

Fabrication of Fe-ACF/TiO₂ composites and their photonic activity for organic dye

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ACF/TiO₂ 복합체의 제조 및 유기 염료에 의한 광활성

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요약: 철 화합물을 처리한 활성탄소섬유(Fe-ACF)를 사용하여 Fe-활성탄소섬유/TiO₂(Fe-ACF/TiO₂) 복합체 촉매를 제조하였다. 또한, Fe-ACF/TiO₂ 복합체 촉매는 BET, SEM, XRD 와 EDX 기기를 사용하여 특성화하였다. BET 표면적은 각각의 복합체들에 대한 흡착 특성과 관계 있음을 나타내었다. SEM 결과는 ACF의 표면에 Fe 화합물과 이산화 티타늄이 분포해 있음을 나타내었다. XRD 결과는 Fe-ACF/TiO₂ 복합체가 철 중간체 화합물과 함께 아나타제 구조를 가지고 있음을 나타내었다. EDX 결과는 Fe-ACF/TiO₂ 복합체내에 C, O, Ti와 Fe 피크의 존재를 보였다. 광촉매 분해 효과로부터, 이들 복합체에 의한 유기염료의 분해를 관찰 하였다. 다른 분해 효과는 Fe의 포토-펜톤 반응의 탓으로 여겨진다. 즉 Fe-ACF/TiO₂의 복합적인 반응은 MB 분해에 대한 강력한 포토-펜톤 반응을 생성한 것으로 여겨진다.

Abstract: Activated carbon fiber treated with iron compound (Fe-ACF) was employed for preparation of Fe-activated carbon fiber/TiO₂ (Fe-ACF/TiO₂) composite catalysts. Then, the prepared Fe-ACF/TiO₂ composite catalysts were characterized by employing BET, SEM, XRD and EDX instruments. It showed that BET surface area was related to adsorption capacity for each composite. The SEM results showed that ferric compound and titanium dioxide were distributed on the surfaces of ACF. The XRD results showed that Fe-ACF/TiO₂ composite mostly contained an anatase structure with a Fe mediated compound. EDX results showed the presence of C, O, and Ti with Fe peaks in Fe-ACF/TiO₂ composites. From photocatalytic degradation effect, it was observed in the organic dye (Methylene blue, MB) degradation by these composites. Different degradation effect can be attributed to the synergetic effects of photo-Fenton reaction of Fe. It was considered that the combined reactions of Fe-ACF/TiO₂ produce powerful photo-Fenton process in the MB degradation.

Key words: Activated carbon fiber, Fe, Methylene blue, Photo-Fenton, SEM

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1. Introduction

Titania (TiO₂) possesses the properties of non-toxic, stable performance, with anti-chemical and optical corrosion, high photocatalytic activity for degradation of organic water pollution in non-selective, complete mineralization, no secondary pollution, etc.¹⁻⁵ So, TiO₂ in different ways was used in photocatalytic degradation, which this method is considered to be environmentally friendly for pollution treatment. Thus, it is highly desirable that TiO₂ can be applied on a large scale for water and wastewater treatment. However, it suffers the shortcoming of lower photonic efficiency and usually be induced only by ultraviolet light, which prevents the large-scale application of this promising method.

Several attempts have been adopted to enhance the photocatalytic performance of TiO₂, such as immobilization of TiO₂ powder onto supports like ACF,^{6,7} and AC.⁸⁻²⁰ At the same time, doping of a variety of metals to TiO₂, increase photocatalytic efficiency, such as Fe,²¹⁻²³ Pt,^{24,25} Au,²⁵ Pd,²⁶ Ru²⁷ have been successfully treated with TiO₂. ACF is highly adsorptive; the micropore surface of ACF greatly enhances the efficiency of pollutant adsorption. On the other hand, it can put pollutants in the water adsorbed on the side, combination of TiO₂ have been able to concentrate on the decomposition of pollutants. So many authors have reported a synergistic effect for ACF-supported TiO₂ systems,^{13,14} such as high adsorptive ability and photosensitivity, therefore, TiO₂/ACF has been already widely used.

Photo-Fenton reactions are widely studied and used in the photocatalytic process,²⁸⁻³² the iron was most commonly used in the photo-Fenton process as a catalyst.³⁰ Doping of iron to TiO₂ has been widely described of photo-Fenton reactions for compose catalysis, because iron doping can give some benefits such as retarding the recombination reaction. But, containing a larger amount of Fe³⁺ was reported to inhibit the photocatalytic activity.^{33,34} However, these studies mainly take attentions to photo-catalytic efficiency for containing Fe compounds, and the photo-catalytic efficiency is affected by the

Fe content.

In this present work, ACF re-treated by ferric nitrate (Fe(NO₃)₃·9H₂O) was selected as an adsorptive support for TiO₂ loading. The Fe-ACF/TiO₂ composites were prepared by a sol-gel method using titanium (IV) oxysulfate hydrate (TOS) as precursor, following by heat treatment at suitable temperature. The characterizations of Fe-ACF/TiO₂ composite catalysts were determined by employing BET, SEM, XRD and EDX instruments. To determine the photocatalytic decomposition of the composites, the photocatalytic activities of different concentrations of Fe on the Fe-ACF/TiO₂ composite were studied for the MB degradation under UV light.

2. Experimental

2.1. Materials

10 g ACFs (EAST ASIS Carbon Fibers Co., Ltd, AnShan, China) were added to 50 ml different concentration of Fe(NO₃)₃·9H₂O (Duksan Pure Chemical Co. (99+%, ACS reagent, Korea) and stirred for 24 h at room temperature. These samples obtained of Fe-ACF were dried naturally at 773 K for 1 h. 5 g powdered of Fe-ACF composites was added to same volume (10 mL) of 1 M titanium (IV) oxysulfate hydrate (TiOSO₄·xH₂O (TOS), Sigma-Aldrich, Germany) solutions and stirred for 5 h at room temperature. clarified and poured out of the super water. The sediments was dried at 373 K, and then heated at 923 K for 1 h. After cooling, the Fe-ACF/TiO₂ composites were obtained. Non-treated ACF/TiO₂ was supplied from former experiment.⁶ The nomenclatures and method of the samples prepared are listed in *Table 1*.

2.2. Characteristics and investigations for the samples

To characterize of Fe-ACF/TiO₂, the BET surface area as N₂ adsorption method was measured at 77 K using a BET analyzer (MONOSORB, USA). The surface state and structure of the Fe-ACF/TiO₂ composites was observed via a SEM (JSM-5200, Japan). XRD (Shimatz XD-D1, Japan) analysis using Cu K α

Table 1. Nomenclatures of Fe-ACF/TiO₂ composites prepared

Preparation process	Nomenclatures
ACF + Titanium iso propoxide	F0T
[{ACF + 0.1 M Fe(NO ₃) ₃ }(773 K) + 1 M TOS/alcohol 10 mL] (923 K)	F1T
[{ACF + 0.25 M Fe(NO ₃) ₃ }(773 K) + 1 M TOS/alcohol 10 mL] (923)	F2T
[{ACF + 0.5 M Fe(NO ₃) ₃ }(773 K) + 1 M TOS/alcohol 10 mL] (923 K)	F3T

radiation was performed to assess the crystalline phases. For the elemental analysis of the Fe-ACF/TiO₂ composites, EDX spectra were also obtained. For the measurement of photo-degradation effects, MB in water was determined by the following procedure. A Fe-ACF/TiO₂ powdered sample of 0.03 g was added into a concentration of 1.0×10^{-5} mol/L in a dark atmosphere at ambient temperature. Each concentration was measured as a function of UV irradiation time. Results were recorded using a Genspec III (Hitachi, Japan) spectrometer.

2.3. Photocatalytic activity

Fe-ACF/TiO₂ photocatalysts were used to degrade MB, in aqueous media under UV light irradiation. For UV irradiation, the reaction tube was placed in the darkness box. The UV lamp was located at the distance of 100 mm from the solution in darkness box. After irradiation at 10 min, 30 min, 60 min, 90 min, 120 min, and 150 min, the samples were extracted from the reactor and removal of dispersed powders through centrifuge. The concentration of MB in the solution was determined as a function of irradiation time from the absorbance change at a UV wavelength line of 220 and 800 nm.

An original data of ACF/TiO₂ was borrowed and used to compare with preparation of Fe-ACF/TiO₂ composites.

3. Result and Discussion

3.1. The structural characteristics of Fe-ACF/TiO₂ composites

The Fe-ACF/TiO₂ catalysts prepared with different concentrations of Fe were denoted as F1T, F2T and F3T. These BET surface areas are listed in Table 2. It can be clearly seen that the specific surface area

Table 2. Specific BET surface areas of Fe-ACF/TiO₂ composite samples

Sample	S _{BET} (m ² /g)
F1T	782
F2T	745
F3T	706

was gradually decreased by increasing the Fe contents of Fe-ACF/TiO₂ composites because of the blocking of the micropores by surface complexes, which introduced through the formation of the Fe-ACF/TiO₂ composites.²² The similar phenomena had also been observed in the references.^{35,36}

SEM micrographs in Fig. 1 show the morphology of Fe-ACF/TiO₂ photocatalysts. According to the Fig. 1, it is observed that TiO₂ particles were agglomerated on the surface of ACF. Compared with different concentrations of Fe in all samples, there was no significant difference. Generally, it is considered that good particle dispersions can produce high photocatalytic activity. In previous studies,^{37,38} ACF/TiO₂ composites treated with nitric acid enhanced the homogenous and uniform distribution of TiO₂ particles. The SEM images showed that the titania particles on the complexes were evenly distributed in all types of the Fe-ACF/TiO₂ composites. Although we could not find out Fe particle in SEM images of Fe-ACF/TiO₂ composites, maybe the size of the Fe particle was very small, it was confirmed in XRD and EDX results.

Fig. 2 showed the XRD analysis results for the catalyst of Fe-ACF/TiO₂. Diffraction peaks corresponding to anatase phase have been marked with 'A', diffraction peaks corresponding to 'FeO+TiO₂' and 'γ-Fe₂O₃' phase have been marked with 'F' and 'O', respectively. XRD patterns of the composites showed that the Fe-ACF/TiO₂ composites contained

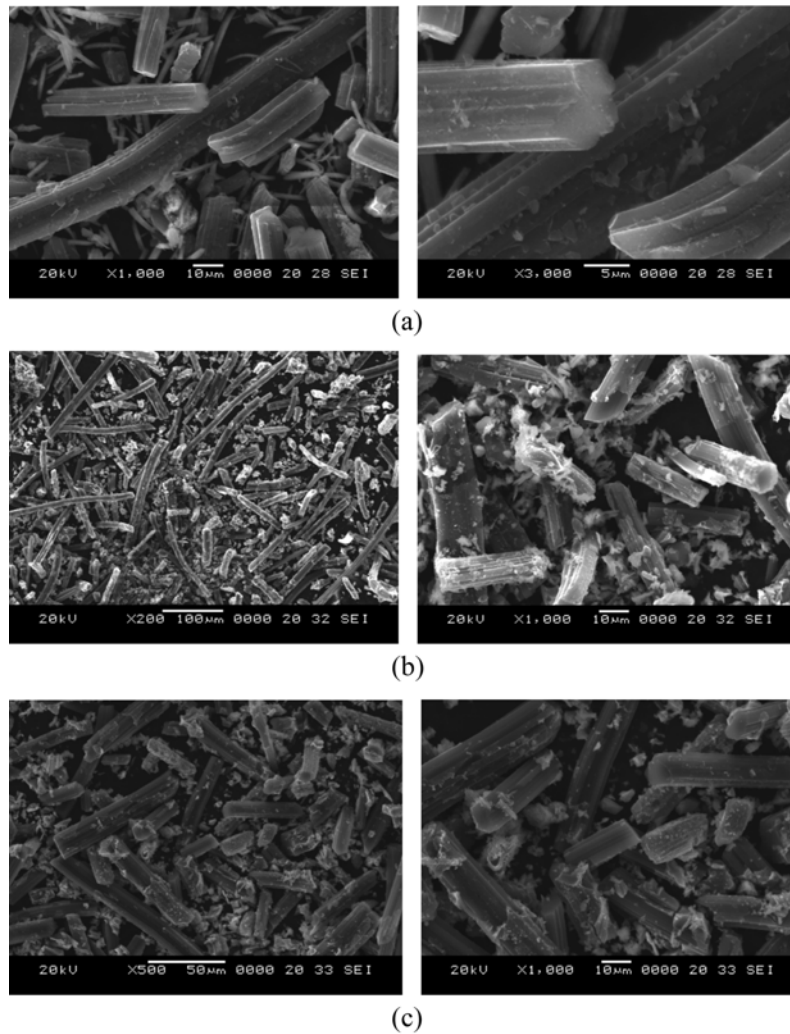


Fig. 1. SEM images obtained from powdered Fe-ACF/TiO₂ composites: (a) F1T, (b) F2T and (c) F3T.

only an anatase phase. The anatase phase was obtained after heat treatment at 773 K. The main diffraction peaks at 25.3, 37.8, 48.0, 53.8 and 62.5 are diffractions of (101), (004), (200), (105) and (204) planes of anatase. Moreover, in the samples of F1T, F2T and F3T, we can clearly find the peaks of 'FeO+TiO₂' in the XRD patterns, respectively. It is noteworthy that the 'FeO+TiO₂' peaks in F3T are higher than other samples. As expected, the intensity of 'FeO+TiO₂' peaks increased with an increase of concentration of Fe source in the solution. 'γ-Fe₂O₃' diffraction peaks were only found in F3T, the main diffraction peaks have characteristic reflections of

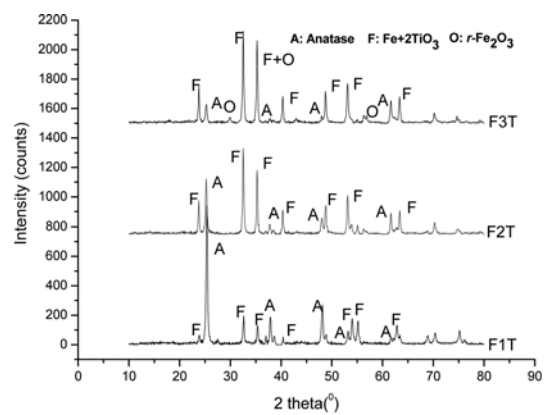


Fig. 2. XRD patterns of powdered Fe-ACF/TiO₂ composites.

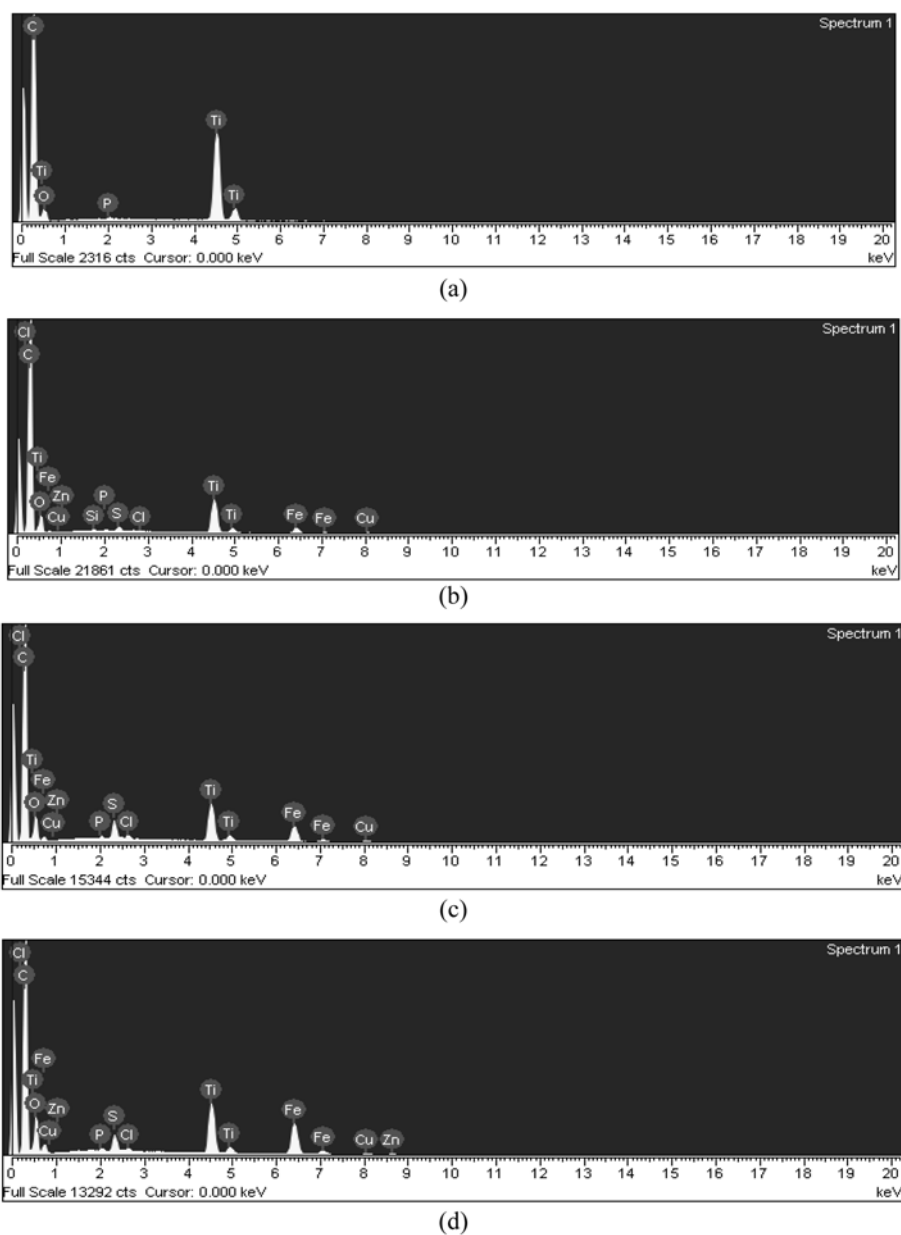


Fig. 3. Typical EDX microanalyses for the ACF/TiO₂ and Fe-ACF/TiO₂ composites: (a) F0T, (b) FIT (c) F2T, and (d) F3T

(110), (210), and (211).³⁹ These nanocrystallites were produced by solvothermal reaction and heat treatment temperature at 773-1173 K.⁴⁰

Fig. 3 showed the results of the EDX for Fe-ACF/TiO₂ and ACF/TiO₂. These spectra exhibit the presence of peaks from the C, O and Ti elements. For the Fe-ACF/TiO₂ composites, we observed the peaks

of the Fe element. And, the numerical contents for the various elements were listed on the Table 3. From the data, we can also see that all of the samples are rich in C, O and Ti elements with a very poor in impure elements. It can be explained the appearance from their SEM observations as mentioned above. On the other hand, it is noticed that the amount of C

Table 3. EDX elemental microanalysis of Fe-ACF/TiO₂ composites

Sample (wt.%)	C	O	Ti	Fe
F0T	65.5	15.4	18.9	0
F1T	71.18	16.82	7.8	2.18
F2T	67.41	17.63	6.52	5.18
F3T	60.04	21.07	7.53	8.65

element of all samples is much more than the amount of Ti and O elements. Other impurity elements may be derived from TOS.

3.2. The photocatalytic activity of Fe-ACF/TiO₂ composites

Fig. 4 showed photocatalytic efficiency of different samples at the same concentrations of MB solution. In Fig. 4(b) and (c), only a sharp absorption peak at around 250 nm was found in UV spectra. It was indicated that the product of MB solution

degradation has a single and homogenous structure, which considered complete mineralization of MB solution. In Fig. 4(a) and (d), absorption maximum peaks located at 660 nm. The absorption peaks were shifted to visible light range, degradation product possibly still comprised of the aromatic compounds containing nitrogen. Which shown that the MB solution was not completely degraded by the composites of Fe-ACF/TiO₂ from analysis of UV spectra and degradation process of MB molecules. In oxidation process of titania-based photocatalytic, two oxidative agents can be considered: the photo-produced holes $h_{\nu b}^+$ (mainly involved in the decarboxylation reaction) and/or the OH^{*} radicals. The $h_{\nu b}^+$ and OH^{*} radicals in aqueous MB solution is not selective,⁴¹ therefore, it means random degradation of the nitrogen substituent on aromatic compounds as well as MB molecules. As shown in the Fig. 4, we can also observe that the absorbance maxima of the sample

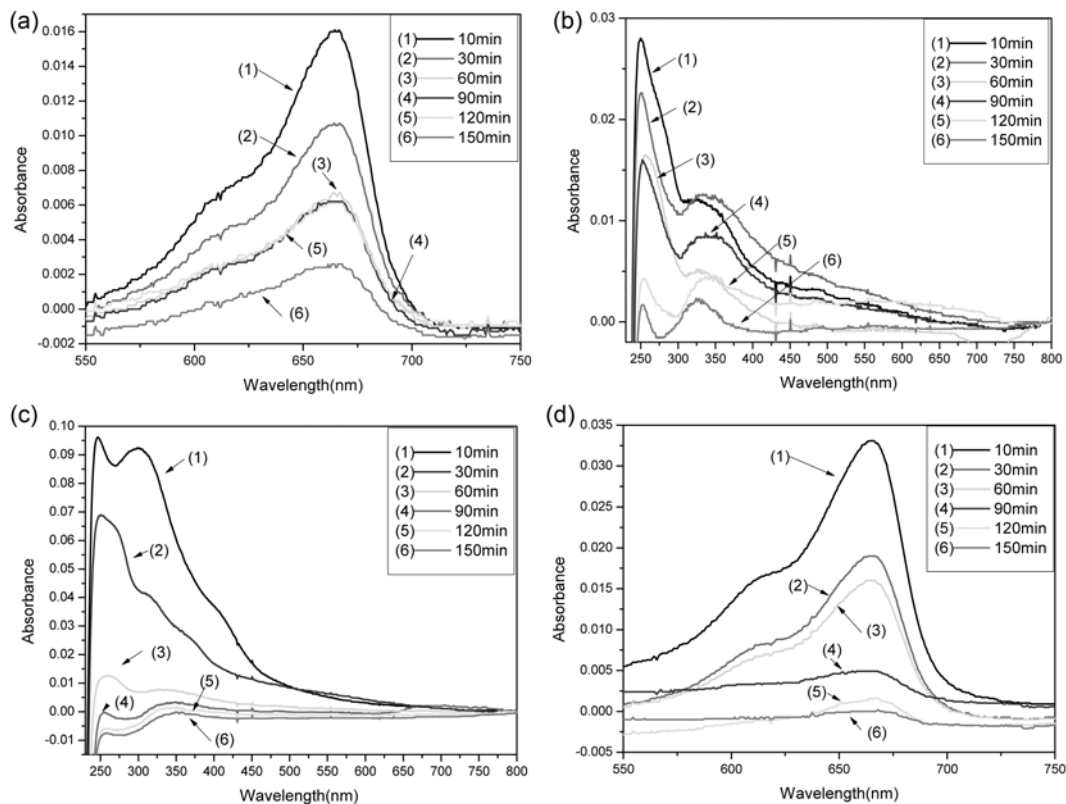


Fig. 4. UV/Vis spectra of MB concentration against the ACF/TiO₂ and Fe-ACF/TiO₂ composite under various time conditions: (a) F0T (b) F1T (c) F2T and (d) F3T

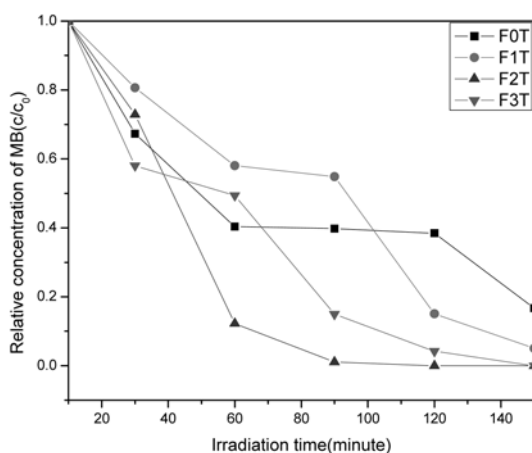


Fig. 5. Dependence of relative concentration of MB in the aqueous solution $\ln \text{Abs}(\text{max})_t / \text{Abs}(\text{max})_0$ on UV irradiation time for the ACF/TiO₂ and Fe-ACF/TiO₂ composites.

Fe-ACF/TiO₂ is much more decreased than that of the sample F0T in the same irradiation time. It was

considered that the photocatalytic activity was increased with introduce of Fe, and showed significant difference between different concentrations of Fe.

Fig. 5 showed dependence of relative concentration of MB in the aqueous solution $\ln \text{Abs}(\text{max})_t / \text{Abs}(\text{max})_0$ on UV irradiation time for ACF/TiO₂ and Fe-ACF/TiO₂ composites. As shown in the Fig. 5, from ACF/TiO₂ to Fe-ACF/TiO₂, the MB degradation efficiency increased distinctly, despite content of Ti is highest in F0T from EDX data shown, it is noteworthy that the Fe modified ACF-TiO₂ enhances the photocatalytic activity greatly. This reaction could be attributed to Fe's photo-Fenton reaction which was showed in equations ((1)~(6)) and Fig. 6.

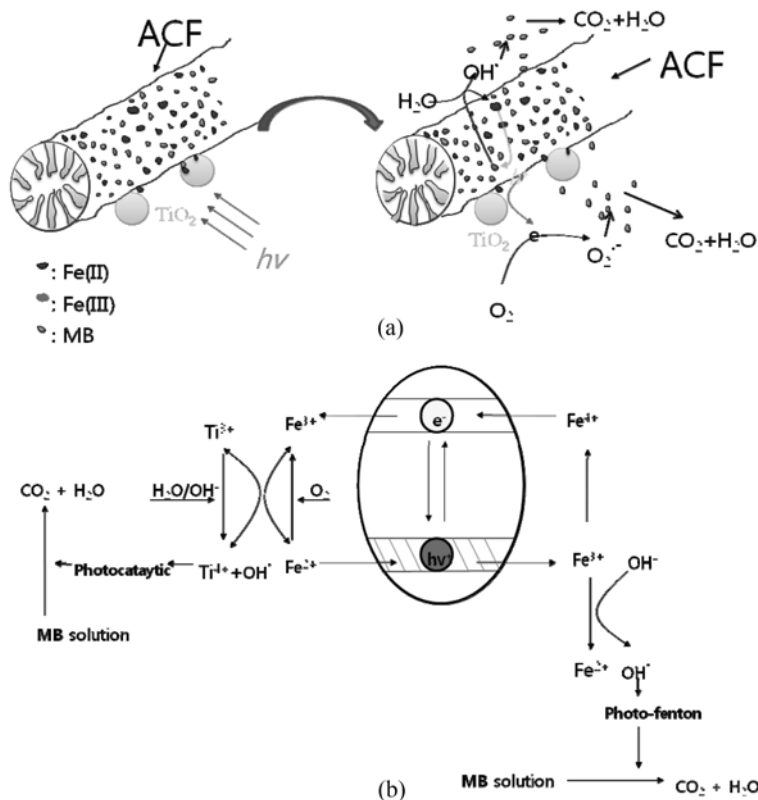
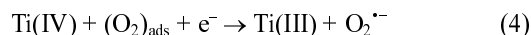
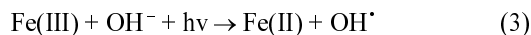
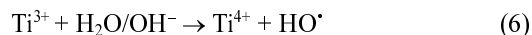
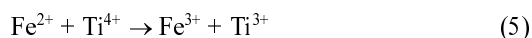


Fig. 6. Fe's photo-Fenton reaction of Fe-ACF/TiO₂ in MB solution; (a) macroscopic diagram and (b) photo-Fenton reaction in TiO₂.



(ads: adsorption)

Comparison with samples of Fe treated-ACF/TiO₂ composites, as shown in the *Table 3*, the content of Ti is approximate equation for each Fe-ACF/TiO₂ composites. Between F1T and F2T, it is considered that photocatalytic activity was enhanced due to increase of iron ions concentration. As shown in the equations ((1)-(4)), low levels of iron doping can retard the recombination rate of electron/hole pair. Although the degradation effect of F3T sample was some lower than expected. The photocatalytic activity of F3T was lower than that of F2T after 60 min. It is attributed to that the superfluous irons can act as recombination centers for the electron/hole pairs.⁴² The proposed reactions were showed in the equations ((2), (7)-(9)):

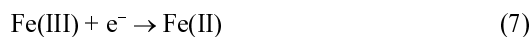


Fig. 6 shows Fe's photo-Fenton reaction of Fe-ACF/TiO₂ in MB solution. As shown microcosmic diagram of Fe-ACF/TiO₂ photocatalytic for MB degradation in the *Fig. 6(a)*, during the photo degradation process, MB was firstly absorbed by strong adsorption capacity of ACF. An important step in the photocatalytic process is the adsorption of reacting substances onto the surface of the catalyst.⁴³ Then the TiO₂ component produce O₂^{•-} radicals and give lone hole due to a photocatalytic reaction. The Fe effect on combining lone hole produce OH[•] radicals due to a photo-Fenton process. This photo assistance reaction conduce gradual rise of OH[•] radicals and O₂^{•-} radicals. *Fig. 6(b)* shows photo-Fenton reaction of Fe in TiO₂-based photocatalytic, we evidently known that introducing iron ion can increase production amount of OH[•] radicals. Otherwise, additional OH[•] radicals were provided due to an associated reaction between iron and titanium ion. Thus, which reveals the modified composites by Fe can enhance the photocatalytic activity greatly.

4. Conclusion

In this study, Fe-ACF/TiO₂ was prepared with Fe-ACF and TOS by sol-gel. Then, the characteristics of the Fe-ACF/TiO₂ composites were analyzed by BET, SEM, EDX and XRD. Fe-ACF/TiO₂ composites of containing different concentrations of Fe were used to investigate photocatalytic activity in MB solution degradation. In the photo degradation process, degradation of MB solution degradation experienced two chemical reactions of Ti photo-degradation and Fe photo-Fenton reaction, compared with the composites without Fe modification and different samples obtained by different concentrations of Fe, the composites of Fe-ACF/TiO₂ can enhance photocatalytic activity due to Fe assistance on the photocatalytic reaction, and photocatalytic activity can attain maximal at certain of concentration. Thus, an important role of Fe was acted in Fe-ACF/TiO₂ composite as a catalyst. An effective controlling of photo-Fenton reaction is an interesting subject for further investigation regarding Fe element.

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