Research Journal of Chemical Sciences ISSN 2231-606X
Vol. **3(11),** 60-65, November **(2013)** *Res. J. Chem. Sci.*

Heterogeneous Photocatalytic Degradation of Azure B: Measurement of Kinetic Parameters and Effluent Treatment using Solar Energy

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Available online at: www.isca.in, www.isca.me
Received 13th October 2013, revised 12th November 2013, accepted 17th November 2013

Abstract

The present work incorporates the study of efficiency of WO_3 for photocatalytic degradation of Azure B dye. Effect of some factors such as catalyst dose, concentration of dye, intensity of light, pH etc., on degradation of the dye was examined. The experimental data prove that the reaction follows pseudo first order kinetics. Participation of OH free radical is confirmed by scavenger studies. Optimum conditions (pH 7.8, dye concentration 5×10^{-6} moles/litre, semiconductor amount 0.12g, light intensity 37 mW/cm^2) were extracted by varying factors. Mineralization of dye produces harmless products.*

Keywords: Tungsten Oxide, Azure B, Scavenger, pH, bleaching.

Introduction

Textile industries are sources of colour dye effluents and these are toxic that induce a lot of damage to the environment. Various methods such as precipitation, air stripping, flocculation, adsorption, reverse osmosis, ultra filtration etc. have been used for removal of them. Heterogeneous photocatalytic oxidation is an effective method to remove low concentrations of organic contaminants. Here semiconductor particles on excitation act as photocatalysts or short-circuited microelectrodes. Semiconductor generates electron-hole pair on excitation which may be used either for reduction or oxidation of the dye.

$$\text{Photocatalyst} + h\nu \longrightarrow e^- + h^+ \text{ (hole)}$$
$$e^- + O_2 \longrightarrow O_2^-$$
$$h^+ + H_2O \longrightarrow OH^{\cdot} + H^+$$

Research in the field of photocatalysis has shown various promising applications based on the use of semiconductors. Vinodgopal et al[1] studied degradation of azo dye by SnO2/TiO2 coupled semiconductor thin films. Photocatalytic degradation of organic dyes on $PbBiO_2Br$, a visible light responsive photocatalyst was studied by Shan et al[2] while photo catalytic degradation of Methyl Orange over nano sized coupled ZnO/SnO_2 was investigated by C. Wang et al[3]. Study of the removal of Malachite Green was studied by Shabudeen[4]. The study was carried out in industrial solid waste. Photocatalytic degradation of Rhodamine B was suggested by Xiaohong et al[5]. They used visible light with Nd-doped titanium dioxide films. Photo-catalytic degradation of organic dyes with different chromophores by nanosize TiO_2 which was synthesized and was used by Hosseinnia et al[6]. Ji et al[7] used N-doped $Sr_2Nb_2O_7$ and visible light for photocatalytic hydrogen production from water-methanol mixtures. 2,4-Dichlorophenol was degraded by heterogeneous fenton like reaction and carbon-Fe catalysts was used for this purpose. The study was carried out by Yinchun et al[8]. Preparation of methyl orange and its photocatalytic degradation was studied by Shihong et al[9]. Magnetically separable $Bi_{12}TiO_{20}$ supported on nickel ferrite was used in water. Degradation of azure B using $Ni_2P_2O_7$ as photocatalyst studied by Khant et al[10]. The effect of pH on the photocatalytic reaction behaviors of dyes using TiO_2 and Nafion-coated TiO_2 was studied by Wang et al[11]. Titanium Dioxide-Mediated Photocatalytic Degradation of Humic Acid under natural sunlight was investigated by He[12].

Dielectric property of barium strontium titanate [$Ba_{0.4}$ $Sr_{0.6}$ TiO_3] thin film was studied by Gupta et al[13]. Methylene blue dye was degraded photocatalytically from aqueous solution using silver ion-doped TiO_2 and its application to the degradation of real textile wastewater was studied by Sahoo et al[14]. An UV-TiO_2 photocatalytic oxidation of commercial dyes was studied by Tang[15] in water. Pt modified TiO_2 loaded on natural Zeolite was used for photocatalytic discolorization of methyl orange solution by Huang et al[16] while Kako et al[17] suggested some preventive method for catalytic poisoning of TiO_2 photocatalyst. Devi et al[18] reported that heat treated TiO_2 acts as photocatalysts in the photocatalytic degradation of p-amino azobenzene and p-hydroxy azobenzene. Chen and Liu[19] studied photocatalytic degradation of glyphosphate by TiO_2 photocatalyst while characterization, adsorption and photocatalytic activity of vanadium-doped TiO_2 and sulfated TiO_2 (rutile) catalysts was reported by Mohamed et al[20] for degradation of methylene blue. Ungelenk et al[21] showed that nanoscale β-Sn_1-nWO4-nα-Sn is a highly efficient photocatalyst for degradation of organic dyes in day light and it was observed to be a real 'green' synthesis. Desilvestro and Spallart[22] observed that WO_3 was used as catalyst for oxygen generation from water. Role of photo sensitizer-reductant for generation of electrical energy in photo galvanic cell was studied by Meena et al[23]. Removal of organic pollutants is of utmost importance as a variety of such organic compounds are synthesized, used and

excreted in the environment polluting it. Looking to the harms caused by these organic pollutants, the present work was incorporated.

Material and Methods

The stock solution of dye (Azure B .030583 g/100 ml = 1 x 10^{-4} M) was prepared in double distilled water and diluted as required. The pH of the solution was determined using pH meter (Hena imported pen type) and was varied using pre-standardized solutions of HCl (Merck) and NaOH (Aldrich). Solution of dye was taken in a beaker; known amount of Tungsten Oxide (Loba Chemie) (0.12 g) was added and covered with water filter to avoid the heat reaction. The solution was irradiated by a 200 watt tungsten lamp (Philips) and the intensity was measured by solarimeter (Suryamapi CEL 201). Optical density at different time intervals was recorded by spectrophotometer (Systronics 106). Controlled experiments were carried out by keeping the setup in presence and absence of light and photo catalyst.

Results and Discussion

Effect of irradiation time: A graph plotted of time and percentage degradation is given in table-1 and figure-2. It is observed that percent degradation increases with irradiation time. The process slows down with time because it stands difficult to convert N-atoms into nitrogen compounds[24]. The difficulty in breakdown of C-N bond has been given by Maillard et al[25]. The dye is degraded by formation of OH* free radical whose formation increases with increase in irradiation time and so increases the percentage degradation.

Table- 1
[Azure B] = 5 x 10^{-6} M, pH = 7.8, Amount of semiconductor = 0.12 g, Intensity of light = 37mW/cm^2

Time (min.)	1 + log O.D.
0.0	0.5263
15.0	0.5105
30.0	0.4814
45.0	0.4424
60.0	0.4183
75.0	0.3783
90.0	0.3424
105.0	0.3010
120.0	0.2764
135.0	0.2479
150.0	0.2227

K = 9.21 ×10^{-5} sec^{-1}

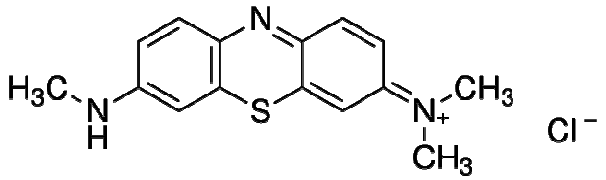

Figure-1
Structure of Azure B

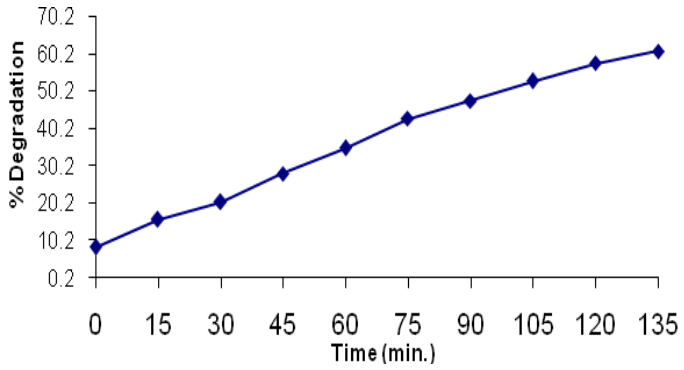

Figure-2
A typical run

Photo catalytic degradation of Azure B was observed at λmax = 648 nm. Reaction mixture was irradiated and an aliquot was withdrawn at different time intervals to record the optical density (O.D.). The plot between 1+log O.D. and time gave a straight line suggesting that the removal of Azure B by semiconductor follows law of pseudo first order kinetics. Rate constant was calculated by –

k = 2.303 x slope

Absence of light and photo catalyst showed no change in the optical density proving that the reaction is neither photoreaction nor catalytic rather it is a photo catalytic process. Participation of OH* free radical was confirmed by use of scavenger that ceased the reaction completely. Degraded products like NO_2, H_2O, CO_2 etc. Were formed which were of no harm to the environment.

Effect of pH: The most important factor is pH of the solution as it governs the generation of the degrading species i.e. the OH* free radical. Thus the effect of was studied on the rate by varying the pH of solution by adding pre standardized HCl and NaOH solutions. All other factors were kept constant. The results are summarized in table-2 and figure-3. The reaction rates are determined in the pH range 5.3–8.6. An increase in the rate of degradation with increase in pH is due to generation of more OH^- ions. These ions loose an electron to the hole generated at the semiconductor surface and OH* free radicals are formed. These formed free radicals cause oxidation of the dye and as a result, first step of degradation takes place. On further increase in pH above 7.8, a decrease in the rate is due to the fact that azure B now becomes negatively charged and so repelled negatively charged OH ions. This force does not allow the approach of OH ions to the surface of semiconductor and free radical generation is retarded.

Effect of dye concentration: The concentration of pollutants is a major parameter to be considered in water treatment. Keeping all other factors constant, concentration of dye was varied (3.0

$x10^{-6}$ to $9.0x10^{-6}$M) and the data are summarized in table-2 and figure-4. It is observed that the rate of degradation increases up to a certain concentration (5×10^{-6} M) because more surface area of dyes is available for OH* free radical to abstract an electron. Above this if the concentration is increased, the rate decreases. This is because this imparts a darker colour to the solution which does not allow larger number of photons to reach the surface of photo catalyst, reducing the rate of degradation.

Effect of catalyst loading: Different weighed amount of WO_3 was taken and all other factors were kept constant. The data are summarized in table-2 and figure-5. The rate was found to increase with increase in amount of catalyst as increase in the active site available on the catalyst surface for the reaction increases the rate of free radical formation. After this, further increase in the weight of photocatalyst decreases the rate. It is because with a higher catalyst loading (above 0.12g), collision with ground state molecules dominates and deactivation takes place thus reducing the rate of reaction.

Effect of light intensity: Variation of was carried out from 23 $mWcm^{-2}$ to 37 $mWcm^{-2}$ and all other factors were kept constant. The results are reported in table-2 and figure-6. It was observed that increase in light intensity increases the rate of degradation[26,27]. Increase in number of photons striking per unit area of the photo catalyst increases causing increased rate of degradation. Higher intensities were not studied as increase in intensity may cause thermal reaction instead of photo catalytic one.

Table-2
Effect of variation of different parameters

Effect of pH		**Effect of dye concentration**		**Effect of amount of photo catalyst**		**Effect of light intensity**	
Dye concentration=5×10^{-6}M Catalyst = 0.12g Light intensity= 37mWcm^{-2} **pH varied**	Rate constant×$10^{-5}S^{-1}$	Catalyst = 0.12g Light intensity= 37mWcm^{-2} pH = 7.8 **Dye concentration× 10^{-6}M Varied**	Rate constant×$10^{-5}S^{-1}$	Dye concentration=5×10^{-6}M pH=7.8 Light intensity= 37mWcm^{-2} **Catalyst amount (g) varied**	Rate constant×$10^{-5}S^{-1}$	Dye concentration= 5×10^{-6}M pH= 7.8 Catalyst = 0.12g **Light intensity (mWcm^{-2}) varied**	Rate constant×$10^{-5}S^{-1}$
5.3	6.31	3.0	8.11	0.04	4.89	**37**	**9.20**
5.8	6.76	4.0	4.50	0.06	5.89	34	7.25
6.3	7.43	**5.0**	**9.20**	0.08	6.65	30	5.44
6.8	7.30	6.0	4.80	**0.12**	**9.20**	27	4.54
7.3	7.23	7.0	4.12	0.14	6.70	23	4.10
7.8	**9.20**	8.0	2.77	0.16	6.86	Nil	Nil
8.3	7.37	9.0	2.31	0.18	6.65	Nil	Nil
8.6	7.43	Nil	Nil	0.20	6.59	Nil	Nil

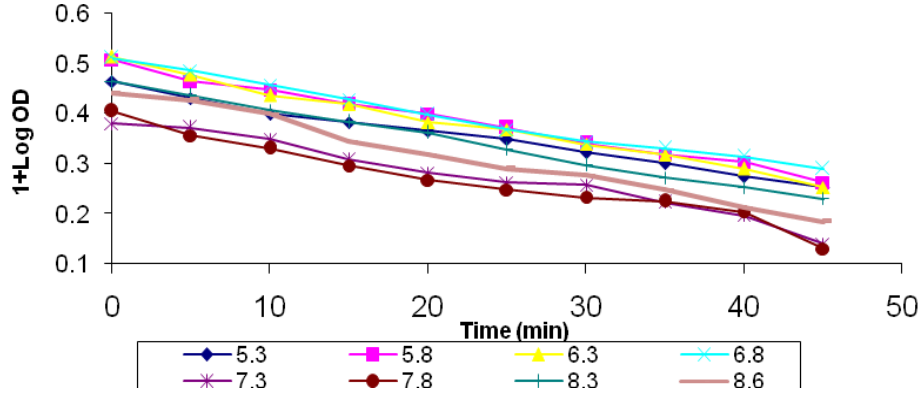

Figure-3
Effect of variation of pH [Azure B] = 5×10^{-6}M, light intensity = 37 mW/cm^2, amount of semiconductor = 0.12g

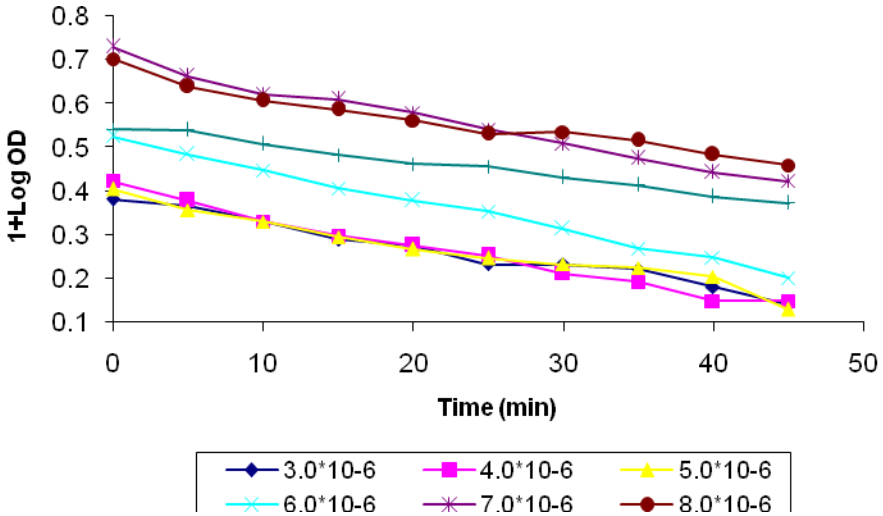

Figure-4
Effect of concentration of dye (in moles/litre) pH = 7.8, light intensity = 37 mW/cm^2 Amount of semiconductor = 0.12g

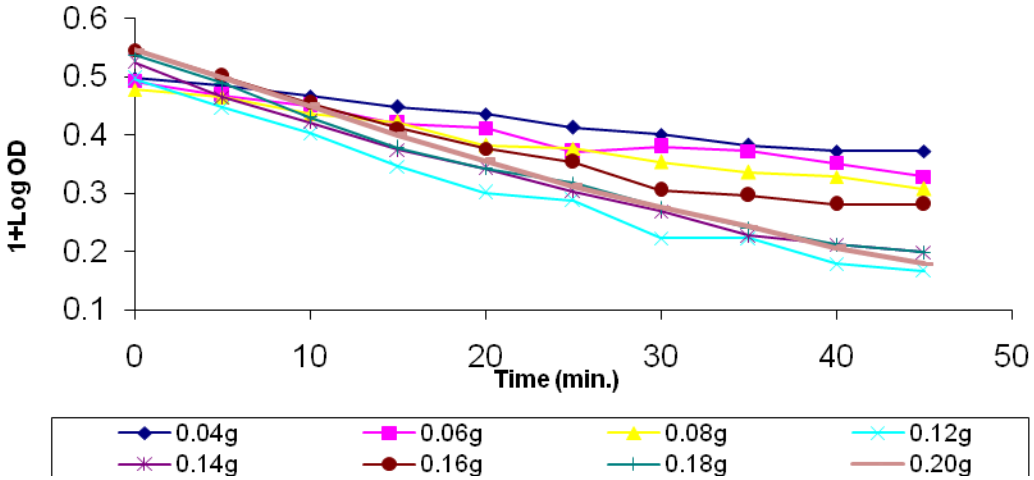

Figure-5
Effect of variation of amount of semiconductor pH = 7.8, light intensity = 37 mW/cm^2 , [Azure B] = 5x10^{-6} M

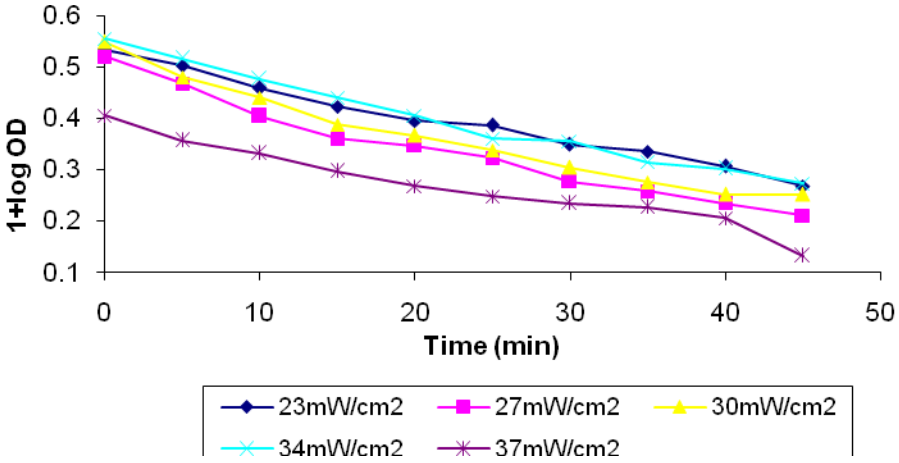

Figure-5
Effect of variation of light intensity [Azure B] = 5 x 10^{-6} M, pH = 7.8, Amount of semiconductor = 0.12 g

Conclusion

It is concluded here by that dyes are being degraded, with the help of photocatalyst and in presence of visible light, into fragments and no harmful products are formed. The proposed mechanism is

$h\nu + Dye \longrightarrow Dye^1$ (Dye in singlet exited state)

In presence of light, dye molecule gets excited to its singlet state.

$Dye^1 \xrightarrow{ISC} Dye^3$ (Dye in triplet exited state)

Then by losing some energy through inter system crossing (ISC), it get converted to its triplet state.

$h\nu + SC \longrightarrow h^+ + e^-$

On the other hand semiconductor absorbs photon and an electron from its valence band jumps to the conduction band leaving a hole behind.

$h^+ + OH^- \longrightarrow h + OH^*$

The hole abstracts an electron from OH^- ion generating OH* free radical and the hole is quenched.

$OH^* + Dye^3 \longrightarrow$ Leuco form dye $\longrightarrow$ degraded products

This free radical abstracts an electron from weaker site of dye causing break down in conjugation and then oxidizing and mineralizing the dye. The degraded products formed are NH_4^+, CO_2, H_2O, SO_4^{2-} etc.

Thus an eco-friendly, cost effective, consuming the natural resource of energy i.e. solar energy and environmental protecting process may be used to make the planet clean and pollution free.

Acknowledgement

The authors are thankful to Professor Suresh C. Ameta, (Director, College of pure and applied Science, Pacific University, Udaipur, Rajasthan, India), for his valuable guidance and kind support.

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