

Fabrication and Physicochemical Properties of Carbon/Titania/Bentonite Monolith for Architecture

Won-Chun Oh^{*†}, Jong-Geun Choi^{*}, Da-Ye Song^{*}, Ha-Rry Kim^{*},
Ming-Liang Chen^{*}, Feng-Jun Zhang^{***} and Tong-So Park^{***}

^{*}Department of Advanced Materials & Science Engineering, Hanseo University, Seosan-si, Chungnam-do, Korea, 356-706

^{**}Anhui Key Laboratory of Advanced Building Materials, Anhui University of Architecture, Anhui Hefei, P. R. China, 230022

^{***}Department of Architectural Engineering, Hanseo University, Seosan-si, Chungnam-do, Korea, 356-706

(Received March 3, 2010 : Received in revised form March 17, 2010 : Accepted March 17, 2010)

Abstract In this study, we used activated carbon (AC) and titanium oxysulfate as a titanium precursor to prepare carbon/titania composites. We then mixed it with bentonite in different ratios to make a carbon/titania/bentonite monolith for use in architecture bricks by using Phenolic rosin (PR) as a bonding agent. The physicochemical properties of the prepared composites were analyzed by BET surface area, scanning electron microscopy (SEM), X-ray diffraction (XRD), energy dispersive X-ray analysis (EDX), self-cleaning effect and bactericidal tests. The BET surface areas increased as the ratio of carbon/titania composites increased. The SEM microscopy showed that the TiO₂ and bentonite were coated on the surface of the AC. The XRD patterns showed a mixture structure of anatase and rutile of TiO₂ with a clear SiO₂ structure. The EDX spectra of the carbon/titania/bentonite monolith confirmed the presence of various elements, namely C, O, Ti and Si, as well as other, impure elements. Moreover, to determine the self-cleaning effect of the carbon/titania/bentonite monolith, we used methylene blue (MB, C₁₆H₁₈N₃S·Cl·3H₂O) in an aqueous solution under the irradiation of visible light. Accordingly, all of the samples had excellent degradation of the MB solution. Furthermore, it was observed that the composites with sunlight irradiation had a greater effect on *E. coli* than any other experimental conditions.

Key words activated carbon, titania, bentonite monolith, self-cleaning effect, bactericidal tests.

1. Introduction

Titanium dioxide (TiO₂) is one of the most intensively studied heterogeneous photocatalysts for the photodegradation of toxic organic pollutants because it is non-toxic, relatively cheap, chemically stable within a wide pH range and robust under UV light irradiation.¹⁻⁶ However, TiO₂ photocatalysts can only absorb UV light due to their band structure. Unfortunately, UV light in sunlight accounts for only 3-5% of the overall energy of the sunlight reaching earth's surface, and the artificial UV light is expensive. Therefore, the applications of TiO₂ in photocatalytic reactions are impeded. Recently, we have reported the photodegradation of some organic dyes using TiO₂ under visible light irradiation.^{5,6} It is significant for both fundamental and practical studies because of its unique mechanism and the perspective in treatment of dye pollutants under sunlight. Besides, for the photocatalysis processes in which fine TiO₂ powders

are used as catalysts, an important issue is to recover fine TiO₂ powders from aqueous suspensions. Since the photocatalytic reactions occur on the catalyst surface, the catalyst with a larger specific surface area is expected to have a higher catalytic activity. The composite mesoporous structures of TiO₂ nano-crystals and clay layers are highly efficient photocatalysts because in such a structure discrete anatase crystals existing on clay layers have a large specific surface area. A composite structure of TiO₂/bentonite with a large surface area can be prepared readily. Moreover, TiO₂/bentonite powders can be easily recovered from aqueous suspensions, and this leads to a potential advantage in downstream separation. Therefore, TiO₂/bentonite can be a superior photocatalyst for practical application.

Several attempts have been also adopted to enhance the photocatalytic performance of TiO₂, such as immobilization of TiO₂ powder onto supports like activated carbon (AC),⁷⁻¹⁵ activated carbon fiber (ACF),¹⁶ and so on. AC is highly adsorptive owing to its developed pore structure and high specific area; moreover the particle size of commercial AC is usually in the micro-scale range.

[†]Corresponding author
E-Mail : wc_oh@hanseo.ac.kr (W. C. Oh)

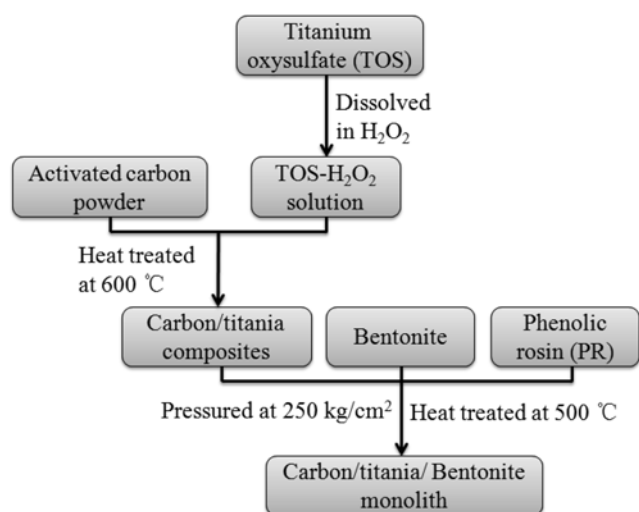


Fig. 1. The procedure of carbon/titania/bentonite monolith.

And it has been indicated that AC/TiO₂ composites could be enhanced the photocatalytic activity of TiO₂ in our previous studies.¹⁷⁻¹⁹⁾

In this study, we used AC, titanium source (TOS, TiOSO₄) and bentonite with phenolic rosin (PR) as a bonding agent to prepare carbon/titania/bentonite monolith for architecture used. And the prepared monolith was characterized by several technologies such as BET, scanning electron microscopy (SEM), X-ray diffraction (XRD) and energy dispersive X-ray analysis (EDX). Moreover, to determine the self-cleaning effect of carbon/titania/bentonite monolith, we used the methylene blue (MB, C₁₆H₁₈N₃S·Cl·3H₂O) in an aqueous solution under the irradiation of visible light. Furthermore, the bactericidal effect of carbon/titania/bentonite monolith irradiated with sunlight on *E. coli* was also evaluated, and the dose-dependent efficacy of monolith was investigated by a colony-forming unit (CFU) assay. The CFU assay is useful for studying the efficacy of bacterial adhesion of monolith.

2. Experimental Procedure

2.1 Materials

A porous and powder 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 minutes. This AC was washed with deionized water and dried overnight in a vacuum drier at over 683 K. The size of used AC is less than 150 mesh. The TOS as titanium source was purchased from Sigma-Aldrich. And the hydrogen peroxide (H₂O₂) was purchased from DaeJung Chemicals & Metals Co., Ltd, to dissolve the TOS. The bentonite (100% sodium) which

Table 1. Nomenclatures of carbon/titania/bentonite monolith.

Preparation ratios	Nomenclatures
(3% carbon/titania composites + bentonite) 10 g + 20% PR	AT3
(6% carbon/titania composites + bentonite) 10 g + 20% PR	AT6
(9% carbon/titania composites + bentonite) 10 g + 20% PR	AT9
(12% carbon/titania composites + bentonite) 10 g + 20% PR	AT12

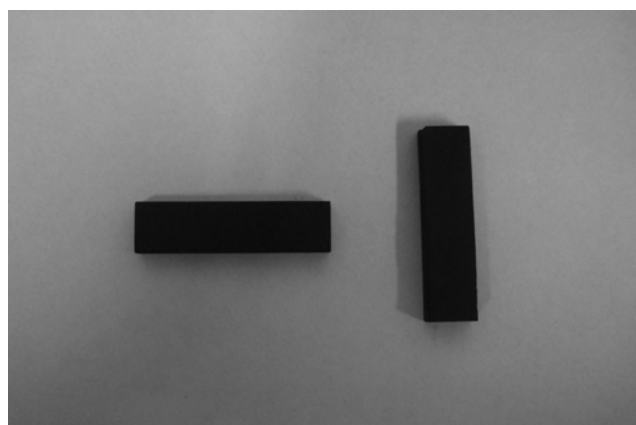


Fig. 2. The photo of prepared monolith.

used as a starting material was obtained from Volclay Korea. Phenolic rosin (PR) was used as a bonding agent, which purchased from KangNam Chemical Co., Ltd.

2.2 Synthesis of carbon/titania/bentonite monolith

2.2.1 Preparation of carbon/titania composites

At first, TOS was dissolved in the H₂O₂ to prepare TOS-H₂O₂ solution. And then AC powder was put into TOS-H₂O₂ solution and stirred at room temperature for 3 hours. After stirring, the mixture was on standing until the solution and solid matters were separated. Dumped the solution and the solid matters were dried at 100°C. After the solid matters heat treatment at 600°C for 1 h, the carbon/titania composites were obtained.

2.2.2 Preparation of carbon/titania/bentonite monolith

Prepared carbon/titania composites were mixed with bentonite by different quality ratios together with a content of PR, and then pressed the monolith into a mould at a pressure of 250 kg/m²; the dimensions of mold were 9.95 × 39.5 × 5.95 mm. The curing temperature of the monolith was at room temperature, and the cured sample was heat treated at 500°C for 1 h to completely cure the binder. This procedure was shown in Fig. 1. And several samples were prepared by changing the ratios of starting materials and the nomenclatures of

Table 2. The BET surface area of carbon/titania/bentonite monolith.

Samples	S_{BET} (m^2/g)
AT3	154.32
AT6	208.75
AT9	306.48
AT12	342.85

samples were listed in Table 1. And the photos of prepared monolith were showed in Fig. 2.

2.3 Characterization of carbon/titania/bentonite monolith

The surface area of the carbon/titania/bentonite monolith was evaluated from an N_2 adsorption isotherm at 77 K with a BET analyzer (Monosorb, USA). A scanning electron microscope (JSM-5200, JEOL, Japan) was used to observe the surface states and structure of the carbon/titania/bentonite monolith. The X-ray diffraction patterns were taken by an X-ray generator (Shimadzu XD-D1, Japan) with $\text{Cu K}\alpha$ radiation. For the elemental analysis of the carbon/titania/bentonite monolith, we also used an EDX technique.

2.4 The self-cleaning effect of carbon/titania/bentonite monolith

The self-cleaning effect of carbon/titania/bentonite mono-

lith was determined by using MB solution under irradiation of visible light (8W, KLD-08L/P/N, Fawoo Technology). The initial MB concentration was 1.0×10^{-5} mol/L (c_0). The amount of suspended composites was kept at 1 g/L in 50 mL MB solution. Before turning on visible lamp, the solution mixed with composites was kept in the dark for at least 2 h, allowing the adsorption-desorption equilibrium to be reached. Then, the solution was irradiated with visible light. The first sample was taken out at the end of the dark adsorption period (just before the light was turned on) in order to determine the MB concentration in solution, which was hereafter considered as the initial concentration (c_{ads}) after dark adsorption. Samples were then withdrawn regularly from the reactor by an order of 30, 60, 90, 120 and 150 min, and immediately centrifuged to separate any suspended solid. The clean transparent solution was analyzed by using a UV/VIS spectrophotometer (250–600 nm).²⁰ The spectra (550–750 nm) for each sample were recorded and the absorbance was determined at characteristic wavelength 660 nm for the each MB solution degraded.

2.5 Bactericidal tests

E. coli strains were used in this study. *E. coli* was grown in Trypticase Soy Broth (TSB badge, ca. 394 K, 15 min) at 37°C for several days under aerobic conditions. The bacteria were harvested by centrifugation at $2500 \times$

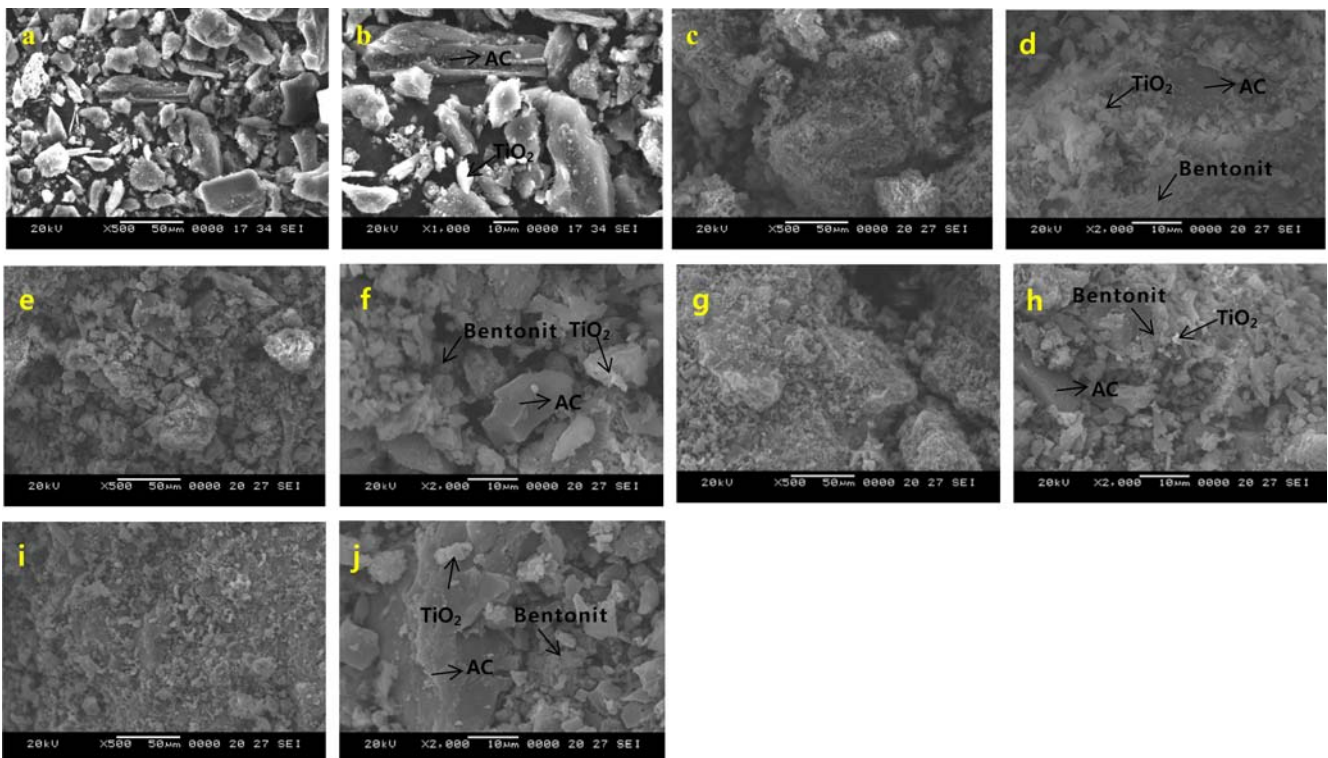


Fig. 3. The SEM images of carbon/titania composites and carbon/titania/bentonite composites; carbon/titania composites (a and b); AT3 (c and d); AT6 (e and f); AT9 (g and h) and AT12 (i and j).

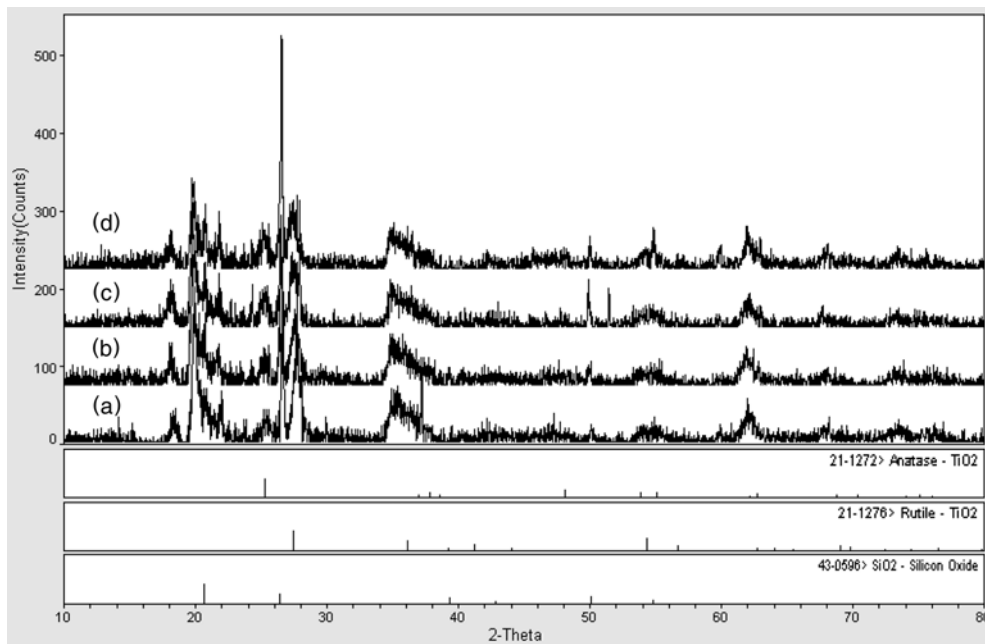


Fig. 4. XRD patterns of carbon/titania/bentonite composites. (a) AT3, (b) AT6, (c) AT9 and (d) AT12.

g and suspended in TSB broth at a concentration of 6.2×10^5 CFU/mL. The carbon/titania/bentonite monolith was then inoculated with 5 μ l of the *E. coli* culture solution, followed by irradiation with sunlight or in dark. The monolith was incubated for 24 h at 37°C under conditions of constant humidity, and the colonies were then counted.

3. Results and Discussions

3.1 Structure and morphology of carbon/titania/bentonite monolith

The values of the BET surface areas of carbon/titania/bentonite monolith are shown in Table 2. Table 2 shows that the BET surface areas of samples AT3, AT6, AT9 and AT12 were 154.32, 208.75, 306.48 and 342.85 m²/g, respectively. These results demonstrate that there is a marked increase in the BET surface area of the carbon/titania/bentonite monolith as the ratios of carbon/titania composites increase.

Fig. 3 shows the SEM image of carbon/titania composites and carbon/titania/bentonite composites. Comparing of SEM image of carbon/titania composites, it can be seen that AC particle is missive with larger particle size; TiO₂ particle have relative smaller size and looked white; bentonite particle have fine structure with very smaller size. Moreover, TiO₂ particles were dispersed and fixed on the surface of AC can be observed from Fig. 2 (a and b). After mixing with bentonite and heat treatment at 500°C, from the Fig. 2 (c-j), we can see that a new material was obtained, and it mixed with TiO₂

together coated on the surface of AC, just bentonite. From the Fig. 2, we can also observe that the size of bentonite is smaller than that of TiO₂, and the amount of bentonite is decreased as increasing the amount of carbon/titania composites.

The XRD spectra of carbon/titania/bentonite monolith are shown in Fig. 4. The structure for the carbon/titania/bentonite monolith shows a mixture of anatase and rutile structures. It is well known that the crystal structure of titanium dioxide is mainly determined by the temperature of the heat-treatment. After heat treatment at 600°C for 1 h, one part of main crystalline phase is transformed to rutile structure. The peaks at 25.3, 37.8, 48.0, 53.8 and 62.5 are diffractions of the (101), (004), (200), (105) and (204) planes of the anatase, and the peaks at 27.4, 36.1, 41.2 and 54.3 belong to the diffraction peaks of (110), (101), (111) and (211) of rutile, indicating that the developed carbon/titania/bentonite monolith exist in a mixture structure anatase and rutile. Because the anatase phase formed below 500°C starts to transform to rutile-type structure above 600°C and changed into single phase of rutile at 700-900°C.²¹⁻²³⁾ Moreover, some other peaks are also found at 20.8, 26.5, 39.2 and 50.2, belong to SiO₂ structure, which derived from the bentonite.

Fig. 5 shows the EDX spectra of the carbon/titania/bentonite monolith. From the Fig. 4, it can be confirmed that the existence of elements, namely C, O, Ti and Si, as well as other impure elements. Table 3 also lists the results of EDX elemental microanalysis (wt. %) of all kinds of elements. It can be observed that the four

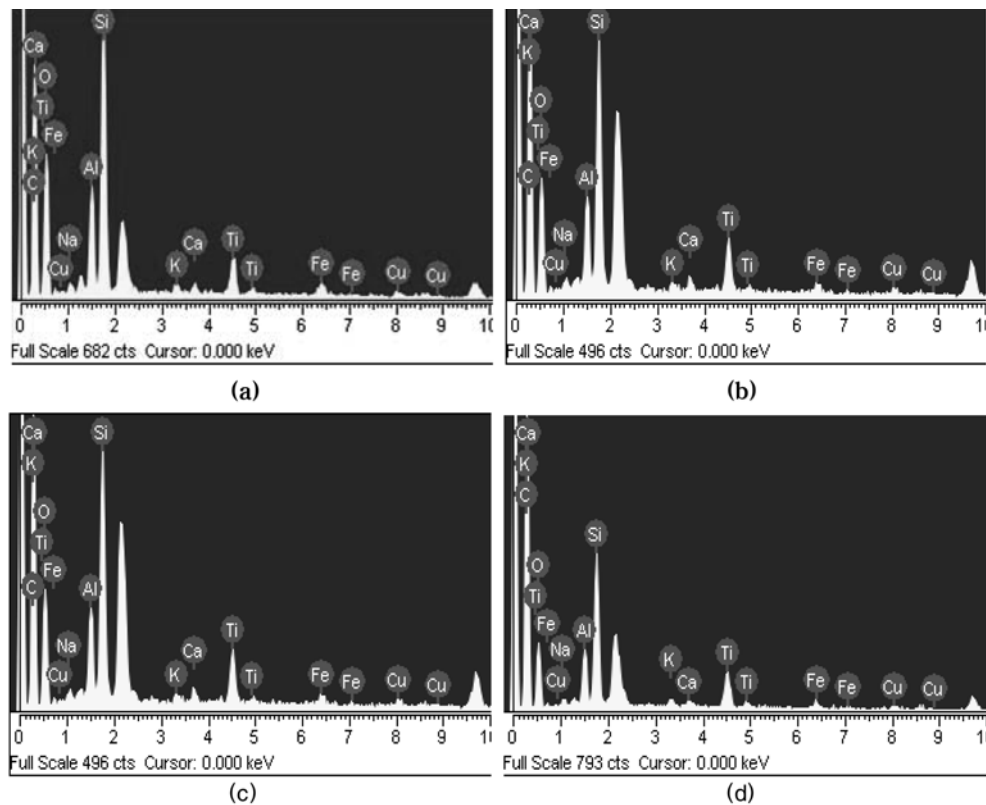


Fig. 5. EDX elemental microanalysis of carbon/titania/bentonite composites; (a) AT3, (b) AT6, (c) AT9 and (d) AT12.

Table 3. EDX Elemental Microanalysis (wt. %) of carbon/titania/bentonite monolith.

Samples	Elements				
	C	O	Ti	Si	others
AT3	48.75	33.17	2.52	8.41	7.15
AT6	52.38	30.33	3.3	7.29	6.7
AT9	59.21	25.98	4.03	5.56	5.22
AT12	61.66	23.88	4.65	5.82	3.99

kinds of main elements (C, O, Ti and Si) percentages are 92.85%, 93.3%, 94.78% and 96.01%, and the impure elements percentages are 7.15%, 6.7%, 5.22% and 3.99% for samples AT3, AT6, AT9 and AT12, respectively. It can be indicated that the prepared samples mainly have four kinds of elements C, O, Ti and Si. Furthermore, the C and Ti content are increased as the ratios of carbon/titania composites increased. It can be considered that the self-cleaning effect would be increased by increasing of C and Ti content.

3.2 Self-cleaning effect of carbon / titania / bentonite monolith

To study the self-cleaning effect of carbon/titania/bentonite monolith, we investigated the decomposition of MB in the water. Fig. 6 shows the changes in the relative concentration (c/c_0) of the carbon/titania/bentonite

monolith in an MB concentration of 1×10^{-5} mol/L under visible light. As mentioned above, before turning on visible light, the MB solution mixed with composites was kept in the dark for at least 2 h, allowing the adsorption-desorption equilibrium to be reached. The adsorption ability of MB solution is 77, 88, 51 and 59% for samples AT3, AT6, AT9 and AT12, respectively. According to BET surface area, samples AT9 and AT12 have bigger surface area than samples AT3 and AT6. However, they have lower adsorption ability than AT3 and AT6. Because the samples AT9 and AT12 have relative more amount of bentonite than samples AT3 and AT6, and these bentonite coated on the surface of AC, and the particle size and pore size of bentonite are much less than that of AC, thus the MB particles are adsorbed by AC easier than bentonite, accordingly, samples AT9 and AT12 have lower adsorption ability than samples AT3

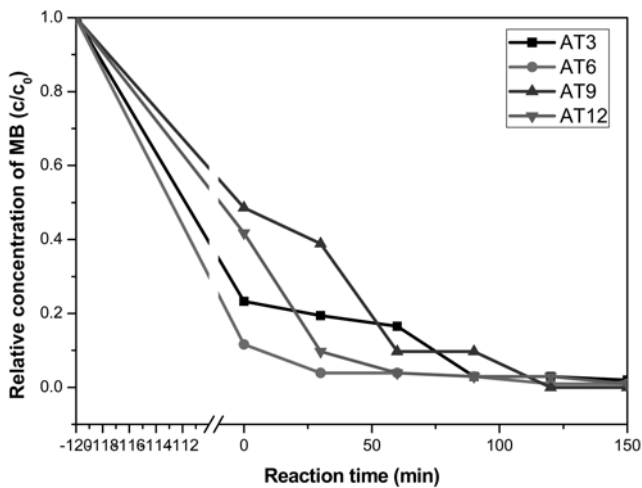


Fig. 6. Dependence of relative concentration of MB in the aqueous solution c/c_0 on time of visible light irradiation for the CNT/TiO₂ composites; the concentration of MB: 1.0×10^{-5} mol/L.

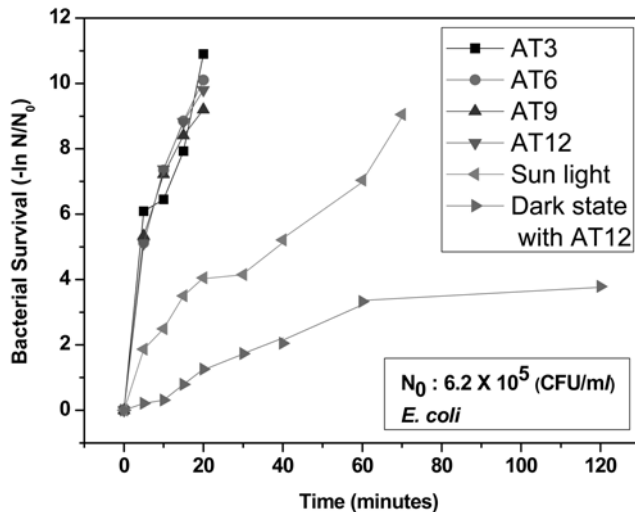


Fig. 7. The bactericidal effect of carbon/titania/bentonite monolith irradiated with sunlight.

and AT6. After adsorption by 2 h, the visible light was turned on, the photocatalytic react is beginning. After irradiation by 150 min, the MB solution is almost decomposed at all for all of samples. However, the photocatalytic activities of samples are different at different period. The concentration of MB solution is decreased a lot after irradiation of visible light by 60 min for samples AT6, AT9 and AT12, and decreased slowly at later 120 min. But the sample AT3 show a smooth decrease at first 60 min of irradiation time, and decreased quickly at period from 60 min to 90 min. It seems that the samples AT9 and AT12 show much more photocatalytic activities than samples AT3 and AT6, which removed 49 and 41% of the MB solution. Due to the samples AT9 and AT12 have much amount

of TiO₂ than the samples AT3 and AT6. In our previous works,^{24,25} carbon can act as an electron sensitizer and donator in the composite photocatalyst to accept the photo-induced electron (e^-) into conduction band of the TiO₂ particles under irradiation of light, thus increasing the amount of electron, thereby increasing the rate of the electron induced redox reaction. So the photocatalytic activity of TiO₂ can be improved.

3.3 Bactericidal tests

Fig. 7 shows the effect of carbon/titania/bentonite monolith on the *E. coli* with or without sunlight as a function of time. The total time of bacterial abatement was shorter under the monolith with sunlight condition than under other conditions. Based on the bacterial survival number, the graph of the $-\ln(N/N_0)$ versus time should give a straight line, where: N represents the bacterial survival number at time (t); N_0 , the initial number of bacteria; and t , the contact time. From Fig. 7, it can be seen that inactivation of *E. coli* was much more effective for the monolith with sunlight than in any other experimental conditions, which almost achieved 100% efficiency of bacterial killing after 20 min irradiation. However, in other two kinds of experimental conditions, only irradiation with sunlight and sample AT12 under dark state, the efficiency of bacterial killing were achieved only 40 and 12%. This result shows that the bactericidal activities of carbon/titania/bentonite monolith with sunlight were higher than other experimental conditions. The similar bactericidal efficacy of carbon/titania/bentonite monolith against *E. coli* observed in our study was in agreement with the result of previous work.²⁶⁾

4. Conclusion

The carbon/titania/bentonite monolith for architecture used has been successfully prepared from AC, TOS and bentonite with PR as a bonding agent. The prepared monolith is characterized by several methods. The BET surface of samples is increased as increasing the ratio of carbon/titania composites. The surface states of samples show that the TiO₂ and bentonite were coated on the surface of AC. The XRD patterns of samples show that a mixture structure of anatase and rutile of TiO₂ with a clear SiO₂ structure. From EDX data, the main elements C, O, Ti and Si are existed, though other impure elements are also existed. All of samples have excellent degradation of MB solution by two effects, adsorption effect by AC and bentonite, and photocatalytic effect by TiO₂. Furthermore, the bactericidal activities against *E. coli* of carbon/titania/bentonite monolith with sunlight were higher than other experimental conditions.

References

1. X. Z. Li and F. B. Li, *Environ. Sci. Technol.*, **35**, 2381 (2001).
2. R. Zanella, S. Giorgio, C. R. Henry and C. Louis, *J. Phys. Chem. B*, **106**, 7634 (2002).
3. H. X. Li, Z. F. Bian, J. Zhu, Y. N. Huo, H. Li and Y. F. Lu, *J. Am. Chem. Soc.*, **129**, 4538 (2007).
4. V. Subramanian, E. E. Wolf and P. V. Kamat, *J. Am. Chem. Soc.*, **126**, 4943 (2004).
5. J. Y. Li, C. C. Chen, J. C. Zhao, H. Y. Zhu and J. Orthman, *Appl. Catal. B*, **37**, 331 (2002).
6. J. Y. Li, C. C. Chen, J. C. Zhao, H. Y. Zhu and Z. Ding, *Sci. China Series. B*, **45**, 445 (2002).
7. J. Matos, J. Laine and J. M. Herrman, *J. Catal.*, **200**, 10 (2001).
8. B. Tryba, A. W. Morawski and M. Inagaki, *Appl. Catal. B*, **41**, 427 (2003).
9. C. H. Ao and S. C. Lee, *Appl. Catal. B*, **44**, 191 (2003).
10. Y. C. Chiang and C. P. Huang, *Carbon*, **39**, 523 (2001).
11. M. Inagaki, Y. Hirose, T. Matsunaga, T. Tsumura and M. Toyoda, *Carbon*, **41**, 2619 (2003).
12. G. M. Colon, C. Hidalgo and M. Macias, *Appl. Catal. A*, **259**, 235 (2004).
13. M. C. Lu and J. N. Chen, *Chemosphere*, **38**, 617 (1999).
14. J. Arana and J. M. Dona, *Appl. Catal. B*, **44**, 161 (2003).
15. S. X. Liu, X. Y. Chen and X. Chen, *J. Hazard. Mater.*, **143**, 257 (2007).
16. W. C. Oh and M. L. Chen, *J. Ceram. Process. Res.*, **9**, 100 (2008).
17. W. C. Oh, M. L. Chen and C. S. Lim, *J. Cera. Process. Res.*, **8**, 119 (2007).
18. W. C. Oh, J. S. Bae, M. L. Chen and Y. S. Ko, *Analy. Sci. Technol.*, **19**, 376 (2006).
19. W. C. Oh, J. S. Bae and M. L. Chen, *Bull. Korean Chem. Soc.*, **27**, 1423 (2006).
20. M. L. Chen, J. S. Bae, W. C. Oh, *Analy. Sci. Technol.*, **19**, 460 (2006).
21. M. Inagaki, Y. Hirose, T. Matsunaga, T. Tsumura and M. Toyoda, *Carbon*, **41**, 2619 (2003).
22. M. L. Chen, J. S. Bae and W. C. Oh, *Analy. Sci. Technol.*, **19**, 301 (2006).
23. M. L. Chen, W. C. Oh, *J. of Korean Association Crystal Growth*, **17**, 23 (2007).
24. W. C. Oh and M. L. Chen, *Bull. Korean Chem. Res.*, **29**, 159 (2008).
25. M. L. Chen, F. J. Zhang and W. C. Oh, *New Carbon Materials*, **24**, 159 (2009).
26. W. C. Oh and T. S. Park, *J. Ind. Eng. Chem.*, **11**, 671 (2005).