



## Heterogeneous Photocatalytic Mineralization of Azo Dye in Aqueous Solution

S. LATHASREE<sup>1,\*</sup> and B. SIVA SANKAR<sup>2</sup>

<sup>1</sup>Department of Chemistry, Sathyabama University, Chennai-600 119, India

<sup>2</sup>Department of Chemistry, Anna University, Chennai-600 025, India

\*Corresponding author: E-mail: latsri18@gmail.com

Received: 3 December 2014;

Accepted: 4 January 2015;

Published online: 30 March 2015;

AJC-17113

The photocatalytic degradation of azo dye acid orange 7 was studied using different semiconductor photocatalyst such as ZnO, TiO<sub>2</sub>, ZnS and WO<sub>3</sub> in a batch reactor configuration in presence of UV light. ZnO was found to a more efficient photocatalyst in the degradation of the dye compared to other photocatalysts. In the presence of UV/ZnO, illumination was done using a 6 W low pressure mercury vapour lamp. The variables studied include catalyst usage, solution pH and effect of wavelength of incident light on the photocatalytic degradation of the dye. The incident light with wavelength of 254 nm was comparatively more effective than 375 nm light. The degradation rate of acid orange 7 was found to increase linearly with increase in pH and the optimum loading of ZnO was found to be 2.0 g/L. Total organic carbon analysis indicated complete mineralization of dye in aqueous solution.

**Keywords:** Acid orange 7, ZnO, Photocatalytic degradation, Mineralization.

### INTRODUCTION

The growing pollution of our hydrosphere has necessitated the implementation of different strategies to treat water for drinking purposes and to treat domestic and industrial wastewaters for recycling. Over the years, the wastewater generated by the textile industry is rated as the most polluting among all industrial sectors<sup>1,2</sup>. In textile finishing and dyeing industries, large amount of water is consumed in dyeing and washing/rinsing of the fabrics. Dyestuffs are widely employed and the wastewater generated from these industries are highly coloured due to residual dyes. The discharge of dye bearing wastewater into natural streams from textile industry had created significant concern, as the dyes impart toxicity and impede light penetration. It is estimated that 10-15 % of the dye is not fixed to the fabric and lost to the environment during the dyeing process in the form of effluent. Synthetic dyes used in textile industries are low cost and readily available and possess good stability towards both photo-degradation as well as in chemical degradation. Advanced oxidation processes (AOPs) involving hydrogen peroxide, ozone and/or Fenton reagents, with or without a source of UV light have been proposed in recent years as potential alternatives for colour and substantial removal of chemical oxygen demand and total organic carbon from textile effluents. Among the various advanced oxidation processes, semiconductor mediated photocatalysis has been accorded great importance over the last few years due to its potential to

destroy a wide range of organic and inorganic pollutants at ambient temperatures and pressures without the production of harmful by products<sup>3-5</sup>. Among the various semiconductors used ZnO is a suitable alternative for TiO<sub>2</sub> and in fact proved to be more effective than TiO<sub>2</sub> in destruction of organics. This study represents part of our investigation on the ZnO mediated photo-destruction of azo dye acid orange 7.

### EXPERIMENTAL

ZnO, TiO<sub>2</sub>, WO<sub>3</sub>, TiO<sub>2</sub> and other chemicals used in the present study are of reagent grade obtained from LOBA, CDH and Merck. The azo dye acid orange 7 (molecular formula, molecular weight and  $\lambda_{\max}$  were C<sub>16</sub>H<sub>11</sub>N<sub>2</sub>O<sub>4</sub>SNa, 350 g/mol and 485 nm respectively) used for experimental studies was obtained from dyestuff suppliers and used without purification. Fig. 1 shows the chemical structure of acid orange 7. Solutions were prepared using double distilled water. Brunauer-Emmett-Teller (BET) surface area of ZnO, TiO<sub>2</sub>, ZnS and WO<sub>3</sub> determined by flow method using Micromeritics Pulse Chemisorb 2700 were found to be 8, 50, 9 and 10 m<sup>2</sup>/g respectively. The pH of the solutions was adjusted to the desired values between 4 and 10 using dilute solutions of dilute HCl or NaOH. All the studies were carried out at 30 °C.

The photodegradation studies were carried out in a batch reactor system. The solutions were illuminated in an open rectangular tray of 16 cm × 5 cm × 5 cm made of borosilicate

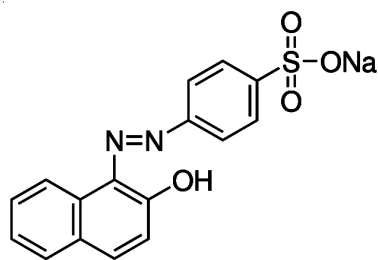


Fig. 1. Structure of acid orange 7

glass mounted on a magnetic stirrer with 6 W lamp used as an irradiation source. The lamp emitted a peak wavelength of 253.7 nm with intensity of  $2.48 \pm 0.1 \times 10^{19}$  quanta per second standardized by ferrioxalate actinometry.

**Procedure:** In all the batch reactor experiments, the optimum conditions used were a batch volume of 250 mL (dye solution), 8 cm distance between UV source and solution with stirring speed of 70 rpm and 0.5 h for adsorption equilibrium. The experimental procedure consisted of irradiation of the dye solution of known concentration mixed with a known weight of catalyst powder with UV light. Samples of 3 mL were withdrawn at regular intervals of time, centrifuged and the absorbance was measured using a Systronics single beam UV-visible spectrophotometer model 118 at  $\lambda_{\text{max}}$  of 485 nm. The concentration of the dye solution was determined using a standard Beer's plot from the measured absorbance value of the irradiated solution. After analysis the solutions were returned back to the reactor. The estimation of total organic carbon was done subjecting dye solution to photocatalytic degradation in a closed reactor to convert the organic carbon to carbon dioxide. The evolved carbon dioxide was trapped in an aqueous KOH solution of known concentration and unreacted KOH was titrated with HCl of known concentration<sup>6</sup>. The experimental procedure adopted is described by Lathasree *et al.*<sup>7,8</sup>. The stability of ZnO was assessed by subjecting the irradiated solution to atomic absorption spectroscopic (AAS, Perkin-Elmer) analysis and the amount of zinc in solution resulting from photo-corrosion was determined. The reusability of the catalyst was evaluated by reclaiming the catalyst after reaction in the batch mode, washing, drying in air at 110 °C and using it for dye degradation under similar experimental conditions.

## RESULTS AND DISCUSSION

**Photodegradability of acid orange 7:** The photodegradability of the dye was investigated by exposing the dye solution to UV light in the absence and in the presence of semiconductor photocatalyst in a batch reactor (Fig. 2). In the absence of the photocatalyst the 50  $\mu\text{M}$  dye solution on irradiation with UV light of wavelength 254 nm was found to be stable and photodegradation was negligible even after 2 h of exposure. In the presence of ZnO and in the absence of UV light the dye solution was stable though adsorption was found to be responsible for the decrease in dye concentration. However, the dye undergoes photodegradation on irradiation with UV light of 254 nm in the presence of ZnO (with a band gap energy of 3.2 eV). Complete mineralization of the dye solution occurred within 1 h of irradiation as determined by total

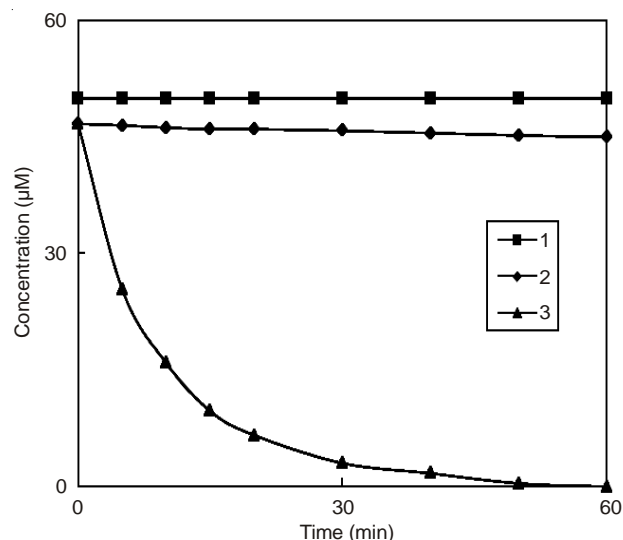


Fig. 2. Photodegradability of acid orange 7; [Acid orange 7] = 50  $\mu\text{M}$ ; pH =  $7.0 \pm 0.1$ ; Catalyst = ZnO (2.0 g/L); Temperature =  $30.0 \pm 0.1$  °C; Incident wavelength = 254 nm; Absorbance measured at 485 nm; (1) Dye solution irradiated with UV light in the absence of ZnO; (2) Dye solution treated with 2.0 g/L of ZnO in the dark; (3) Dye solution irradiated with UV light in the presence of ZnO

organic carbon analysis. Carbon dioxide content determined experimentally was found to tally with the theoretical value on the basis of known molecular structure of the dye, molecular weight and concentrations employed. The organic nitrogen and sulphur contents of the dye molecule were apparently converted to a mixture of nitrate, nitrite, sulphate and sulphite, which were identified and quantitatively estimated after the completion of the irradiation.

**Comparison of catalytic activity of different semiconductors:** Different semiconductor metal oxides and metal sulphides were investigated for their effectiveness in the degradation of the dye solutions. The effect of different catalysts on the photodegradability of acid orange 7 as a function of time is shown in Fig. 3. TiO<sub>2</sub> Degussa P-25 primarily of anatase form with surface area 50 m<sup>2</sup>/g and ZnO Merck sample of surface area 8 m<sup>2</sup>/g was found to be more effective in photocatalytic degradation of the dye compared to WO<sub>3</sub> and ZnS. ZnO was found to function as more efficient photocatalyst in the degradation of dye compared to TiO<sub>2</sub><sup>9,10</sup>. Since ZnO is low-cost compared to TiO<sub>2</sub> the dye degradation studies were conducted using ZnO.

**Effect of incident light on the photocatalytic degradation of dye:** The photocatalytic degradation of acid orange 7 was investigated by exposing the dye solution to light of incident wavelengths 375 and 254 nm and in the presence of ZnO. The photocatalytic degradation of the dye in presence of ZnO involves the light absorption of wavelength (380 nm) higher than band gap energy of 3.2 eV. A sample of 50 M of the dye solution on irradiation with 254 nm light was found to undergo complete mineralization within 1 h. Under similar conditions, with 375 nm light, only 40 % of the degradation was observed. Fig. 4 shows the effect of incident light wavelength on the photodegradability of acid orange 7 as a function of time. The improved effectiveness of 254 nm light compared to 375 nm light may be due to the fact that the shorter wavelength light is absorbed more strongly by the catalyst particles

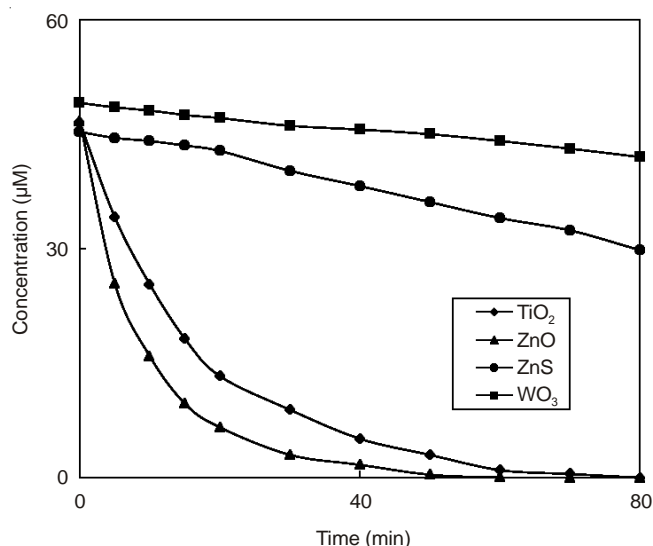


Fig. 3. Catalytic activity of different semiconductors on the photocatalytic degradation of acid orange 7; [Acid orange 7] = 50 µM; pH = 7.0 ± 0.1; Incident wavelength = 254 nm; Absorbance measured at 485 nm; Weight of catalyst = (2.0 g/L); Temperature = 30 ± 0.1 °C

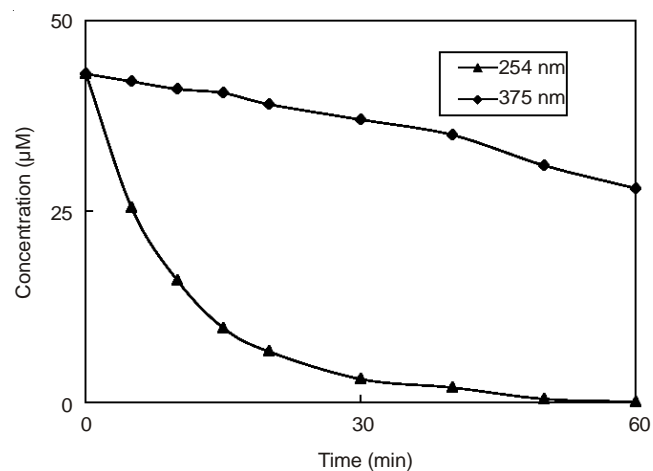


Fig. 4. Effect of wavelength of incident light on the photocatalytic degradation of acid orange 7 [Acid orange 7] = 50 µM; pH = 7.0 ± 0.1; Temperature = 30.0 ± 0.1 °C; Absorbance measured at 485 nm; Catalyst = ZnO (2.0 g/L)

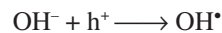
than the longer wavelength light. Hence the penetration distance of photons into the particle is shorter and photoelectrons and holes are formed closer to the surface of the particle. Therefore they take less time to migrate to the surface of the particle and hence have less time to participate in energy wasting recombination reactions before useful surface reaction take place. Many organic molecules are excited by 254 nm light and are degraded as a result of direct action. But the direct degradation rate is very small compared to the rate in the presence of a photocatalyst. Similar observation was reported by Mathews and McEvoy<sup>11</sup>. Therefore the photocatalytic degradation reaction studies were carried out using 254 nm light.

**Effect of solution pH:** The photocatalytic degradation of acid orange 7 was studied in the pH range of 4-10. It was observed that, with the increase in pH value from 4 to 10 the time required for degradation decreased from 80 to 30 min. This pH dependency may be explained on the basis of increase

in the generation of OH• radicals with increase in pH. In acid and neutral solutions, the reactions occurring is represented as:



whereas in alkaline solution, increased adsorption of hydroxide ions may give rise to a greater concentration OH• radicals:



A similar influence of pH on the initial photocatalytic degradation rate of acid red 3B was reported by Shourong *et al.*<sup>12</sup>. Fig. 5 shows the linear increase in the initial rate of degradation in the pH range 4-9. The initial rate value lies in the range of 1.7-6.1 µM/min.

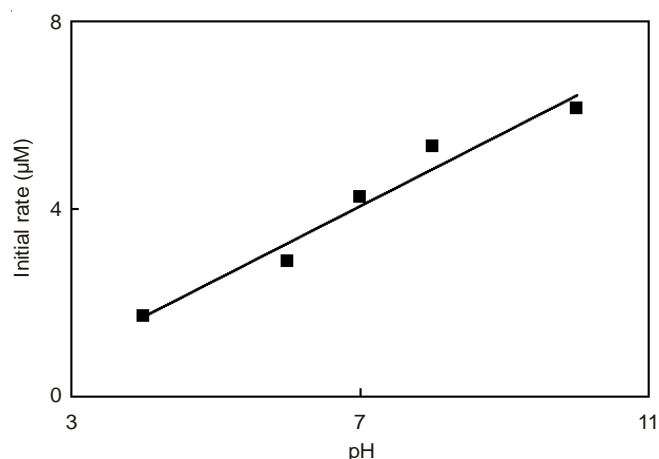


Fig. 5. Effect of pH on the initial rate of photodegradation of acid orange 7 [Acid orange 7] = 50 µM; pH = 7.0 ± 0.1; Temperature = 30.0 ± 0.1 °C; Absorbance measured at 485 nm; Catalyst = ZnO (2.0 g/L)

**Effect of catalyst weight:** The effect of catalyst weight on the photodegradation of the dye was studied in the range 1-3 g/L. The time required for the degradation of the dye was found to decrease with increase in weight of the catalyst. As the amount of catalyst increases, there is rise in the number of ZnO particles and therefore the number of dye molecule adsorbed increases. However, the initial rate of photodegradation was found to increase with increase in catalyst weight in the range 1.0-2.0 g/L and further increase in catalyst loading was found to show a negative effect as shown in Fig. 6. The optimum weight of the catalyst loading was found to be 2.0 g/L. At higher catalyst loading the initial rate decreases possibly due to a screening effect of excess catalyst particle in the solution on light<sup>13</sup>.

**Reusability of ZnO catalyst:** The solutions resulting from photocatalytic degradation was filtered and the filtrate was subjected to AAS analysis to assess the loss of Zn<sup>2+</sup> to solution as a result of dissolution of ZnO. Under the experimental conditions, photo-corrosion of ZnO was found to be negligible (0.04 % loss of zinc was observed during 2 h of reaction time) though literature survey has indicated that ZnO suffers from photocorrosion induced by self oxidation<sup>14</sup>. In the present study it was observed that the photocatalyst was used repeatedly without any treatment and the catalytic activity of the reused catalyst was found to be the same as that of original catalyst even after five batch reactions.

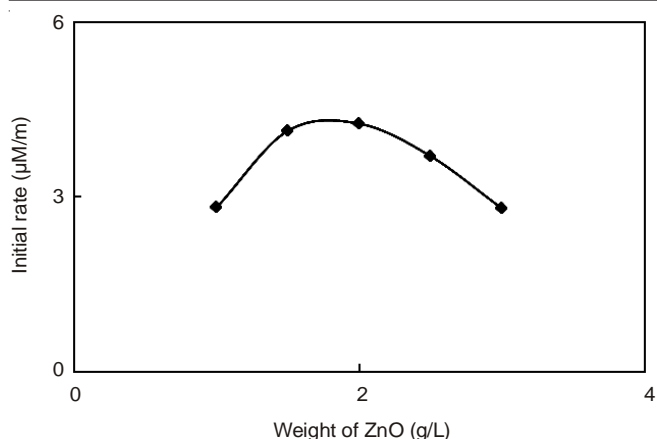


Fig. 6. Effect of catalyst weight on the initial rate of photo-catalytic degradation of acid orange 7 [Acid orange 7] = 50 µM; pH = 7.0 ± 0.1; Incident wavelength = 254 nm; Absorbance measured at 485 nm; Temperature = 30.0 ± 1 °C

### Conclusion

The azo dye acid orange 7 was completely mineralized by photocatalytic degradation on ZnO surface. Compared to other semiconductors used, ZnO was found to more efficient photocatalyst in the photodegradation of dye in the presence of UV light. The incident light of wavelength 254 nm was found to be comparatively more effective in the degradation of acid orange 7 than incident light of wavelength 375 nm. The degradation of the dye was favourable in the alkaline pH range. Experimental results indicated that the initial rate of photodegradation increased with increase in pH. The photodegradation of the dye were studied in the initial catalyst weight

ranging from 1-3 g/L. The initial rate of the photodegradation reaction was found to increase with increase in catalyst weight upto an optimum loading. Further increase in the catalyst weight showed a negative effect. ZnO was stable and undergone photo-corrosion only to a negligible extent. The photocatalytic activity of ZnO was retained even upto five cycles.

### REFERENCES

1. A. Mishra, T. Arockiadoss and S. Ramaprabhu, *Chem. Eng. J.*, **162**, 1026 (2010).
2. A. Maleki, A.H. Mahvi, R. Ebrahimi and Y. Zandsalimi, *Korean J. Chem. Eng.*, **27**, 1805 (2010).
3. B. Neppolian, H.C. Choi, S. Sakthivel, B. Arabindoo and V. Murugesan, *Chemosphere*, **46**, 1173 (2002).
4. B. Pare, S.B. Jonnalagadda, H. Tomar, P. Singh and V.W. Bhagwat, *Desalination*, **232**, 80 (2008).
5. C. Guillard, J. Disdier, M. Herrmann, C. Lehaut, T. Chopin, S. Malato and J. Blanco, *Catal. Today*, **54**, 217 (1999).
6. R.W. Matthews, M. Abdullah and G.K.-C. Low, *Anal. Chim. Acta*, **233**, 171 (1990).
7. S. Lathasree, A.N. Rao, B. SivaSankar, V. Sadasivam and K. Rengaraj, *J. Mol. Catal. Chem.*, **223**, 101 (2004).
8. I. Prabha and S. Lathasree, *Mater. Sci. Semicond. Process.*, **26**, 603 (2014).
9. J.P. Percherancier, R. Chapelon and B. Pouyet, *J. Photochem. Photobiol. Chem.*, **87**, 261 (1995).
10. I. Poullos, M. Kositzi and A. Kouras, *J. Photochem. Photobiol. Chem.*, **115**, 175 (1998).
11. R.W. Matthews and S.R. McEvoy, *J. Photochem. Photobiol. Chem.*, **66**, 355 (1992).
12. Z. Shourong, H. Qingguo, Z. Jun and W. Bingkun, *J. Photochem. Photobiol. Chem.*, **108**, 235 (1997).
13. L.C. Chen and T.C. Chou, *Ind. Eng. Chem. Res.*, **32**, 1520 (1993).
14. M.A. Fox and M.T. Dulay, *Chem. Rev.*, **93**, 341 (1993).