

## Photocatalytic degradation of rhodamine B dye using hydrothermally synthesized ZnO

K BYRAPPA\*, A K SUBRAMANI, S ANANDA<sup>†</sup>, K M LOKANATHA RAI<sup>†</sup>, R DINESH<sup>††</sup> and M YOSHIMURA<sup>††</sup>

Department of Geology, <sup>†</sup>Department of Chemistry, University of Mysore, Manasagangotri, Mysore 570 006, India

<sup>††</sup>Materials Structures Laboratory, Centre for Materials Design, Tokyo Institute of Technology, 4259, Nagatsuta, Midori, Yokohama 226, Japan

MS received 15 February 2006; revised 6 July 2006

**Abstract.** The sunlight mediated photocatalytic degradation of rhodamine B (RB) dye was studied using hydrothermally prepared ZnO ( $T = 150^{\circ}\text{C}$  and  $P \sim 20\text{--}30$  bars). Zinc chloride was used as the starting material along with sodium hydroxide as a solvent in the hydrothermal synthesis of ZnO. Different durations were tried to obtain pure ZnO phase, which was later confirmed through powder X-ray diffraction. The photocatalytic behaviour of the prepared ZnO was tested through the degradation of RB. The disappearance of organic molecules follows first-order kinetics. The effect of various parameters such as initial dye concentration, catalyst loading, pH of the medium, temperature of the dye solution, on the photo degradation of RB were investigated. The thermodynamic parameters of the photodegradation of RB, like energy of activation, enthalpy of activation, entropy of activation and free energy of activation revealed the efficiency of the process. An actual textile effluent containing RB as a major constituent along with other dyes and dyeing auxiliaries was treated using hydrothermally synthesized ZnO and the reduction in the chemical oxygen demand (COD) of the treated effluent revealed a complete destruction of the organic molecules along with colour removal.

**Keywords.** Photocatalysis; hydrothermal; synthetic ZnO; dyes; rhodamine B; textile effluent.

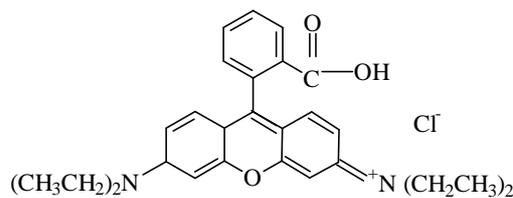
### 1. Introduction

Dyes are extensively used in the textile industry. They are the copious source of coloured organics emanating as a waste from the textile dyeing process. Due to the high concentration of organics in the effluents and the higher stability of modern synthetic dyes, the conventional biological treatment methods are ineffective for the complete colour removal and degradation of organics and dyes (Souther and Alspaugh 1957; Hamza and Hamoda 1980). Other conventional methods of colour removal from an aqueous medium include techniques like coagulation, filtration, adsorption by activated carbon and treatment with ozone (Lorimer *et al* 2001). Each method has its own advantages and disadvantages. For example, the use of charcoal is technically easy but has a high waste disposal cost. While in filtration, low-molar-mass dyes can pass through the filter system. Coagulation, using alum, ferric salts or lime is a low cost process. However, the disposal of toxic sludge is a severe drawback in all the above methods. Lastly, the ozone treatment does not require disposal but suffers from high cost.

Advanced oxidation processes are of ample interest currently for the effective oxidation of a wide variety of organics and dyes (Kang and Hoffman 1998; Boye *et al* 2002). Amongst them, top priority goes to semiconductor assisted photocatalytic degradation. Most of the photocatalytic studies use either synthetic or commercial  $\text{TiO}_2$  as the photocatalyst (Grzechulska and Morawski 2002; Noorjahan *et al* 2002). However, recently some studies have been carried out to evaluate the priority of other metal oxides (Reutergardh and Iangphasuk 1997; Hu *et al* 1999). Among the other semiconductors, ZnO appears to be a highly promising photocatalyst (Stanford *et al* 1996; Carlos *et al* 2000). The focus of the present work is to synthesize ZnO under mild hydrothermal conditions ( $T = 150^{\circ}\text{C}$  and  $P \sim 20\text{--}30$  bars) and use it in the photocatalytic degradation of RB (C.I. No: 45170, formula weight = 479.02, structure shown below), using sunlight illumination. The rate determining parameters like initial dye concentration, catalyst loading, pH of the medium, temperature of the dye solution on the photodegradation of RB were studied in detail. The thermodynamic parameters were calculated. The study of RB degradation and understanding its reaction kinetics helped to consider actual effluent for the photocatalytic study, in view of its complexity in containing diverse types of dyes and other

\*Author for correspondence (byrappak@yahoo.com)

chemicals. The effluent was collected from a textile industry located on the outskirts of Mysore city, India.



Structure of Rhodamine B dye.

## 2. Experimental

### 2.1 Hydrothermal synthesis

In the synthesis of ZnO, reagent grade ZnCl<sub>2</sub> (M/s Ranbaxy, India) was used as the starting material. A required amount of ZnCl<sub>2</sub> was taken in a Teflon liner and the mineralizer solution (NaOH 1 M) was added into it, which was then placed inside an autoclave, and heated to 150°C. In the initial runs the pressure was measured directly using the Bourdon gauge fixed to the autoclave neck. In the subsequent experiments the pressure was adjusted to the desired volume using percent fill. The experimental temperature, type and molarity of the solvent and % fill, controls the size and morphology of the resultant product (Byrappa *et al* 2000; Zhu *et al* 2003). After the experimental run for a particular duration, the autoclave was quenched in air jet and cold water and the liner was taken out. The resultant product inside the liner was separated from the solution and then rinsed with HCl (0.2 M) to remove any residual alkalinity in the product and thoroughly washed with double distilled water till the pH of the wash became neutral. The product was finally dried at 35–40°C in a dust proof environment. The X-ray powder diffraction pattern of synthesized ZnO was recorded using Rigaku Miniflex X-ray diffractometer (Model IGC2, Rigaku Denki Co. Ltd., Japan) and the  $2\theta$  range was kept between 10 and 80°. The identification of the crystalline phase was accomplished by comparison with JCPDS using PCPDF Win version 2.01.

### 2.2 Photocatalytic degradation

In photocatalytic experiments, RB dye (50 ml) and the catalyst (ZnO), were taken in a beaker and exposed to sunlight (intensity of sunlight,  $4.993 \times 10^{16}$  quanta/s by uranyl oxalate method) for up to 180 min. Dye samples of about 2–3 ml were taken out at a regular interval from the test solution, centrifuged for 4–5 min at 950–1000 rpm and their absorbance were recorded at 555 nm using a spectrophotometer (Model: Minispec SL 171, Elico, India). COD was estimated before and after the treatment using K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> oxidation method. The same photocatalytic experimental set up was employed in the case of textile effluent

treatment. As-received effluent was suitably diluted in order to facilitate light penetration. The photodegradation efficiency was calculated from the equation given below

$$\text{Photodegradation efficiency} = \frac{\text{Initial}_{\text{COD}} - \text{Final}_{\text{COD}}}{\text{Initial}_{\text{COD}}} \times 100. \quad (1)$$

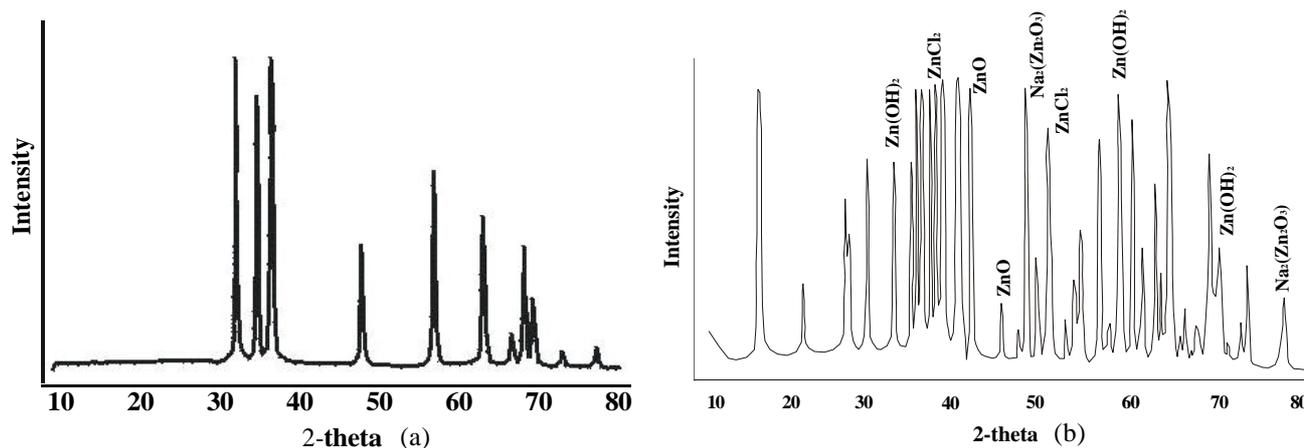
## 3. Results and discussion

### 3.1 ZnO synthesis and characterization

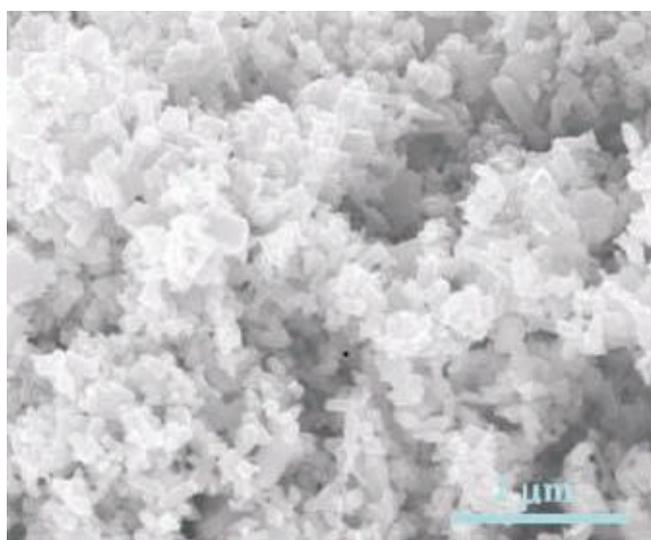
The characteristics of the final product of any hydrothermal synthesis or treatment depends mainly on the experimental parameters like starting materials, experimental temperature and pressure, pH of the medium, mineralizer, experimental duration, etc (Byrappa *et al* 2000). From the previous study on the hydrothermal treatment of ZnO, it is clear that a raise in the NaOH concentration and experimental temperature increased the ZnO particle size (Hasegawa *et al* 2003). The focus of the present study is to obtain fine particles of ZnO as the photodegradation efficiency is proportional to the particle size of the photocatalyst used (Ding *et al* 2000). Hence, in the present study a mild experimental temperature (150°C) and a low concentration (1 M NaOH) solvent were considered for the hydrothermal synthesis experiment. The hydrothermal experimental duration was increased from 5–50 h and its effect on the formation of pure ZnO phase was studied. The X-ray powder diffraction pattern and SEM photograph of ZnO obtained with a hydrothermal experimental duration of 50 h are shown in figures 1a and 2, respectively. The identification of crystalline phase of ZnO was accomplished by comparison with JCPDS files (PDF: 800075). Only after 40 h of experimental duration pure ZnO phase was observed. Mixed phases of ZnO, hydroxide and chlorides (e.g. Zn(OH)<sub>2</sub>, ZnCl<sub>2</sub>, Na<sub>2</sub>(Zn<sub>2</sub>O<sub>3</sub>), etc. PDF: 7617781, 741752, 850325) were observed when the experimental duration was 5–35 h. The SEM (figure 2) shows that the particles are uniform in shape and well dispersed. Figure 1b shows a representative X-ray powder diffraction pattern of the product containing mixed phases obtained with the experimental duration of 5–35 h.

### 3.2 Photodegradation studies of RB

Photodegradation process assisted by a semiconductor depends on various parameters like nature and concentration of the organic substrate, concentration and type of the semiconductor, light source and intensity, pH, temperature, etc (Ferraz *et al* 1999). Several earlier studies reported that, the photocatalytic degradation of dyes follows first-order kinetics (Panduranga *et al* 2001; Lachheb *et al* 2002). The present investigation also reveals that ZnO induced photocatalysis of RB follows the first order kine-



**Figure 1.** X-ray diffraction patterns: (a) hydrothermally synthesized ZnO with an experimental duration of 50 h and (b) mixed phases.

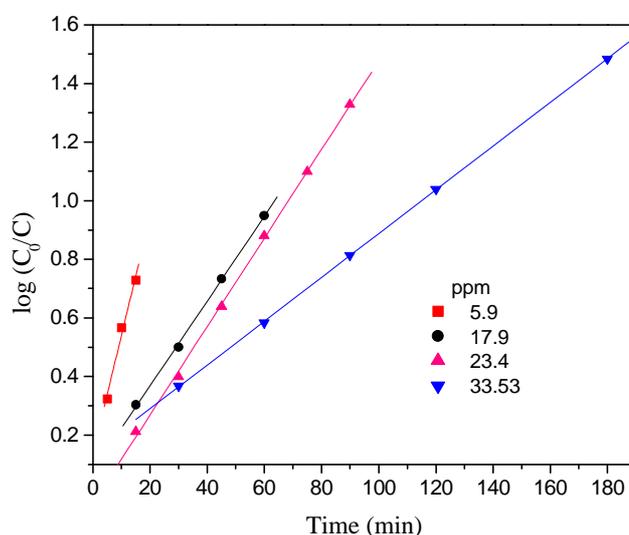


**Figure 2.** SEM photograph of pure ZnO particles obtained under hydrothermal conditions.

**Table 1.** Rate constant ( $k$ ) and half-life ( $t_{1/2}$ ) values for different concentrations of the dye solution at 298 K.

Rhodamine B (ppm)	$K$ ( $m^{-1}$ ) ( $10^{-2}$ )	$t_{1/2}$
9.58	3.74	18.52
17.9	3.33	20.81
19.16	3.21	21.58
23.4	3.47	19.97
28.74	3.208	21.65
33.53	1.72	40.29

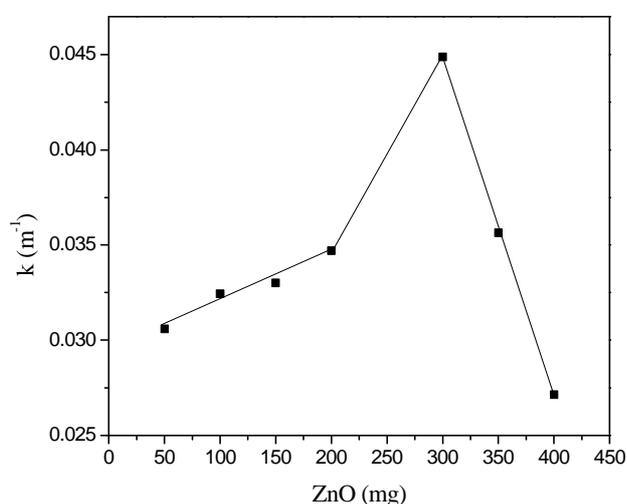
tics with respect to RB concentration. Table 1 shows the rate constant and  $t_{1/2}$  values for different concentrations of RB. All the experimental results discussed herein are based on the first order plots ( $\log C_0/C$  vs time) or the rate constants derived from the first order plots.



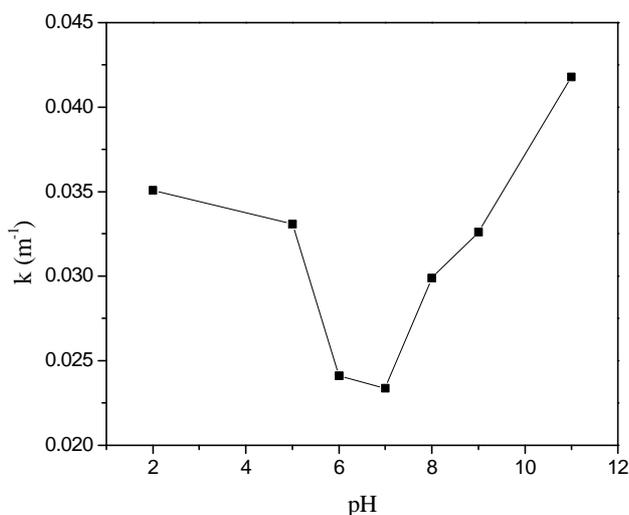
**Figure 3.** Effect of initial dye concentration on the photodegradation efficiency of RB.

**3.2a Effect of initial dye concentration:** The effect of initial RB concentration on the degradation efficiency was studied by varying the concentration from 5.9–33.53 ppm and keeping ZnO (200 mg/50 ml) as constant. The degradation efficiency of RB was found to decrease with an increase in the initial dye concentration (figure 3). The active surface on the catalyst available for reaction is very crucial for the degradation to take place, but as the dye concentration is increased and the catalyst amount is kept constant, results in fewer active sites for the reaction. With increased dye molecules the solution became more intense coloured and the path length of photons entering the solution decreased thereby only fewer photons reached the catalyst surface. And therefore, the production of hydroxyl and superoxide radicals were limited. At still higher concentration of the dye, the path length was further reduced and the photodegradation was found to be negligible.

**3.2b Effect of ZnO loading:** Experiments were carried out taking different amounts of ZnO and keeping dye concentration constant at 23.4 ppm (figure 4). It was found that the rate constant increases up to 300 mg/50 ml of the dye solution, beyond which it shows a drastic reduction. The increase in the degradation efficiency of RB with an increase in the catalyst amount may be due to an increase in the active sites available on the catalyst surface for the reaction, which in turn increases the rate of radical formation. The reduction in the rate constant when the catalyst amount is increased beyond 300 mg/50 ml, is due to light scattering and reduction in light penetration through the solution. With a higher catalyst loading the deactivation of activated molecules by collision with ground state molecules dominates the reaction, thus reducing the rate of reaction (Neppolian et al 2001).

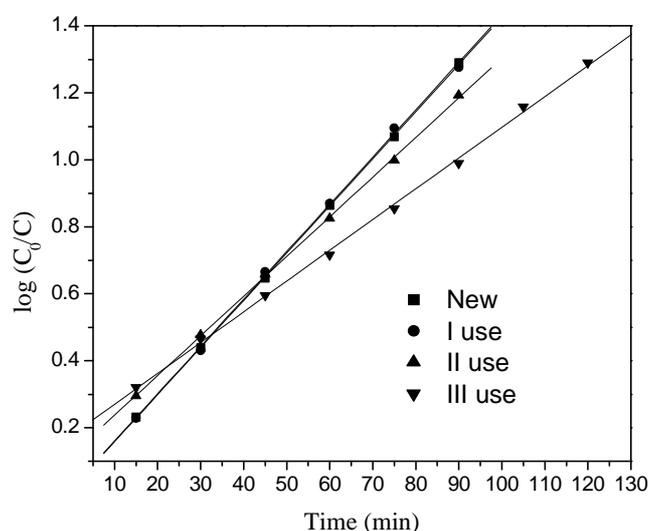


**Figure 4.** Effect of ZnO loading on rate constant of the photodegradation of RB.

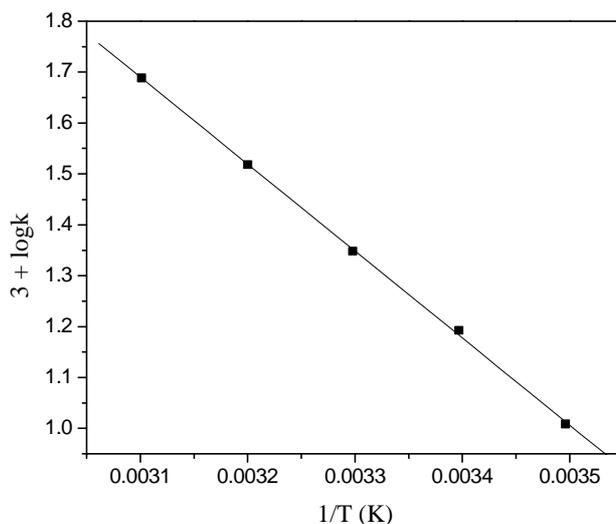


**Figure 5.** Effect of pH on rate constant of the photodegradation of RB.

**3.2c Effect of pH:** The pH of the dye solution in the present study was adjusted using varying concentrations of HNO<sub>3</sub> or NaOH. The minimum rate constant was recorded at pH 7 and increased with acidic as well as alkaline pH values (figure 5). The pH affects not only the surface properties of ZnO but also the dissociation of dye molecules and the formation of hydroxyl radicals (Serpone and Pelizzetti 1989; Alberici and Jardim 1994). Enforcement of the reaction rate under alkaline condition could be attributed to the increase of hydroxyl ions, which induces more hydroxyl radical formation. In the acidic condition, the perhydroxyl radical can form hydrogen peroxide, which in turn gives rise to the hydroxyl radical. Thus an increase or decrease in pH from neutral value increases the rate of reaction, because the formed OH radicals also



**Figure 6.** Photodegradation efficiency of the catalyst when reused.



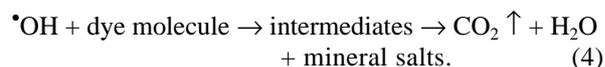
**Figure 7.** Effect of temperature on the photocatalytic degradation of RB.

initiate the degradation reaction. We attempted to achieve high degradation efficiency at neutral pH, however, it was found to be good at extreme acidic or alkaline pH conditions.

**3.2d Efficiency of reused catalyst:** The ZnO used in the photocatalytic treatment was centrifuged, dried at 30–40°C in a hot air oven before it was reused as such in the succeeding photocatalytic experiment. The photodegradation efficiency of ZnO shows only a marginal change after repetitive use (figure 6). These results indicate the cost effectiveness of this method.

**3.2e Effect of temperature:** The photocatalytic degradation was studied at various temperatures in the range 281–321°K and rate constant,  $k$ , was determined from the first-order plots. An increase in temperature helps the reaction to compete more efficiently with  $e^-/H^+$  recombination (Mills and Hunte 1977). The energy of activation,  $E_a$ , was calculated from the Arrhenius plot of  $\log k$  vs  $1/T$  (figure 7). The other thermodynamic parameters viz. enthalpy of activation ( $\Delta H^\ddagger$ ), entropy of activation ( $\Delta S^\ddagger$ ) and free energy of activation ( $\Delta G^\ddagger$ ) were calculated (table 2) using the energy of activation.

**3.2f Reaction scheme:** The possible reaction scheme for the photocatalytic degradation of RB dye is given in (2)–(4).



The proposed reaction scheme is also supported by the fairly high positive values of the free energy of activation and enthalpy of activation, which indicates that the transition state is highly solvated. While the small  $\Delta S^\ddagger$  suggests that the intermediate complex is less ordered than the reactants, which supports higher degree of degradation of the dye molecule into simple products.

**3.2g Estimation of chemical oxygen demand (COD):** The chemical oxygen demand test is widely used as an effective technique to measure the organic strength of wastewater. The test allows the measurement of waste in terms of the total quantity of oxygen required for the oxidation of organic matter to  $\text{CO}_2$  and water. The COD of the dye solution before and after the treatment was estimated. The reduction in COD values of the treated dye solution indicates the mineralization of dye molecules along with the colour removal. Table 3 gives COD values of blank and treated dye solutions.

### 3.3 Photocatalytic treatment of textile effluent

In any textile plant diverse dyes and chemicals are used to impart attractive colours to the textile. In this process enormous amount of wastewater with high concentration of persistent dyes and chemicals are generated. An effluent with such diverse composition has been considered for the photocatalytic degradation in the present study. The visible spectrum of the textile effluent employed in the present study was recorded and  $I_{\max}$  was found to be 530 nm. The effluent was used in the photodegradation studies with a required dilution. The initial COD of the effluent was 1278.44 mg/l and the %T (measured at 530 nm) was found

**Table 2.** Kinetics and thermodynamic parameters for the photocatalytic degradation of RB.

$T$ (K)	$k$ ( $\text{m}^{-1}$ ) ( $10^{-2}$ )	$E_a$ (KJ $\text{mol}^{-1}$ )	$\Delta H^\ddagger$ (KJ $\text{mol}^{-1}$ )	$\Delta S^\ddagger$ (JK $^{-1}$ $\text{mol}^{-1}$ )	$\Delta G^\ddagger$ (KJ $\text{mol}^{-1}$ )
281	1.02		29.97		79.56
291	1.56		29.89		81.33
301	2.23	32.30	29.80	-0.17	83.10
311	3.3		29.71		84.87
321	4.87		29.64		86.64

**Table 3.** COD values of initial and treated RB dye solutions.

Dye concentration (ppm)	Initial COD (mg/l)	Final COD (mg/l)	Photodegradation efficiency (%)
38.32	19.12	6.32	66.94
47.90	23.9	0	100
95.80	47.8	15.5	67.57
191.60	95.6	8.85	90.74
383.21	191.2	21.86	88.56

**Table 4.** Photocatalytic treatment of the effluent.

Exposure duration (h)	%T	Final COD	Photodegradation efficiency (%)
1	67	1018.72	20.31
2	75	962.64	24.7
4	86	705.81	44.79
6	93	458.7	64.12
8	96	320.52	74.92
10	96	179.5	85.95

to be 53% after dilution. Sun light was used as the source of illumination. Table 4 gives results of the photocatalytic treatment of industrial effluent using hydrothermally synthesized ZnO. The reduction in COD confirms the destruction of the organic molecules in the effluents along with colour removal.

#### 4. Conclusions

Preparation of photocatalytic ZnO was carried out under mild hydrothermal conditions ( $T = 150^{\circ}\text{C}$  and  $P = 20\text{--}30$  bars). The required pure ZnO phase was obtained by increasing the hydrothermal experimental duration beyond 40 h. The photocatalytic degradation of RB was found to be dependent on various kinetic parameters like nature and concentration of the dye, concentration of the semiconductor and pH, temperature of the dye solution, etc. The ZnO can be reused for a number of cycles, which will reduce the cost of operation. The thermodynamic parameters of the degradation of RB have been reported. Fairly high positive  $\Delta H^{\ddagger}$  and  $\Delta G^{\ddagger}$  obtained indicate that the transition state is highly solvated. In the present case the value of  $\Delta S^{\ddagger}$  is  $-0.17$  which is almost positive, so that the complex formed is less ordered than the reactants and the bands are not strongly associated. Initially the complex formed is unstable and degradation of the reactants into products is not very slow, but takes place rapidly under present experimental conditions.

Textile effluent with diverse composition was effectively treated using hydrothermally synthesized ZnO. The reduction in COD of the effluent suggests that the dye molecules were completely mineralized along with colour removal. It can be concluded that the ZnO assisted photocatalytic degradation of textile dyes and textile effluent may be a versatile, economic, environmentally benign and efficient method of treatment.

#### Acknowledgements

The authors are indebted to the University Grants Commission, New Delhi, for financial support to carry out this work. Also the authors wish to acknowledge the referee for his valuable suggestions.

#### References

- Alberici R M and Jardim W F 1994 *Water Res.* **28** 1845
- Boye B, Dieng M M and Brillas E 2002 *Env. Sci. & Technol.* **36** 3030
- Byrappa K, Lokanatha Rai K M and Yoshimura M 2000 *Env. Technol.* **21** 1085
- Carlos A K, Wypych G F, Moraes Sandra G, Duran N, Nagata N and Peralta P Z 2000 *Chemosphere* **40** 433
- Ding Z, Lu G Q and Greenfield P F 2000 *Colloid. & Interf. Sci.* **232** 1
- Ferraz A M C M, Maser S and Jonhaeuser M 1999 *Fuel* 1567
- Grzechulska J and Morawski A W 2002 *Appl. Catal. B: Environ.* **36** 45
- Hamza A and Hamoda M F 1980 *Proc. 35th Purdue industrial waste congress, West Lafayette, IN, USA*
- Hasegawa H, Uchida S and Tomiha M 2003 in *Proc. seventh international symposium on hydrothermal reactions* (ed.) S H Feng (Japan: Nishimura Tosha-do Ltd) p. 517
- Hu X, Lei L, Chu H P and Yue P L 1999 *Carbon* **37** 631
- Kang J and Hoffman M R 1998 *Env. Sci. & Technol.* **32** 3194
- Lachheb H, Puzenat E, Houas A, Ksibi M, Elaloui E, Guillard C and Herrmann J M 2002 *Appl. Catal. B: Environ.* **39** 75
- Lorimer J P, Mason T J, Plattes M, Phull S S and Walton D J 2001 *Pure & Appl. Chem.* **12** 1957
- Mills A and Hunte S L 1977 *J. Photochem. & Photobiol. A: Chem.* **108** 1
- Neppolian B, Sakthivel S, Banumathi A, Palanichamy M and Murugesan V 2001 *Indian J. Chem. Technol.* **8** 36
- Noorjahan M, Durga Kumari V and Subramanyam M 2002 *Indian J. Environ. Prot.* **22** 1162
- Panduranga A, Kamala S, Uma S, Palanichamy M and Murugesan V 2001 *Indian J. Chem. Technol.* **8** 496
- Reutergardh R and Iangphasuk M 1997 *Chemosphere* **35** 585
- Serpone N and Pelizzetti E 1989 *Photocatalysis* (New York: John Wiley and Sons)
- Souther R H and Alspaugh T A 1957 *J. Water Pollution Control Federation* **29** 804
- Stanford U, Gray K A and Kamat D V 1996 *Het. Chem. Rev.* **3** 77
- Zhu K, Yanagisawa K, Onda H and Kajiyoshi K 2003 in *Proc. seventh international symposium on hydrothermal reactions* (ed.) S H Feng (China) p. 289