Available online at www.sciencedirect.com
ScienceDirect
Dyes and Pigments 75 (2007) 207–212
DYES and PIGMENTS
www.elsevier.com/locate/dyepig

Influence of TiO_2 and ZnO photocatalysts on adsorption and degradation behaviour of Erythrosine

M.M. Uddin [a], M.A. Hasnat [a,*], A.J.F. Samed [a], R.K. Majumdar [b]

[a] *Department of Chemistry, Shahjalal University of Science and Technology, Sylhet 3114, Bangladesh*
[b] *Atomic Energy Commission, Savar, Bangladesh*

Received 21 May 2005; received in revised form 24 October 2005; accepted 30 April 2006

Abstract

The photocatalytic degradation of Erythrosine, an anionic dye (λ_{max} at 526 nm, $\varepsilon_{max} = 7.24 \times 10^4$ L mol^{-1} cm^{-1}), has been investigated over TiO_2 and ZnO photocatalysts, irradiated by UV–vis light. Spectrum of the dye has been found, unaffected in the pH range 4.86–11.56. The adsorption over TiO_2 and ZnO surface followed Langmuir and Freundlich adsorption isotherms. The extent of adsorption decreased with the rise of pH. But the percent of decolourization fluctuated over this pH range. Increment of initial dye concentration adversely affected the decolourization efficiency but proportionately affected with the catalyst loading until it gets attenuated after 2.0 g/L. The presence of H_2O_2 in lower concentration (ie, 4×10^{-4} M) with the catalysts decelerated the degradation but accelerated at higher concentration (ie, 300×10^{-4} M). Kinetic studies including order of the reaction, rate constant and half-life have also been performed in the presence of TiO_2 and ZnO.

Keywords: Erythrosine; Adsorption; Photocatalysis; Degradation; TiO_2; ZnO

1. Introduction

With the triumph of science and technology the application of dyes and pigments have increased in a considerable way. A lot of industries have been set up to mitigate the continuously increasing demand of dyes and pigments. Dyes are used in textiles, food and beverage industries and printing processes. A large number of such type of industries have been set up in an unplanned manner in many urban and suburban areas of developing countries like Bangladesh. But most of the industries generally discharge their untreated effluents into sewer systems or nearby watercourses because of the unavailability of an economically and technically favorable process. The chromophores in ionic and nonionic dyes are mostly azo groups or anthraquinone type. Thus dyestuffs have a complex chemical structure which is hard to degrade biologically and numerous biodegradability studies on dyes have shown that azo dyes are not likely to be biodegradable under aerobic condition [1–8]. Although dyes may not be directly toxic, they may generate carcinogenic compounds such as aromatic amines from azo dyes during their anaerobic degradation [9–14].

So new methods are necessary to destroy or mineralize this dye pollutants and thus converting it into harmless compounds, without much expense. Heterogeneous photocatalysis is one important destructive technology leading to complete mineralization of dye [1–10]. The process uses atmospheric oxygen as the oxidant and leads to the complete mineralization of organic pollutants to CO_2 and H_2O, sulphates, nitrates, etc [3–12]. TiO_2 and ZnO are most extensively used photocatalysts in recent years. They are known as inexpensive, nontoxic and very effective semiconductor photocatalysts. These photocatalysts are applicable to wide range of organic synthetic dyes.

The photocatalytic degradation mechanism of dye by UV–vis light follows different mechanisms. The well-established visible light mechanism [1] suggested is given below:

$$\text{Dye} + h\nu \rightarrow \text{Dye}^*$$

---

* Corresponding author.
E-mail address: mah-che@sust.edu (M.A. Hasnat).

0143-7208/$ - see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.dyepig.2006.04.023

$$\text{Dye}^* + TiO_2 \rightarrow \text{Dye}^+ + TiO_2(e)$$

$$TiO_2(e) + O_2 \rightarrow TiO_2 + O_2^{\bullet -}$$

$$O_2^{\bullet -} + 2H_2O \rightarrow H_2O_2 + e^-$$

$$H_2O_2 + e \rightarrow {}^{\bullet}OH + OH^-$$

$$\text{Dye}^{\bullet +} + O_2(\text{or } O_2^{\bullet -} \text{ or } {}^{\bullet}OH) \rightarrow \text{peroxide or hydroxyl intermediate} \rightarrow \rightarrow \text{degraded products.}$$

The well-established UV light mechanism can be written as follows [1,16]. When the light energy is greater than the band gap energy of semiconductor, it produces electron (e^-) and hole (h^+) pairs.

$$TiO_2 + h\nu \rightarrow e^- + h^+$$

$$(O_2)_{ads} + e^- \rightarrow (O_2^{\bullet -})_{ads}$$

$$Ti(IV) - OH + h^+ \rightarrow Ti(IV)HO^{\bullet}$$

$$Ti(IV) - H_2O + h^+ \rightarrow Ti(IV)HO^{\bullet} + H^+$$

$$\text{Dye} + h^+ \rightarrow \text{Dye(oxidation)}.$$

The primary oxidants, $O_2^{\bullet -}$, $HO^{\bullet}$, are capable of initiating a series of oxidative degradation reactions of adsorbed organic molecules.

Recently we showed the comparative studies of adsorption–degradation of a cationic dye and an anionic dye on TiO_2 surface [4]. This study deals with the comparative investigation of photocatalytic degradation of anionic dye Erythrosine, using two photocatalysts TiO_2 and ZnO. Experiments were conducted to investigate the effect of various variables including pH, catalyst loading, initial dye concentration, H_2O_2 concentration, and other things on process performance. Studies of adsorption isotherm such as Langmuir and Freundlich isotherms, kinetic studies such as reaction order, half-life, etc. have also been made.

2. Experimental

2.1. Materials

Semiconductors employed as photocatalysts are TiO_2 (Degussa P25, band gap energy 3.0 eV), powdered form, specific surface area 50 m^2/g, crystalline mode is 80% anatase and 20% rutile and ZnO (Fluka, surface area 100 m^2/g and band gap energy 3.2 eV). The dye chosen for this research purpose is Erythrosine (laboratory grade) having complex organic structure (Fig. 1).

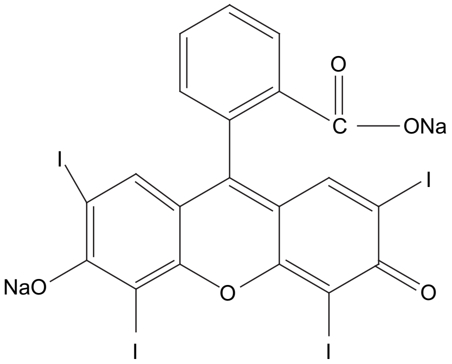

Fig. 1. The molecular structure of Erythrosine.

2.2. Apparatus

The reaction mixture was kept in a cylindrical Pyrex vessel of 5 cm. diameter and positioned 10 cm apart from the light source. In order to maintain the temperature, the vessel was surrounded by a water jacket, consisting of one inlet and another outlet for the passage of cold water. The vessel contains a stirring rod supported by a magnetic stirrer. The light source used is low-pressure mercury lamp (PASCO scientific light source, Hg Light Source OS-9286) of 125 W. The reactor was set in open air. The change of concentration of dye solution was measured spectrophotometrically using Shimadzu-160 double beam spectrophotometer.

2.3. Experimental procedure

The aqueous suspension was prepared by adding 0.025 g of TiO_2 in a 50 mL volumetric flask containing little water and then Erythrosine solution was added to the volumetric flask in such a way that the final concentration of the solution becomes the desired one. pH was adjusted by adding 0.01 M HCl or 0.01 M NaOH. The experiments were carried out at medium pH ca. 8.0 and 9.5 for TiO_2 and ZnO, respectively. Then the solution was stirred by magnetic stirrer for 30 min and kept overnight to reach adsorption–desorption equilibrium. Exactly the same procedure was adopted for the preparation of solution in the presence of ZnO. During the experiments 5 mL samples of suspension were withdrawn at regular intervals and were centrifuged at 3500 rpm for 12 min and filtered with a filter paper of pore size 0.2 μm to completely remove catalyst particles.

3. Results and discussion

3.1. Characterization of Erythrosine

Erythrosine is a synthetic anionic (ER^{2-}) dye. It has a complex organic structure (Fig. 1). Its characteristic λ_{max} is at 526 nm and molar absorption coefficient is 7.24×10^4 $L\,mol^{-1}\,cm^{-1}$. At pH range 4.86–11.56 the dye was stable and no significant change in spectrum was observed.

3.2. Degradation of Erythrosine

The degradation of Erythrosine has been investigated spectrophotometrically to study whether mineralization occurs when the dye solution was irradiated with UV–vis light in the presence of TiO_2 and ZnO suspension. Solution after certain time intervals has been taken and the spectrum has been taken by the spectrophotometer. The initial dye concentration was 11.0×10^{-6} M and 9.0×10^{-6} M for TiO_2 and ZnO, respectively. Figs. 2 and 3 suggest that the dye molecules have undergone mineralization and no new peak in the UV–vis range has been noticed.

3.3. Adsorption isotherm

The analysis of isotherm data is important to develop the equations that represent the results and would be useful to design degradation purposes [15]. For heterogeneous photocatalysis adsorption on catalyst surface is a prerequisite condition [16]. It has been observed that the amount of adsorption per gram of adsorbate increases with the rise of concentration. In this study two isotherms, Langmuir and Freundlich isotherms have been selected to evaluate the adsorption capacity of the adsorbents (TiO_2 and ZnO). The equation of Langmuir isotherm (1) is given as

$$[D]_e/(x/m) = [D]_e/k' + 1/k_1k' \tag{1}$$

where $[D]_e$ is the equilibrium concentration of dye and (x/m) is the amount of dye adsorbed per gram of TiO_2/ZnO, k_1 is the adsorption constant and k' is the adsorption coefficient. On the other hand the Freundlich empirical Eq. (2) is given as

$$\log(x/m) = \log k + (1/n)\log C_e \tag{2}$$

A plot of log (x/m) vs log C_e will give a straight line. Here x is the amount of dye adsorbed (mg/L), m is the weight of the adsorbent used (g/L), and C_e is the equilibrium concentration of the dye in the solution (mg/L). From the slope $(1/n)$, we can obtain the value of n. To study the adsorption isotherm, initial dye concentration was taken as 8.0×10^{-6}–26.0×10^{-6} M for TiO_2 catalyst and in the presence of ZnO, 7.0×10^{-6}–22.0×10^{-6} M dye concentration was taken. Figs. 4 and 5 suggest that the adsorption follows both the Langmuir and Freundlich isotherms. The values of adsorption constant (k_1) and adsorption coefficient (k') obtained from Fig. 4 and Freundlich constant (n) obtained from Fig. 5 have been listed in Table 1.

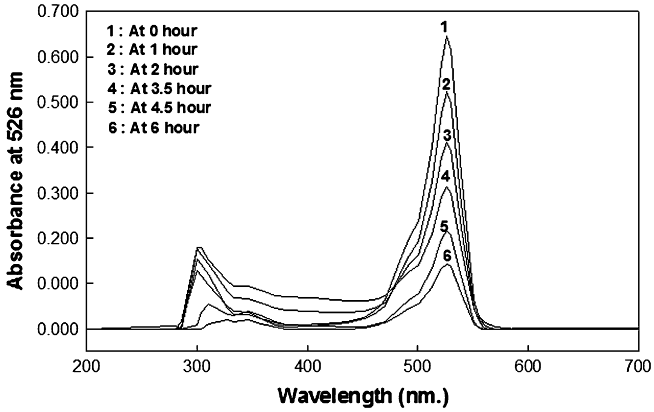

Fig. 2. Variation of the absorption spectra of Erythrosine solution in the presence of TiO_2 suspension under irradiation with UV–vis light at different time intervals.

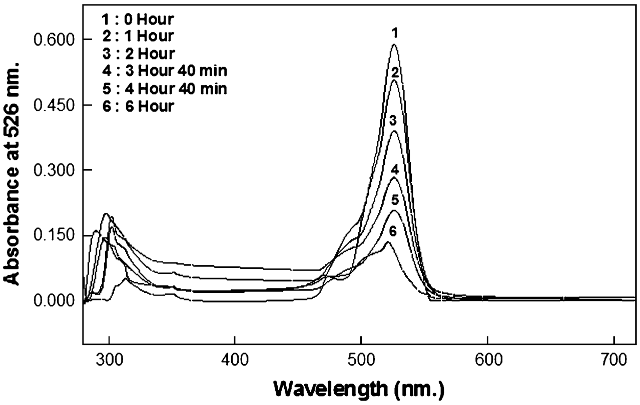

Fig. 3. Variation of the absorption spectra of Erythrosine solution in the presence of ZnO suspension under irradiation with UV–vis light at different time intervals.

3.4. pH effect

Because of the amphoteric behaviour of most of the semiconductor oxides, an important parameter in the reaction taking place on the semiconductor particle surface is the pH of dispersions, since it influences the surface charge properties of photocatalyst [6]. The zero point charge (zpc) is 6.8 for TiO_2 (Degussa P25) and 8.9 for ZnO [3,6]. So at lower pH the surface of the catalyst is positively charged but at higher pH it becomes negatively charged. From Fig. 6 it has been observed that the amount of the adsorption of dye molecules per gram of adsorbate (x/m) decreased with the rise of pH. But the percent of decolourization did not show the same trend. From Fig. 6 it has been observed that the percent (%) of decolourization efficiency has been fluctuating throughout this pH range upon 120 min photolysis. The decolourization efficiency was found to be

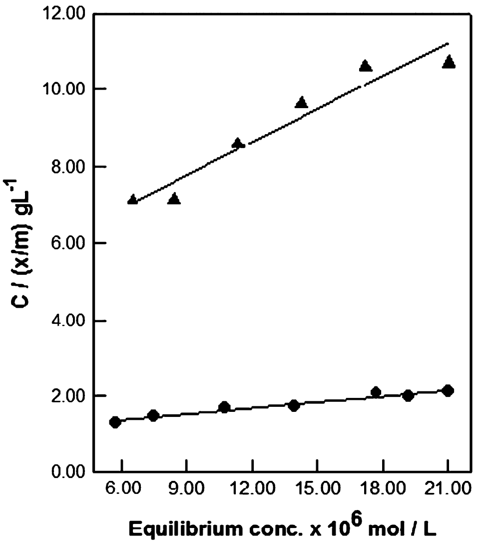

Fig. 4. Langmuir isotherm in the presence of ZnO (▲) and in the presence of TiO_2 (●).

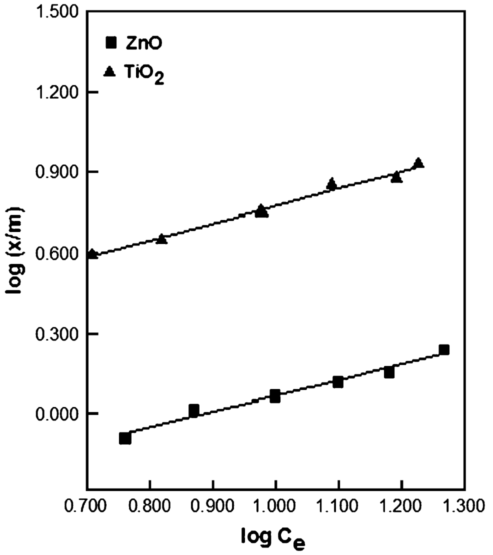

Fig. 5. Freundlich isotherm in the presence of ZnO and TiO_2.

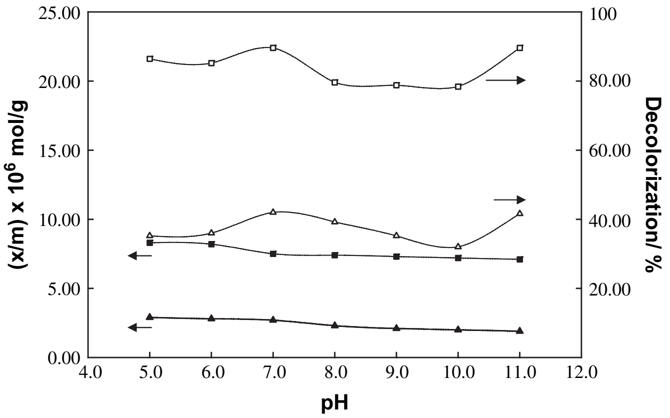

Fig. 6. The effect of pH: (▲) (*x*/*m*) vs pH in the presence of ZnO, (■) (*x*/*m*) vs pH in the presence of TiO_2, (△) percent of decolourization in the presence of ZnO, and (□) percent of decolourization in the presence of TiO_2.

maximum in the presence of TiO_2 suspension at pH ~6.75 and ~10.10 and in the presence of ZnO suspension maximum efficiency was found at pH ~7.21 and ~10.08. This is because, at higher pH the catalyst surface is negatively charged by means of adsorbed OH^- ions which favor the formation of $^{\bullet}OH$ radicals [8], the principal oxidant. On the other hand, the anionic dye molecule is negatively charged, so low pH favors adsorption on the catalyst surface. Consequently, pH affects process performance by influencing dye adsorption and $^{\bullet}OH$ radical creation on catalyst surface in a conflicting manner [8].

3.5. Effect of initial dye concentration

The effect of initial dye concentration on decolourization efficiency has been investigated by varying the initial dye concentration from 8.0×10^{-6} M to 24.0×10^{-6} M in the presence of TiO_2 suspension and 0.7×10^{-6} M to 24.0×10^{-6} M in the presence of ZnO suspension. Fig. 7 suggests that the decolourization and degradation efficiencies are inversely related to the dye concentration. By increasing dye concentration, the equilibrium adsorption of dye on catalyst surface sites increases, and as a result $^{\bullet}OH$ radical formation rate decreases due to the hindered OH^- ion adsorption at the same sites. In addition to that the path lengths of photons entering the solution also decrease according to the Beer–Lambert law, which causes lower photonic adsorption on catalyst particles [8,9] and hence the photocatalytic reaction rate decreases.

Table 1
Adsorption constants and adsorption coefficients

Catalyst	Langmuir adsorption constant, K_1 (mol L^{-1})	Langmuir adsorption coefficient, K'	Freundlich constant, *n*
TiO_2	0.48×10^5	1.97×10^{-5}	1.6
ZnO	0.55×10^5	3.48×10^{-6}	1.7

3.6. Effect of catalyst loading

To investigate the effect of catalyst loading on decolourization efficiency, two sets of experiments were conducted employing TiO_2 and ZnO photocatalysts. The varying amounts of catalysts ranging from 0.50 to 2.50 g/L were used. The result obtained, shown in Fig. 8, suggests that both the catalysts showed the same trend, ie, decolourization efficiency increased with increasing catalyst loading until a plateau was reached at concentration above 2.0 g/L. This is because catalyst loading exhibits conflicting effects on the photocatalytic process; at lower loading levels, photonic adsorption controls the reaction extent due to the limited catalyst surface area, while at higher loading levels, light scattering by catalyst particles predominates over photonic adsorption [8,9].

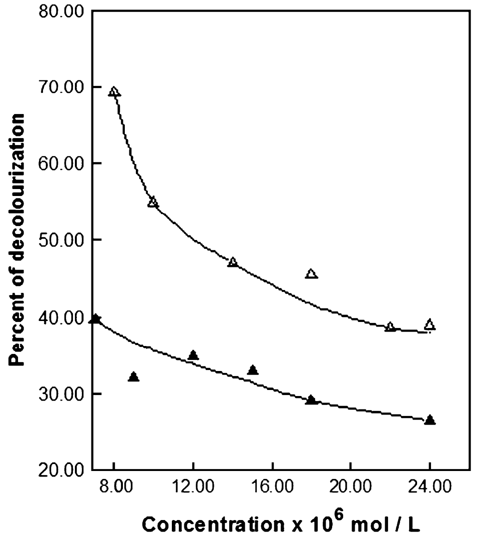

Fig. 7. The percent of decolourization with varying initial dye concentration: in the presence of TiO_2 (△) and in the presence of ZnO (▲).

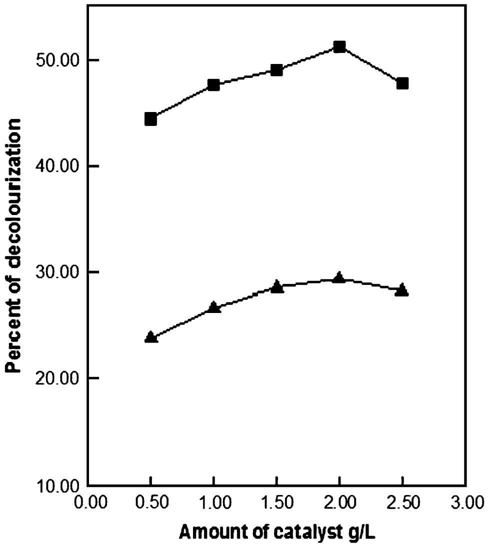

Fig. 8. Percent of decolourization in the presence of TiO_2(■) and in the presence of ZnO (▲).

3.7. Effects of H_2O_2 on degradation

The effect of H_2O_2 on degradation of the dye has been shown in Fig. 9. The initial concentration of dye was 12.0×10^{-6} M. It has been observed that the combination of the catalysts (TiO_2 and ZnO) with low H_2O_2 concentration (4.0×10^{-4} M) leads to a decrease of the degradation rates, but at high H_2O_2 concentration (30.0×10^{-4} M) leads to an increase of the degradation rates due to the higher concentration of the hydroxyl radicals generated from the synergetic effect of the semiconductor with hydrogen peroxide [11].

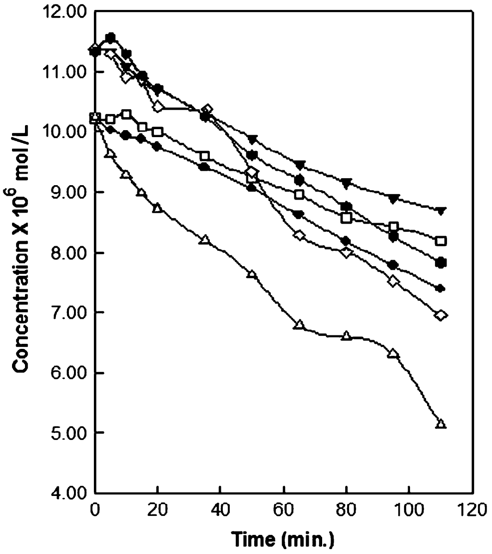

Fig. 9. Change in concentration of Erythrosine with time upon irradiation under UV–vis light: (▼) in the presence of ZnO (0.50 g/L) and 4×10^{-4} M H_2O_2, (●) in the presence of ZnO (0.50 g/L), (◇) in the presence of ZnO (0.50 g/L) and 300×10^{-4} M H_2O_2, (□) in the presence of TiO_2 (0.50 g/L) and 4×10^{-4} M H_2O_2, (◆) in the presence of TiO_2 (0.50 g/L), and (△) in the presence of TiO_2 (0.50 g/L) and 300×10^{-4} M H_2O_2.

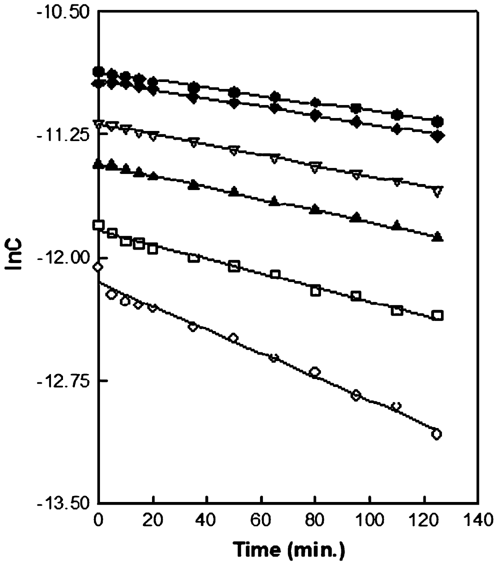

Fig. 10. Plot of ln *C* vs time graph: (○) initial concentration of dye 8.0×10^{-6} M, (□) initial concentration of dye 10.0×10^{-6} M, (▲) initial concentration of dye 14.0×10^{-6} M, (▽) initial concentration of dye 18.0×10^{-6} M, (◆) initial concentration of dye 22.0×10^{-6} M, and (●) initial concentration of dye 24.0×10^{-6} M.

3.8. Kinetic study

The integrated rate Eq. (3) was tested in the presence of both TiO_2 and ZnO catalysts.

$$\ln C_t = -kt + \ln C_0 \tag{3}$$

where C_t is the concentration of the dye at time t and C_0 is the initial concentration of the dye. The plot of $\ln C_t$ vs t will give a straight line with slope $-k$, where k is the rate constant. From Figs. 10 and 11 it has been confirmed that degradation follows first-order kinetics in the presence of both TiO_2 and ZnO

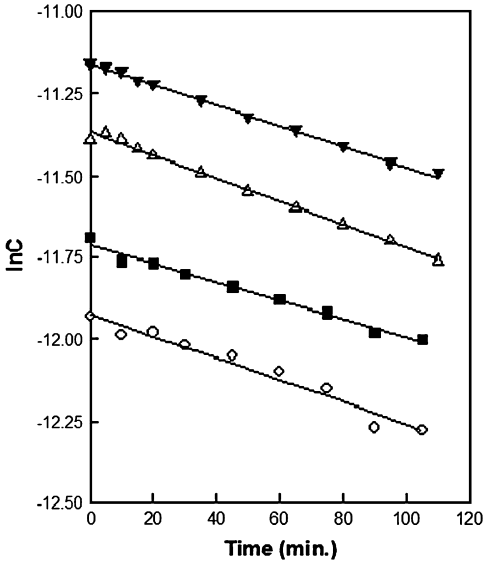

Fig. 11. Plot of ln *C* vs time: (○) initial concentration of dye 7.0×10^{-6} M, (■) initial concentration of dye 9.0×10^{-6} M, (△) initial concentration of dye 12.0×10^{-6} M, and (▼) initial concentration of dye 15.0×10^{-6} M.

Table 2
First order rate constant and half life

Catalyst	K (min^{-1})	$t_{1/2}$ (min)
TiO_2	3.85×10^{-3}	180.1 (at pH 6.75)
ZnO	3.23×10^{-3}	214.5 (at pH 9.11)

suspension. The rate constant (k) and half-life ($t_{1/2}$) obtained have been listed in Table 2.

4. Summary

Both TiO_2 and ZnO are active catalysts for adsorption and photocatalytic degradation of Erythrosine. Due to different unique physical properties of the catalysts and Erythrosine molecules, the most effective decolorization/degradation occur mainly in the basic pH of the dispersion medium. Photonic effect and active surface area of the catalysts triggered the opposite effects and these effects lead to the maximum decolorization at ca. 2.0 g/L of catalyst loading in the case of both catalysts. Nonetheless, ZnO has double the surface area than TiO_2; the experimental result showed that TiO_2 is a more effective photocatalyst than ZnO for decolorization of Erythrosine. This conflicting effect might be due to the larger band gap energy of ZnO (3.2 eV) than TiO_2 (3.0 eV, anatase).

Acknowledgements

Heartiest thanks to Almighty first as we could successfully completed this work with His mercy and forgiveness. Then the authors are indebted to Professor A.J. Mahmood (Rtd.), Department of Chemistry, Dhaka University, Bangladesh for providing related literatures and important discussion. The authors reverberate the supports provided by Dr. S.M. Saiful Islam, Dr. S.S. Alam, Dr. M. Younus and Dr. A. Sobhan, Department of Chemistry, Shahjalal University of Science and Technology, Sylhet, Bangladesh during this work. Ministry of Science, Information Communication and Technology, Bangladesh is gratefully acknowledged for inspiring one of the authors (M.A. Hasnat) by awarding an expert fellowship in 2002–2003 financial year for a similar research work.

References

[1] Wu Taixing, Liu Guangming, Zhao Jincai, Hidaka Hisao, Serpone Nick. J Phys Chem B 1999;103:4862–7.

[2] Lin Jun, Yu Jimmy C, Lo D, Lam SK. J Catal 1999;183:368–72.

[3] Mahmood Abu Jafar, Jabbar MA, Akhtar Shirin, Hasnat MA. J Bangladesh Chem Soc 2003;16(1):57–70.

[4] Hasnat MA, Siddiquey IA, Nuruddin A. Dyes Pigments 2005;66:185–8.

[5] Liu Guangming, Wu Taixing, Zhao Jincai, Hidaka Hisao, Serpone Nick. Environ Sci Technol 1999;33:2081–7.

[6] Zhang Fenglei, Zhao Jincai, Shen Tao, Hidaka Hisao, Pelizzetti Ezio, Serpone Nick. Appl Catal B Environ 1998;15:147–56.

[7] Wu Taixing, Lin Tong, Zhao Hncaai, Hidaka Hisao, Serpone Nick. Environ Sci Technol 1999;33:1379–87.

[8] Akyol A, Yatmaz HC, Bayramoglu M. Photocatalytic degradation of Remazol Red RR in aqueous ZnO suspension. Appl Catal B Environ 2004;54:19–24.

[9] Kiriakidou Fotini, Kondarides Dimitris I, Verykios Xenophon E. Catal Today 1999;54:119–30.

[10] Ma Wanhong, Huang Yingping, Li Jing, Cheng Mingming, Song Wenjing, Zhao Jincai. R Soc Chem; 2003.

[11] Poulios I, Makri D, Prohaska X. Global Nest Int J 1999;1(1):55–62.

[12] Pagga U, Brown D. The degradation of dyestuff: part II. Behaviour of dyestuffs in aerobic biodegradation tests. Chemosphere 1986;15:1479–91.

[13] Ince NH, Gonenc DT. Treatability of a textile azo dye by UV/H_2O_2. Environ Technol 1997;18:179–85.

[14] Ledakowicz S, Solecka M, Zylla R. Biodegradation, decolourization and detoxification of textile wastewater enhanced by advanced oxidation processes. J Biotechnol 2001;89:175–84.

[15] Namasivayam C, Jeyakumar R, Yamuna RT. Waste Manage 1994;14:643–8.

[16] Hasnat MA, Siddiquey IA, Saiful SM. Indian J Chem 2002;42A:1865–7.