STUDY ON PROCESS FOR DEGRADATION OF RHODAMINE B DYE BY Ag/TiO_2 CATALYST UNDER VISIBLE IRRADIATION

NGHIÊN CỨU SỰ PHÂN HỦY CỦA RHODAMINE B BỞI CHẤT XÚC TÁC QUANG HÓA Ag/TiO_2 DƯỚI ÁNH SÁNG KHẢ KIẾN

Vo Thi Thu Nhu[1], Đo Quang Minh[2], Nguyen Quoc Hien[3]
[1] Ho Chi Minh City University of Technology and Education
[2] Ho Chi Minh City University of Technology
[3]Research and Development Center of Radiation Technology

Received 10/09/2016, Peer reviewed 10/12/2016, Accepted for publication 25/12/2016

ABSTRACT

*TiO_2 (P25) doped with silver nanoparticles (Ag/TiO_2) synthesized by γ-irradiation method was used for the photocatalytic degradation of Rhodamine B (RB) dye. The effects of operational parameters such as catalysts amount, initial dye concentration, pH were studied for the photocatalytic degradation of Rhodamine B by Ag/TiO_2 catalyst. Catalytic testing of RB showed that Ag nano/TiO_2 photocatalyst exhibited better photocatalytic activity compared to that of TiO_2 under the same reaction condition and TiO_2 doped with 1.5 % (w/w) Ag gave high photodegradation efficiency (*95.59%*) of 10^{-5}M Rhodamine B at pH 6 using 2 g/L catalyst within 2 hours. The possible intermediate products during the photocatalytic degradation has been suggested, which was based on the electrospray ionization mass spectrometry (ESI-MS) analysis. The complete mineralization of RB dye (10^{-5}M) was confirmed by high performance liquid chromatography (HPLC) analysis. Results demonstrated that the Ag/TiO_2 catalyst can effectively degrade RB dye with optimum conditions.*

Keywords: *TiO_2; silver nanoparticles; photocatalyst; Rhodamine B; degradation.*

TÓM TẮT

Ag nano pha tạp TiO_2 (Ag/TiO_2) tổng hợp bằng phương pháp chiếu xạ tia γ đã được sử dụng làm chất xúc tác cho sự phân hủy quang của thuốc nhuộm Rhodamine B (RB). Ảnh hưởng của các yếu tố như lượng chất xúc tác, nồng độ thuốc nhuộm ban đầu, độ pH đã được nghiên cứu cho sự phân hủy quang của Rhodamine B bằng chất xúc tác Ag/TiO_2. Kết quả cho thấy Ag nano/TiO_2 làm tăng sự phân hủy quang hóa RB so với TiO_2 ở cùng điều kiện khảo sát và TiO_2 pha tạp với 1,5% Ag cho hiệu suất phân hủy quang hóa cao (95.59%) với nồng độ Rhodamine B: 10^{-5}M, pH 6, hàm lượng vật liệu 2 g/L trong 2 giờ. Các sản phẩm trung gian trong quá trình phân hủy RB đã được xác đinh dựa trên phương pháp phân tích khối phổ (ESI-MS). Sự phân hủy hoàn toàn của thuốc nhuộm RB (10^{-5}M) đã được khẳng định bởi phương pháp phân tích sắc ký lỏng cao áp (HPLC). Kết quả chứng minh rằng chất xúc tác quang hóa Ag/TiO_2 phân hủy RB có hiệu quả cao.

Từ khóa: *TiO_2; Ag nano; chất xúc tác quang hóa; Rhodamine B; phân hủy.*

1. INTRODUCTION

Photocatalytic reaction catalyzed by semiconductors has been approved as a promising process for solving energy and environmental issues [1]. Among the semiconductor catalysts, TiO_2 has been studied extensively owing to its special property [2]. However, the wide application of TiO_2 is limited in the condition of solar irradiation due to its wide band gap [3, 4]. Therefore, considering energy conservation and environmental pollution issue, it is necessary and indispensable to develop high efficient and visible light-driven photocatalysts. Several approaches for TiO_2 modification have been proposed: metal-ion implanted TiO_2 (using transition metals: Cu, Co, Ni, Cr, Mn, Mo, Nb, V, Fe, Ru, Au, Ag, Pt) [5-7], reduced TiO_2 photocatalysts [8,9], non-metal doped-TiO_2 (N, S, C, B, P, I, F) [10-12], doping metal ions into the TiO_2 lattice, dye photosensitization on the TiO_2 surface, an addition of inert support and deposition of noble metals. Noble metals doped or deposited on TiO_2 are expected to have various effects on the photo-catalytic activity of TiO_2.

Silver doped TiO_2 (Ag/TiO_2) has been one of the extensively studied doped TiO_2 photocatalysts due to its wider applications in environmental remediation, antimicrobial activity, catalytic oxidation reactions, etc. [13−20] Generally, Ag/TiO_2 catalysts are synthesized by either deposition or doping of silver (in optimum amount) in TiO_2 to improve its photocatalytic efficiency.

In the present investigation, to explore the possibility of Ag/TiO_2 for photocatalytic degradation of RB dye in visible light has been carried out. The effects of various parameters such as catalyst amount, initial dye concentration, pH have been investigated on the photocatalytic degradation of RB in the presence Ag/TiO_2 as a photocatalyst under irradiation of visible light. The complete mineralization of RB dye was further confirmed by high performance liquid chromatography (HPLC) analysis. Intermediate products during the photocatalytic degradation have been identified based on electrospray ionization mass spectrometry (ESI-MS) to confirm the photocatalytic degradation of dyes under visible light.

2. MATERIALS AND METHODS

2.1 Materials

Titanium dioxide (*Degussa* P-25) was purchased from Degussa Corporation, Germany). Ethanol and silver nitrate (99% purity) was purchased from China. Rhodamine B with 97% purity was purchased from India. The molecular structure and chemical properties of RB are given in Fig. 1.

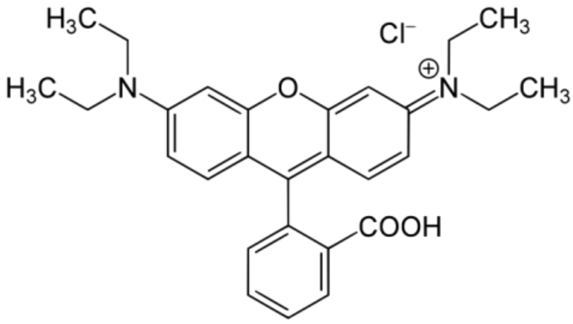


Figure 1. *Structure of Rhodamine B*

2.2 Preparation of Ag nano/TiO_2

2 g of TiO_2 and 5 ml ethanol were added into 95 ml distilled water. $AgNO_3$ was then added to the TiO_2 suspension mixture with ration of Ag/TiO_2: 1.5/100 (1.5%, w/w). The reduction of Ag^+ was carried out by γ-irradiation on a γ- ^{60}Co source at 2.7 kGy. The modified TiO_2 photocatalyst were separated by centrifugation, washed by distilled water and dried at 60^{o}C.

2.3 Photocatalysis experiment

The concentration of RB dye (λmax = 554 nm) in the irradiated solution was determined using a calibration curve of RB concentration versus absorbance and concentration versus peak area of known concentrations using

UV-vis spectrophotometer (Biochrom, Libra S32) and JASCO high performance liquid chromatography (HPLC) equipped with UV–vis diode array detector using C18 column (4.6 mm×250 mm) in the reverse phase mode. The HPLC separation was carried out using mixed eluent (CH_3CN:H_2O = 1:1 by volume, pH = 3.5) at a flow rate of 1 mL/min.

Intermediate products of degradation RB process was studied using electro spray ionization mass spectra (ESI-MS) experiments performed on a micro TOF – QII Bruker instrument.

3 RESULTS AND DISCUSSIONS

3.1 Photocatalytic activity

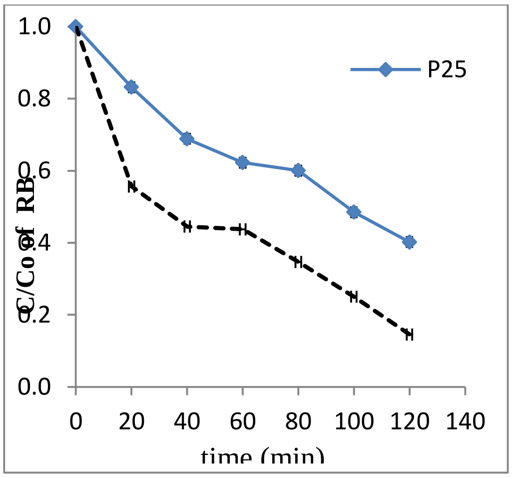


Figure 2. *Comparison between the photocatalytic activity of TiO_2-P25 and Ag1.5%/TiO_2 in degradation of Rhodamine B under visible light irradiation.*

'Figure 2 shows the photocatalytic degradation of RB on TiO_2 and Ag doped TiO_2 photocatalytic. Under visible light, the Rhodamine B photodegradation by pure TiO_2 is lower than by TiO_2 modified with Ag. The results demonstrated that after 120 min of irradiation, nearly 86% of RB was degraded in presence of Ag-TiO_2 whereas the percentage degradation of RB dye was 60% for pure TiO_2.

3.2 Effect of catalyst amount

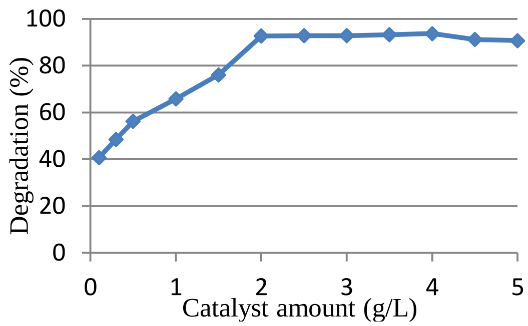


Figure 3. *Effect of Ag//TiO_2 catalyst amount on degradation of RB under visible light.*

To find out the optimum amount of Ag1.5%/TiO_2 catalyst for highest photocatalytic degradation, the amount of catalyst was varied from 0.1 to 5.0 g/L. The concentration of RB (10^{-5}M), irradiation time (1h) was kept constant in all experiments. Fig. 3 shows the effect of catalyst amount on the degradation of RB dye in visible light. The results demonstrated that the percentage degradation of RhB dye increased with the increase of catalyst amount up to 2.0 g/L. When the photocatalyst amount was increased from 2.0 to 5.0 g/L, the percentage degradation was remain or slightly decreased. This may be due to the increase in the turbidity of the solution, results in decrease of visible light penetration and photo activated volume. The results suggested that an optimal amount of the catalyst (2.0 g/L) is necessary for higher degradation rate and reducing needless waste.

3.3 Effect of dye concentration

In order to study the effect of dye concentration on the photocatalytic degradation of RB dye under visible light irradiation, the concentration of dye was varied in the range of 10^{-5} – 10^{-4} M with same amount of catalyst (2.0 g/L) and irradiation time (1 hour) in all experiments. The results are shown in Fig. 4. Results demonstrated that the percentage degradation of RB was decreased with increase in initial dye concentration from 10^{-5} to 10^{-4} M. The percentage degradation was 93% in the case of 10^{-5}M and 31% for 10^{-4} M. When increasing the initial concentration of dye, the amount of dye adsorbed on the catalyst surface get increases that make only fewer photons reach at the surface of photocatalyst. This results decrease in concentration of $^{\bullet}OH$ and $O_2^{\bullet -}$ radicals thereby decrease in photocatalytic activity.

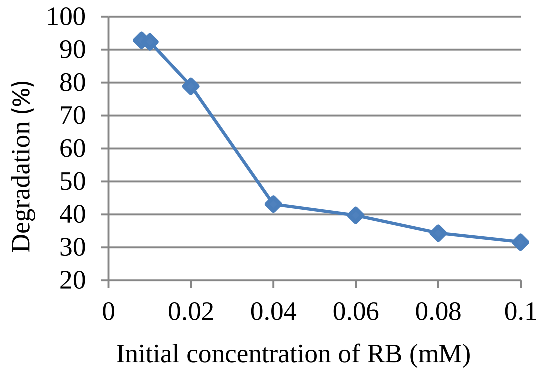


Figure 4. *Effect of dye initial concentration on degradation of RB by Ag/TiO₂ catalyst under visible light.*

3.4 Effect of pH

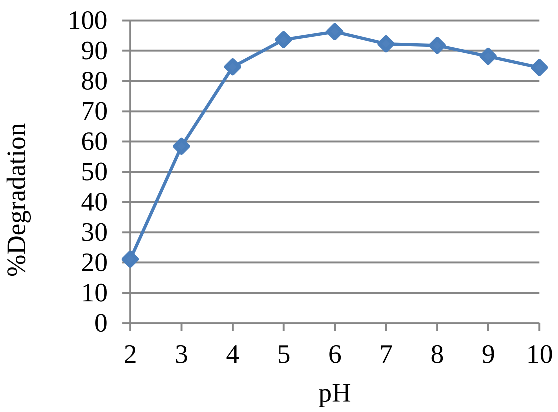


Figure 5. *Effect of pH on degradation of RB of Ag/TiO_2 under visible light.*

The effect of pH is one of the most important factors on the photocatalytic degradation process. In order to find out the optimal pH for the degradation of RB dye, the pH of reaction mixture was varied from 2 to 10 by keeping the RB dye concentration (10^{-5} M) and catalyst amount (2.0 g/L) constant in all reactions. The pH was adjusted by the addition of appropriate amounts of NaOH or HCl solution. The results shown in Fig.5 demonstrated that the greatest degradation was obtained at pH6, with 95.59%. When pH was in range from 4 to 6, the percentage degradation was increased from 84.65 to 95.59%. Further pH in range from 6 to 10, the percentage degradation was decreased from 95.59 to 84.42%. Thus, the pH at 6.0 should be the optimal value. This may explain the highest degradation at acidic condition rather than alkaline.

3.5 Mineralization

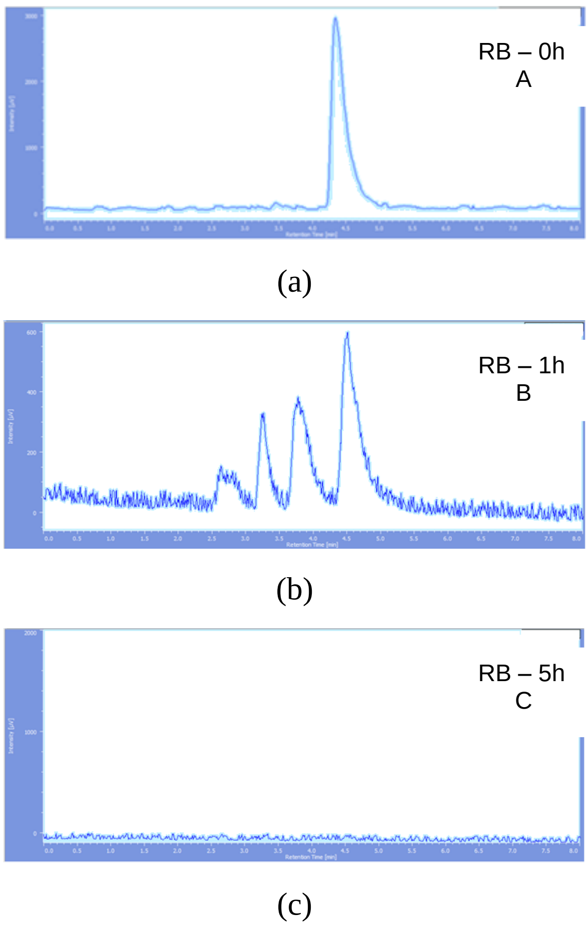


Figure 6. *HPLC chromatogram of degraded samples of different time intervals (A) 0 h, (B) 1 h and (C) 5h.*

To confirm the mineralization, the photocatalytic degradation reactions of RB by Ag/TiO_2 were carried out up to 5 h and then the irradiated samples were analyzed by HPLC. HPLC chromatogram of 0, 1 and 5 h samples are shown in Figure 6A-6C. HPLC analysis results showed that, RB dye (peak A) was identified at the retention time of 4.35 min. From the HPLC chromatogram, the formations of N-deethylated intermediate were observed after the photocatalytic degradation of RB dye. The N-deethylated intermediates were further confirmed by the shifting of wavelength range for the samples taken out at different time intervals during the photocatalytic experiments. Percentage degradation of RB dye determined by HPLC analysis confirms that there was no formation of harmful final products. Furthermore, it was observed that 100 % of dye was degraded at the end of 5 h reaction (Fig. 6C).

To identify the possible intermediate products during the photocatalytic degradation, electro spray ionization mass spectra (ESI-MS) experiments were conducted. ESI mass spectra of the irradiated aqueous solutions of RB at 1 hour were observed. Major intermediates during the degradation process were proposed by using m/z values of the mass spectra. It shows in the figures 7A-7D.

Table 1. *Identification of RB and N-de-ethylation intermediates by LC/MS*

m/z	Retention time (min)	N-De-ethylation intermediates
415	15.6	N,N-Diethyl-N-ethylrhodamine (DER)
387	9.2	N-Ethyl-N-ethylrhodamine (EER)
359	7.2	N-Ethylrhodamine (ER)
331	5.5	Rhodamine (R)

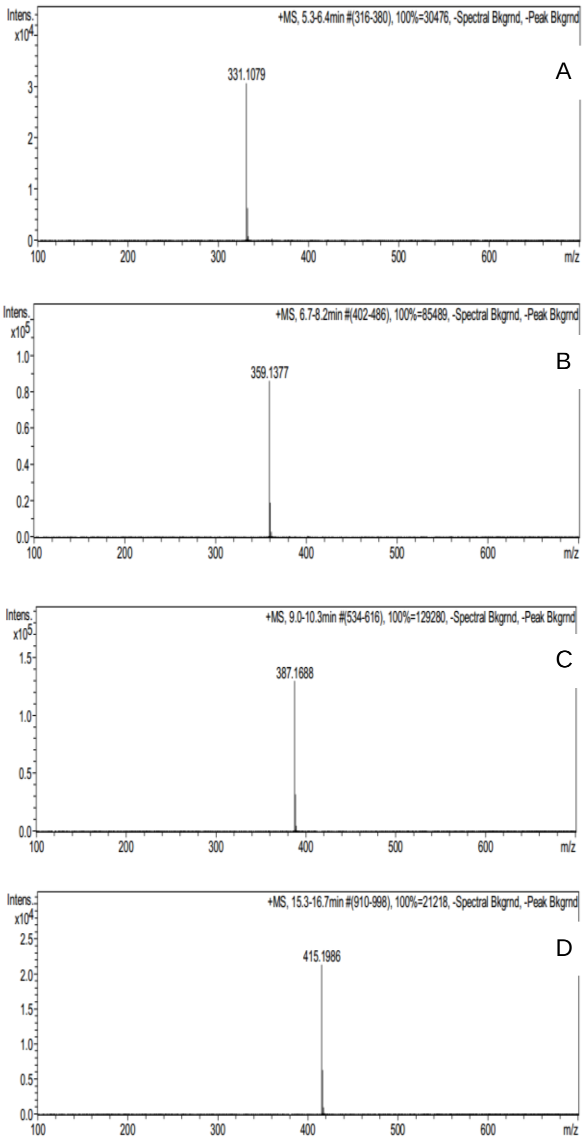
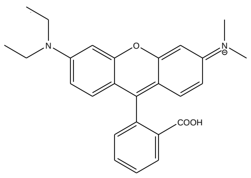
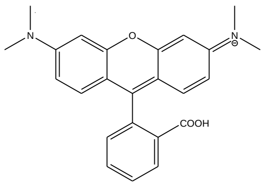
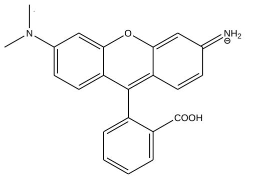
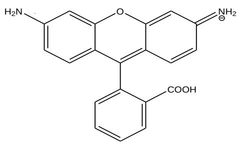


Figure 7. *Typical LC–MS chromatogram at the irradiation for 60 min (A: DER; B: EER; C: ER; D: R).*

The identification and structure of intermediates of RB are listed in Table 1 and 2. From the mass spectra, the main intermediate with m/z value of 415, 387, 359, 331 were those of N-de-ethylated intermediates such as N,N-diethyl-N-ethylrhodamine, N-diethyl-N-ethylrhodamine, N-ethyl-N-ethylrhodamine, N-ethylrhodamine and Rhodamine, respectively. The results indicated that the ethyl groups in the RB structure were removed one by one, and finally transformed into R. In Figure 6C, all chromatogram peaks disappeared after 5 hours irradiation which proved that RB and the intermediates were degraded completely in Ag/TiO_2 under visible light.

Table 2. *Structural formula of N-de-ethylation intermediates*

N-De-ethylation intermediates	**Structural formula**
N,N-Diethyl-N-ethylrhodamine	
N-Ethyl-N-ethylrhodamine	
N-Ethylrhodamine	
Rhodamine	

4 CONCLUSION

The prepared Ag/TiO_2 catalysts showed higher photocatalytic efficiency for RB degradation under visible light irradiation compared to pure TiO_2 (P25). The optimized amount of catalyst and pH for higher degradation was 2.0 g/L, and 6.0, respectively. The degradation of RB dye was further confirmed by HPLC analysis. LC/MS technique was used to analyze the degradation process, and photocatalytic degradation of RB dye by Ag/TiO_2 was mainly a stepwise N-de-ethylation.

ACKNOWLEDGMENTS

The authors thank for support of the Technology Environment Lab - HCMC University of Technology and Education.

REFERENCES

[1] X. Chen, S.S. Mao, Titanium dioxide nanomaterials: synthesis, properties, modifications, and applications, *Chemical Review*, 107, pp. 2891–2959, 2007.

[2] T.L. Thompson, J.T. Yates, Surface science studies of the photoactivation of TiO_2 - new photochemical processes, *Chemical Review*, 106, pp. 4428–4453, 2006.

[3] S.Y. Chai, Y.J. Kim, M.H. Jung, A.K. Chakraborty, D. Jung, W.I. Lee, Heterojunctioned BiOCl/Bi_2O_3 - a new visible light photocatalyst, *Journal of Catalysis*, 262, pp. 144–149, 2009.

[4] X. Li, J. Ye, Photocatalytic degradation of Rhodamine B over $Pb_3Nb_4O_{13}$/Fumed SiO_2 composite under visible light irradiation, *Journal of Physic and Chemical. C*,111, pp. 13109–13116, 2007.

[5] M. Anpo, Use of visible light. Second-generation titanium dioxide photocatalysts prepared by the application of an advanced metal ion-implantation method, *Pure and Applied Chemistry*, 72, pp. 1787-1792, 2000.

[6] M.D.H.A. Fuerte, A.J. Maira, A. Martinez-Arias, M. Fernadez-Garcia, J.C. Conesa, and J. Soria, Visible light-activated nanosized doped-TiO_2 photocatalysts, *Chemical Communication*, 24, pp. 2718-2719, 2001.

[7] H. Yamashita, M. Harada, J. Misaka, et al., Application of ion beam techniques for preparation of metal ion-implanted TiO_2 thin film photocatalyst available under visible light irradiation: Metal ionimplantation and ionized cluster beam method, *Journal of Synchrotron Radiation,* 8, pp. 569-571, 2001.

[8] T. Ihara, M. Miyoshi, M. Ando, S. Sugihara, and Y. Iriyama, Preparation of a visible light active TiO_2 photocatalyst by RF plasma treatment, *Journal of Material Science,* pp. 4201-4207, 2001.

[9] K. Takeuchi, I. Nakamura, O. Matsumoto, S. Sugihara, M. Ando, and T. Ihara, Preparation of visible-light-responsive titanium oxide photocatalysts by plasma treatment, *Chemistry Letters*, 29, pp. 1354-1355, 2000.

[10] T. Ohno, T. Mitsui, and M. Matsumura, Photocatalytic activity of S doped TiO_2 photocatalyst under visible light, *Chemistry Letters,* 32, pp. 364-365, 2003.

[11] Y. Liu, X. Chen, J. Li, and C. Burda, Photocatalytic degradation of azo dyes by nitrogen-doped TiO_2 nanocatalysts, *Chemosphere,* 61, pp11-18, 2005.

[12] J.C. Yu, L. Zhang, Z. Zheng, and J. Zhao, Synthesis and characterization of phosphated mesoporous titanium dioxide with high photocatalytic activity, *Chemistry of Materials,* 15, pp. 2280 -2286, 2003.

[13] T. T. Y. Tan, C. K. Yip, D. Beydoun, R. Amal, Effects of nano-Ag particles loading on TiO_2 photocatalytic reduction of selenate ions, *Chemical Engineering Journal,* 95, pp. 179−186, 2003.

[14] V. Vamathevan, R. Amal, D. Beydoun, G. Low, S. McEvoy, Photocatalytic oxidation of organics in water using pure and silver modified titanium dioxide particles, *Journal of Photochemistry and Photobiology A*, 148, pp. 233−245, 2002.

[15] L. Zhang, J.C. Yu, A simple approach to reactivate silver coated titanium dioxide photocatalyst, *Catalysis Communication,* 6, pp. 684−687, 2005.

[16] N. Sobana, M. Muruganadham, M. Swaminathan, Nano-Ag particles doped TiO_2 for efficient photodegradation of direct azo dyes, *Journal of Molecule Catalysis A: Chemical,* 258, pp. 124−132, 2006.

[17] X.G. Hou, M.D. Huang, X.L. Wu, A.D. Liu, Preparation and studies of photocatalytic silver loaded TiO_2 films by hybrid sol gel method, *Chemical Engineering Journal*, 146, pp. 42−48, 2009.

[18] Zielinska, E. Kowalska, J. W. Sobczak, I. Lacka, M. Gazda, B. Ohtani, J. Hupka, A. Zalesk, Silver-doped TiO_2 prepared by microemulsion method: surface Properties, bio- and photoactivity, *Separation and puritication technology,* 72, pp. 309−318, 2010.

[19] Q. Liu, Y. Cao, W. L. Dai, J. F. Deng, The oxidative dehydrogenenation of methanol over a novel low-loading Ag-SiO_2-TiO_2 catalyst, *Catalysis Letter,* 55, pp. 87−91, 1998.

[20] A.L. de Oliveira, A. Wolf, F. Schuth, Highly selective propene epoxidation with hydrogen/oxygen mixtures over Titania-supported silver catalysts, *Catalysis Letter,* 73, pp.157−160, 2001.

<u>Corresponding author:</u>
Vo Thi Thu Nhu
Ho Chi Minh City University of Technology and Education
E-mail: nhuvtt@hcmute.edu.vn