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Effect of Fe Contents in Fe-AC/TiO_2 Composites on Photodegradation Behaviors of Methylene Blue

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ABSTRACT

Activated carbon/TiO_2 (AC/TiO_2) composites modified with different concentrations of Fe were prepared. The N_2 adsorption data showed that the composites had decreased surface area compared with the pristine activated carbon. This indicated the blocking of the micropores on the surface of AC, which was further supported by observation via SEM. XRD results showed patterns for the composites and an anatase typed titanium dioxide structure with a small part of rutile in a higher Fe concentration (>1.0 mol/L). EDX results showed the presence of C and, O, with Ti peaks on the composites of Fe-AC/TiO_2 with relatively lower Ti concentration, which may be due to the higher Fe concentration incorporated into the composites. Subsequently, the photocatalytic effects on methylene blue (MB) were investigated. The improved decomposition of MB showed the combined effects of adsorptions and photodegradation. Especially, the composites modified by Fe revealed enhanced photodegradation behaviors of MB.

Key words*: *Activated carbon, Titanium dioxide, SEM, EDX, XRD, Photodegradation

1. Introduction

In last decades, the decomposition of environmental pollutants using TiO_2 photo catalysts has been studied widely due to their excellent photocatalytic activity. Especially, in treating organic toxic compounds, which are generally difficult to decompose, TiO_2 shows great advantages other environmental technology.[1-3] For practical application, the TiO_2 power generally are mounted on porous materials or coated on the surface of supporting media, since bare TiO_2 has lower efficiency due to the molecule polarity polar on the TiO_2 surface which is unfavorable for contact with the non-polarity organics. At the same time, it is hard to recycle in actual wastewater treatment.[4-6] However, in general absorbable media, the decomposition of pollutants is limited mainly due to the slow diffusion into the surface of TiO_2 particles. According to former studies, composites of AC/TiO_2 showed advantages, such a high photocatalytic activity, photosensitivity and high adsorptive ability.[7-10] AC/TiO_2 composites are typically used to obtain the combined effects of the photoactivity of TiO_2 and the adsorption of carbons. Generally, it is considered that organic molecules could be adsorbed into the carbon layer, diffused into the surface to the surface of TiO_2, and decomposed under UV.[11-16] It is expected that these effects would be enhanced if the TiO_2 was well dispersed on the surface of AC. However, the penetration of TiO_2 in the pores of AC is limited when using general mechanical methods of immersion of AC in a TiO_2 solution through mechanical grinding of AC with TiO_2.[17] Recently, a method for the preparation of AC/TiO_2 composites involving the penetration of titanium n-butoxide (TNB) solution into AC was developed.[13] This method is expected to have some advantages compared with using liquid solvents for the coating process due to its high diffusivity, on-condensation and weak salvation properties. The concept is that the TNB could penetrate into micropore and mesopore structures of AC and become adsorbed in pores as TNB molecules. The absorbed TNB on the solid surface would then be converted to TiO_2 through thermal decomposition and hydrolysis. As another means of improving photocatalytic activity, reducing the recombination of holes and electrons by doping TiO_2 with transition metals has been proposed. It is generally assumed that a higher photoactivity for Fe-coated TiO_2 is possible in comparison with the undoped material, principally because Fe^{3+} can act as both holes and electrons shallow traps to enhance lifetimes of electrons and holes.[18,19]

In this study, we focused on the preparation of composites involving TiO_2 immobilized on Fe-AC. Then, the decomposition of pollutants from MB dye was investigated to explore photodegradation effects of the composites of Fe-AC/TiO_2. The main objectives of this study were as follows: (1) to investigate the possible unique characteristics of the Fe-AC/TiO_2 composites. (2) to determine the photocatalytic effects of the composites Fe-AC/TiO_2 on deposition of MB to find

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Table 1. The Simple Properties of the Pristine Titanium Dioxide used

Parameter	Crystal type	Primary Particle Size (μm)	Secondary particle size (μm)	BET surface area (m^2/g)
	Anatase	30-50	80-150	125

Table 2. Nomenclatures of Pristine Activated Carbon and Fe-AC/TiO$_2$ Composites Prepared with Different Concentrations of Ferric (III) Nitrate to Activated Carbon

Preparation method	Nomenclatures
Activated Carbon	AC
Activated Carbon+Non ($Fe(NO_3)_3$)+Titanium n-butoxide (99.99%)	ACT
Activated Carbon+0.5M $Fe(NO_3)_3$+Titanium n-butoxide (99.99%)	F05ACT
Activated Carbon+1.0M $Fe(NO_3)_3$+Titanium n-butoxide (99.99%)	F10ACT
Activated Carbon+1.5M $Fe(NO_3)_3$+Titanium n-butoxide (99.99%)	F15ACT

the potential factors concerning with materials themselves.

2. Experimental Procedures

2.1. Materials

A porous and granular AC used in this study was prepared from coconut. The coconut shell was pre-carbonized first at 773 K, and then activated by steam diluted with nitrogen in a cylindrical quartz tube at 1023 K for 30 min. This AC was washed with deionized water and dried overnight in a vacuum drier at over 683 K. For comparison, the commercially available TiO_2 photocatalyst are listed in Table 1. The anatase-type titanium dioxide powder had a relatively large BET surface area of 125 m^2/g and a diameter range of 30-50 μm. 5 g of activated carbon prepared as above were added to 100 ml of different concentrations of Fe $(NO_3)_3 \cdot 9H_2O$: 0.5, 1.0 and 1.5 mol/L, respectively. The $Fe(NO_3)_3 \cdot 9H_2O$ was supplied from Duksan Pure Chemical Co. (Korea). Then the mixture was stirred for 1 h, clarified and poured out of the super water. The sediments of Fe/AC were dried naturally at 378 K. 5 g powdered Fe/AC prepared above was mixed into 20 ml of titanium n-butoxide (TNB, $C_{16}H_{36}O_4Ti$, Acros Orgnis, USA) aqueous solution and stirred for 5 h at 333 K. Before heat treatment, the solvent in the mixtures were vaporized at 343 K for 1 h. Then the mixtures were heated at 973 K for 1 h. The nomenclatures of the samples prepared are listed in Table 2.

2.2. Characteristics and investigations of the samples

To characterize of Fe-AC/TiO$_2$, an N_2 adsorption isotherm was measured at 77 K using a BEL Sorp Analyzer (BEL, Japan). Then, the BET surface area was calculated by nitrogen adsorption. The pore size distribution was calculated by the BJH method. The morphology of the Fe-AC/TiO$_2$ composites was examined via a scanning electron microscope (SEM, JSM-5200, Japan). The crystalline phases were determined using X-ray diffraction (XRD) with Cu Kα radiation (Shimats XD-D1, Japan). For the elemental analysis of the TiO$_2$/AC composites, energy dispersive X-ray analysis (EDX) was also employed. Characterization of Methylene blue ($C_{16}H_{18}N_3S$, MB) in water was determined by the following procedure. An Fe-AC/TiO$_2$ powdered sample of 0.05 g was dispersed in an aqueous solution with a concentration of 1.0×10^{-5} mol/L in a dark atmosphere at room temperature. Each concentration was measured as a function of UV irradiation time from the absorbance in the range of 200-550 nm wavelength of MB, as measured by the UV/VIS spectrophotometer.

2.3. Photocatalytic activity

For MB, an initial concentration was set to about 10^{-5} mol/L. Then, each of the 0.5 g composite photocatalysts (as listed in table 2) was used to decompose MB. For UV irradiation, a UV lamp (20 W, 365 nm) was used at the distance of 100 mm from the solution in darkness box. After irradiation at 10 min, 30 min, 60 min, 120 min, and 200 min, the samples were examined to test the change of MB concentration to compare the different photocatalytic effects between the Fe-TiO$_2$/AC composites. Specifically, by sampling 3 mL of solution after removal of the dispersed powders using a centrifuge, the concentration of MB in the solution was determined as a function of irradiation time from the absorbance change at a wavelength of 660 nm.

3. Results and discussion

3.1. The surface characteristics

The Fe-AC/TiO$_2$ catalysts prepared with different concentration of Fe component were denoted as F05ACT, F10ACT and F15ACT. Nitrogen adsorption isotherms and pore size distributions for pristine AC and Fe-AC/TiO$_2$ are shown in Fig. 1 and Fig. 2. The formation of Type I adsorption isotherms confirmed mainly micropores on the surface of the pristine AC and Fe-AC/TiO$_2$. The BET surface area of the original AC was 1083 m^2/g, which decreased greatly to about 400 m^2/g when Fe-AC/TiO$_2$ composites were formed. These BET surface areas decreased gradually and slightly from 416.4 to 357.9 m^2/g. The results are summarized in Table 3. Accordingly, average pore size also decreased from 2.79 to 2.13 nm. From the pore size distribution results, the maximum peaks were formed around 0.7 nm for three kinds of samples of Fe-AC/TiO$_2$. In addition, it can be seen that there was little change in the micropore size distribution for

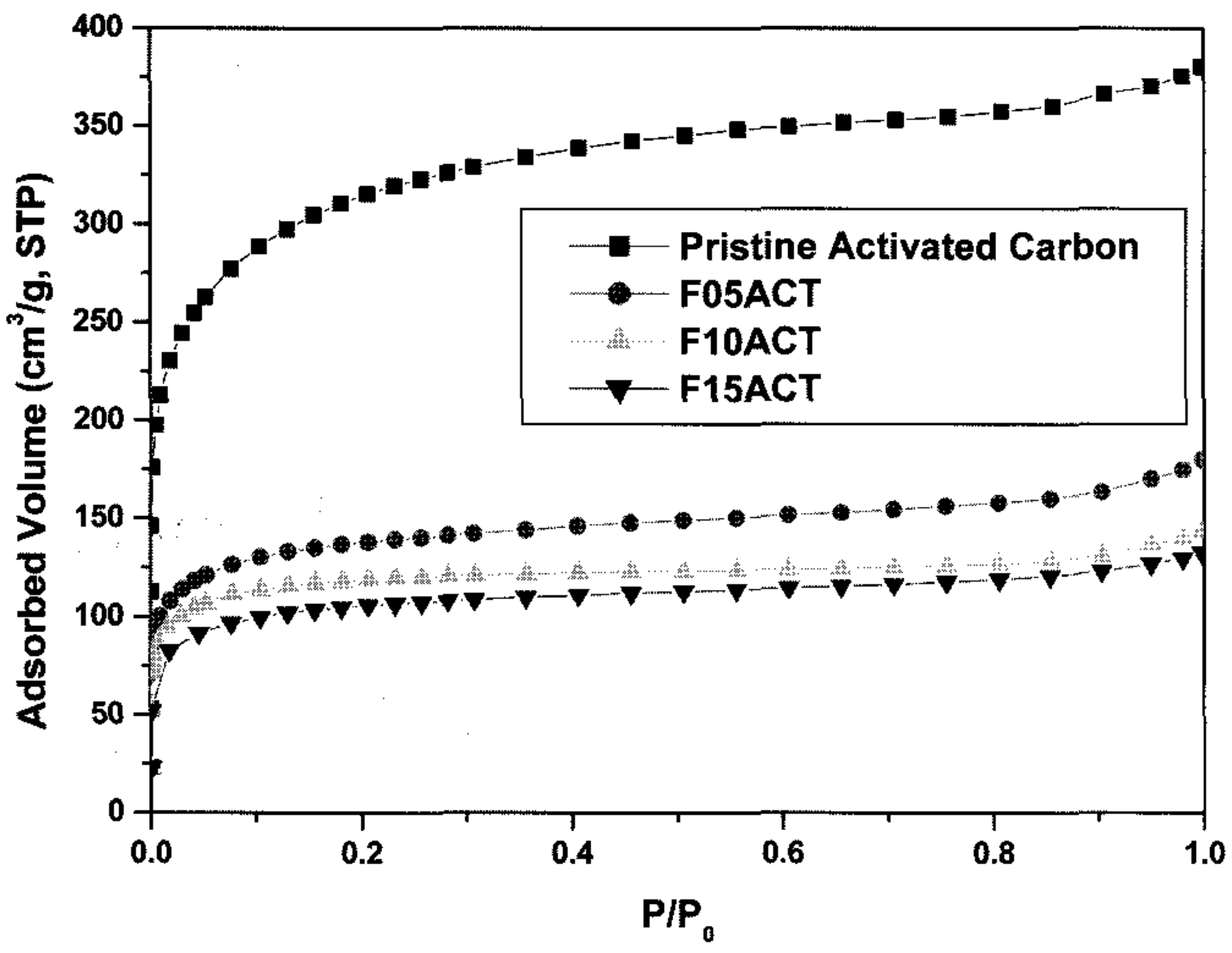


Fig. 1. Nitrogen adsorption isotherms obtained from the pristine activated carbon and powdered Fe-AC/TiO_2 composites.

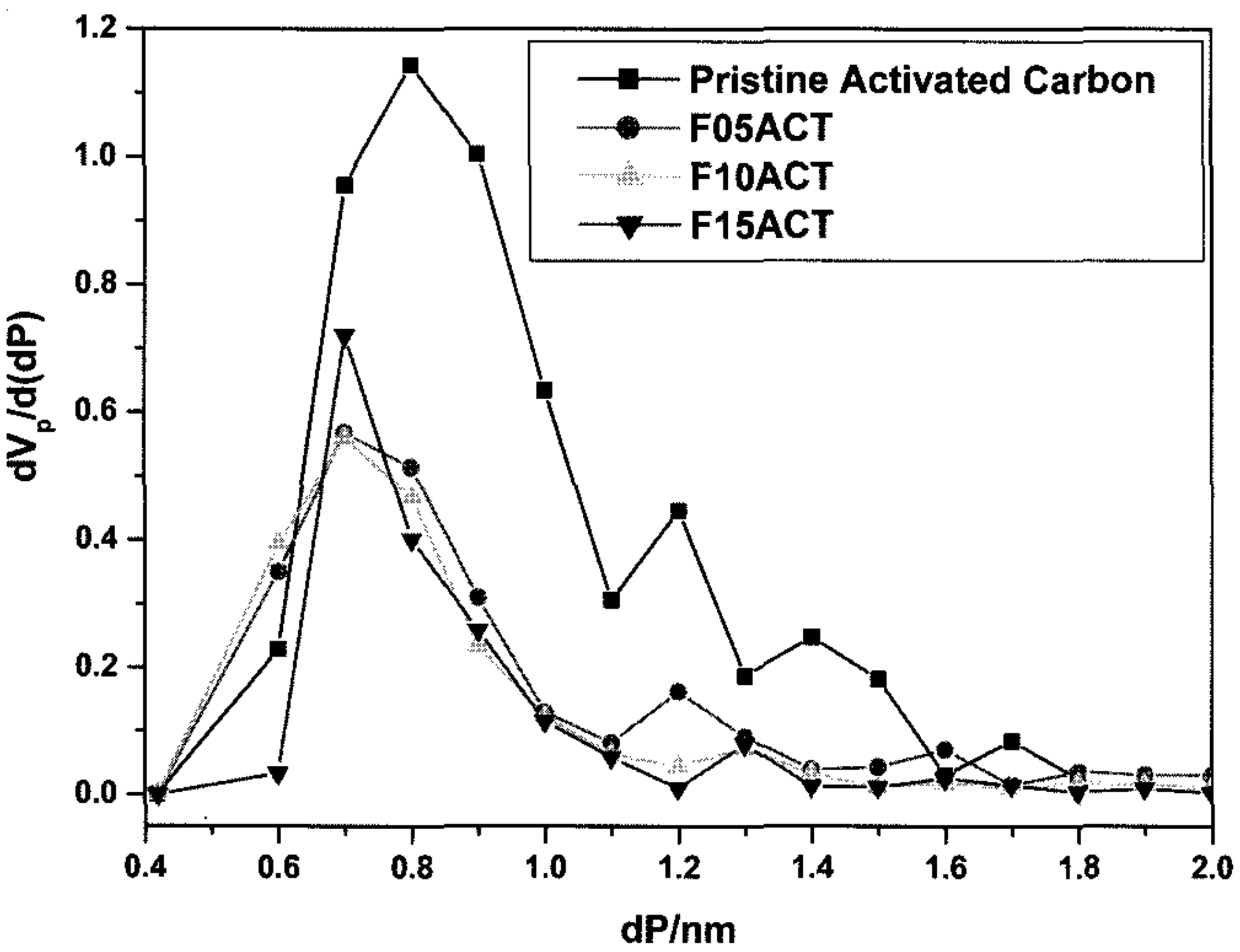


Fig. 2. Comparison of pore size distribution for the pristine activated carbon and Fe-AC/TiO_2 composites.

Table 3. Textural Properties of Pristine Materials and Fe-AC/TiO_2 Composite Samples

Sample	Parameter		
	S_{BET} (m^2/g)	Micropore Volume (cm^3/g)	Average Pore Diameter (nm)
As-received AC	1083	0.5665	2.79
F05ACT	416.4	0.2320	2.59
F10ACT	414.8	0.2127	2.14
F15ACT	357.9	0.1902	2.13

Table 4. EDX Elemental Microanalysis of Fe-AC/TiO_2 Composites

Sample (wt%)	C	O	Ti	Fe
F05ACT	65.7	26.1	7.54	0.63
F10ACT	62.2	26.1	9.79	1.90
F15ACT	61.2	26.7	9.10	2.78

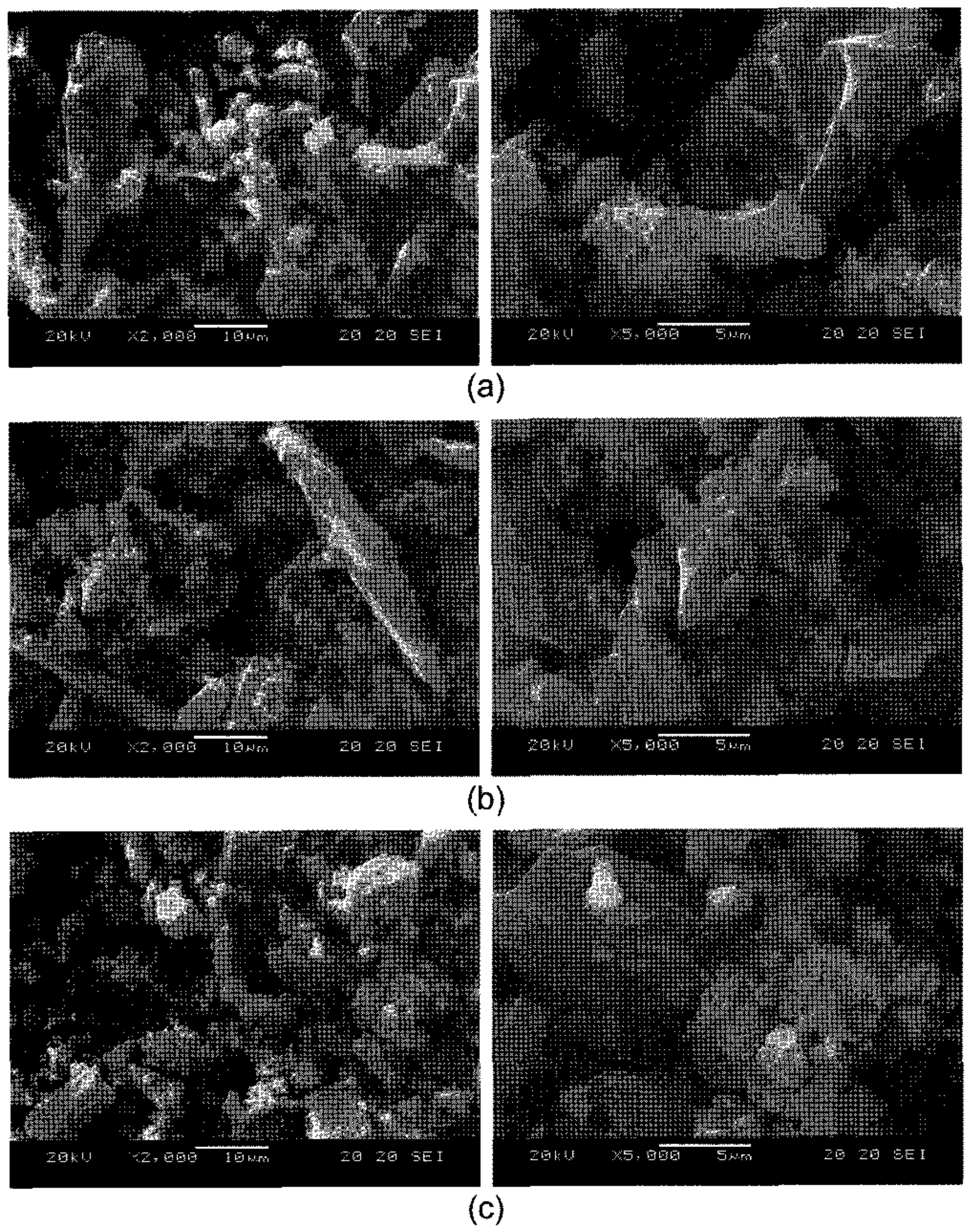


Fig. 3. SEM images obtained from powdered Fe-AC/TiO_2 composites: (a) F05ACT, (b) F10ACT, and (c) F15ACT.

Fe-AC/TiO_2 composites compared with that of corresponding AC. This result indicated that although the total surface area decreased after formation of TiO_2 particles by TNB treatment, these composites kept the normal pore structure of AC. Pristine AC showed relative wide pore size distributions. But, the Fe-AC/TiO_2 composites presented a very similar pore distribution.

Generally, the BET surface area is thought decrease due to the blocking of the micropores by surface complexes introduced through the formation of the AC/TiO_2 composites.[11] The BET surface area and pore volume to average pore diameters confirmed the formation of complexes on the surface of AC. The variation of surface parameters was probably caused by the TiO_2 and Fe compounds.

SEM imagines of pristine AC and Fe-AC/TiO_2 catalysts are shown in Fig. 3. From Fig. 3, we can observe that the TiO_2 particles are fine and agglomerated on the surface of AC, but are not uniform. Especially, the attachment to the pores of AC can be observed, which was consistent with the N_2 adsorption experiment. Compared with different concentrations of Fe in AC, there was no significant difference. Generally, it is considered that good particle dispersions can produce high photocatalytic activity. In previous studies,[14] a nitric acid treatment on AC/TiO_2 composites enhanced the homogenous and uniform distribution of TiO_2 particles.

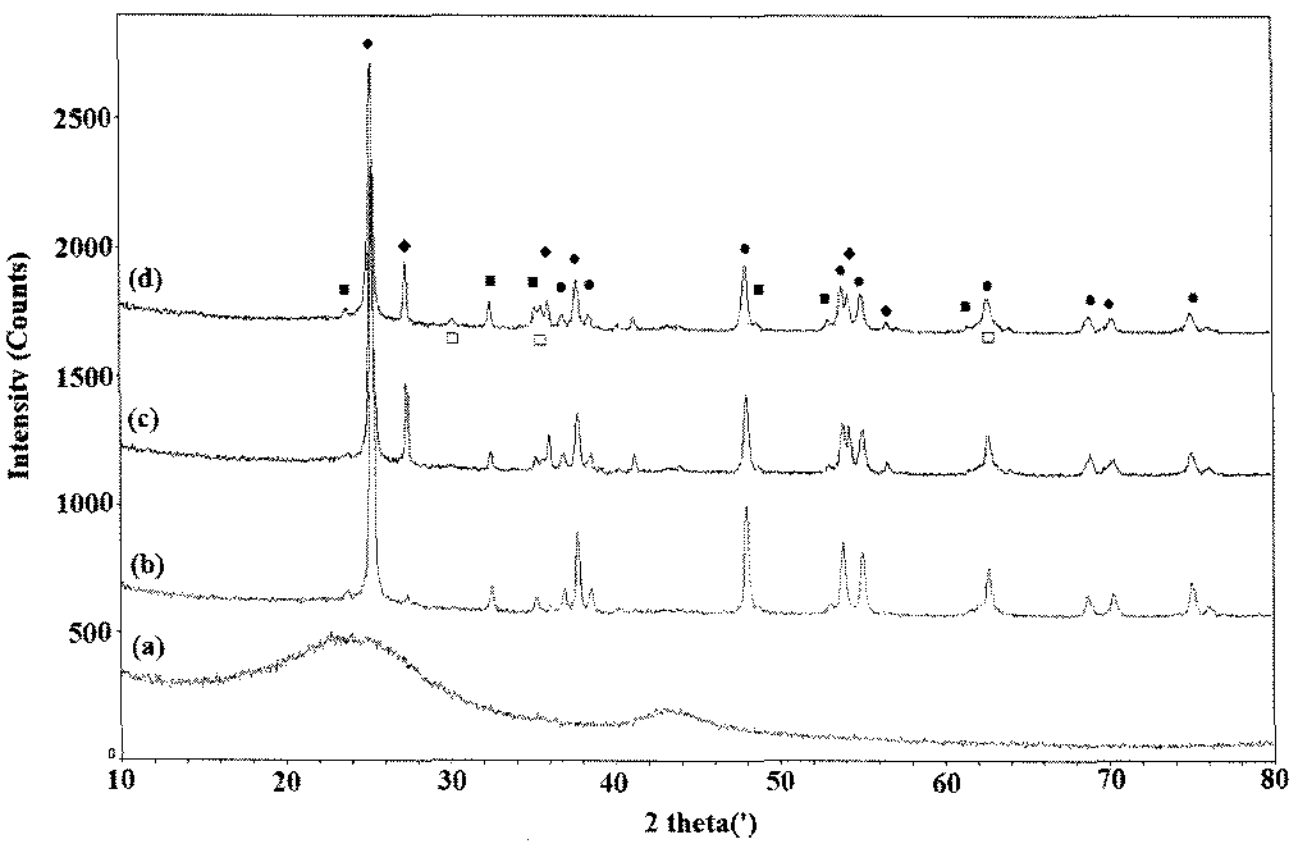
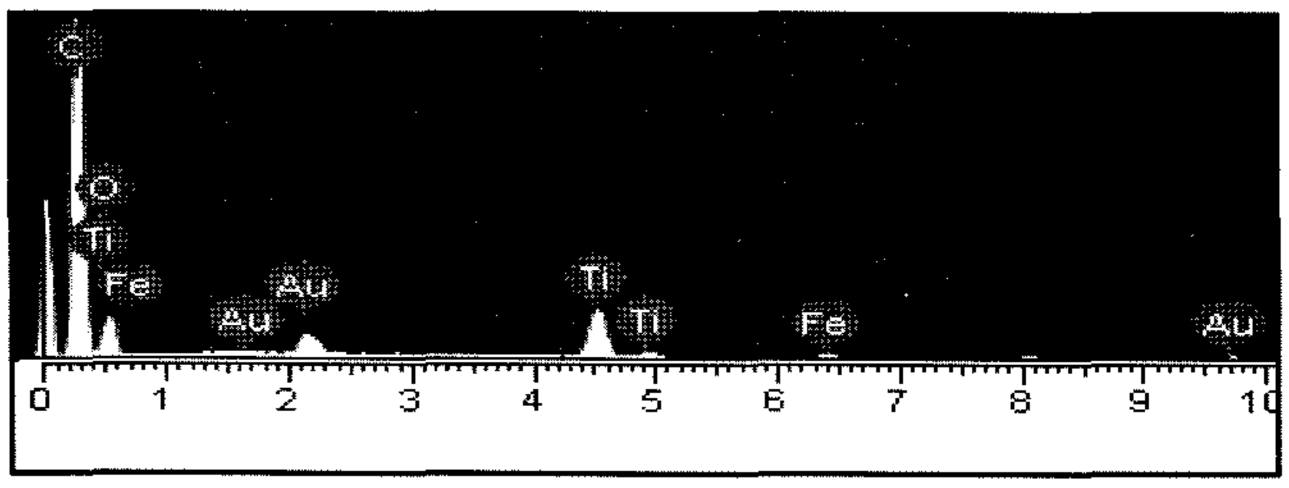
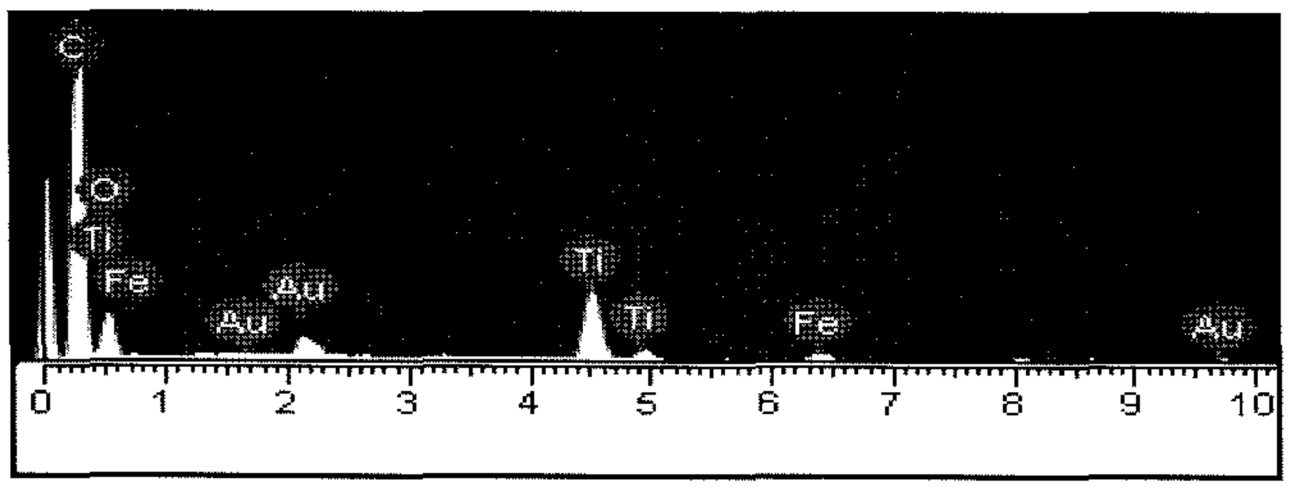


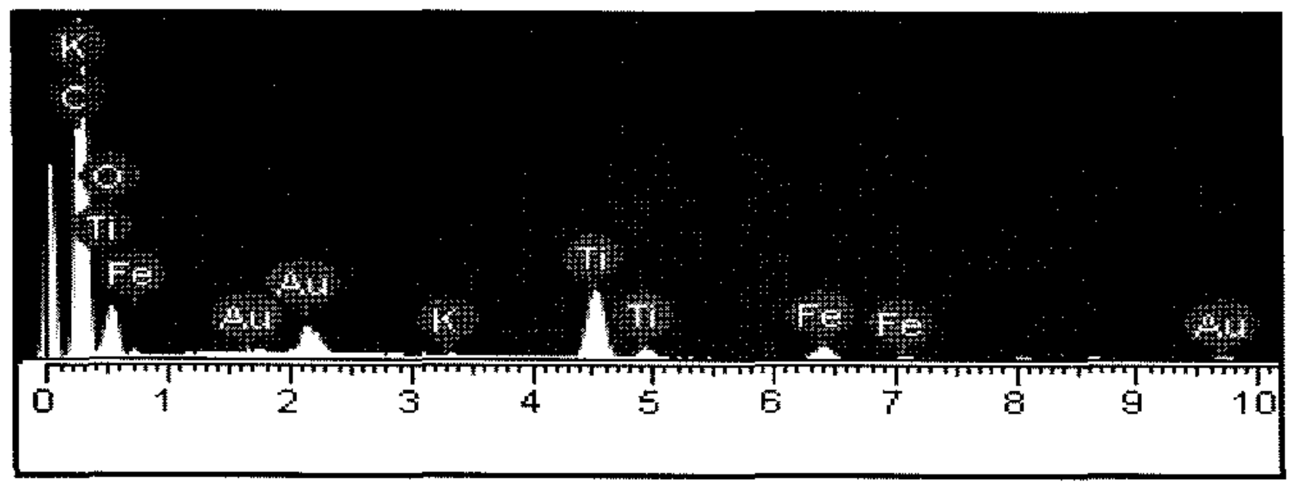
Fig. 4. XRD patterns of the pristine activated carbon and powdered Fe-AC/TiO_2 composites: (a) pristine activated carbon, (b) F05ACT, (c) F10ACT, and (d) F15ACT. (■ : Fe+2TiO_3, ● : Anatase, ◆ : Rutile and □ : Fe_2O_3).



(a)



(b)



(c)

Fig. 5. Typical EDX microanalyses for the Fe-AC/TiO_2 composites: (a) F05ACT, (b) F10ACT, and (c) F15ACT.

3.2. The composition of TiO_2/AC composites

The XRD results (Fig. 4.) indicate that the phase transition from TNB to dominantly anatase takes place at 973 K, which is in accordance with previous studies.[18] Meanwhile, there were small peaks of rutile in F10ACT and F15ACT, which have relatively higher Fe concentrations than that of F05ACT. This result indicated that the high concentration of Fe incorporated into the composites influences the structure of the crystal phases. Therefore, the amount of Fe dropped into the composites has to be considered thoughtfully. In addition, there were Fe+2TiO_3 composites in all Fe-AC/TiO_2, which may be important for the functions of photoactivity.

Actually, $FeTiO_3$, with a band gap of 2.58-2.9 eV, has been used as a chemical catalyst and photocatalyst. It was observed that under UV irradiation the TiO_2-Fe_3O_4 mixed oxide coatings exhibited higher photocatalytic efficiency than the naked TiO_2 due to the formation of $FeTiO_3$, which may form a p-n junction with TiO_2, and may induce the spatial separation of the photogenerated electrons and holes. It has been suggested that the $FeTiO_3$ formation can extend the absorption wavelength to the visible region and thereby enhance the photocatalytic activity in the TiO_2-Fe_3O_4 mixed oxides. The detailed role of $FeTiO_3$ was further investigated to show excellent photocatalytic activity.[19]

Fig. 5 shows the results of the EDX. The spectra show the presence of C, O and Fe with Ti peaks. Table 4 summarizes the specific element contents in the Fe-AC/TiO_2 composites. As expected, the Fe element contents in the composites increased with the addition of a high amount of Fe $(NO_3)_3$. However, the Ti contents were some lower than expected, indicating the relatively smaller TiO_2 particles in the composites. In a previous study,[14] the content of Ti was higher than in this study, around 18% versus 10% in this study. This might be due to the influence of Fe elements, since the contents of Fe were very strong in the composites. Whether this influence was present needs further investigation. In another respect, the oxidants of Fe could form, according a study characterizing Fe species incorporated into TiO_2 particles with defferent high Fe concentrations.[20]

3.3. The decomposition of pollutants

Fig. 6 shows the UV/VIS spectra of MB degradation as a function of radiation time. MB treated only by AC (Fig. 6(a)) has a rather wide band of absorption peaks, from 250 nm to 330 nm, which indicated the variability of structures and groups in MB molecules. At the same time the absorbance of MB gradually decrease along with the time, which shows the absorption effect of AC on MB molecules. However, MB treated with the composites of AC/TiO_2 (Fig. 6(b)) shows a completely different result as compared with that treated by AC. There is only a sharp absorption peak at around 250 nm. This actually indicated that the decomposition product of MB by the composites of AC/TiO_2 has a single and homogenous structure. Around 120 min, it reaches a stable state. The other figures show the decomposition of MB by the composites of Fe-AC/TiO_2 (Figs. 6(c)-(e)) with different concentration of Fe, respectively. These spectra differed from that of the AC/TiO_2 composites. Becides the peak at 250 nm, there was another small peak around 330 nm for an Fe concentration of 0.5 mol/L and 1.0 mol/L Fe ((b) and (c)), while no peaks were observed with a 1.5 mol/L Fe addition (e). The difference structures of degradation products of MB probably showed the photocatalytic selection of individual composites. Fig. 7 shows a comparison of phothocata-

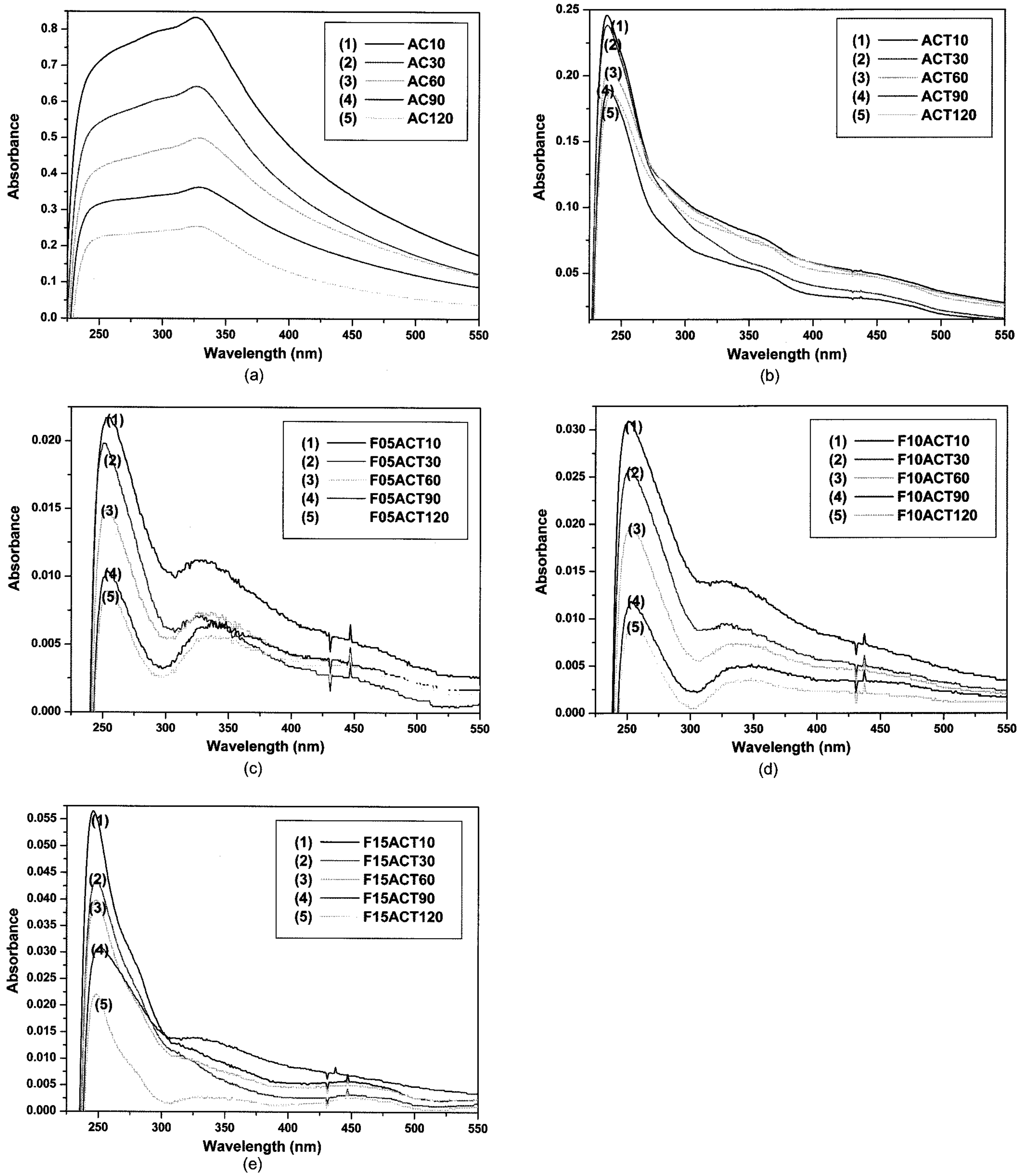


Fig. 6. UV/VIS spectra of MB concentration against the Fe-AC/TiO_2 composite under various time conditions: (a) AC, (b) ACT, (c) F05ACT, (d) F10ACT, and (e) F15ACT.

lytic efficiency between AC, AC/TiO_2, and Fe-AC/TiO_2. As shown in the figure, from AC to Fe-AC/TiO_2, the MB degradation efficiency increased gradually. This clearly indicates the combination effect on the organic pollutants decomposition as discussed before.[9-14] In these composites, it is considered that the AC component absorbed the organic molecule and then the TiO_2 component degrades due to a photocatalytic reaction. It is noteworthy that the Fe modified AC-TiO_2

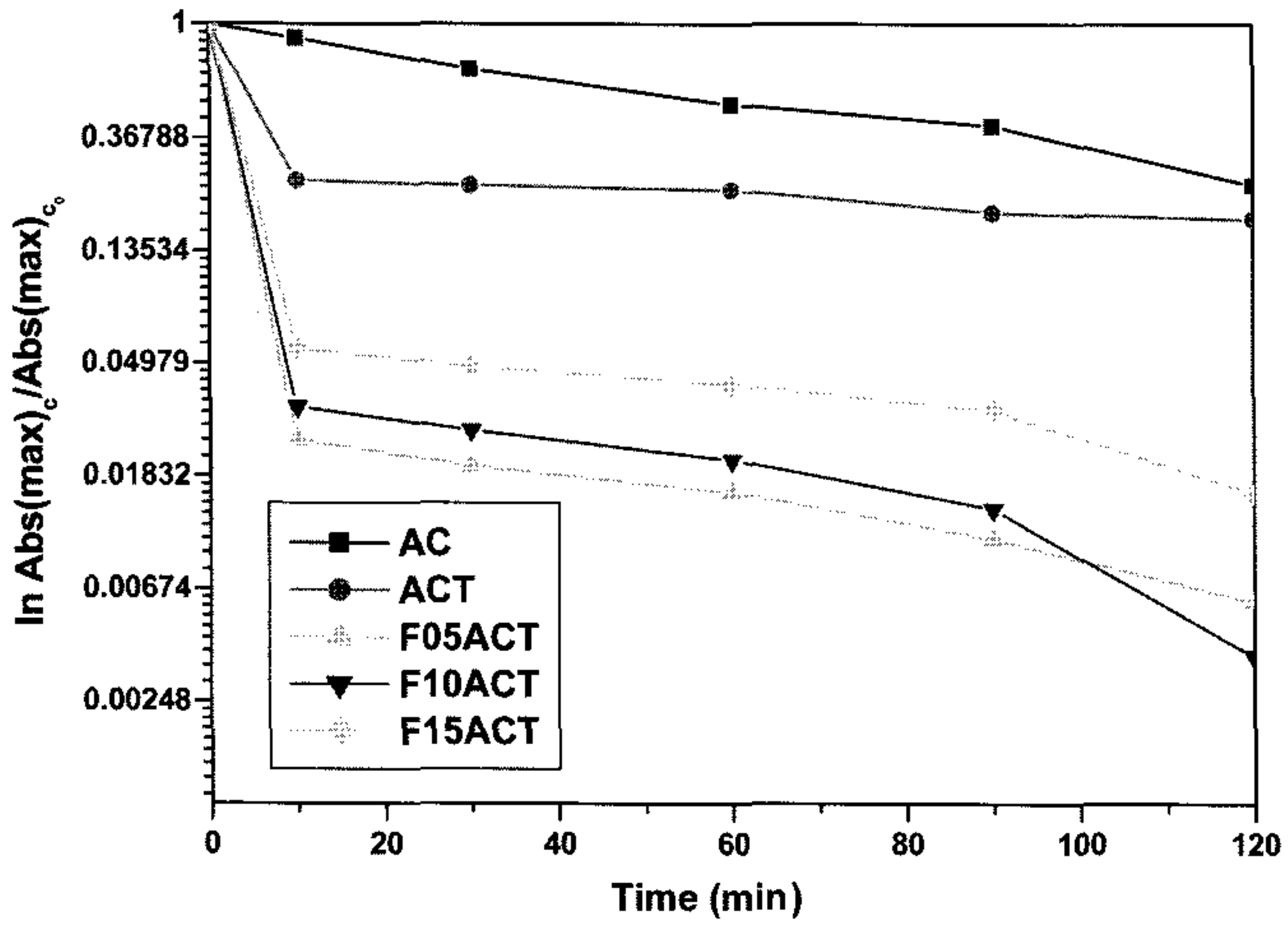


Fig. 7. Dependence of relative concentration of MB in the aqueous solution ln Abs(max)$_c$/Abs(max)$_{c0}$ on UV irradiation time for the Fe-AC/TiO$_2$ composites prepared from the different Fe mole ratios.

enhances the photocatalytic activity greatly, although there is no significant difference between different concentration of Fe. The Fe effect on accelerating the photocatalytic ability is due to a photo-Fenton process. In photo-Fenton reactions, the process of metal oxidation and reduction occur after each other, giving rise to $OH^{\cdot}$ radicals, which are known to be responsible for the degradation of organic compounds. Iron is the most commonly used metal as a Fenton reagent in this process.[21,22] It was reported that the rate of pollutant decomposition via a photo-Fenton process was governed by the amount and ratio of Fe^{2+}/Fe^{3+}. When enough Fe^{2+} is obtained after a Fe^{3+} reduction, a significant acceleration of pollutant degradation via a photo-Fenton process proceeds.[23-26] In summary, the individual composites can decompose the MB to different structure products, which reveals an interesting subject for further investigation regarding the degradation of Fe-AC/TiO$_2$ on organic pollutants. At the same time, the modified composites by Fe can enhance the photocatalytic activity greatly and show the prcatical benefits for industrial application.

4. Conclusion

Composites of Fe-AC/TiO$_2$ were synthesized by immobilizing TiO$_2$ particles on the surface of AC. Then, the characteristics of the Fe-AC/TiO$_2$ composites were analyzed by an N_2 adsorption experiment, SEM, and EDX. Next, the Fe-AC/TiO$_2$ composites were used to investigate photocatalytic activity on an MB solution. The photodegration of MB by the Fe-AC/TiO$_2$ shows excellent photocatalytic effects. Furthermore, the MB decomposition processes confirmed the adsorption and photocatalytic reaction on the composites. Compared with the composites without Fe modification, the composites of Fe-AC/TiO$_2$ enhanced the photocatalytic activity due to Fe assistance on the photocatalytic reaction.

REFERENCES

1. A. L. Linsebigler, G. O. Lu, and J. T. Yates, "Photocatalysis on TiO$_2$ Surfaces: Principles, Mechanisms, and Selected Results," *Chem. Rev.*, **95** 735 (1995).
2. M. Inagaki, T. Imai, T. Yoshikawa, and B. Tryba, "Photocatalytic Activity of Anatase Powders for Xxidation of Methylen Blue in Water and Diluted NO Gas," *Appl. Catal.B-Environ.*, **51** 247-54 (2004).
3. A. K. Ray and Design, "Modelling and Experimentation of a New Large-scale Photocatalytic Reactor for Water Treatment," *Chem Eng Sci.*, **54** 3113-25 (1999).
4. M. E. Fabiyi and R. L. Skelton, "Photocatalytic Mineralisation of Methylene Blue Using Buoyant TiOt-coated Polystyrene Beads," *Photochem. Photobio., A Chem.*, **132** 121-28 (2000).
5. T. Torimoto, Y. Okawa, N. Takeda, and H. Yoneyama, "Effect of Activated Carbon Content in TiO$_2$-loaded Activated Carbon on Photodegradation Behaviors of Dichloromethane," *J. Photochem. Photobio., A: Chem.*, **103** 153-57 (1997).
6. P. F. Fu, Y. Luan and X. G. Dai, "Preparation of Activated Carbon Fibers Supported TiO$_2$ Photocatalyst and Evaluation of its Photocatalytic Reactivity," *J. Molecular Catalysis A: Chemical*, **221** 81-8 (2004).
8. M. Inagaki, S. Kobayashi, F. Kojin, N. Tanaka, T. Morishita, and B. Tryba, "Pore structure of Carbons Coated on Ceramic Particles," *Carbon*, **42** 31-53 (2004).
9. W. C. Oh, M. L. Chen, and C. S. Lim, "Preparation with Different Mixing Ratios of Anatase to Activated Carbon and their Photocatalytic Performance," *J. Ceramic Proceeding Research*, 8 119 (2007).
10. W. C. Oh, M. L. Chen, and Y. S. Ko, "Preparation of AC/TiO$_2$ Composites from Activated Carbon Modified by HNO$_3$ and their Photocatalytic Activity," *Carbon Science*, 8 6 (2007).
11. W. C. Oh, J. S. Bae, M. L. Chen, and Y. S. Ko, "Characterisation of Composite Prepared with Different Mixing Ratio of TiO$_2$ to Activity Carbon and their Photocatalytic Activity," *Analytical Science & Technology*, **19** 376 (2006).
12. W. C. Oh, J. S. Bae, and M. L. Chen, "Characterisation of AC/TiO$_2$ Composite Prepared with Pitch Binder and their Photocatalytic Activity," *Bull. Korean Chem. Soc.*, **27** 1423 (2006).
13. W. C. Oh, J. S. Bae, and M. L. Chen, "Photocatalytic Effect for the Pitch-coated TiO$_2$," *Analytical Science & Technology*, **19** 301 (2006).
14. W. C. Oh and M. L. Chen, "Formation of TiO$_2$ Composites on Activated Carbon Modified by Nitric Acid and their Photocatalytic Activity," *J. Ceramic Processing Research*, **316** (2007).
15. W. C. Oh and Y. R. Na, "Photocatalytic Oxidation for Organic Dye using Phenol Resin-based Carbon- titania Composites," *J. Kor. Ceram. Soc.*, **45** [1] 36-42 (2008).
16. W.C. Oh and A. R. Jung, "Properties and Photocatalytic Activity of Pitch-binded ACF/TiO$_2$ Composites," *J. Kor. Ceram. Soc.*, **45** [3] 150-56 (2008).
17. Eva Piera, M. Isabel Tejedor, Michael E. Zorn, and Marc A. Anderson, "Relationship Concerning the Nature and Con-

centration of Fe(III) Species on the Surface of TiO_2 Particles and Photocatalytic Activity of the Catalyst," *Applied Catalysis B: Environmental*, **46** 671-85 (2003).

18. B. Tryba, A. W. Morawski, M. Inagaki, and M. Toyoda, "Effect of the Carbon Coating in Fe-C-TiO_2 Photocatalyst on Phenol Decomposition under UV Irradiation via Photo-Fenton Process," *Chemosphere*, **64** 1225-32 (2006).
19. B. F. Gao, Y. J. Kim, A. K. Chakraborty, and W. I. Lee, "Efficient Decomposition of Organic Compounds with $FeTiO_3$/TiO_2 Heterojunction under Visible Light Irradiation," *Applied Catalysis B: Environmental*, **83** 202-07 (2008).
20. S. Y. Zhu, T. F. Shi, W. H. Liu, S. Q. Wei, Y. N. Xie, C. Z. Fan, and Y. Z. Li, "Direct Determination of Local Structure Around Fe in Anatase TiO_2," Physica B **396** 177-80 (2007).
21. B. Tryba, "Immobilization of TiO_2 and Fe-C-TiO_2 Photocatalysts on the Cotton Material for Application in a Flow Photocatalytic Reactor for Decomposition of Phenol in water," *J. Hazardous Materials*, **151** 623-27 (2008).
22. B. Tryba, M. Toyoda, A.W. Morawski, and M. Inagaki, "Modification of Carboncoated TiO_2 by Iron to Increase Adsorptivity and Photoactivity for Phenol," *Chemosphere*, **60** 477-84 (2005).
23. B. Tryba, A.W. Morawski, M. Inagaki, and M. Toyoda, "The Kinetics of Phenol Decomposition under UV Irradiation with and without H_2O_2 on TiO_2, Fe-TiO_2 and Fe-C-TiO_2 Photocatalysts," *Appl. Catal. B: Environ.*, **63** 215-21 (2006).
24. B. Tryba, M. Toyoda, A.W. Morawski, and M. Inagaki, "Modification of Carbon Coated TiO_2 by Iron to Increase Adsorptivity and Photoactivity for Phenol," *Chemosphere*, **60** 477-84 (2005).
25. B. Tryba, A.W. Morawski, M. Inagaki, and M. Toyoda, "The Kinetics of Phenol Decomposition under UV Irradiation with and without H_2O_2 on TiO_2, Fe-TiO_2 and Fe-C-TiO_2 Photocatalysts," *Appl. Catal. B: Environ.*, **63** 215-21 (2006).
26. S. Mozia, M. Toyoda, M. Inagaki, B. Tryba, and A.W. Morawski, "Application of Carbon-coated TiO_2 for Decomposition of Methylene Blue in a Photocatalytic Membrane Reactor," *J. Hazard. Mater.*, **140** 369-75 (2007).