Asian Journal of Chemistry; Vol. 27, No. 5 (2015), 1889-1893

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2015.18382

Preparation of TiO_2/Fe_2O_3/Chitosan Nanocomposite Films and Its Photocatalytic Degradation of Rhodamine B

J. Jia and Ping Du*

Department of Chemical Engineering, Binzhou University, Binzhou, Shandong Province, P.R. China

*Corresponding author: Fax: +86 543 3190097; Tel: +86 15169991068; E-mail: enzyme_008@163.com

Received: 28 June 2014; *Accepted*: 23 September 2014; *Published online*: 20 February 2015; AJC-16914

A new photocatalytic thin films TiO_2/Fe_2O_3/chitosan was synthesized by a solution casting technology to degrade the azo coloured compounds in the industrial waste water. The prepared TiO_2/Fe_2O_3/chitosan was characterized by X-ray diffraction, scanning electron microscopy and high-resolution transmission electron microscopy (HRTEM). TiO_2 and Fe_2O_3 were entrpped in the chitosan film uniformly. The catalytic ability of TiO_2/Fe_2O_3/chitosan was evaluated by photodegradtion of Rhodamine B. About 99.4 % Rhodamine B were photodegraded by 0.5 g L^{-1} photocatalyst under solar lights irradiation for 120 min. The influence of the reaction pH has been well investigated. And TiO_2/Fe_2O_3/chitosan has good stability and reusability, it is suitable for the practical industrial waste water treatment.

Keywords: TiO_2, Fe_2O_3, Chitosan, Photocatalytic degradation.

INTRODUCTION

Printing and dyeing pollution is an important source of organic pollutants. Every year about 7,000,000 tons textile dyes are synthesized by the global industries[1]. Half of them are azo compounds with chromophore (-N=N-) in their molecular structures. And 15 % of the coloured compounds are lost and discharged in the process of textile printing as effluents[2]. The dye containing waterwaste are charactered with deep chromaticity, high chemical oxygen demand (COD), toxicity, low biodegradability and resistant to decolourization. It is important to remove the organic dyes from the wastewater before it released into all kinks of open waters. Nowadays it is confirmed that the catalytic oxidation methods are effective for the degradation of the dye pollutants[3]. TiO_2 has attracted great concern and has been widely applied in the course of heterogeneous photocatalysis for its strong oxidizing power, non-toxicity and long term photostability[4-7]. However, TiO_2 is only effective to ultraviolet light for a wide band gap of 3.2 eV (anatase), which also resulted in high recombination rate of electron/hole pairs and the reduction of quantum yield[8-11]. In order to extend the photo responses of TiO_2 and achieve the complete mineralization of organic dyes in solar irradiation, many researches have been made by doping the transition metal and nanocomposites[12]. Meanwhile, Fe_2O_3/TiO_2 has been proven as an effective and prospect photocatalyst in the presence of visible light[13-15]. The nanosized interfaces and microstructure may play an important part in the improved photocatalytic activity of composite photocatalysts[16]. However, nanosized materials have a trend to aggregate by the van der Waals forces and it is difficult to be separated from the solution[17] after degradation.

Chitosan is obtained from chitin by N-deacetylation and contains high contents of amino and hydroxyl functional groups. Chitosan has good adsorption and chelating properties[16]. As a result, chitosan is a wonderful biological matrix for the immobilization of nanosized photocatalysts. In addition, chitosan can avoid the aggregation of the nanosized photocatalyst and facilitate the collection and the recycle use[18-20].

In this study, TiO_2/Fe_2O_3/chitosan thin film composite was synthesized under mild condition. Rhodamine B was selected as a model azo dye to evaluate the photocatalytic activity of the photocatalyst under imitate solar lights. This newly prepared composites combined with the advantages of TiO_2, Fe_2O_3 and chitosan. It is resulted that the photodegradation with TiO_2/Fe_2O_3/chitosan composite is a green, economical and low cost method for the treatment of the azo dyes wastewater.

EXPERIMENTAL

Titanium dioxide (TiO_2) (20 nm, Tianjing Topstar Co., Ltd, China); chitosan (99 %, molecular weight: about 2×10^5, Henan Deda Chemical Co., Ltd, China); Rhodamine B (Tianjin Guangfu Chemical Reagent Co., Ltd, China), $FeNO_3$ (Nanjing Chemical

Reagent Co., Ltd, China); glutaraldehyde (v/v, 25 %, Shanghai Chemical Reagent Co., Ltd, China). All of the materials were used as received.

Preparation of TiO_2/Fe_2O_3/chitosan nanocomposite films: The TiO_2/Fe_2O_3/chitosan nanocomposite films were prepared according to the solution casting technology[21]. Firstly, 2 g of chitosan was dissolved in 100 mL 2 % (v/v) acetic acid solution under magnetic stirring. After 1.5 h, 0.2 g TiO_2 and 1.53 g of Fe_2O_3 were added into the above chitosan solution. The mixture were continued to stir strongly for 1.5 h. Ferric nitrate was used as the precursor of nanosized Fe_2O_3. The pH was adjusted at 4.5. 25 mL of the viscous reaction mixture was cast on a glass plate (10 cm × 20 cm) and dried at room temperature to receive thin and flat film. Secondly, the films casted on the plates were immersed into 0.2 mol L^{-1} NaOH solution for the coagulation and separation. The films were kept in 60 °C homothermal water bath for 3.5 h and then were immersed into the 0.5 % glutaraldehyde solution for 1 h for the crosslinking reaction. The films were rinsed by ethanol and double distilled water for several times. Finally the nanocomposite thin films (TiO_2/Fe_2O_3/chitosan) was obtained after dried in oven at about 200 °C. TiO_2/chitosan and Fe_2O_3/chitosan were also received with the similar methods.

X-ray diffraction (XRD) of TiO_2, Fe_2O_3, chitosan and TiO_2/Fe_2O_3, TiO_2/Fe_2O_3/chitosan were recorded by an X'pert pro X-ray diffractometer (PAN Analytical, Holland) with CuK_α radiation and the step scan range was from10° to 80° (2θ). Scanning electron microscopy (SEM, JEOL, X-650, Japan) was used to observe the surface physical morphology of chitosan, TiO_2/chitosan, Fe_2O_3/chitosan and TiO_2/Fe_2O_3/chitosan. High-resolution transmission electron microscopy (HRTEM) photographs were obtained on a JEOL machine (Tokyo, Japan) at an accelerating voltage of 200 kV.

Photocatalytic degradation of rhodamine B under simulated solar irradiation: To evaluate the photocatalytic activity of TiO_2/Fe_2O_3/chitosan, the photocatalytic degradation experiment was carried out by the degradation of rhodamine B present in the wastewater on the XPA (XuJiang Electromechanical Plant, Nanjing) photochemical reactor. And simulated solar irradiation for the tube containing the reaction suspension were provided by a 300 W xenon lamp with an optical filter to get rid of light of wavelength less than 400 nm.

The reaction temperature was controlled at about 20 °C with circulating water during the whole experiment. The rhodamine B solution were completely dissolved in the 100 mL quartz tube. A certain amount of TiO_2/Fe_2O_3/chitosan photocatalyst was added to the rhodamine B solution. And the air was pumped through the reaction solution in order to mix the reactant solution sufficiently. And the pH of rhodamine B solution was measured as 4.5. Firstly the experiment was carried out with vigorous stirring in the dark to reach adsorption-desorption equilibrium. Then the mixture was bubbled with air and catalyzed under the visible lights irradiation. The photodegradation samples were collected at well-regulated intervals of time and measured by Agilent 8453 UV-visible spectrometer to evaluate the photoactivity of the new catalyst by the degradation of the dyes in the irradiation process. The concentration of rhodamine B was calculated by its standard curves.

RESULTS AND DISCUSSION

Characteristics of TiO_2/Fe_2O_3/chitosan composites: Fig. 1 showed the XRD patterns of (a) chitosan, (b) Fe_2O_3, (c) TiO_2, (d) TiO_2/Fe_2O_3, (e) TiO_2/Fe_2O_3/chitosan. TiO_2 exhibits the typical patterns of anatase and rutile.

Chitosan has the typical crystalline peaks at 2θ of 13.38°, while Fe_2O_3 exhibits peaks at 2θ of 30.4°, 35.7°, 53.8°, 43.4°, 57.4° and 63.0°of cubic spinel structure. And the peak shapes and positions of TiO_2/chitosan is identical with the patterns raw TiO_2. This indicated that the introduction of chitosan in the TiO_2/chitosan had no effect on the crystalline phase of TiO_2. The TiO_2/Fe_2O_3/chitosan pattern is basically in accordance with patterns of TiO_2/chitosan and Fe_2O_3/chitosan, except that the crystalline peak of chitosan shifted to about 17.80°. The possible reason was that the intermolecular interaction of chitosan has been destroyed by the modification of TiO_2 and Fe_2O_3 in the process of TiO_2/Fe_2O_3/chitosan nanocomposite thin films.

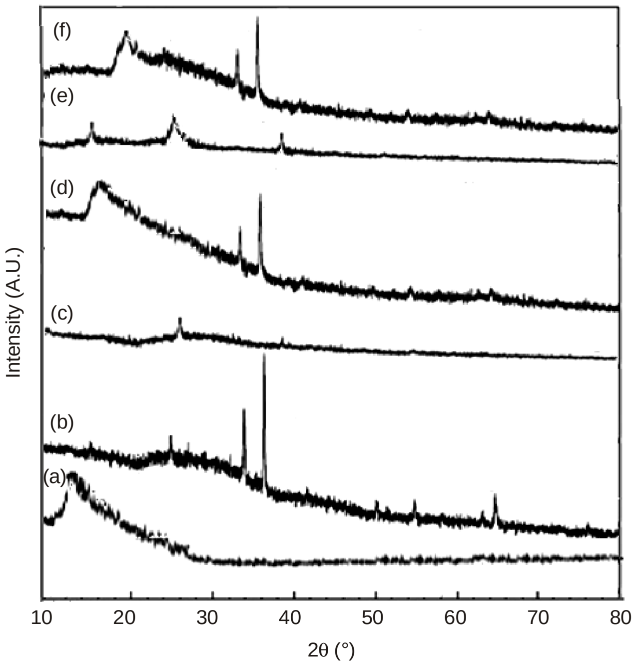

Fig. 1. XRD patterns of (a) chitosan, (b) Fe_2O_3, (c) TiO_2, (d) Fe_2O_3/chitosan, (e) TiO_2/chitosan, (f) TiO_2/Fe_2O_3/chitosan

SEM images for chitosan, Fe_2O_3/chitosan, TiO_2/chitosan and TiO_2/Fe_2O_3/chitosan NTFs were shown in Fig. 2. As shown, the chitosan film is relatively smooth. After the addition of Fe_2O_3, Fe_2O_3 granules have good dispersions in the membrane (Fig. 2-B). TiO_2/chitosan(Fig. 2-C) is more rough than 2-A. The TiO_2 particles were immobilized irregularly in the film. The TiO_2/Fe_2O_3/chitosan thin film in Fig. 2-D, the surface morphology is similar with TiO_2/chitosan. That suggested that TiO_2 and Fe_2O_3 were embedded in the surface of TiO_2/Fe_2O_3/chitosan, which were in good agreement with those of XRD. A representative HRTEM image is shown in Fig. 3, which resulted that the particle diameters were in the range of 20-30 nm.

Photocatalytic activity of the prepared TiO_2/Fe_2O_3/chitosan: 0.5 g L^{-1} TiO_2/Fe_2O_3/chitosan was mixed with

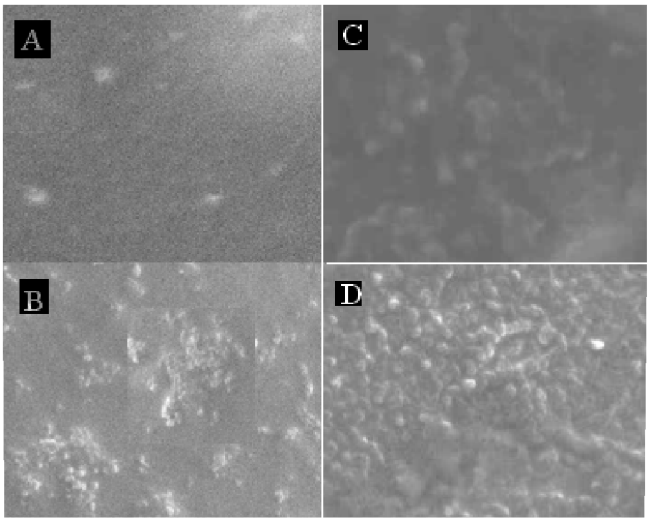

Fig. 2. SEM images for pure chitosan film (A), Fe_2O_3/chitosan (B), TiO_2/chitosan (C) and TiO_2/Fe_2O_3/chitosan NTFs (D)

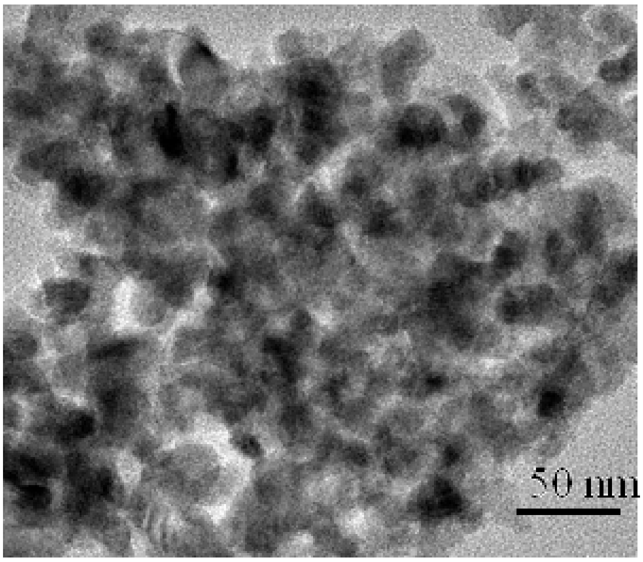

Fig. 3. TEM images for TiO_2/Fe_2O_3/chitosan NTFs

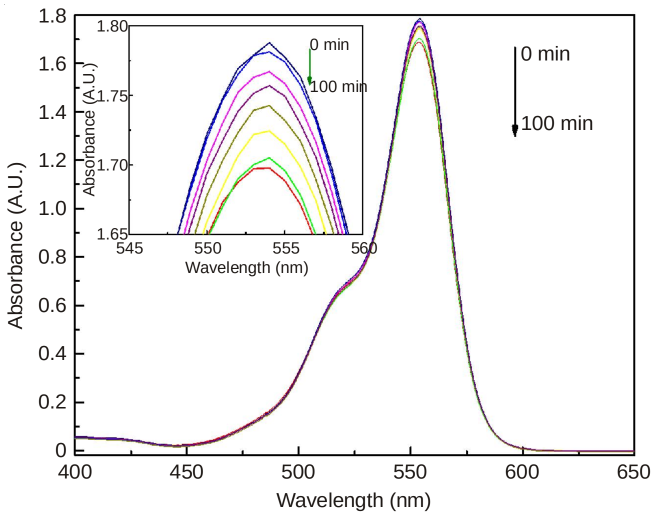

Fig. 4. UV-visible absorption spectra of rhodamine B solution by TiO_2/Fe_2O_3/chitosan in dark; Time (up to down):0, 10, 25, 40, 60, 80, 90, 100 min

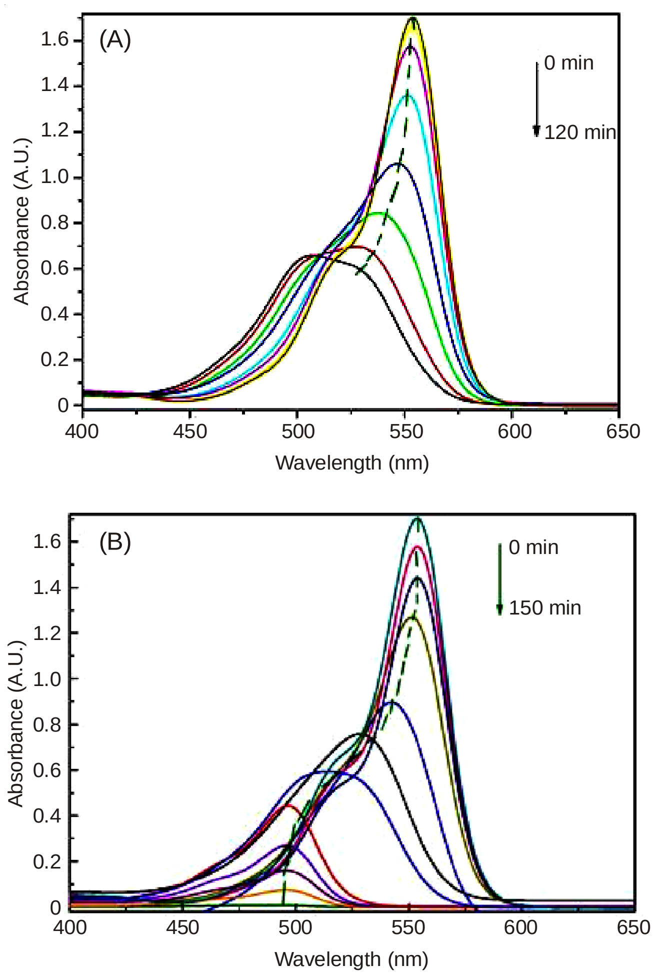

Fig. 5. UV-visible absorption spectra of rhodamine B solution by TiO_2/Fe_2O_3/chitosan under the visible light irradiation (A) with the optical filter; (B) without the the optical filter to throw away the UV

rhodamine B (2×10^{-4} mol L^{-1}) aqueous solution and the pH of the reaction suspension was adjusted to 4.5. Adsorption capacity of catalyst are sigificant to photocatalytic reactions since it is well-known that the degraded material are firstly adsorbed onto the surface of the catalyst or free molecules arrive at the photocatalyst surface[22]. Ahead of irradiation, the suspensions was kept in dark for 100 min to reach adsorption equilibrium with vigorous stirring. UV-visible absorption spectra of aqueous solution of rhodamine B in dark for the adsorption equilibrium is shown in Fig. 4. The adsorption rate of TiO_2/Fe_2O_3/chitosan was about 17.7 %. Subcequently, the mixture was bubbled with air and catalyzed under the visible lights irradiation. The spectral changes of rhodamine B solution by TiO_2/Fe_2O_3/chitosan are illustrated in Fig. 5. Fig. 5-A was received under xenon lamp with an UV-cut filter for 120 min and Fig. 5-B is received without an UV-cut filter for 150 min.

0.5 gL^{-1} TiO_2/chitosan and 0.5 gL^{-1} Fe_2O_3/chitosan was also mixed with rhodamine B (2×10^{-5} mol L^{-1}) aqueous solution, respectively. In order to compare the photocatalytic activity of the above three photocatalysts, the photodegradation experiments were also done as shown in Fig. 6. The photocatalytic activity was evaluated according to the concentration of rhodamine B in the process of the degradation. This results noted that TiO_2/Fe_2O_3/chitosan has strongest adsorption ability and photocatalytic activity under the same experimntal conditions.

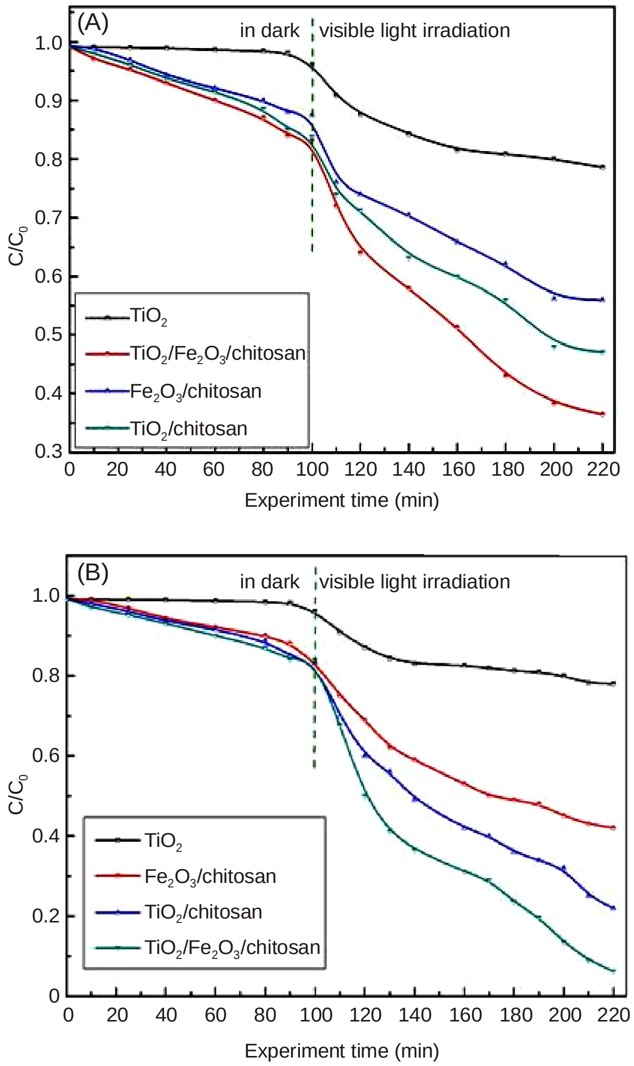

Fig. 6. Photodegradation of rhodamine B with TiO_2/Fe_2O_3/chitosan, TiO_2/chitosan and Fe_2O_3/chitosan under visible irradiation. A: with the optical filter (time: 0, 10, 20, 40, 60, 80, 100, 120 min); (B) without the the optical filter (time: 0, 10, 20, 30, 45, 60, 70, 80, 90, 100, 110, 120, min)

Fig. 6A displayed the photocatalytic effect of TiO_2/Fe_2O_3/chitosan, Fe_2O_3/chitosan and TiO_2/chitosan under visible lights with a optical filter of $\lambda \leq 400$ nm. The degradation rate of rhodamine B reached to 63.5, 44.0 and 50.2 %, respectively. Compared with Fig. 6A, 6B was the performance of the three above mentioned photocatalysts without the optical filter. It was apparent shown that the overall photodegradation rates had increased trends. The degradation rate was about 99.4, 78 and 58 %, respectively. At the same time, it was also noted that the degradation ability under the imitated solar irradiation without a fliter had a remarkable enhance. The possible reasons were listed as followes. Firstly, with the catalysis of TiO_2/Fe_2O_3/chitosan, the UV-visible absorption spectrum of rhodamine B had a hypsochromic shift from 550 nm to about 490 nm. It may be mainly due to the double band (N=N) in the molecule of rhodamine B, which were the most active oxidative groups[11,23]. Therefore, it could be inferred that the corresponding band gap energy has also been changed. Secondly, UV lights were outputed accompanied with the visible lights irradiation without optical fliter. The electrons which were photogenerated by TiO_2/Fe_2O_3/chitosan possibly had been transferred into TiO_2, while the generated band gap energy remain in TiO_2/Fe_2O_3/chitosan[24].

Influence of pH of the photodegradation by TiO_2/Fe_2O_3/chitosan: The value of pH is a important factor that affect the catalytic activity of the reaction. The pH of the solution was adjusted with HCl and NaOH. The adsorption and degradation experiments were carried out on different value of pH. From Table-1, it is illustrated that the experiment results have a widely variation. According to the study of Schme-lling *et al.*[25], the adjustment of the value of the pH could lead to the change of the Fermi energy level. So pH 4.5 was chosen as the reaction pH.

TABLE-1
ADSORPTION AND DEGRADATION RATE WITH DIFFERENT pH

Dye	pH	$C_{absorption}/C_0$ (t = 100 min)	$C_{degradation}/C_0$ (t = 120 min)
	3.0	0.1000	0.2056
Rhodamine B	4.5	0.1893	0.0632
	10.5	1.000	0.9455

Stability and reusability of TiO_2/Fe_2O_3/chitosan: In order to verify the stability and reproducibility, the photodegradation experiment was carried out by TiO_2/Fe_2O_3/chitosan under the same condition. After each catalytic experiment of rhodamine B, the reaction solution was filtrated for the catayst. The TiO_2/Fe_2O_3/chitosan was washed by double diatilled water for several times and then dried at 100 °C for 40 min. The photodegradation efficiency of each experiment was shown in Fig. 7. The degradation rate changed only from 99.4 to 85.2 % after five times of reaction. As the results shown, TiO_2/Fe_2O_3/chitosan was considered to have a good stability and reusability. For this judgment, TiO_2/Fe_2O_3/chitosan is suitable for the practical industrial waste water treatment.

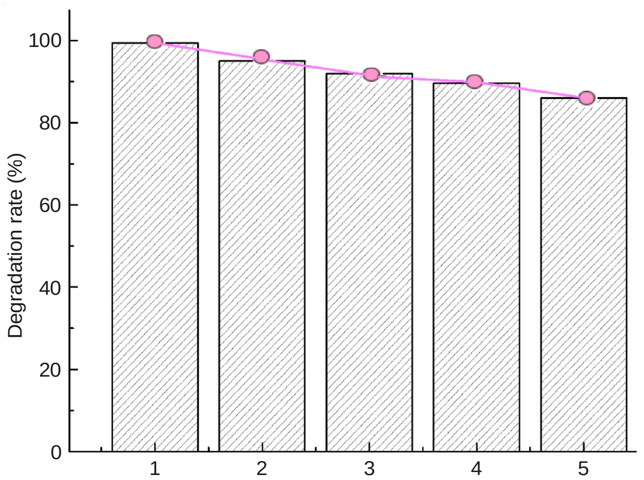

Fig. 7. Reproducibility experiment of TiO_2/Fe_2O_3/chitosan; (2×10^{-5} mol/LRB, 0.5 g/L catalyst, 120 min irradiation time without optical filter)

Conclusion

In this work, a new photocatalyst TiO_2/Fe_2O_3/chitosan composite was synthesized and characterized by XRD, SEM and HRTEM. It is found that the prepared new TiO_2/Fe_2O_3/

chitosan has better photocatalitic activity under the imitate solar lights and after 120 min, the degradation rate of rhodamine B was almost 99.4 % at pH 4.5. It was investigated that the TiO_2/Fe_2O_3/chitosan has good stability and reusability and suitable for the practical treatment of the dye containing wastewater.

ACKNOWLEDGEMENTS

This work was partially supported by the Doctor Foundation of Binzhou University (2009Y02), the Science and Technology Development Program Foundation of Binzhou City (2013ZC1603) and Innovation and Entrepreneurship Training Programm for the National College Students (No. 201410449017).

REFERENCES

1. H. Park and W. Choi, *J. Photochem. Photobiol. Chem*., **159**, 241 (2003).
2. H. Zhu, R. Jiang, Y. Fu, Y. Guan, J. Yao, L. Xiao and G. Zeng, *Desalination*, **286**, 41 (2012).
3. R. Andreozzi, V. Caprio and A. Insola, *Catal. Today*, **53**, 51 (1999).
4. M. Makita and A. Harata, *Chem. Eng. Process*., **47**, 859 (2008).
5. W. Du, Q. Sun, X. Lv and Y. Xu, *Catal. Commun*., **10**, 1854 (2009).
6. H.Y. Zhu, L. Xiao, R. Jiang, G.M. Zeng and L. Liu, *Chem. Eng. J*., **172**, 746 (2011).
7. R.J. Tayade, P.K. Surolia, R.G. Kulkarni and R.V. Jasra, *Sci. Technol. Adv. Mater*., **8**, 455 (2007).
8. M. Stylidi, D.I. Kondarides and X.E. Verykios, *Appl. Catal. B*, **47**, 189 (2004).
9. S. Kaur and V. Singh, *Ultrason. Sonochem*., **14**, 531 (2007).
10. K.M. Parida, N. Sahu, N.R. Biswal, B. Naik and A.C. Pradhan, *J. Colloid Interf. Sci*., **318**, 231 (2008).
11. M.A. Behnajady, N. Modirshahla and H. Fathi, *J. Hazard. Mater*., **136**, 816 (2006).
12. J.A. Navio, G. Colon, M. Macias, C. Real and M.I. Litter, *J. Appl. Catal. A*, **177**, 111 (1999).
13. M.A. Mahadik, S.S. Shinde, V.S. Mohite, S.S. Kumbhar, A.V. Moholkar, K.Y. Rajpure, V. Ganesan, J. Nayak, S.R. Barman and C.H. Bhosale, *J. Photochem. Photobiol. B*, **133**, 90 (2014).
14. X.X. Yu, S.W. Liu and J.G. Yu, *Appl. Catal. B*, **104**, 12 (2011).
15. H. Tang, D. Zhang, G. Tang, X. Ji, W. Li, C. Li and X. Yang, *Ceram. Int*., **39**, 8633 (2013).
16. A. Deshpande, P. Shah, R.S. Gholap and N.M. Gupta, *J. Colloid Interf. Sci*., **333**, 263 (2009).
17. I. Sopyan, M. Watanabe, S. Murasawa, K. Hashimoto and A. Fujishima, *J. Photochem. Photobiol. Chem*., **98**, 79 (1996).
18. H.Y. Zhu, R. Jiang, L. Xiao, Y.H. Chang, Y.J. Guan, X.D. Li and G.M. Zeng, *J. Hazard. Mater*., **169**, 933 (2009).
19. R. Jiang, H.Y. Zhu, X.D. Li and L. Xiao, *Chem. Eng. J*., **152**, 537 (2009).
20. Q. Li, H.J. Su and T.W. Tan, *Biochem. Eng. J*., **38**, 212 (2008).
21. U.G. Akpan and B.H. Hameed, *J. Hazard. Mater*., **170**, 520 (2009).
22. C. Tang and V. Chen, *Water Res*., **38**, 2775 (2004).
23. N.M. Mahmoodi, M. Arami, N.Y. Limaee and N.S. Tabrizi, *Chem. Eng. J*., **112**, 191 (2005).
24. H. Zhu, R. Jiang, L. Xiao, L. Liu, C. Cao and G. Zeng, *Appl. Surf. Sci*., **273**, 661 (2013).
25. D.C. Schmelling, K.A. Gray and P.V. Kamat, *Water Res*., **31**, 1439 (1997).