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**Research Article** 

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# Role of 13X zeolite for photochemical degradation of antibiotic oxytetracycline in aqueous solution: Comparison between TiO2 and TiO2/13X system

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# ABSTRACT

Oxytetracycline (OTC), as one of the most used antibiotics, is ubiquitous in aqueous environment and considered as a worldwide issue. In the study, the photocatalytic degradation of oxytetracycline was investigated. A novel composite of 15% TiO<sub>2</sub>/13X (15%T13X) as photocatalyst was synthesized with TiO<sub>2</sub> and 13X zeolite. Moreover, the adsorption of OTC by 15%T13X and TiO<sub>2</sub> was individually investigated. Besides, OTC photodegradation with pH was studied and an optimum of 9 was reached, and the influence of radical scavengers and humic acid were also investigated. The mineralization and toxicity change during photocatalytic processes was detected by TOC analyzer and standardized by bioluminescence assay on Vibrio qinghaiensis sp.-Q67 (Q67). The results showed that the composite of 15%T13X had better performance in photodegradation and detoxification than TiO<sub>2</sub> because of its combined effects of adsorption and photooxidation. Overall, it is concluded that the composite photocatalyst of 15%T13X was effective in treating oxytetracycline in aqueous solution.

Keywords: Titanium dioxide; 13X; Oxytetracycline; Photocatalysis degradation; Detoxification

# INTRODUCTION

Antibiotics are worldwide concerned for their widespread use in therapy and agriculture. Nawaz et al. reported that 23000 tons of antibiotics' consumption each year on average in U.S., in which 40% were used in veterinary applications [1]. Thus, a large amount of antibiotics is released into aquatic environment through agricultural runoff, discharges of pharmaceutical manufacturers and municipal wastewater treatment plants [2]. The concentration of antibiotics in aquatic environment is ubiquitous from ng/L to  $\mu$ g/L [3-4]. Although the level of antibiotics is low, they may induce the broadcasting of the resistant gene of bacteria, and finally cause antagonistic effects to humans [5].

Oxytetracycline (OTC) is a broad spectrum antibiotic, which is widely used as veterinary drugs for treating disease, keeping health and improving growth rate. OTC is an organic compound with partially conjugated four-ring structure and a serial of functional groups. OTC is also hydrophilic, so it can be easily dissolved and transferred in water.

So far, it has been found that OTC was hardly removable by conventional treatment [6]. Hence,  $TiO_2$  photocatalytic process is proposed to be an option. To improve the photoactivity and efficiency of titania photocatalysts, different types of modified  $TiO_2$  have been developed, including mesoporous clay supported  $TiO_2$  [7-8]. As mesoporous material, zeolites are induced into photocatalyst to enhance adsorption of contaminants and reduce UV scattering [8]. 13X zeolite is a kind of zeolite with a pore size around 1 nm. In this study, a composite catalyst, 13X zeolite supported  $TiO_2$ , was adopted to investigate the degradation and detoxification of OTC in aqueous solution.

Moreover, the adsorption property and photo-degradation performance with adding radical scavengers were studied to reveal the mechanism of the composite catalyst by comparing between 15%T13X and nano-TiO<sub>2</sub>.

# **EXPERIMENTAL SECTION**

# Chemicals

Oxytetracycline hydrochloride (CAS No. 2058-46-0) was purchased from Sigma. TiO<sub>2</sub> P-25 (surface area 50 m<sup>2</sup>/g, particle size 27 nm) was obtained from Degussa Co., Ltd, and zeolites of 13X with particle size of 3  $\mu$ m on average were supplied by Shanghai Zeolite Molecular Sieve Co., Ltd. The other chemicals were analytical grade. All working solutions were prepared with ultrapure water (Millipore, Watford, UK) and were freshly prepared.

### Preparation of TiO<sub>2</sub>/13X photocatalyst

The synthesized 15%T13X catalyst was prepared by solid-state dispersion (SSD) method as reported earlier [9]. Required amount of  $TiO_2$  (15 wt%) is loaded on 13X zeolite.

# Photolysis and photocatalytic experiments

The photocatalyst system consisted of two 16 W UV sterilization lamps (Light Sources Co., Ltd, USA) with wavelength at 254 nm and a light intensity of 845  $\mu$ W/cm<sup>2</sup> on average. For all experiments, the amount of TiO<sub>2</sub> or 15%T13X catalyst used was 0.015 g and 0.1 g, respectively. The catalyst was added to OTC solution (50 mg/L, 200 mL) in an open dish reactor ( $\varphi$ 10.5 cm×4 cm). The pH of mixture was adjusted with HCl or NaOH, and then agitated by a magnetic stirrer at 200 rpm. After 210 min, the mixture pH was readjusted to 11 and stirred for another 30 min to desorb the adsorpted OTC. Prior to light experiments, dark experiments were carried out to evaluate adsorption and desorption of OTC. For other studies, different amount of methanol, tert-butanol or humic acid were added to OTC solution before light experiment.

#### Analytical method

The OTC was measured by HPLC (LC-2010AHT, Shimadzu) coupled with a C18 column (250 mm×4.6 mm). The analysis was conducted with a mixture of methanol/acetonitrile/ 0.1 M oxalic acid solution (10/20/70, v/v) at a flow rate of 0.8 mL/min and detection wavelength at 355 nm. The TOC change was measured by TOC analyzer (TOC-VCPH, Shimadzu), and *V. qinghaiensis sp.*-Q67 toxicity was monitored by Veritas<sup>TM</sup> luminometer (Turner BioSystems Inc., USA).

#### **RESULTS AND DISCUSSION**

#### Effect of adsorption and desorption

It is found that pre-adsorption of contaminants on the surface of  $TiO_2$  leads to a more efficient degradation due to the enhanced electron transfer [10]. To estimate the adsorption capacity of the composite catalyst, adsorption experiment was carried out at pH 7, and then the solution pH was adjusted to 11 for another 30 min to desorb the adsorpted OTC on catalysts. As shown in Fig. 1, the maximum adsorption of nearly 90% is reached within 90 min. It indicates OTC could be well adsorbed by 13X due to the porous structure of zeolite. After 30 min desorption, the concentration of OTC nearly recovered to initial concentration. Thus, the 30 min desorption of OTC could be representative of the OTC adsorbed earlier, and it is used in all the future experiments.





Fig. 1 Adsorption and desorption of TOC on 13X.

Fig. 2 Photodegradation by TiO<sub>2</sub> and 15%T13X at different pH

# Effect of initial pH

The pH value is crucial in photocatalysis as it can alter both charge of the contaminant and the catalyst. The initial pH of the solution was adjusted into 5, 7, 9 and 11. The comparison of degradation by two catalysts is depicted in Fig. 2, where both are sensitive to pH value. At the pH range from 5 to 9, the degradation of OTC by 15%T13X was faster than TiO<sub>2</sub>. The effect of pH could be attributed to the change of substrates surface charge, which would further affect pre-adsorption. The dissociation of OTC differs as pH varies, and OTC presents as OTC<sup>+</sup>, OTC<sup>0</sup>,

 $OTC^{-}$  and  $OTC^{2-}$  at pH 5, 7, 9 and 11. Furthermore, the surface charge of catalysts is also related to their points of zero charge. Moreover, for photodegradation, the oxidation potential of hydroxyl radicals and the Fermi level of the  $TiO_2$  were reported to be affected by pH values [11].

Therefore, at acidic condition, the electrostatic interaction between OTC and catalysts was limited. As both of them presented positive charges, and a low degradation rate was resulted. At basic condition, the production of hydroxyl radicals is enhanced due to more  $OH^-$  in the solution while the adsorption of OTC on catalysts was inhibited. Thus, the two effects determined the total photocatalytic efficiency of OTC, and an optimum pH of 9 for both of the catalysts. However, considering the potential application of photocatalysts in natural water treatment, pH 7 was chosen for the following experiments.

# Changes of TOC in photolysis and photocatalysis

The changes of TOC in photolysis and photocatalysis were monitored by TOC analyzer and shown in Fig. 3(a). After irradiation for 10 h, the reduction of TOC by photolysis was 5.8%. The low percentage of mineralization indicated that the OTC was partly degraded instead of mineralized. TOC reduction by photocatalysis in 10 h was of 18.9%, which leads to removal efficiency to be more than three times compared with photolysis. It implies that the composite catalyst is more effective in mineralizing OTC. However, similar to Dalmázio's research [12], it is still a low removal of TOC. This is because the main structure of OTC, naphthol ring, is hard to cleave. For the pathway of OTC by photolysis proposed by Jiao, *et al.[13]*, the naphthol ring of OTC remained intact in the whole process and a relatively low mineralization efficiency was presented.

# Changes of toxicity in photocatalysis processes

The combined toxicity change of OTC solution was expressed by inhibition percentage, and a similar trend by TiO<sub>2</sub> and 15%T13X was found as shown in Fig. 3(b). The inhibition percentage increased in the first 60 min and then dropped slowly. It indicated that the first degradation byproducts seemed to be more toxic than OTC itself, and they are easily further degraded. It has been reported that the degradation byproducts of OTC were more toxic than OTC itself [14-15]. Moreover, the OTC oxidized products often make the molecular more polar, which is easier to be transported into the cellular and increase toxicity to bacteria. Overall, during slow mineralization of OTC, the toxicity decreased. It was also found that the combined toxicity of 15%T13X system roses smaller than TiO<sub>2</sub>, which implies the composite catalyst could reduce toxicity of photocatalysis by adsorption of toxic degradation byproducts.



Fig. 3 Change of TOC (a) and toxicity (b)

# Influence of adding radical scavengers

To assess the participation of free radicals in photocatalysis, methanol and tert-butanol were used as hydroxyl radical scavengers, and the effects are shown in Fig. 4 and Fig. 5.

Tert-butanol and methanol can react with  $\cdot$ OH to produce inert products with a rate constant as high as  $6 \times 10^8$  M<sup>-1</sup>s<sup>-1</sup> and  $9.7 \times 10^8$  M<sup>-1</sup>s<sup>-1</sup>, respectively[16]. The results showed that adding tert-butanol had suppressed TiO<sub>2</sub> photocatalytic reaction significantly. On the contrary, the photocatalytic progresses by the composite catalyst had only been affected slightly. However, the removal rate of OTC by 15%T13X was much faster than TiO<sub>2</sub> alone. A similar trend by the two catalysts can also be observed with methanol. According to Hoffmann's report, among the highly active free radicals in photocatalysis,  $\cdot$ OH is the most effective for its highest redox potential [17]. The mechanism of the better performance by composite catalyst is proposed as follows: (i) adsorption of OH<sup>-</sup> and zwitterionic OTC on 13X zeolite is easier than that of neutral radical scavengers due to electrostatic interaction. Thus the effect of radical scavengers was suppressed. (ii) Although zeolite could not produce more hydroxyl radicals' amount, it can prolong the existence of radicals [7], which increases the oxidation of OTC.



Fig. 5 Effect of tert-butanol on photocatalysis

# Effect of humic acid

Humic acid is the main component of DOM in natural aqueous environment. To appraise the composite catalyst application in natural water treatment, humic acid was added and the results are shown in Fig. 6. The photodegradation by  $TiO_2$  was sensitive to humic acid which indicated a competition effect between OTC and humic acid. However, 15%T13X showed better degradation rate as humic acid concentration increasing. It was reported that humic acid could serve as  $\cdot$ OH source or photosensitizer [18], which resulted an enhanced degradation rate by 15%T13X. Whereas, high concentration of humic acid would also bring negative effects on photocatalysis since it can act as an irradiation filter and/or hydroxyl radical sink. In general, the composite catalyst 15%T13X performs better than  $TiO_2$  alone at the presence of humic acid, which suggested it has a potential application in treating raw water.



Fig. 6 Effect of humic acid at different initial concentration

# CONCLUSION

The present study revealed that the composite catalyst 15%T13X was highly active for photodegradation of OTC. The composite catalyst presents a high adsorption of OTC due to the large specific surface of 13X support. The pH value is a key parameter of OTC photodegradation. Besides, the reaction rate enhanced with the increasing of pH from 5 to 9, and reached the highest at pH 9, while the removal rate dropped down at pH 11 for the poor adsorption of OTC by catalysts. Photocatalysis presented a better TOC removal efficiency than photolysis. For toxicity change, 15%T13X showed a more temperate change during photocatalysis. Moreover, the composite catalyst had better performance when radical scavengers existed or was in synthetic raw water, which indicated that the composite catalyst was suitable for natural water treatment. However, the degradation pathway of OTC and the chronic toxicity of OTC and its degradation byproducts were still unknown and would be the focus of future studies.

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