

# Photocatalytic Degradation of Oxytetracycline Using Co-precipitation Method Prepared Fe<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub> Nanocomposite

Yuefa Jia<sup>1</sup>, Chunli Liu<sup>1\*</sup>, and Rong Li<sup>2\*</sup>

<sup>1</sup>Department of Physics and Oxide Research Center, Hankuk University of Foreign Studies, Yongin 17035, Korea

<sup>2</sup>Research Center of Nano Science and Technology, Shanghai University, Shanghai 200444, China

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Fe<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub> nanocomposite were successfully synthesized by co-precipitation method using Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O and Ti(SO<sub>4</sub>)<sub>2</sub> 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 Fe<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub> 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. Cu<sup>2+</sup>, NH<sub>4</sub><sup>+</sup>, C<sub>3</sub>H<sub>8</sub>O and EDTA in the aqueous suspension were found to suppress the degradation rate of OTC, whereas the effect of NO<sub>3</sub><sup>-</sup> and H<sub>2</sub>C<sub>2</sub>O<sub>4</sub> can be ignored.

**Keywords :** Fe<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub>, 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%TiO<sub>2</sub>-5A molecular sieve composite and 13X loaded with TiO<sub>2</sub> photocatalysis showed a faster OTC removal and degradation speed than unsupported TiO<sub>2</sub> under ultra-violet (UV) light [11, 12]. Pereira *et al.* studied TiO<sub>2</sub>-assisted heterogeneous photocatalytic degradation and fully removal of OTC under solar UV energy [13]. In addition to UV light, visible light responsive TiO<sub>2</sub>, such as nitrogen and fluorine doped TiO<sub>2</sub> film,

have also been investigated in the photodegradation experiments, and exhibited good degradation efficiency of OTC [14]. Recently, the photocatalytic response of OTC using Fe<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub> nanocomposite has been investigated in details regarding the pH value and reaction mechanism [3], proposing that Fe<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub> nanocomposite can be used as a promising material for OTC removal under visible light. The existence of Fe<sub>2</sub>O<sub>3</sub> 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 Fe<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub> nanocomposite under UV and visible lights.

## 2. Experimental Section

### 2.1. Preparation of Fe<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub> nanocomposite

Using Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O and Ti(SO<sub>4</sub>)<sub>2</sub> as raw materials, Fe<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub> nanocomposite were synthesized using a co-precipitation method. A certain amount of Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O and Ti(SO<sub>4</sub>)<sub>2</sub> 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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\*Co-corresponding author: Tel: +82-31-330-4733

Fax: +82-31-330-4566, e-mail: chunliliu@hufs.ac.kr

Tel/Fax: +86-21-66137276, e-mail: lirong376@hotmail.com

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  $\text{SO}_4^{2-}$  could be tested with  $\text{Ba}^{2+}$ , 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  $\text{TiO}_2$  and hematite  $\text{Fe}_2\text{O}_3$  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.

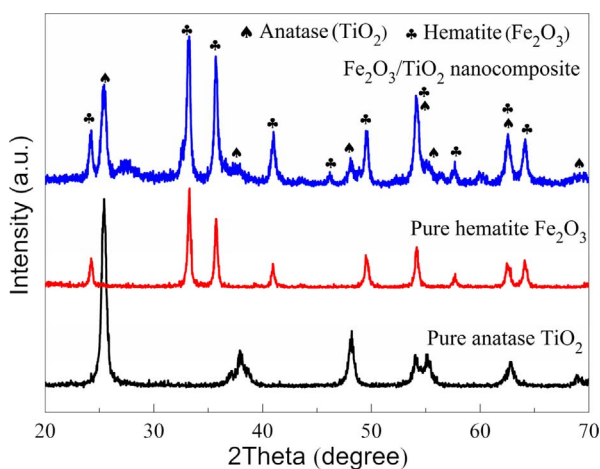
The phases of the co-precipitation products were analyzed by a D/Max-2200(Japan) X-ray diffractometer. The microstructure of  $\text{Fe}_2\text{O}_3/\text{TiO}_2$  nanocomposite was observed via a field emission scanning electron microscopy (FESEM, Hitachi-S4800, Japan) equipped with energy-dispersive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



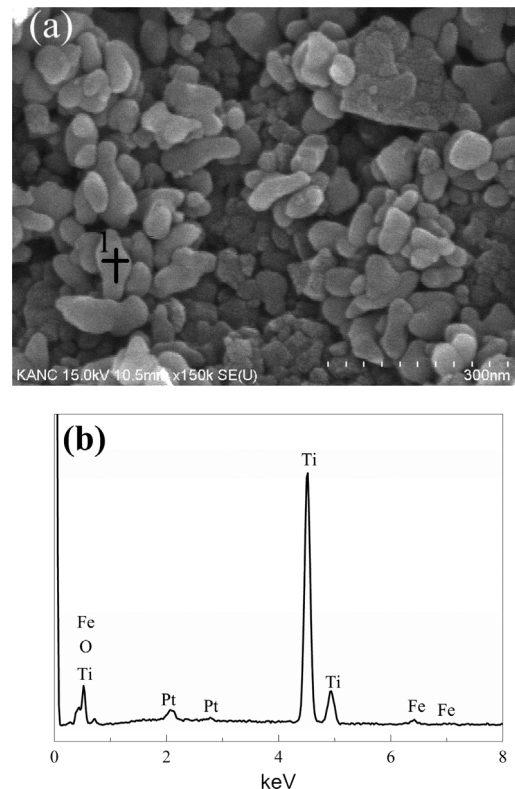
**Fig. 1.** (Color online) XRD pattern of  $\text{Fe}_2\text{O}_3/\text{TiO}_2$  nanocomposite, pure anatase  $\text{TiO}_2$  and hematite  $\text{Fe}_2\text{O}_3$ .

$\text{Fe}_2\text{O}_3$  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  $\text{TiO}_2$  (JCPDS card No.21-1272) and hematite  $\text{Fe}_2\text{O}_3$  (JCPDS card No.33-0664). Through the Scherrer equation:

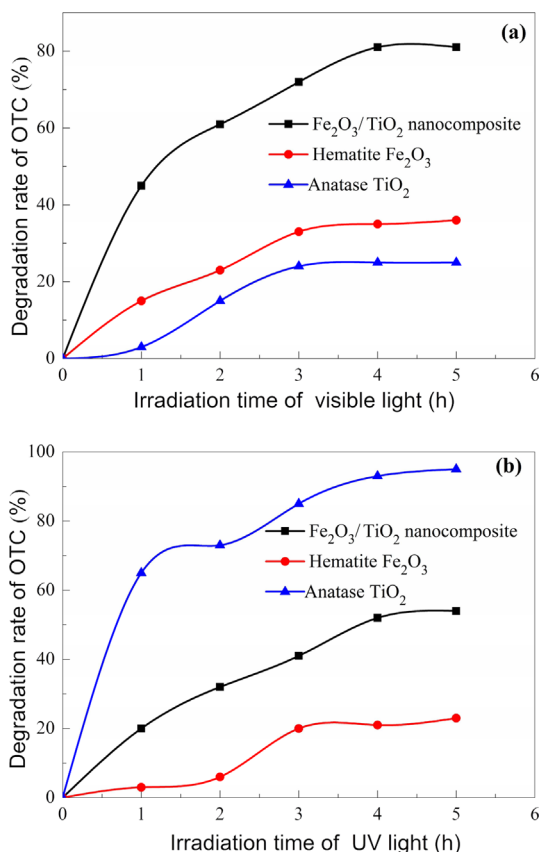
$$D = \frac{K\lambda}{\beta \cos \theta}$$

where  $K$  refers to a constant of 0.89,  $\beta$  is the full width at half maximum (FWHM) of the XRD peak at the diffraction angle  $\theta$ , and  $\lambda$  is X-ray wavelengths of 0.154 nm, the grain size  $D$  is estimated as 25 nm and 17 nm for  $\text{TiO}_2$  and  $\text{Fe}_2\text{O}_3$  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  $50 \pm 2$  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.

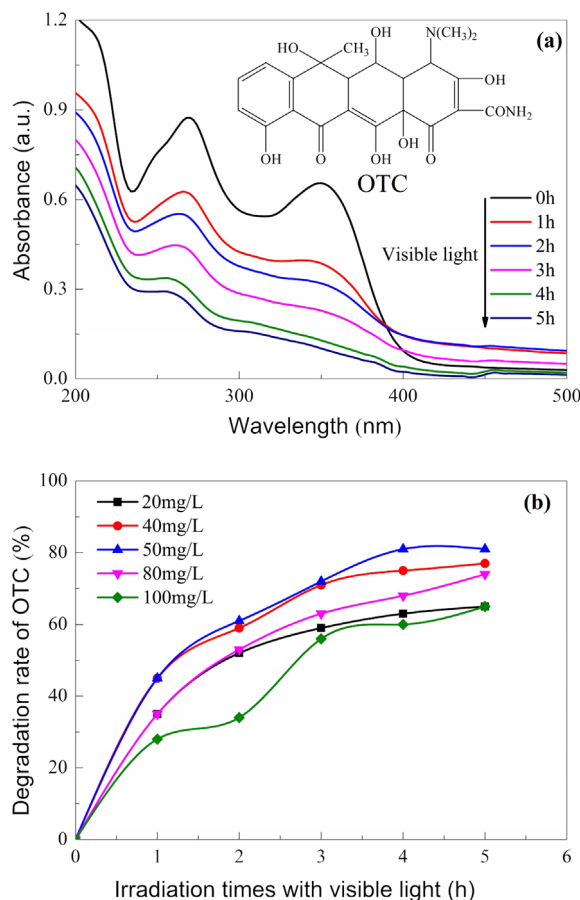


**Fig. 3.** (Color online) Degradation rate of OTC over pure anatase TiO<sub>2</sub>, hematite Fe<sub>2</sub>O<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub> nanocomposite ( $C_0 = 50$  mg/L) under visible light (a) and UV (b).

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 TiO<sub>2</sub> and hematite Fe<sub>2</sub>O<sub>3</sub> are also given for comparison. Under visible light for 5 h, the photodegradation rates of 81%, 36% and 25% can be observed for Fe<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub> nanocomposite, hematite Fe<sub>2</sub>O<sub>3</sub> and pure anatase TiO<sub>2</sub>, respectively. With similar conditions but UV light, photodegradation rates are 54%, 23% and 95% for Fe<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub> nanocomposite, hematite Fe<sub>2</sub>O<sub>3</sub> and pure anatase TiO<sub>2</sub>, respectively. Since visible light occupies about 50% of the solar spectrum, Fe<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub> nanocomposite are good candidates for further application in the waste water treatment containing OTC or similar materials.

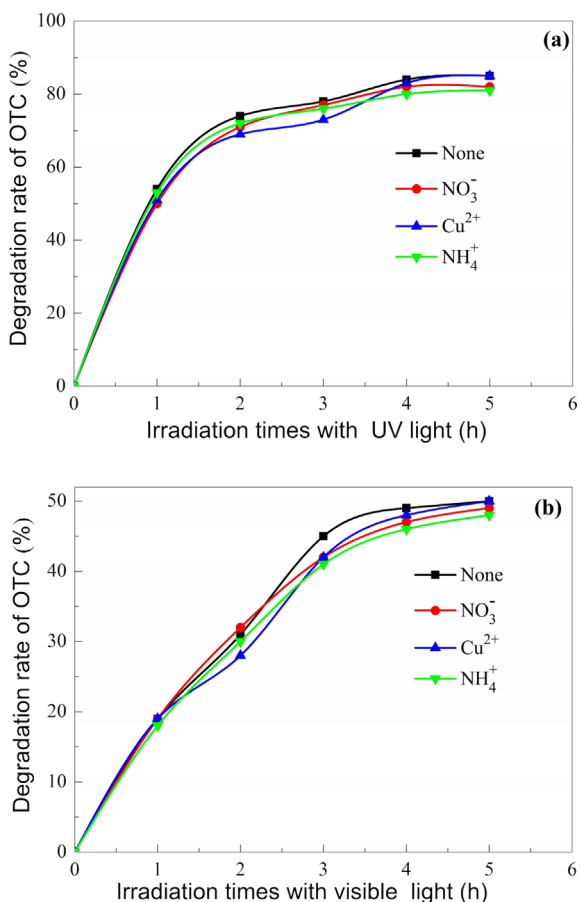
### 3.3. Effect of initial OTC concentration on the photocatalytic degradation

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 Fe<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub> 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.

Fe<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub> 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 Fe<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub> 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 Fe<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub> nanocomposite.

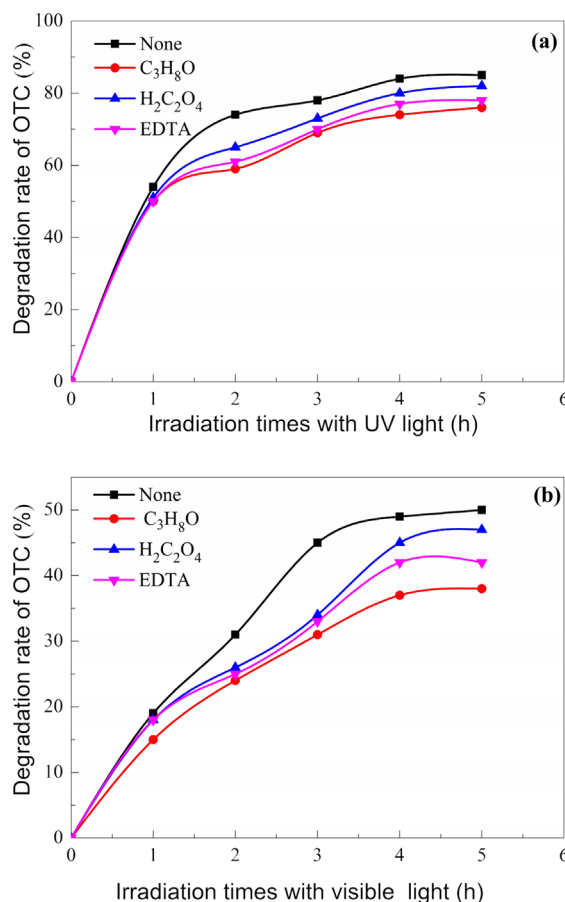


**Fig. 5.** (Color online) Effect of competitive ions (0.5 mmol/L) on degradation rate (%) of OTC solution (50 mg/L) under UV (a) and visible light (b) with  $\text{Fe}_2\text{O}_3/\text{TiO}_2$  nanocomposite.

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

$\text{NO}_3^-$ ,  $\text{NH}_4^+$ ,  $\text{Cu}^{2+}$ ,  $\text{C}_3\text{H}_8\text{O}$ , 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,  $\text{NaNO}_3$ ,  $\text{NH}_4\text{Cl}$ ,  $\text{CuCl}_2$ , 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  $\text{NO}_3^-$ ,  $\text{NH}_4^+$ ,  $\text{Cu}^{2+}$ ,  $\text{C}_3\text{H}_8\text{O}$ , 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  $\text{NO}_3^-$ ,  $\text{NH}_4^+$ ,  $\text{Cu}^{2+}$  (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  $\text{NO}_3^-$  and  $\text{Cu}^{2+}$  ions exhibited minimal or negligible impacts,  $\text{NH}_4^+$  showed a much significant effect in suppressing the degradation efficiency. Normally, the  $\text{NO}_3^-$  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  $\text{Cu}^{2+}$  enhanced the adsorption of tetracyclines (TC) via acting as a bridge ion to form goethite-  $\text{Cu}^{2+}$ -tetracycline surface complex [18]. Since the structure of OTC is similar to TC,  $\text{Cu}^{2+}$  can also enhanced adsorption of OTC on the surface of  $\text{Fe}_2\text{O}_3/\text{TiO}_2$  nanocomposite. However, the  $\text{NH}_4^+$  have greatly suppressed on degradation rate of OTC, because the relationship between  $\text{Fe}_2\text{O}_3/\text{TiO}_2$  nanocomposite and  $\text{NH}_4^+$  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  $\text{HC}_2\text{O}_4^-$  generated from  $\text{H}_2\text{C}_2\text{O}_4$  can compete with neutral-zwitterionic ( $\text{H}_3\text{OTC}^\pm$ ) generated from OTC for preferential adsorption on the surface of catalyst [19], reaction between  $\text{H}_2\text{C}_2\text{O}_4$  and  $\text{Fe}^{2+}$  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 C<sub>3</sub>H<sub>8</sub>O and EDTA can be understood considering the fact that C<sub>3</sub>H<sub>8</sub>O is known as ·OH radical scavengers [21] and Fe<sup>3+</sup>-EDTA can be formed by reactions of EDTA<sup>2-</sup> with iron oxides at pH < 7 [22], which inhibited the degradation rate of OTC.

#### 4. Conclusions

In summary, we synthesized Fe<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub> nanocomposite by co-precipitation method using Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O and Ti(SO<sub>4</sub>)<sub>2</sub> as raw materials, and characterized by XRD, HR-SEM and EDX. These results showed that Fe<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub> nanocomposite consisted of hematite Fe<sub>2</sub>O<sub>3</sub> and anatase TiO<sub>2</sub> with particle size of 50 ± 2 nm. The photocatalytic measurements indicated that by using Fe<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub> 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 NO<sub>3</sub><sup>-</sup> and H<sub>2</sub>C<sub>2</sub>O<sub>4</sub> can be ignored, Cu<sup>2+</sup>, NH<sub>4</sub><sup>+</sup>, C<sub>3</sub>H<sub>8</sub>O and EDTA in aqueous suspension significantly inhibited the degradation efficiency of OTC.

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