

Decolourization of Methylene Blue in Water Using Bentonite Impregnated with Ti and Ag as Photocatalyst

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ABSTRACT: This article used bentonite impregnated with titanium and silver, respectively, as photocatalyst, to degrade methylene blue (MB) under conditions of MB solutions exposed to sodium lamp and sunlight. Due to the semi-conducting properties of synthesized bentonite catalysts, when exposed to sodium lamp and sunlight, catalyst particles are excited for photocatalysis to achieve decolourization. After an FT-IR analysis, this study finds that smectite catalysts have significant and complicated wave crests between the fingerprint area with wave numbers 415~600 cm^{-1} and 750~1170 cm^{-1} . The bentonite impregnated with Ti^{4+} (Sm-Ti) and with Ag^+ (Sm-Ag) removes MB through the mechanisms of adsorption and degradation, while the commercial product of titanium dioxide (TiO_2) only exhibits the capability of MB degradation. At present, a heterogeneous photocatalytic system has been fully applied for use in daily life, with its efficiency determined by the free radical action of electrons and holes, the generation efficiency of $\cdot\text{OH}$. *Water Environ. Res.*, **87**, 727 (2015).

KEYWORDS: bentonite, photocatalyst, methylene blue, clay catalyst, sodium lamp.

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Decolourization of dye effluents has received increasing attention. Traditional physico-chemical techniques (adsorption on activated carbon, ultra-filtration, reverse osmosis, oxidation by chemical agents, etc.) can generally be used efficiently. Nevertheless, they are non-destructive since they just transfer organic compounds from water to another phase, causing secondary pollution (Chang et al., 2008; Yu et al., 2010). Dyes are extensively used in the textile, plastic, leather, food, paper, cosmetics, and pharmaceutical industries. Effluents from such industries are important sources of colour pollution. Dyes present in water streams do not allow the passage of light through them and damage the aquatic life. Disposal of dyes into water streams causes skin allergies, cancer and eye irritation in human beings. Among the various frequently used dyes, crystal violet is an important one that is used as a biological stain, for finger printing, veterinary medicine, poultry feed additive, as well as the dyeing and paper industries. Crystal violet dye also causes mutagenic effects in human beings; hence, it needs to be

removed before discharges into water bodies (Dincer et al., 2007; Chiang et al., 2007; Sekhar et al., 2009).

Methylene blue is a class of heterocyclic aromatic compounds often used as chemical indicator, dye, biological dye, and drugs. In the oxidizing environment, the water solution of methylene blue is blue, but when it encounters a deoxidant such as zinc and ammonia water, it returns to the colourless state. Methylene blue has often been applied as the titrating indicator of redox reaction in chemical analysis; for the application of dye, methylene blue is used for the dyeing of linen, silk and paper; for biological application, Methylene blue is also utilized as a dyeing and preservative agent of bacteria or cells. In medical application, methylene blue will be discharged via urine between 30 minutes (injection) and after a couple of hours (oral admission) after entering the human body; because this results in a temporary blue colour of urine, it is also used to measure kidney function.

The photocatalyst carrier used in this study is mainly Bentonite. Bentonite is a term in petrology because it is named after the Fort Benton Formation in Rock Creek, Wyoming. Bentonite, montmorillonite, and smectite have different definitions. They are alternatively used, but in fact, they are different. Bentonite mainly contains montmorillonite, a type of clay mineral of the smectite series. The smectite series, according to the position of its metal ions, can be categorized into montmorillonite, saponite and nontronite (montmorillonite belongs to the smectite series). Moreover, due to the fine particles with a specifically large surface area, is not only expansive and plastic, but also has such characteristics as high water absorption ability, contractility, cohesion, "stickability" and dispersal force in water. Among silicate minerals, bentonite has the strongest colloid property. This study uses montmorillonite of the smectite series.

Conventional treatments have been used to decolorize industrial textile wastewaters, such as adsorption (Faria et al., 2005; Roy et al., 2010); chemical coagulation; chemical oxidation processes, some of which utilize Fenton reagent (Perez et al., 2002); and the combined action of these oxidants or any of them with H_2O_2 and electrochemical oxidation (Mohammadian et al., 2010). Biological processes have also been used to decolorize effluents from the textile industry, and in particular on azo dyes (Shaw et al., 2002), but they are not always effective in removing colour because of the low biodegradability of textile dyes, so tertiary treatments are needed to decolorize dye effluents before discharge (Ramose et al., 2012).

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Table 1—Results of the bentonite composition analysis.

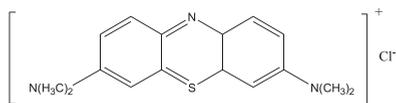
composition	(%)
SiO ₂	61.40
Al ₂ O ₃	22.21
Fe ₂ O ₃	0.50
CaO	2.06
MgO	4.45
Na ₂ O	9.26
K ₂ O	0.11
TiO ₂	0.01

^a The value is determined by ICP, expressed by the oxidation state of the element.

In terms of the selection of agent, due to the similar reactions and functions of crystal violet and methylene blue, they both can be applied to chemical analysis, dyeing agents, medicine and bacteria dyeing agents; the crystal violet has the more serious concern of carcinogenesis than methylene blue does. On the other hand, methylene blue is more widely applied in daily life and has greater availability than crystal violet. It is easier to be dissolved in water and alcohol; the preparation of methylene blue solution is simpler. Hence, the researchers use methylene blue as the agent source in this study. This study modified bentonites through impregnation with metal ions of Ti⁴⁺ and Ag⁺, respectively, and investigated the usefulness of the modified bentonites in degrading methylene blue, commonly found in dye wastes.

Materials and Methods

Materials. Chemicals. Analyzed Reagent of methylene blue (molecular weight 373.91, C₁₆H₁₈N₃SCl · 3H₂O) was purchased from J. T. Baker Chemical Co. The compound contains 60.08%, H 5.67%, Cl 11.09%, N 13.14% and S 10.03%. This chemical has a deep green colour, is either crystal or powder, can be dissolved in water, alcohol or chloroform, and has the following structure:



The other chemicals used in this study include alcohol (purity 99%, MERCK), TiCl₄ (99%, SHOWA), and AgNO₃ (99.8%, MERCK). The catalysts carrier (Sm) is made from Wyoming bentonite—2:1 (Colloid, USA).

Instrumental Analysis. The light source was a high pressure sodium lamp, having wave length 589.44 nm and 0~400 W (in this study 100 W was employed). The reactor was a closed wood-box, 75 cm high, 33 cm wide, with a lamp located in the centre of the reactor.

- (1) Ultraviolet spectrophotometry: used for determining methylene blue concentration (Hitachi U-3300, Scan Speed: 400 nm/min, 200~800nm).
- (2) Infrared spectrophotometry: used for determining the bond structure of clay mineral in FT-IR radicals (Bruker Vector 22, KBr disk, scan range 4000 cm⁻¹-400 cm⁻¹).
- (3) X-Ray analysis (Rigaku RINT 2000): Used for determining the difference of mineral structure and crystal before and after treatments, such as potassium-saturated, magnesium-saturated and glycerine stifling (Zhuang and Wang, 1995).

Methods. Preparation of Carriers. With a weight of 60 g, bentonite was placed in a 2L beaker. After the bentonite was completely swollen, the sand was separated by 300 mesh screener, and the filtrate was poured into a 1L Imhoff cone allowing for sedimentation. After 8 h, about 10 centimetres of supernatant were placed in a centrifuge at 1000 rpm. The settled bentonite was mixed with NaCl, de-ionized water, and alcohol; the mixture was then placed on shaker for shaking, and finally for centrifugation. The water-saturated bentonite was frozen, dried and grinded as powder before it was used in the test.

Property Determination. The purified bentonite was digested with acids (Baker and Amacher, 1982), followed by ICP-AAS analysis. The cation exchange capacity was determined by sodium acetate method.

Catalysts of Sm-Ti and Sm-Ag Preparation. The 0.1N TiCl₄ and AgNO₃ solutions were prepared respectively, and placed the water-saturated bentonite in these solutions. The bentonite-added solutions were kept in 40 °C water bath and mixed for 48 h. After the solutions were centrifuged, 50% alcohol (chloride ions had been removed) was added to obtain the modified bentonites of the Sm-Ti and Sm-Ag catalyst. These catalysts were frozen, dried and ignited at 350 °C for 2 h before they were stored in ambient temperature for use.

Calibration Curve for Determination of Methylene Blue. The artificial dye waste was prepared with methylene blue having a concentration of 30 mg/L. A series of concentrations of methylene blue, including: 0, 0.1, 0.5, 1, 5, 10 and 15 mg/L, were prepared for plotting the calibration curve. The calibration curve with r² = 0.9994 of methylene blue was obtained by measuring light adsorption at 644 nm wave length using ultraviolet spectrophotometer.

Decolourization Tests. The light sources were the sun and a sodium lamp, respectively, during the study on the degradation of methylene blue. Batch tests were performed, where catalysts of 0.01% bentonite, Sm-Ti and Sm-Ag, were added to three beakers, respectively. Each beaker contained 50 mL of 30 mg/L methylene blue.

Under the exposure of sunlight, from 9 a.m. to 3 p.m. (for a period of 6 h), changes in pH, temperature, light intensity and MB concentration, were measured each hour. When a sodium lamp was used as light source, its light intensity was set in accordance with that obtained in the test exposed to sunlight: 50 lux. Similar measurements were conducted every half hour. Additionally, the effectiveness of degrading methylene blue by commercial TiO₂ under different light sources was also conducted. The controls that received no light were carried out in dark room.

Assessment of Pseudo-First-Order Kinetic Model of Heterogeneous Photocatalytic System. This study adopts pseudo-first-order kinetic model to examine the decolourization effect of MB after degradation by three types of photocatalysts under exposure to a sodium lamp and sunlight; the reaction equation is:

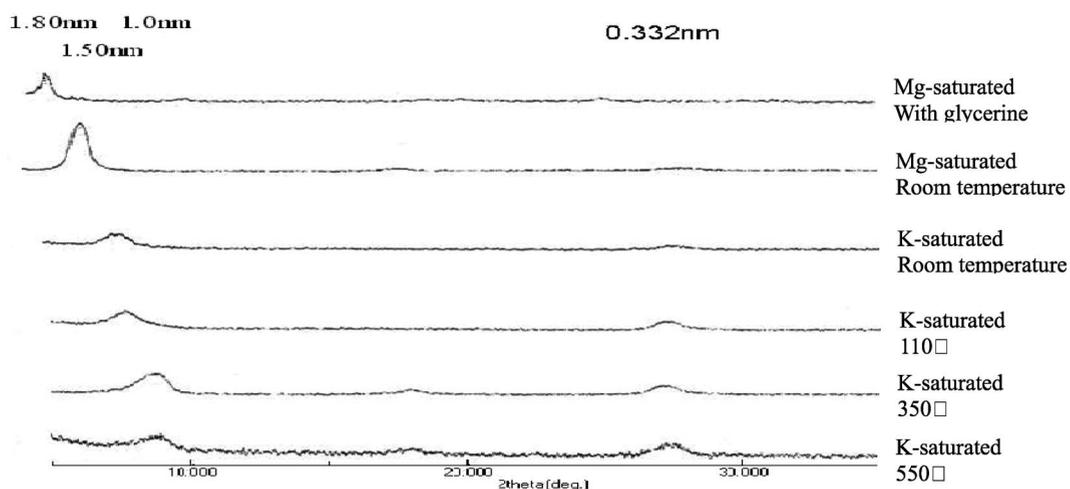
$$\ln\left(\frac{C}{C_0}\right) = -k \times t$$

where

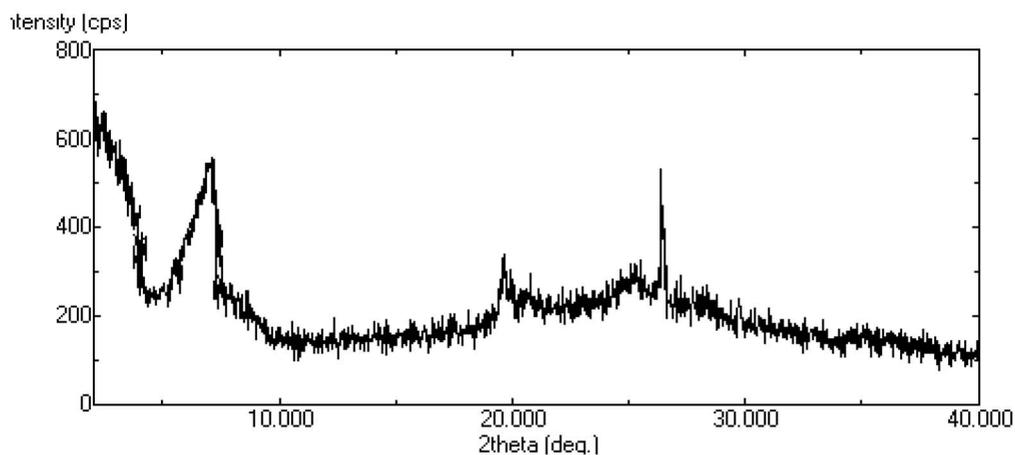
C₀ = MB's initial concentration (mg/L);

C = MB's concentration after the decolourization reaction (mg/L)

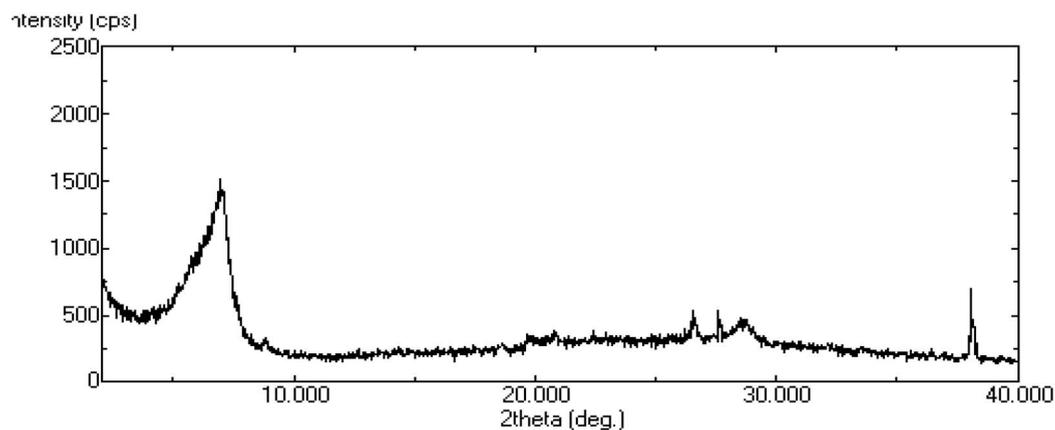
k = Constant of reaction speed (min⁻¹); t: Reaction time (min)



(a) Bentonite

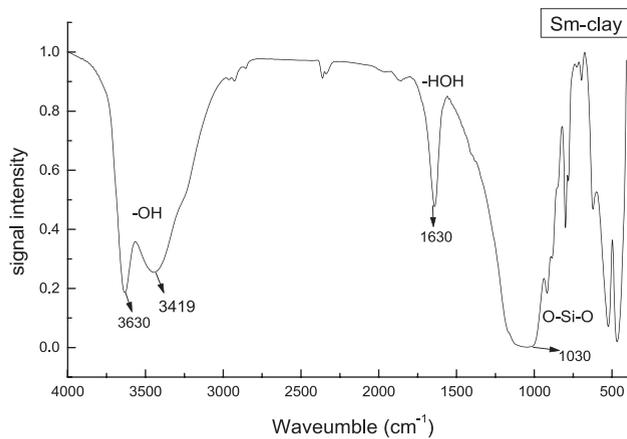


(b) Sm-Ti

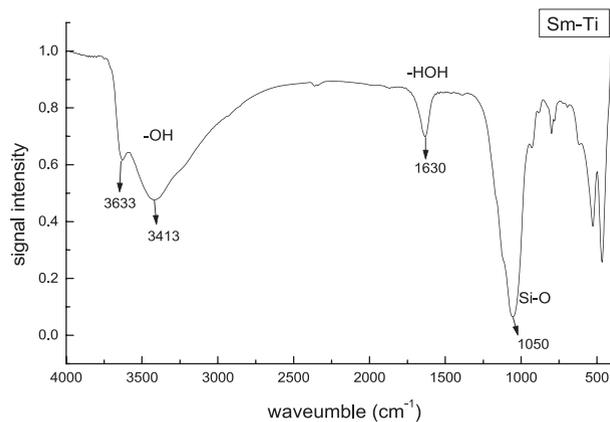


(c) Sm-Ag

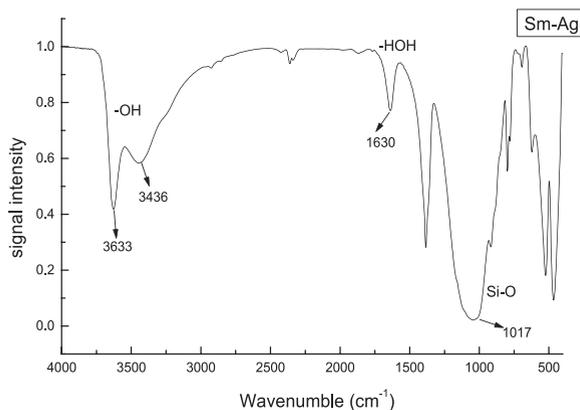
Figure 1—Spectra of X-Ray analysis for bentonite, Sm-Ti and Sm-Ag



(a) Sm-clay



(b) Sm-Ti



(c) Sm-Ag

Figure 2—Spectra of FT-IR for bentonite, Sm-Ti and Sm-Ag

Results and Discussion

Basic Property. As shown in Table 1, because of the inside silicate layers (tetrahedral), the bentonite structure of part of Si^{4+} is replaced by Al^{3+} and many metal ions in the metal ion layer (octahedral) enter the inner layer to promote bending and vibration of $-\text{OH}$, forming different absorption characteristics, primarily consisting of Si (61.40%) and Al (22.21%). Other elements include: Fe (0.5%), Ca(2.06%), Mg(4.45%), Na (9.21%), K (0.11%) and Ti (0.01%). The CEC was 93.70 cmole/kg, to serve well as the catalyst carrier.

X-Ray Analysis. After the bentonite was examined by X-Ray analysis, the clay mineral appeared to be highly purified, and the peaks were distinguished after treatment with potassium-saturated and magnesium-saturated. The bentonite exhibited a swollen phenomenon after it was treated with magnesium-saturated and vaporized with glycerine; the shrinking phenomenon was due to water loss also occurring after heating. Figure 1(a) shows that reflection occurs at 1.5 nm after treatment with magnesium-saturated, and swollen at 1.8 nm after treatment with glycerine. The bentonite treated with potassium had a reflection at 1.1 nm, swollen between layers to 1.0 nm after being heated to 550 °C; the reflection at 0.322 nm indicates the presence of quartz.

The spectra of X-Ray analysis for Sm-Ti are shown in Figure 1(b) and Sm-Ag in Figure 1(c). At 4 nm there appears a reflection, indicating that the bentonite structure was not destroyed. For Sm-Ti, at $2\theta = 26^\circ$, there was a peak, implying that the prime component is anatase. Bentonite 2:1 is a clay mineral, easily swollen by adsorption of water; however, after modification with metal ions and heating, the mineral tends to shrink due to water loss, but the space between molecular layers is still sufficient to allow the larger metal to enter.

FT-IR Radicals Identification. Figure 2 illustrates the spectra for Sm-Ti and Sm-Ag, where the peak shrinking occurs at 1630 cm^{-1} due to $-\text{OHO}$ adsorption. In Figure 2(a), at 415–600 cm^{-1} and 750–1170 cm^{-1} , there are complex peaks, indicating Si-O and O-Si-O bonds from non-purified silica minerals; at 3200–3700 cm^{-1} , peak deviation and fragments arise from $-\text{OH}$ adsorption, and Al is substituted for Si.

Even after 2 h of heating, the molecular structure of the bentonite minerals was not destroyed, as indicated in Figures 2(b) and 2(c), where the original buffering adsorption layers remained unchanged, although the peak of water decreased. In Figure 2(b), at 3413 cm^{-1} , the more reactive site is available, which increases the $-\text{OH}$ signal; it can be attributed to the combination of strong oxidant of Ti^{4+} with the substitution of bentonite (Wu et al., 2011)

Decolourization Background Experiment. To examine the non-photocatalysis decolourization level of water, it is necessary to objectively address the actual decolourization result after irradiation by sodium light without photocatalysts. An example is used without adding any photocatalysts, simply by projecting the sodium lamp on water. The experiment's result indicates that they did not achieve the decolourization effect. Especially, after being placed in sodium light for 300 min, the temperature of water increased to 50~60 °C, but there was no change in methylene blue concentration. This result indicates that under the exposure to sodium light, the methylene blue solution increased the temperature, but the lack of a catalytic effect of photocatalysts resulted in the failure of decolourization.

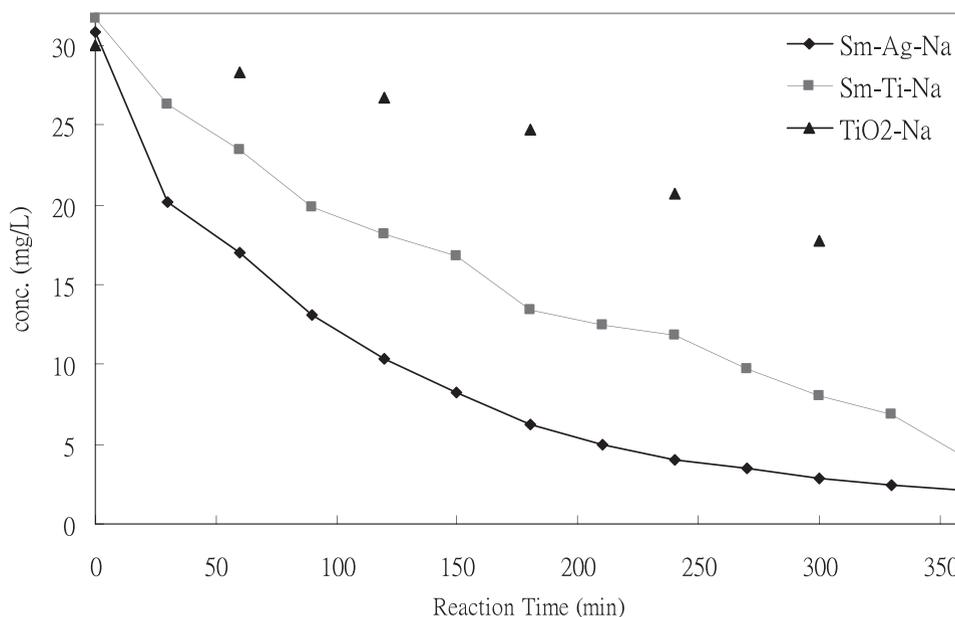


Figure 3—Methylene blue degradation by the additions of different catalysts under exposure to sodium lamp light

Therefore, the influence of the factor mentioned above may be ignored.

Decolourization of Methylene Blue. *Exposure to a sodium lamp.* Figure 3 indicates the decolourization results of methylene blue with initial concentration of 30 mg/L subject to a sodium lamp when different catalysts were added. The addition of 0.01% Sm-Ti brings about colour removal of 86.1%, with the residual MB concentration of 4.17 mg/L. The 0.01% Sm-Ag achieved colour removal of 93.1% and residual methylene blue concentration 2.06 mg/L. However, The TiO_2 only yielded colour removal of 47.7%, and residual MB concentration reached 15.70 mg/L. This means that when photocatalysts are irradiated by sodium light, the photocatalysts are excited sufficiently to carry

out a photocatalytic reaction (Kuo and Liao, 2006; Tsai et al., 2011). At this time, irradiation of photocatalysts with photons of energy equal to, or greater than, its band-gap results in the promotion of electrons from the valence band (vb) to the conduction band (cb) of the catalyst particles. This process results in a region of positive charge termed holes (h_{VB}^+) in the vb and a free electron (e_{CB}^-) in the cb:



For example, with silver particles on the Sm-Ag catalyst particle surface, the holes react with the surface hydroxyl groups (OH^-) and adsorb H_2O , to form OH free radicals:

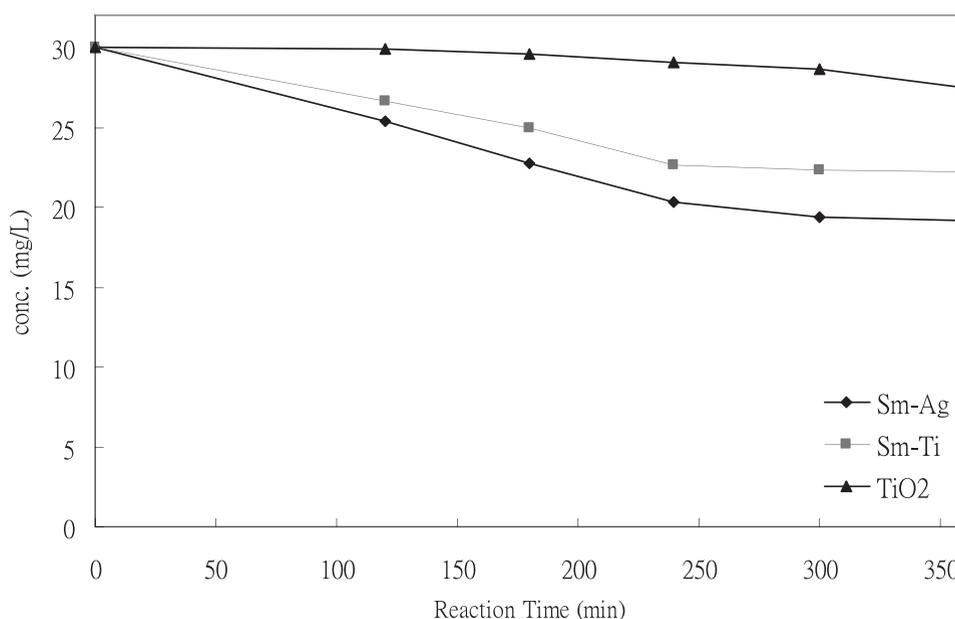


Figure 4—Methylene blue degradation by the additions of different catalysts in a dark room

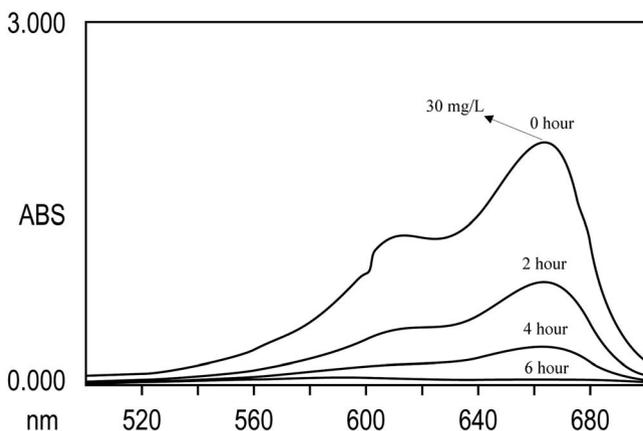
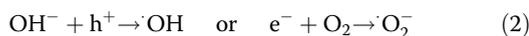


Figure 5—Spectra of UV/VIS for methylene blue in different irradiation times by Sm-Ag



The $\cdot\text{OH}$ free radicals and $\cdot\text{O}_2^-$ free radicals are all vigorous and provide high levels of activity (Huang et al., 2011). The $\cdot\text{OH}$ free radicals, in particular, have the ability to remove MB in the presence of the Ag/Ti/TiO₂ catalyst.

In the photocatalytic rate constant (k) of the pseudo-first-order kinetic model, k of Sm-Ti is 0.0055 (min⁻¹); k of Sm-Ag is 0.0074 (min⁻¹); and k of TiO₂ is 0.0018 (min⁻¹). The above analysis clearly shows that the catalytic degradation of Sm-Ag after 350 min achieves the optimal decolourization effect to methylene blue, followed by Sm-Ti and then TiO₂.

Additionally, this study also found more significant decolourization effects of synthesized Sm-Ag and Sm-Ti on methylene blue than that of TiO₂. This is because the specific surface areas of Sm-Ag and Sm-Ti catalyst are larger than that of TiO₂ (Kuo and Liao, 2006). When a photocatalyst has a larger specific surface area, the area exposed to the sodium lamp is larger, and this results in relatively better results in degrading MB. In this study, various modified bentonite catalysts provide semiconductor properties, so the sodium lamp can stimulate the bentonite catalyst particles to undertake photocatalysis and achieve the goal of decolourization. On the other words, the exchanged bentonite catalysts can excite photocatalysis of catalyst particles through irradiation by sodium light and generate decolourization.

In the dark room (as shown Figure 4), the MB removal efficiencies by the additions of Sm-Ti, Sm-Ag and TiO₂ were 26.0, 38.1 and 8.3%, respectively, indicating that adsorption occurred in the control test. During the tests by the sodium lamp, the temperature was 50~60 °C and pH = 4.84~5.75, which indicates that high temperature enhances degradation.

Furthermore, Figures 5 and 6 show the results of removal levels of methylene blue for Sm-Ag and Sm-Ti under different irradiation time for 0~6 h, respectively. The illustration reveals that the absorptivity of the two catalysts will be increased if the illuminated time is longer. It also means that the methylene blue has been successfully decolourized. Furthermore, as shown in Figures 5 and 6, Sm-Ag demonstrated better results of MB decolourization than Sm-Ti, while methylene blue decolouriza-

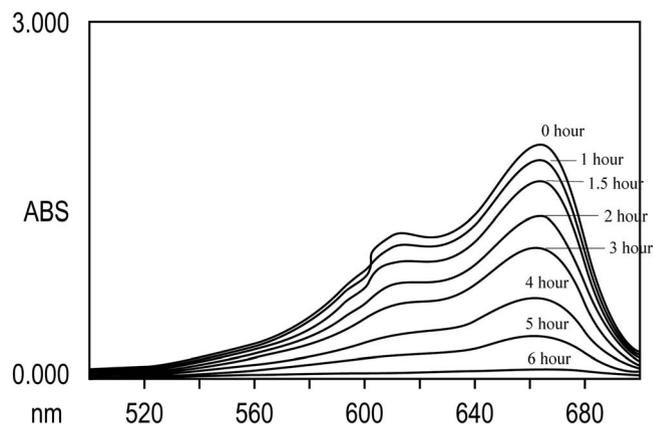


Figure 6—Spectra of UV/VIS for methylene blue in different irradiation times by Sm-Ti

tion of TiO₂ was poorer than that of Sm-Ag and Sm-Ti because after cation exchange, the specific surface areas of Sm-Ag and Sm-Ti significantly increase (Kuo and Liao, 2006), and after catalytic degradation, methylene blue's concentration is significantly reduced. Accordingly, when MB's transmittance (T%) under UV/VIS spectrometers increases, its absorbance (ABS) decreases.

Exposure to Sunlight. Figure 7 indicates the methylene blue degradation under sunlight. After exposure to the sunlight over 6 h, the methylene blue with initial 30 mg/L was greatly removed by the addition of Sm-Ti as photocatalyst; the methylene blue removal efficiency was 94.3%. The addition of Sm-Ag resulted in MB removal efficiency of 26.2%. In the dark room (as shown in Figure 4), the methylene blue removal efficiencies were 26.0, 38.1 and 8.3%, respectively, for which Sm-Ti, Sm-Ag and TiO₂ were added. Under sunlight, the methylene blue solutions received light intensity which varied from 10~90 klux. The main reason for the Sm-Ag and Sm-Ti photocatalysts having better removal efficiency on methylene blue is that the surface of these photocatalysts is super-hydrophilic (Liu and Tian, 2003), and the photocatalysis with light has been proven to be a highly effective process for the complete degradation of pollutants (Vohra et al., 2006; Tsai et al., 2011). When they are in the dark, the contact angle with water is not zero, but when exposed to light, the contact angle with water tends to zero, and these photocatalysts become super-hydrophilic. When the surface of these photocatalysts is exposed to light, strong oxidants ($\cdot\text{OH}$ and $\cdot\text{O}_2^-$) will be released and the water molecules are able to form strong hydrophilic bonds (Liao and Kuo, 2007).

In the photocatalytic rate constant (k) of the pseudo-first-order kinetic model, k of Sm-Ti is 0.0046 (min⁻¹); k of Sm-Ag is 0.0080 (min⁻¹); and k of TiO₂ is 0.0008 (min⁻¹). The above analysis clearly shows the catalytic degradation of Sm-Ag after 350 min; results identical to those exposed to a sodium lamp are found: the optimal decolourization effect of MB catalyzed by Sm-Ag, followed by Sm-Ti and then TiO₂.

At present, a heterogeneous photocatalytic system has been fully applied for use in daily life, with its efficiency determined by the free radical action of electrons and holes, the generation efficiency of $\cdot\text{OH}$. Furthermore, many aspects in the solution affect the feature of the photocatalytic surface and change its

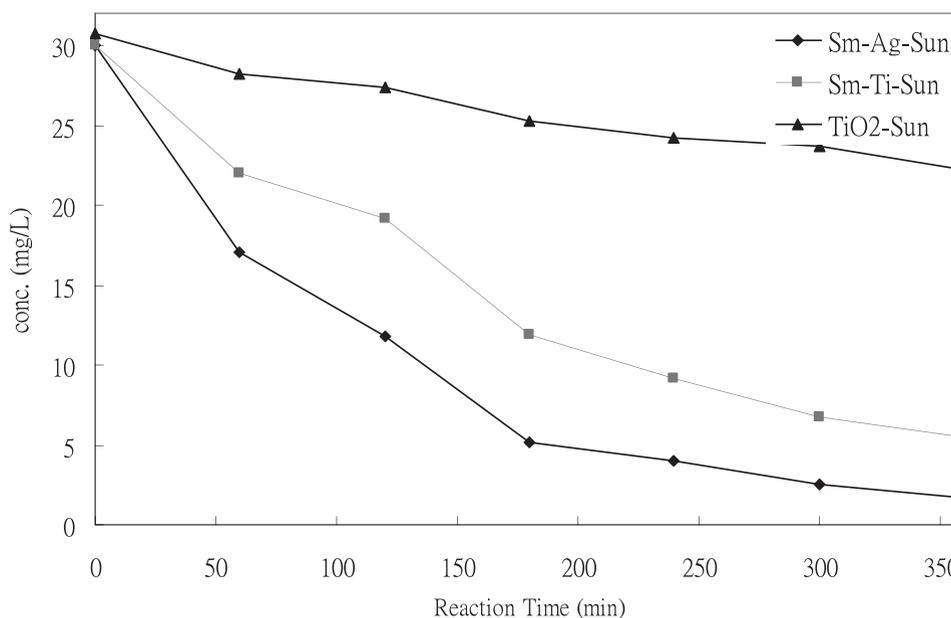


Figure 7—Methylene blue degradation by the additions of different catalysts under exposure to sunlight

absorption. For example, when a photocatalyst is used to treat pollutants in the water, it helps to completely degrade pollutants in wastewater via oxidation. However, more time and effort are required to separate water treated with nano photocatalysts. These issues require more in-depth discussion in future studies on heterogeneous photocatalytic systems.

Conclusions

This study utilized the theory of heterogeneous photocatalytic with self-synthesized photocatalysts, incorporate with the exposure to a sodium lamp to trigger photocatalytic degradation, to achieve decolourization of methylene blue in water. Due to the semi-conducting properties of synthesized bentonite catalysts, when exposed to a sodium lamp, catalyst particles are excited for photocatalysis, to achieve decolourization. Bentonite offers a great amount of cation exchange capacity, which is beneficial for use as a carrier of metal catalyst. Various smectite bentonite catalysts have been modified to provide semiconductor properties. A sodium lamp can stimulate the bentonite catalyst particles to trigger photocatalysis and achieve the goal of decolourization.

In this study, the modified catalysts of Sm-Ti and Sm-Ag can adsorb and degrade MB, while TiO₂ only degrades MB due to its low adsorption capacity, about 2.51 mg/L. When the MB solutions of 30 mg/L were exposed to sodium lamp light, the MB decolourization efficiencies were 86.1, 93.1 and 47.7%, respectively, under the additions of Sm-Ti, Sm-Ag and TiO₂. This demonstrated that the bentonite impregnated with metal ions exhibited greater effectiveness in degrading organics. While the MB solutions were exposed to sunlight, the methylene blue removal efficiencies were 81.6, 94.3 and 26.2% under the additions of Sm-Ti, Sm-Ag and TiO₂, respectively.

At present, a heterogeneous photocatalytic system has been fully applied in daily life and its efficiency depends on the free radical reaction of electrons and holes, the production efficiency of ·OH. Additionally, the application of immobilization and

different pH values of solution affect not only the surface properties of catalysts but also the absorbance properties of continuous photocatalysts. These issues shall be more widely examined in future studies.

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