Journal of Ceramic Processing Research. Vol. 8, No. 2, pp. 119~124 (2007)

JOURNAL OF
Ceramic Processing Research

Preparation with different mixing ratios of anatase to activated carbon and their photocatalytic performance

Ming-Liang Chen, Chang-Sung Lim and Won-Chun Oh*
Department of Advanced Materials & Science Engineering, Hanseo University, Chungnam 356-706, Korea

Pitch/activated carbon/TiO_2 composites photocatalysts were prepared by a CCl_4 solvent mixing method with different mixing ratios. Since two types of carbon in the particles had porous structures, the pitch/activated carbon/TiO_2 composite series showed a good adsorptivity and photo-degradation activity. The result of the textural surface properties demonstrates that there is a slight increase in the BET surface area of composite samples with an increase in the amount of activated carbon. The surface properties seen by SEM present a characterization of the porous texture on the pitch/activated carbon/TiO_2 composites and homogenous compositions in the particles for all the materials used. From XRD data, a weak and broad carbon peak of graphene remained and rutile peaks kept some of the anatase structure were observed in the X-ray diffraction patterns for the pitch/activated carbon/TiO_2 composites. The EDX spectra for the elemental identification showed the presence of C, O and S with strong Ti peaks. Most of these samples are richer in carbon and Ti metal than any other elements. From the photocatalytic results, the excellent activity of the pitch/activated carbon/TiO_2 composites of MB (methylene blue) and UV irradiation time could be attributed to both the effects between the photocatalysis of the supported TiO_2 and adsorptivity of the two kinds of carbons.

Key words: Activated carbon, BET surface area, SEM, XRD, EDX, Photocatalytic activity.

Introduction

Porous carbons have been extensively used as adsorbents in industrial technologies related to environmental pollution control due to their well-developed pore structure and excellent adsorption capacity [1-3]. Titanium oxide has also been widely studied as a promising material for an environmental protection approach for the past few decades because of its excellent photocatalytic activity. A number of studies have shown their unique performance in photodegradation of most toxic organic compounds in wastewater [4, 5]. According to former studies for carbon sources, the carbonization of an unlinked resorcinol resin with titanium tetrabutoxide [6], immersion of activated carbon in a TiO_2 sol [7], and mechanical grinding of activated carbon with TiO_2 [8] have been reported for the preparation of carbon/TiO_2 composites.

A composite product of activated carbon and TiO_2 photocatalysts perhaps be offers the merits of an adsorption effect on the porous structure and a light excitation source for the photocatalytic degradation for the pollutants. Among the various supports, activated carbon is very promising for the several reasons ; its adsorption and release capability for the pollutants onto the surface of TiO_2, an increase of charge transfer between the activated carbon and TiO_2 by acidification of surface hydroxyl groups and adsorption of intermediates produced during degradation. We have developed a method for the preparation of activated carbon/TiO_2 composites involving CCl_4 dissolution pitch coating. The CCl_4 dissolution method is expected to have some advantages due to the high diffusivity with a homogenous distribution by non-condensation of pitch in the CCl_4 solution.

In this study, we have prepared hybrid composites of activated carbon and titanium oxide which have the synergistic effects by the combined function of adsorptivity and photoactivity. The CCl_4 dissolution method used the pitch/activated carbon/TiO_2 system in order to optimize mixing effects between TiO_2 and the activated carbon employed. The pitch used was chosen as the precursor to the binding material. The catalysts developed were characterized by BET surface area measurements, X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive X-ray (EDX) spectroscopy and UV/VIS spectrophotometer. The catalytic efficiency of the catalysts developed was evaluated by the photodegradation of methylene blue (MB).

Experimental

Materials

A granular type activated carbon used in this study was prepared from coconut shell. The coconut shell was carbonized first at 773 K, and then activated by steam diluted with nitrogen in a cylinderical quartz

*Corresponding author:
Tel : +82-41-660-1337
Fax: +82-41-688-3352
E-mail: wc_oh@hanseo.ac.kr

Table 1. Nomenclatures of Samples Prepared with Different Mixing Ratios of Anatase to Activated Carbon

Sample	Mixing Ratios	Nomenclatures
Pitch + Activated Carbon + TiO_2	15 : 25 : 60	PAT1
	15 : 30 : 55	PAT2
	15 : 35 : 50	PAT3

tube at a temperature of 1023 K for 30 minutes. These activated carbons were washed with deionized water and dried overnight at ambient temperature. The pitch was used as the carbon precursor for the preparation of pitch/activated carbon/TiO_2 composite photocatalysts. The granular pitch was supplied from Jungwoo Chemical Co. (Korea). The TiO_2 photocatalysts were the commercially available (Duk-San Pure Chemical Co., Korea), which were composed of a single phase of anatase with secondary particles of about 80-150 μm aggregated from the primary particles of about 30-50 μm. This anatase-type titanium dioxide powder had a relatively large BET surface area of about 125 m^2/g. To dissolve the pitch, carbon tetrachloride (Dae-Jung Chemical Co., Korea) was used as solvent. After melting of pitch in CCl_4 solution, TiO_2 powder and activated carbon was mixed with pitch-CCl_4 solution. The powder mixtures prepared with different mixing ratios of anatase to activated carbon were heated at 333 K for 1 h. The solvent in the mixtures was vaporized at 353 K for 6 hours. The agglomerates of pitch/activated carbon/TiO_2 was heated at 1023 K for 1 h and then crushed in an auto miller. The nomenclatures of the samples prepared were listed in Table 1.

Characterization

For the physical parameter measurements, nitrogen isotherms were measured using an ASAP 2010 instruments (Micromeritics, U.S.A) at 77 K. Scanning electron microscopy (SEM, JSM-5200 JOEL, Japan) was used to observe the surface state and structure of pitch/activated carbon/TiO_2 samples prepared through the CCl_4 dissolution method. For the elemental analysis of pitch/activated carbon/TiO_2 samples, energy dispersive X-ray analysis (EDX) was also used. X-ray diffraction patterns were taken using an X-ray generator (Shimatz XD-D1, Japan) with Cu Kα radiation. As part of the analysis of photocatalytic activity, a UV/VIS spectrophotometer (Genspec III (Hitachi), Japan) was used to characterize of catalytic efficiency of pitch/activated carbon/TiO_2 composite photocatalysts. Characterization by methylene blue ($C_{16}H_{18}N_3S$, MB) in water was determined by the following procedure. A pitch/activated carbon/TiO_2 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 environment at room temperature. Each concentration was measured as a function of UV irradiation time from the absorbance in the wavelength range of 550-750 nm of MB measured by a UV/VIS spectrophotometer.

Photocatalytic effect

In order to reveal the photocatalytic effect of the prepared samples, the decomposition reaction of MB in water was followed. Powdered samples of 0.05 g were dispersed by ultrasonication for 3 minuntes. For UV irradiation a UV lamp (20 W, 365 nm) was used at a distance of 100 mm from the solution in a dark box. By sampling 3 ml of solution after removal of the dispersed powders by centrifuging, 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.

Results and Discussion

Surface properties

Table 2 shows the textural properties of the raw materials and pitch/activated carbon/TiO_2 composites. The results of this table demonstrate that there is a slight increase in the BET surface area of composite samples with an increase in the amount of activated carbon. However, almost all surface textural parameters of the composites represent a considerable decrease compared to that of the pristine activated carbon. This can be attributed to the blocking of micropores during the pitch coating. It is expected that the dissolved pitch can block the pores in the activated carbon, but the porosity of then carbons can be recovered by heat treatment. It is noteworthy that increases of surface parameters among the composite series are related to the removal efficiency of MB by adsorptivity. Figure 1 depicts SEM micrographs of the pitch/activated carbon/TiO_2 composite samples. It was observed that the pitch was covered with activated carbon/TiO_2 particles. The TiO_2 particles were regularly distributed around the activated carbon and the carbon precursor pitch. Also some large clusters were found when the amount of activated carbon was increased (PAT3). In contrast, a homogenous activated carbon and TiO_2 distribution with a good particle dispersion was observed when the mixing ratio was 35 :55 between activated carbon and TiO_2. It is considered

Table 2. Textural Properties of Pristine Materials and Pitch/Activated Carbon/TiO_2 composite samples

Sample	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	1829	0.412	1597	17.28
PAT1	728	0.298	572	15.54
PAT2	762	0.310	637	15.83
PAT3	811	0.318	688	16.01

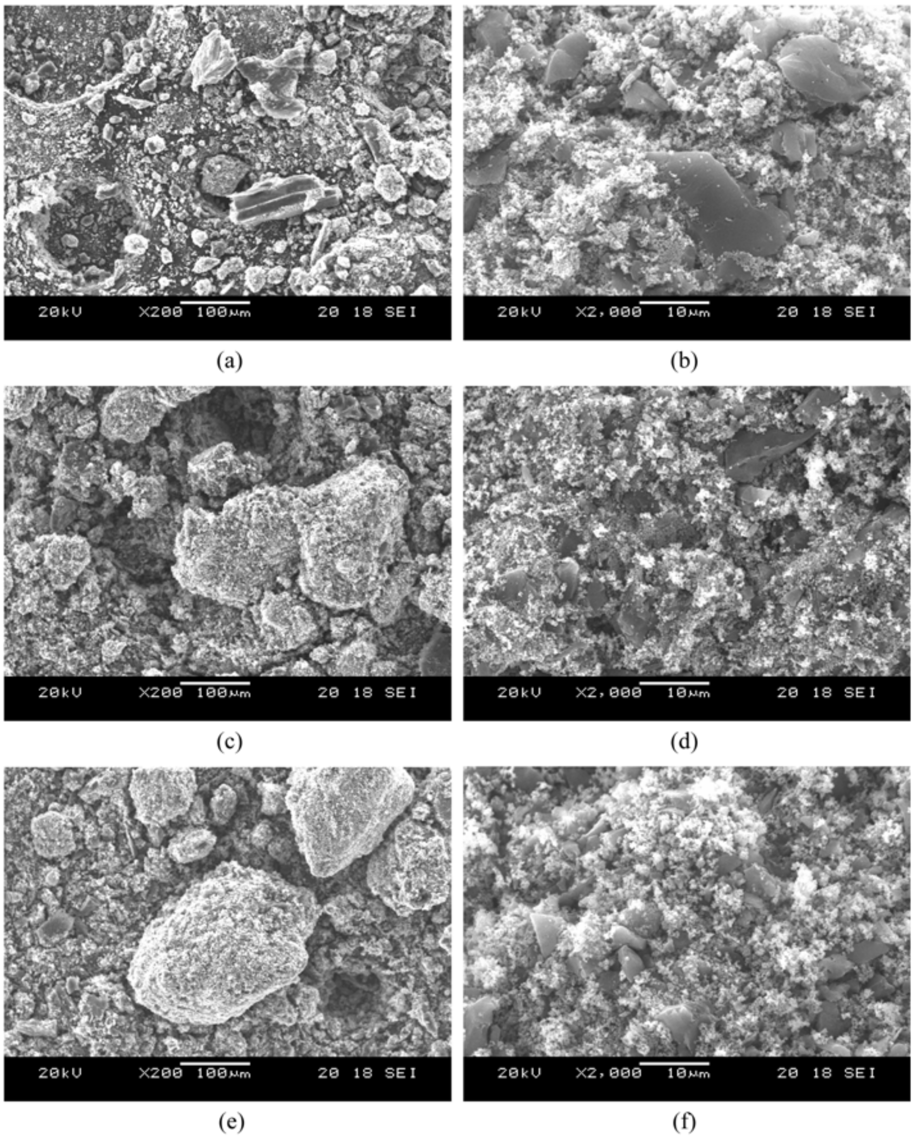


Fig. 1. SEM micrographs of pitch/activated carbon/TiO_2 composites prepared with different mixing ratios; (a) PAT1, (b) PAT1, (c) PAT2, (d) PAT2, (e) PAT3 and (f) PAT3.

that a good dispersion of small particles would provide more reactive sites for the reactants than aggregated particles. It has been reported [9] that the quantum efficiency of an electron from the interior of a photocatalyst particle to the surface and the recombination rate of electron-hole pairs of the photocatalyst is lower. Accordingly, a high photocatalytic yield is expected from a homogenous and small TiO_2 particle distribution (PAT2). Therefore, the higher photocatalytic activity of the sample prepared (PAT2) might be attributed to the homogenous distribution and adsorptivity between TiO_2 and activated carbon produced by the binding effect by the good dispersion of pitch. The TiO_2 particles become pronounced and coarse by the pitch treatment and the size of the particles is kept large. On the other hand, many granular particles with regular surfaces are observed for activated carbon/TiO_2 treated with pitch, which are supposed to be due to the coagulation by pitch as the binder.

Structural and elemental identifications

In Fig. 2, changes in the XRD pattern are shown for the raw TiO_2 and a pitch/activated carbon/TiO_2 composite prepared with a heat treatment at 1023 K. Before the heat treatment, the TiO_2 structure shows the typical anatase type pattern. After the heat treatment at 1023 K for 1 h, however, the main crystalline phase has transformed to rutile structure. Weak and broad amorphous carbon peaks of graphene with rutile peaks were observed in the XRD patterns for the pitch/activated carbon/TiO_2 composites. Even after heat treatment at 1023 K, some anatase phase still remained. The major peaks at 25.3, 37.8, 48.0, 53.8, 54.9 and 62.5 degrees are reflections from (101), (004), (200), (105), (211) and (204) planes of anatase, indicating the TiO_2 developed existed in the anatase state. In the case of pitch/activated carbon/TiO_2

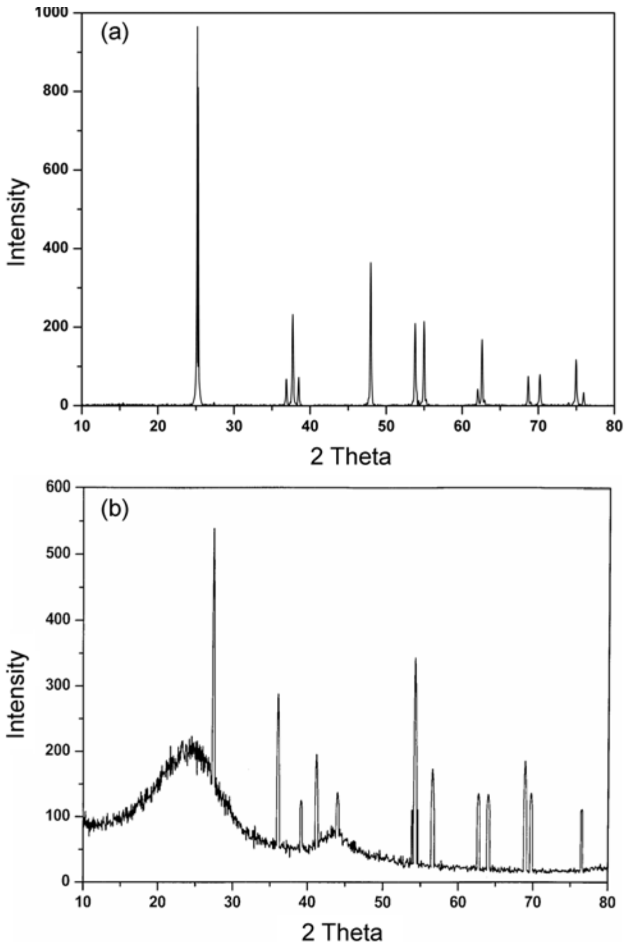


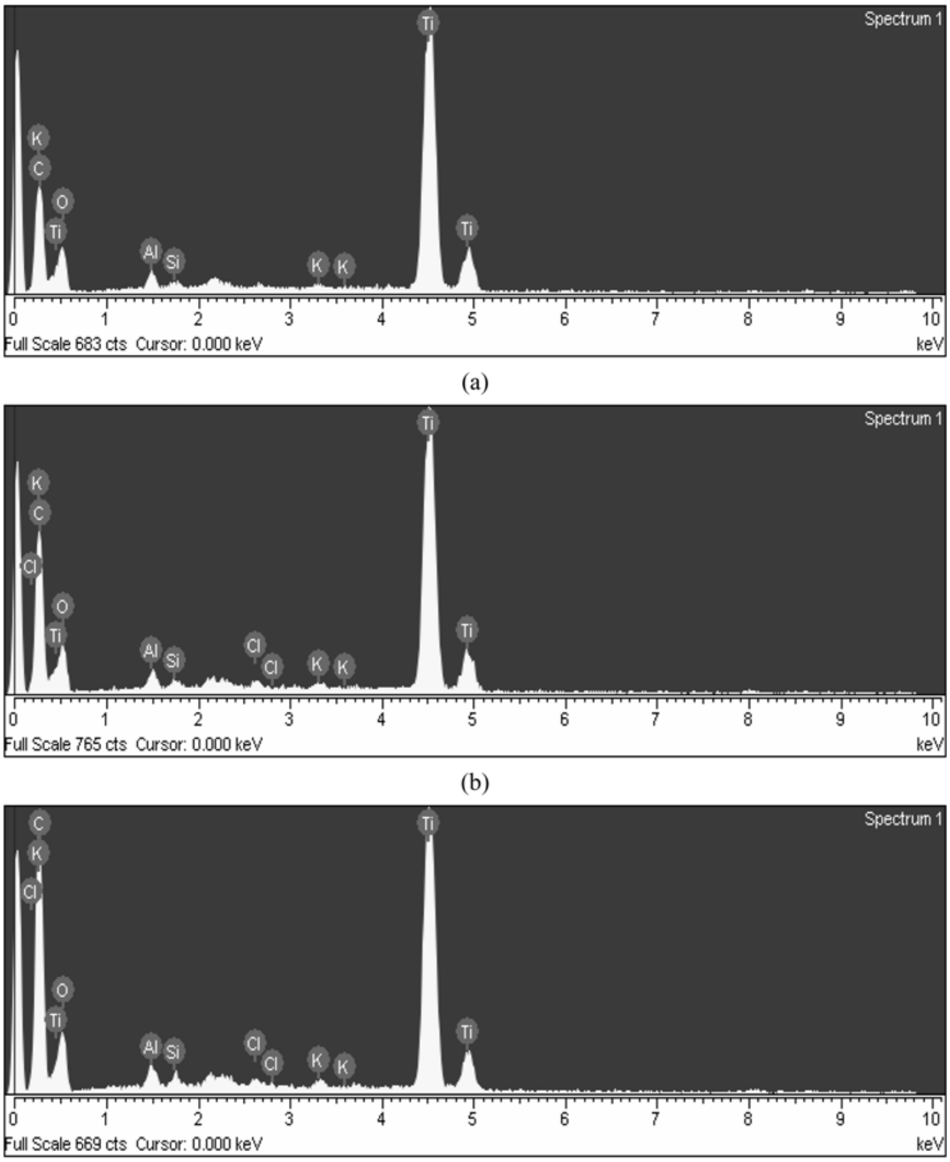
Fig. 2. XRD patterns of (a) raw TiO_2 and (b) a pitch/activated carbon/TiO_2 composite heat-treated at 1023 K (PAT1, PAT2 and PAT3 are commonly presented the same position).

composites, this are major peaks found at 27.4, 36.1, 41.2 and 54.3 degrees that belong to the diffraction peaks from (110), (101), (111) and (211) of rutile. It can be concluded that the pitch/activated carbon/TiO_2 composites developed have a mixture structures between anatase and rutile.

For the elemental microanalysis of pitch/activated carbon/TiO_2 composite samples as a function of mixing ratios, these samples were analyzed by EDX. These EDX spectra of the pitch/activated carbon/TiO_2 composites are shown in Fig. 3. These spectra show the presence of C, O and S with strong Ti peaks. Most of these samples are richer in carbon and major Ti metal than any other elements. The results of EDX elemental microanalysis of the pitch/activated carbon/TiO_2 composite series are listed in Table 3. In the case of most of the samples, carbon and Ti were present as major elements in the pitch/activated carbon/TiO_2 samples. These results were observed for each sample show the spectra corresponding to almost all samples rich in C with an increase of the amount of activated carbon content. It should be note that a decrease of the C and S (impurity element derived from pitch) content with an increase of the Ti content is observed for all the sample series.

Photocatalytic activity

The UV/VIS spectra of MB concentration against the pitch/activated carbon/TiO_2 composites for various times are shown in Fig. 4. As can be seen from the spectra, the absorbance maxima for the all samples slowly decreased with an increase of the UV irradiation time. This implies that the transparency of the MB concentration increased greatly by the photocatalytic degradation effect of the pitch/activated carbon/TiO_2 composites. Figure 5 shows changes in MB concentration under UV light irradiation in the solution. MB removal with pitch/activated carbon/TiO_2 composite photocatalysts was carried out to observe the UV photolysis effect for the MB solution. The changes are plotted on the relative concentration (c/c_o) of MB in the aqueous solution with UV irradiation time for the sample series. It is observed that the MB solution is quite unstable with a variation of concentration when it is irradiated under UV with pitch/activated carbon/TiO_2 composites, suggesting the disappearance of MB is caused by UV irradiation. The relationship showed approximately linear properties depending on irradiation time, as reported on similar modified TiO_2 samples [10, 11]. Because the presence of the pitch and activated carbon in pitch/activated carbon/TiO_2 composite samples had a large adsorptivity, as mentioned above, it is believed that the decrease of MB concentration in the aqueous solution can be related to two physical phenomena such as adsorption by two types of carbon and the photocatalytic decomposition by TiO_2. According to an earlier study [12], MB adsorbed on the activated carbon particles can be eventually degraded by the TiO_2 particles in the solution for the case of the TiO_2 and activated carbon mixture. This suggests that the TiO_2 deposited on the surface of activated carbon can retain its catalytic activity. The synergistic effect has been ascribed [8] to the enhanced adsorption of the pollutants on activated carbon followed by a transfer through an interphase to titania where it is photodegraded. In this study, the excellent photocatalytic activity of pitch/activated carbon/TiO_2 samples could be attributed to the homogeneous coating of pitch on the external surfaces coated by the CCl_4 solvent method and the excellent adsorptivity of activated carbon. From the MB removal results in the solution measured periodically over 50 minutes, an increase in the content of activated carbon results in a significant degradation effect with a decrease in the relative concentration (c/c_o) of MB. In the case of photocatalytic activity, the curve for PAT2 of the relative concentration (c/c_o) of MB represents lower values than that of PAT3. According to earlier workers [13], MB molecules absorb energy from the irradiation, thereby shifting their delocalized electrons from bonding to antibonding orbitals. Since MB adsorption probably occurs *via* π-π interactions between its delocalized electrons and the carbon's graphene layers, it is reasonable to suggest that shifts in the



(a)

(b)

(c)

Fig. 3. EDX elemental microanalysis of pitch/activated carbon/TiO_2 composites prepared with different mixing ratios; (a) PAT1, (b) PAT2 and (c) PAT3.

Table 3. EDX Elemental Microanalysis of Samples Prepared with Different Mixing Ratios of Anatase to Activated Carbon

Nomenclatures	C	O	S	Ti	Others
PAT1	31.3	30.1	1.09	36.9	0.56
PAT2	38.6	27.6	0.95	31.9	0.66
PAT3	45.5	26.5	0.84	26.1	0.70

electron orbitals would alter adsorption. Because the photocatalytic reaction is light excited, carbon deep inside TiO_2 is not easily accessible to light because of enhanced reflection and scattering by the support and the long traveling distance. For all the pitch/activated carbon/TiO_2 composite samples prepared with different mixing ratios, a linear slope relationship between relative concentration (c/c_o) of MB and UV irradiation time were observed at 1.0×10^{-4} mol/l of MB concentration. From the results between the relative concentration (c/c_o) of MB and UV irradiation time, it was observed that the removal efficiency of MB for the pitch/activated carbon/TiO_2 composites is much better then that of pristine TiO_2 for all the samples. Based on these observations, we therefore can conclude that the decrease of MB concentration should be attributed to both effects between photocatalysis of the supported TiO_2 and adsorptivity of the two kinds of carbons.

Conclusions

In this study, we have prepared pitch/activated carbon/TiO_2 composite photocatalysts through a carbon tetra-

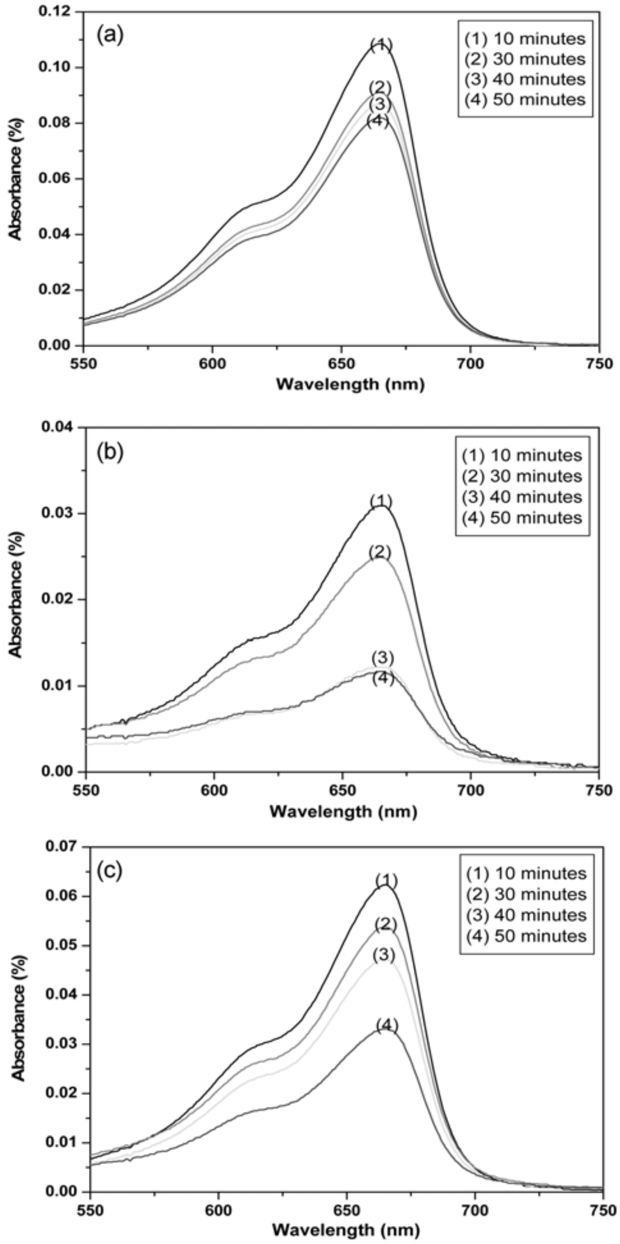


Fig. 4. UV/VIS spectra of MB concentration against the pitch/activated carbon/TiO_2 composites for various times ; (a) PAT1, (b) PAT2 and (c) PAT3.

chloride solvent method. The samples developed were characterized in terms surface properties, structural crystallinity between activated carbon and TiO_2, elemental identification and photocatalytic activity. The result of the textural surface properties demonstrates that there is a slight increase in the BET surface area of composite samples with an increase in the amount of activated carbon. The SEM results give a characterization of the porous texture on the pitch/activated carbon/TiO_2 composites and confirm homogenous compositions in the particles for all the materials used. From the XRD data, a weak and broad carbon peak of graphene remained rutile peaks replaces part of the anatase structure were

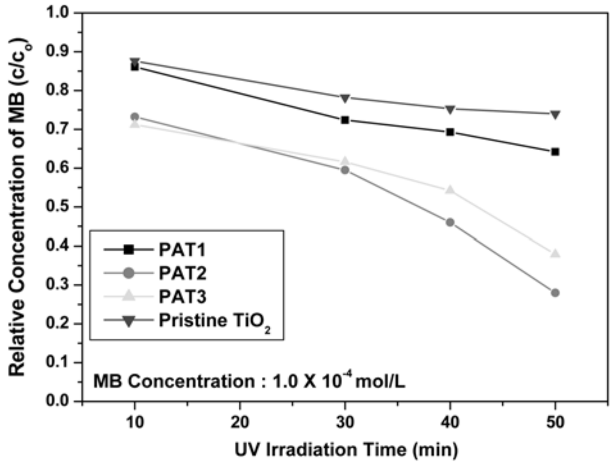


Fig. 5. Dependence of relative concentration (1.0×10^{-4} mol/l) of MB in the aqueous solution c/c_0 on time of UV irradiation for the pitch/activated carbon/TiO_2 composites prepared from the different mixing ratios.

observed in the X-ray diffraction patterns for the pitch/activated carbon/TiO_2 composite samples. The EDX spectra show the presence of C, O and S with strong Ti peaks. Most of these samples are richer in carbon and Ti than any other elements. Finally, the excellent photocatalytic activity of the pitch/activated carbon/TiO_2 composite samples with the relative concentration (c/c_o) of MB and UV irradiation time could be attributed to both the effects between photocatalysis of the supported TiO_2 and adsorptivity by the two types of carbons.

References

1. W.C. Oh, C.S. Park, J.S. Bae, and Y.S. Ko, Carbon Science 7[3] (2006) 180-187.
2. W.C. Oh, C.S. Park, C.S. Lim, and Y.S. Lee, J. Ceramic Processing Research 7[1] (2006) 37-48.
3. W.C. Oh, J.S. Bae, and Y.S. Ko, Carbon Science 7[2] (2006) 105-113.
4. A.L. Linsebigler, G.Q. Lu, and J.T. Yates, Chem. Rev. 95 (1995) 735-58.
5. J. Motos, J. Laine, and J.M. Hermann, J. Catal. 200 (2001) 10-20.
6. F.J. Maldnano-Hodar, C. Moreno-Castilla, and J. Rivera-Utrilla, Appl. Catal. A 203[1] (2000) 151-9.
7. T. Torimto, S. Ito, S. Kuwabata, and H. Yoneyama, Environ. Sci. Technol. 30[4] (1996) 1275-81.
8. J. Matos, J. Laine, and J.M Hermann, Carbon 37[11] (1999) 1870-2.
9. M. Graetzel, and A.J. Frank, J. Phys Chem. 86 (1982) 2964-7.
10. X. Zhang, M. Zhou, and L. Lei, Carbon 44 (2006) 325-33.
11. W.C. Oh, C.S. Park, C.Y. Park, A.R. Jung, and M.L. Chen, Conference Proceeding of Korea Carbon Society p.94 (2006).
12. X. Zhang, M. Zhau, and L. Lei, Carbon 43 (2005) 1700-1708.
13. R.P. Schwarzenbach, P.M. Gschwend, and D.M. Imboden, *Environmental organic chemistry,* 2nd Ed., John Wily and Sons (2002).