



pH Dependence on the Degradation of Rhodamine B by Fe-ACF/TiO₂ Composites and Effect of Different Fe Precursors

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Fe-ACF/TiO₂ 복합체에 의한 로다민 B 용액의 분해에 있어서 pH 의존성 및 여러 가지 Fe 전구체의 효과

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ABSTRACT : Iron-loaded activated carbon fibers (Fe-ACF) supported titanium dioxide (TiO₂) photocatalyst (Fe-ACF/TiO₂) was synthesized using a sol-gel method. Three different types of Fe-ACF/TiO₂ were obtained by treatment with different precursor of Fe, and characterized using BET, SEM, XRD and EDX analysis. The photocatalytic activity of Fe-ACF/TiO₂ was investigated by the degradation of Rhodamine B (Rh.B) solution under UV irradiation. From the experimental results, it was revealed that Fe-ACF/TiO₂ composites show considerable photocatalytic ability for the removal of Rh.B by comparing non-treated ACF/TiO₂ composites. And photo-Fenton reaction with Fe element was incoordinately influenced due to different precursor of Fe. It clearly indicates that Fe-ACF/TiO₂ composites prepared using FeCl₃ provided the highest photo-Fenton activity, then, which was affected by pH changes on the degradation of Rh.B.

요약 : 졸-겔 방법을 사용하여 Fe-ACF/TiO₂ 복합체 광촉매를 제조하였다. 여러 가지 철 전구체를 사용하여 세 가지 Fe-ACF/TiO₂ 복합체를 제조하고 BET, SEM, XRD 및 EDX를 사용하여 특성화 하였다. UV 조사에서 Rh.B 용액의 분해에 의거하여 Fe-ACF/TiO₂ 복합체의 광촉매 특성을 파악 하였다. 실험 결과로부터, Fe-ACF/TiO₂ 복합체는 ACF/TiO₂ 복합체 보다 Rh.B의 제거 효과가 더 우수함을 나타내었다. 또한 여러 가지 Fe 전구체 사용으로 인한 Fe 원소의 포토-펜톤 효과는 다르게 나타났다. FeCl₃를 사용하여 제조된 Fe-ACF/TiO₂ 복합체는 가장 우수한 포토-펜톤 효과를 나타내었고, pH 변화에 의존하여 Rh.B 용액 분해에 대하여 영향을 주었다.

Keywords : Fe-ACF/TiO₂ composites; Fe precursors; Rh.B; photo-Fenton; photocatalytic activity

I. Introduction

In the last decade, titania has variable applications in paints,¹ pigments, hydrogen gas evolution² and environmental purification systems.³ It is widely used due to its low cost, non-toxicity, chemical stability and complete mineralization.⁴⁻⁸ However, the existent drawback of titania is its relatively low quantum yield due to high electron/hole pairs recombination rate. A high degree of recombination between charge carriers is a waste of radiation energy. Intuitively, efficient separation of charge carriers can assist photocatalytic system. Therefore, many attempts have been focused on reduced electron/hole pairs recombination rate, which includes dye sensitization, metal ion doping, nonmetal doping, etc.⁹⁻¹¹ It is well known when

titania is treated with metal or metal oxides, its properties are remarkably modified. And the prevalent candidate of iron dopant in the titania matrix significantly influenced charge carrier recombination rate and interfacial electron-transfer rate, hence increasing the quantum yield of photocatalysts.¹²⁻¹⁴ Namely the inimitable character of iron possesses different valence, and each other can easily transform with electron/hole pairs, hereby to reduce electron/hole pairs recombination rate, enhancing the photocatalytic activity. As reported in recent literatures,¹⁵⁻²⁰ iron ions were able to work in photo-Fenton process to enhance the photocatalytic activity by formation of OH· Radicals.

As we know, there are no reports concerning the change of photo-Fenton reaction by different precursor of Fe. However, the photo-Fenton process can be governed by the amount and ratio of Fe²⁺/Fe³⁺, it was well known that an optimal ratio would give an ideal work in photo-Fenton reaction. Many au-

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thors reported that the Fe²⁺ can be effectively oxidized to Fe³⁺ by adjustment of solution pH.²¹⁻²² It was considered that the effective oxidation of Fe²⁺ to Fe³⁺ can enhance the effect of photo-Fenton reaction due to less active Fe²⁺. Moreover, many studies also indicated that the pH of a reaction solution is an important parameter in the photocatalytic degradation of organic compounds using photocatalyst as TiO₂.²³⁻²⁴ It was considered that the interfacial electron transfer and the photo-redox process were affected by the influence of the surface charge of the photocatalyst due to various pH of initial reaction solution.²⁵ However, according to the former studies,²⁶⁻²⁷ the contrary degradation effect were obtained by change of pH.

In this study, ACF was selected as the support for TiO₂ and Fe loading due to the good adsorption and uniform pore structure.²⁸⁻²⁹ In addition, ACF in the form of felt or cloth is preferable for handling, compared with granular supports.³⁰⁻³¹

In this paper, we synthesized Fe-ACF/TiO₂ composites using different Fe precursors (FeCl₃ · 6H₂O, Fe(NO₃)₃ · 9H₂O and Fe₂(SO₄)₃ · 9H₂O) by a sol-gel method. The synthesized catalyst has been characterized by BET, SEM, XRD and EDX. And their photocatalytic degradation properties were compared with ACF/TiO₂ by degradation of Rh.B solution, and degradation activity was discussed among the Fe-ACF/TiO₂ composites. Furthermore, effect of different initial solution pH on the degradation of Rh.B by using the synthesized photocatalyst was studied in detail.

II. Experimental

1. Materials

Activated Carbon Fiber (ACF) was purchased from EAST ASIS Carbon Fibers Co., Ltd, (Anshan, China). Hydrogen Peroxide (H₂O₂) was purchased from Daejung Chemicals Metals Co., Ltd, (Korea). Titanium (IV) oxysulfate hydrate (TiOSO₄ · xH₂O (TOS), Sigma-Aldrich, Germany) was selected as a titanium source for the preparation of ACF/TiO₂ composites, and FeCl₃ · 6H₂O as the ferric source was purchased from Duksan Pure Chemical Co., Ltd, (Korea). Fe(NO₃)₃ · 9H₂O was also purchased from Duksan Pure Chemical Co., Ltd, (Korea). Fe₂(SO₄)₃ · 9H₂O was purchased from Yakuri Pure Chemical Co., Ltd, (Japan). The Rh.B was purchased from Samchun Pure Chemical Co., Ltd, Korea. The sodium hydroxide (NaOH) was purchased from Duksan Pure Chemical Co., Ltd, (Korea), and the hydrochloric acid (HCl) was purchased from Daejung Chemicals & Metals Co., Ltd, (Korea).

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

Samples	Nomenclatures
ACF + Titanium iso propoxide	F ₀ AT
ACF+ 0.25M FeCl ₃ + 1M TOS/alcohol	F ₁ AT
ACF+ 0.25M Fe(NO ₃) ₃ + 1M TOS/alcohol	F ₂ AT
ACF+ 0.5M Fe ₂ (SO ₄) ₃ + 1M TOS/alcohol	F ₃ AT

2. Preparation of samples

In this experimental process, 5 g ACF power was added into to 50 ml 0.25M Fe precursors (FeCl₃ · 6H₂O, Fe(NO₃)₃ · 9H₂O and Fe₂(SO₄)₃ · 9H₂O) solution and the mixtures were stirred 24 h using a non-magnetic stirrer at room temperature. After heat treatment at 773 K, we obtained the Fe-ACF. The Fe-ACF was put into the mixture of TOS and ethanol. Then the mixed solution was stirred for 5 h in an air atmosphere. After stirring solution was transformed to gel state, and these gels were heat treated at 923 K for 1h. And then the Fe-ACF/TiO₂ composites were obtained. The nomenclatures of prepared samples are listed in Table 1. At the same time, an original sample of ACF/TiO₂ was quoted from former experiment³² and compared with that of Fe-ACF/TiO₂ composites obtained.

3. Characteristics and investigations of the samples

The BET surface area by N₂ adsorption method was measured at 77 K using a BET analyzer (Monosorb, USA). XRD (Shimadzu XD-D1, Japan) result used to identify the crystallinity by Cu K α radiation. SEM used to observe the surface state and structure of Fe-ACF/TiO₂ composites using an electron microscope (JSM-5200 JOEL, Japan). EDX spectra were also obtained for determining the elemental information of ACF/TiO₂ and Fe-ACF/TiO₂ composites. UV-vis absorption parameters for the MB solution decomposed by ACF/TiO₂ and Fe-ACF/TiO₂ composites under UV lamp irradiation were recorded using a Spectronic (USA) spectrometer.

4. Photocatalytic activity of Fe-ACF/TiO₂

The photocatalytic decomposition was tested by different Fe-ACF/TiO₂ composites powder and an aqueous solution of MB in a 100 mL glass container and then irradiation system with 20W UV light at 365 nm, which was used at the distance of 100 mm from the solution in darkness box. The same amount of Fe-ACF/TiO₂ composites (0.03 g) was suspended in 50 mL of 5.0 × 10⁻⁵ mol/L Rh.B solution. The photocatalytic activities of the prepared Fe-ACF/TiO₂ composites were inves-

tigated using the photodegradation rate of Rh.B, which was measured for 0 min, 30 min, 60 min, 90 min and 120 min. The red color of the solution faded gradually with time due to the adsorption and decomposition of Rh.B. For reactions in different pH media, the initial pH of the suspensions was adjusted by the addition of either NaOH or HCl solutions. And then the concentration of Rh.B in the solution was determined as a function of irradiation time from the absorbance change at a wavelength of 550 nm.

III. Results and discussion

1. The surface characteristics

The value of BET surface area of pristine ACF, ACF/TiO₂ and Fe-ACF/TiO₂ samples are shown in Table 2. As shown results of Table 2, the BET surface area of the as-received ACF was 1842 m²/g. It can be clearly seen that the specific surface area was decreased by treated with TiO₂. This result is thought that the decrease is due to the blocking of the micro-

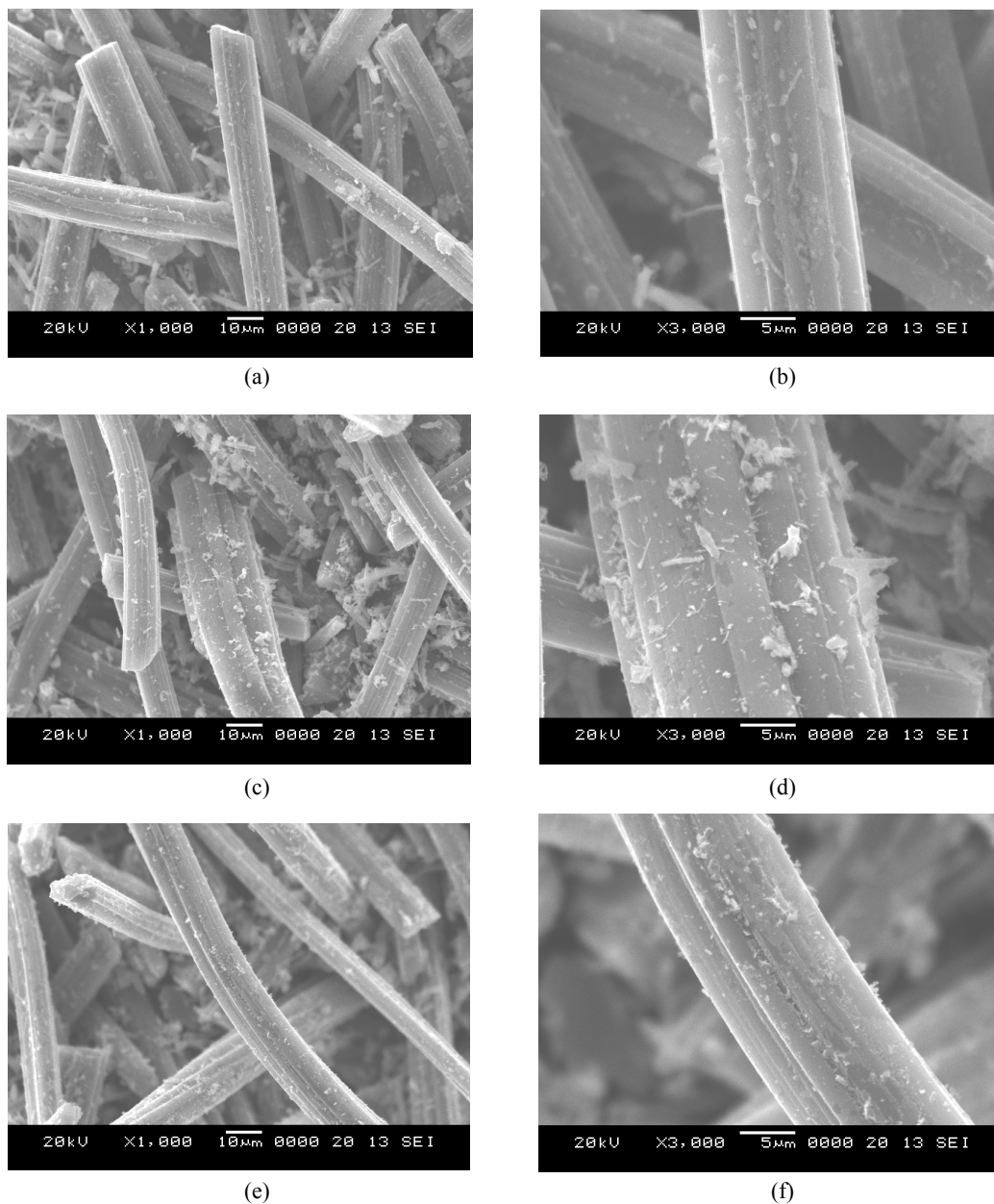


Figure 1. SEM images of ACF/TiO₂ and Fe-ACF/TiO₂ composites: F₁AT: (a)×1000, (b)×3000; F₂AT: (c)×1000, (d)×3000 and F₃AT: (e) ×1000, (f)×3000.

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

Sample	S _{BET} (m ² /g)
Pristine ACF	1842
F ₀ AT	1268
F ₁ AT	1047
F ₂ AT	960
F ₃ AT	1012

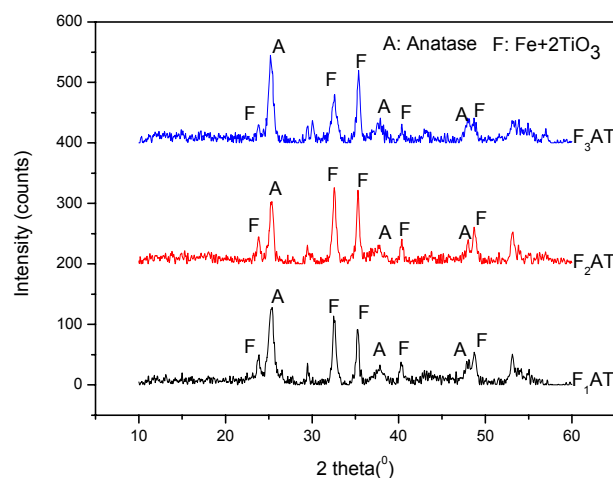
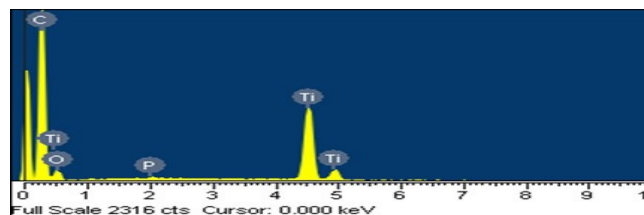
pores by surface complexes introduced through the formation of the ACF/TiO₂ composites. Especially, the variation of surface parameters for Fe-ACF/TiO₂ composites was probably caused by the TiO₂ and Fe compounds. The similar phenomena had also been observed in the references.³³⁻³⁴

The SEM images of Fe-ACF/TiO₂ composites are shown in Figure 1. It shows that TiO₂ particles uniformly covered the surface of ACF, which was beneficial for the photocatalytic reaction because the photocatalytic reaction is carried out on the external surfaces of the TiO₂/ACF composites catalysts by existing reactants using UV light and the nano-size structured catalyst could provide a more effective surface for MB adsorption and UV light absorption.³⁵ In the comparison with different precursors of Fe in all samples, there was no significant difference. In previous studies,³⁶⁻⁴¹ a nitric acid treated on AC/TiO₂ composites enhanced the homogenous and uniform distribution of TiO₂ particles. It was considered that Fe-ACF/TiO₂ composites could have much more activity because the TiO₂ particles were mixed well with the ACF. We could not find out the Fe particle in SEM imagines of Fe-ACF/TiO₂ composites, due to the small size of Fe particle. But it was confirmed in XRD and EDX results.

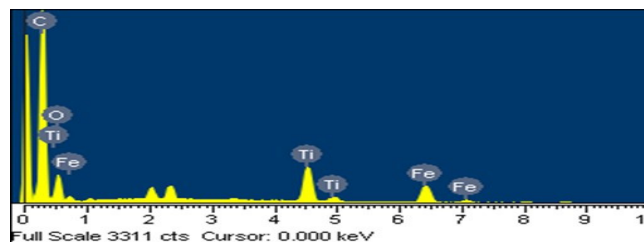
2. The composition of ACF/TiO₂ and Fe-ACF/TiO₂

According to the former studies,^{38,42} it is well known that the crystal structure of the TiO₂ is mainly determined by the heat treatment temperature. Figure 2 depicts XRD patterns of Fe-ACF/TiO₂ composites prepared at 927 K for 1 h. The peaks at 25.3, 37.8, 48.0, 53.8, 54.9 and 62.5° are the diffractions of (101), (004), (200), (105), (211) and (204) planes of anatase. There are no peaks found at 27.4, 36.1, 41.2 and 54.3° that belong to the diffraction peaks of (110), (101), (111) and (211) of rutile. It indicated that the developed Fe-ACF/TiO₂ composites only existed in anatase state. According to the former studies,^{38,41} Pure anatase nanocrystallites can provide higher photocatalytic activity.

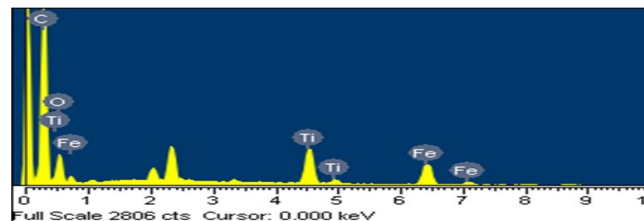
Figure 3 showed the results of the EDX for Fe-ACF/TiO₂ and ACF/TiO₂. These spectra show the presence of the C, O and Ti elements. TiO₂ particles show a peak around 0.2

**Figure 2.** XRD patterns of powdered Fe-ACF/TiO₂ composites (F₁AT, F₂AT and F₃AT).

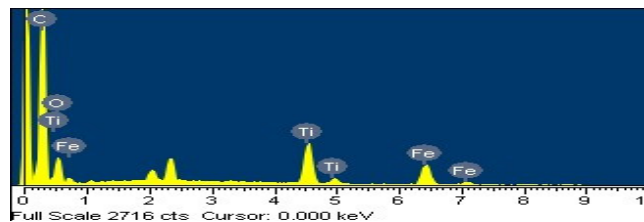
(a)



(b)



(c)

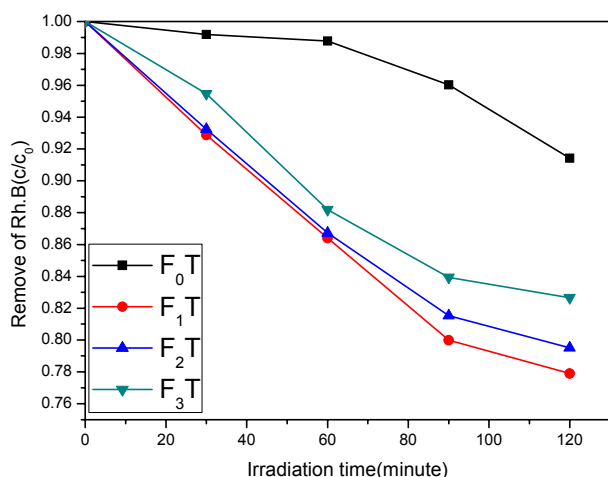


(d)

Figure 3. EDX elemental microanalysis of ACF/TiO₂ and Fe-ACF/TiO₂ composites: (a) F₀AT, (b) F₁AT (c) F₂AT and (d) F₃AT.

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

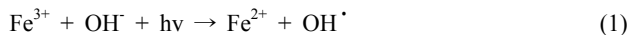
Samples	Elements (wt.%)			
	C	O	Ti	Fe
F ₀ AT	65.5	15.4	18.9	0
F ₁ AT	61.85	22.89	7.98	7.27
F ₂ AT	59.32	23.96	7.47	9.25
F ₃ AT	59.73	23.50	8.53	8.24

**Figure 4.** Remove of Rh.B in the aqueous solution on UV irradiation time for the ACF/TiO₂ (F₀AT) and Fe-ACF/TiO₂ (F₁AT, F₂AT and F₃AT) composites.

keV and another intense peak appears at 4.5 keV. The intense peak is assigned to TiO₂ in the bulk form and the less intense peak is assigned to TiO₂ surface.⁴³ The peaks due to Fe were clearly distinct in Fe-ACF/TiO₂ at 7.1 and 6.4 keV. Because of coating by Au for preparation of EDX images, some peaks appeared around 9.6 keV were omitted. Elemental composition analyses of the composite series were listed in Table 3.

3. Photocatalysis activity

Figure 4 showed remove of Rh.B in the aqueous solution on UV irradiation time for ACF/TiO₂ and Fe-ACF/TiO₂ composites. As the results of Figure 4, the Rh.B degradation efficiency was increased distinctly due to appearance of Fe. It is noteworthy that the Fe modified ACF-TiO₂ enhances the photocatalytic activity greatly via photo-Fenton reaction. This reaction could be showed in following equation:

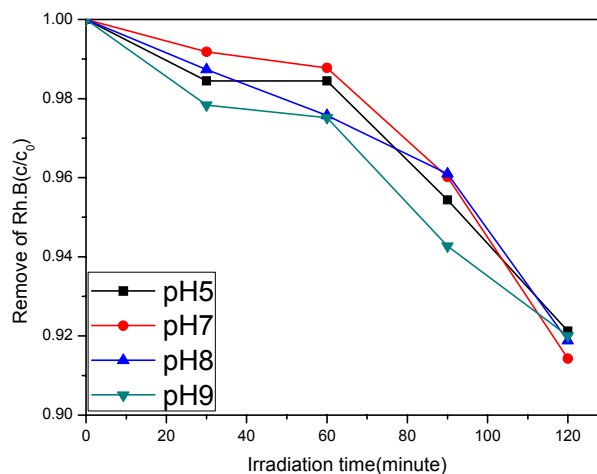


As above mentioned, the reduction of Fe³⁺ to Fe²⁺ in OH⁻

solution under UV light gave rise of OH[•] radicals. However, the one-step reaction has limitations, because recuperation of Fe³⁺ is slow and difficult due to pH below 7 in reaction solution after using photocatalysts degradation.⁴⁴⁻⁴⁵ Therefore, for the photocatalytic activity of three Fe-ACF/TiO₂ composites, this was directly affected by an amount of Fe³⁺ in initial synthesized Fe-ACF/TiO₂ composites.

To evaluate the actual photocatalytic activity of the Fe-ACF/TiO₂ photocatalysts, comparison of different Fe-ACF/TiO₂ photocatalysts prepared, the preparation of Fe-ACF/TiO₂ composites using FeCl₃ · 6H₂O has been found to be more photoactive than that of Fe(NO₃)₃ · 9H₂O and Fe₂(SO₄)₃ · 9H₂O. It can be attributed to that a higher amount of Fe³⁺ was formed during the preparation of Fe-ACF/TiO₂. Generally, the formation of Fe-ACF composites can be inhibited by inorganic acid ions in different degree, which can be attributed to a decrease of an effective combination of Fe and ACF because of the formation of more reactive Fe³⁺ complexes with anions during the preparation of Fe-ACF. According to the former studies,⁴⁶⁻⁴⁷ sulfonamides undergo photocatalytic degradation in processes conducted in the presence of Fe³⁺ salts. The highest catalytic activity was provided by FeCl₃ due to formation of more reactive inorganic radicals, while among the heterogeneous catalysts. This fact was also confirmed by the results of our experiments, which is particularly clear for Cl⁻.

Remove of Rh.B in the aqueous solution on UV irradiation time for F₀AT composites under various pH are showed in Figure 5. The results indicated that the photocatalytic activity of ACF/TiO₂ is unchanged in different pH conditions. It was considered that the beneficial electron transfer had been occurred on ACF and/or Fe.²⁸ And TiO₂ surface is not positively or negatively charged in different pH conditions. It can be attributed to that the adsorption capability of TiO₂ is neglected in the presence of ACF.

**Figure 5.** Remove of Rh.B in the aqueous solution on UV irradiation time for F₀AT composites under varying pH.

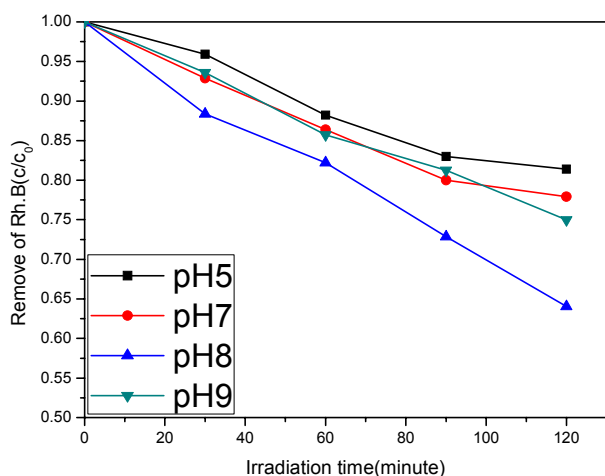
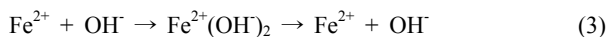


Figure 6. Remove of Rh.B in the aqueous solution on UV irradiation time for F₁AT composites under varying pH.

Remove of Rh.B in the aqueous solution on UV irradiation time for F₁AT composites under various pH are showed in Figure 6. The results indicated that the degradation rate is highest at pH 8. It can be explained that Fe²⁺ is rapidly oxidized to Fe³⁺ under a mild alkaline condition. And ion complex Fe²⁺(OH)₂ formed can be completely hydrolyzed under a mild alkaline condition, according to the following reactions:



Therefore, the photo-Fenton reduction of Fe³⁺ to Fe²⁺ was accelerated by the powerful oxidation of Fe²⁺ at pH 8. However, when the pH value of reaction solution is up to 9, on the contrary, the degradation rate of Rh.B is decreased with the increase of alkaline. The explanation of this phenomenon can be that the hydrolysis balance of ion complex Fe²⁺(OH)₂ is destroyed under an over-based condition. These precipitated ion complexes Fe²⁺(OH)₂ are detrimental for the oxidation of Fe²⁺, thus the photocatalytic activity of the Fe-ACF/TiO₂ is decreased. In addition, degradation rate of Rh.B proceed much slower under an acidic condition. The phenomenon can be explained that the ion complex Fe³⁺(OH)₃ is deposited in lower pH. Gel of Fe³⁺ is not reduced to Fe²⁺ and OH[•] radicals is not formed via photo-Fenton reaction.

IV. Conclusion

In this study, we present the fabrication of Fe-ACF/TiO₂ composites using different Fe precursors and characterization of these composites. The effect of degradation for Rh.B dyes was also studied. The BET data showed that the composite

had decreased surface area compared with the pristine ACF. XRD data revealed that the structure for the Fe-ACF/TiO₂ composite showed a single anatase phase. The SEM microphotographs of Fe-ACF/TiO₂ composite showed that TiO₂ particles were fine fixed on the surface of the ACF, and the distribution was uniform. From the EDX data, the main elements such as C, O, Ti and Fe were existed. The Fe-ACF/TiO₂ could enhance its photoactivity for decomposition of Rh.B under the condition of UV due to production of photo-Fenton reaction via compared with the composites without Fe modification. And fabrication of Fe-ACF/TiO₂ composites using FeCl₃ · 6H₂O solution as Fe precursors can provide higher photo-Fenton reaction than that of Fe(NO₃)₃ · 9H₂O and Fe₂(SO₄)₃ · 9H₂O. And the Fe-ACF/TiO₂ composites can display a higher photocatalytic activity at pH 8.

References

1. J. H. Braun, A. Baidins, and R. E. Marganski, "TiO₂ pigment technology: a review", *Prog. Org. Coat.*, **20**, 105 (1992).
2. N. Dubey, N. K. Labhsetwar, S. S. Rayalu, and S. Devotta, "Hydrogen evolution by water splitting using novel composite zeolite-based photocatalyst", *Catal. Today.*, **129**, 428 (2007).
3. C. A. Linkous, G. J. Carter, D. B. Locuson, A. J. Ouellette, D. K. Slattery, and L. A. Smitha, "Photocatalytic Inhibition of Algae Growth Using TiO₂, WO₃, and Cocatalyst Modifications", *Environ. Sci. Technol.*, **34**, 4754 (2000).
4. M. R. Hoffmann, S. T. Martin, W. Y. Choi, and D. W. Bahnemann, "Environmental applications of semiconductor photocatalysis", *Chem. Rev.*, **95**, 69 (1995).
5. A. L. Linsebigler, G. Q. Lu, and J. T. Yates, "Photocatalysis on TiO₂ surfaces: principles, mechanisms, and selected results", *Chem. Rev.*, **95**, 735 (1995).
6. N. Negishi, T. Iyoda, K. Hashimoto, and A. Fujishima, "Preparation of transparent TiO₂ thin-film photocatalyst and its photocatalytic activity", *Chem. Lett.*, **24**, 841 (1995).
7. I. Sopyan, M. Watanabe, and S. Murasawa, "Efficient TiO₂ powder and film photocatalysts with rutile crystal structure", *Chem. Lett.*, **1**, 69 (1996).
8. T. Torimoto, S. Ito, S. Kuwabata, and H. Yoneyama, "Effects of Adsorbents Used as Supports for Titanium Dioxide Loading on Photocatalytic Degradation of Propylamide", *Environ. Sci. Technol.*, **30**, 1275 (1996).
9. W. Choi, A. Termin, and M. Hoffmann, "The Role of Metal-Ion Dopants in Quantum-Sized TiO₂: Correlation between Photoreactivity and Charge-Carrier Recombination Dynamics", *J. Phys. Chem.*, **98**, 13669 (1994).
10. W. Shockley and W. T. Read, "Statistics of the Recombinations of Holes and Electrons", *J. Phys. Rev.*, **87**, 835 (1952).
11. A.sahi,T.Morikawa, T. Ohwaki, K. Aoki, and Y. Taga, "Visible-Light Photocatalysis in Nitrogen-Doped Titanium Oxides", *Science*, **293**, 269 (2001).
12. V. Vamathevan, H. Tse, R. Amal, G. Low, and S. McEvoy,

- “Effects of Fe^{3+} and Ag^+ ions on the photocatalytic degradation of sucrose in water”, *Catal. Today.*, **68**, 201 (2001).
13. C. Huang, W. P. Hsieh, J. R. Pan, and S. M. Changa, “Characteristic of an innovative TiO_2/Fe^0 composite for treatment of azo dye”, *Sep. Purif. Technol.*, **58**, 152 (2007).
 14. T. K. Ghorai, S. K. Biswas, and P. Pramanik, “Photooxidation of different organic dyes (RB, MO, TB, and BG) using Fe(III) -doped TiO_2 nanophotocatalyst prepared by novel chemical method”, *Appl. Surf. Sci.*, **254**, 7498 (2008).
 15. M. Pera-Titus, V. Garc'ia-Molina, M. A. Baños, J. Giménez, and S. Esplugas, “Degradation of chlorophenols by means of advanced oxidation processes: a general review”, *Appl Catal B: Environ.*, **47**, 219 (2004).
 16. M. Neamtu, A. Yediler, I. Siminiceanu, and A. Ketrup, “Oxidation of commercial reactive azo dye aqueous solutions by the photo-Fenton and Fenton-like processes”, *J. Photochem. and Photobio. A: Chem.*, **161**, 87 (2003).
 17. M. I. Franch, J. A. Ayllón, J. Peral, and X. Doménech, “ Fe(III) photocatalyzed degradation of low chain carboxylic acids implications of the iron salt”, *Appl. Catal. B: Environ.*, **50**, 89 (2004).
 18. H. Fallmann, T. Krutzler, R. Bauer, S. Malato, and J. Blanco, “Applicability of the Photo-Fenton method for treating water containing pesticides”, *Catal. Today.*, **54**, 309 (1999).
 19. R. Bauer, G. Waldner, H. Fallmann, S. Hager, M. Klare, T. Krutzler, S. Malato, and P. Maletzky, “The photo-fenton reaction and the TiO_2/UV process for waste water treatment novel developments”, *Catal. Today.*, **53**, 131 (1999).
 20. K. Zhang, Z. D. Meng, W. B. Ko, and W. C. Oh, “Fabrication of Fe-ACF/TiO_2 Composites and Their Photonic Activity for Organic Dye”, *Anal. Sci. Technol.*, **22**, 254 (2009).
 21. A. Ninh Phama, A. L. Rosea, A. J. Feitza and T. David Waite, “Kinetics of Fe(III) precipitation in aqueous solutions at pH 6.0-9.5 and 25 °C”, *Geochimica et Cosmochimica Acta.*, **70**, 640 (2006).
 22. J. Subrt, V. Stengl, and M. Skokánek, “Decomposition of ferrihydrite prepared from $\text{Fe(NO}_3)_3$ aqueous solutions under varying Ph”, *Thermochimica Acta.*, **211**, 107 (1992).
 23. E. Evgenidou, K. Fytianos, and I. Poullos, “Photocatalytic oxidation of dimethoate in aqueous solutions”, *J. Photochem. Photobiol. A: Chem.*, **175**, 29 (2005).
 24. A. Piscopo, D. Robert and J.V. Weber, “Influence of pH and chloride anion on the photocatalytic degradation of organic compounds: Part I. Effect on the benzamide and para-hydroxybenzoic acid in TiO_2 aqueous solution”, *Appl. Catal. B: Environ.*, **35**, 117 (2001).
 25. X. Zhu, C. Yuan, Y. Bao, J. Yang, and Y. Wu, “Photocatalytic degradation of pesticide pyridaben on TiO_2 particles”, *J. Mol. Catal. A.*, **229**, 95 (2005).
 26. H. S. Son, G. Ko, and K. D. Zoh, “Kinetics and mechanism of photolysis and TiO_2 photocatalysis of triclosan”, *J. Hazard. Mater.*, **166**, 954 (2009).
 27. C. S. Lu, C. C. Chen, F. D. Mai, and H. K. Li, “Identification of the degradation pathways of alkanolamines with TiO_2 photocatalysis”, *J. Hazard. Mater.*, **165**, 306 (2009).
 28. W. C. Oh, F. J. Zhang, M. L. Chen, Y. M. Lee, and W. B. Ko, “Characterization and relative photonic efficiencies of a new Fe-ACF/TiO_2 composite photocatalysts designed for organic dye decomposition”, *J. Indust. Engin. Chem.*, **15**, 190 (2009).
 29. W. C. Oh and M. L. Chen, “Electrochemical Preparation of TiO_2/ACF Composites With TNB Electrolyte and Their Photocatalytic Effect”, *J. Ceram. Process. Res.*, **9**, 100 (2008).
 30. F. SuarezGarca, A. Martnez-Alonso, and J. M.D. Tascon, “Activated carbon fibers from Nomex by chemical activation with phosphoric acid”, *Carbon.*, **42**, 1419 (2004)
 31. Z. H. Huang, F. Y. Kang, W. L. Huang, J. B. Yang, K. M. Liang, M. L. Cui, and Z. Y. Cheng, “Pore structure and fractal characteristics of activated carbon fibers characterized by using HRTEM”, *J. Colloid Interface Sci.*, **249**, 453 (2002).
 32. Y. G. Go, F. J. Zhang, M. L. Chen, and W. C. Oh, “Fabrication of Zn-treated ACF/TiO_2 Composites and Their Photocatalytic Activity for Degradation of Methylene Blue”, *J. Mater. Res.*, **19**, 142 (2009).
 33. F. J. Zhang, M.L. Chen, and W.C. Oh, “Synthesis and Characterization of CNT/ TiO_2 Photoelectrocatalytic Electrodes for Methylene Blue Degradation”, *Kor. J. Mater. Res.*, **doi: 10.3740/MRSK.2008.18.9.000**.
 34. W. D. Wang, P. Serp, P. Kalck, and J. L. Faria, “Visible Light Photodegradation of Phenol on MWNT- TiO_2 Composite Catalysts Prepared by a Modified Sol-Gel Method”, *J. Mole. Catal.A: Chem.*, **235**, 194 (2005).
 35. M. L. Chen, C. S Lim, and W. C. Oh, “Photocatalytic Effect For TiO_2/ACF Composite Electrochemically Prepared With TNB Electrolyte”, *Carbon lett.*, **8**, 177 (2007).
 36. W. C. Oh and M. L. Chen, “Formation of TiO_2 composites on activated carbon modified by nitric acid and their photocatalytic activity”, *J. Ceram. Proc. Res.*, **8**, 316 (2007).
 37. W. C. Oh, S. B. Han, and J.S. Bae, “Preparation of Fullerene/ TiO_2 Composite and Its Photocatalytic Effect”, *Anal. Sci. Technol.*, **20**, 279 (2007).
 38. M. L. Chen, J. S. Bae, and W.C. Oh, “Preparation of Carbon-Coated TiO_2 at Different Heat treatment Temperatures and Their Photocatalytic”, *Carbon. Sci.*, **7**, 259 (2006).
 39. M. L. Chen, J. S. Bae, and W.C. Oh, “Characterization of AC/TiO_2 Composite Prepared with Pitch Binder and Their Photocatalytic Activity”, *Bull. Kor. Chem. Soc.*, **27**, 1423 (2006).
 40. M. L. Chen, J. S. Bae, Y.S. Ko, and W.C. Oh, “Characterization of composite prepared with different mixing ratios of TiO_2 to activated carbpn and their photocatalytic activity”, *Anal. Sci. Technol.*, **19**, 376 (2006).
 41. M. L. Chen, J. S. Bae, and W.C. Oh, “Photocatalytic effect for the pith-coated TiO_2 ”, *Anal. Sci. Technol.*, **19**, 301 (2006).
 42. M. Inagaki, Y. Hirose, T. Matsunage, T. Tsumura, and M. Toyoda, “Carbon coating of anatase-type TiO_2 through their

- precipitation in PVA aqueous solution”, *Carbon.*, **41**, 2619 (2003).
43. K. Nagaveni, M.S. Hedge, and G. Madras, “Structure and Photocatalytic Activity of Ti_{1-x}M_xO_{2±δ} (M = W, V, Ce, Zr, Fe, and Cu) Synthesized by Solution Combustion Method”, *J. Phys. Chem. B.*, **108**, 20204 (2004).
 44. C. Guillard, H. Lachheb, A. Houas, M. Ksibi, E. Elaloui, and J.M. Herrmann, “Influence of chemical structure of dyes, of pH and of inorganic salts on their photocatalytic degradation by TiO₂ comparison of the efficiency of powder and supported TiO₂”, *J. Photochem and Photobio A: Chem.*, **158**, 27 (2003).
 45. M. Carrier, N. Perol, J.M. Herrmann, C. Bordes, S. Horikoshi, J.O. Paise, R. Baudot, and C. Guillard, “Kinetics and reactional pathway of Imazapyr photocatalytic degradation Influence of pH and metallic ions”, *Appl. Cata.B: Environ.*, **65**, 11 (2006).
 46. W. Baran, E. Adamek, A. Sobczak, and A. Makowski, “Photocatalytic degradation of sulfa drugs with TiO₂, Fe salts and TiO₂/FeCl₃ in aquatic environment-Kinetics and degradation pathway”, *Appl. Catal. B: Environ.*, **90**, 516 (2009).
 47. W. Baran, E. Adamek, A. Sobczak, and J. Sochacka, “The comparison of photocatalytic activity of Fe-salts, TiO₂ and TiO₂/FeCl₃ during the sulfanilamide degradation process” *Catal. Communications.*, **10**, 811 (2009).