www.sphinxsai.com

International Journal of ChemTech Research
CODEN(USA): IJCRGG ISSN : 0974-4290
Vol.2, No.3, pp 1537-1543, July-Sept 2010

Dual Effect of Photocatalysis and Adsorption in Degradation of Azorubine Dye Using Nanosized TiO_2 and Activated Carbon Immobilized with Different Techniques

Jatinder Kumar[1], **Ajay Bansal**[2]

Department of Chemical Engineering, Dr B R Ambedkar National Institute of Technology Jalandhar-144011, Punjab, India

Corres.author: ***[1]replytojk@yahoo.com; [2]bansala@nitj.ac.in***

Abstract: Combination of photodegradation and adsorption processes induces strong beneficial effects in removal of dyes. Addition of high adsorption capacity activated carbon to photoactive titanium dioxide in photodegradation of dyes improves the efficiency of dye mineralization. The present study involves the preparation of immobilized TiO_2 films by two different techniques to overcome the drawbacks encountered with the powdered suspensions. The photocatalytic performance of the prepared films for degradation of Azorubine dye has been evaluated and compared. The activated carbon has also been immobilized along with titanium dioxide to examine the dual effect of photodegradation and adsorption in removal of Azorubine. The dual effect showed better dye degradation capabilities.

Keywords: Titanium dioxide, photocatalysis, adsorption, activated carbon, Azorubine.

Introduction and Experimental

The treatment of coloured waste water containing hazardous dyes is one of the growing needs of the present time. To meet increasingly stringent regulations, waste water treatment plants have applied additional processes like coagulation, adsorption and filtration for the removal of dyes. However, these processes simply transfer pollutants from one source to another rather than completely eliminating them [1]. Photocatalysis using nanosized titanium dioxide has been widely studied as alternate to conventional processes for complete degradation of dyes [2]. In recent years, TiO_2 photocatalysis has been successfully applied to remove chemical pollutants and to inactivate microorganism [3-5].

Most of the studies related to photodegradation have been carried out using the suspension of powdered TiO_2 in aqueous solutions. However, the use of aqueous suspensions is limited for practical application by filtration problems due to the nanosize of TiO_2 particles. Alternatively, the catalyst may be immobilized on to a solid inert support, which eliminates the need of filtration of catalyst for reuse. Many techniques have been developed to obtain immobilized films of nano-crystals of TiO_2. The films of TiO_2 nanoparticles are routinely produced through the sol-gel process [6-7]. The sol-gel method of immobilization requires expensive precursors of TiO_2 and thermal treatment of the film between 400-500 °C [8].

The present investigation highlights the immobilization of TiO_2 with the help of polyvinyl alcohol –formaldehyde binder and using acrylic emulsion. Both of these methods do not require expensive precursors and thermal treatment at higher temperatures. The photocatlytic performance of the prepared films for degradation of Azorubine was evaluated and compared. The dual effect of photocatalysis and adsorption was also evaluated by immobilizing the activated carbon along with titanium dioxide.

Materials

The chemicals in this study were used as purchased. Titanium dioxide powder (nano-crystals) Degussa P25 (size of crystallites =30 nm, surface area = 55±15 m^2/g) was procured from Degussa, Germany. Polyvinyl alcohol LR, Formaldehyde LR and Azorubine ($C_{20}H_{11}N_2O_{10}S_3Na_3$) dye powder were obtained from s d Fine-Chem Ltd, Mumbai. Activated carbon was procured from Merck (India) Ltd Mumbai. Acrylic binder was obtained from Golden Chemical Works, Delhi.

Preparation of Degussa P25 films using polyvinyl alcohol-formaldehyde binder

TiO_2 suspension was prepared by adding 1 gm of TiO_2 in 10 ml of double distilled water followed by continuous stirring for 1 hour. Similarly, TiO_2-activated carbon suspension was prepared by mixing 0.5 gm of TiO_2 and 0.5 gm of activated carbon in 10 ml of double distilled water followed by stirring for 1 hour to ensure homogeneity. A 6.25% w/v polyvinyl alcohol-formaldehyde binder was prepared under constant stirring in a 70 °C water bath until transparent, sticky polymer glue is formed. The binder was kept in a sealed bottle to prevent it from rapid hardening. The fiberglass slides (75 mm × 50 mm × 1mm) were first applied with a thin layer of binder on one side of the slide. The TiO_2 suspension was then brushed onto the layer of binder to immobilize it. The film prepared by this method was given an identity FP1. The same procedure was carried out to immobilize TiO_2-activated carbon on fiberglass sheet to examine the combined effect of adsorption and photodegradation. This film was given an identity FP2.

Preparation of Degussa P25 films using acrylic binder

The TiO_2 films using acrylic binder were prepared by adding 1 gm of TiO_2 in 25 ml of water followed by addition of 1ml of acrylic emulsion under vigorous stirring for proper mixing. The TiO_2-acrylic emulsion was then applied over one side of the microscope glass slides (75 mm × 50 mm × 1mm) with the help of a brush. The coated film was left for air-drying. Coating was repeated twice to get a uniform film without pin holes. The film prepared in this way was given an identity GA1. In a similar way, 0.5 gm of TiO_2 and 0.5 gm of activated carbon were added in 25 ml of double distilled water followed by addition of 1ml of acrylic binder under vigorous stirring for proper mixing. The resultant emulsion was applied over microscope glass slides to form TiO_2-activated carbon film in the same way as discussed above. This film was given an identity GA2.

Photocatalytic performance test

All of the prepared films were used for photocatalytic degradation of Azorubine dye. Photocatalytic degradation experiments were carried out in a photocatalytic chamber containing two 15W lamps as source of UV light to evaluate the photocatalytic performance of the sol-gel derived films. A dye solution of 50ml with concentration of 10ppm was poured into a beaker having cross sectional area of 86.6 cm^2. The slide carrying film of TiO_2 was placed in the beaker in such a manner that the total available surface of photocatalyst was 50 mm × 75 mm. The beaker was then placed onto the working area of the photocatalytic reactor. A magnetic stirrer was used to provide mixing. Two UV light sources were then switched on and the solution was irradiated with the ultraviolet light The concentration of the dye at different reaction times were determined by measuring the absorbance intensity at λ_{max} = 520 nm with the help of the UV-Vis spectrophotometer. The decrease in concentration of the Azorubine was plotted with respect to time for analysis. The experiment was repeated for all kind of prepared TiO_2 films.

Kinetic Modeling

It has been agreed that the expression for the rate of degradation of dyes with irradiated TiO_2 follows the Langmuir –Hinshelwood (L-H) law of heterogeneous photocatalytic reactions [9]. According to L-H model, when initial concentration C_o is very small the following pseudo-first order rate equation is followed.

$$\ln\frac{C}{Co} = -kt$$

where k is pseudo- first order rate constant and t is time. A plot of ln (C/Co) versus time represents a straight line, the slope of which upon linear regression equals the pseudo-first order rate constant k.

Scanning Electron Microscopy (SEM)

The SEM analysis of the used films, after being coated with gold, was done with the help of scanning electron microscope JSM 6100 (JEOL) operated at 25 kV.

Results and Discussion

The photocatalytic degradation of Azorubine was performed with films FP1 and GA1 separately for a period of 5 hours in each case. The decrease in concentration of dye was recorded with respect time and is shown in Figure 1. The recorded data was best fitted by exponential equations with regression coefficient as high as 0.9904 and 0.9938 for FP1 and GA1 films respectively. It was observed that there was 83.2% decrease in the concentration of dye after 5 hours of UV light illumination in case of FP1 film. A decrease of 45.2% of dye concentration was monitored for the same period of illumination in case of GA1 film. The ln(C/Co) values were calculated and plotted with respect to time for FP1 and GA1 films as shown in Figure 2. The plotted data for both types of films was best fitted by straight line of different slopes which indicate that the reactions followed pseudo-first order kinetics according to the Langmuir – Hinshelwood (L-H) law. The pseudo-first order reaction rate constants were determined from the slopes of the plot ln(C/Co) versus time.

Table 1 shows the values of half life time ($t_{1/2}$) and pseudo-first order reaction rate constant (k) for FP1 and GA1 films. It is obvious that the films formed by polyvinyl alcohol binder gave fast photocatalytic degradation of Azorubine than film prepared using acrylic binder. The half life time was less and reaction rate constant was higher in case of film formed by polyvinyl alcohol-formaldehyde binder (FP1). One of the main reasons for the remarkable difference could be the solid-liquid interface between the TiO_2 particles and the aqueous solution. The polyvinyl alcohol-formaldehyde binder films contained very slightly physically adsorbed TiO_2 aggregates on the support that's why these films were not dense and had a large contact area of TiO_2. Moreover, the formaldehyde (a large portion of the binder) gets evaporated at room temperature providing the more TiO_2 surface area for degradation. The acrylic binder film (GA1) was less active because TiO_2 was more firmly bounded to the surface and acrylic binder does not evaporate at room temperature resulting in less surface area available for degradation.

In the similar way, the photocatalytic degradation of Azorubuine was also performed with films FP2 and GA2 separately for a period of 2.5 hours. The decrease in concentration of dye was plotted with respect to time and is shown in Figure 3. The recorded data was fitted by exponential equations with regression coefficient of 0.9972 in both of the cases. About 79.5% and 28.9% of the dye was photodegradad within 2.5 hours of UV light illumination for FP2 and GA2 films respectively. The plots of ln(C/Co) versus time for these films were best fitted by straight lines of different slopes as shown in Figure 4. It is obvious from the Figure 4 that the photocatalytic reactions followed pseudo-first order kinetics according to the Langmuir –Hinshelwood (L-H) law. The pseudo-first order reaction rate constants were determined from the slopes of the plot ln(C/Co) versus time.

Table 2 shows the values of half life time ($t_{1/2}$) and pseudo-first order reaction rate constant (k) for FP2 and GA2 films. These films gave comparatively better results than the FP1 and GA1 films due to the combined effect of adsorption and photodegradation. Activated carbon acts as an adsorbent in adsorbing the dye molecules from the solution. The adsorbed molecules on the surface of the activated carbon then come in contact with TiO_2 which causes photodegradation. TiO_2-activated carbon films act as semiconductor as well as adsorbent to give dual effect to the dye removal regardless the characteristics of the dye. In the present case, the activated carbon adsorption worked well in combination with TiO_2 photodegradation for removal of dye. The dual effect was capable of increasing the efficiency or performance of the whole degradation system. The film prepared using polyvinyl alcohol-formaldehyde binder (FP2) showed higher degradation rates than the films prepared by acrylic binder (GA2) due to the earlier mentioned reasons.

The SEM images of the used FP2 and GA2 films were also taken and shown in Figures 5 and 6. From the micrographs it was observed that the TiO_2 and activated carbon particles were present on the surface of the film even after use indicating the reusability of the film. The TiO_2 and activated carbon particles were not covered fully by the binders.

Table 1: Half life time ($t_{1/2}$) and rate constant (k) for immobilized films containing only TiO_2

Film Identity	Immobilization Technique	Content	Half Life Time ($t_{1/2}$), hours	Rate Constant (k), hour^{-1}
FP1	Polyvinyl alcohol – formaldehyde binder	TiO_2	2.07	0.3370
GA1	Acrylic binder	TiO_2	5.56	0.1255

Table 2: Half life time ($t_{1/2}$) and rate constant (k) for immobilized films containing both TiO_2 and activated carbon

Film Identity	Immobilization Technique	Content	Half Life Time ($t_{1/2}$), hours	Rate Constant (k), hour^{-1}
FP2	Polyvinyl alcohol – formaldehyde binder	TiO_2 & Activated carbon	1.16	0.588
GA2	Acrylic binder	TiO_2 & Activated carbon	4.84	0.1513

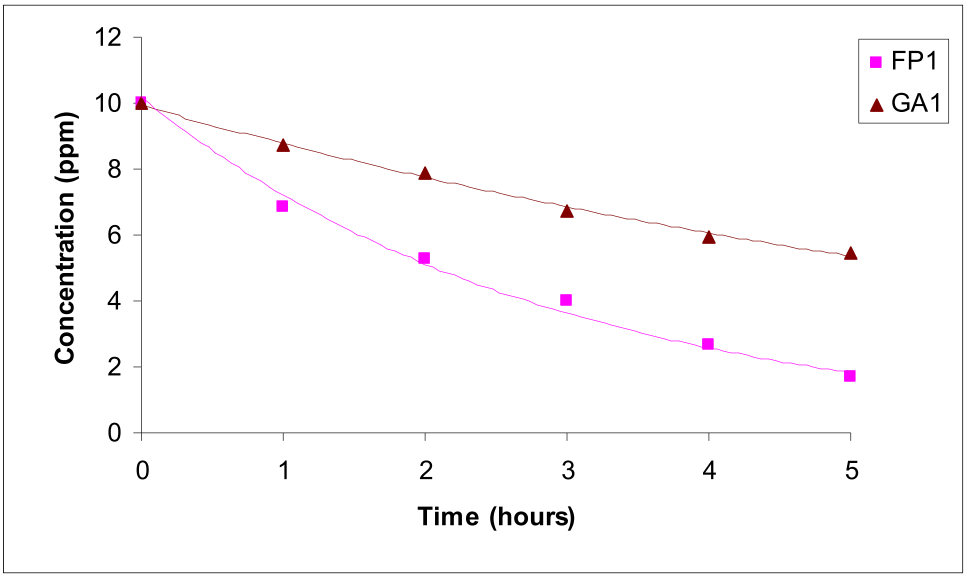

Figure 1: Time effect on photocatalytic degradation of Azorubine for immobilized films containing only TiO_2

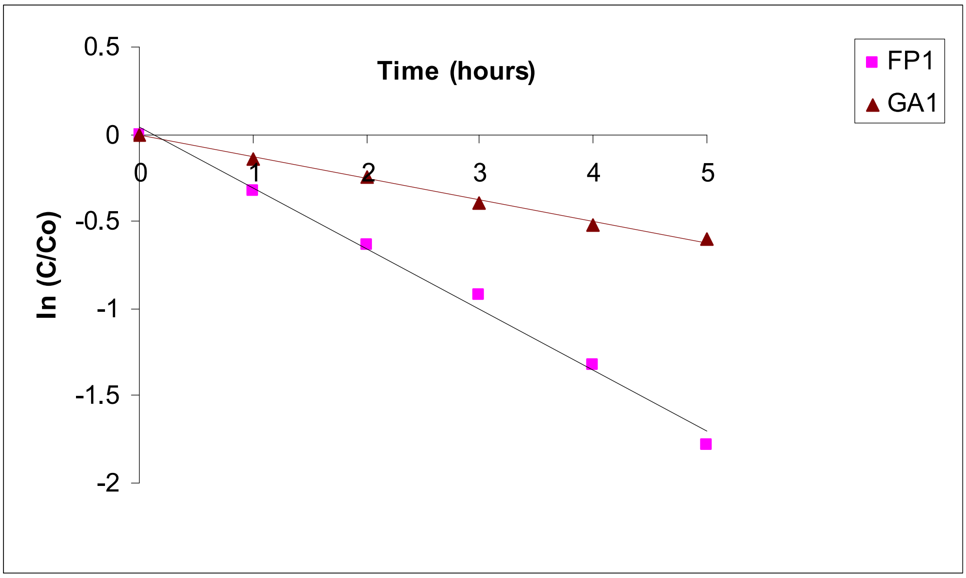

Figure 2: Kinetics of photocatalytic degradation of Azorubine for immobilized films containing only TiO_2

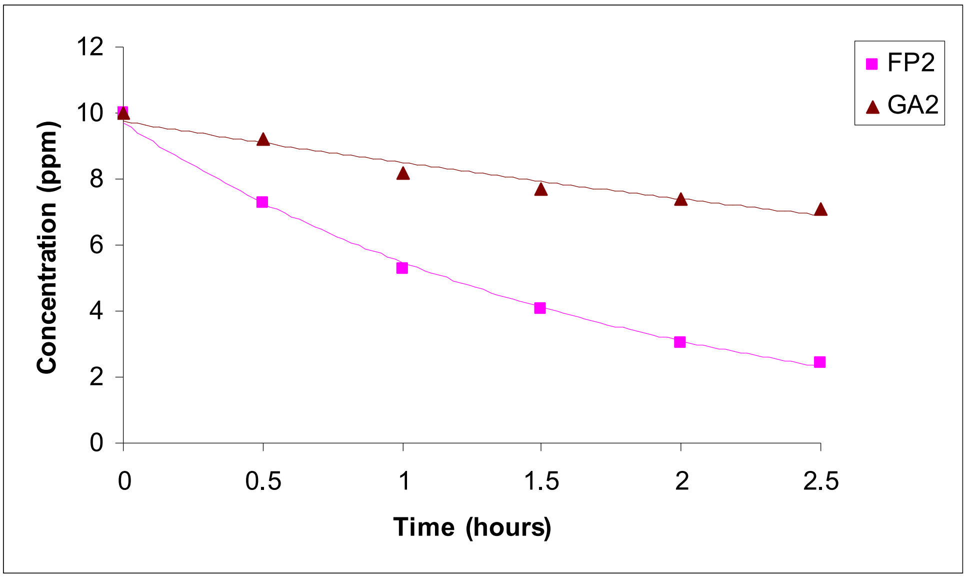

Figure 3: Time effect on photocatalytic degradation of Azorubine for immobilized films containing both TiO_2 & activated carbon

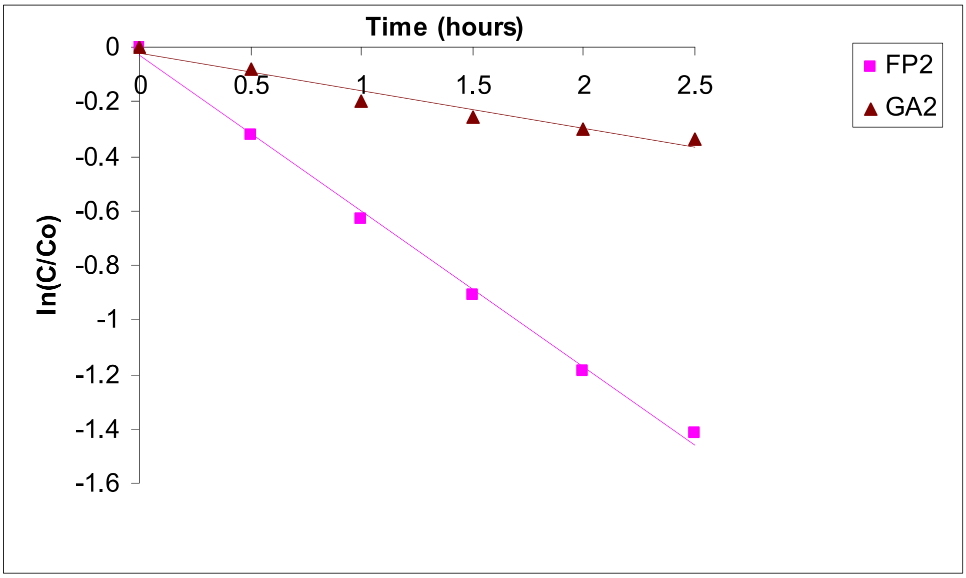

Figure 4: Kinetics of photocatalytic degradation of Azorubine for immobilized films containing both TiO_2 & activated carbon

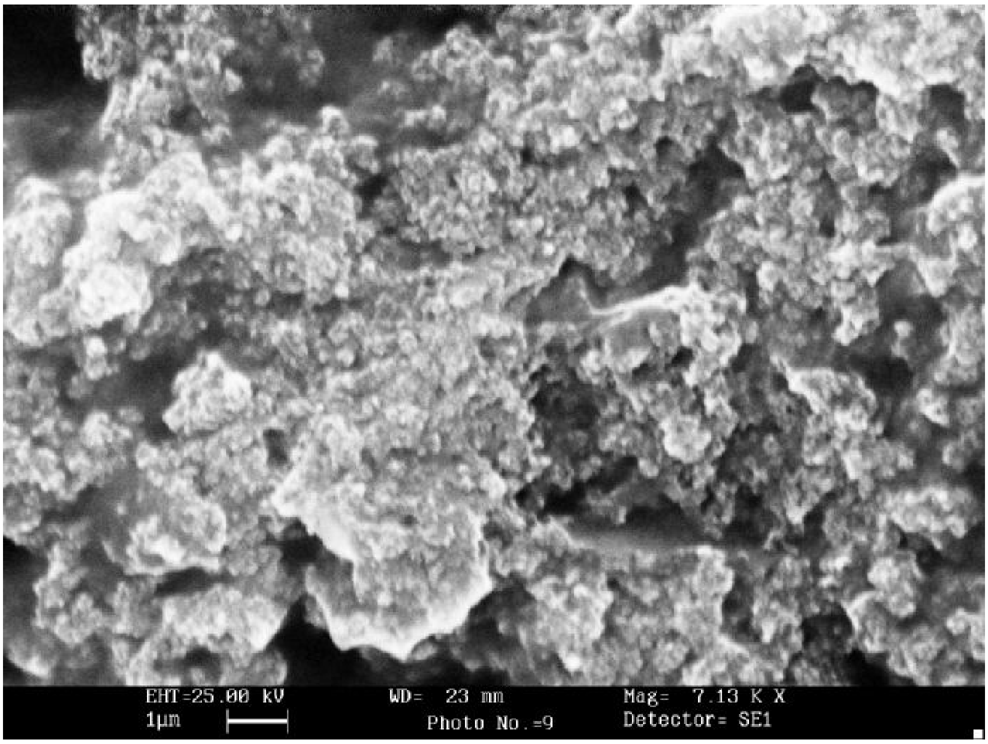

Figure 5: SEM image of TiO_2-activated carbon film prepared using polyvinyl-alcohol formaldehyde binder

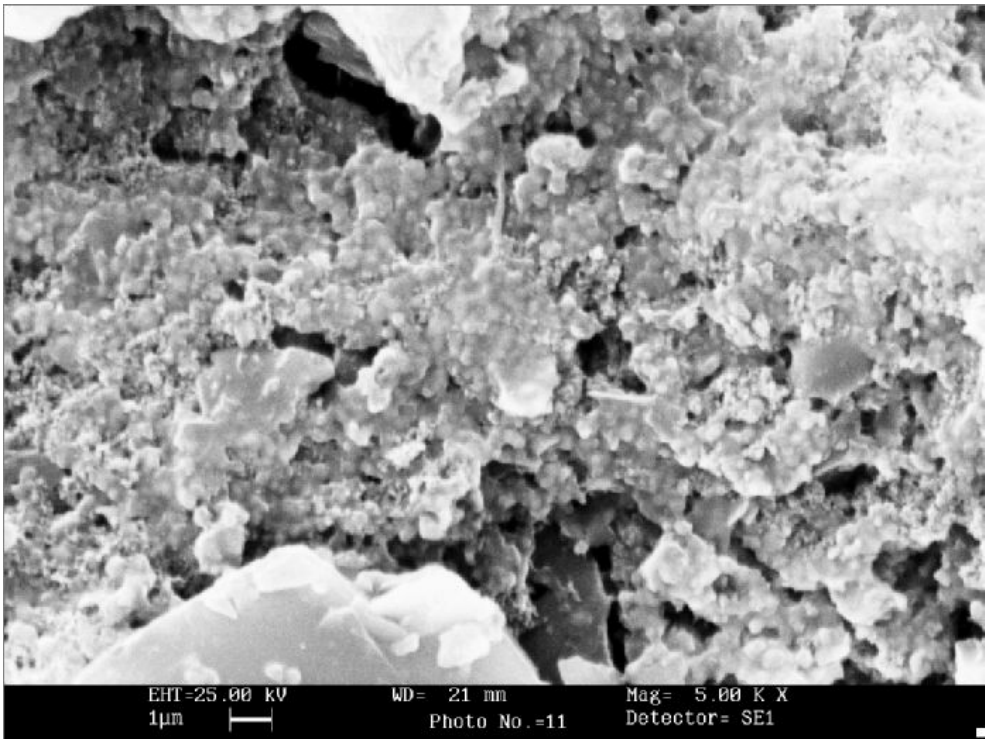

Figure 6: SEM image TiO_2-activated carbon film prepared using acrylic binder

Conclusion

The catalyst was immobilized on inert supports by two different methods, which eliminated the need of filtration of catalyst for further use. It is found that the TiO_2 films formed with the help of polyvinyl alcohol – formaldehyde binder showed better results than films formed using acrylic emulsion for photocatalytic degradation of Azorubine solution. The addition of activated carbon to the films enhanced the photocatalytic activity due to the combined effect of photodegradation and adsorption. The present results suggest that the polyvinyl alcohol-formaldehyde binder films are efficient for the treatment of aqueous solution of Azorubine. The application of these films should be extended for treatment of industrial wastewater.

References

1. Jain R., Sikarwar S., Photodestruction and COD removal of toxic dye erioglaucine by TiO_2- UV Process: Influence of operational parameters, International Journal of Physical Sciences, 2008, 3(12), 299-305.

2. Černigoj U., Lavrenčič Štangar U., Trebše P., Opara Krašovec U., Gross S., Photocatalytically active TiO_2 thin films produced by surfactant-assisted sol-gel processing, Thin Solid Films, 2006, 495, 327-332.

3. Lawton L.A., Robertson P.K.J., Cornish B.J.P.A., Jaspars M., Detoxification of microcystins (cyanobacterial hepatotoxins) using TiO_2 photocatalytic oxidation, Environmental Science and Technology, 1999, 33, 771-775.

4. Fernandez-Ibanez P., Blanco J., Sichel C., Malato S., Water disinfection by solar photocatalysis using compound parabolic collectors, Catalysis Today, 2005, 101, 345-352.

5. Hoffmann M.R., Martin S.T., Choi W., Bahnemann D.W., Environmental applications of semiconductor photocatalysis, Chemical Reviews, 1995, 95, 69-96.

6. Černigoj U., Photodegradation of organic pollutants in aqueous solutions catalyzed by immobilized titanium dioxide:Novel routs towards higher effeiceincy, PhD thesis, University of Noval Gorica, Graduate School, Nova Gorica, 2007.

7. Habibi M.H., Esfahani M.N., Egerton T.A., Photochemical characterization and photocatalytic properties of a nanaostructure composite TiO_2 film, International Journal of Photoenergy, 2007, 13653, 1-8.

8. Noorjahan M., Reddy M.P., Kumar V.D., Lavedrine B., Boule P. Subrahmanyam M., Photocatalytic degradation of H-acid over a novel TiO_2 thin film fixed bed reactor and in aqueous suspensions, Journal of Photochemistry and Photobiology A: Chemistry, 2003, 156,179-187.

9. Kumar J., Bansal A., Photocatalytic degradation of amaranth dye over immobilized nano-crystals of TiO_2, In proceedings of international conference on Energy & Environment, University of Cambridge, UK, 2010.

10. Divya N., Bansal A., Jana A K., Surface modification, characterization and photocatalytic performance of nano-sized titania modified with silver and bentonite clay, Bulletin of Chemical Reaction Engineering & Catalysis, 2009, 4(2), 43-53.

11. Keng C. S., Zainal Z., Abdullah A. H., Removal of cationic and anionic dyes by immobilized titanium dioxide loaded activated carbon, The Malaysian Journal of Analytical Sciences, 2008, 12 (2), 451-457

12. Karkmaz M., Puzenat E., Guillard C., Herrmann J.-M., Photocatalytic degradation of the alimentary azo dye amaranth. Mineralization of the azo group to nitrogen, Applied Catalysis B: Environmental, 2004, 51, 183-194.

13. Mills A., Le Hunte S., An overview of semiconductor photocatalysis, Journal of Photochemistry and Photobiology A: Chemistry, 1997, 108, 1-35.

14. Piccinini P., Minero C., Vincenti M., Pelizzetti E., Photocatalytic mineralization of nitrogen-containing benzene derivatives, Catalysis Today, 1997, 39, 187-195.

*****