

## Diclofenac photodegradation under simulated sunlight: Effect of different forms of nitrogen and Kinetics

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### ARTICLE INFO

#### Article history:

Received 22 March 2011

Received in revised form 2 May 2011

Accepted 14 May 2011

Available online 23 May 2011

#### Keywords:

Diclofenac

Inorganic nitrogen

Kinetics

Self-sensitization

Simulated sunlight

### ABSTRACT

A synthetic non-steroidal anti-inflammatory drug diclofenac is one of the most frequently detected pharmaceuticals in various water samples. One of the most important degradation processes relating to diclofenac is its photodegradation in the aquatic environment. This paper studies the kinetic model for diclofenac degradation in water and the variation of the photodegradation of diclofenac in the presence of different forms of nitrogen changes with different pE values in the aquatic environment under simulated sunlight. The results demonstrate that degradation pathways proceed via pseudo first-order kinetics in all cases and the photodegradation of diclofenac is the sum of the degradation by direct photolysis and self-sensitization.  $\text{NO}_3^-$  and  $\text{NO}_2^-$  have inhibiting effects on the photodegradation of diclofenac. The different forms of nitrogen changes with different pE values and this has a significant influence on the photodegradation of diclofenac. The results show that when  $\text{NH}_4^+$  and  $\text{NO}_2^-$  coexist in the aquatic environment, the inhibiting effect on the photodegradation of diclofenac is less than the sum of the partial inhibiting effects. The results indicated that  $\text{NO}_2^-$  had an obvious antagonistic action for  $\text{NH}_4^+$ . When  $\text{NO}_3^-$  and  $\text{NO}_2^-$  coexisted in the aquatic environment, a similar antagonistic action between  $\text{NO}_3^-$  and  $\text{NO}_2^-$  was observed.

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### 1. Introduction

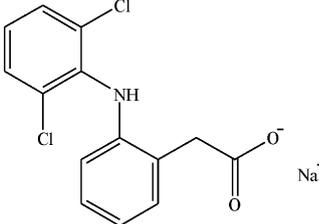
In recent years, Pharmaceutical and Personal Care Products (PPCPs) have been found polluting a wide range of aquatic environments including groundwater, surface water and drinking water [1]. Accordingly, this important emerging environmental pollution by PPCPs and their metabolites in the aquatic environment has raised increasing concern [2]. Pharmaceutical pollution is increasing in the aquatic environment since many pharmaceuticals are incompletely removed during their passage through wastewater treatment plants. PPCPs consist of a wide range of compounds whose behavior is difficult to predict because it is often controlled by interactions with specific functional groups or complicated pH-dependent speciation and so on [3]. Therefore, it is important to study the environmental behavior of pharmaceuticals.

Diclofenac (DCF) is a synthetic non-steroidal anti-inflammatory drug (NSAD), mostly used as its sodium salt in medical care as an analgesic, antiarthritic and antirheumatic. It is also an important drug in outpatient care. The chemical characteristics of DCF are described in Table 1. The global consumption of diclofenac is estimated to be 940 tons per year, with a defined daily dose of 100 mg [4–7]. DCF enters the aquatic environment by direct disposal in households, excretion or human and animal medical care and so on [8]. However, a low degradation rate of diclofenac in communal sewage treatment plants has been recorded. In the WWTP, the level of DCF removal efficiency is still very uncertain, ranging from 0% up to 80%, but mainly in the range 21–40% [9]. Since the degradation by wastewater treatment plants is incomplete, diclofenac is frequently detected in natural water and diclofenac has been detected in concentrations of up to 28.4  $\mu\text{g/L}$  in surface water. It is also detected in concentrations of 0.59  $\mu\text{g/L}$  in groundwater [10]. Nowadays, the harmful effects of DCF on different organisms in realistic aquatic environments have been demonstrated [11]. Compounds such as diclofenac can cause renal failure in the Indian gyps vulture and alterations of the gills of rainbow trout, with effects observed with concentrations as low as 1  $\mu\text{g/L}$  [12–14]. Diclofenac can also influence the biochemical functions of fish and lead to tissue damage [15]. It is clear that we should be much more concerned about DCF in the aquatic environment. Recently, most studies have been

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**Table 1**  
Chemical characteristics of Diclofenac.

Drug	CAS	Chemical structure	Molecular weight (g/mol)	$\lambda_{\max}$ (nm)
Diclofenac	15307-86-5		318.13	276

focused on DCF treatment methods in order to achieve degradation, such as via Fenton reactions and under UV-light irradiation in the presence of  $\text{H}_2\text{O}_2$  or ozone [16–18]. However, there have been few studies of the environmental behavior of DCF in natural water. So, it is necessary to study.

Nitrogen, in its various forms, plays an important role in natural water and has been extensively studied. Natural waters contain or produce nitrogen (up to  $10^{-3}$  mol/L) through bacterial nitrification and usually receive nitrogenous fertilizers and so on [19]. Inorganic nitrogen, mainly in the form of  $\text{NH}_4^+$  and  $\text{NO}_3^-$ , is usually present in the aquatic environment. The intermediate oxidation state of nitrogen, represented by  $\text{NO}_2^-$ , exists in surface water under certain conditions. Furthermore, the photolysis of nitrate and nitrite ions in the aquatic environment cannot be neglected. In the last 20 years, a great deal of research work has proven that  $\cdot\text{OH}$  is generated in natural waters by the photolysis of nitrite and nitrate. Therefore, nitrate is the major source of  $\cdot\text{OH}$  in natural water [20]. It is meaningful to study the interactions of different forms of nitrogen on the photodegradation of DCF under simulated sunlight irradiation.

The objective of this study was to investigate the kinetic model for DCF degradation and the effect of different forms of nitrogen changes with different pE values on the photodegradation of DCF under simulated sunlight in the aquatic environment. Furthermore, quenching experiments and the kinetic model for DCF degradation were used to test whether the DCF underwent self-sensitization or not. The experimental results were analyzed to explain the effects of different forms of nitrogen on the photodegradation of DCF.

## 2. Experimental

### 2.1. Chemicals

Diclofenac, 2-[(2,6-dichlorophenyl)amino]benzeneacetic acid, sodium salt (98% purity), was purchased from J&K Chemical Co. Ltd. (Beijing, China). High performance liquid chromatography (HPLC) graded methanol. HPLC-grade methanol was obtained from Suqian Guoda Chemical Reagent Co. Ltd. (Jiangsu, China). Sodium nitrate, sodium nitrite, ammonium sulfate were all obtained from Tianjin Guangfu Chemical Reagents Co. Ltd. (Tianjin, China). All of chemicals used were of analytical grade without further purification. Ultra-pure water from a Milli-Q water process (Millipore, USA) was used for preparing all aqueous solutions.

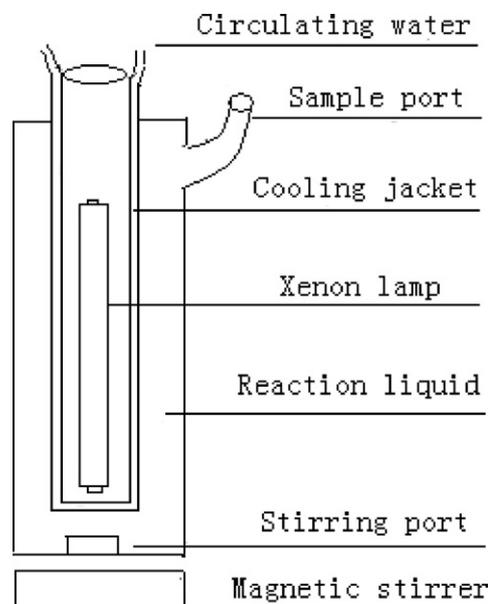
### 2.2. Photodegradation experiments

Photolysis experiments were performed on the equipment that had a 250 mL hollow cylindrical quartz tube photoreactor (SGY-1, Nanjing STO Co. Ltd.), as shown in Scheme 1. The reaction liquid of DCF and other additives were stirred by a magnetic stirrer throughout the experiments in order to remain homogeneous in the quartz tube which was put vertically outside a double-walled

quartz cooling jacket. A 350 W xenon lamp was put in the double-walled quartz cooling jacket and temperature was controlled by the constant-temperature liquid-circulating apparatus. DCF and other additives were placed into the 250 mL volumetric flask and diluted with Milli-Q water, then put the reaction liquid into the quartz tube. During the whole experiments, 2 mL reaction liquid was taken out every 3 min from the quartz tube periodically using a pipette and immediately analyzed by reversed-phase high-performance liquid chromatography system.

### 2.3. Analytical methods

The concentrations of DCF solutions was determined by reversed-phase high-performance liquid chromatography system, which consisted of two Waters 1525 Binary HPLC pumps and Waters 2998 Photodiode Array detector (Waters, Massachusetts, USA). Analytical column temperatures were controlled with a Model 1500 Column Heater (Waters, and Product of Singapore). The analytical column was a 150 mm  $\times$  4.6 mm Waters C18 column, (particle size 5  $\mu\text{m}$ ). A Waters guard column (C18, 4.6 mm  $\times$  20 mm, particle size 5  $\mu\text{m}$ ) was used to protect the analytical column (both purchased from Waters). The injection volume was 20  $\mu\text{L}$ . The mobile phase was mixtures 75% HPLC-grade methanol and 25% MilliQ-water (containing 1% Acetic acid) at a constant flow rate of 1.0  $\text{mL min}^{-1}$ , the detection wavelength was set at 276 nm.

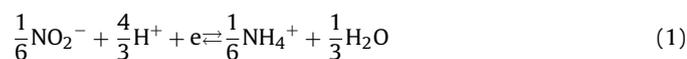


**Scheme 1.** Photoreactor for the degradation of DCF under the simulated sunlight system.

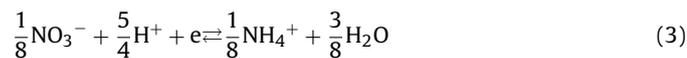
#### 2.4. Redox transformation of inorganic nitrogen

Inorganic nitrogen mainly in the form of  $\text{NH}_4^+$  and  $\text{NO}_3^-$  exists in surface water. Intermediate oxidation state of  $\text{NO}_2^-$  exists in surface water under certain conditions. The pE value is the negative log of electronic density in oxidation–reduction equilibrium system. According to the existence forms of nitrogen, pE value are divided into three intervals as below (Suppose the total nitrogen concentration is  $1.00 \times 10^{-4}$  mol/L and the pH value of water is:

(i) pE value is less than 5,  $\text{NH}_4^+$  is the main form:

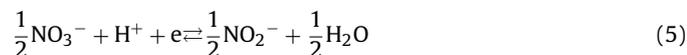


$$\text{pE} = 5.82 + \lg \frac{[\text{NO}_2^-]^{1/6}}{[\text{NH}_4^+]^{1/6}} \quad (2)$$



$$\text{pE} = 6.15 + \lg \frac{[\text{NO}_3^-]^{1/8}}{[\text{NH}_4^+]^{1/8}} \quad (4)$$

(ii) pE value is about 6.5,  $\text{NO}_2^-$  is the main form:



$$\text{pE} = 7.15 + \lg \frac{[\text{NO}_3^-]^{1/2}}{[\text{NO}_2^-]^{1/2}} \quad (6)$$

(iii) pE value is more than 7,  $\text{NO}_3^-$  is the main form:

$$\text{pE} = 7.15 + \lg \frac{[\text{NO}_3^-]^{1/2}}{[\text{NO}_2^-]^{1/2}} \quad (7)$$

$$\text{pE} = 6.15 + \lg \frac{[\text{NO}_3^-]^{1/8}}{[\text{NH}_4^+]^{1/8}} \quad (8)$$

This research was investigated the effect of different pE values (according to the existence forms of nitrogen) on photodegradation of DCF under the simulated sunlight.

#### 2.5. Kinetics of DCF degradation

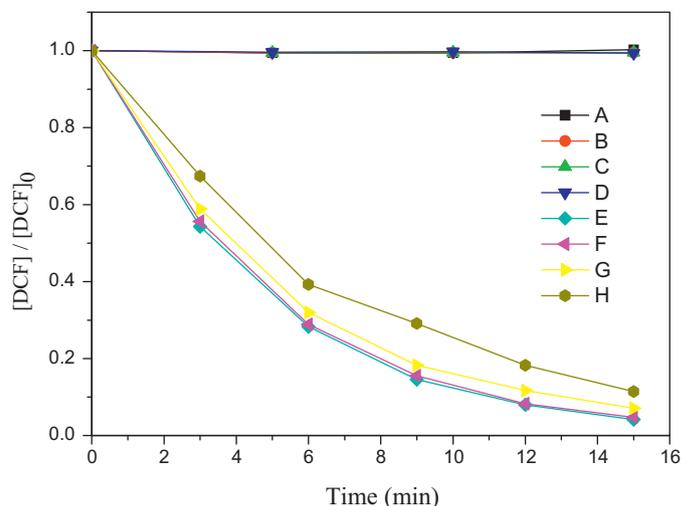
First-order kinetics is generally used to express the photodegradation of a micropollutant [21]. The rate constant  $k$  was calculated from the first-order equation:

$$\frac{dC}{dt} = -kC \quad (9)$$

where  $C$  is the concentration of DCF;  $k$  is the rate constant;  $t$  is the reaction time. By integrating the equality, the following equations could be obtained:

$$\ln \frac{C_t}{C_0} = -kt \quad (10)$$

where  $C_t$  is the DCF concentration at time  $t$ ,  $C_0$  is the initial concentration of DCF. Furthermore, when the concentration of DCF reduces to 50% of its initial concentration, the half-life can be calculated from the rate constant as the equation:  $t_{1/2} = \ln 2/k$ .



**Fig. 1.** Photodegradation of four different initial DCF concentrations under dark and light condition Dark: (A)  $[\text{DCF}]_0 = 0.015$  mmol/L; (B)  $[\text{DCF}]_0 = 0.03$  mmol/L; (C)  $[\text{DCF}]_0 = 0.045$  mmol/L; (D)  $[\text{DCF}]_0 = 0.06$  mmol/L; Light: (E)  $[\text{DCF}]_0 = 0.015$  mmol/L; (F)  $[\text{DCF}]_0 = 0.03$  mmol/L; (G)  $[\text{DCF}]_0 = 0.045$  mmol/L; (H)  $[\text{DCF}]_0 = 0.06$  mmol/L.

### 3. Results and discussion

#### 3.1. Effect of initial DCF concentration on the photodegradation of DCF

The effect of different initial concentrations of DCF on the degradation of DCF in the absence of simulated sunlight or the presence of any other illumination was investigated (Fig. 1). It can be seen that DCF shows hardly any decompose in the absence of simulated sunlight. In contrast, more than 90% of the DCF was degraded in 15 min under simulated sunlight irradiation (350 W xenon lamp). These results indicate that the degeneration of DCF is the result of photon absorption. Experiments conducted the linear plots of  $[\text{DCF}]/[\text{DCF}]_0$  versus time for initial DCF concentrations of 0.015, 0.030, 0.045 and 0.060 mmol/L, showed degradation rates of 95.81%, 95.25%, 92.93%, and 88.54%, respectively.

It can be seen that the degradation rate of DCF increased as the initial concentration of DCF decreased. This result can be explained by considering the competition for absorption of the limited quantity of available photons by the DCF. Because the initial concentration of DCF increased but the number of available photons did not change, the number of photons available per molecule of DCF decreased, so the degradation rate of DCF decreased.

#### 3.2. Mechanisms and kinetic models for the photodegradation of DCF

Quenching experiments were used to test whether the DCF underwent self-sensitization via a reactive oxygen species (ROS). As can be seen from the Fig. 2, the addition of isopropanol ( $\bullet\text{OH}$  quencher) [22], sodium azide ( $\bullet\text{OH}$  and  $^1\text{O}_2$  quencher) [23] and p-quinone ( $\text{O}_2^{\bullet-}$  quencher) [24] each showed an inhibition effect on the DCF degradation. The experimental results led to the conclusion that photooxidation was involved in the photodegradation of DCF via  $\bullet\text{OH}$ ,  $^1\text{O}_2$  and  $\text{O}_2^{\bullet-}$  under simulated sunlight in water. It has been reported that organic pollutants will absorb actinic photons and transfer energy or electrons, resulting in the generation of ROS, which subsequently oxidized and degraded the organic pollutants. The degradation process has been referred to as the self-sensitized photooxidation of pollutants [25–27]. It is therefore possible that the photodegradation of DCF includes a self-sensitization photooxidation process via  $\bullet\text{OH}$ ,  $^1\text{O}_2$  and  $\text{O}_2^{\bullet-}$  under simulated sunlight.

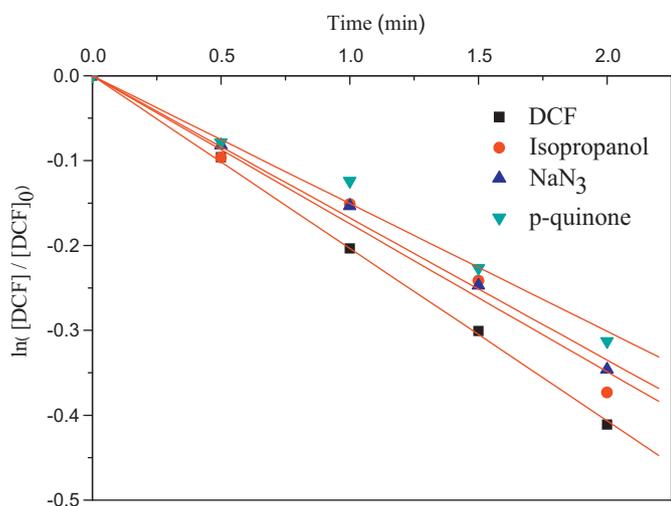


Fig. 2. Effect of isopropanol, NaN<sub>3</sub> and p-quinone photodegradation kinetics of DCF ([DCF]<sub>0</sub> = 0.03 mmol/L) under simulated sunlight.

Scheme 2 shows the reactions that may occur during DCF photodegradation.

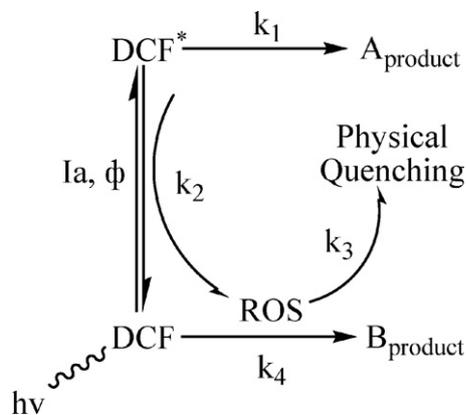
According to the literatures [27,28], we can estimate the contribution of •OH, <sup>1</sup>O<sub>2</sub> and O<sub>2</sub><sup>•-</sup> to the overall photodegradation of DCF as follows:

$$R_{\bullet\text{OH}} = \frac{k_{\bullet\text{OH}}}{k} \approx \frac{k - k_{\text{isopropanol}}}{k} \quad (11)$$

$$R_{^1\text{O}_2} = \frac{k_{^1\text{O}_2}}{k} \approx \frac{k_{\text{isopropanol}} - k_{\text{NaN}_3}}{k} \quad (12)$$

$$R_{\text{O}_2^{\bullet-}} = \frac{k_{\text{O}_2^{\bullet-}}}{k} \approx \frac{k - k_{\text{p-quinone}}}{k} \quad (13)$$

where  $R_{\bullet\text{OH}}$ ,  $R_{^1\text{O}_2}$  and  $R_{\text{O}_2^{\bullet-}}$  are the contribution rates of self-sensitized photodegradation via •OH, <sup>1</sup>O<sub>2</sub> and O<sub>2</sub><sup>•-</sup>, respectively;  $k_{\bullet\text{OH}}$ ,  $k_{^1\text{O}_2}$  and  $k_{\text{O}_2^{\bullet-}}$  are the rate constants of self-sensitized photodegradation via •OH, <sup>1</sup>O<sub>2</sub> and O<sub>2</sub><sup>•-</sup>, respectively;  $k_{\text{isopropanol}}$ ,  $k_{\text{NaN}_3}$  and  $k_{\text{p-quinone}}$  are the rate constants for the addition of isopropanol, sodium azide and p-quinone in water.  $k$  is the rate constants of photodegradation of DCF. It can be calculated that  $R_{\bullet\text{OH}}$  is 14.99%,  $R_{^1\text{O}_2}$  is 3.36%,  $R_{\text{O}_2^{\bullet-}}$  is 26.59%. It can be concluded from above results that direct photodegradation contributed to the main degradation of DCF with little contributed of self-sensitization.



Scheme 2. The proposed pathway for photolysis of DCF.

To take <sup>1</sup>O<sub>2</sub> for an example, Scheme 2 simplified can be obtaining simplified reaction scheme as follow:



where  $I_a$  is the rate of light absorption by DCF,  $\phi$  is the quantum yield for DCF\*,  $k_1$  is the direct photodegradation rate constant of DCF,  $k_2$  is the second-order rate constant between DCF\* and <sup>3</sup>O<sub>2</sub>,  $k_3$  is the first-order rate constant for physical quenching of <sup>1</sup>O<sub>2</sub> by water,  $k_4$  is second-order rate constant between <sup>1</sup>O<sub>2</sub> and DCF. Reaction (15) is direct photodegradation process; Reaction (18) is photooxidation process of DCF via <sup>1</sup>O<sub>2</sub>.

The steady-state approximation for ground state DCF is:

$$-\frac{d[\text{DCF}]}{dt} = k_{\text{self-sensitized}} + k_{\text{direct}} = k_4[{}^1\text{O}_2][\text{DCF}] + k_1[\text{DCF}^*] \quad (19)$$

The steady-state approximation for [DCF\*] is:

$$\frac{d[\text{DCF}^*]}{dt} = \phi I_a - k_1[\text{DCF}^*] - k_2[\text{DCF}^*][{}^3\text{O}_2] = 0 \quad (20)$$

$$[\text{DCF}^*] = \frac{\phi I_a}{k_1 + k_2[{}^3\text{O}_2]} \quad (21)$$

The steady-state approximation for [<sup>1</sup>O<sub>2</sub>] is:

$$\frac{d[{}^1\text{O}_2]}{dt} = k_2[\text{DCF}^*][{}^3\text{O}_2] - k_4[\text{DCF}][{}^1\text{O}_2] - k_3[{}^1\text{O}_2] = 0 \quad (22)$$

$$[{}^1\text{O}_2] = \frac{k_2[\text{DCF}^*][{}^3\text{O}_2]}{k_3 + k_4[\text{DCF}]} \quad (23)$$

The value of  $k_3$  for <sup>1</sup>O<sub>2</sub> is  $2.5 \times 10^5 \text{ s}^{-1}$  [22], so  $k_3$  will be much greater than  $k_4$ ,  $I_a = I_0(1 - e^{-\epsilon b[\text{DCF}]})$ , The initial concentration of DCF in thin study was 0.03 mM, so  $k_3 \gg k_4[\text{DCF}]$ , Eq. (23) can be simplified to:

$$[{}^1\text{O}_2] = \frac{k_2[\text{DCF}^*][{}^3\text{O}_2]}{k_3} \quad (24)$$

According to the Beer-Lambert law,

$$I_a = I_0(1 - e^{-\epsilon b[\text{DCF}]}) \quad (25)$$

Because of the initial concentration of DCF in thin study was 0.03 mM, so  $\epsilon b[\text{DCF}] \ll 1$ , Eq. (25) can be simplified to:

$$I_a = I_0 \epsilon b[\text{DCF}] \quad (26)$$

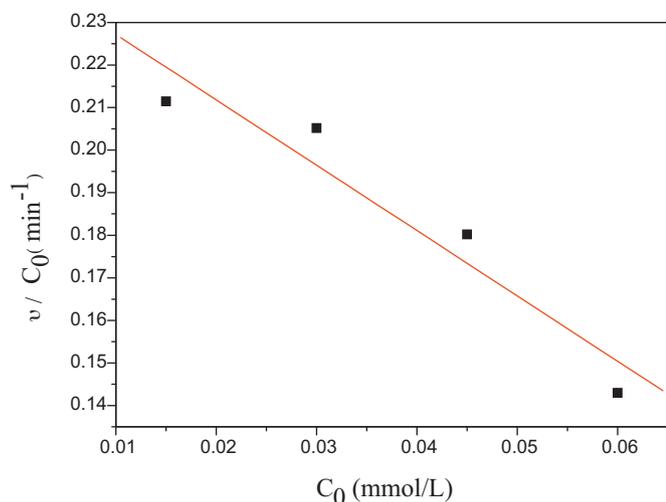
Rearranging Eq. (24) yields:

$$[{}^1\text{O}_2] = \frac{k_2[\text{DCF}^*][{}^3\text{O}_2]}{k_3} = \frac{\phi I_0 \epsilon b[\text{DCF}] k_2 [{}^3\text{O}_2]}{k_3(k_1 + k_2[{}^3\text{O}_2])} \quad (27)$$

$$\begin{aligned} v = -\frac{d[\text{DCF}]}{dt} &= k_4[{}^1\text{O}_2][\text{DCF}] + k_1[\text{DCF}^*] \\ &= \frac{\phi I_0 \epsilon b[\text{DCF}] k_2 [{}^3\text{O}_2] k_4 [\text{DCF}]}{k_3(k_1 + k_2[{}^3\text{O}_2])} + \frac{\phi I_0 \epsilon b k_1 [\text{DCF}]}{k_1 + k_2[{}^3\text{O}_2]} \end{aligned} \quad (28)$$

$$\frac{v}{[\text{DCF}]} = \frac{\phi I_0 \epsilon b k_2 k_4 [{}^3\text{O}_2]}{k_3(k_1 + k_2[{}^3\text{O}_2])} [\text{DCF}] + \frac{\phi I_0 \epsilon b k_1}{k_1 + k_2[{}^3\text{O}_2]} \quad (29)$$

In accordance with Eq. (29), linear plots of  $C_0$  versus  $v/C_0$  obtained the y-intercepts was the rate constants of the direct photodegradation which is consistent with the report by some



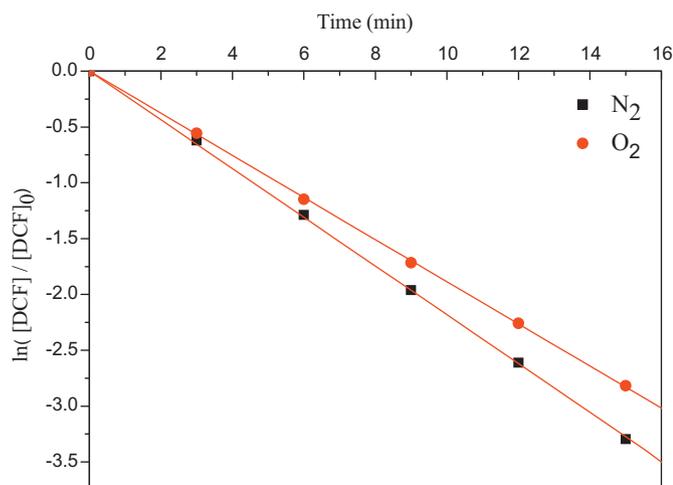
**Fig. 3.** The initial rate of DCF photodegrade vs. various initial concentrations under simulated sunlight.

literatures [24,25]. From Fig. 3, the rate constants of the direct photodegradation resulting from extrapolation to  $C_0=0$ , the rate constants of the direct photodegradation is  $0.227 \text{ min}^{-1}$ .

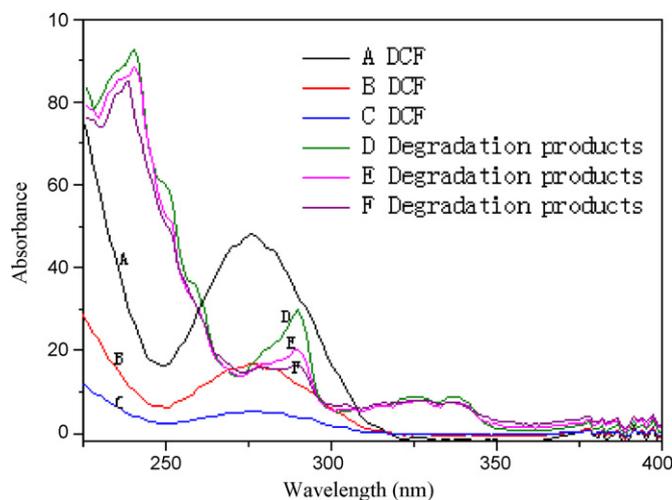
### 3.3. Effect of oxygen concentration on the photodegradation of DCF

Experiments were conducted to study the effect of varying the oxygen concentration in the solution, using nitrogen or oxygen as purging gas, on the photodegradation of DCF. As can be seen from Fig. 4, the lower the oxygen content, the more rapid the degradation rate.

In accordance with simplified reaction can inferences the photodegradation process of DCF: ① DCF absorbs actinic photons and forms an excited DCF, followed by direct photodegradation, ② excited DCF transfers energy to dissolved oxygen in water with the formation of reactive oxygen species, which subsequently cause the photooxidation of DCF (self-sensitized process of DCF). It can be seen there are two effects of dissolved oxygen: on the one hand, the dissolved oxygen can absorb the energy of the excited DCF and form reactive oxygen species, which then promote the self-sensitized degradation of DCF; on the other hand, dissolved oxygen



**Fig. 4.** Kinetics of DCF photodegradation at various dissolved oxygen contents,  $[DCF]_0 = 0.03 \text{ mmol/L}$ .



**Fig. 5.** UV-Vis spectra comparison of degradation products of DCF,  $[DCF]_0 = 0.03 \text{ mmol/L}$ . Spectra were acquired by separating DCF and the degradation products via HPLC and detecting with a photodiode array detector. Reaction time: DCF: (A) 0 min; (B) 5 min; (C) 10 min. DCF and its degradation products: (D) 5 min; (E) 10 min; (F) 15 min.

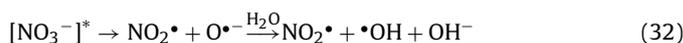
quenches the excited DCF and, in this way, has an inhibiting effect on the direct photodegradation of DCF. It has been verified that the photodegradation of DCF can be predominantly attributed to direct photolysis. So the probability that dissolved oxygen inhibits the photodegradation of DCF is high. As can be seen from Fig. 4, dissolved oxygen inhibits the DCF degradation. It can be seen that the experimental results agree well with the theoretical analysis.

Furthermore, the reaction liquid was colorless and transparent after 15 min in the presence of  $\text{N}_2$  and the reaction liquid was yellow after 15 min in the presence of  $\text{O}_2$ . It was also observed that a different degradation product was obtained with different oxygen content. The results indicated that the  $B_{\text{product}}$  was yellow in color. Fig. 5 shows the UV-Vis spectra of  $B_{\text{product}}$  and DCF in water. It can be seen that the  $B_{\text{product}}$  absorption wavelength region overlaps with the absorbance region of DCF (Fig. 5). With the self-sensitized processes, the concentration of  $B_{\text{product}}$  increased so the competition for photons will also be more intense.

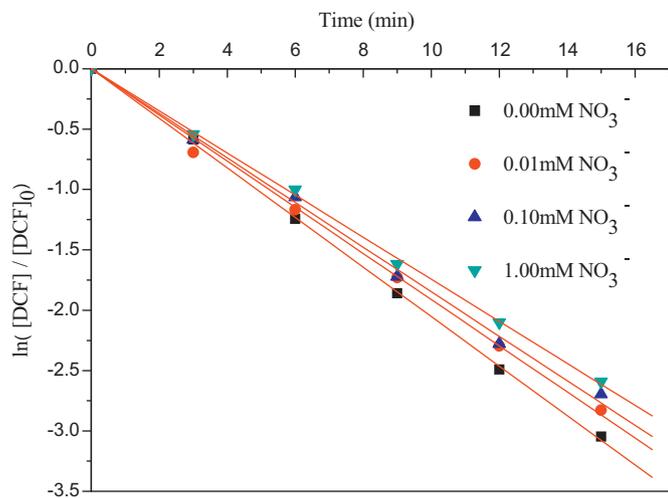
To sum up the above arguments, it is concluded that dissolved oxygen inhibits the photodegradation of DCF.

### 3.4. Effect of nitrate ion on the photodegradation of DCF

The effect of different concentrations of  $\text{NO}_3^-$  on the degradation of DCF under simulated sunlight is shown in Fig. 6 Linear plots of  $\ln([DCF]/[DCF]_0)$  versus time obtained with  $\text{NO}_3^-$  concentrations of 0.0, 0.01, 0.1 and 1.0 mmol/L, gave correlation coefficients ( $R^2$ ) of 0.9996, 0.9982, 0.9972 and 0.9990, respectively. The calculated rate constants ( $k$ ) were 0.205, 0.191, 0.185 and  $0.174 \text{ min}^{-1}$  at  $\text{NO}_3^-$  concentrations of 0.0, 0.01, 0.1 and 1.0 mmol/L, respectively. It can be seen that the nitrate ion inhibits the DCF degradation whatever the concentration of nitrate, and the degradation rate of DCF was reduced with increasing nitrate ion concentration.



On the one hand, nitrate ion can form  $\cdot\text{OH}$  radicals under UV irradiation [29]. The  $\cdot\text{OH}$  radicals can promote DCF degradation. In contrast, the contribution rate of self-sensitization photooxidation via  $\cdot\text{OH}$  is 14.99%. The photodegradation of DCF has been predom-



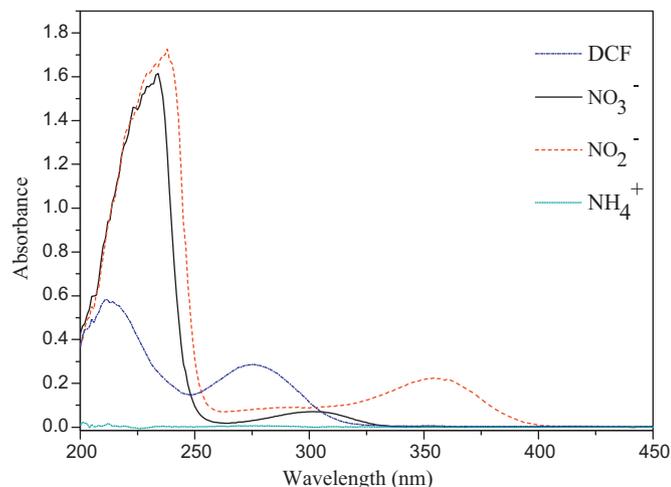
**Fig. 6.** Effect of  $\text{NO}_3^-$  concentration under simulated sunlight photodegradation kinetics of DCF ( $[\text{DCF}]_0 = 0.03 \text{ mmol/L}$ ) in water.

inantly attributed to direct photolysis. So, the promotion effect via  $\bullet\text{OH}$  plays only a small part in the entire photodegradation process.

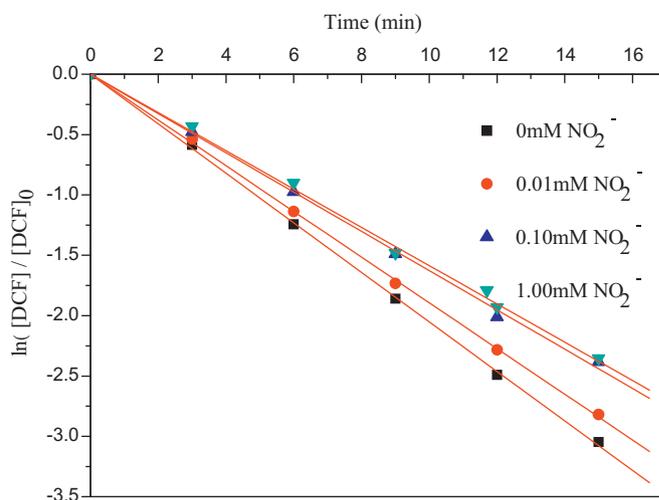
On the other hand, nitrate ion can absorb light in the UV range under UV or sunlight irradiation. Nitrate ion absorbs photons in the emission spectrum of a Xenon lamp, and this wavelength region overlaps with the absorbance wavelength region of DCF (Fig. 7). Therefore, this result can be explained as competition of DCF and nitrate ion for the limited number of available photons, leading to a reduction of the degradation rate of DCF with increased nitrate ion concentration. The result is consistent with the report by Wenzhen Li et al.

### 3.5. Effect of nitrite ion on the photodegradation of DCF

The effect of different  $\text{NO}_2^-$  concentrations on the degradation of DCF under simulated sunlight is shown in Fig. 8. Experiments conducted at  $\text{NO}_2^-$  concentrations of 0.0, 0.01, 0.1 and 1.0 mmol/L produced rate constants of 0.205, 0.189, 0.163 and 0.159  $\text{min}^{-1}$ , respectively. The rate constants decreased with increasing concentration of  $\text{NO}_2^-$ , showing the same trend as for  $\text{NO}_3^-$ . It is worth mentioning that when  $[\text{inducer}]_0$  is 1.0 mmol/L, the rate constants are 0.174 and 0.159  $\text{min}^{-1}$  for  $\text{NO}_3^-$  and  $\text{NO}_2^-$ , respectively. It can be seen that  $\text{NO}_2^-$  appears to show greater inhibition than  $\text{NO}_3^-$ , a result which can be explained because the  $\text{NO}_2^-$  absorption wave-



**Fig. 7.** UV-Vis spectra comparison of isolated DCF,  $\text{NO}_3^-$ ,  $\text{NO}_2^-$  and  $\text{NH}_4^+$ .



**Fig. 8.** Effect of  $\text{NO}_2^-$  concentration under simulated sunlight photodegradation kinetics of DCF ( $[\text{DCF}]_0 = 0.03 \text{ mmol/L}$ ) in water.

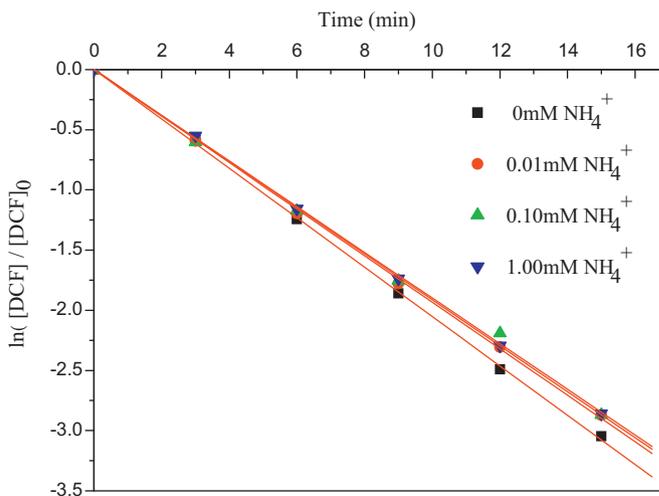
length overlaps the absorbance wavelength region of DCF more than that of  $\text{NO}_3^-$  (Fig. 7) [30].

### 3.6. Effect of ammonium ion on the photodegradation of DCF

Fig. 9 shows the effect of different concentrations of ammonium ion on the photodegradation of DCF. Linear plots of  $\ln([\text{DCF}]/[\text{DCF}]_0)$  versus time obtained at  $\text{NH}_4^+$  concentrations of 0.0, 0.01, 0.1 and 1.0 mmol/L, gave rate constants of 0.205, 0.193, 0.190 and 0.191  $\text{min}^{-1}$ , respectively. The rate constants for the photodegradation of DCF showed little change with increase of the concentration of ammonium ion. The results indicate that  $\text{NH}_4^+$  has little effect on the photodegradation of DCF.

### 3.7. Effect of pE value on the photodegradation of DCF

The simulated pE values corresponding to different forms and concentrations of inorganic N are listed in Table 2. A series of experiments was designed to investigate the influence of the pE value (4.82–8.15) on the photodegradation of DCF. The experimental results are shown in Table 3 and demonstrate that the rate constants decreased gradually when the pE value changed from 4.82



**Fig. 9.** Effect of  $\text{NH}_4^+$  concentration under simulated sunlight photodegradation kinetics of DCF ( $[\text{DCF}]_0 = 0.03 \text{ mmol/L}$ ) in water.

**Table 2**  
Different pE value corresponding inorganic N concentration,  $[DCF]_0 = 0.03$  mmol/L.

Simulate pE value	Inorganic N concentration/mmol/L		
	$NO_3^-$	$NO_2^-$	$NH_4^+$
4.82	0.00	0.00	1.00
5.82	0.00	0.50	0.50
5.92	0.00	0.80	0.20
6.85	0.20	0.80	0.00
7.15	0.50	0.50	0.00
8.15	1.00	0.00	0.00

**Table 3**  
Kinetics of DCF photodegradation at different pE value,  $[DCF]_0 = 0.03$  mmol/L.

pE value	$k/\text{min}^{-1}$	$t_{1/2}/\text{min}$	$R^2$	Actual inhibition rate/%	Theoretical inhibition rate/%
4.82	0.191	3.62	0.9998	7.10	7.10
5.82	0.169	4.09	0.9980	21.01	35.20
5.92	0.162	4.27	0.9988	26.33	36.69
6.85	0.155	4.47	0.9994	32.25	40.53
7.15	0.165	4.21	0.9960	24.56	41.42
8.15	0.174	3.98	0.9998	17.75	17.75

to 6.85, and then increased gradually when the pE value changed from 6.85 to 8.15.

These results can be related to the form of inorganic N. When the pE value is less than 5,  $NH_4^+$  is the main form but when the pE value is about 6.5,  $NO_2^-$  is the main form. When the pE value is more than 7,  $NO_3^-$  is the main form.  $NO_2^-$  and  $NO_3^-$  have inhibiting effects on the photodegradation of DCF. The inhibiting effect of  $NO_2^-$  was stronger than that of  $NO_3^-$ . Ammonium ion had little effect on the photodegradation of DCF. Therefore, as the concentration of  $NO_2^-$  increased ( $NH_4^+$  decreased) when the pE value changes from 4.82 to 6.85, the inhibition rate is increased. Similarly, as the concentration of  $NO_2^-$  decreased ( $NO_3^-$  increased) when the pE value changes from 6.85 to 8.15, so the inhibition rate was decreased.

Comparing the actual inhibition rate with the theoretical inhibition rate, it is clear that when  $NH_4^+$  and  $NO_2^-$  coexist in the aquatic environment, the actual inhibiting effect on the photodegradation of DCF is less than the sum of the partial inhibiting effects. The results indicated that  $NO_2^-$  had an obvious antagonistic action for  $NH_4^+$  and when  $NO_3^-$  and  $NO_2^-$  coexist in the aquatic environment, a similar antagonistic action is present between  $NO_3^-$  and  $NO_2^-$ .

#### 4. Conclusions

In this study the kinetic model and the effect of different forms of nitrogen on the photodegradation of DCF under simulated sunlight in the aquatic environment was investigated in detail. The following conclusions can be drawn:

- (1) Degradation pathways proceed via pseudo first-order kinetics in all cases. The photodegradation of DCF is the sum of the degradation by direct photolysis and self-sensitization. The photodegradation of DCF can be predominantly attributed to direct photolysis.
- (2) Dissolved oxygen inhibits the photodegradation of DCF.
- (3)  $NO_3^-$  and  $NO_2^-$  has inhibiting effects on the photodegradation of DCF. The inhibiting effect of  $NO_2^-$  was stronger than that of  $NO_3^-$  and  $NH_4^+$  had no effect on the photodegradation of DCF.
- (4)  $NO_2^-$  had an obvious antagonistic action for  $NH_4^+$  and a similar antagonistic action between  $NO_3^-$  and  $NO_2^-$ .

#### Acknowledgements

This work is supported by the National Natural Science Foundation of China (No. 20677012), the Scientific Research Project of the Union of Guangdong Province and Education Ministry (No. 2009B090300342), and the Government Key Project of Water Pollution Controlling of China (No. 2009ZX07211-005-03).

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