

# Preparation of Fe-ACF/TiO<sub>2</sub> Composites and their Photocatalytic Degradation of Waste Water

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## ABSTRACT

In this study, we prepared Fe-activated carbon fiber(ACF)/TiO<sub>2</sub> composites with titanium (VI) n-butoxide (TNB) as the titanium source for ACF pre-treated with iron compounds through the impregnation method. In terms of textural surface properties, the composites demonstrate a slight decrease in the BET surface area of the samples and an increase in the amount of iron compounds treated. The surface morphology of the Fe-ACF/TiO<sub>2</sub> composites was characterized by means of SEM. The composites have a porous texture with homogenous compositions of Fe and titanium dioxide distributed on the sample surfaces. The phase formation and structural transition of the iron compounds and titanium dioxide were observed in X-ray diffraction patterns of the Fe-ACF/TiO<sub>2</sub> composites. The chemical composition of the Fe-ACF/TiO<sub>2</sub> composites, which was investigated with EDX shows strong peaks for the C, O, Fe and Ti elements. The photo degradation results confirm that the Fe-ACF/TiO<sub>2</sub> composites show excellent removal activity for the COD in piggery waste due to photocatalysis of the supported TiO<sub>2</sub>, radical reaction by Fe species, and the adsorptivity and absorptivity of ACF.

**Key words :** Activated carbon fiber, TiO<sub>2</sub> Composite, BET, XRD, SEM, Piggery waste

## 1. Introduction

Carbon/titania complexes are common photocatalysts in oxidation studies of organics, in both the aqueous and gas.<sup>1-3)</sup> However, the photocatalytic oxidation rates of many target pollutants are too slow to be of practical interest. Considerable research has been undertaken for the purpose of speeding up these processes or reducing the volume of photocatalytic reactors by particularly by using a carbon matrix to optimize certain system parameters such as the type of composite.<sup>4-6)</sup> One of the most common techniques of preserving porosity is the use of a titanium compound with porous carbons, such as activated carbon and its fibers. These hybrid materials have great potential in applications such as catalyst and porous supports or as adsorbents in electrode preparation, or in optical applications and the reinforcement of elastomeres and plastics. Carbon/titania catalysts can produce synergetic or cooperative effects between the metal oxide phase and the carbon phase. Recently, the physical mixture of titania and activated carbon has been shown to produce a synergetic effect on the photodegradation of organic compounds.<sup>6,7)</sup> On the other hand, a carbon/titania composite catalyst has recently been used in the improved methylene blue removal reaction with a high level of selectivity due to cooperation between the

metal oxide phase and the carbon matrix.<sup>8)</sup> This effect is expected to be enhanced if another metal species is well dispersed on the carbon phase. In most cases, iron is used to form iron salts as a homogeneous catalyst because of its highly efficient degradation of organic compounds in solutions. In our study, however, heterogeneous catalysts such as Fe-carbon/TiO<sub>2</sub> have an interesting reaction in waste water because of possible multiple uses of the catalyst. This system can be used in the decomposition of many organic compounds, such as phenols, dyes, pesticides and waste water. Metallic Fe ion may act as an electron or hole trap and alter the recombination rate of electron-hole pairs. The reaction mechanism of the decomposition of organic compounds by means of an iron complex reaction under light irradiation is not completely clear. However, many authors suggest that the degradation is probably caused by the formation of an iron complex.<sup>9,10)</sup> Some Fe-supported catalysts have extensively studied in the photo-Fenton process.<sup>11,12)</sup> In the degradation of organic compounds in the photo-Fenton process, iron complexes are important because organic compounds are generally degraded through the oxidation of Fe complexes.

In this study, we focus on the characterization of the Fe-ACF/TiO<sub>2</sub> composite obtained from the porous ACF and the formation of TiO<sub>2</sub> from titanium n-butoxide (TNB). The conversion of TNB to TiO<sub>2</sub> during heat treatment is important for the preparation of Fe-ACF/TiO<sub>2</sub> composites. Moreover, the morphology of the converted TiO<sub>2</sub> is strongly affected by the porous structure of Fe-ACF, provided the TiO<sub>2</sub> on the fiber surface is properly formed in the restricted space of Fe-

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**Table 1.** Nomenclature of the Fe-ACF/TiO<sub>2</sub> Composite Prepared with ACT Treated with Fe Salts and TNB

Synthesis Procedure	Nomenclature
0.5 M FeCl <sub>3</sub> pre-treated Activated Carbon Fiber+Titanium (IV) n-butoxide	FAFT1
1.0 M FeCl <sub>3</sub> pre-treated Activated Carbon Fiber+Titanium (IV) n-butoxide	FAFT2
1.5 M FeCl <sub>3</sub> pre-treated Activated Carbon Fiber+Titanium (IV) n-butoxide	FAFT3

ACF. For our investigation of the physicochemical properties and morphological structure of Fe-ACF/TiO<sub>2</sub> composites, we use adsorption, X-ray diffraction (XRD), scanning electron microscopy (SEM), and an energy dispersive X-ray (EDX) technique. The results from a UV/VIS spectrophotometer confirm that Fe-ACF/TiO<sub>2</sub> composites have excellent activity with regard to the decomposition of piggery waste.

## 2. Experimental

### 2.1. Materials

Self-made ACFs, which were used as raw material, were prepared from commercial PAN fibers (T-300 Amoco, USA). The carbonized PAN fiber was heated at 823 K for the burn off, and the carbon fibers were activated by steam diluted with nitrogen in a cylinder quartz glass tube for 30 min. at a temperature of 1073 K. These ACFs were washed with deionized water and dried for 24 h at an ambient temperature. For a comparison of photocatalytic effects, we used commercially available TiO<sub>2</sub> photocatalysts (Duk-San Pure Chemical Co., Korea). For the treatment of Fe sources to an ACF matrix, we obtained FeCl<sub>3</sub>·6H<sub>2</sub>O from the Duksan Pure Chemical Co. (99+%, ACS reagent, Korea) and used it as received. During the metal treatment, 20 g of ACF was dipped into 100 ml of 0.5, 1.0 and 1.5 M ferric nitrate solutions and stirred for 24 h at room temperature. The air and bubbles in the solution were then removed under a vacuum pressure of about 1.33 Pa for 20 min and the solution was discarded. Next, the samples were dried at 383 K for 48 h in an air atmosphere. For the TNB treatment to Fe-ACF, we prepared Fe-containing ACF slurry solutions with pristine concentrations of 20 mL of TNB (C<sub>16</sub>H<sub>36</sub>O<sub>4</sub>Ti, Acros Organics, USA) for the preparation of Fe-ACF/TiO<sub>2</sub> composites. For the preparation, we mixed 5 g of powdered Fe-ACF in 20 ml of a TNB aqueous solution and stirred the mixture for 5 h at 333 K. After that, the solvent in the mixture was vaporized at 343 K for 1 h. The powder mixtures of TNB to Fe-ACF were heated at 973 K for 1 h. The simple preparation method and nomenclature of the prepared samples are listed in Table 1. The effluent characterization involved treatment of an aqueous piggery urine effluent with chemical oxygen demand (COD) levels exceeding 50000 mg/l. The levels can be reduced to less than 155~165 mg/l by applying a physicochemical primary treatment step (coagulation and air-blowing). Samples with lower COD levels were used for characterization of powdered Fe-ACF/TiO<sub>2</sub> composites.

### 2.2. Characterization

To investigate the textural surface properties, we obtained nitrogen adsorption isotherms by using a BEL Sorp analyzer (BEL, Japan) at 77 K. Furthermore, to analyze the crystallinity and phase transition of the synthesized catalysts, we used an XRD (Shimatz XD-D1, Japan) with Cu K $\alpha$  radiation. A SEM (JSM-5200 JOEL, Japan) was used to observe the surface state and structure of the Fe-ACF/TiO<sub>2</sub> composites, and an elemental analyzer was used to obtain EDX spectra of the prepared composites. In addition, UV-VIS spectra of the aqueous solutions decomposed with Fe-ACF/TiO<sub>2</sub> composites were recorded with a Genspec III (Hitachi, Japan) spectrometer so that we could measure the photodegradation effects. Finally, the COD analyses were measured with a cell test spectrophotometer (PhotoLab S6, WTW, Germany) in accordance with standard cell test methods (Merck, Germany).

### 2.3. Photocatalytic activities

Photocatalytic activities were evaluated by measuring the degradation of piggery waste in aqueous media under UV light irradiation. For the UV irradiation, the reaction tube was located axially and held in a UV lamp (20 W, 365 nm) black box. The lamp was used in a darkness box at a distance of 100 mm from the aqueous solution. The amount of suspended Fe-ACF/TiO<sub>2</sub> composites was kept at 0.005 g/mL. When the illumination was turned on, the suspension of piggery waste and Fe-ACF/TiO<sub>2</sub> composites was stirred with a magnetic stirrer in a dark condition for the irradiation time to establish a chemical equilibrium. The suspension was irradiated with UV light as a function of irradiation time. The samples were withdrawn regularly from the reactor and the dispersed powders were removed through a centrifuge. The clean transparent solutions were tested with a COD cell test photometer and analyzed by means of UV/VIS spectroscopy. With regard to the piggery waste, the trial absorption in the 215 nm to 350 nm region was examined by means of UV/VIS spectroscopy so that we could assess how the Fe-ACF/TiO<sub>2</sub> composite affected the photodegradation.

## 3. Results and discussion

### 3.1. Surface characterization of the samples

Nitrogen adsorption isotherms of N<sub>2</sub> at 77 K in pristine ACF and Fe-ACF/TiO<sub>2</sub> composites are shown in Fig. 1. The shape of the isotherms (Type I classification in the IUPAC) clearly confirms that the pores in the prepared composites

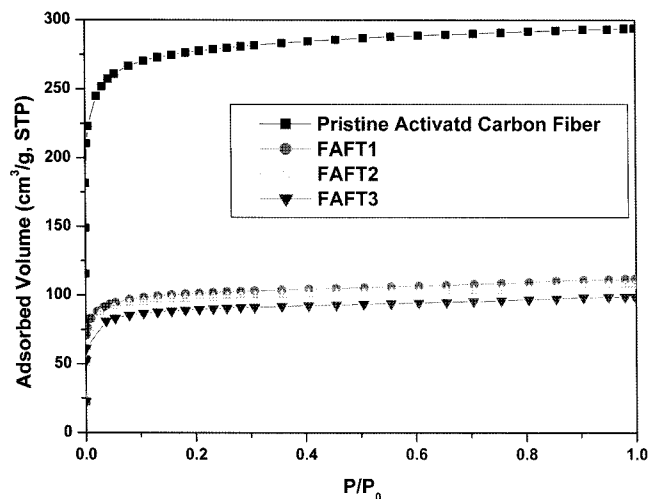


Fig. 1. Nitrogen adsorption isotherms obtained from the pristine ACF and the powdered Fe-ACF/TiO<sub>2</sub> composites.

Table 2. Textural Properties of Pristine Materials and Fe-ACF/TiO<sub>2</sub> Composite Samples

Sample	Parameter		
	S <sub>BET</sub> (m <sup>2</sup> /g)	Micropore Volume (cm <sup>3</sup> /g)	Average Pore Diameter (nm)
As-received ACF	967.4	0.4530	2.70
FAFT1	344.8	0.1717	1.99
FAFT2	338.9	0.1644	1.94
FAFT3	287.0	0.1521	1.91

are micropores. All of the Fe-ACF/TiO<sub>2</sub> composites have Type I isotherms: they have a plateau that is nearly horizontal to the  $p/p_0$  axis in the middle region, and the adsorbed volume increases catastrophically in a low relative pressure region. This classification implies that all the Fe-ACF/TiO<sub>2</sub> composites have a micropore structure. These isotherms confirm that the adsorbed volume decreases with an increase in the amount of treated iron salt.

The specific surface area of the photocatalysts decreases linearly when the Fe content in the Fe-ACF/TiO<sub>2</sub> composites is increased. This phenomenon occurs because the pristine ACF has a much greater specific surface area (967.4 m<sup>2</sup>/g) than TiO<sub>2</sub> (125 m<sup>2</sup>/g). Table 2 summarizes the surface textural properties for the pristine ACF and Fe-ACF/TiO<sub>2</sub> composites. The results clearly confirm that the TiO<sub>2</sub> composite derived from TNB in the presence of ACF has a significantly higher specific surface area than the pristine TiO<sub>2</sub>. Furthermore, the surface area values seem to be correlated with the C/Fe ratios. The higher the Fe content, the smaller the surface area. Accordingly, the decrease in the surface area must be directly related to the iron salt. In addition, all the surface textural parameters of the composites are considerably lower than those of the pristine ACF due to the pore structural transformation caused by the iron and titanium complexes on the ACF surface. The formation

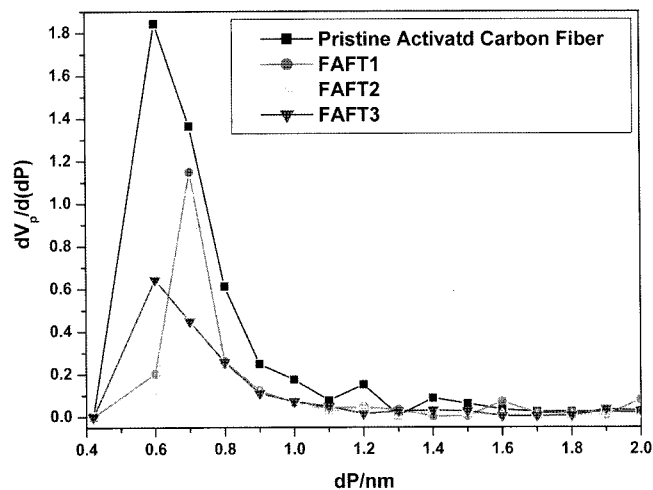
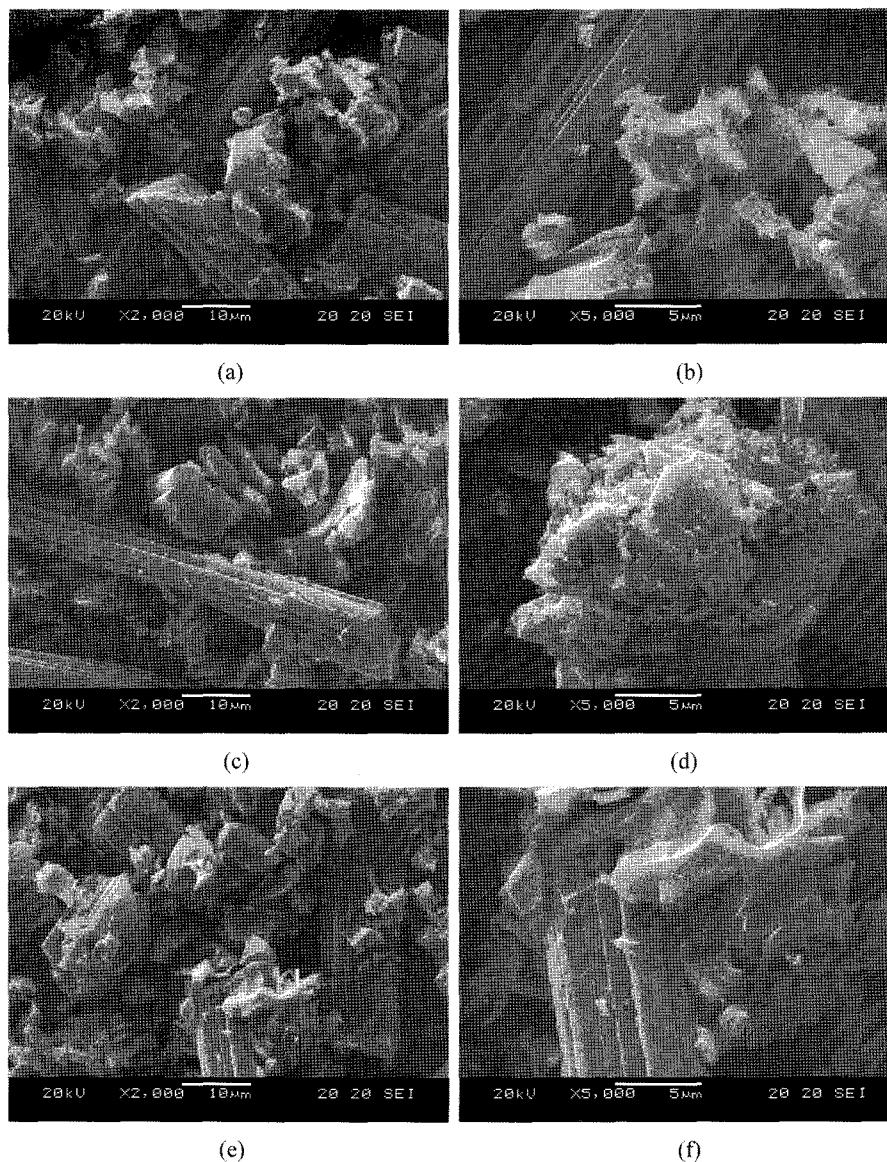


Fig. 2. Comparison of the pore size distribution of the pristine ACF and the Fe-ACF/TiO<sub>2</sub> composites.

of iron and titanium complexes in the pores can be block the pores on the ACF surfaces. The deformation of surface parameters at the composites may be related to efficiency at which organic compounds are removed from piggery waste solutions. In earlier studies,<sup>13,14</sup> the BET surface areas of carbon-titania composites were considerably smaller because surface complexes such as pre-treated acid and titanium deformed the narrow pores.

Fig. 2 shows the evolution of the pore size distribution in the three series together with the Fe content. Two clear pore families can be observed in the distribution: one family has a major pore size of about 0.4 to 0.9 nm (for the pristine ACF and FAFT3); the other family has a major pore size of about 0.6 to 0.9 nm (FAFT1 and FAFT2). The major peak in all the samples occurs in the micropore range. Because of the surface transition in the Fe-ACF/TiO<sub>2</sub> composites, the pore volume tends to decrease when the amount of iron salt is increased. Colon *et al.*<sup>15</sup> reported that the pore size distribution of the carbon-titania composites that are derived by means of a sol-gel method from titanium *iso*-propoxide and activated carbon depend considerably on the amount of carbon matrix.

The SEM images show that the structure evolves gradually as the amount of Fe salt increases. The agglomerates around the ACF consist of small particles of 5 to 10  $\mu\text{m}$ ; some coagulated particles can also be observed. The number of particles appears to increase as the Fe content increases around the ACF. The SEM images show that the titanium complexes contain evenly distributed particles in all the types of Fe-ACF/TiO<sub>2</sub> composites. The average particle size estimated from SEM observations is not very large in the composites prepared from iron and titanium sources. Although the titanium complex particles on the carbon surface become pronounced and coarse, we observed no iron complex particles due to the size of the ions. The figures show that the TiO<sub>2</sub> grains grow from the starting TNB, the particles of which are small. The distribution of titanium

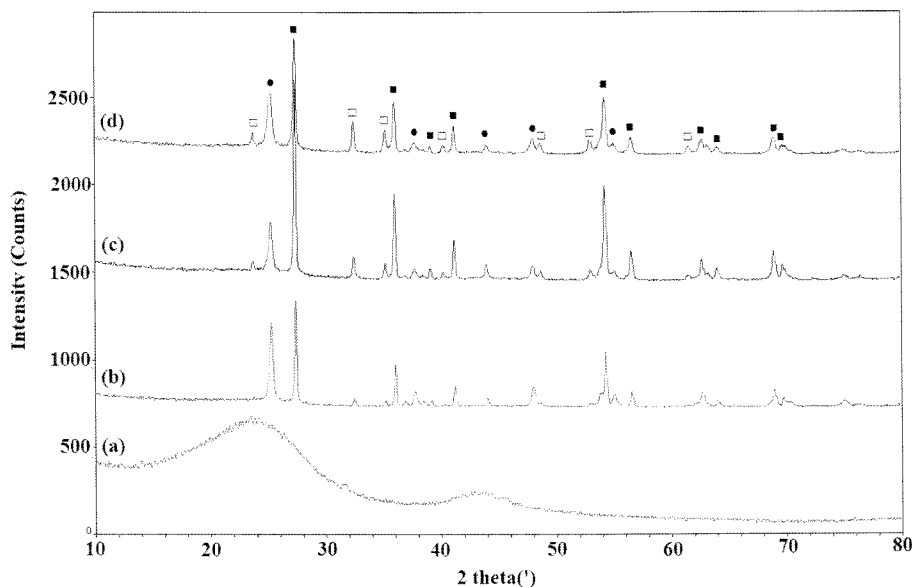


**Fig. 3.** SEM images obtained from the powdered Fe-ACF/TiO<sub>2</sub> composites: (a) FAFT1 (overall scale), (b) FAFT1 (close up), (c) FAFT2 (overall scale), (d) FAFT2 (close up), (e) FAFT3 (overall scale), and (f) FAFT3 (close up).

dioxide on the large surface area can enhance the catalytic efficiency of the removal of organic dyes and the COD. Furthermore, the dispersion of small particles can apparently provide more reactive sites for the reactants than the agglomerated particles. Moreover, one disadvantage of the aggregated particles is that a considerable portion of the iron and titanium complexes becomes encapsulated in the three-dimensional matrix and cannot be accessed by organic dyes in the photodegradation process. Studies confirm that the quantum efficiency of the photoreaction depends on the average transit time of an electron from the photocatalyst particle interior to the surface and the combination rate of an electron-hole pair of photocatalysts.<sup>16)</sup> Accordingly, high quantum yields are expected from additives comprised of small TiO<sub>2</sub> particles and iron complexes.

### 3.2. Identification of the crystal structure and chemical components

The crystal structure of synthesized composites is mainly determined by the XRD method. Fig. 4 shows changes in the XRD patterns on the pristine ACF and the Fe-ACF/TiO<sub>2</sub> composites. None of the XRD patterns of any of the composites have any carbon matrix diffraction peaks that correspond to the inorganic amorphous phase. However, the XRD patterns in Fig. 4 show diffraction peaks of the mixture of anatase and rutile. Anatase is a metastable polymorphic form of titania that transforms to rutile when heated.<sup>3)</sup> For pure oxides, the transformation is rapid at temperatures above 973 K, though the phase transition temperature seems to depend on the impurity contents, particle size and surface area.<sup>3,17,18)</sup> After heat treatment at 973 K for 1 h, the main diffraction peaks at 25.3, 37.8, 48.0, 53.8, 54.9 and

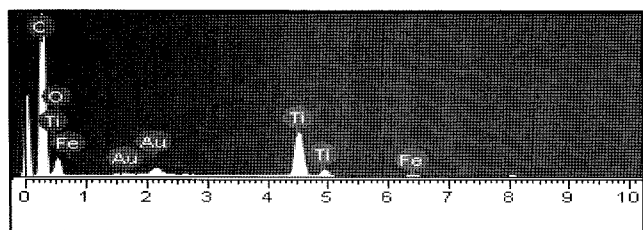


**Fig. 4.** XRD patterns of the pristine ACF and the powdered Fe-ACF/TiO<sub>2</sub> composites: (a) pristine ACF, (b) FAFT1, (c) FAFT2, and (d) FAFT3 (□: Fe+2TiO<sub>3</sub>, ●: anatase and ■: rutile).

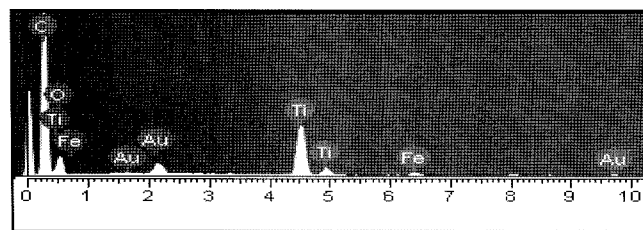
62.5 correspond to diffractions of the (101), (004), (200), (105), (211) and (204) planes of anatase, indicating that the prepared TiO<sub>2</sub> exists in an anatase state. Another crystal phase is marked by peaks at 27.4, 36.1, 41.2 and 54.3, which correspond to diffraction peaks of the (110), (101), (111) and (211) planes of rutile. The Fe+2TiO<sub>2</sub> phase can be attributed

to the addition of iron to the TiO<sub>2</sub> catalyst. Thus, the Fe+2TiO<sub>2</sub>-developed Fe-ACF/TiO<sub>2</sub> composites are formed during the transformation of TNB to TiO<sub>2</sub> as a result of the heat treatment of all the samples.

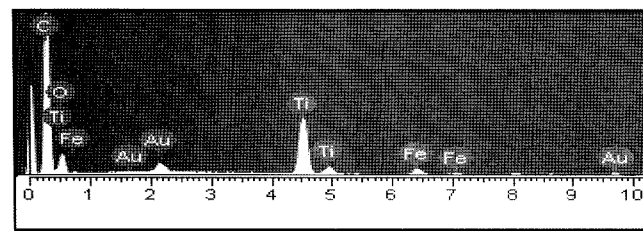
To analyze the Fe-ACF/TiO<sub>2</sub> composites in relation to the iron salt treatments, we used EDX for the elemental microanalysis. Fig. 5 shows EDX spectra of the Fe-ACF/TiO<sub>2</sub> composites. These spectra show that the main elements of C, O and Fe have strong Ti peaks. Most of these samples have a more abundant supply of carbon and major oxygen than any other elements. The data of the EDX analyses of the Fe-ACF/TiO<sub>2</sub> composites are listed in Table 4. The elements of C, Fe and Ti are confirmed as componential elements in most of the Fe-ACF/TiO<sub>2</sub> samples. The spectra results confirm that almost all the samples show a decrease in the C element and an increase in the O, Fe and Ti elements. The elemental analyses of the solid particles confirm the presence of carbon and composite-type carbon on various types of titania.<sup>19,20</sup> Thus, quantitative analysis is important for determining the componential elements of carbon-titania photocatalysts.



(a)



(b)



(c)

**Fig. 5.** Typical EDX microanalyses of the Fe-ACF/TiO<sub>2</sub> composites: (a) FAFT1, (b) FAFT2, and (c) FAFT3.

### 3.3. Photocatalytic activity in the piggery waste

Catalysts were used to degrade piggery waste under a UV photoreactor to demonstrate their reaction activity. Analytical results of primitive piggery waste have been described in

**Table 3.** EDX Elemental Microanalysis of Fe-ACF/TiO<sub>2</sub> Composites

Sample (wt%)	C	O	Ti	Fe
FAFT1	62.7	22.7	13.7	0.90
FAFT2	61.0	22.8	14.6	1.68
FAFT3	59.0	23.6	14.7	2.66

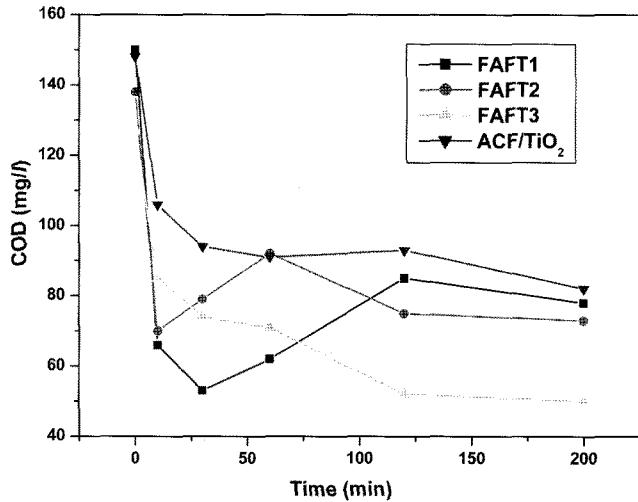


Fig. 6. Results of COD removal efficiencies by the Fe-ACF/ $\text{TiO}_2$  composites for the piggery waste.

the literature.<sup>21,22</sup> The average value of the initial COD of raw waste exceeds 50,000 mg/L. The average COD values of the waste in the first chemical coagulation and physical air-blowing treatment were distributed between 127 and 150 mg/L. Fig. 6 shows the removal rates of piggery waste in terms of the COD removal efficiency as a function of irradiation time. After treatment with Fe-ACF/ $\text{TiO}_2$  composites, these piggery waste values dropped to less than 85 mg/L; in fact, most samples showed a significant COD removal efficiency in the range of 50 to 85 mg/L. The considerably lower removal efficiency rate of the FAT3 sample helped reduce the COD. The COD removed by the treatment with Fe-ACF/ $\text{TiO}_2$  composites seems to have an excellent removal effect in all cases. However, the values of the COD removal effect in relation to the period of degradation caused by Fe-ACF/ $\text{TiO}_2$  composites in the piggery waste show an unstable tendency. In terms of COD values, the Fe-ACF/ $\text{TiO}_2$  composites reveal a much greater removal efficiency than that of the ACF/ $\text{TiO}_2$  prepared without any iron component. This phenomenon may be due to the photocatalytic reactions that occur on the surface of the composite catalysts; moreover, the addition of iron compounds can increase the number of catalytic active sites. The large increase in the decomposition reaction of Fe compounds in the composite derived from organic compounds is attributed to the photocatalytic degradation effect of the Fe-ACF/ $\text{TiO}_2$  composite. This implies that Fe compounds in the composite operate as a new synergistic factor.

The photocatalytic experiments show that three kinds of composites can photocatalyze the degradation of piggery waste. Because the results of the UV/VIS spectra obtained from the piggery waste after photolysis correspond highly to variations in the concentration of the solution, we attempted to compare the relative yields of the photodegraded products that formed at different irradiation times. Fig. 7 shows UV spectra of the piggery waste in relation to the Fe-ACF/ $\text{TiO}_2$  composite under various time conditions.

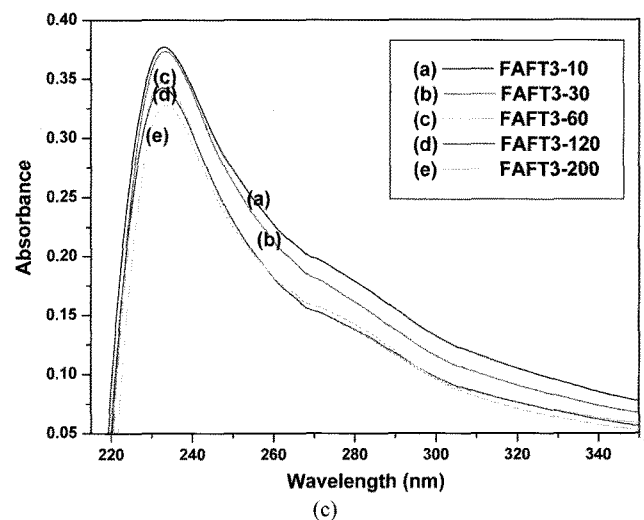
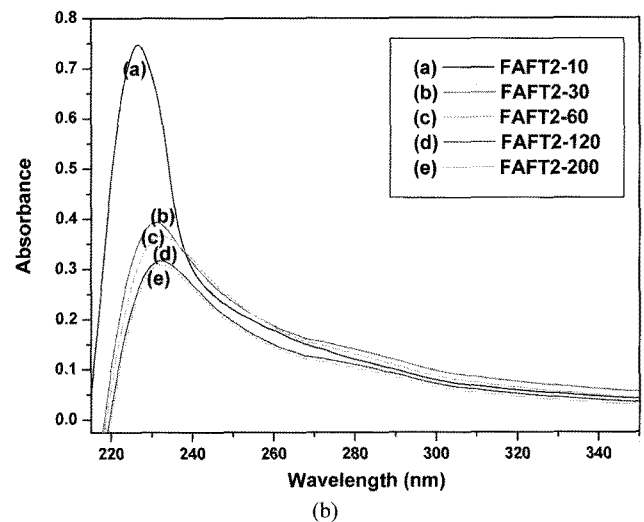
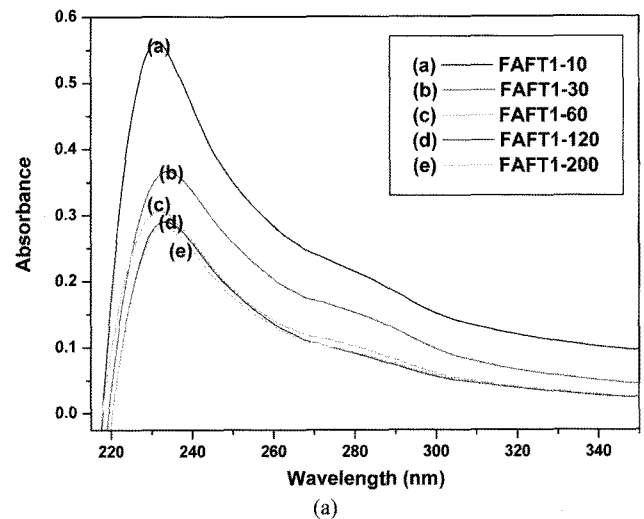


Fig. 7. UV spectra of the piggery waste against the Fe-ACF/ $\text{TiO}_2$  composites under various irradiation time conditions: (a) FAFT1, (b) FAFT2, and (c) FAFT3.

The photodegradation caused by the Fe-ACF/ $\text{TiO}_2$  composite was tested in piggery waste products in a trial absorp-

tion of the 215 nm to 350 nm region. The figures show a decrease in absorbance, which is related to the degradation of the piggery waste. Although the difference in the absorbance level is small, the sharp decrease in absorbance, as shown in Fig. 7, can be attributed to a degradative reaction. The decrease in the absorbance maxima is proportional to the decrease in the concentration of transient organic material that forms after the UV light excitation. The maxima values tend to decrease in the lower absorbance region as the irradiation time increases. This tendency explains why the photocatalytic combination causes an increase in light transparency when the concentration of piggery waste decreases. An earlier study<sup>23)</sup> confirms that the decrease in absorbance for the Rhodamine degradation can be attributed to the degradative reaction of photocatalysts. The photoactivity of the Fe-ACF/TiO<sub>2</sub> composite is governed by two stages: namely, the photocatalytic activity of TiO<sub>2</sub>; and the reduction of Fe<sup>3+</sup> to Fe<sup>2+</sup> in an OH<sup>-</sup> solution under UV light, which gives rise to OH· radicals. The high Fe content in the Fe-containing ACF/TiO<sub>2</sub> composites is responsible for the high photoactivity of the piggery waste. Moreover, the removal effect of organic materials in a solution is also governed by the physisorption of porous ACF. This kind of behavior, as mentioned above, can be explained by the photo-Fenton reaction of the Fe<sup>3+</sup> reduction to Fe<sup>2+</sup> under UV irradiation.

#### 4. Conclusion

In this study, we present the synthesis and characterization of Fe-ACF/TiO<sub>2</sub> composites prepared from ACF and TNB. The adsorption and surface properties, as well as the structural and chemical composition, were investigated in terms of the synthesis of the Fe-ACF/TiO<sub>2</sub> composite. The data of the textural surface properties reveal that the BET surface area and the pore size of the composites decrease slightly as the amount of Fe salt is increased. The surface properties are confirmed by SEM images of the texture of the Fe-ACF/TiO<sub>2</sub> composite, but we were unable to observe the particles of the iron complexes because of the size of the ions. The X-ray diffraction patterns vary with strong peaks of the anatase, rutile and Fe+2TiO<sub>2</sub> phases of the Fe-ACF/TiO<sub>2</sub> composite. The EDX spectra show that the major elements of C, Fe and O have strong Ti peaks. Finally, the COD removed by the photocatalytic reaction of the Fe-ACF/TiO<sub>2</sub> composites confirms the excellence of the removal effect in all cases. Thus, the degradation of the piggery waste by the Fe-ACF/TiO<sub>2</sub> composites can be attributed to a combination of effects such as the radical formation of the Fe species, the photocatalytic reactions of TiO<sub>2</sub>, and the physisorption of porous ACF.

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