Journal of Chemical Engineering, IEB
Vol. ChE 28,No. 1, December, 2013

A novel polystyrene-supported titanium dioxide photocatalyst for degradation of methyl orange and methylene blue dyes under UV irradiation

Seema Singh[1]*, Aniket Chaki[1], Devesh Pratap Chand[1], Avinash Raghuwanshi[1], Pramod Kumar Singh[1] and Hari Mahalingam[1*]

[1]*Department of Chemical Engineering, Jaypee University of Engineering and Technology, Guna, Madhya Pradesh, India.*

Abstract: The commercialization of titanium dioxide-based heterogeneous photocatalysis continues to suffer from various limitations, the major shortcoming being the costly and time consuming post-treatment separation of very fine titanium dioxide particles. In order to eliminate this major hindrance, immobilization of titanium dioxide particles on various substrates continues to be an active area of research. In this work, polystyrene-supported titanium dioxide photocatalyst was prepared using a facile method. The photocatalytic activity of the developed photocatalysts was investigated by photodegradation of aqueous solutions of methylene blue andmethyl orange dyes under UV light for 24 h under non-stirred conditions. The recovery and reuse of the prepared photocatalysts was also investigated. The maximum percentage degradation of methyl orange and methylene blue dyes by the developed photocatalysts was found to be around 60 % and 66 % respectively. The ease of separation after use in addition to a facile, low cost-based method of fabrication and appreciable photocatalytic activity of the developed photocatalyst makes it a promising candidate to be explored further for large scale applications.

1. INTRODUCTION

In 1972, Akira Fujishima and Kenichi Honda first reported the photoinduced decomposition of water on titanium dioxide (TiO_2) electrodes. Since then, heterogeneous photocatalysis using semiconductor titanium dioxide photocatalyst has been an active and ever increasing area of research [1, 2].

TiO_2 has been reported as one of the most efficient and promising photocatalyst because of the following properties: (i) high physical and chemical stability, (ii) strong oxidizing power, (iii) high photocatalytic activity, (iv) non-toxic nature, (v) high turnover, (vi) complete mineralization of organic pollutants, (vii) economical, (viii) relatively low band gap, (ix) can be supported on various substrates and (x) stability against photo corrosion [3-7].

Although the TiO_2photocatalyst is considered to be an ideal photocatalyst yet it suffers from two major limitations:

1) It is active only under UV light.
2) Recombination of photo-generated holes (h^+) and electrons (e^-) that leads to reduction in the overall quantum efficiency [8, 9].

For large scale commercial applications of TiO_2photocatalysis, extensive research is being carried out to modify TiO_2so as to make it effective in solar light that is freely and abundantly available. Some of the various approaches being tried for making titanium dioxide effective in visible light are doping, capping, dye sensitization, coupling and surface modification by noble metals [3, 5].

TiO_2 is conventionally available in the form of powder. It can be applied to wastewater either in the form of powder, i.e., in slurry form or can be supported over a suitable substrate. Although when used in the form of powder, it shows greater surface area and efficiency yet it suffers from a major obstacle of post-treatment recovery that is both time and money consuming. Moreover, the light utilization efficiency of suspended photocatalyst is lowered due to the attenuation loss suffered by light raysas it travels in the water surface. To overcome these drawbacks, continuous efforts are being made to immobilize TiO_2 on various substrates [5, 10].

In the literature, various substrates for supporting titanium dioxide photocatalyst have been reported. Few of these are inorganic carbon-fabrics [11], Indium tin oxide glass [12], plastics [13],natural fabrics [14], synthetic fabrics [15],polymers [16], glass mats [17], glass plates, raschig rings [18], fly ash, vycor glass, hollow glass spheres, reactor walls, fiber glass, silica gel, fabric or wool, anodised iron, micro-porous cellulose membranes, quartz optical fibres, zeolites, alumina clays, ceramic membranes and monoliths, stainless steel [19].

Of the above stated substrates,the polymer substrates for supporting titanium dioxide photocatalyst have been attracting a lot of recent attention. This is attributed to their following unique properties: (i) chemical inertness, (ii) mechanical stability, (iii) high durability, (iv) hydrophobicnature, (v) low cost, (vi) ease of availability, (vii) thermosoftening properties, (viii) high UV-resistance and (ix) low density for most of them [3].

---

[*] Corresponding Authors: Seema Singh, HariMahalingam
E-mail: *seemchem@gmail.com ; hari.mahalingam@juet.ac.in*

A variety of methods for supporting titanium dioxide on polymer substrate have been reported in the literature. Some of them are sol-gel method [20], chemical vapour deposition (CVD) [21] thermal treatment method [22], hydrothermal methods [23], sol-spray methods [24] and electrophoretic deposition [25].

Due to the need of high temperature calcination along with complex procedures and expensive instruments, most of the above mentionedtechniques do not find their use in coating polymer substrate with TiO_2.As per our literature survey, it appears that sol–gel and sputtering have been the main low-temperature deposition techniques for supporting titanium dioxide nanoparticleson various polymeric substrates. Although sol–gel methodis very convenient yet the photocatalytic activities of TiO_2 films supported on substrates by this method are limited. This is due to the fact that efficient photo-induced holes and electrons are generated only in well crystallized phases of titanium dioxide. To obtaindesired crystal phase from amorphous sol–gel TiO_2films, thermal treatment at relatively high temperatures(generally 300°C and above) is required post deposition. This restricts the applicationof sol–gel method for supporting titania only on those polymeric substrates that have good thermal stability [3].

In this paper, a novel, facile and low cost-based method is used to immobilize commercial TiO_2 powder on polystyrene (PS) substrate. For photocatalytic degradation studies, methylene blue (MB) and methyl orange (MO) dyes were employed as model organic dye compounds. The photodegradation of MB and MO dyes by the prepared polystyrene-supported titanium dioxidephotocatalysts was investigated.

2. EXPERIMENTAL DETAILS

2.1 Materials, Equipment and Methods

The chemicals used in this study were: xylene (AR,SDFCL), polystyrene beads(Sigma-Aldrich), P25 TiO_2 (Evonik Degussa AG, Germany; BET surface area 50±15 m^2g^{-1}), methylene blue ($C_{16}H_{18}N_3SCl$, Merck, India), methyl orange ($C_{14}H_{14}N_3NaO_3S$, Merck, India). Distilled water was used throughout this study. Images were obtained by using an optical microscope (NIKON Eclipse E600 POL). The TiO_2 slurry samples were centrifuged using REMI R-8C Laboratory centrifuge. The calibration curves for MB and MO dyes and their photodegradation under UV illumination (Hg lamp, 254 nm, 15W, Philips) was investigated with the help of UV-visspectrophotometer (ELICO SL159).

2.2 Preparation of (TiO_2/PS) photocatalysts

The TiO_2/PS photocatalysts were prepared by mixing TiO_2 (Degussa P25) powder in polystyrene (PS) dissolved in xylene at 80^0C. Different TiO_2samples, namely $TiO_{2(0.02)}$/PS, $TiO_{2(0.03)}$/PS, $TiO_{2(0.04)}$/PS were prepared by taking 0.02g, 0.03g and 0.04g amount of TiO_2 respectively.The suspension was casted into a petridish and left at room temperature for solvent to evaporate. Then the petridish was kept in an oven at 80^0C for about 20h to obtain a thick sheet of photocatalyst. The sheets were washed several times with distilled water, air-dried and stored.

2.3 Preparation of calibration curves for MB and MO

Different concentrations of MB and MO solutions were prepared from stock solutions of 50 ppm and the calibration curves for MB and MO solutions were obtained by using UV-vis spectrophotometer at absorption maximum of 664 nm and 465 nm respectively.

2.4 Photocatalytic study

During the photocatalytic study, small pieces of TiO_2/PS photocatalyst samples weighing 3g were placed in a 100mL beaker containing 50 mL of MB solution (5 ppm). A similar setup was used for studying the photodegradation of MO dye. The solutions were then kept in dark for a period of 60min to reach adsorption equilibrium. To avoid oxygenation of the solutions, no stirring was used in the reactions. After 1h of adsorption period, the initial absorbance was recorded at a wavelength of 664 nm for MBsolution and 465 nm for MO solution. Subsequently, the irradiation was started by turning on the UV light kept at 10 cm above the solution surface. The photodegradation of MB and MO solutions was analysed after 6h, 18h and 24h of UV irradiation. For this, 5mL sample of MB and MO solutions was retrieved from the beaker, analyzed and then returned to the beaker.

A comparative study employing a similar setup was also undertaken using 0.02g of commercial TiO_2 (Degussa P25) in slurry form. The solution samples retrieved from the beaker were centrifuged to obtain clear solutions before spectrophotometric analysis.

3. OBSERVATIONS, RESULTS AND DISCUSSIONS

3.1 TiO_2/PS photocatalyst characterization

The preliminary images (Fig.1) of the prepared TiO_2/PS photocatalysts were obtained by using an optical microscope. The images suggest the presence of TiO_2 particles on the polystyrene surface. The TiO_2/PS photocatalyst sample with higher loading amount of TiO_2 show higher TiO_2 agglomerates. Further investigation using electron microscopy (SEM/TEM) needs to be undertaken.

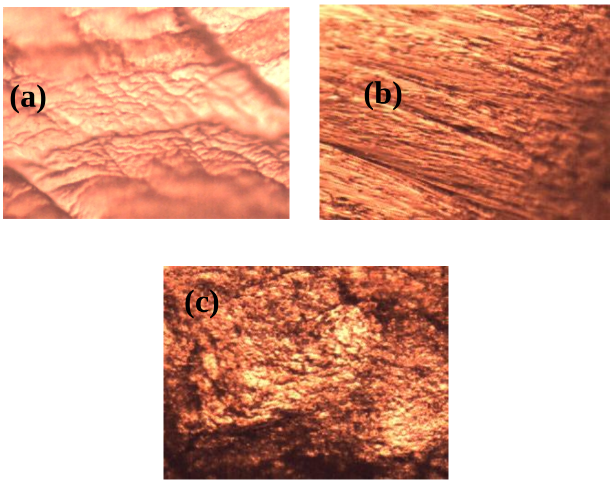

Fig.1: Optical microscope images of TiO_2/PS photocatalysts on 20X magnification scale (a) $TiO_{2(0.02)}$/PS, (b) $TiO_{2(0.03)}$/PS, (c) $TiO_{2(0.04)}$/PS

3.2 Calibration curves for MB and MO

Straight lines were obtained for the calibration curve of both MB and MO solutions (with R^2 = 0.9937and 0.9997 respectively)**(Fig. 2).**

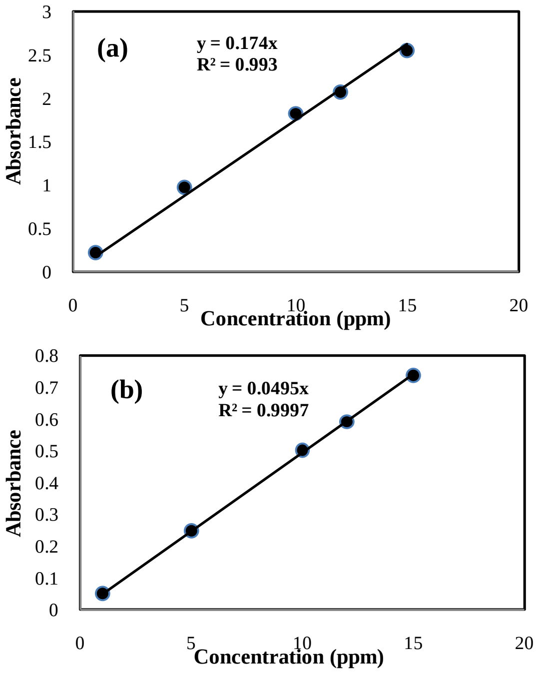

Fig. 2: Calibration curves for (a) methylene blue, (b) methyl orange

3.3 Photocatalytic reactions

After 1 h of adsorption period in the dark, it was found out that the $TiO_{2(0.02)}$/PS sample showed lowerabsorbance as compared to $TiO_{2(0.03)}$/PS, $TiO_{2(0.04)}$/PS and TiO_2 (Degussa P25, slurry form) photocatalyst samples. This could be attributed to the lower adsorption of the dye molecules by relatively lesser amount of TiO_2particles present in $TiO_{2(0.02)}$/PS sample. In the absence of the photocatalyst in MB and MO solutions (blank experiment-I) as well as in presence of only PS beads in MB and MO solutions (blank experiment-II), no significant discoloration of MB and MO solutions under UV irradiation was observed. This confirmed that the photocatalytic activity was due to TiO_2 particles present in the PS substrate.

The photocatalytic studies were carried out by investigating the degradation of dyes, MB and MO as organic probe molecules under UV light irradiation after 6h, 18h and 24h. It was observed that the prepared TiO_2/PS photocatalysts could degrade both the MB and MO. The percentage degradation for all the three prepared photocatalysts increased as the irradiation time increased from 6h to 18h and subsequently 24h.The experimental data for the percentage degradation of MBand MO solutions by different samples of the photocatalystsis shown in **Fig. 3.**

The percentage degradation of MO and MB solutions by various prepared samples of TiO_2/PS photocatalysts under UV irradiation (λ=254nm) was found to be around 60% and 66% respectively.The percentage degradation of MO solution increased with time as well as loading amount of TiO_2 in the photocatalyst. For MB solution, $TiO_{2(0.02)}$/PS and $TiO_{2(0.03)}$/PS photocatalyst samples showed almost similar degradation efficiencies but $TiO_{2(0.04)}$/PS photocatalyst exhibitedslightly lesser percentage degradation for MB. The result suggests that the amount of TiO_2 has a significant influence on the photocatalytic activity of the photocatalyst and thus, optimization of loading amount of TiO_2 in the photocatalyst needs further investigation. For comparison, a similar experimental setup was made to investigate the photocatalytic degradation by 0.02g of TiO_2 (Degussa P25)in slurry form. It was observed that the slurry form of titaniacompletely degraded both, the MB and MO solutions, within 2.5h of UV irradiation. This could be attributed to the greater surface area offered by the photocatalysts in powder form as compared with the supported forms.

On investigation, it was found the polystyrene-supported TiO_2photocatalysts scored over slurry form of TiO_2 in ease of post-treatment recovery. Recyclability of the prepared TiO_2/PS photocatalysts was also investigated by using the TiO_2/PS photocatalysts (without any intermittent cleaning) for degradation of fresh MO dye solutions. It was observed that after second reaction run, the photocatalytic activity of the TiO_2/PS sheets decreased only slightly.

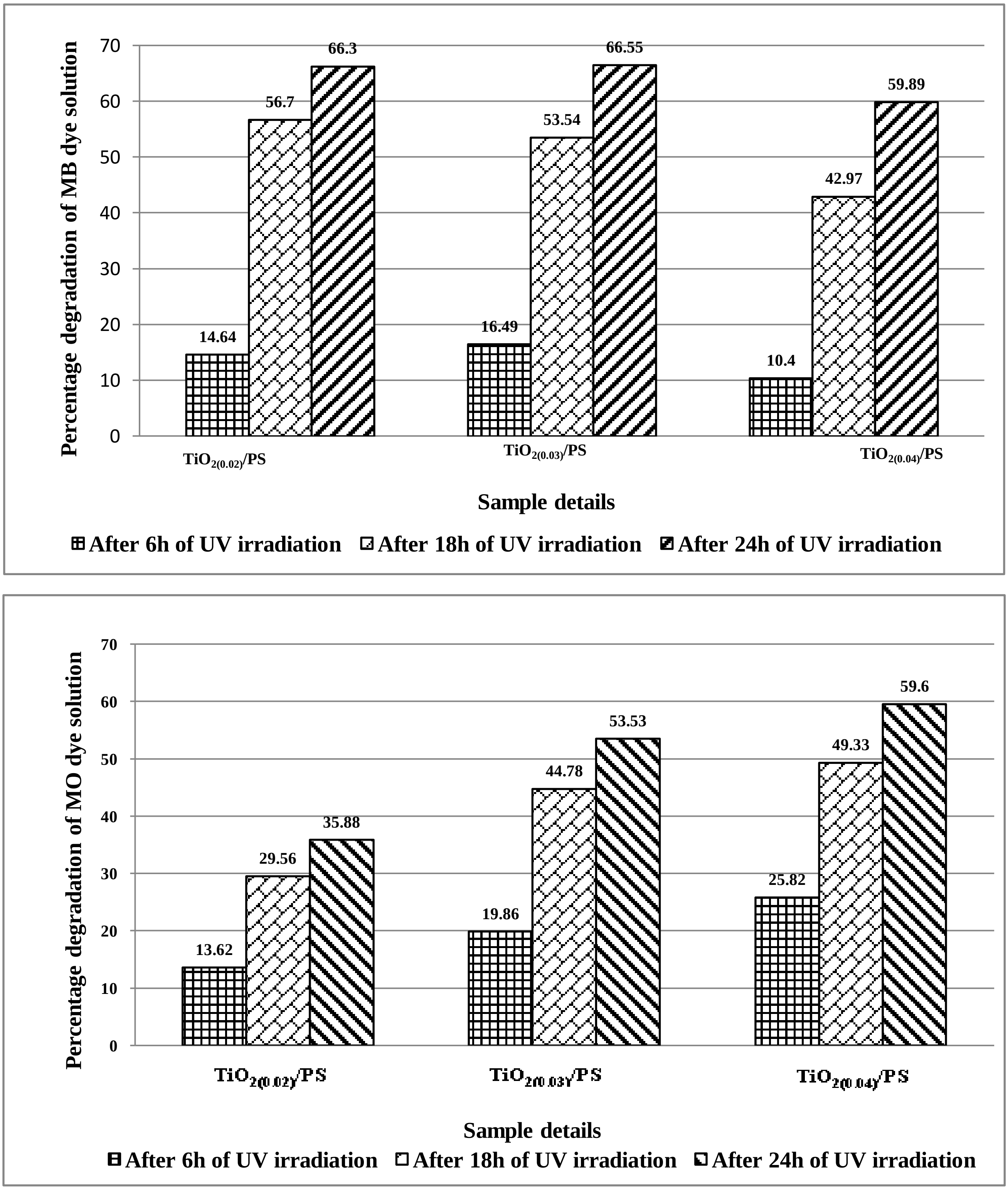

Fig. 3: Photodegradation of MB and MO dye solutions by prepared TiO_2/PS photocatalysts.

4. CONCLUSIONS

A novel and simple method for preparing polystyrene-supported TiO_2photocatalysts has been described. All the prepared TiO_2/PS photocatalyst samples could degrade both the MBand MOsolutions under UV irradiation. The percentage degradation by the TiO_2/PS photocatalysts was lower than that exhibited by slurry form of TiO_2. However, the ease of separation after use in addition to a facile and low cost-based method of fabrication and appreciable photocatalytic activity of the developed polystyrene-supported TiO_2photocatalyst makes it an attractive and promising candidate to be explored further for large scale applications like degradation of recalcitrant pollutants from wastewater. Due to the promising nature of the prepared polystyrene-supported TiO_2photocatalysts, further investigation in terms of characterizing the physico-chemical properties of the photocatalysts using scanning electron microscopy, optimization and influence of various parameters like amount of titanium dioxide in the photocatalyst, pH and temperature of the dye solution and recyclability over multi-reaction runs needs to be undertaken.

REFERENCES

[1] A. Fujishima, K. Honda, Nature 238 (1972) 37-38.

[2] K. Hashimoto, H. Irie, A. Fujishima, AAPPS Bulletin 17 (6)(2007) 12-28.

[3] S. Singh, H. Mahalingam, P.K. Singh, Appl. Catal., A 462– 463 (2013) 178– 195.

[4] S.M. Gupta, M.Tripathi, Chinese Sci Bull, 56 (16) (2011) 1639−1657.

[5] H.Han, R.Bai, Ind. Eng. Chem. Res. 48 (2009) 2891–2898.

[6] J. Kasanen, J. Salstela, M. Suvanto, T.T.Pakkanen, Appl. Surf. Sci. 258 (2011) 1738– 1743.

[7] J. Kasanen, M. Suvanto, T.T. Pakkanen, J.Appl.Polym. Sci. 119 (2011) 2235–2245.

[8] M. Pelaez, N.T. Nolan, S.C. Pillai , M. K. Seery, P. Falaras, A.G. Kontos, P.S.M. Dunlop, J.W.J. Hamilton, J.A. Byrne, K.O'Shea, M.H. Entezari, D.D. Dionysiou, Appl. Catal., B 125 (2012) 331–349.

[9] U.G. Akpan, B.H. Hameed, J. Hazard. Mater. 170 (2009) 520–529.

[10] J.A. Byrne, B.R. Eggins, N.M.D. Brown, B. McKinney, M. Rouse, Appl.Catal.,B 17 (1998) 25-36.

[11] T. Yuranova, O. Enea, E. Mielczarski, J. Mielczarski, P. Albers, J. Kiwi, Appl. Catal., B 49 (2004) 39–50.

[12] S.B. Sankapal, M.Ch. Steiner, A. Ennaoui, Appl. Surf. Sci. 239 (2005) 165-170.

[13] C.H. Kwon, H. Shin, J.H. Kim, W.S. Choi, K.H. Yoon, Mater. Chem. Phys. 86 (2004) 78-82.

[14] T. Yuranova, R. Mosteo, J. Bandara, D. Laub, J. Kiwi, J. Mol. Catal. A 244 (2006) 160–167.

[15] A. Bozzi, T. Yuranova, J. Kiwi, J. Photochem. Photobiol. A 172 (2005) 27–34.

[16] J.H. Yang, Y.S. Han, J.H. Choy, Thin Solid Films 495 (2006) 266-271.

[17] M. Dhananjeyan, J. Kiwi, P. Albers, O. Enea, Helv. Chim. Acta 84 (2001) 3433–3445.

[18] Y. Zhiyong, H. Keppner, D. Laub, E. Mielczarski, J. Mielczarski, L.K-Minsker, A. Renken, J. Kiwi, Appl.Catal., B 79 (2008) 63–71.

[19] M.E. Fabiyi, R.L. Skelton, J. Photochem. Photobiol., A 132 (2000) 121–128.

[20] Y. Chen, E. Stathatos, D.D. Dionysiou, Surf. Coat. Technol. 202 (2008) 1944–1950.

[21] C. Kuo, Y. Tseng, C. Huang, Y. Li, J. Mol. Catal. A 270 (1–2) (2007) 93–100.

[22] K. Tennakone, C.T.K. Tilakaratne, I.R.M. Kottegoda, J. Photochem. Photobiol., A 87 (1995) 177–179.

[23] S. Liu, X. Chen, J. Chem. Technol. Biotechnol. 82 (2007) 453–459.

[24] A.Y. Shan, T.I.M. Ghazi, S.A. Rashid, Appl. Catal., A 389 (2010) 1–8.

[25] M.S. Djosic, V.B. Miskovic-Stankovic, Dj. T. Janackovic, Z.M. Kacarevic-Popovic, R.D. Petrovic, Colloids Surf. A 274 (2006) 185–191.