrical reactor were maintained in suspension by means of sparged air and magnetic stirring under the irradiation. At different intervals, the samples were withdrawn and centrifuged at 4000 r/min for 30 min, and then the supernatant was collected. Finally, the concentration of Norfloxacin was determined by the high-performance liquid chromatograph (HPLC, L6, Pgrandsil STC C18 column, 4.6 mm × 150 mm, 5 μm, Pgenernal Co., China) with UV detector at 277 nm. The mobile phases consisted of an 85/15 ratio of aqueous phase to acetonitrile (V/V) with a flow rate of 1.5 mL/min, and the aqueous phase was 2.5 mmol/L sodium-1-heptane sulfonate adjusted to pH 2 with H_3PO_4.

2 Results and discussion

2.1 Photodegradation of Norfloxacin in the absence and presence of algae

Figure 1 shows that the time series for the photochemical degradation of Norfloxacin in the absence or in the presence of algae as well as the corresponding dark controls. In the dark, only small amount of Norfloxacin (2.3% and 5.0%, respectively) was lost from the solution in the absence and presence of algae due to the physical absorption to the inner surface of reactor and the chemical attenuation (dark reaction). Under the medium pressure mercury lamp (15 W), 9.1% of Norfloxacin was degraded after 60 min irradiation in solution without the algae, this phenomenon could arise the direct photolysis, the chemical attenuation and the physical absorption of Norfloxacin.

Furthermore, the degradation rate of Norfloxacin was enhanced by the presence of algae on the basis of photolysis (Fig. 1). The degradation rate of Norfloxacin reached to 36.9% after 60 min irradiation, indicating that the

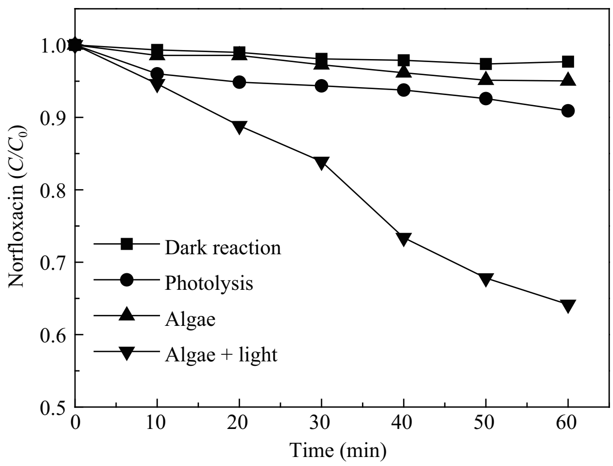

Fig. 1 Norfloxacin concentration as a function of time in different solutions. Initial Norfloxacin concentration: 20 mg/L; Algae concentration: 1.7×10^8 cell/L; pH = 5.

photolycatalysis of algae, *C. vulgaris* could promote the degradation of Norfloxacin. The algae can generate some lower molecular weight organics through the secretion of algae (O' Driscoll et al., 2006; Deng et al., 2008), and the lower molecular weight organics may produce the hydroxyl radical under UV irradiation (Zepp et al., 1983; Liu et al., 2003; Peng et al., 2006). The enzymatic reaction at the algae cell surface may be another reason involved in the degradation of Norfloxacin. Therefore, the degradation of Norfloxacin could arise from both the photolysis and algae effect.

2.2 Effect of algae concentration on the photodegradation of Norfloxacin

Algae concentration plays an important role in the degradation of Norfloxacin because it may influence the yield of photoactive compound. Suspensions of algae, *C. vulgaris* at four initial algae concentrations, 1.7×10^9, 1.7×10^8, 1.7×10^7 and 1.7×10^6 cell/L, at pH 5 were irradiated under a medium pressure mercury lamp (15 W). As shown in Fig. 2, the faster degradation of Norfloxacin is with the higher algae concentration, and the increase of algae concentration greatly shortened the photodegradation time. After 60 min irradiation, 35.9% and 40.1% of Norfloxacin was degraded at the algae concentration of 1.7×10^7 and 1.7×10^6 cell/L respectively. A higher algae concentration results in a faster photoproduction of small dissolved organic matter (Zuo et al., 1996; Deng et al., 2010). Franke and Franke (1999) noted that there were the dissolved organic matters (humic and fulvic acid etc.) in the secretion of algae, which could serve as photosensitizer in the generation of hydroxyl radical. Therefore, the higher algae concentration causes the higher yield of hydroxyl radical due to the increase of photosensitizer in suspension under irradiation.

2.3 Effect of pH on the photodegradation of Norfloxacin

The wastewater of antibiotics may be discharged at different pH values, thus it is important to study the role of pH in the photodegradation of Norfloxacin. The experiments were conducted at pH range 3–6 with the initial concentration of Norfloxacin 20 mg/L, algae 1.7×10^8 cell/L,

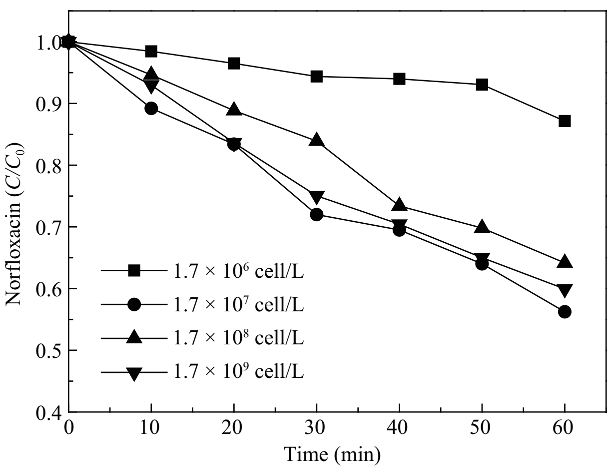

Fig. 2 Effect of algae concentration on the photodegradation of Norfloxacin. Initial Norfloxacin concentration: 20 mg/L; pH = 5.

the results are illustrated in Fig. 3. It is observed that the photodegradation of Norfloxacin was influenced by the pH value, and the degradation rates of Norfloxacin were: pH 5 > pH 4 > pH 6 > pH 3. At pH 5, up to 35.9% of Norfloxacin was degraded from the suspension after 60 min irradiation. However, only 13.7% of Norfloxacin was degraded from the suspension at pH 3 after 60 min irradiation. Effect of pH on the photodegradation of Norfloxacin demonstrates that pH plays an important role in the photochemical degradation of Norfloxacin in aqueous solution containing algae.

The dependence on the pH may be considered to mainly result from the two aspects. First, algae may be easier to release more dissolved organic matter in the weak acidic environment, and the lower molecular organic acid in the dissolved organic matters can serve as photosensitizer to photoinduce the generation of hydroxyl radical under irradiation (Zepp et al., 1983; Sandvik et al., 2000; Liu et al., 2004). Deng et al. (2008, 2010) noted that algae could release acidic dissolved organic matters during the process of irradiation under the acid condition, and the dissolved organic matters such as humic acid and fulvic acid could act as photosensitizer. Zuo et al. (1996) indicated that the dissolved organic matters could form the photochemical reactive substance under irradiation. Moreover, the survival of algae may be inhibited on the strong acid condition, which can influence its secretion. Second, pH may affect the formation of active substance in the generation of hydroxyl radial. In the algae-induced photodegradation of Norfloxacin, there may be a series of reaction of HO· build-up in the solution (Eqs. (1)–(5)). However, the determining step occurs in the generation of hydroxyl radical, which is the formation of $HO_2\cdot$ (the active substance), and the secretion release of algae and the yield of hydroxyl radical may rise higher degree under the weak acid condition. Liu et al. (2004) indicated that pH could influence the yield of hydroxyl radical in aqueous solution containing algae.

$$DOC + h\nu \longrightarrow DOC\cdot \quad (1)$$

$$DOC\cdot + O_2 \longrightarrow \cdot DOC^+ + \cdot O_2^- \quad (2)$$

$$H^+ + \cdot O_2^- \longleftrightarrow HO_2\cdot \quad (3)$$

$$2HO_2\cdot \longrightarrow H_2O_2 + O_2 \quad (4)$$

$$H_2O_2 + h\nu \longrightarrow 2HO\cdot \quad (5)$$

2.4 Effect of Fe(III) on the photodegradation of Norfloxacin

Iron is a widespread inorganic compound in the aquatic environment and could form strong ligand-to-metal charge absorption bands with carboxylic anion in the near-UV and visible region (Li et al., 2010). Algae could release the acidic dissolved organic matters which contain the humic acid and the fulvic acid etc. (Franke and Franke, 1999). Thus, it is interesting to investigate the effect of Fe(III) on the degradation of Norfloxacin in the suspension of algae. The degradation rate of Norfloxacin in the suspension of algae containing Fe(III) was tested. As shown in Fig. 4, the

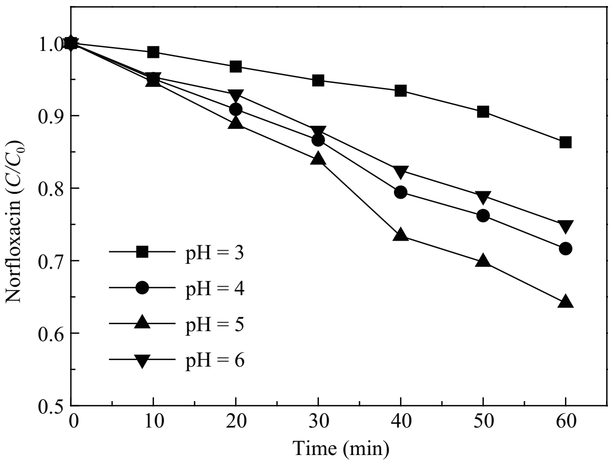

Fig. 3 Effect of pH on the photodegradation of Norfloxacin. Initial Norfloxacin concentration: 20 mg/L; algae concentration: 1.7×10^8 cell/L.

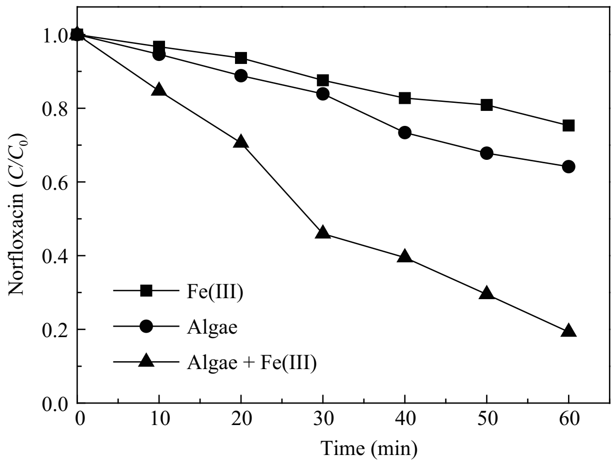

Fig. 4 Effect of Fe(III) on the photodegradation of Norfloxacin. Initial Norfloxacin concentration: 20 mg/L; algae concentration: 1.7×10^8 cell/L; Fe(III): 20 μmol/L; pH = 5.

degradation rate of Norfloxacin could be greatly enhanced in the suspension containing both algae and Fe(III). After 60 min irradiation, the degradation rates of Norfloxacin were 24.7% and 35.9% by Fe(III) photocatalysis and algae photocatalysis respectively, and the degradation rate of Norfloxacin reached to 80.3% by the cooperation action of Fe(III) and algae. Thus, Fe(III) can result in a faster degradation of Norfloxacin in the suspension of algae. It is known that iron can form the complexes with carboxylic anion as Fe(III)-carboxylate complexes (Goldberg et al., 1993; Li et al., 2010), which is more photoreactive for producing the hydroxyl radical under irradiation. Also, it has been reported that algae may release acidic dissolved organic matters which contain the low molecular weight carboxylic acids (Deng et al., 2010). Thus, the degradation rate of Norfloxacin is greatly enhanced when the greater amounts of photoactive iron occur in the suspension of algae. The mechanism of formation of hydroxyl radical photolyzed by both Fe(III) and carboxylic acid secreted by the algae are as the following Eqs. (6) –(11):

$$\text{Fe(III)-L} + h\nu \longrightarrow \text{Fe(II)} + \text{L}\cdot \quad (6)$$

$$\text{L}\cdot + O_2 \longrightarrow \cdot O_2^- + \text{Other photoproducts} \quad (7)$$

$$\text{Fe(II)} + \cdot O_2^- + H^+ \longrightarrow \text{Fe(III)} + H_2O_2 \quad (8)$$

$$\text{Fe(II)} + H_2O_2 \longrightarrow \text{Fe(III)} + HO\cdot + HO^- \quad (9)$$

$$> \text{L} + \text{Fe(III)} \longrightarrow \; > \text{Fe(III)-L} \quad (10)$$

$$> \text{Fe(III)-L} + h\nu \longrightarrow \text{Fe(II)} + \text{L}' \quad (11)$$

where, Fe(III)-L represents the Fe(III)-carboxylate complex, > represents the surface complex, L• and L' represent the carboxylate radical and its oxidized product respectively.

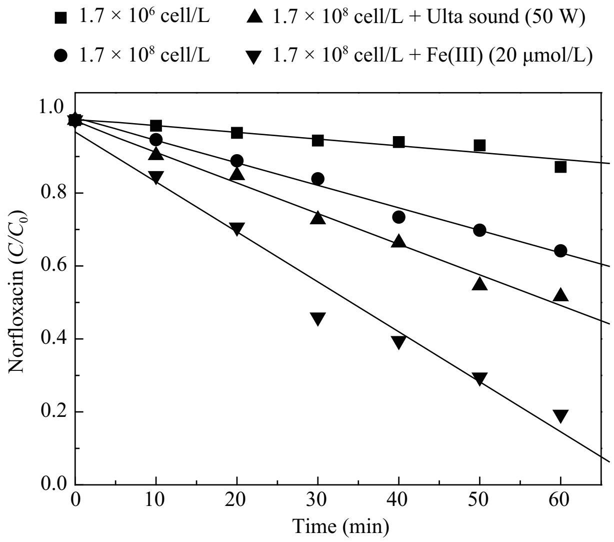

Fig. 5 Photodegradation of Norfloxacin in aqueous solution with algae. Initial Norfloxacin concentration: 20 mg/L; pH = 5.

2.5 Analysis of degradation kinetics

The degradation experiments were carried out in order to probe the characteristic of degradation kinetics. The results are shown in Fig. 5 and the kinetics analysis results are listed in Table 1. $R_1{}^2$ and $R_2{}^2$ are the correlation coefficients of pseudo zero-order equation and the correlation coefficients of pseudo first-order equation respectively (Table 1). It is observed that the model of pseudo-zero order kinetics can describe the degradation process of Norfloxacin well in solution containing only algae, and the analytic results show that the values of $R_1{}^2$ are higher than the values of $R_2{}^2$ when the reaction solutions contain

Table 1 Photodegradation kinetics analysis

No.	Pseudo zero-order equation		Pseudo first-order equation	
	Kinetics equation	R_1^2	Kinetics equation	R_2^2
I	$C/C_0 = 1.003 - 0.00185t$	0.9532	$\ln C/C_0 = 0.00469 - 0.00197t$	0.9474
II	$C/C_0 = 1.006 - 0.00616t$	0.9950	$\ln C/C_0 = 0.0195 - 0.00761t$	0.9929
III	$C/C_0 = 0.995 - 0.00839t$	0.9943	$\ln C/C_0 = 0.0238 - 0.0116t$	0.9921
IV	$C/C_0 = 0.968 - 0.0137t$	0.9870	$\ln C/C_0 = 0.0905 - 0.0272t$	0.9904

Initial Norfloxacin concentration is 20 mg/L. I: 1.7×10^6 cell/L; II: 1.7×10^8 cell/L; III: 1.7×10^8 cell/L (50 W); IV: 1.7×10^8 + Fe(III) (20 μmol/L).

only algae, thus photodegradation of Norfloxacin should be the pseudo-zero order reaction in solution containing only algae. However, the photodegradation of Norfloxacin can be described well by the pseudo first-order kinetics model when reaction solution contained both algae and Fe(III) since R_2^2 is higher than R_1^2 according to the results (Table 1), thus photodegradation of Norfloxacin should be the pseudo-first order reaction under the cooperation action of algae and Fe(III).

2.6 Effect of temperature and ultrasound on the photodegradation of Norfloxacin

The growth of algae is influenced by the temperature due to its biological property, thus the amount of algae secretion is naturally affected by different temperatures. Also, the wastewater of antibiotic usually has different temperatures in the natural environment, it is necessary to study the effect of temperature on the photodegradation of Norfloxacin. The degradation experiments were carried out under different temperatures in order to probe the effect of temperature. As shown in Fig. 6a, degradation rate of Norfloxacin gradually increased with the increase of temperature in the range of 15°C to 25°C, indicating that the increase of reaction temperature results in the increase of degradation rate of Norfloxacin for algae photocatalytic reaction under the experimental condition. Moreover, the degradation rate of Norfloxacin decreased when reaction temperature rose to 45°C (data not shown here due to lack of practical significance for the natural environment).

The possible reason here have two aspects for the above phenomenon. First, algae can grow in a logarithmic growth phase under the suitable temperature (Peng et al., 2006; Deng et al., 2010), and accordingly algae may be release more secretion which can photoinduce the rapid degradation of Norfloxacin under the suitable temperature. Liu et al. (2004) indicated that algae could grow in a logarithmic growth phase at about 25°C. Second, the activity of algae may be influenced by the unsuitable temperature, and the degradation rate of Norfloxacin at 35°C was higher than that at 25°C, this phenomenon could arise from the release of lower molecular organic acids which are from the break of algae cell at the high temperature.

To probe the effect of break of algae cell, the experiments were performed with the ultrasound treatment. As shown in Fig. 6b, the degradation rate of Norfloxacin was enhanced in the presence of ultrasound. Up to 40.6% of Norfloxacin was degraded with the ultrasound assistance in the solution containing algae after 60 min irradiation. The observed effect of ultrasound demonstrates that the break of algae cell can enhance the degradation rate of Norfloxacin. Also, it is beneficial to the diffusion of active oxygen generated by Chlorophyll in the algae cell under the ultrasound condition since the active oxygen is an important matter in the generation of hydroxyl radical. Liu et al. (2004) noted that Chlorophyll could produce the active oxygen through a serious complicated reaction under UV irradiation.

2.7 Analysis of degradation pathway

The main product is the dissolved organic carbon (DOC) for the secretion of algae under irradiation, and the DOC can serve as the photosensitizer to induce the generation of hydroxyl radical. Meanwhile, algae may release some enzymes under the induced condition, which can result in the degradation of Norfloxacin. Also, the carboxylic acid released by algae can react with Fe(III) to form the Fe(III)-carboxylate complexes, which is more photoreactive. Similar aspects of organic compound degradation by algae photocatalysis are available in the research literature. Liu et al. (2003) and Peng et al. (2006) reported that Chlorophyll could produce the active oxygen under UV irradiation. Zuo et al. (1996) noted that DOC could serve as the photosensitizer which induced the generation of active oxygen. Liu et al. (2004) and Li et al. (2010) indicated that Fe(III)-oxalate complexes was more photoactive and it could produce the hydroxyl radical under simulated sunlight conditions. The mechanism of photocatalytic degradation of Norfloxacin in solution containing algae is considered to have many important photochemical processes for degradation of Norfloxacin catalyzed by algae, including the enzymatic degradation at the algae cell surface, the degradation by dissolved organic carbon produced via the photolysis of algae under UV irradiation, as shown in Fig. 7. Moreover, the degradation of Norfloxacin

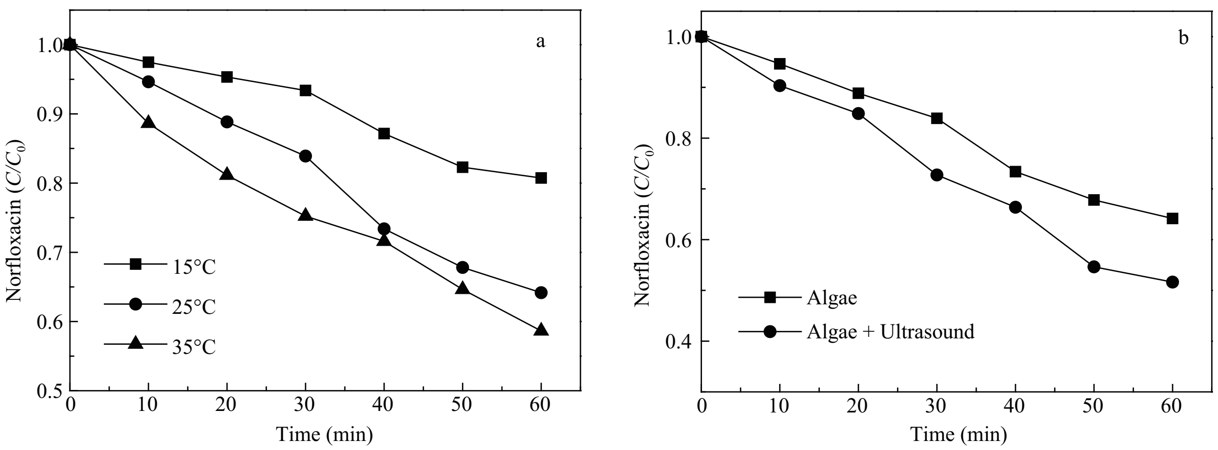

Fig. 6 Effect of temperature (a) and ultrasound (b) on the photodegradation of Norfloxacin. Initial Norfloxacin concentration: 20 mg/L; algae concentration: 1.7×10^8 cell/L; pH = 5.

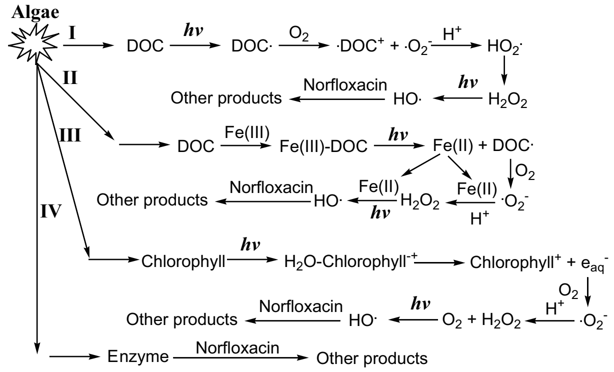

Fig. 7 Pathway of Norfloxacin photodegradation in the solution containing both algae and Fe(III).

by the dissolved organic carbon may be faster than the enzymatic catalysis or the Chlorophyll catalysis since the lower molecular weight of dissolved organic carbon can act as photosensitizer, which can promote the generation of hydroxyl radical. The same mechanisms may also act in natural water since both algae and Fe(III) are commonly present in nature aquatic environment.

3 Conclusions

Under a UV lamp (λ_{max} = 365 nm, photo flux 1.32×10^{-4} Einstein/(L·min)), the rapid degradation of Norfloxacin in the solution containing the algae takes place via oxidation with hydroxyl radical generated by the algae. The algae could significantly accelerate the photodegradation of Norfloxacin under irradiation. The photodegradation rate of Norfloxacin increased with increasing concentration of algae. The photodegradation of Norfloxacin catalyzed by the algae was pH-dependent. The photodegradation rate of Norfloxacin increased with increased pH value of solutions in the range of 3–5, and the degradation efficiency of Norfloxacin decreased when pH value was more than 5. In addition, the removal efficiency of Norfloxacin could be enhanced by the addition of Fe(III) or ultrasound in the suspensions of algae. A certain extent of increase for the reaction temperature was beneficial to the degradation rate of Norfloxacin. Furthermore, the degradation kinetics of Norfloxacin were the pseudo zero-order reaction in solution containing algae and the pseudo first-order reaction in solution containing containing both algae and Fe(III). Three reactions may have been involved in the algae enhanced degradation of Norfloxacin, including the degradation by the Chlorophyll and the dissolved organic carbon produced via the photolysis of algae under irradiation, the enzymatic degradation at the algae cell surface. Finally, algae could accelerate the degradation of Norfloxacin by addition of Fe(III). This research will be helpful for understanding photochemical degradation of antibiotics in aqueous environment in the presence of algae.

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