

Catalytic activity of TiO₂/sepiolites in the degradation of rhodamine B aqueous solution

Nguyen Tien Thao^{1*}, Doan Thi Huong Ly¹, Dinh Minh Hoan¹, Han Thi Phuong Nga^{1,2}

¹Faculty of Chemistry, VNU University of Science – Vietnam National University, Hanoi

²Faculty of Environment, Vietnam National University of Agriculture

Received 7 July 2016; Accepted for publication 11 April 2017

Abstract

TiO₂/sepiolite catalysts were prepared by suspension of titanium dioxide and support in solvent accompanying by calcination. The characterization of the obtained powder has been examined by some physical means including XRD, SEM, FT-IR, and UV-vis. The sepiolite support possesses fibrous structure. X-ray diffraction analysis pointed out that the TiO₂ particles are firmly distributed on fibrous sepiolite matrix. All TiO₂/sepiolite samples were tested for the degradation of rhodamine B and showed a high catalytic activity. The experimental data showed that the degradation efficiency of rhodamine B is correlated with the amount of TiO₂ loadings and oxidant behavior. At room temperature, the conversion of rhodamine B reaches to 99-100 % over 6.0 wt% TiO₂/sepiolite catalyst.

Keywords. TiO₂, rhodamine B, sepiolite, degradation, photocatalysis.

1. INTRODUCTION

The development of economy and industry in Vietnam also leads to some environmental issues during the last decades. A large quantity of organic contaminants in wastewater was exhausted into environments [1, 2]. Many of them are highly chemically stable, low biodegradable, and potentially harmful to the human society. As Law on Environmental Protection came into effect from January 01, 2015 in Vietnam, all toxic contaminants in exhausted wastewater must be treated before releasing water into rivers, fields, etc. Organic dyes and colored compounds are the source of considerable water consumption and contamination. Thus, the complete oxidation of these dyes in their aqueous solutions offers an opportunity of direct removal of these chemicals or their transformation into non-toxic products [2, 3]. However, efficiency of the classical oxidation processes for their removal from wastewater is still limited. For this reason, new advanced oxidation techniques are quite promising. They use active catalysts activated by sunlight irradiation for the dye degradation under ambient conditions [2-4]. Among heterogeneous photocatalysts used, TiO₂ is reported as an effective semiconductor catalyst for removing stable organic compounds [3-5]. However, its catalytic activity sometimes varies with light frequency, phase,

particle domain, dispersion... [4, 5]. Thus, distribution of TiO₂ on matrix leads to an increased dispersion of active centers and improves catalytic activity. Among various inorganic materials reported, sepiolite a clay mineral having a unique structure related to its functional properties and adsorbability [6, 7]. Many works have reported the potential adsorption ability of dyes on this clay [8-10]. This adsorptive property is an advantage to exploit its catalytic activity if this material is consisted of active components such as ZnO, FeO_x, and TiO₂.

The purpose of the present study is to prepare TiO₂ on fibrous sepiolite carrier as catalysts for the oxidation of rhodamine B.

2. EXPERIMENTAL

2.1. Catalyst preparation and characterization

Sepiolite was purchased from Fluka Chemical Company and used without further purification. TiO₂ was purchased from Wako Company. A certain amount of TiO₂ was added into 25 mL of absolute ethanol under magnetic stirring at room temperature. The suspension was stirred for 10 minutes prior to adding a weighted quantity of dried sepiolite. The mixture was further stirred at room temperature for 3 hours and then evaporated at 70-75 °C for 15 hours

to the yield white powder. The solid was then calcined at 400 °C for 2 hours to give TiO₂/sepiolite samples.

Powder X-ray diffraction (XRD) patterns were recorded on a D8 Avance-Bruker instrument using CuK_α radiation ($\lambda = 1.59 \text{ \AA}$). Fourier transform infrared (FT-IR) spectra were obtained in 4000-400 cm⁻¹ range on a FT/IR spectrometer (DX-Perkin Elmer, USA). The scanning electron microscopy (SEM) microphotographs were obtained with a JEOS JSM-5410 LV. UV-Vis spectra were collected with UV-Visible spectrophotometer.

2.2 Degradation of rhodamine B

In photocatalytic experiments, 75 mL solution of 20 ppm of rhodamine B dye (RhB) and 0.45 grams of catalyst were added in to a beaker under magnetic stirring at room temperature. Then, either 75 mL solution of H₂O₂ (30%) was dropwised into the beaker or 5.0 mL/min flowrate of air was bubbled into the reaction mixture 2-5 mL of dye samples were taken out at a regular interval (20 min) from the solution test, filtered and their absorbance was recorded at 553 nm using a CARY 100 UV-vis spectrophotometer (Shimadzu). The degradation level is estimated by the following equation:

$$\text{Degradation} = \frac{[\text{RhB}]_{\text{initial}} - [\text{RhB}]_{\text{final}}}{[\text{RhB}]_{\text{initial}}} \times 100$$

3. RESULTS AND DISCUSSION

3.1 Catalyst Characterization

All TiO₂/sepiolite samples with different loadings were prepared and their XRD patterns were represented in figure 1. As seen in figure 1, the

reflection signals at 2-theta of 20.6, 23.8, 26.7, 28.0, 35.6, 37.9, 39.9, 43.8° are indexed to the sepiolite phase (Joint Committee on Powder Diffraction Standards (JCPDS) Card No. 00-013-0558) [6, 7, 9]. Some weaker signals at 2-theta of 25.5, 37.8, 55.1° are essentially assigned to the TiO₂ anatase (CPJS 00-021-1272). These peaks are rather broadening, implying the formation of nanocrystalline titanium dioxide loaded on the support [4, 5, 11].

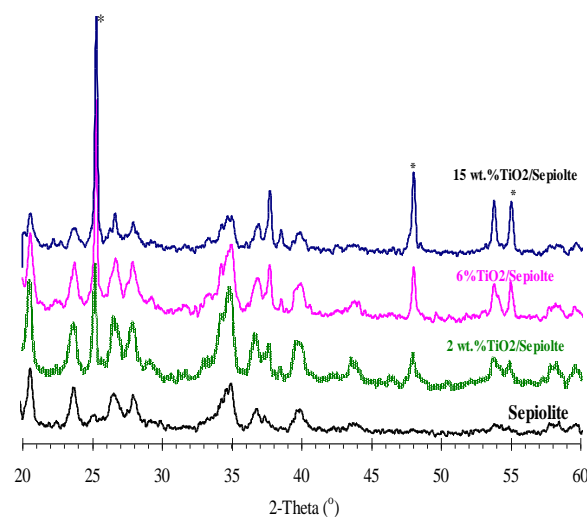


Figure 1: XRD patterns for TiO₂/sepiolite catalysts

Morphology and microstructure of the raw sepiolite and TiO₂/support are observed using scanning electron microscope and their micrographs are displayed in Fig. 2. The solid is consisted of a stick-like aggregation made up of lots of fibers and the length of sticks is approximately 1μm. The diameter of sticks is about 80 nm [12, 13]. No remarkable changes in the shape and size of Mg-O-Si sepiolite fibers were observed for the TiO₂ loading samples (Fig. 2B).

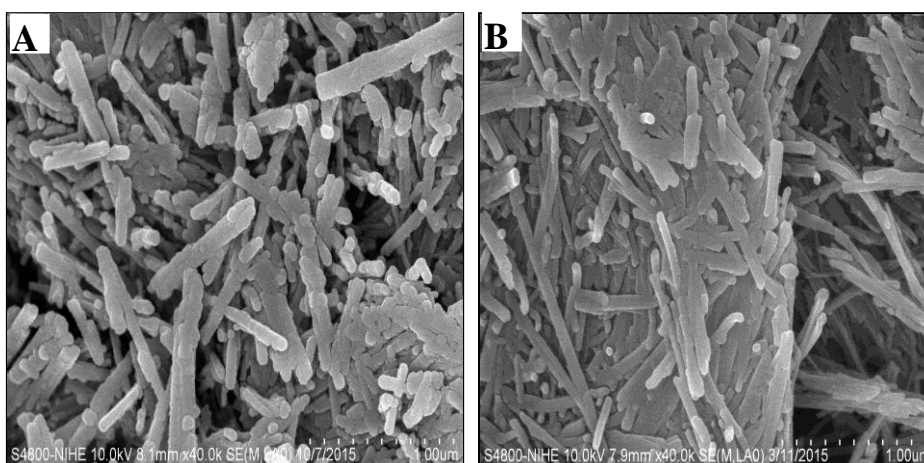


Figure 2: SEM images of sepiolite (A) and sample 15.0 wt% TiO₂/sepiolite (B)

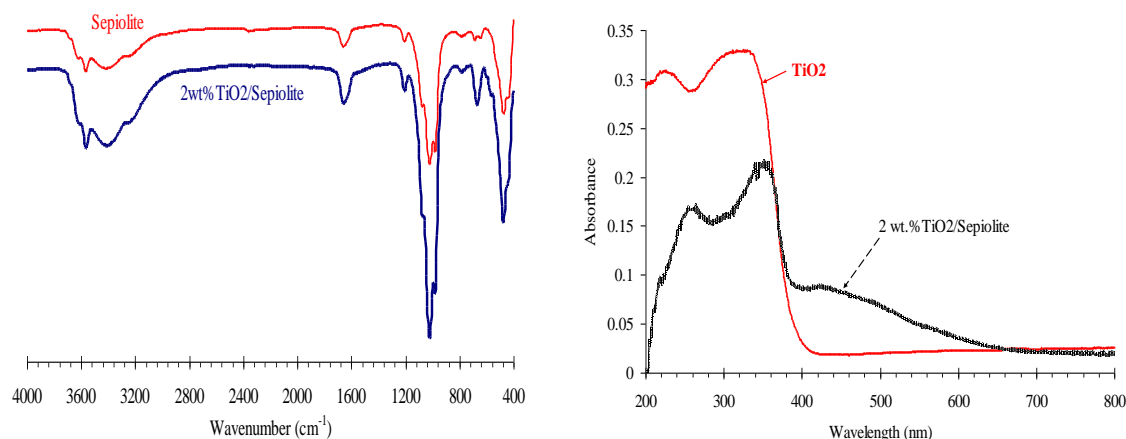


Figure 3: IR spectra (left) and UV-spectra (right) of TiO₂ and TiO₂/sepiolite samples

FT-IR spectra of raw sepiolite and the TiO₂/support are illustrated in Fig. 3A. The weak bands at 3610 and 3415 cm⁻¹ for the three samples are assigned to the stretching vibrations of hydroxyl groups in the octahedral Mg sheet and external surface [8, 12, 13]. The band at 1650 cm⁻¹ is due to the bending vibration of O-H bond of chemisorbed water on the surface of the solids. The bands around 1026 and 472 cm⁻¹ which originate from stretching of Si-O in the Si-O-Si groups of the tetrahedral sheet still exist, indicating that the basic structure of sepiolite is well preserved [12, 13]. Fig. 3A also indicates no significant difference between the spectra of the TiO₂/clay before and after suspension of TiO₂.

Figure 3B presents the UV-Vis diffuse reflectance spectra of TiO₂/sepiolite. It is observed that two samples show a similar wavelength of the adsorption edge at 392 nm ($E_g \approx 3.20$ eV), in line with the theoretical value of TiO₂ photocatalysts [5, 14, 15]. Thus, no chemical interaction between

titanium and sepiolite was observed. The results suggest that the TiO₂/sepiolites have a suitable band gap for photocatalytic reactions [16].

3.2. Degradation of rhodamine B

The degradation of rhodamine B was investigated in water at room temperature, laboratory lamp-light with air flow rate or 30% H₂O₂ solution as oxidant. For a comparison a blank test was carried out under the same conditions and a small amount of rhodamine B was converted, confirming the stability of organic dye [10]. Figure 4A shows that TiO₂ pure oxide was also tested for the removal oxidation of rhodamine B with air. It is not supervising to see a gradually increased degradation degree of rhodamine B with reaction time since TiO₂ is a typical photocatalyst. Figure 4B displayed the temporal changes in UV-vis spectra of the rhodamine B in the solution with reaction time.

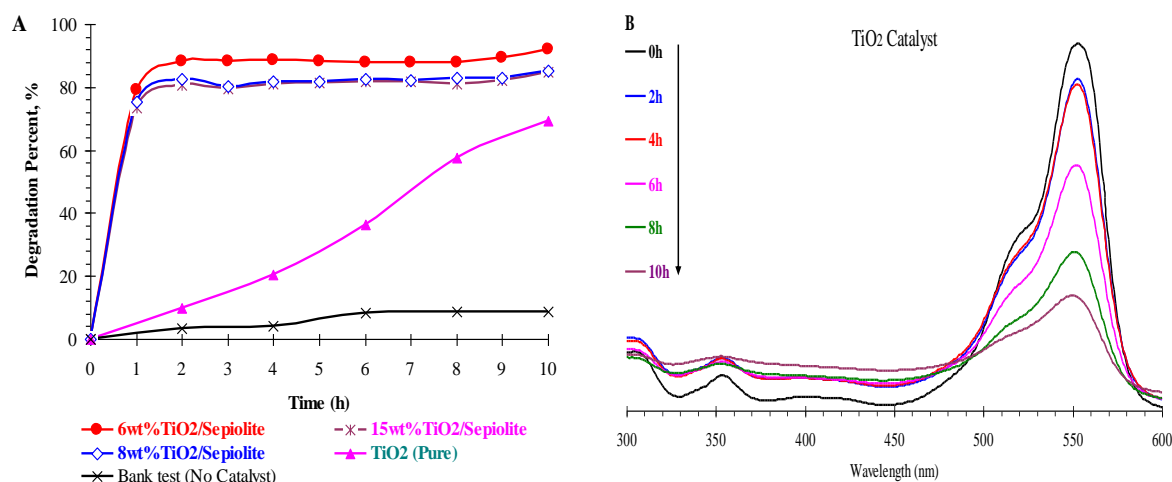


Figure 4: Catalytic activity of TiO₂/sepiolite samples (A) and UV-vis absorption spectra of rhodamine B during visible light irradiation over TiO₂ pure catalysts (20 ppm of rhodamine B, 0.30 grams of catalyst, room temperature)

A gradual decrease in the intensity of the strong absorption band with the peak maximum at 553 nm is observed during the photocatalytic degradation of RhB white no wavelength shift of the band at 553 nm, implying the de-ethylation process of rhodamine B over the catalyst (Fig. 4B) [4, 5, 17, 18]. However, the degradation efficiency of rhodamine B sharply goes up as TiO₂ particles were dispersed on sepiolite support. Indeed, the three TiO₂/sepiolite catalysts exhibit rather high photocatalytic activity as compared with that of TiO₂ pure experiment (Fig. 4).

Figure 4A shows that the degradation level reaches nearby 100 % after 4-8 hours on time. In order to expedite degradation process, air flowrate was replaced by H₂O₂ oxidant. The oxidation of rhodamine B aqueous solutions with H₂O₂ was carried out over TiO₂/sepiolite catalyst under ambient conditions. The catalytic activity of rhodamine B discoloration is represented in Figure 5. All catalyst samples show good activity in the oxidation of rhodamine B by H₂O₂. The discoloration reaction occurs more quickly and the degradation efficiency of rhodamine B increases after initiating reaction as seen in Fig. 5 [2, 18-20]. Evidently, the degradation efficiency of rhodamine B goes linearly up during 50 minute-reaction period and then gradually approaches about 100 %.

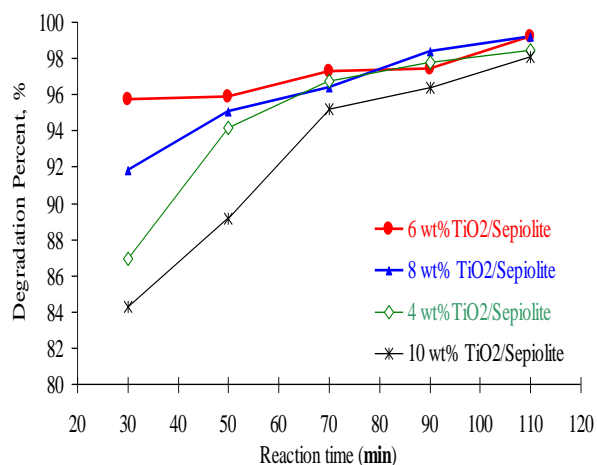


Figure 5: Catalytic activity of TiO₂/sepiolite samples in the degradation of rhodamine B in the presence of H₂O₂ at room temperature, 0.3 grams of catalyst, 20 ppm RhB

Figure 5 also reveals the comparative activity among catalyst samples. As seen in Fig. 5. The catalytic activity can be arranged in order of 6.0 wt% TiO₂/sepiolite ≥ 8.0 wt% TiO₂/sepiolite > 4.0 wt% TiO₂/Sepiolite > TiO₂. A higher photocatalytic activity for TiO₂/sepiolite is explained by the high dispersion of TiO₂ on the sepiolite surface, which provides more available active sites for the

photocatalytic reaction. Furthermore, sepiolite was known as a good adsorbent and thus the catalyst surface may be the accumulation of rhodamine B molecules [7-10]. As a result, rhodamine B molecules have more chances to reach active sites and are therefore decolorized into intermediates [17-19]. However, a higher TiO₂ loading may lead to form large crystallite titania clusters which cover the sepiolite surface and finally decrease the photocatalytic activity. This explained a lower catalytic activity on 8.0 wt% TiO₂/sepiolite [3, 15].

4. CONCLUSION

Sepiolite was used as support for TiO₂ catalysts in the oxidative removals of rhodamine B. The support has layered structure with fibrous morphology. TiO₂ was distributed on the sepiolite through the suspension and calculation route. TiO₂/sepiolite was an excellent catalyst for the photodegradation of rhodamine B in the presence of H₂O₂ or air. Under the same experimental conditions, H₂O₂ was more oxidative than air in the discoloration of rhodamine B. The catalytic activity was related to the amount of TiO₂ loadings and oxidant nature. An increased amount of TiO₂ led to a decreased degradation efficiency of rhodamine B. The highest conversion of rhodamine B was observed on 6.0 wt% TiO₂/sepiolite with the degradation efficiency of 99 % using either H₂O₂ or air as oxidant.

Acknowledgment. This research is funded by Vietnam National Foundation for Science and Technology Development (NAFOSTED) under grant number 104.05-2014.01.

REFERENES

1. Simphiwe P. Buthelezi, Ademola O. Olaniran, and Balakrishna Pillay. *Textile Dye Removal from Wastewater Effluents Using Biofloculants Produced by Indigenous Bacterial Isolates*, *Molecules*, **17**, 14260-14274 (2012).
2. Nguyen Tien Thao, Do Thi Trang. *Decolorization of methylene blue from aqueous solution using Mg-Fe-Al layered double hydroxides with H₂O₂*, *Asian Journal of Chemistry*, **25**, 8097-8101 (2013).
3. Meiqing Fan, Songxia Hu, Bo Ren, Jun Wang, Xiaoyan Jing. *Synthesis of nanocomposite TiO₂/ZrO₂ prepared by different templates and photocatalytic properties for the photodegradation of Rhodamine B*, *Powder Technol.*, **235**, 27-32 (2013).
4. Youji Li, Shuguo Sun, Mingyuan Ma, Yuzhu Ouyang, Wenbin Yan. *Kinetic study and model of the*

- photocatalytic degradation of rhodamine B (RhB) by a TiO₂-coated activated carbon catalyst: Effects of initial RhB content, light intensity and TiO₂ content in the catalyst*, Chem. Eng. J., **142**, 147-155 (2008).
5. Noureddine Barka, Samir Qourzal, Ali Assabbane, Abederrahman Nounah, Yhya Ait-Ichou. *Factors influencing the photocatalytic degradation of Rhodamine B by TiO₂-coated non-woven paper*, Journal of Photochemistry and Photobiology A: Chemistry, **195**, 346-351 (2008).
 6. Maria Jesus Belzunce, Safrario Mendiros and Jerzy Haber. *Modification of sepiolite by treatment with fluorides: Structural and Textural Changes*, Clays and Clay Minerals, **46(6)**, 603-614 (1998).
 7. E. Galan. *Properties and Applications of Palygorskite-Sepiolite Clays*, Clay Minerals, **31**, 443-453 (1996).
 8. Mehmet Uqurlu. *Adsorption of a textile dye onto activated sepiolite*, Microporous and Mesoporous Materials **119(1-3)**, 276-283 (2009).
 9. Osman Duman, Sibel Tunc, Tulin Gurkan Polat. *Adsorptive removal of triarylmethane dye (Basic Red 9) from aqueous solution by sepiolite as effective and low-cost adsorbent*, Microporous and Mesoporous Materials, **210**, 176-184 (2015).
 10. Nguyen Tien Thao, Doan Thi Huong Ly, Ta Thi Huyen, Han Thi Phuong Nga. *Characteristics and Rhodamine B Adsorption Ability of modified sepiolite*, VNU Journal of Science, Submitted (2016).
 11. Nguyen Tien Thao, Trinh Dang Tuan. *Oxidation of styrene over TiO₂/Di Linh clay catalysts*, Vietnam Journal of Chemistry, **49**, 517-521 (2011).
 12. A. Esteban-Cubillo, R. Pina-Zapardiel, J. S. Moya, M.F. Barba, C. Pecharroman. *The role of magnesium on the stability of crystalline sepiolite structure*, Journal of the European Ceramic Society, **28**, 1763-1768 (2008).
 13. Debajyoti Mahanta, Giridhar Madras, S. Radhakrishnan, and Satish Patil. *Adsorption and Desorption Kinetics of Anionic Dyes on Doped Polyaniline*, J. Phys. Chem. B, **113**, 2293-2299 (2009).
 14. E. Eren, O. Cubuk H. Ciftci, B. Eren, B. Caglar. *Adsorption of basic dye from aqueous solutions by modified sepiolite: Equilibrium, kinetics and thermodynamics study*, Desalination, **252**, 88-96 (2010).
 15. Yalei Zhang, Daojie Wang, Gaoke Zhang, *Photocatalytic degradation of organic contaminants by TiO₂/sepiolite composites prepared at low temperature*, Chem. Eng. J., **173**, 1-10 (2011).
 16. Vu Van Nhuong, Nguyen Van Noi, Nguyen Tien Thao, *Synthesis and characterization of TiO₂/SBA-15 materials used as catalysts for the treatment of red phenol in water*, Vietnam Journal of Chemistry, **50(4A)**, 346-350 (2012).
 17. T. Aarthi and Giridhar Madras, *Photocatalytic Degradation of Rhodamine Dyes with Nano-TiO₂*, Ind. Eng. Chem. Res., **46**, 7-14 (2007).
 18. Oliver Merka, Viktor Yarovyi, Detlef W. Bahnemann, and Michael Wark. *pH-Control of the Photocatalytic Degradation Mechanism of Rhodamine B over Pb₃Nb₄O₁₃*, J. Phys. Chem. C **115**, 8014-8023 (2011).
 19. Nguyen Tien Thao, Nguyen Thi Tuoi, Do Thi Trang, *Degradation of methylene blue in water over Mg-Fe-Al hydrotalcites*, Vietnam Journal of Chemistry, **51(5)**, 534-538 (2013).
 20. Bai Cuiping, Gong Wenqi, Feng Dexin, Xian Mo, Zhou Qi, Chen Shaohua, Ge Zhongxue, Zhou Yanshui, *Natural graphite tailings as heterogeneous Fenton catalyst for the decolorization of rhodamine B*, Chem. Eng. J., **197**, 306-313 (2012).

Corresponding author: **Nguyen Tien Thao**

Faculty of Chemistry, Vietnam National University Hanoi

19 Le Thanh Tong Str., Hoan Kiem District, Hanoi, Viet Nam

E-mail: ntthao@vnu.edu.vn/nguyentienthao@gmail.com; Tel.: +84.043.8253503.