



Degradation of antibiotic norfloxacin in aqueous solution by visible-light-mediated C-TiO₂ photocatalysis

Meijuan Chen, W. Chu*

Department of Civil and Structural Engineering, Research Centre for Environmental Technology and Management, The Hong Kong Polytechnic University, Hung Hom, Kowloon, Hong Kong

ARTICLE INFO

Article history:

Received 6 February 2012

Received in revised form 26 March 2012

Accepted 28 March 2012

Available online 5 April 2012

Keywords:

Norfloxacin

Photocatalysis

Visible-light-mediated C-TiO₂ process

ABSTRACT

A visible-light-mediated C-TiO₂ photocatalytic process (Vis/C-TiO₂) was employed to degrade antibiotic norfloxacin. The influences of catalyst dosage, initial probe compound concentration and solution pH levels on the decay performance and reaction kinetics were investigated and optimized. Based on the experimental results, an equation was established to predict the observed rate constant under neutral pH. In addition, the decay rate was accelerated under weak alkali in the presence of moderate OH⁻ anions. Hydroxyl radical was confirmed to play a major role in the Vis/TiO₂ process, where in the presence of •OH quencher and electron acceptor, retardation and improvement were found respectively. Furthermore, an original schematic diagram describing the surface property of C-TiO₂ was built and further verified, in which, NH₄⁺ cations normally served as hole scavengers showed a negligible effect because the adsorbed OH⁻ formed a barrier for NH₄⁺ ions to approach the holes, and the F⁻ anions presented a significant suppression on norfloxacin decay due to the formation of hydrogen bond (O—H...F) around the C-TiO₂ surface. Besides, the recycling and sedimentation tests justified that the Vis/C-TiO₂ process is a cost-effective and feasible way for wastewater treatment.

© 2012 Elsevier B.V. All rights reserved.

1. Introduction

The release of antibiotics into aquaculture has increased significantly in recent years [1]. Norfloxacin belongs to fluoroquinolone antibiotics, which has been used to treat common and complicated urinary tract infections. It was frequently detected in sewage and the concentration reached up to 3.54 μg/L in Hong Kong [2]. Because the inefficient removal ability of antibiotics in traditional sewage plants [3], pollution of these chemicals has been observed in various water sources, including sewage treatment plant effluents [4], surface water [5], seawater [6], groundwater [7] and drinking water [8]. The norfloxacin in aqueous system might lead to adverse environmental effects [9], including the development of antibiotic resistance to aquatic bacteria [10], direct toxicity to microorganism and possible risks to human health through drinking water and/or food-chain [10].

In the past decade, efforts have been made on the removal of norfloxacin. Among the studies, adsorption is found to be a useful method, since norfloxacin can be absorbed by activated sludge [11], activated carbon [12], carbon nanotubes [12], and silica/alumina [13]. However, the “removed” norfloxacin only physically resides

in sorbent and brings a risk of being released into aquatic environment if the used sorbent is improperly disposed. Therefore, methods resulting in direct or full decomposition are required.

Researchers have examined the degradation of norfloxacin in aqueous systems by different methods, such as ozonation, UV, ClO₂, KMnO₄, UV/O₃ and UV/TiO₂ [14–16]. Thereinto, photocatalysis technique has received intensive attention with key advantage of low cost and enduring stability. However, the popularly used photocatalyst, namely TiO₂, can only be excited by UV light with an irradiation wavelength less than 380 nm, which significantly limits its application. To broaden the utilizable range of light, the investigation on visible-light-driven photocatalysts has become one of the most active research areas. Therefore, various photocatalysts responding to visible light have been developed, including TiO₂-based catalyst comprised by doping element [17–19] or composing with other substances [20,21]. Carbon-doped TiO₂ (C-TiO₂) has attracted considerable attention due to its high efficiency and long-term stability [22]. Most previous studies focus on the improvement of C-TiO₂ morphology to enhance the performance on pollutants decomposition. However, investigation on the degradation performance considering the environmental parameters effects is limited.

In this study, a visible light mediated C-TiO₂ photocatalytic process (Vis/C-TiO₂) was employed to degrade antibiotic norfloxacin. To our best knowledge, this is the first time to employ Vis/C-TiO₂

* Corresponding author. Tel.: +852 2766 6075; fax: +852 2334 6389.
E-mail address: cechu@polyu.edu.hk (W. Chu).

process in the norfloxacin decay. Environmental parameters, including C-TiO₂ dosage, norfloxacin initial concentration, and pH levels were investigated and optimized. To elucidate the reaction principle of this Vis/C-TiO₂ process, an original schematic diagram was built and selected inorganic ions was added into the process to verify the model. Meanwhile, the involved radical was confirmed. Furthermore, to evaluate the potential use of this process for real application, the reuse ability and settling properties of C-TiO₂ were carried out as well.

2. Materials and methods

2.1. Materials

Chemicals for the synthesis of C-TiO₂ including titanium tetrachloride (TiCl₄), diethanolamine (C₄H₁₁NO₂) and ethanol were purchased from Sigma–Aldrich Inc., USA. The probe compound of norfloxacin (1-ethyl-6-fluoro-4-oxo-7-piperazin-1-yl-1H-quinoline-3-carboxylic acid, C₁₆H₁₈FN₃O₃) was purchased from Wako Pure Chemical Industries, Japan. Other chemicals, including methanol (CH₃OH), hydrochloric acid (HCl), orthophosphoric acid (H₃PO₄), sodium hydroxide (NaOH), potassium iodate (KIO₃), sodium nitrate (NaNO₃), sodium chloride (NaCl), sodium fluoride (NaF) and ammonium chloride (NH₄Cl) were all obtained from Sigma–Aldrich Inc., USA. All chemicals are of analytical grade and used as obtained without further purification. The mobile phase solvents (i.e. acetonitrile) are of HPLC grade from Tedia Company, USA. The stock solution was prepared in deionized water with a resistivity of 18.2 MΩ from a Bamstead NANOpure water system (Thermo Fisher Scientific Inc., USA).

2.2. Synthesis of C-TiO₂ photocatalyst

The C-TiO₂ photocatalyst was synthesized by a solution phase carbonization method synthesis as reported by Huang et al. [22]. First, 10 mmol of titanium tetrachloride was added dropwise into 30 mL of ethanol with continuous stirring to form a transparent yellowish solution. Then 4 mL of diethanolamine was added into the above solution and continuously stirred for 24 h at ambient temperature. The mixture was dried at 100 °C, and followed by raising the temperature to 500 °C with a heating rate of 1 °C/min and maintained for 5 h. After calcination, the obtained powder was washed by DI water for several times. For comparison, pure TiO₂ was synthesized in the same procedure in parallel with the absence of diethanolamine. The phases of C-TiO₂ and pure TiO₂ were examined and confirmed by X-ray powder diffraction (XRD) characterization (date not shown).

2.3. Norfloxacin degradation procedures

The photocatalytic reaction was conducted in a computerized Luzchem CCP-4V photochemical reactor containing 12 low-pressure mercury lamps. The irradiation wavelength of these lamps is mainly located at 420 nm as stated previously [23]. Prior to the reaction, a predetermined amount of C-TiO₂ was added into 100 mL of norfloxacin solution in a quartz beaker/cylinder, and stirred in darkness for 1 h to achieve adsorption equilibrium (Remark: pH drop was observed during this period likely due to the adsorption of hydroxyl ions onto the C-TiO₂ as discussed later). After equilibrium, the degradation was started by exposing to the pre-heated light source. At preset intervals, exact 1 mL of sample was withdrawn and filtered through a 0.2 μm PTFE membrane for further analysis. The experiments were carried out at room temperature (air-conditioned) at 23 ± 1 °C in duplicate and the error is less than 5.0%.

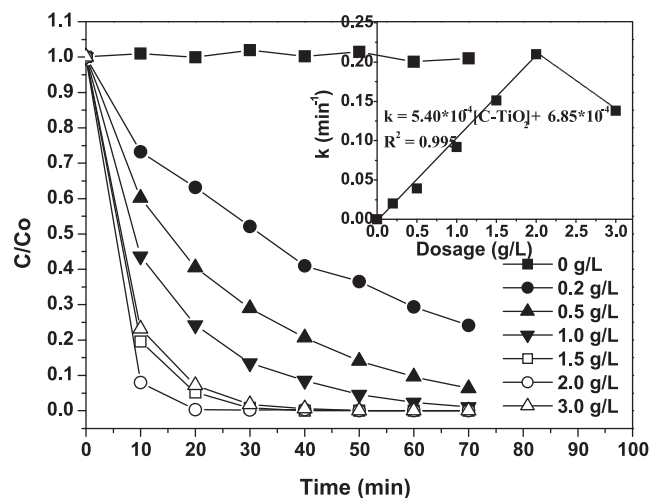


Fig. 1. Effect of catalyst dosage ([norfloxacin]₀ = 0.0313 mM).

2.4. Analysis

The remaining norfloxacin after reaction was quantified by HPLC, which was comprised of a Waters 515 HPLC pump, Waters 2487 Dual λ Absorbance Detector, Waters 717 plus Autosampler, and a Restek C18 column (5.0 μm, 0.46 cm × 25 cm). The absorption wavelength was selected as 280 nm for norfloxacin. The mobile phase was consisted of a mixture of 50% acetonitrile and 50% of water adjusting the pH level to 3 by H₃PO₄, and run at a flow rate of 0.8 mL/min. The pH level was measured by a digital pH meter (HANNA instrument, B417). The turbidity of C-TiO₂ suspension was monitored by a Hach 2100 Series Laboratory Turbidimeter. The effective diameters of C-TiO₂ at different pH levels were measured by Zeta Plus/Zeta Potential Analyzer (Brookhaven Instruments Corporation).

3. Results and discussion

3.1. Catalyst dosage and initial concentration

It was found that the probe norfloxacin is inert to sole visible light without C-TiO₂ existence (Fig. 1), while in the presence of 0.2 g/L C-TiO₂, 78% of norfloxacin was removed in 70 min and the decay curve presented a pseudo first-order kinetics. In contrast, the decay of norfloxacin in pure TiO₂ was 25% (data not shown) under other identical conditions, indicating that the Vis/C-TiO₂ process is much effective than Vis/TiO₂ process. In Fig. 1, the norfloxacin decay curves was investigated as the C-TiO₂ dosage, [C-TiO₂], varying from 0 to 3.0 g/L. It was found that all decay curves followed pseudo first-order kinetics and the rate constants (k , min⁻¹) were shown in the inset of Fig. 1. In general, the rate constant increases with the increment of catalyst dosage from 0 to 2.0 g/L. The optimum dosage was observed at a dosage of 2.0 g/L in this process, in which the norfloxacin was completely degraded in 20 min. However, a significant drop was observed when the dosage further increased to 3.0 g/L, which needed 40 min for norfloxacin thoroughly decomposition. This retardation might be ascribed to the reduction in the light penetration resulting from the abundance of C-TiO₂ particles. Therefore, an unlimited increase in C-TiO₂ dosage is not always favorable in real operation. It is also interesting to note that there is a linear correlation between k and catalyst dosage in the range of 0–2.0 g/L.

To elucidate the effect of probe concentration, the Vis/C-TiO₂ process was examined with different initial concentrations of norfloxacin, [norfloxacin]₀ (Fig. 2). It can be observed that lower initial

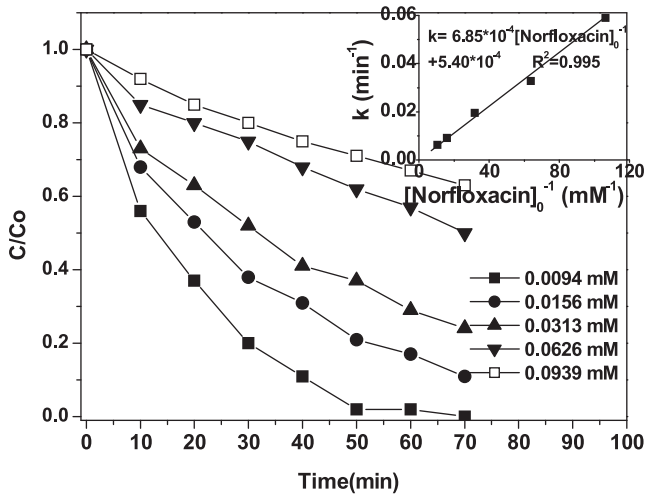


Fig. 2. Effect of norfloxacin initial concentration ($[C\text{-TiO}_2] = 0.2 \text{ g/L}$).

concentration leads to higher removal efficiency of norfloxacin, i.e. when the $[\text{norfloxacin}]_0$ increased from 0.0094 to 0.0939 mM, the final degradation at 70 min decreased from 100 to 37%. Again, a linear correlation between k and $[\text{norfloxacin}]_0^{-1}$ can be established as shown in the insert of Fig. 2.

By using multiple regression from above two linear correlations, the observed pseudo first-order rate constant (k , min^{-1}) of this Vis/C-TiO₂ process becomes predictable in terms of $[\text{norfloxacin}]_0$, mM and $[C\text{-TiO}_2]$, g/L, as shown below:

$$k = 5.44 \times 10^{-4} [\text{norfloxacin}]_0^{-1} + 0.10 [C\text{-TiO}_2] - 1.99 \times 10^{-2} (R^2 = 0.998) \quad (1)$$

In addition, the Langmuir–Hinshelwood (LH) model is used to evaluate this heterogeneous reaction if the solid–liquid interface is the location dominating the process. The LH model is shown as follows [24,25]:

$$\frac{1}{k} = \frac{[\text{norfloxacin}]_0}{k_{\text{LH}}} + \frac{1}{k_{\text{LH}}K_{\text{L}}} \quad (2)$$

where k_{LH} is the apparent rate constant of the reaction occurring on the catalyst surface (mM min^{-1}), k is the observed pseudo first-order rate constant (min^{-1}), and K_{L} is the equilibrium adsorption constant of norfloxacin on C-TiO₂ surface (mM^{-1}). The experimental results fit well with the kinetic model with a R^2 of 0.996, which confirms that the norfloxacin decay in the Vis/C-TiO₂ process dominantly occurs on C-TiO₂ surfaces. Besides, it can be judged from Eq. (2) that the adsorption is of importance to the pollutant decay.

The K_{L} was determined separately to be $2.37 \times 10^3 \text{ mM}^{-1}$ from the original data. By combining above Eqs. (1) and (2), a general form of the apparent rate constant of our Vis/C-TiO₂ process (k_{LH}) can be predicted as Eq. (3).

$$k_{\text{LH}} = 0.10 [C\text{-TiO}_2] [\text{norfloxacin}]_0 - 1.99 \times 10^{-2} [\text{norfloxacin}]_0 + 2.30 \times 10^{-7} [\text{norfloxacin}]_0^{-1} + 4.22 \times 10^{-5} [C\text{-TiO}_2] + 5.44 \times 10^{-4} \quad (3)$$

Within the test range of this study, the 3rd and 4th terms on the right-hand side are about 2–3 log lower than the others, and can be neglected. The k_{LH} therefore is abbreviated to be as follows,

$$k_{\text{LH}} = 0.10 [C\text{-TiO}_2] [\text{norfloxacin}]_0 - 1.99 \times 10^{-2} [\text{norfloxacin}]_0 + 5.44 \times 10^{-4} \quad (4)$$

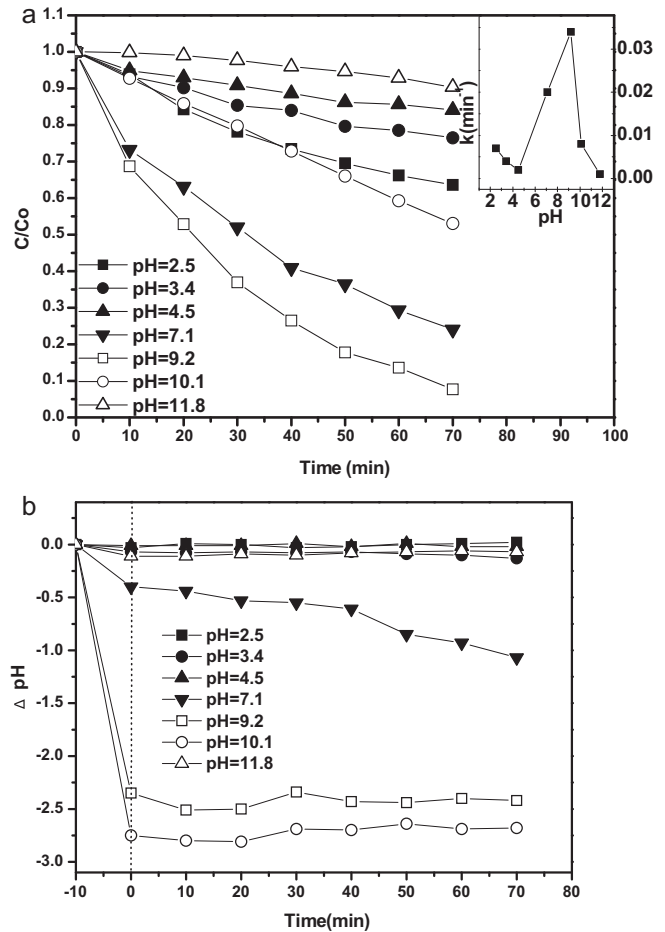


Fig. 3. (a) Decay performance of norfloxacin at different pH levels, and (b) pH variation during reaction ($\Delta\text{pH} = \text{pH}_t - \text{pH}_{\text{initial}} (X = -10)$) ($[C\text{-TiO}_2] = 0.2 \text{ g/L}$, $[\text{norfloxacin}]_0 = 0.0313 \text{ mM}$).

3.2. Effect of pH levels

The influence of pH levels on norfloxacin decay by the Vis/C-TiO₂ process was shown in Fig. 3(a). The pH values were measured by the initial norfloxacin solution in the absence of C-TiO₂. It was obvious that the pH level strongly affects the performance of norfloxacin degradation, where the decay is much faster in weak basic pH (9.2) than those of acidic (2.5, 3.4 and 4.5), neutral (7.1) or alkaline (10.1 and 11.8) conditions. Besides, the pH variation during adsorption (X axis from -10 to 0) and photocatalytic reaction was also examined (X axis from 0 to 70) as shown in Fig. 3(b). It was noted that a significant pH drop occurred at adsorption, especially when the pH level is 9.2 and 10.1. It suggests that the surface of C-TiO₂ is of acid property, thereby, it favors OH⁻ anions and will lead to a redistribution/adsorption of OH⁻ anion from solution to the surface of C-TiO₂, as illuminated in Scheme 1. It is deserved to note the pH variation during the photocatalytic reaction as initial pH of 7.1 (without pH adjustment), where a gradually pH drop was found. It implies that the continuous consumption and redistribution/adsorption of OH⁻ occurs in the Vis/TiO₂ process as well, where the imperceptible pH variation under other pH conditions might be ascribed to their buffer capacity.

At weak alkaline condition, the addition of OH⁻ into the process leads to the increase in its adsorbed amount on C-TiO₂ surface, resulting in a larger amount of hydroxyl radicals (see Eq. (6)).

Table 1
Effective particle diameter of C-TiO₂ in distilled water at different pH levels.

pH	2.5	3.4	4.5	5.5	7.1	9.2	10.1	11.8
Effective diameter ^a (nm)	300	467	498	894	583	283	258	338

^a The effective diameter is the biggest at pH of point of zero charge. It is because the like charges of C-TiO₂ particles repelled each other at pH away from pzc, as a result, the C-TiO₂ presented a small effective particle size in aqueous solution.

Thereby, the decay performance at pH of 9.2 is superior to that of 7.1. However, as the pH further increased to the 10.1 or 11.8, a repulsive force between C-TiO₂ and norfloxacin quickly builds up due to their like surface charges. To verify this, the point of zero charge (pzc) of C-TiO₂ was determined to be around pH 5.5 (as indicated in Table 1), while norfloxacin has two acid dissociation constants pK_{a1} and pK_{a2} at 6.24 and 8.75, respectively [26]. The negative charge on both sides (i.e. the repulsive force) restrains the norfloxacin approaching to the surface of C-TiO₂, leading to the suppression of norfloxacin degradation. At acidic condition, similar charge repulsion (both at positive charges) occurs. In summary, the Vis/C-TiO₂ process performed well at weak basic pH, especially when moderate OH⁻ ions present in the suspension.

It is interesting to note that the degradation performance at extreme acidic pH follows the order of $k_{pH\ 2.5} > k_{pH\ 3.4} > k_{pH\ 4.5}$. The faster rate at extreme acidic condition is likely due to the effective particle size of C-TiO₂ in suspension solution, as shown in Table 1, where the smaller size of C-TiO₂ at lower pH offers larger surface area and provides more opportunities to contact with norfloxacin molecules and absorb the visible light.

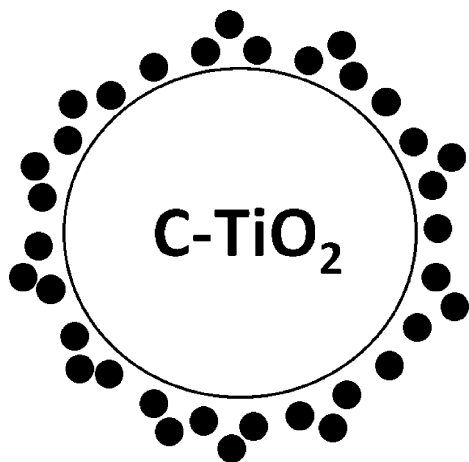
3.3. Principle study of the Vis/C-TiO₂ process

In photocatalytic reaction, it is compulsory to illumine semiconductor catalyst with sufficient light energy. The effective incidence light wavelength (λ) can be calculated according to the following equation [27]:

$$\lambda = \frac{hc}{E_{bg}} \quad (5)$$

where E_{bg} is the band gap of semiconductor catalyst (e.g. C-TiO₂ of 2.64 eV [22]); h is Plank's constant, 4.14×10^{-15} eV; and c is the light speed, 3×10^{10} cm/s.

As a result, λ is calculated to be 480 nm, which indicates that light with irradiation wavelength less than 480 nm has the potential to participate in a photocatalytic reaction. In this study, the irradiation wavelength selected was 420 nm from low-pressure mercury lamps [23]. Obviously, these low pressure lamps are proven useful to activate C-TiO₂ to generate electron (e^-) and hole (h^+) pairs.



Scheme 1. (○) represents C-TiO₂, and (●) represents OH⁻ anion.

Subsequently, the h^+ reacts with surface OH⁻ to produce \bullet OH radicals via following equation [28]:



To verify the involvement of \bullet OH radicals in our Vis/TiO₂ process, methanol was added as a hydroxyl radical quencher, due to its high-rate constant reaction with the \bullet OH radical [29] ($k = 1.01 \times 10^{12}$ mL molecule⁻¹ s⁻¹). As indicated in Fig. 4(a), in the presence of 1.2 M methanol, a retardation was found. Therefore, the generation of hydroxyl radicals is confirmed in the Vis/C-TiO₂ process. From Eq. (6) and Scheme 1, more hydroxyl radicals will be produced as the increase of OH⁻ anions on C-TiO₂ surface. As a result, higher norfloxacin decay rate was observed in weak alkali.

On the other hand, photo-generated electrons will immigrate to the surface of catalyst, then react with dissolved oxygen in aqueous solution to produce peroxide radicals [28]:

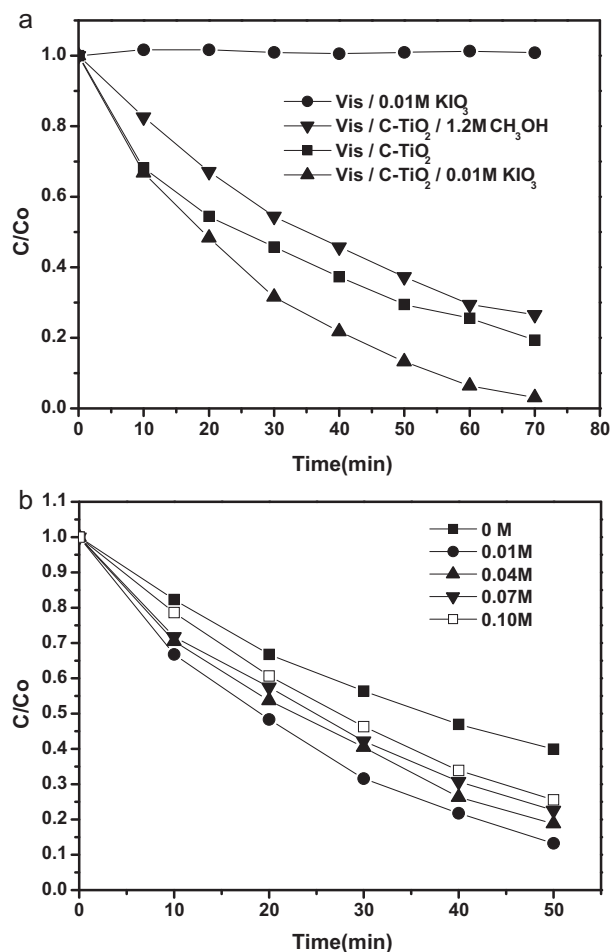


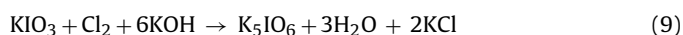
Fig. 4. (a) Effect of methanol and KIO₃ on the norfloxacin degradation, and (b) decay performance at different KIO₃ dosage ([C-TiO₂] = 0.2 g/L, [norfloxacin]₀ = 0.0313 mM).

To verify the presence of the above electron mechanism, an electron acceptor KIO_3 was added to the reaction, and the degradation of norfloxacin was improved as illuminated in Fig. 4(a). It is because the involvement of KIO_3 terminates the recombination of e^- and h^+ [30] through the capture of electrons ejected from C-TiO₂ surface by following equation:



As a result, the number of separated h^+ is increased which will be beneficial to the generation of hydroxyl radicals.

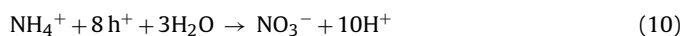
However, it should be noted that the further increment of KIO_3 from 0.01 M to 0.1 M will reduce the decay rates as shown in Fig. 4(b). It might partly be due to the generation of I^- (Eq. (8)), which was reported as an effective hole scavenger to react with photogenerated h^+ [31], resulting in the reduction of hydroxyl radicals (Eq. (6)). In addition, it was known that the KIO_3 can be oxidized by Cl_2 and generate IO_6^{5-} (a weaker oxidant than KIO_3) as shown in Eq. (9)



The above reaction occurs at basic condition, while the OH^- is likely to accumulate and be concentrated at the surface of C-TiO₂ (Scheme 1), which makes the hydroxyl radicals (also generated at C-TiO₂ surface) have a very good chance to perform a similar oxidation process due to its much higher reduction potential (2.0–2.8) than Cl_2 (1.36). The possible consumption of valuable $\bullet\text{OH}$ therefore resulted in a slower rate of the norfloxacin decay as KIO_3 was overdosed.

3.4. Effect of inorganic ions

In Fig. 5(a), norfloxacin decay in the Vis/TiO₂ process was investigated in the presence of various inorganic ions. In view of nitrogen and fluoride are elements of norfloxacin, the effect of inorganic ion containing these ions, such as NH_4^+ , NO_3^- and F^- , was investigated. Previous studies showed that NH_4^+ ion is a scavenger for photo-generated holes in photocatalytic process [32,33]:



However, no effect was found with the addition of 0.10 M NH_4^+ ion in this study. The positive charge on NH_4^+ ions apparently make them difficult to approach to the holes as negatively-charged groups (i.e. $-\text{OH}^-$) have formed a barrier on the surface and trap the NH_4^+ . As a result, Eq. (10) is invalid or minor in this process and the structure of catalyst as shown in Scheme 1 is reconfirmed. Besides, there was no apparent effect in the addition of [NO_3^-] ions to the process, this is because the oxidation state of NO_3^- is already high, the further oxidation of it is difficult and no radical or hole consumption was observed.

In the presence of 0.10 M F^- anions, the norfloxacin decay was suppressed. Additional tests with various F^- concentrations were conducted to verify this repressive effect, and the results were shown in Fig. 5(b), which indicated that the reaction rate progressively decreased with the increment of fluoride concentration. Parallel tests of the adsorption of norfloxacin (prior to initialize the photocatalytic reaction) in the presence of F^- were also investigated and the results showed that, almost no norfloxacin was adsorbed onto C-TiO₂ at 0.20 M [F^-], while 2.3, 5.4 and 5.6% of norfloxacin were adsorbed at 0.10, 0.01 and 0 M [F^-], respectively. This observation suggests that fluoride ions may restrain the norfloxacin approaching to C-TiO₂ surface, leading to the retardation of the heterogeneous reaction. However, it is interesting to note that the chloride ions (0.10 M), which possess similar chemical property to fluoride ions, did not show an appreciable effect on norfloxacin decay. Therefore, the repressive effect of F^- ions might

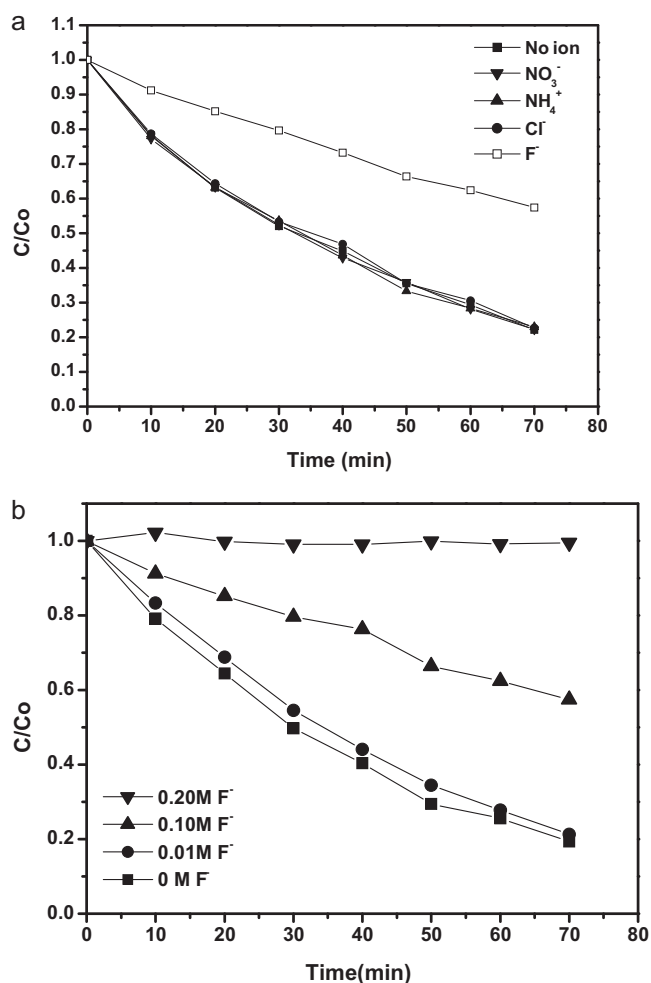


Fig. 5. (a) Effect of inorganic ions (all 0.10 M), and (b) effect of fluoride ion at different concentration ($[\text{C-TiO}_2] = 0.2 \text{ g/L}$, $[\text{norfloxacin}]_0 = 0.0313 \text{ mM}$).

be ascribed to the exclusive hydrogen bond ($\text{O-H} \cdots \text{F}$), which most likely formed around the C-TiO₂ surface (as shown in Scheme 1). This additional bonding kindly tied up the hydroxyl ions so that the surface property of C-TiO₂ was changed, and then the norfloxacin approaching was restrained. In addition, the formation of hydroxyl radical could be hindered as the hydroxyl ions were bided.

3.5. Reuse of C-TiO₂ catalyst

In real applications, it is necessary to demonstrate whether, after photocatalysis and liquid/solid separation, the reuse of catalyst is feasible. To find out the reuse possibility of C-TiO₂, the efficiency of the process by using recycled catalyst was studied, in which 0.2 g of C-TiO₂ was dispersed into 100 mL 0.313 mM norfloxacin solution. After 70 min of photocatalytic reaction, the C-TiO₂ was separated and washed with DI water for several times, then dried in an oven at 80 °C. Very little weight loss was observed during the separation and wash process (less than 5%). For a fair test, the weight difference was made up by adding fresh catalyst into the next run to reach the same weight. The removal efficiency of each trial (one fresh and four reuses) was 42.23, 40.73, 40.36, 40.87 and 40.99 in sequence. No obvious efficiency degrade was observed with using the same batch of catalyst. This demonstrates that the chemical stability of the synthesized C-TiO₂ is excellent and the C-TiO₂ catalyst has good potential to be used in water/wastewater treatment.

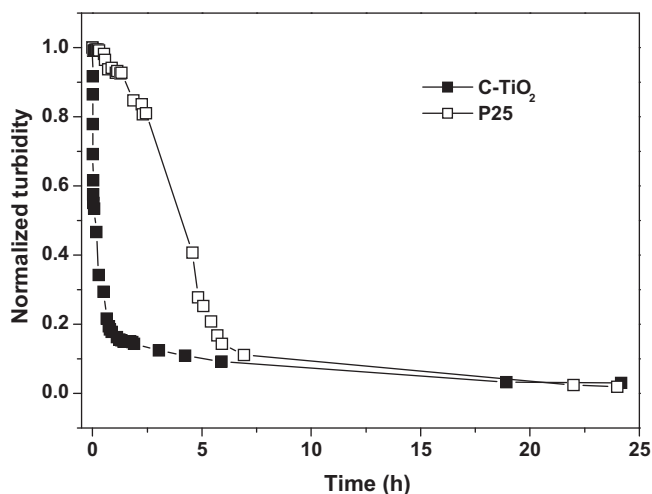


Fig. 6. Turbidity variation of suspensions (■) synthesized C-TiO₂, and (□) commercial Degussa P25 by using gravity settling ($[C-TiO_2] = 0.2 \text{ g/L}$, $[norfloxacin]_0 = 0.0313 \text{ mM}$).

3.6. Sedimentation property of C-TiO₂ catalyst

The sedimentation property of suspended photocatalyst is of importance in water treatment, since most photocatalysts possessing fine particle, e.g. Degussa P25 (80% anatase, 20% rutile) of average particle size of 25–30 nm, are difficult to be separated from water by self-sedimentation once enter into aquatic phase [34]. Thereby, a high operating cost is needed for their separation [35]. The sedimentation study was carried out on dispersions of the C-TiO₂ and Degussa P25 in norfloxacin solution. The profile of turbidity versus settling time was shown in Fig. 6. It can be noted that most of C-TiO₂ can be easily settled from the suspension in a short time, around 85% of C-TiO₂ was removed/recycled in 1 h, while it took 6 h for the Degussa P25 to reach the same removal performance. Because the settling time is reasonably fitted into the scale of a conventional sedimentation tank in water/wastewater treatment process, the fast settling property C-TiO₂ becomes an advantage in real application.

4. Conclusion

In this study, a visible-light-mediated C-TiO₂ photocatalytic process was employed to degrade antibiotic norfloxacin. The influences of dosage, initial concentration and pH levels on the decay performance and reaction kinetics were investigated. The norfloxacin degradation was found to be a pseudo first order kinetics and the observed rate constant (k , min^{-1}) can be simply expressed with $k = 5.44 \times 10^{-4} [norfloxacin]_0^{-1} + 0.10 [C-TiO_2] - 1.99 \times 10^{-2}$. The reaction rationale of the Vis/C-TiO₂ process was proposed to dominantly occur on the C-TiO₂ surface, and the apparent rate constant of the surface reaction (k_{LH} , mM min^{-1}) can be predicted by the equation of $k_{LH} = 0.10 [C-TiO_2] [norfloxacin]_0 - 1.99 \times 10^{-2} [norfloxacin]_0 + 5.44 \times 10^{-4}$. Hydroxyl radical was confirmed to play a major role in the Vis/C-TiO₂ process. It was also found that the addition of slight OH⁻ anions in to the system could accelerate the reaction with producing more radicals. Besides, the process was benefited from a small suspension particle of C-TiO₂ which offers larger surface area for reaction. An original schematic diagram for deciphering the surface property of C-TiO₂ was built from the observation of redistribution/adsorption of OH⁻ in the treatment process. Furthermore, this model was confirmed by various tests, in which, the hole scavenger of NH₄⁺ cations showed an inappreciable effect

because the OH⁻ formed a barrier for NH₄⁺ ions to approach the holes, and the F⁻ anions presented a significant suppression due to the formation of hydrogen bond (O–H···F). Besides, the recycling and sedimentation tests justified that the Vis/C-TiO₂ process is a cost-effective and feasible way for water treatment.

Acknowledgment

The authors are grateful for the financial support of a research grant from the Hong Kong Polytechnic University (RPHC).

References

- [1] A.L. Giraldo, G.A. Peñuela, R.A. Torres-Palma, N.J. Pino, R.A. Palominos, H.D. Mansilla, Degradation of the antibiotic oxolinic acid by photocatalysis with TiO₂ in suspension, *Water Res.* 44 (2010) 5158–5167.
- [2] H.W. Leung, T.B. Minh, M.B. Murphy, J.C.W. Lam, M.K. So, M. Martin, P.K.S. Lam, B.J. Richardson, Distribution, fate and risk assessment of antibiotics in sewage treatment plants in Hong Kong, South China, *Environ. Int.* 42 (2012) 1–9.
- [3] A.L. Batt, I.B. Bruce, D.S. Aga, Evaluating the vulnerability of surface waters to antibiotic contamination from varying wastewater treatment plant discharges, *Environ. Pollut.* 142 (2006) 295–302.
- [4] R.H. Lindberg, P. Wennberg, M.I. Johansson, M. Tysklind, B.A.V. Andersson, Screening of human antibiotic substances and determination of weekly mass flows in five sewage treatment plants in Sweden, *Environ. Sci. Technol.* 39 (2005) 3421–3429.
- [5] J.M. Cha, S. Yang, K.H. Carlson, Rapid analysis of trace levels of antibiotic polyether ionophores in surface water by solid-phase extraction and liquid chromatography with ion trap tandem mass spectrometric detection, *J. Chromatogr. A* 1065 (2005) 187–198.
- [6] W.H. Xu, G. Zhang, S.C. Zou, X.D. Li, Y.C. Liu, Determination of selected antibiotics in the Victoria Harbour and the Pearl River, South China using high-performance liquid chromatography-electrospray ionization tandem mass spectrometry, *Environ. Pollut.* 145 (2007) 672–679.
- [7] A.L. Batt, D.S. Aga, Simultaneous analysis of multiple classes of antibiotics by ion trap LC/MS/MS for assessing surface water and groundwater contamination, *Anal. Chem.* 77 (2005) 2940–2947.
- [8] A.J. Watkinson, E.J. Murby, D.W. Kolpin, S.D. Costanzo, The occurrence of antibiotics in an urban watershed: from wastewater to drinking water, *Sci. Total Environ.* 407 (2009) 2711–2723.
- [9] Y.J. Lee, S.E. Lee, D.S. Lee, Y.H. Kim, Risk assessment of human antibiotics in Korean aquatic environment, *Environ. Toxicol. Pharmacol.* 26 (2008) 216–221.
- [10] T.P.H. Phan, S. Managaki, N. Nakada, H. Takada, A. Shimizu, D.H. Anh, P.H. Viet, S. Suzuki, Antibiotic contamination and occurrence of antibiotic-resistant bacteria in aquatic environments of northern Vietnam, *Sci. Total Environ.* 409 (2011) 2894–2901.
- [11] B. Li, T. Zhang, Biodegradation and adsorption of antibiotics in the activated sludge process, *Environ. Sci. Technol.* 44 (2010) 3468–3473.
- [12] Z.Y. Wang, X.D. Yu, B. Pan, B.S. Xing, Norfloxacin sorption and its thermodynamics on surface-modified carbon nanotubes, *Environ. Sci. Technol.* 44 (2010) 978–984.
- [13] O. Lorphensri, J. Intravijit, D.A. Sabatini, T.C.G. Kibbey, K. Osathaphan, C. Saiwan, Sorption of acetaminophen, 17 alpha-ethynyl estradiol, nalidixic acid, and norfloxacin to silica, alumina, and a hydrophobic medium, *Water Res.* 40 (2006) 1481–1491.
- [14] T.C. An, H. Yang, W.H. Song, G.Y. Li, H.Y. Luo, W.J. Cooper, Mechanistic considerations for the advanced oxidation treatment of fluoroquinolone pharmaceutical compounds using TiO₂ heterogeneous catalysis, *J. Phys. Chem. A* 114 (2010) 2569–2575.
- [15] J. Rivas, A. Encinas, F. Beltran, N. Graham, Application of advanced oxidation processes to doxycycline and norfloxacin removal from water, *J. Environ. Sci. Health A* 46 (2011) 944–951.
- [16] P. Wang, Y.L. He, C.H. Huang, Oxidation of fluoroquinolone antibiotics and structurally related amines by chlorine dioxide: reaction kinetics, product and pathway evaluation, *Water Res.* 44 (2010) 5989–5998.
- [17] T.L. Su, Y.L. Kuo, T.J. Wu, F.C. Kung, Experimental analysis and optimization of the synthesizing property of nitrogen-modified TiO₂ visible-light photocatalysts, *J. Chem. Technol. Biotechnol.* 87 (2012) 160–164.
- [18] J.P. Wang, H.C. Yang, C.T. Hsieh, Visible-light photodegradation of dye on Co-doped titania nanotubes prepared by hydrothermal synthesis, *Int. J. Photoenergy* 2012 (2012) 1155–1164.
- [19] H.J. Cho, P.G. Hwang, D. Jung, Preparation and photocatalytic activity of nitrogen-doped TiO₂ hollow nanospheres, *J. Phys. Chem. Solids* 72 (2011) 1462–1466.
- [20] Y. Liu, C.S. Xie, H.Y. Li, H. Chen, T. Zou, D.W. Zeng, Improvement of gaseous pollutant photocatalysis with WO₃/TiO₂ heterojunctional-electrical layered system, *J. Hazard. Mater.* 196 (2011) 52–58.
- [21] L.C. Chen, C.M. Huang, C.S. Gao, G.W. Wang, M.C. Hsiao, A comparative study of the effects of In₂O₃ and SnO₂ modification on the photocatalytic activity and characteristics of TiO₂, *Chem. Eng. J.* 175 (2011) 49–55.
- [22] Y. Huang, W.K. Ho, S.C. Lee, L.Z. Zhang, G.S. Li, J.C. Yu, Effect of carbon doping on the mesoporous structure of nanocrystalline titanium dioxide and

- its solar-light-driven photocatalytic degradation of NO_x , *Langmuir* 24 (2008) 3510–3516.
- [23] Y.F. Rao, W. Chu, Linuron decomposition in aqueous semiconductor suspension under visible light irradiation with and without H_2O_2 , *Chem. Eng. J.* 158 (2010) 181–187.
- [24] H. Al-Ekabi, N. Serpone, Kinetics studies in heterogeneous photocatalysis. I. Photocatalytic degradation of chlorinated phenols in aerated aqueous solutions over titania supported on a glass matrix, *J. Phys. Chem.* 92 (1988) 5726–5731.
- [25] D. Keane, S. Basha, K. Nolan, A. Morrissey, M. Oelgemöller, J. Tobin, Photodegradation of famotidine by integrated photocatalytic adsorbent (IPCA) and kinetic study, *Catal. Lett.* 141 (2011) 300–308.
- [26] H.R. Park, K.Y. Chung, H.C. Lee, J.K. Lee, K.M. Bark, Ionization and divalent cation complexation of quinolone antibiotics in aqueous solution, *Bull. Korean Chem. Soc.* 21 (2000) 849.
- [27] C.A. Arancibia-Bulnes, S.A. Cuevas, Modeling of the radiation field in a parabolic trough solar photocatalytic reactor, *Sol. Energy* 76 (2004) 615–622.
- [28] A.L. Linsebigler, G. Lu, J.T. Yates, Photocatalysis on TiO_2 surfaces: principles, mechanisms, and selected results, *Chem. Rev.* 95 (1995) 735–758.
- [29] Y.P. Chin, P.L. Miller, L. Zeng, K. Cawley, L.K. Weavers, Photosensitized degradation of bisphenol A by dissolved organic matter, *Environ. Sci. Technol.* 38 (2004) 5888–5894.
- [30] W.K. Choy, W. Chu, Photo-oxidation of o-chloroaniline in the presence of TiO_2 and IO_3^- : a study of photo-intermediates and successive IO_3^- dose, *Chem. Eng. J.* 136 (2008) 180–187.
- [31] S.H. Yoon, J.H. Lee, Oxidation mechanism of As(III) in the UV/ TiO_2 system: evidence for a direct hole oxidation mechanism, *Environ. Sci. Technol.* 39 (2005) 9695–9701.
- [32] X. Zhu, S.R. Castleberry, M.A. Nanny, E.C. Butler, Effects of pH and catalyst concentration on photocatalytic oxidation of aqueous ammonia and nitrite in titanium dioxide suspensions, *Environ. Sci. Technol.* 39 (2005) 3784–3791.
- [33] C.R. Chenthamarakshan, K. Rajeshwar, E.J. Wolfrum, Heterogeneous photocatalytic reduction of Cr(VI) in UV-irradiated titania suspensions: effect of protons, ammonium ions, and other interfacial aspects, *Langmuir* 16 (2000) 2715–2721.
- [34] Z. Ding, X. Hu, G.Q. Lu, P.L. Yue, P.F. Greenfield, Novel silica gel supported TiO_2 photocatalyst synthesized by CVD method, *Langmuir* 16 (2000) 6216–6222.
- [35] P. Le-Clech, E.K. Lee, V. Chen, Hybrid photocatalysis/membrane treatment for surface waters containing low concentrations of natural organic matters, *Water Res.* 40 (2006) 323–330.