

Properties and Photocatalytic Activity of Pitch-binded ACF/TiO₂ Composites

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ABSTRACT

Pitch-binded activated carbon fiber(ACF)/TiO₂ composite photocatalysts were prepared by Carbon Tetra Chloride (CTC) solvent mixing method with different mixing ratios of anatase to ACF. The result of the textural surface properties demonstrated that there is a slight increase in the Brunauer, Emmett and Teller (BET) surface area of composites with an increase of the amount of ACF. The surfaces structure morphologies of the composites were observed using an Scanning Electron Microscope (SEM). In the XRD patterns for all ACF/TiO₂ composites, the diffraction peaks showed the formation of anatase crystallites. The EDX spectra showed the presence of C, O and Si with strong Ti peaks. Most of these samples were richer in carbon and major Ti metal than any other elements. From the photo-decomposition results, the excellent activity of the ACF/TiO₂ composites between c/c₀ for methylene blue and UV irradiation time could be attributed to both the effects of the photocatalysis of the supported TiO₂ and adsorptivity of activated carbon fiber and another carbon derived from pitch.

Key words : Activated carbon fiber, Anatase, BET surface area, SEM, XRD, EDX, Photocatalysis

1. Introduction

Porous carbon materials such as activated carbon and the fibers made from it are undoubtedly versatile, as demonstrated by the variety of structures and the wide range of applications in which they are found: indeed, they can be used for everything from gas storage to catalyst supports, molecular sieves, adsorbents, electrodes in electrical devices, environmental pollutant filters and medical derivatives.¹⁻³⁾ Using general mechanical methodology different composite mixed oxides have also been prepared. The introduction of a second component in such a composite structure can stabilize the textural properties upon thermal treatment, which modifies the distributions of active sites and generally enhances the catalytic activity of the pure oxides.⁴⁾ These composites have specialized properties as the materials of which they are composed exhibit cooperative or synergistic effects. A great deal of research has focused on the optimization of the catalytic properties of TiO₂ which depend on its surface area, porosity and acid-base nature. For some practical applications, the particles of titania were not only mounted on adsorbents, such as activated carbons and their fiber and other porous materials, but also fixed on a substrate by using a binder. One of the most important applications of TiO₂ is to behave as photocatalyst for chemical reactions in water contaminated with organic pollutants

such as dyes and aromatic or cyclic compounds. The synergistic effects of the titania/carbon composite surface have also been remarked elsewhere.^{5,6)} Generally, the MB molecules could be adsorbed onto adsorbents, and they were not readily decomposed by the TiO₂/carbon photocatalyst mainly because of the slow diffusion speed of the pollutants on the adsorbent surface to the TiO₂/carbon particles. For a number of applications, however, the practical use of TiO₂ in powder presents some drawbacks : for example, the immobilization of TiO₂ on fixed supports was found to reduce the functional efficiency of the material, as evidenced by researchers working on a de-pollution assessment. The use of mesoporous carbon supports could assure the mass transfer and diffusion of reacting species. The aim of this work is to prepare TiO₂/ACF composites to obtain a material with a well-developed microporosity in which well-mixed fine TiO₂ particles are binded with pitch. The resultant composite should combine the advantages that can be gained from the acid-base properties of the titanium oxide with the benefits of the surface area and porosity contributed by the ACF constituent.

Accordingly, we have synthesized a hybrid composite of ACF and titanium oxide with synergistic effects arising from these combined functions of adsorptivity and photoactivity. The unique preparation method used the ACF/TiO₂ system in order to optimize the mixing of TiO₂ and ACF. The pitch-binded ACF/TiO₂ photocatalysts were characterized by BET surface area, X-ray diffraction (XRD), scanning electron microscope (SEM), energy dispersive X-ray (EDX) and UV/VIS spectrophotometer. The catalytic efficiency of the studied catalysts was evaluated by the photo-degradation of methylene blue (MB).

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Table 1. Nomenclatures of Pitch-binded ACF/TiO₂ Composite Prepared with Different Mixing Ratios

Sample	Mixing Ratios	Nomenclatures
	9.0:27.0:64.0	AFT1
Pitch + Activated	9.0:36.0:55.0	AFT2
Carbon Fiber+TiO ₂	9.0:45.5:45.5	AFT3
	9.0:55.0:36.0	AFT4

2. Experimental Method

2.1. Materials

Self-made ACFs used as a raw material were prepared from commercial PAN fibers (T-300 Amoco, USA). The carbonized PAN fiber was first heated at 823 K for burn off, and the carbon fibers were activated by steam diluted with nitrogen in a quartz glass tube at 1073 K for 30 min. These ACFs were washed with deionized water and dried for 24 h at ambient temperature. The 0.01 M diluted sulfuric acid at boiling temperature was used in the oxidation treatment to increase the formation of functional groups without damage to the ACF surface. The oxidation was carried out at boiling temperature for 1 h. The oxidized ACFs were washed and dried at 323 K for 24 h. Pitch was used as a carbon precursor as well as for a binder in the preparation of the ACF/TiO₂ composite. The granular pitch was supplied from Jungwoo Chemical Co. (Korea). The TiO₂ photocatalysts were commercially available (Duk-San Pure Chemical Co., Korea), and were composed of a single phase of anatase with particles of about 30-50 μm. This anatase-type titanium dioxide powder had a relatively large BET surface area of about 125 m²/g. To melt the pitch, carbon tetrachloride (CTC, Dae-Jung Chemical Co., Korea) was used as solvent. After melting the pitch in CCl₄ solution, TiO₂ powder and ACF were mixed with the pitch-CCl₄ solution. Powder mixtures prepared with different mixing ratios of anatase to ACF were heated at 333 K for 1 h. The solvent in the mixtures was vaporized at 353 K for 6 hours. The agglomerates of ACF/TiO₂ were heated at 1023 K for 1 h. The nomenclatures of the prepared samples are listed in Table 1.

2.2. Characterization

To assess the surface textural properties, nitrogen isotherms were measured using an ASAP 2010 instruments

(Micromeritics, U.S.A) at 77 K. SEM (JSM-5200 JOEL, Japan) was used to observe the surface state and structure of the ACF/TiO₂ prepared through the CTC dissolution method. For the elemental analysis of the ACF/TiO₂, EDX was also used. XRD patterns were taken using an X-ray generator (Shimatx XD-D1, Japan) with Cu Kα radiation. As one analysis of photocatalytic activity, UV/VIS spectrophotometer (Genspec III (Hitachi), Japan) was used to characterize the catalytic efficiency of the ACF/TiO₂ composite. Characterization of methylene blue (C₁₆H₁₈N₃S, MB) in water was determined by the following procedure. An ACF/TiO₂ powdered sample of 0.05 g was dispersed in an aqueous solution with a concentration of 1.0×10⁻⁴ 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 550-750 nm wavelength of MB measured by a UV/VIS spectrophotometer.

2.3. Photocatalytic effect

For the identification of the photocatalytic effect of the prepared samples, the decomposition reaction of MB in water was followed. 0.05 g powdered samples were dispersed in ultra sonicate for 3 min. For UV irradiation a UV lamp (20 W, 365 nm) was used at the distance of 100 mm from the solution in darkness box. 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. Surface characterization

The surface textural properties of the ACF/TiO₂ composite prepared from mechanical mixing ratios are compiled in Table 2. The textural properties of a pristine TiO₂ and ACF are also included in the table. The TiO₂ only presented some macropores and did not present either mesopores or micropores. Consequently, they had low surface area value. The result in the table demonstrates that there is a slight increase in the BET surface area of composite samples with an increase of the amount of ACF. However, almost all surface textural parameters for the composites decreased considerably more than did those of the pristine ACF. This

Table 2. Textural Properties of Pristine Materials and ACF/TiO₂ Composites

Samples	Parameter			
	S _{BET} (m ² /g)	Micropore Volume (cm ³ /g)	Internal Surface Area (m ² /g)	Average Pore Diameter (Å)
As-received TiO ₂	125.0	-	87	-
As-received Activated Carbon Fiber	1989	0.443	1645	17.56
AFT1	872	0.268	657	14.55
AFT2	876	0.301	667	14.88
AFT3	881	0.312	678	15.01
AFT4	915	0.327	693	15.87

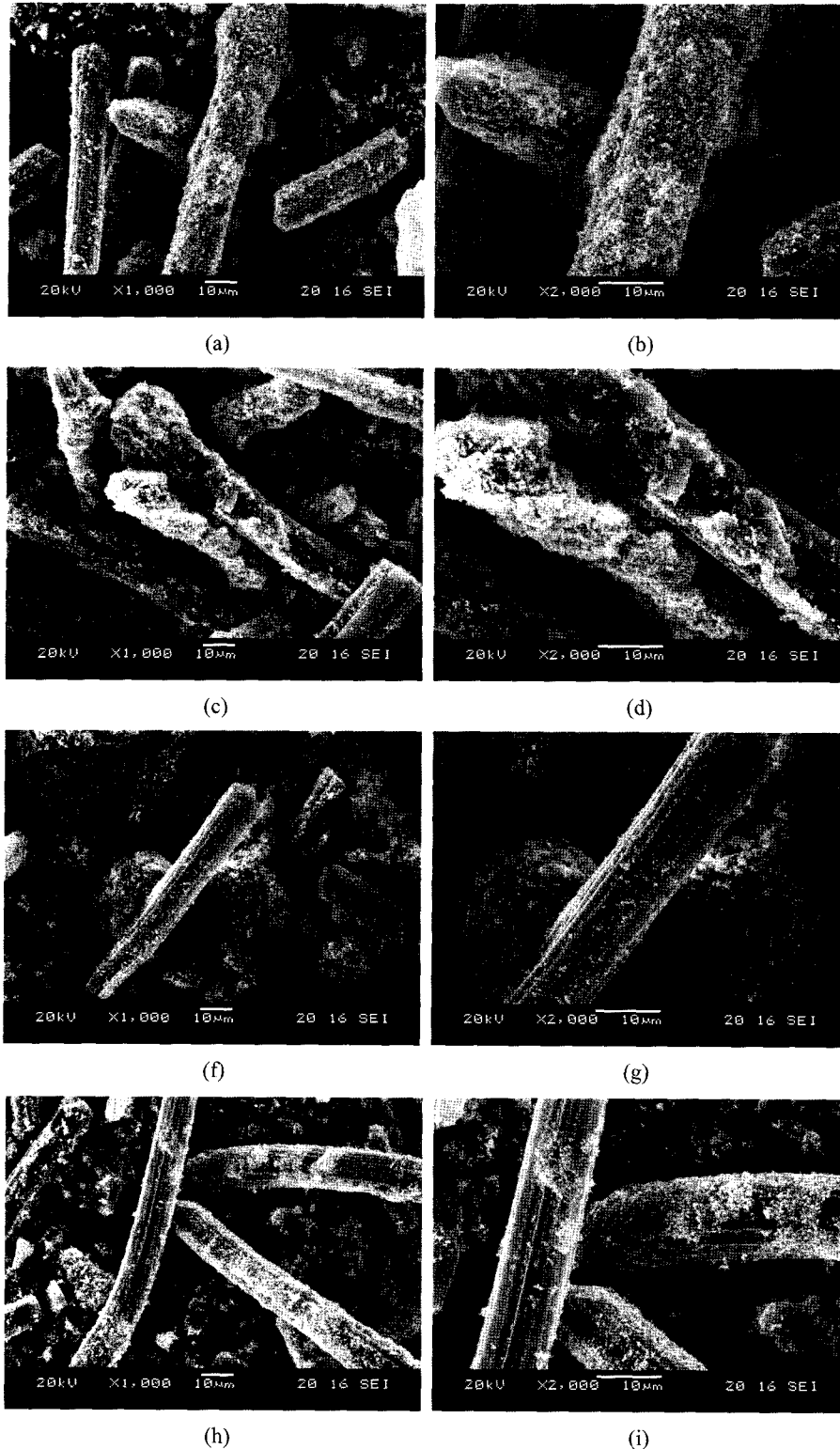


Fig. 1. SEM images of ACF/TiO₂ composite prepared with different mixing ratios; (a) AFT1 ($\times 1000$), (b) AFT1 ($\times 2000$), (c) AFT2 ($\times 1000$), (d) AFT2 ($\times 2000$), (e) AFT3 ($\times 1000$), (f) AFT3 ($\times 2000$), (h) AFT4 ($\times 1000$), and (i) AFT4 ($\times 2000$).

could be attributed to the blocking of micropores during pitch coating. It is considered that the dissolved pitch can block the ACF pore, but the porosity of carbons is reproduced by heat treatment. It may be the case that increases

of composite surfaces porosity allow for more efficient removal pollutants through adsorption.

SEM images of ACF/TiO₂ composites are shown in Fig. 1. It was observed that the pitch was covered with ACF/TiO₂

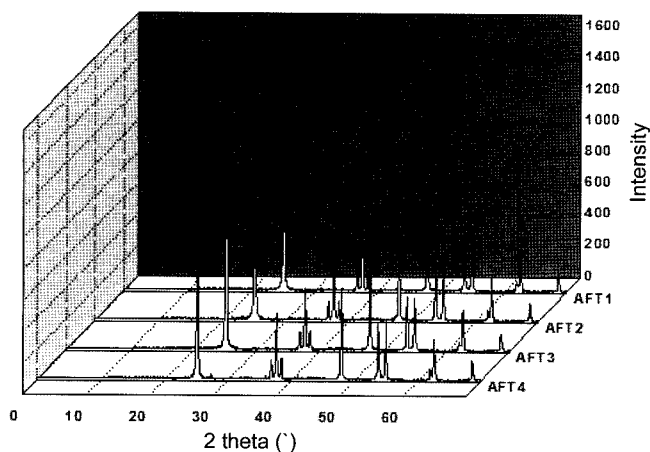
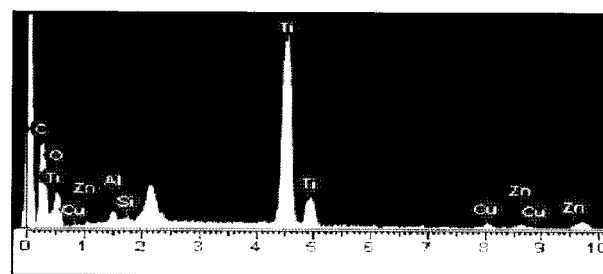


Fig. 2. XRD patterns of ACF/TiO₂ composites heat-treated at 1023 K.

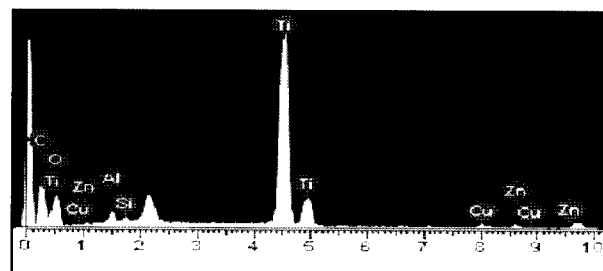
particles. The TiO₂ particles irregularly mounted on and around the ACF with carbon precursor pitch. Some large clusters occurred when the amount of TiO₂ increased (AFT4). In contrast, homogenous ACF and TiO₂ distribution with good particle dispersion was observed when the mixing ratio was 9.0:55.0:36.0 (AFT1) between ACF and TiO₂. It is considered that a good dispersion of small particles could provide more reactive sites on the composite surface for the pollutants than aggregated particles. The quantum efficiency of the electron from the photocatalyst particle interior to the surface and the recombination rate of electron-hole pairs of the photocatalyst were investigated in.⁷⁾ In this study, the samples obtained after heating with pitch and TiO₂ with various mixing ratios of ACF were shown to have a granular and stick-like form above 1023 K. Accordingly, high photocatalytic yields were expected for homogenous and small TiO₂ particle distributions (AFT3). Therefore, the higher degradation activity of the sample prepared (AFT3) might be attributed to the photo-decomposition and adsorptivity between the TiO₂ and ACF produced through the binding effect of good pitch dispersion. These carbon-coated solid particles have been investigated and reported for the various types titania.^{8,9)} The ACF and TiO₂ particles became pronounced and coarse through pitch treatment, and the size of the particles remained large. Aggregated particles with a diameter size of around 10~20 μm were observed. Most of the particles and stick-like forms were sintered together, and became predominantly aggregated, though a limited amount of small particles still remained. On the other hand, when ACF/TiO₂ was treated with pitch, many granular particles with regular surface observed, which we suppose was due to the coagulation by pitch as a binder.

3.2. Structural and elemental analyses

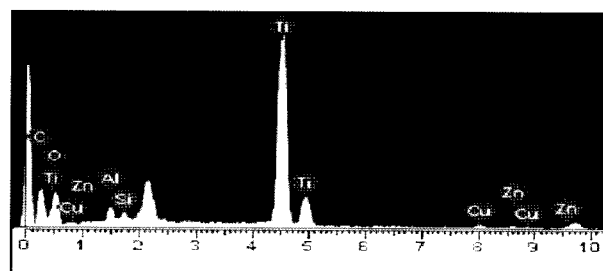
The changes in XRD pattern on the ACF/TiO₂ composites prepared with heat treatment at 1023 K are shown in Fig. 2. In the XRD patterns for all ACF/TiO₂ composites, diffraction peaks of carbon were not observed because of the low crystallinity of this amorphous carbon. The XRD patterns of



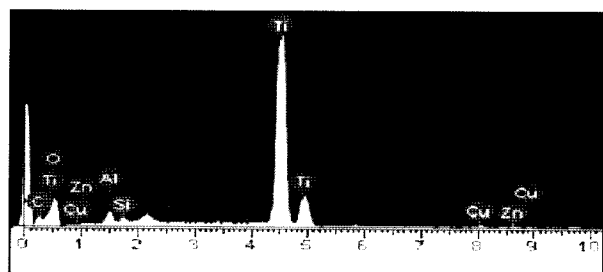
(a)



(b)



(c)



(d)

Fig. 3. EDX elemental microanalysis of ACF/TiO₂ composites prepared with different mixing ratios; (a) AFT1, (b) AFT2, (c) AFT3 and (d) AFT4.

the ACF/TiO₂ composite showed the formation of anatase crystallites. Also, the XRD patterns of the ACF/TiO₂ composite did not have any diffraction peaks corresponding to the inorganic phase, with the exception of anatase peaks. This indicates that it was well dispersed inside and outside the ACF matrix, with the formation of a crystal. The increase in the carbon contents is not affected to TiO₂ structural formation progress. The major peaks at 25.3, 37.8, 48.0, 53.8, 54.9 and 62.5 are diffractions of (101), (004), (200), (105), (211) and (204) planes of anatase, respectively, indicating the developed TiO₂ existed in anatase state. After the heat treatment at 1023 K for 1 h, the main crystalline

Table 3. EDX Elemental Microanalysis of ACF/TiO₂ Prepared with Different Mixing Ratios

Samples	C	O	Si	Ti	Others
AFT1	21.5	26.5	0.84	51.9	0.70
AFT2	19.4	27.3	0.56	47.4	
AFT3	22.6	25.3	0.45	41.3	0.66
AFT4	32.7	28.3	0.37	34.0	0.56

phase was not transformed to rutile structure.

These composites were analyzed by EDX for the quantitative microanalysis of C and Ti as major elements for the ACF/TiO₂ composites as a function of mixing ratios. These EDX spectra of ACF/TiO₂ composites are shown in Fig. 3. The carbon-coated solid particles and composite typed carbon for the elemental analyses have been reported on for the various types titania.^{5,6,10} In this study, the spectra were shown the presence as major elements of C, O and Si with strong Ti peaks. Most of these samples were richer in carbon and major Ti metal than in any other elements. The numerical results of EDX quantitative microanalysis of the ACF/TiO₂ composite series are listed in Table 3. In the case

of most of the samples, carbon and titanium were present as major elements with small quantities of other elements in the ACF/TiO₂ samples. These results were presented the tendency of each sample and show that spectra corresponding to almost all samples become rich in C with an increase of the amount of ACF. It should be noted that a decrease of the C content was observed for all the composite samples as Ti content increase.

3.3. Photocatalytic activity

The various UV/VIS spectra of MB concentration against the ACF/TiO₂ composites as a function of various time conditions are shown in Fig. 4. As can be seen from the spectra, the absorbance maxima of MB concentration for all samples slowly decrease with increase of UV irradiation time. This implies that the transparent of the MB concentration highly increases due to the photocatalytic degradation effect of the ACF/TiO₂ composites. These results clearly show two types of adsorption of MB into the ACF/TiO₂ samples. The first one is the adsorption of MB into the micropores of the ACF and the surface coated carbon derived from pitch that is supposed to have a high surface area. The second type of

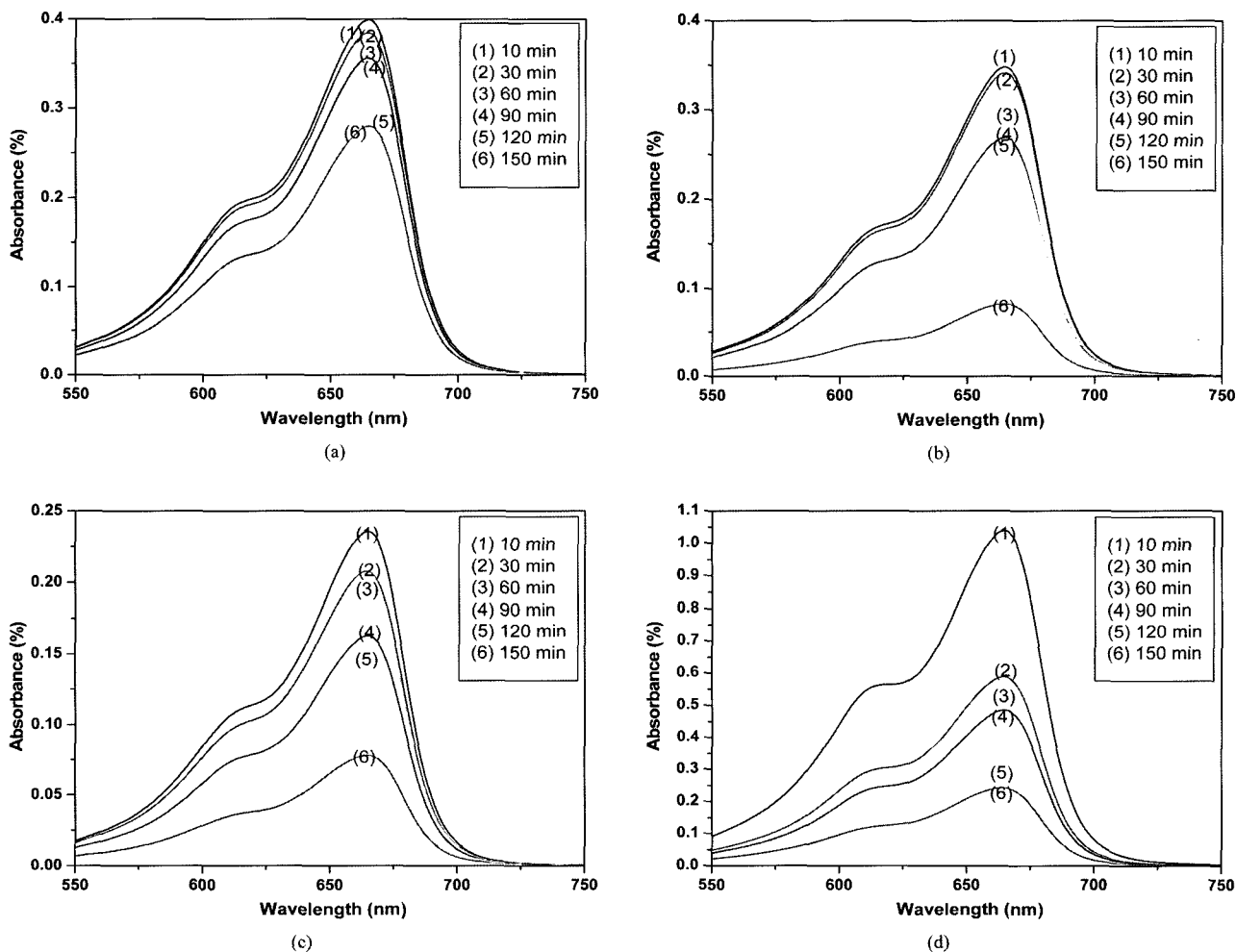


Fig. 4. UV/VIS spectra of MB concentration against the ACF/TiO₂ composites under various time conditions ; (a) AFT1, (b) AFT2, (c) AFT3, and (d) AFT4.

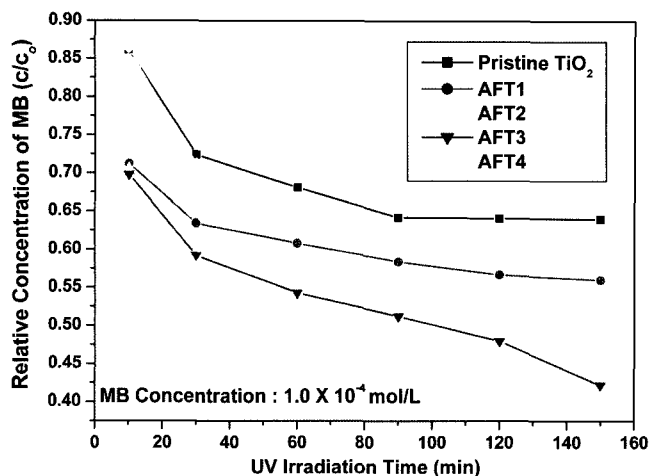


Fig. 5. The plots of relative concentration (c/c_0) of MB in the aqueous solution on time of UV irradiation for the ACF/TiO₂ composites prepared from the different mixing ratios.

adsorption is decomposition via the TiO₂ photocatalytic effect. From the present results, the speed of color fading can be concluded to be faster for the samples (AFT3 and AFT4) with an increased amount of ACF than for the samples (AFT1 and AFT2) with an increased amount of TiO₂. Fig. 5 shows changes in relative MB decomposed concentration under UV light irradiation in the solution as a function of time. The MB decomposition with ACF/TiO₂ composite was carried out to observe the UV photolysis effect for the MB solution. The changes were presented on the relative concentration (c/c_0) of MB in the aqueous solution as a function of UV irradiation time for the samples. In this study, the MB solution was quite unstable with concentration variations when it was irradiated under UV light with ACF/TiO₂ composites. It can be concluded that the disappearance of MB was caused by UV irradiation. The relationship on the c/c_0 of MB in aqueous solution as a function of UV irradiation time has been shown to have approximately linear properties depending on irradiation time, as reported for modified TiO₂ samples.^{11,12} Because the pitch and ACF in the ACF/TiO₂ composites had a large adsorptivity with a high surface area, as mentioned above, it is believed that the decrease of MB concentration in the aqueous solution could have occurred through two physical phenomena such as adsorption by two kinds of carbons and photocatalytic decomposition by TiO₂. According to Oh et al.,^{5,6,10} MB adsorbed on the activated carbon particles can be eventually degraded by the TiO₂ particles in solution for the case of a TiO₂ and activated carbon mixture. It is considered that the TiO₂ deposited on the surface of activated carbon can retain its photo-decomposition activity. In this paper, the excellent decomposition activity of ACF/TiO₂ composites could be attributed to the combined effects of the photo-degradation of TiO₂ on the external surface by the CCl₄ solvent method and the excellent adsorptivity of ACF. The combination effect between carbon and TiO₂ has been ascribed^{13,14} to the enhanced adsorption of the pollutants on activated carbon

followed by a transfer through an interphase to titania where it is photo-degraded. From the decomposition results of MB in the solution measured periodically over 150 min, the increase in the contents of ACF results in a significant decomposition effect with decrease of c/c_0 . In terms of photocatalytic performance, it was obtained that the curve for AFT3 of c/c_0 for MB represents lower values than that of any other sample. According to earlier research,¹⁵ MB molecules absorbed energy from irradiation, thereby shifting their delocalized electrons from a bonding to an antibonding orbital. Since MB adsorption likely occurs via π - π interactions between its delocalized electrons and the carbon's graphene layers, it is reasonable that shifts in its electron orbital would alter adsorption. For all the ACF/TiO₂ composites prepared from different mixing ratios, the slope relationships between c/c_0 for MB and UV irradiation time were observed at 1.0×10^{-4} mol/l of MB concentration. From the photo-decomposition results between c/c_0 for MB and UV irradiation time, it was observed that the decomposition efficiencies of MB for the ACF/TiO₂ composites were excellent, and better than that of pristine TiO₂ for all samples. Based on these observations, we therefore can conclude that the decrease of MB concentration should be attributed to both the effects of the photocatalysis of the supported TiO₂ and the adsorptivity of the two kinds of carbons. The photocatalytic decomposition of MB occurs on TiO₂ particles, even on those coated by carbon, and MB adsorption and decomposition occurred on carbon particles. This may be due to the fact that the photo-decomposition reaction is light-excited, and carbon deep inside TiO₂ is not easily accessible to light because of enhanced reflectivity and scattering because of the support and the long traveling distance.

4. Conclusion

In this study, we have prepared pitch-binded ACF/TiO₂ composite through the CTC solvent method. The studied photocatalysts were characterized with surface textural properties and SEM morphology, structural crystallinity and elemental identification between ACF and TiO₂, and photo-degradation performance. The measured textural surface properties demonstrate that there is a slight increase in the BET surface area in composite samples with an increase of the amount of ACF. The SEM morphologies present on the surface structure of the ACF/TiO₂ composites. In the XRD patterns for all ACF/TiO₂ composites, the diffraction peaks showed the formation of anatase crystallites. The EDX spectra showed the presence of C, O and Si with strong Ti peaks. Most of these samples were richer in carbon and major Ti metal than in any other elements. Finally, the excellent decomposition activity of the ACF/TiO₂ composites between c/c_0 for MB and UV irradiation time could be attributed to the both the effects of the photocatalysis of the supported TiO₂ and adsorptivity of the ACF and another carbon derived from pitch.

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