

Photocatalytic Degradation of Oxytetracycline Using Co-precipitation Method Prepared Fe₂O₃/TiO₂ Nanocomposite

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Fe₂O₃/TiO₂ nanocomposite were successfully synthesized by co-precipitation method using Fe(NO₃)₃·9H₂O and Ti(SO₄)₂ as raw materials. Structural and textural features of the mixed oxide samples were characterized by X-ray diffractometer, field emission scanning electron microscopy and energy-dispersive X-ray. The effects of initial concentration of oxytetracycline (OTC), different competitive ions and organics on the photocatalytic degradation rate of OTC by the Fe₂O₃/TiO₂ nanocomposite were analyzed under UV and visible light irradiation. The results indicate that the optimized initial concentration of OTC was 50 mg/L to achieve the best photocatalytic efficiency. Cu²⁺, NH₄⁺, C₃H₈O and EDTA in the aqueous suspension were found to suppress the degradation rate of OTC, whereas the effect of NO₃⁻ and H₂C₂O₄ can be ignored.

Keywords : Fe₂O₃/TiO₂, photocatalyst, competitive ions and organics, OTC

1. Introduction

Oxytetracycline (OTC) is one of the most widely used antibiotics in many fields [1, 2], but has been frequently found to be contained in water bodies and sediments in many countries due to their poor absorption by human beings or livestock [3, 4]. To prevent the contamination of drinking water due to the spreading of OTC, various technologies, such as advanced oxidation processes (AOPs), biodegradable compounds and activated carbons adsorption [5-9], have been explored to remove OTC from the waste water system. Additionally, photocatalysis has been proposed as a promising approach due to the high efficiency in photodegradation of OTC [10]. Zhao *et al.* reported that 15%TiO₂-5A molecular sieve composite and 13X loaded with TiO₂ photocatalysis showed a faster OTC removal and degradation speed than unsupported TiO₂ under ultra-violet (UV) light [11, 12]. Pereira *et al.* studied TiO₂-assisted heterogeneous photocatalytic degradation and fully removal of OTC under solar UV energy [13]. In addition to UV light, visible light responsive TiO₂, such as nitrogen and fluorine doped TiO₂ film,

have also been investigated in the photodegradation experiments, and exhibited good degradation efficiency of OTC [14]. Recently, the photocatalytic response of OTC using Fe₂O₃/TiO₂ nanocomposite has been investigated in details regarding the pH value and reaction mechanism [3], proposing that Fe₂O₃/TiO₂ nanocomposite can be used as a promising material for OTC removal under visible light. The existence of Fe₂O₃ in the composite has been shown to widen the light absorption beyond the UV range and enhance the electron-hole separation, which consequently improve the photocatalytic efficiency of OTC [3]. In this work, we report the effect of initial OTC concentration and competitive species on the photocatalytic decomposition of OTC using Fe₂O₃/TiO₂ nanocomposite under UV and visible lights.

2. Experimental Section

2.1. Preparation of Fe₂O₃/TiO₂ nanocomposite

Using Fe(NO₃)₃·9H₂O and Ti(SO₄)₂ as raw materials, Fe₂O₃/TiO₂ nanocomposite were synthesized using a co-precipitation method. A certain amount of Fe(NO₃)₃·9H₂O and Ti(SO₄)₂ was firstly dissolved in 10 ml diluted sulfuric acid, then mixed with 500 ml ethanol to form a metal ion solution. Next, the ammonia solution was added drop by drop to the metal solution with continuously stirring at room temperature to maintain the pH value of

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the solution around 8-9. Red colored precipitates were obtained after the solution was aged overnight. The precipitates were filtered, washed with deionized water till no SO_4^{2-} could be tested with Ba^{2+} , and dried at 100 °C for 12 h to obtain the precursor. Finally, the precursors were calcined at 500 °C for 4 h. For comparison, pure anatase TiO_2 and hematite Fe_2O_3 were also synthesized by precipitation method as A. K. Tripathi *et al.* and M. Mishra *et al.* reported [15, 16].

2.2. Characterization of Physical properties and photocatalytic activity.

The phases of the co-precipitation products were analyzed by a D/Max-2200(Japan) X-ray diffractometer. The microstructure of $\text{Fe}_2\text{O}_3/\text{TiO}_2$ nanocomposite was observed via a field emission scanning electron microscopy (FESEM, Hitachi-S4800, Japan) equipped with energy-dispersive X-ray (EDX).

The photocatalytic degradation experiments were carried out using oxytetracycline hydrochloride (OTC·HCl, 95% purity, Aladdin Chemistry Co., Ltd, Shanghai, China) and the $\text{Fe}_2\text{O}_3/\text{TiO}_2$ nanocomposite under both UV and visible light radiation. A 300 W iodine tungsten lamp and high-pressure mercury lamp (main wavelength of 250-400 nm) was used as the visible/UV light source. The detailed measurement process has been reported in our previous work [3].

3. Results and Discussion

3.1. Crystallinity and morphology of the $\text{Fe}_2\text{O}_3/\text{TiO}_2$ nanocomposite

The crystallographic information associated with $\text{Fe}_2\text{O}_3/\text{TiO}_2$ nanocomposite, pure anatase TiO_2 , and hematite

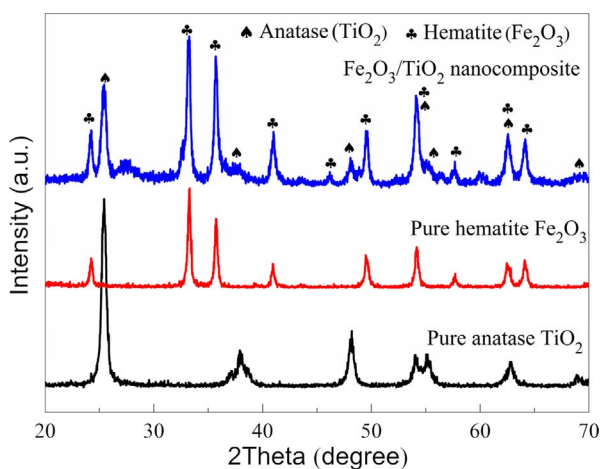


Fig. 1. (Color online) XRD pattern of $\text{Fe}_2\text{O}_3/\text{TiO}_2$ nanocomposite, pure anatase TiO_2 and hematite Fe_2O_3 .

Fe_2O_3 has been investigated by XRD, as illustrated in Fig. 1. The main phases in $\text{Fe}_2\text{O}_3/\text{TiO}_2$ nanocomposite are anatase TiO_2 (JCPDS card No.21-1272) and hematite Fe_2O_3 (JCPDS card No.33-0664). Through the Scherrer equation:

$$D = \frac{K\lambda}{\beta \cos \theta}$$

where K refers to a constant of 0.89, β is the full width at half maximum (FWHM) of the XRD peak at the diffraction angle θ , and λ is X-ray wavelengths of 0.154 nm, the grain size D is estimated as 25 nm and 17 nm for TiO_2 and Fe_2O_3 particles in the $\text{Fe}_2\text{O}_3/\text{TiO}_2$ nanocomposite, respectively. No other impurity diffraction peak is seen, which confirms the purity of the sample. HRSEM images of $\text{Fe}_2\text{O}_3/\text{TiO}_2$ nanocomposite are shown in Fig. 2 (a). Two morphologies including nanorod and nanosphere were observed in the nanocomposite. The particle size of $\text{Fe}_2\text{O}_3/\text{TiO}_2$ nanocomposite is about 50 ± 2 nm. In addition, EDX was detected at point 1 and the spectrum is shown in Fig. 2(b). The observed elements are Ti, O and Fe present in the given sample.

3.2. Photodegradation rate of OTC by $\text{Fe}_2\text{O}_3/\text{TiO}_2$ nanocomposite

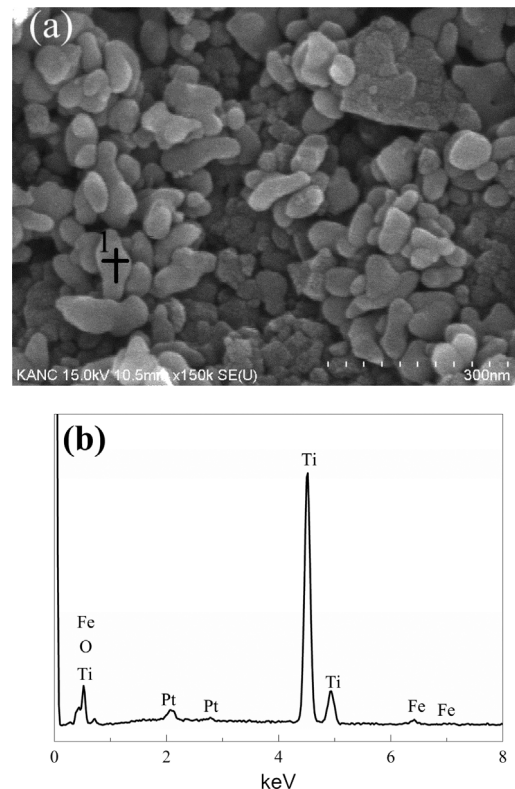


Fig. 2. HRSEM of $\text{Fe}_2\text{O}_3/\text{TiO}_2$ nanocomposite (a) and (b) EDX analysis of point 1.

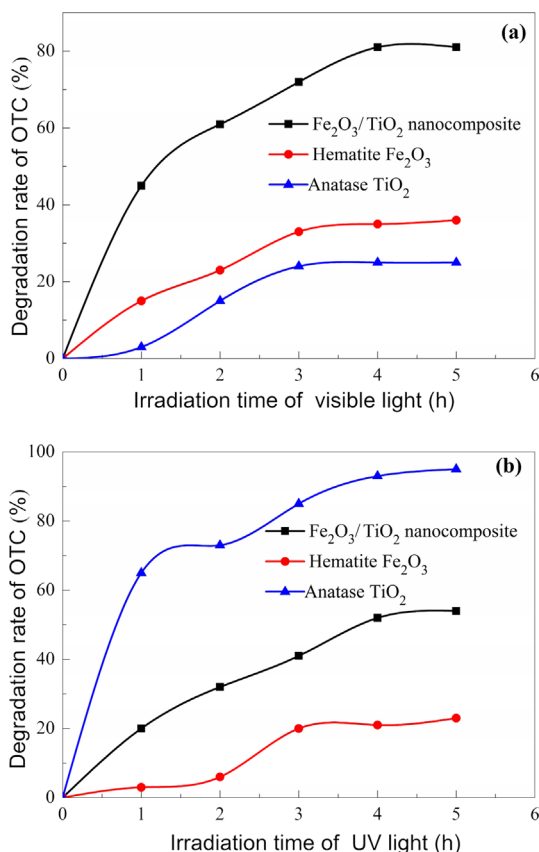


Fig. 3. (Color online) Degradation rate of OTC over pure anatase TiO₂, hematite Fe₂O₃ and Fe₂O₃/TiO₂ nanocomposite ($C_0 = 50$ mg/L) under visible light (a) and UV (b).

Fig. 3 gives the photocatalytic degradation rate of OTC under UV/visible light as a function of irradiation time. The degradation curve using pure anatase TiO₂ and hematite Fe₂O₃ are also given for comparison. Under visible light for 5 h, the photodegradation rates of 81%, 36% and 25% can be observed for Fe₂O₃/TiO₂ nanocomposite, hematite Fe₂O₃ and pure anatase TiO₂, respectively. With similar conditions but UV light, photodegradation rates are 54%, 23% and 95% for Fe₂O₃/TiO₂ nanocomposite, hematite Fe₂O₃ and pure anatase TiO₂, respectively. Since visible light occupies about 50% of the solar spectrum, Fe₂O₃/TiO₂ nanocomposite are good candidates for further application in the waste water treatment containing OTC or similar materials.

3.3. Effect of initial OTC concentration on the photocatalytic degradation

As shown in the inset of Fig. 4(a), OTC has a quite stable naphthacene ring structure, which results in its antibiotic and hydrophilic characteristics. Therefore, OTC is hard to remove by the conventional water treatment processes. The photocatalytic degradation of OTC using

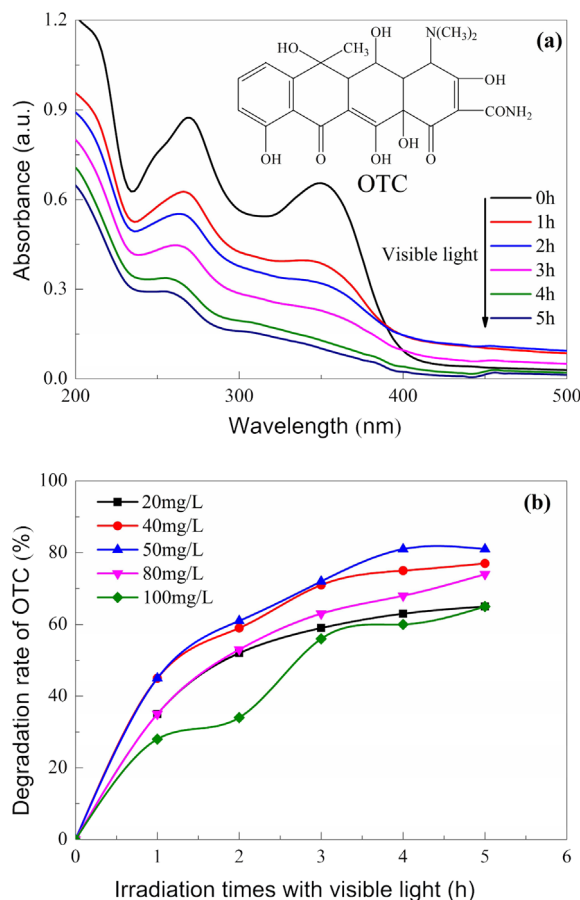


Fig. 4. (Color online) (a) UV-vis spectral variation of OTC solution with reaction time over Fe₂O₃/TiO₂ nanocomposite ($C_0 = 50$ mg/L) under visible light, inset figure shows chemical structures of OTC. (b) The variation of degradation rate (%) of OTC on different initial concentration ($C_0 = 20, 40, 50, 70$ and 100 mg/L) under visible light.

Fe₂O₃/TiO₂ nanocomposite as a function of the visible light irradiation time is shown in Fig. 4(a). The main absorption peaks of OTC ($C_0 = 50$ mg/L) at 270 nm and 353 nm are significantly reduced after 5 h, indicating the removal of a large amount of OTC by Fe₂O₃/TiO₂ nanocomposite under the visible light irradiation. Additionally, testing solutions with various initial concentration of OTC (20, 40, 50, 70 and 100 mg/L, under visible light) were used as shown in Fig. 4(b). One can notice a remarkable increase in the degradation rate of OTC with the initial concentration increasing to 50 mg/L, which implying a balance point between the surface area of the catalyst and the amount of reactive intermediates in the testing solution. Further increase of the initial OTC concentration causes a lower degradation rate, which can be attributed to the insufficient contact between OTC and the photocatalyst due to the presence of more reactive intermediates on the surface of the Fe₂O₃/TiO₂ nanocomposite.

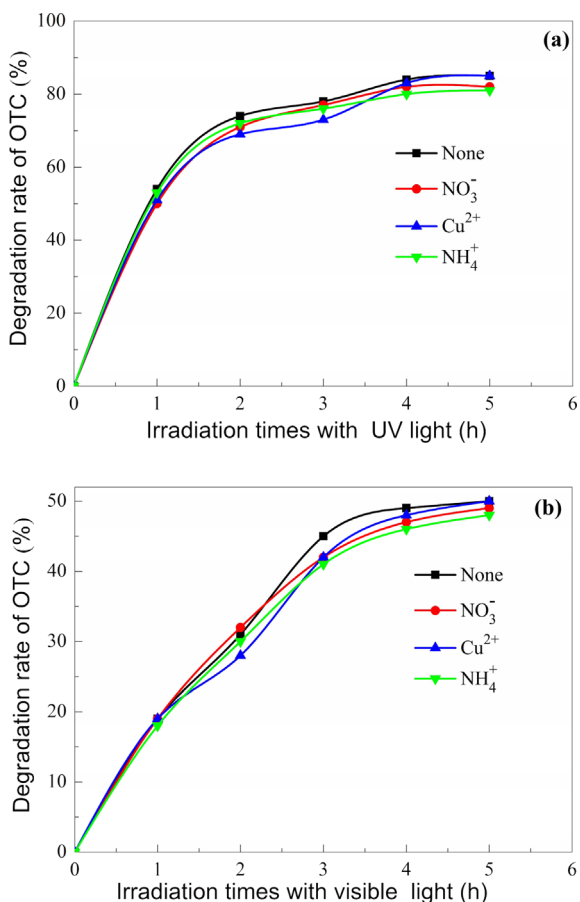


Fig. 5. (Color online) Effect of competitive ions (0.5 mmol/L) on degradation rate (%) of OTC solution (50 mg/L) under UV (a) and visible light (b) with $\text{Fe}_2\text{O}_3/\text{TiO}_2$ nanocomposite.

3.4. Effect of competitive ions and organics on the photocatalytic degradation

NO_3^- , NH_4^+ , Cu^{2+} , $\text{C}_3\text{H}_8\text{O}$, EDTA, or $\text{C}_2\text{H}_2\text{O}_4$ often exist in the waste water environment, and their presence could affect the degradation rate of OTC by attaching or reacting with the active sites of the photocatalyst. Therefore, NaNO_3 , NH_4Cl , CuCl_2 , isopropano ($\text{C}_3\text{H}_8\text{O}$), ethylene diamine tetraacetic acid (EDTA) or oxalic acid ($\text{C}_2\text{H}_2\text{O}_4$) were dissolved in distilled water together with OTC to study the effect of different competitive ions and organics. The concentrations of NO_3^- , NH_4^+ , Cu^{2+} , $\text{C}_3\text{H}_8\text{O}$, EDTA, or $\text{C}_2\text{H}_2\text{O}_4$ were all adjusted as 0.5 mmol/L.

In Fig. 5(a) and (b), competitive ions NO_3^- , NH_4^+ , Cu^{2+} (0.5 mmol/L) all showed a general trend of reducing the degradation rate of OTC (50 mg/L) under UV and visible light. While NO_3^- and Cu^{2+} ions exhibited minimal or negligible impacts, NH_4^+ showed a much significant effect in suppressing the degradation efficiency. Normally, the NO_3^- exhibited minimal or negligible impacts on degradation efficiency of OTC, because reactive species

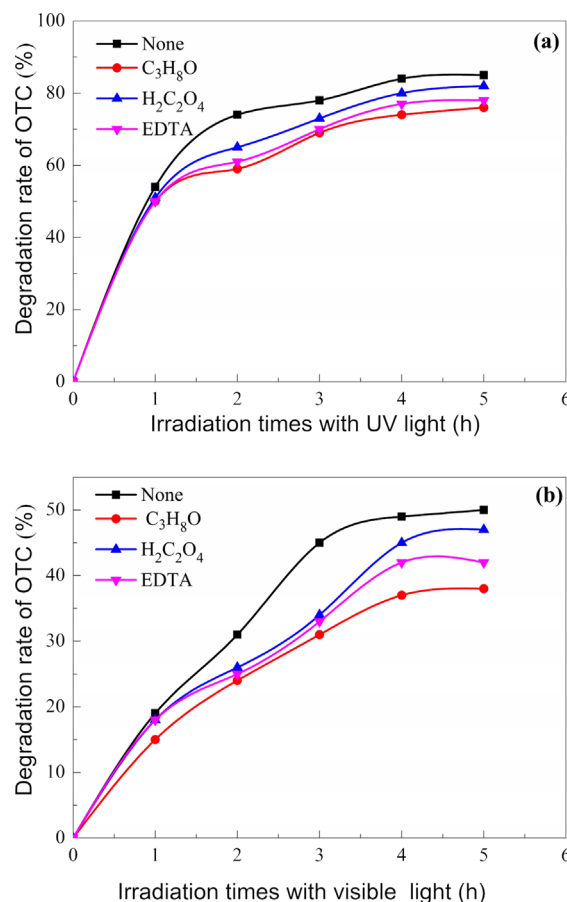


Fig. 6. (Color online) Effect of competitive organics (0.5 mmol/L) on degradation rate (%) of OTC solution (50 mg/L) under UV (a) and visible light (b) with $\text{Fe}_2\text{O}_3/\text{TiO}_2$ nanocomposite.

can be generated in nitrate solution which elevated OTC photolysis efficiency [17]. It has been reported that Cu^{2+} enhanced the adsorption of tetracyclines (TC) via acting as a bridge ion to form goethite- Cu^{2+} -tetracycline surface complex [18]. Since the structure of OTC is similar to TC, Cu^{2+} can also enhanced adsorption of OTC on the surface of $\text{Fe}_2\text{O}_3/\text{TiO}_2$ nanocomposite. However, the NH_4^+ have greatly suppressed on degradation rate of OTC, because the relationship between $\text{Fe}_2\text{O}_3/\text{TiO}_2$ nanocomposite and NH_4^+ is only competitive adsorption.

Effect of competitive organic (0.5 mmol/L) on the degradation rate of OTC (50 mg/L) solution are shown in Fig. 6. Among the three different organic species tested in this work, $\text{H}_2\text{C}_2\text{O}_4$ showed less effect than $\text{C}_3\text{H}_8\text{O}$ and EDTA. Although HC_2O_4^- generated from $\text{H}_2\text{C}_2\text{O}_4$ can compete with neutral-zwitterionic (H_3OTC^\pm) generated from OTC for preferential adsorption on the surface of catalyst [19], reaction between $\text{H}_2\text{C}_2\text{O}_4$ and Fe^{2+} under irradiation can also form the highly active intermediate

·OH radicals, which may improve the decomposition rate of OTC [20]. The significant suppression of the photocatalytic efficiency with the presence of C₃H₈O and EDTA can be understood considering the fact that C₃H₈O is known as ·OH radical scavengers [21] and Fe³⁺-EDTA can be formed by reactions of EDTA²⁻ with iron oxides at pH < 7 [22], which inhibited the degradation rate of OTC.

4. Conclusions

In summary, we synthesized Fe₂O₃/TiO₂ nanocomposite by co-precipitation method using Fe(NO₃)₃·9H₂O and Ti(SO₄)₂ as raw materials, and characterized by XRD, HR-SEM and EDX. These results showed that Fe₂O₃/TiO₂ nanocomposite consisted of hematite Fe₂O₃ and anatase TiO₂ with particle size of 50 ± 2 nm. The photocatalytic measurements indicated that by using Fe₂O₃/TiO₂ nanocomposite of 1 g/L, the highest efficiency of OTC degradation can be achieved when the initial concentration of OTC was 50 mg/L. Additionally, the investigation of the competitive ions and organics showed that although the existence of NO₃⁻ and H₂C₂O₄ can be ignored, Cu²⁺, NH₄⁺, C₃H₈O and EDTA in aqueous suspension significantly inhibited the degradation efficiency of OTC.

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