



Role of pH on photolytic and photocatalytic degradation of antibiotic oxytetracycline in aqueous solution under visible/solar light: Kinetics and mechanism studies

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ABSTRACT

In this study, the photochemical degradation of the antibiotic oxytetracycline (OTC) at different pH values was investigated in aqueous solution under visible and solar light irradiation. Particular emphasis was given to the kinetics and mechanism during the photolytic and photocatalytic degradation of OTC. A comparative study of the photolysis of OTC under solar light, with different initial concentrations and in the presence of scavengers of reactive oxygen species (ROS), revealed a self-photosensitization pathway with evidence of singlet oxygen generation at pH 8.5 and 11.0 during OTC photolysis. The three-dimensional fluorescence spectra of OTC at different pH values demonstrate that OTC only exhibits significant emission spectra at pH 8.5 and 11.0. The change of the internal electrostatic force between the electron withdrawing group and the dehydrogenation moiety of OTC as a function of solution pH values was proposed as a critical factor influencing the energy states and observed reaction pathways of OTC under light irradiation. Moreover, the mechanism of photochemical degradation of OTC was investigated with nitrogen and fluorine doped titanium dioxide (NF-TiO₂) film at different pH values under visible and solar light in the presence of *tert*-butyl alcohol (TBA), sodium azide (NaN₃), potassium iodine (KI) and catalase as scavengers. Five pathways, including direct photolytic degradation, UV/vis light-induced photocatalytic oxidation and reduction, and visible light-induced self-photosensitized oxidation and reduction, were proposed and verified during the photocatalytic degradation of OTC with NF-TiO₂ film.

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1. Introduction

Antibiotics are one of the most widespread pharmaceutical groups and personal care products (PPCPs) in aqueous environments, which is a rising issue of global concern. Specifically, the family of antibiotic tetracyclines (TCs) is produced in great amounts for disease treatment for humans as well as disease prevention and as growth promoters in livestock around the world. Among all the antibiotics, OTC is one of the most frequently detected TCs in water bodies and sediments in many countries with the implication in the development of antibiotic-resistant genes [1–3]. Moreover, due to the antibiotic nature, hydrophilic property and stable naphthacene

ring structure, several studies have shown that OTC is hardly removable by conventional water treatment processes, including biological and chlorination processes [4,5]. Therefore, the spread of OTC in water bodies has been considered as a threat to the safety of drinking water for humans [6,7].

Advanced oxidation processes (AOPs), such as catalytic ozonation, Fenton, photo-Fenton oxidation, and heterogeneous photocatalysis, have shown great efficiency in recent years as possible future complementary methods to conventional water treatment. Among these AOPs, TiO₂ photocatalysis is gradually developed as an affordable, effective, environmentally friendly, reusable, and sustainable technology in water treatment. To extend the potential application, significant efforts have been made to activate TiO₂ catalyst under visible light wavelengths by doping various elements in its crystal lattice. Among such modified materials, N-F-codoped TiO₂ film has achieved promising success under visible light, exhibiting stable characteristics and performance in water treatment applications [8,9]. Besides, OTC has been demonstrated

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to be slowly hydrolysable [10] in water and to undergo photolysis under UV [11] or solar irradiation [12].

During research aimed at studying the phototoxicity for tetracycline (TC), a close family member of OTC with the same main structure but different functional groups, the photosensitized emission of singlet oxygen ($^1\text{O}_2$) radical was observed in TC solution [13]. Equally, the superoxide anion ($\text{O}_2^{\cdot-}$) was found both in TC and OTC aqueous solutions upon exposure to UV light [14]. OTC was considered to be a potential photosensitizer as TC, which generated ROS depending on the wavelengths of irradiation and solution pH [15]. Moreover, recent publications also have demonstrated successful oxidation as well as an effective antibacterial inactivation of OTC by TiO_2 photocatalysis under UV [16] or solar light [17]. However, the underlying mechanistic details of the photolytic and photocatalytic degradation of OTC need clarification, especially at different pH values and under different light wavelengths.

As the photochemical transformation of OTC by photocatalysis employing NF- TiO_2 film involves photolytic and photocatalytic processes, the focus of this research is to assess the effects of photolysis and photocatalysis on the photo-removal efficiency of OTC under visible and solar light irradiation. The effect of solution pH on the photolytic and photocatalytic degradation was investigated to elucidate the different mechanisms at diverse pH values and light wavelengths. Moreover, the formation and specific roles of different reactive species, superoxide radical, and singlet oxygen were probed using selective scavengers. Finally, the transformation pathways of OTC by photolysis and photocatalysis were proposed and probed.

2. Materials and methods

2.1. Chemicals

Oxytetracycline hydrochloride (CAS No. 2058-46-0) was obtained from Sigma. Zonyl FS-300(FS) and titanium(IV) isopropoxide (TTIP, 97%) were purchased from Aldrich (Fluka). Isopropanol, acetic acid and anhydrous ethylenediamine were obtained from Fisher. The other reagents used were all of analytical grade. All aqueous solutions were prepared with ultra pure water (resistivity 18.2 M Ω cm) from a lab Millipore Water purification water unit (Millipore, Watford, UK).

2.2. Preparation of the NF- TiO_2 film and undoped TiO_2 film

The NF- TiO_2 film and undoped TiO_2 film were made of 7 layers of coating on glass with prepared NF- TiO_2 sol-gel and TiO_2 sol-gel, respectively. The detailed process for synthesizing the NF- TiO_2 or TiO_2 film as well as the properties of catalysts have been previously investigated and have been reported by Pelaez et al. [8].

2.3. Photochemical experiments

The photochemical experiments were carried out in a borosilicate vessel (i.d. 9 cm) under two 15 W fluorescent lamps (Cole-parmer) mounted with or without UV block filter (UV420, Opticology) for simulating visible or solar light, respectively. The UV block filter is effective to eliminate irradiation with spectral range below 420 nm. The light intensity was determined using a broadband radiant power meter (Newport Corporation) for a total visible light intensity of 0.399 mW/cm² and a solar light intensity of 0.475 mW/cm². All the aqueous solutions were previously adjusted at the desired pH with corresponding phosphate buffer solutions (0.05 M) and then were spiked with an aliquot amount of freshly prepared OTC solution to achieve the required initial OTC concentration. The solution pH was maintained at the desired values during the reaction (\pm pH 0.2) and the hydrolysis of OTC during the

whole process was found to be negligible. All the experiments were conducted in triplicate and the samples were stored in a refrigerator and analyzed within 7 h.

2.4. Analyses of OTC

The OTC samples were monitored by a HPLC system (LC, Agilent Series 1100) equipped with a C_{18} reverse phase column (150 mm \times 4.6 mm, 5 μm) with methanol/acetonitrile/(0.01 mol/L) oxalic acid solution (20/20/60, v/v %) as the mobile phase at a flow rate of 0.4 ml/min. The detection was monitored at 355 nm while 4 calibration curves were applied for detecting OTC at pH values of 2.0, 5.5, 8.5 and 11.0, respectively. To investigate the absorption and emission spectra of OTC at pH values of 2.0, 5.5, 8.5 and 11.0, a UV-vis spectrophotometer (Shimadzu 2250) and a fluorescence spectrophotometer (Cary Eclipse) were applied.

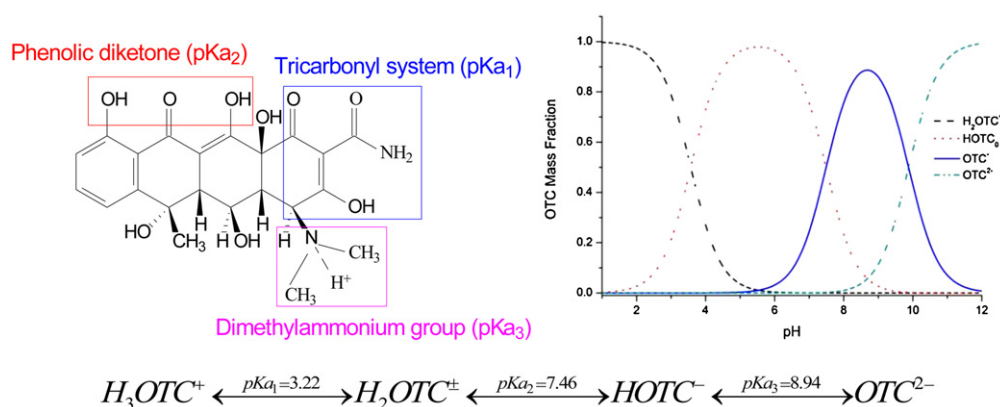
3. Results and discussion

3.1. Photolysis of OTC

The photolytic degradation of OTC was carried out at pH 2.0, 5.5, 8.5 and 11.0 under visible and solar light irradiation. As shown in Scheme 1, OTC has four species at different pH ranges [18], and each species has a unique electric charge state, which may have an important influence on its photolytic and photocatalytic degradation under different light wavelengths. As illustrated in Fig. 1, with the increase in pH, the light absorption of OTC exhibits a red shift to visible light, paralleled to the change of the protonation states of OTC. We chose pH 2.0, 5.5, 8.5 and 11.0 for investigation, because these pH values were the peak values for each of the OTC species. At pH=2.0, OTC is almost fully protonated as H_3OTC^+ . When the pH is increased to 5.5, the majority of OTC changed to zwitterions form (H_2OTC^\pm) by losing a hydrogen at the tricarbonyl group, which is corresponding to $\text{pK}_{\text{a}1}$. Besides, the OTC at pH 8.5 is primarily represented for the fraction of HOTC^- while the OTC mainly exists as OTC^{2-} at pH 11 [12,18]. The fractions of HOTC^- and OTC^{2-} have a visible light absorption above 420 nm while the fractions of H_3OTC^+ and H_2OTC^\pm have only UV light absorption below 420 nm. In addition, the relative intensity of light sources for solar and visible light is also shown in Fig. 1 for comparing the absorption spectra of OTC at different solution pH values. The wavelength range of solar light ranged from 311 nm to 600 nm while that of the simulated visible light was from 420 nm to 600 nm. Light peaks appeared at the wavelengths of 311, 365, 404, 436, 546, 575 and 580 nm, individually.

For the photolytic process alone, the degradation of OTC was enhanced with increasing pH as shown in Fig. 2 under both visible and solar light. At pH 2.0 and 5.5, OTC cannot be degraded under visible light due to the poor visible light absorption while only a minor amount of OTC was degraded under solar light at pH 5.5. On the contrary, the OTC at pH 8.5 and 11.0 had a significant degradation rate under visible and solar light. These results are in agreement with the absorption spectra of OTC at these pH values.

In addition, the photolytic degradation of OTC with initial concentration varying from 5 to 40 mg/L was investigated under solar and visible light at pH 5.5 and 8.5. As shown in Figs. 3 and 4, the initial OTC degradation rate at pH 5.5 hardly increased with enhanced initial concentration while the initial OTC degradation rate per unit of concentration gradually increased with enhanced initial concentration at pH 8.5 under solar and visible light, respectively. These results implied a different OTC photolytic degradation mechanism at pH 5.5 and pH 8.5.



Scheme 1. Molecular structure of OTC and the different protonation/deprotonation equilibria.

3.2. Mechanism on photolysis of OTC

During the photosensitized photolysis reaction of tetracycline, free radicals and ROS were proposed to be produced by Type I and Type II reaction, individually [15]. Moreover, Seto et al., detected singlet oxygen (1O_2) as well as superoxide anion radical ($O_2^{\cdot-}$) directly during the photolysis of OTC by UVA/B at pH 7.4 [19]. Thus, the proposed possible pathway of OTC photolytic degradation is illustrated in Scheme 2. To further investigate the mechanism of OTC photolytic degradation, a series of radical/ROS scavengers and methods were added during photolytic processes at pH 5.5, 8.5 and 11.0 under solar light for comparison. Singlet oxygen, an excited state of molecular oxygen, is readily quenched by NaN_3 . Greater than 90% of dissolved oxygen in aqueous media can be removed with a steady purge with N_2 gas [20]. While the rate of photolytic degradation of OTC decreases by purging with N_2 and in the presence of NaN_3 at pH 8.5 (OTC^-) and 11.0 (OTC^{2-}), no significant change is observed at pH 5.5 ($HOTC^\pm$) as illustrated in Fig. 5. The result suggests the mechanism responsible for OTC photolysis under solar light at pH 8.5 and 11.0 may be the combined paths (1) and (2), while the mechanism for OTC photolysis at pH 5.5 may involve only path (1). Regardless, the

direct degradation of OTC (path 1) was predominant in the photolytic degradation at pH 8.5 and 11.0 when OTC was excited to singlet (S_1) or triplet (T_1) states (OTC^*), analogous to a previous report on the photolysis of tetracycline [15]. Superoxide anion radical (SOAR) and hydroxyl radical scavengers, 4-benzoquinone and TBA or methanol, were used to scavenge SOAR and hydroxyl radicals at pH 5.5, 8.5 and 11.0, respectively. However, no obvious interference of OTC degradation was found with these quenchers. Therefore, the path (3) was not considered contributive to OTC degradation even it had been proved in the literature by Seto [19].

Also, the results further support the proposal that 1O_2 can only be generated at pH 8.5 and 11 by photolysis under simulated solar light. Based on these results, the self-photosensitized reactions only occurred with negatively charged states (OTC^- and OTC^{2-} states). The self-sensitized photoproducts of OTC were verified by quenching experiments and were detected with LC/ESI-DAD-MS by Chen [21]. The photosensitization of sensitizer generates an electronically excited states (singlet (S_1) or triplet (T_1)), and subsequent interaction with 3O_2 can result in Type I photooxidation electron transfer from excited sensitizer to 3O_2 to produce superoxide anion radical ($O_2^{\cdot-}$). Type II photooxidation involves energy transfer from

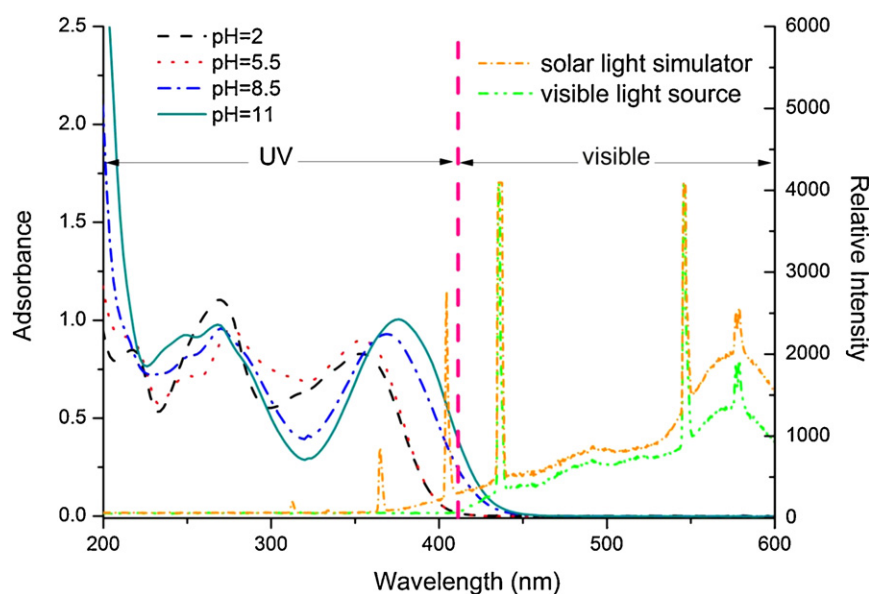
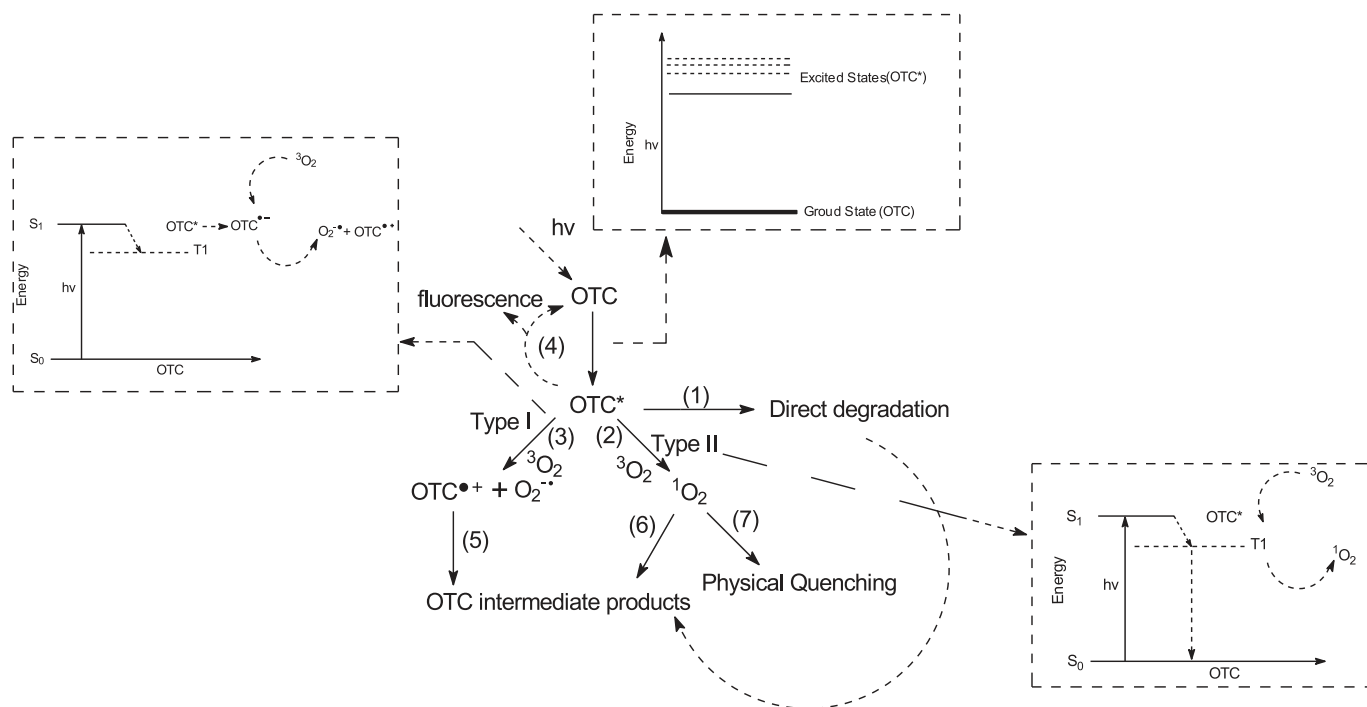


Fig. 1. Absorption spectra of different species of OTC (30 mg/L): pH = 2.0, fully protonation form, H_3OTC^+ ; pH 5.5, zwitterionic form, H_2OTC^\pm ; pH 8.5, monoanion form, $HOTC^-$; pH 11.0, dianion, OTC^{2-} and the relative intensity of the light source used in the experiment with and without UV glass filter. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)



Scheme 2. The proposed pathway of OTC photolytic degradation.

singlet (S_1) or triplet (T_1) states of the sensitizer to 3O_2 , resulting in the formation of singlet oxygen (1O_2) [22]. As the singlet oxygen (1O_2) was only found with negatively charged states of OTC, we propose that the different protonation/deprotonation state of OTC under different pH solution should have a close relationship with the process of OTC transferring from ground state (S_0) to electronic excited states (S_1 and T_1) under light irradiation. The results of three-dimensional fluorescence spectra of OTC at different pH values as shown in Fig. 6 confirm our hypothesis. OTC had significant emission spectra at pH 8.5 and 11.0, but not under acidic conditions. The changes as a function of pH are rationalized based on the different levels of protonation/charge. The results can be plausibly explained as follows: the dimethylammonium group, which is positively charged for H_3OTC^+ , $HOTC^\pm$ and OTC^- , can retard the electron nearby the tricarbonyl group jumping to excited state by electrostatic force for H_3OTC^+ and $HOTC^\pm$ at pH 2.0 and 5.5, respectively, under solar/visible light irradiation. However, the phenolic diketone loses a proton and becomes negatively charged at pH 8.5 (OTC^-), the electron there can be activated to excited state more easily due to the out range of the electrostatic force from positively charged dimethylammonium group, as the electrostatic force between two point-like charges is inversely proportional to the square of the distance between the objects according to Coulomb's law. Furthermore, when the dimethylammonium group turns into neutral charged at pH 11.0 (OTC^{2-}) by losing the positively charged hydrogen, the electrostatic force is completely removed from the system and the electrons from tricarbonyl and phenolic diketone system are much easier to be activated to electronically excited states, which leads to a surprisingly rapid OTC degradation rate under simulated solar or visible light at pH 11.0. Therefore, it is suggested that the change of internal electrostatic force in OTC molecule, which exists between electron drawing group (dimethylammonium group) and dehydrogenation group (tricarbonyl group and phenolic diketone) and based on the pH value (deprotonation of OTC), is responsible for the red shift to the visible light spectrum as well as the dramatically increased photolytic degradation rate with increase in pH in the OTC solution.

3.3. Photocatalytic degradation of OTC

The combined photolytic and photocatalytic degradation of OTC was carried out with NF-TiO₂ film at pH 2.0, 5.5, 8.5 and 11.0 under the same conditions as those in the photolysis experiment of OTC. As shown in Fig. 7, OTC was degradable under solar/visible light except at pH 2.0 under visible light irradiation. However, the degradation rate of OTC under solar light irradiation was greatly improved during photocatalysis at pH 2.0 and 5.5 and at pH 5.5 and 8.5 under visible light irradiation. Yet, the degradation rates of OTC at pH 8.5 under solar light only slightly increased compared with photolysis. The degradation rates of OTC at pH 11.0 under solar/visible light hardly had any improvement compared with photolysis. These results are probably due to the poor adsorption of OTC molecule on NF-TiO₂ films at pH 11.0 as illustrated in Fig. 8. As ROS are formed mainly at the surface of the catalyst, the electrostatic interactions between the substrate and the catalyst, influence the photocatalytic efficiency of the system [23]. Moreover, the dimethylammonium group is mainly positively charged below pH 8.94, while the NF-TiO₂ is positively charged under pH 6.0 and negatively charged above pH 6.0, according to the point of zero charge (PZC) [24]. The TiO₂ film is negatively charged at pH 11.0 while the negatively charged OTC^{2-} is also primary at this pH. Thus, the electron repulsion between NF-TiO₂ and OTC^{2-} makes the adsorption difficult at pH 11.0 as shown in Fig. 8.

3.4. The proposed mechanism of OTC photocatalytic degradation with NF-TiO₂

Significant OTC degradation is observed by photolysis under solar and visible light in alkaline solution. Since the indirect band gap value of NF-TiO₂ is 2.85 eV and the absorption spectrum of NF-TiO₂ is extended to the visible range of 400–500 nm [8,24], both the UV and visible light can excite NF-TiO₂ to promote electrons to the conduction band. Besides, it has been reported that the organic sensitizer could be degraded with anatase TiO₂

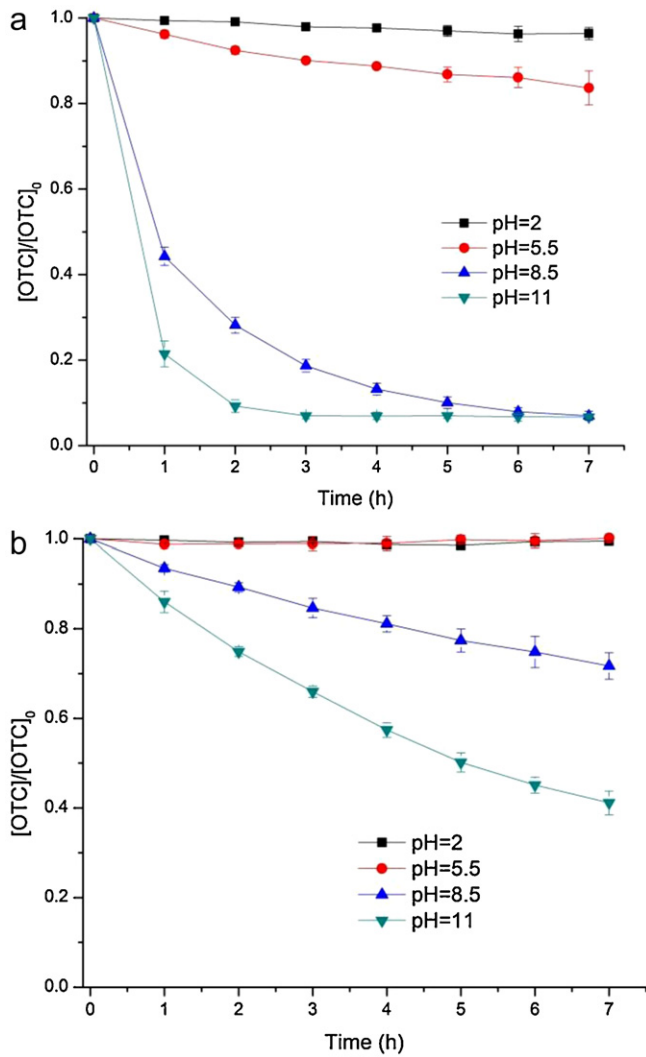


Fig. 2. Photolytic degradation of OTC at different pH values under solar light (a) and visible light (b) (OTC 5 mg/L).

under visible light by self-photosensitized oxidation and reduction [25]. Thus, the photochemical degradation of OTC with NF-TiO₂ film could occur via a number of competing reaction processes: direct photolytic degradation as shown in Scheme 2, UV/vis light-induced photocatalytic oxidation and reduction, and visible light-induced self-photosensitized oxidation and reduction as discussed below.

3.4.1. UV/vis light-induced photocatalytic oxidation and reduction

The electrons and holes can be separated by the excited NF-TiO₂ under UV light (Eq. (a1)) while electrons from localized electronic states can be introduced by bulk N impurities (N_b[−] or N_b[•]) in the lattice of TiO₂ to be promoted to the conduction band under visible light (Eqs. (a2) and (a3)) [9,26]. Then, a series of active oxygen species are produced by the following reactions (Eqs. (a4)–(a10)), which could lead to the oxidative degradation of OTC.

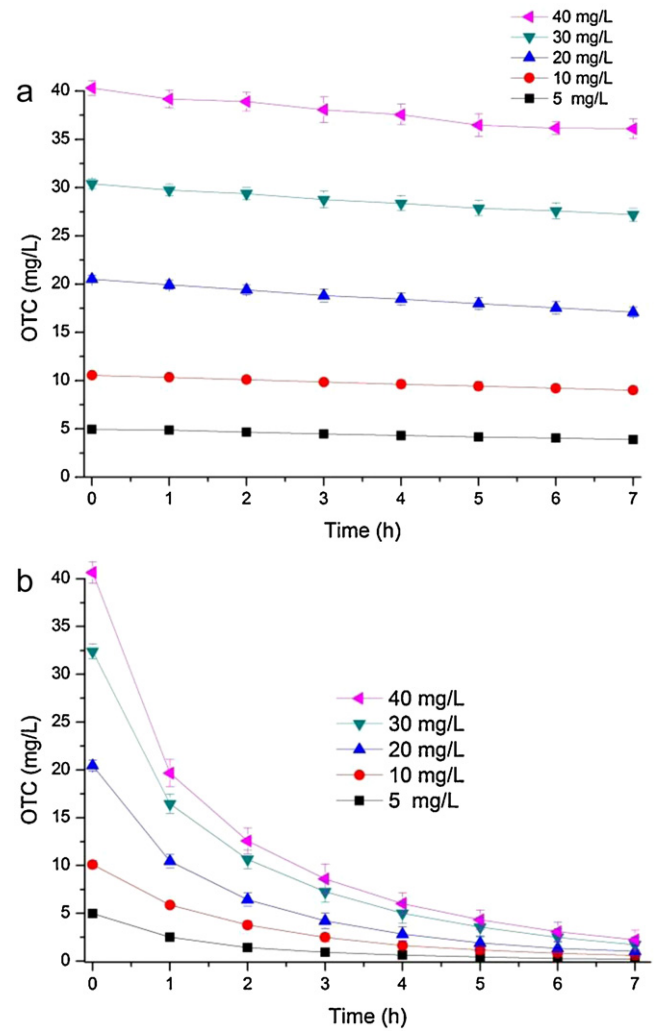
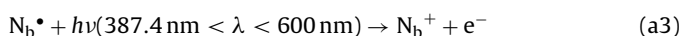
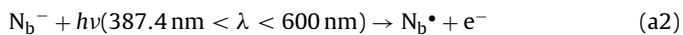
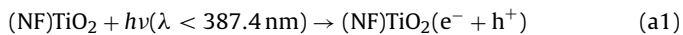
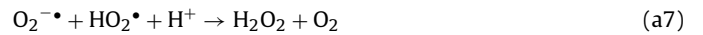
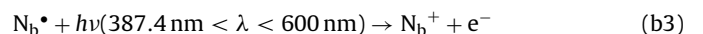
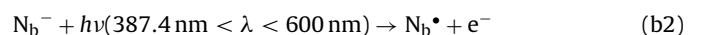
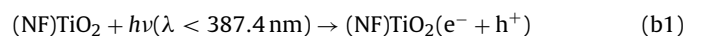
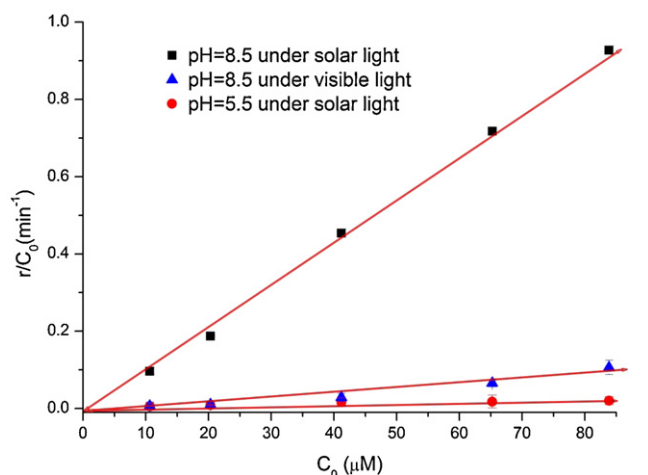


Fig. 3. Photolytic degradation of OTC under solar light at different initial concentrations and pH 5.5 (a) and pH 8.5 (b).



Meanwhile, OTC can serve as an electron scavenger on the NF-TiO₂ surface as well when the dimethylammonium group is positively charged as in the case of H₃OTC⁺, H₂OTC[±] and HOTC[−] (Eqs. (b4) and (b5)). The transfer of electron from NF-TiO₂ film to H₂OTC[±] and HOTC[−] by photocatalysis can release the internal electrostatic force in OTC for easier electron excitation under light irradiation and improve the degradation rate by photolysis indirectly (Eqs. (b6) and (b7)). As shown in the previous section in Fig. 2, HOTC[−] and OTC^{2−} display a much faster photolytic degradation rate than H₂OTC[±] and HOTC[−] under solar/visible light, respectively.





Note: the solar and visible light didn't have the same light flux. Thus, they were not comparable for OTC degradation.

Fig. 4. The initial rate of OTC photolytic degradation per unit of concentration at various initial concentrations at pH 5.5 and 8.5 under visible and solar light.



3.4.2. Visible light-induced self-photosensitized oxidation and reduction

Under the irradiation of visible light at pH > 5.5, HOTC^- is easily excited to singlet state, which can readily intersystem cross to the triplet state (HOTC^{*-}) as shown in Eq. (c1). Then, HOTC^{*-} may inject an electron into the conduction band of TiO_2 or $^3\text{O}_2$ directly to produce superoxide anion radical ($\text{O}_2^{\cdot-}$) while HOTC^{*-} is transferred to HOTC^* (Eqs. (c2) and (c3) and Scheme 3(a)). Meanwhile, the injected electron on the NF- TiO_2 can react with $\text{O}_2/\text{H}_2\text{O}_2$ to produce ROS leading to the oxidation of OTC (Eqs. (c4)–(c6)).

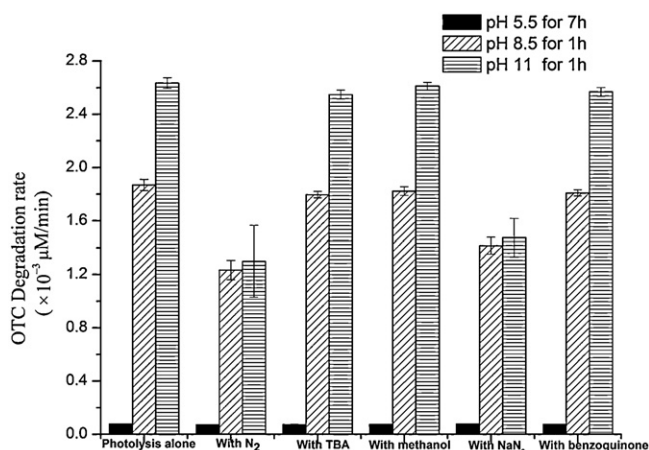
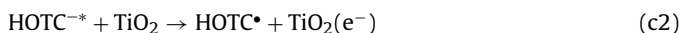
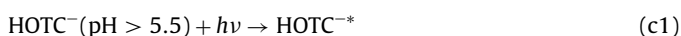
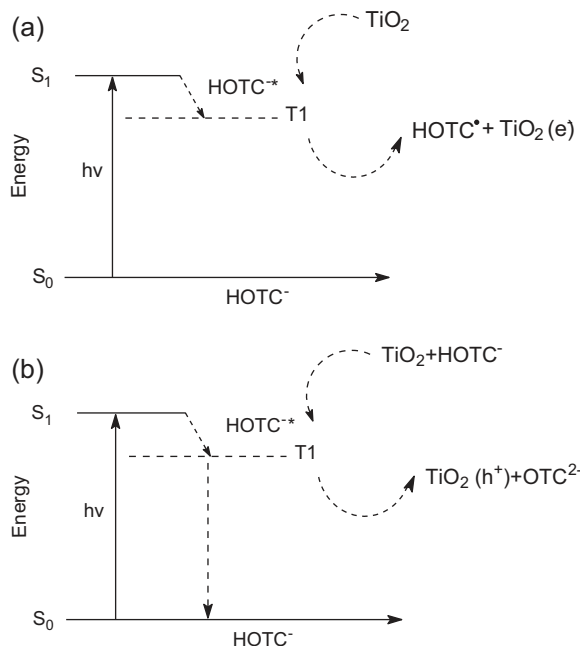


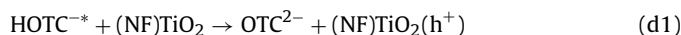
Fig. 5. Comparison of photolytic degradation of OTC in the absence and presence of N_2 atmosphere and different scavengers at pH 5.5, 8.5 and 11.0 under solar light (OTC 5 mg/L, Purging with N_2 for 40 min, with 10 mM TBA, 10 mM methanol, 5 mM NaN_3 and 8 mM 1, 4-benzoquinone).



Scheme 3. The proposed pathway of visible-induced OTC self-photosensitized oxidation (a) and reduction (b) with TiO_2 .



Alternatively, energy transfer from HOTC^{*-} to TiO_2 is possible (Eq. (d1)). The presence of electron withdrawing group (dimethylammonium group) on the HOTC^- may also act as an electron scavenger during the photosensitization of HOTC^- under visible light to form OTC^{2-} (Eq. (d2) and Scheme 3(b)). As shown in the previous section in Fig. 2(b), OTC^{2-} exhibited a much faster photolytic degradation rate than HOTC^- under visible light.



3.4.3. Verification of the proposed photocatalytic mechanisms

To probe the mechanisms and reaction pathways, a series of radical/ROS scavengers were applied during the OTC photocatalytic degradation under solar and visible light at pH 5.5 and 8.5.

As shown in Figs. 9 and 10, TBA depresses the degradation rate of OTC slightly with NF- TiO_2 film under both solar and visible light at pH 5.5 and 8.5. As TBA is considered an effective hydroxyl radical scavenger, these results indicate that hydroxyl radicals do not play a significant role in OTC degradation with NF- TiO_2 film. However, the degradation rate of OTC at pH 5.5 did improve significantly with the addition of NF- TiO_2 film under solar or visible light relative to photolysis alone. To further explore the roles of ROS that may be involved in the degradation of OTC, sodium azide and catalase were applied to scavenge singlet oxygen and hydrogen peroxide in the system during reaction, individually. The results showed that the two scavengers only reduced the degradation rate slightly. Besides, KI was applied as scavenger for hydroxyl radicals and positive holes at the same time during the reaction. As illustrated in Figs. 9 and 10, KI accelerates the degradation rate at both pH 5.5 and pH 8.5. As illustrated in Fig. 11, the adsorption experiment shows that the addition of KI in the solution did not significantly increase the adsorption of OTC on NF- TiO_2 film at pH 5.5 while it did increase the adsorption of OTC on NF- TiO_2

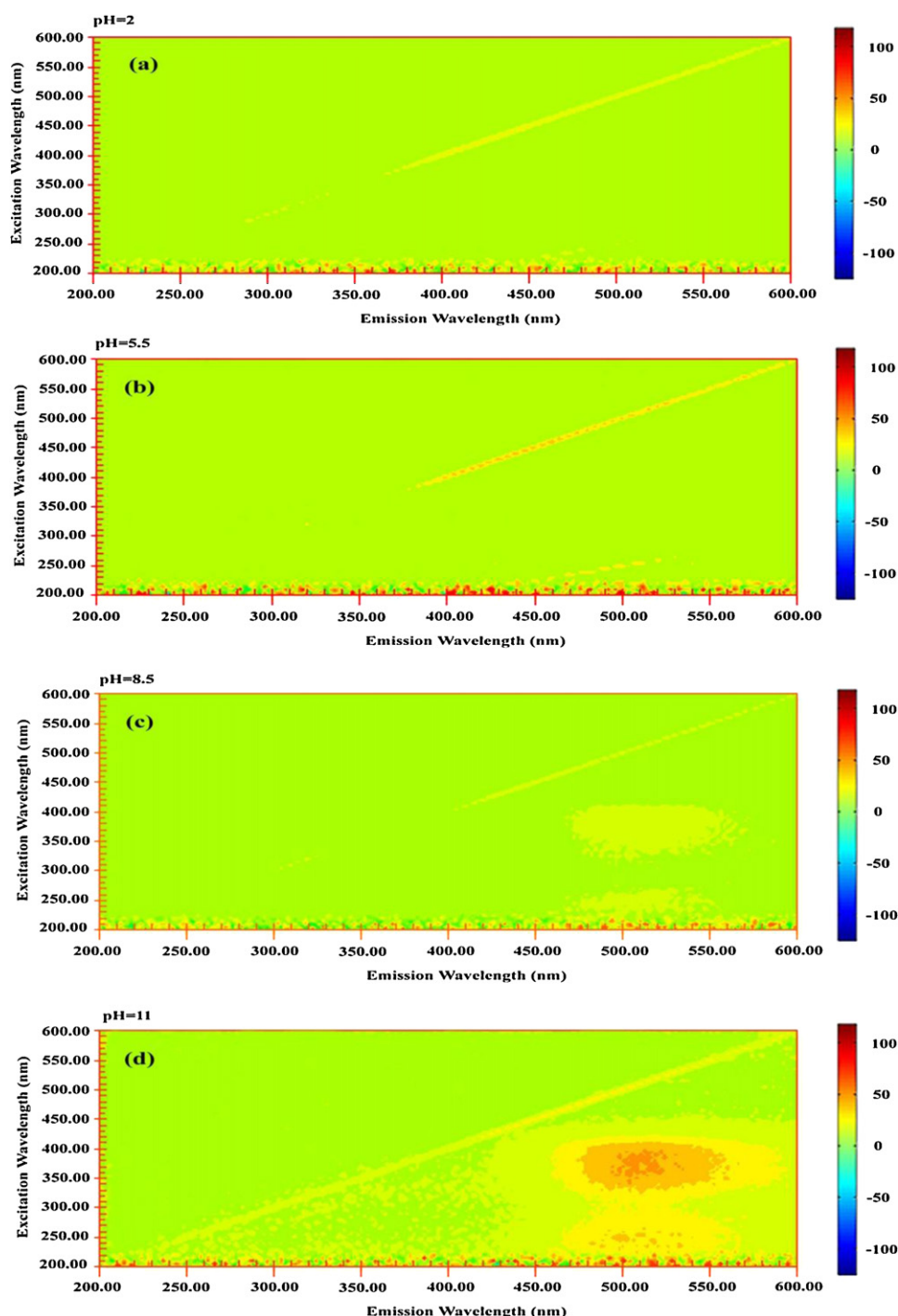


Fig. 6. Comparison of three-dimensional fluorescence spectra of OTC at pH 2.0 (a), pH 5.5 (b), pH 8.5 (c) and pH 11.0 (d) (OTC 10 mg/L). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

film significantly at pH 8.5. As KI is considered an effective positive hole and hydroxyl radical scavenger, the addition of KI can promote the separation of hole and electron on TiO_2 to generate more electrons in Eq. (a1). Therefore, it suggests that the main mechanism responsible for the degradation of OTC with NF-film at pH 5.5 is electrons (charge transfer) that were produced by photocatalysis (Eqs. (b1)–(b7)). Jeong and Song also found that the reaction rate constant of OTC by γ irradiation with solvated electrons was $(2.3 \pm 0.1) \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ while the reaction rate constant with hydroxyl radical was $(5.6 \pm 0.1) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ at pH 7.0 [27]. However, we speculated that OTC was not reduced by

electron directly in the photocatalytic process as Jeong proposed in the γ irradiation process. Based on the detailed study in the photolytic degradation of OTC at different pH, we deduced that the electron should react with OTC at the positive dimethylammonium group first, which changes the internal electrostatic force in the OTC molecule (Eq. (b4)). Then, the negatively charged OTC with free electron can be activated by light irradiation more easily, which lead to a quicker degradation by photolysis as shown in Scheme 2. This hypothesis is helpful for understanding the results that H_3OTC^+ at pH 2.0 can hardly be degraded under visible light even with NF- TiO_2 film. As the H_3OTC^+ at pH 2.0 does

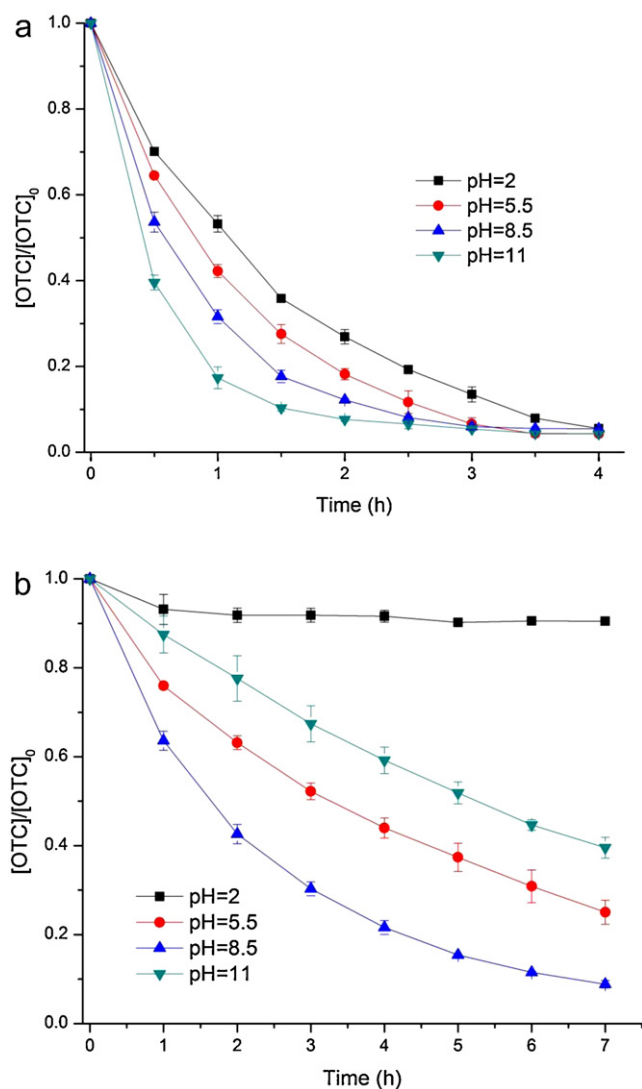


Fig. 7. Photocatalytic degradation of OTC by NF-TiO₂ film at different pHs under solar light (a) and visible light (b) (OTC 5 mg/L).

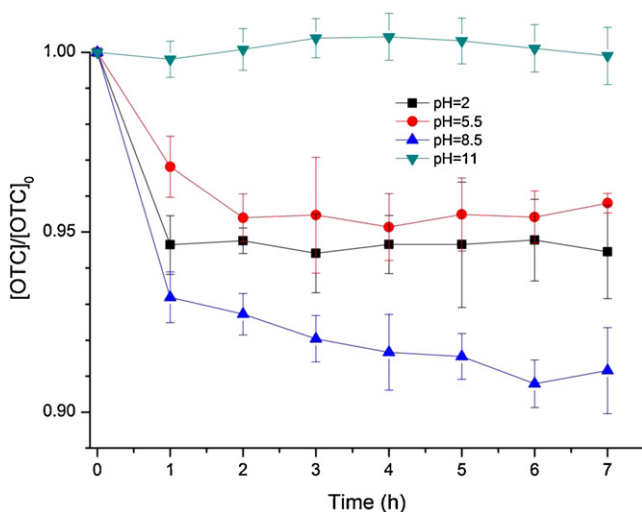


Fig. 8. Adsorption of OTC on NF-TiO₂ film at different pHs (OTC 5 mg/L).

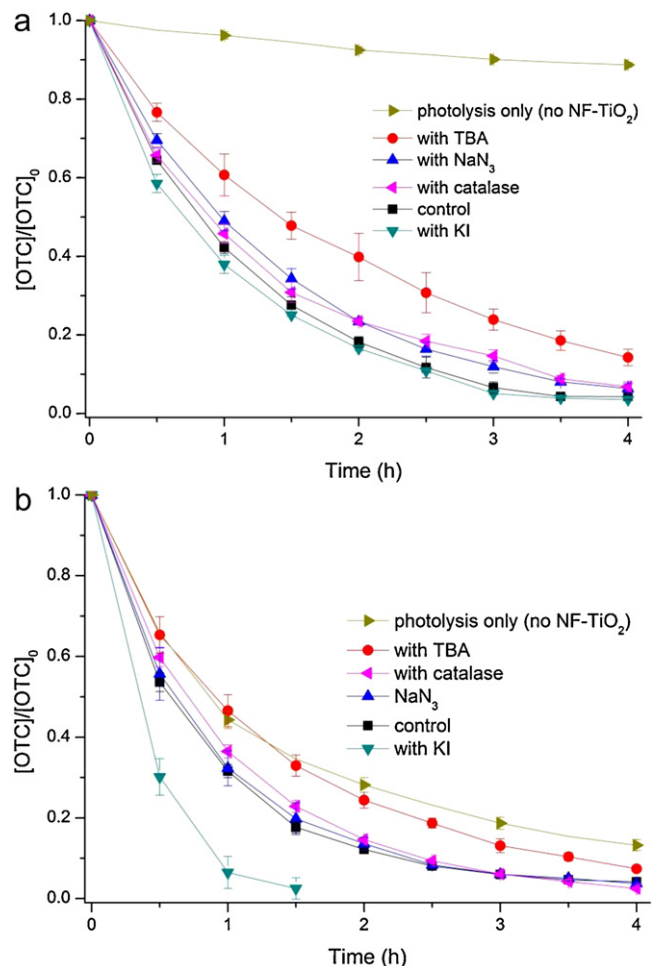


Fig. 9. Influence of TBA (10 mM), NaN₃ (5 mM), KI (10 mM) and catalase (6 unit/L) on photocatalytic degradation of OTC by NF-TiO₂ under solar light at pH 5.5 (a) and 8.5 (b) (OTC 5 mg/L).

not have any free electron, no electron can be activated to electronically excited states in H₃OTC⁺ as in the case of H₂OTC[±] and HOTC⁻.

In addition, it is known that NF-TiO₂ films cannot generate positive hole under visible light (Eq. (a2) and (a3)) to produce hydroxyl radical in Eq. (a4) directly. The generation of hydroxyl radical under visible light is through Eqs. (a5)–(a8). Thus, the existence of hydrogen peroxide in solution is a key factor for producing hydroxyl radical under visible light for NF-TiO₂ film. As shown in Figs. 9 and 10, the reduction of OTC degradation rate with NF-TiO₂ film by TBA is higher than by catalase under solar light, but lower than by catalase under visible light, which implies a different mechanism for hydroxyl radical production by NF-TiO₂ film under different light wavelengths.

Moreover, to reveal the self-photosensitized oxidation and reduction of OTC with TiO₂ during the reaction, undoped TiO₂ film was prepared to degrade OTC under visible light, as undoped TiO₂ film should be inactive under visible light. As illustrated in Fig. 12(a), the degradation rate of OTC at pH 5.5 under visible light with undoped TiO₂ is negligible, compared with OTC adsorption on TiO₂ in the dark. However, as shown in Fig. 12(b), the degradation rate of OTC at pH 8.5 is obviously accelerated with undoped TiO₂, compared with photolytic degradation of OTC, implying the existence of self-photosensitized mechanism in Eqs. (c1)–(c6). Under alkaline condition, the addition of TBA does not completely inhibit the accelerated OTC degradation rate, compared

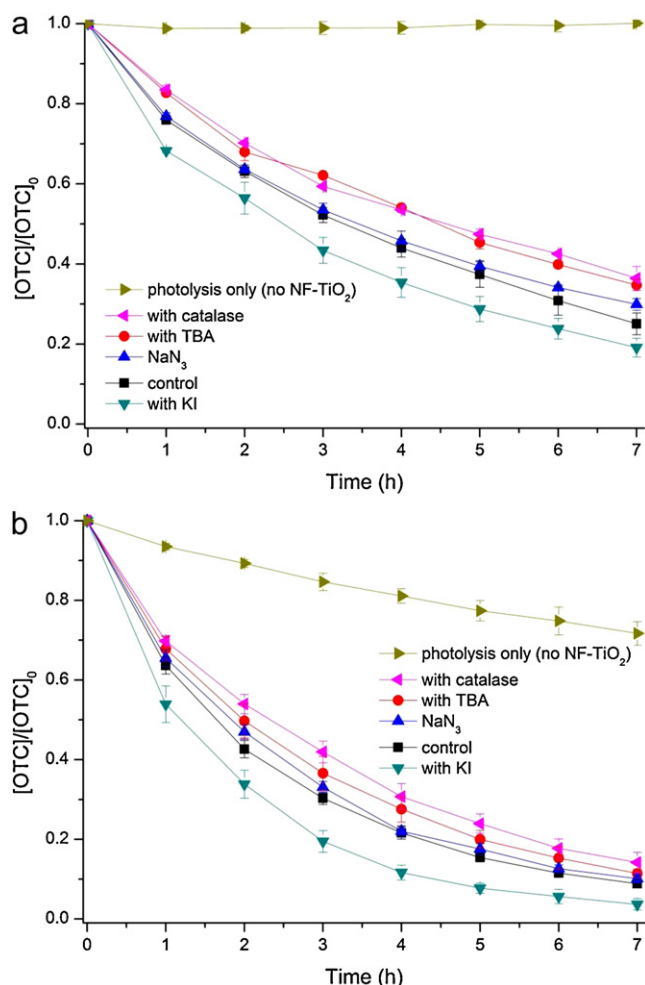


Fig. 10. Influence of TBA (10 mM), NaN₃ (5 mM), KI (10 mM) and catalase (6 unit/L) on photocatalytic degradation of OTC by NF-TiO₂ under visible light at pH 5.5 (a) and 8.5 (b) (OTC 5 mg/L).

with the photolytic degradation rate at pH 8.5. These results suggest the self-photosensitized reduction (Eqs. (d1) and (d2)) may be responsible for part of the improvement of degradation for HOTC under visible light.

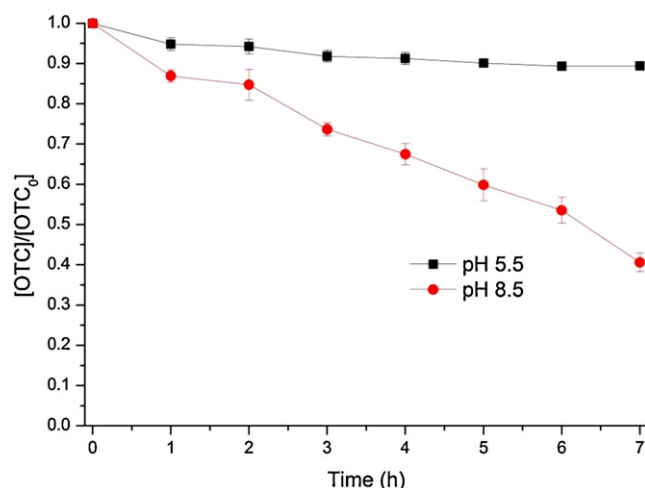


Fig. 11. Adsorption of OTC by NF-TiO₂ film with KI (10 mM) at pH 5.5 and 8.5 in dark (OTC 5 mg/L).

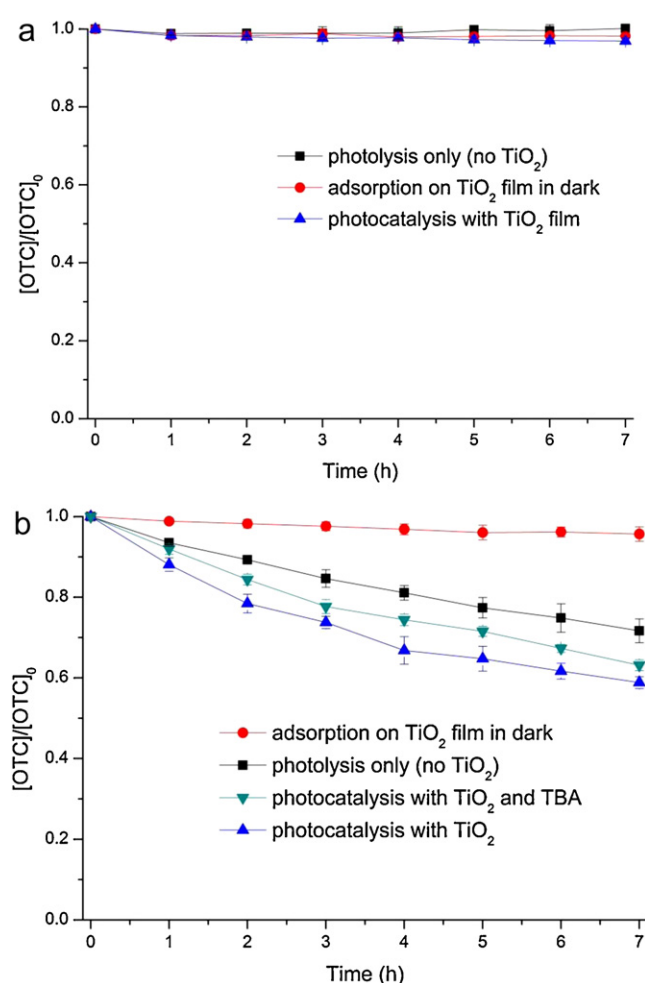


Fig. 12. Photocatalytic degradation of OTC under visible light and adsorption of OTC in dark by undoped TiO₂ film at pH 5.5 (a) and pH 8.5 (b) (OTC 5 mg/L and TBA 10 mM).

4. Conclusions

It has been demonstrated that the degradation rate of OTC by photolysis and photocatalysis under visible or solar light with NF-TiO₂ film is largely influenced by the solution pH, which determines the different electric charge state of OTC species. With the increasing in pH, the light absorption of OTC exhibits red shift to the visible light while the degradation rate of OTC by photolysis under solar/visible light is significantly accelerated. Experiments using a series of ROS scavengers also indirectly proved that singlet oxygen can be generated by OTC photosensitization under solar light at high pH like pH 8.5 and 11.0, and is responsible for part of the OTC degradation. Based on these results, it is suggested that the different electric charge state of OTC, which is based on solution pH, should display a different capability for exciting electron from the ground state to the excited state under light irradiation. Moreover, by analyzing the structure of OTC molecule, we propose that the change of the internal electrostatic force between the electron withdrawing moiety and dehydrogenation moiety of OTC with the pH of the solution should be the key factor for the electron excitation of OTC molecule by light irradiation. Meanwhile, the parallel study for the photocatalytic degradation of OTC with NF-TiO₂ film under solar/visible light suggests that 5 pathways were involved in the reaction: direct photolytic degradation, UV/vis light-induced photocatalytic oxidation and reduction and visible light-induced OTC self-photosensitized oxidation and reduction.

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