## Available online at <u>www.pelagiaresearchlibrary.com</u>



Pelagia Research Library

Advances in Applied Science Research, 2011, 2 (3):280-286



# Removal of Indigo Caramine dye by using nanosized Semiconducting Photocatalyst in aqueous media

Vinod S. Shrivastava

Nanochemistry Research Laboratory, G.T.P. College, Nandurbar (M.S.), India

## ABSTRACT

The present communication deals with the study of photocatalytic degradation of Indigo Caramine in aqueous suspension of nanosized TiO<sub>2</sub> particles. Photocatalytic degradation of Indigo Caramine have been studied with the help of variety of parameters which are catalyst dose, dye concentration, pH and contact time. The optimum condition for the degradation of the dye was 40 mg/L, pH 8, catalyst dose 60mg/L and contact time 20 minutes. The changes of dye concentration were determined by UV–Visible double beam spectrophotometer at  $\lambda$ max 610 nm in our laboratory. The SEM studies were carried out for morphological features and size of the TiO<sub>2</sub> particles.

Keywords: Photocatalytic degradation, Indigo Caramine, TiO<sub>2</sub>, SEM.

## **INTRODUCTION**

Purification of wastewater contaminated with these pollutants is very difficult since they are resistant to conventional treatment techniques. Azo dyes are the largest group of the dyes used for dyeing cotton fabrics in the industry. Cotton is the most widely used fabric among all textile materials, hence azo dyes are discharged frequently and in large quantities into the environment. The color and high COD of effluents from dye house cause serious environmental contamination problems nowadays [1]. In particular, azo dyes represent about half of the dyes used in the textile industry and, as a consequence, a relevant problem of pollution related to the release of these products in the environment is taking place [2]. Although there were several other technologies available for the removal of color and COD from azo dye wastewater such as biodegradation [3], sorption [4-6], electrochemical and oxidative degradation [7-11], chlorine dioxide (ClO<sub>2</sub>) catalytic oxidation was a very attractive and useful technique for treatment of dye house effluents [12-14].

In view of the above the present communication deals with the degradation of Indigo Caramine by nanosiozed  $TiO_2$  particles.

#### **MATERIALS AND METHODS**

#### Materials and Methods

For the present study water soluble Indigo Caramine dye, molecular formula  $C_{16}H_8N_2Na_2O_8S_2$ , molecular weight (466.35 g/mole) was selected. TiO<sub>2</sub> was provided from Himedia. 200 mg/L stock solution of Indigo Caramine was prepared in 1000ml of distilled water. All chemicals were of analytical grade and used without purification. In 100ml of dye solution of desired concentration, different catalyst dose added and irradiated with UV lamp to provide excitation to TiO<sub>2</sub>. To ensure efficient mixing of semiconductor photocatalyst in the reactor. At specific time intervals suitable aliquot of the sample was withdrawn and analyzed after centrifugation. The concentration of dye was determined on a double beam UV-Visible Spectrophotometer (Systronics-2203) at  $\lambda$ max 610 nm. All the experiments were carried out at room temperature. Structure of Indigo Caramine as shown in fig.1.

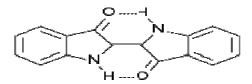


Fig.1: Structure of Indigo Caramine Dye

#### Instrumentation

The photocatalytic degradation study was carried out in photocatalytic reactor. The reactor consist of mercury lamp, tin reflector and reaction flask. Irradiation was conducted using 400 watt mercury lamp placed inside the tin reflector. The lamp emmits pre-dominately UV radiation of 37.4 mW/cm<sup>2</sup> of intensity. Intensity of radiation was measured by Illuminancemeter (Agronics). The pH metric measurements were made on Equiptronics digital pH meter (Model - E610) fitted with glass electrode which was previously standardized with buffers of known pH in acidic and basic medium respectively.

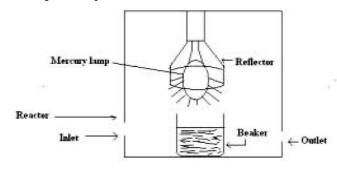
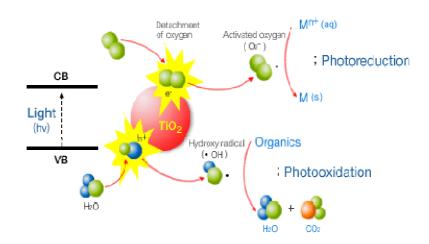


Fig.2(a): Schematic arrangement of Photocatalytic Reactor

## Vinod S. Shrivastava

#### Mechanism:



### Effect of Catalyst dose

The effect of photocatalyst dose on the degradation kinetics of Indigo Caramine was investigated employing different dose of varying from 10mg/L to 100mg/L (Fig.3) Photodegradation of Indigo Caramine increases rapidly with increasing the amount of catalyst. The no. of active sites on the TiO<sub>2</sub> surface which in turn increases the no. of OH<sup>-</sup> and O<sub>2</sub><sup>-</sup> radicals. It observed that 60mg/L of TiO<sub>2</sub> was the optimum dose for efficient degradation of Indigo Caramine dye.

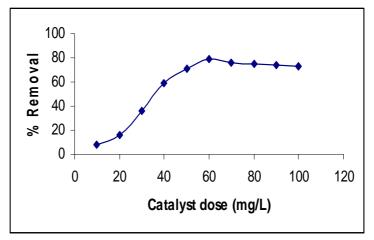


Fig.3 Effect of catalyst dose on percerntage removal of Indigo caramine at dye concentration 40mg/L, contact time 20minutes, pH 8

#### Effect of dye concentration

The photocatalytic degradation of Indigo Caramine dye has been investigated in aqueous suspension of  $TiO_2$  as a function of irradiation time (fig.4). The rate of photodegradation of Indigo Caramine dye was studied by varying the dye concentration from 10mg/L to 100mg/L. The experiment was carried at fixed pH 8 and catalyst dose 60mg/L. It was found that photocatalytic degradation decreases from 100mg/L to 10mg/L. It observed that 40mg/L of dye concentration was the optimum concentration for efficient degradation of Indigo Caramine dye.

Because for a fixed concentration of active sites remaining the same, the no. of substrates ions accommodated in the interlayer space increases so that the degradation decreases. This may be due to the fact that with increase in initial concentration of the dye, more dye molecules are also adsorbed on the surface of TiO<sub>2</sub>. Thus, increase in the number of substrate ions accommodating in inter layer spacing inhibit the action of catalyst which thereby decreases the reactive OH<sup>-</sup> and  $O_2^{-}$  Free radicals attacking the dye molecules and photodegradation efficiency.

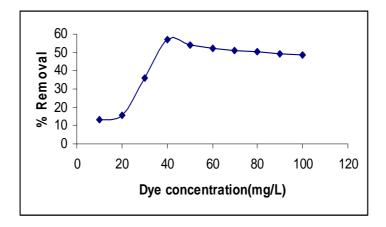


Fig.4: Effect of dye concentration percerntage removal of Indigo caramine catalyst dose 60mg/L, contact time 20minutes, pH 8

## Effect of pH

The photocatalytic degradation of dye was studied at different pH values as it is an important parameter for reaction taking place an particulate surface. The role of pH on the rate of photocatalytic degradation of Indigo Caramine dye was studied in the pH range 3-12 at dye concentration 40 mg/L and catalyst dose 60 mg/L. It was apparent that the rate of degradation of Indigo Caramine with an increase in the pH values up to 8 and beyond the rate of photocdegradation becomes constant. This effect may be attributed to more efficient generation of hydroxyl radical by TiO<sub>2</sub> with an increasing concentration of OH ion (fig.5).

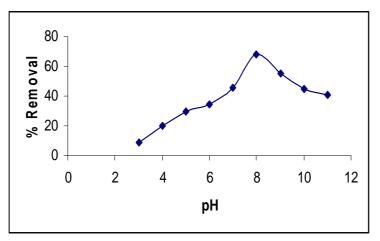


Fig.5: Effect of pH on percerntage removal of Indigo Caramine dye concentration 40mg/L ,catalyst dose 60mg/L and contact time 20minutes

### Vinod S. Shrivastava

#### Effect of contact time

The effect of contact time for the removal of Indigo Caramine dye by semiconductor  $TiO_2$  was shown in fig. 6. The dye was rapidly degraded in the first 20 minutes and then degradation rate decreased gradually and reached equilibrium in about 150 min. It observed that 20 minutes was the agitation time for removal of Indigo Caramine dye. At the beginning, degradation rate was fast as the dye ions were adsorbed by the exterior onto the pores of the adsorbent  $TiO_2$  and were adsorbed by the interior surface of particle. This phenomenon takes a relatively long contact time.

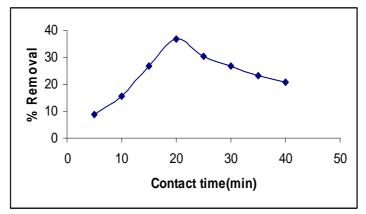


Fig.6: Effect of contact time on percerntage removal of Indigo Caramine dye concentration 40mg/L catalyst dose 60mg/L and pH 8.

#### Effect of Electron Acceptor

It is observed that molar  $H_2O_2$  concentration is key factor that can significantly influence the degradation of Indigo Caramine dye because  $H_2O_2$  concentration is directly related to the no. of OH radicals generated in the photoassisted reaction .The degradation rate of Indigo Caramine dye increases as the  $H_2O_2$  concentration increases until critical  $H_2O_2$  concentration is achieved. When using a higher  $H_2O_2$  molar concentration, the further generation of OH radical in aqueous solution is expressed as,

 $H_2O_2 + OH \longrightarrow HO_2 + H_2O$ 

Thus, experimental were conducted with different amount ranging from 1 mg/L to 10mg/L at fixed pH 8, dye concentration 40mg/L and catalyst dose 60mg/L. It is apparent that rate of degradation is markedly enhanced in the presence of  $H_2O_2$  additive.  $H_2O_2$  is not only known to inhibit the electron-hole recombination process but also generates hydroxyl radicals on abstraction of an electron from the conduction band.

$$H_2O_2 + e_{cb} \longrightarrow OH + OH$$

It was found that the critical molar  $H_2O_2$  concentration for the degradation of Indigo Caramine dye is 4mg/L, the degradation of efficiency remains constant. This is due to hydroxyl radical scavenging effect of  $H_2O_2$ .

$$\begin{array}{ccc} H_2O_2 + OH & \longrightarrow HO_2 + H_2O \\ HO_2 + OH & \longrightarrow H_2O+O_2 \end{array}$$

## Vinod S. Shrivastava

## SEM analysis

Scanning electron microscopy (SEM) is widely used to study the morphological features and surface characteristics of photocatalyst materials. The  $TiO_2$  was analyzed by SEM before and after treatment of Indigo Caramine dye. They show surface texture and porosity of  $TiO_2$  particles.

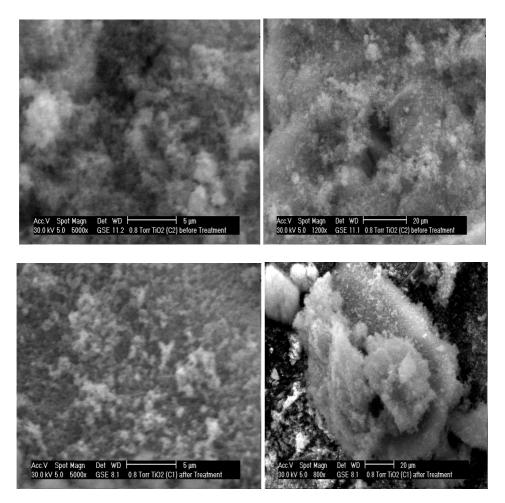


Fig.7: SEM images of TiO<sub>2</sub> and exposed TiO<sub>2</sub> by Indigo Caramine

## CONCLUSION

Photocatalytic degradation using nanosized  $TiO_2$  and UV light was successfully applied for Indigo Caramine dye. The degradation rate was increased significantly by increasing the amount of photocatalyst. While on increasing dye concentration decolorisation decreases. Alkaline pH condition have found to be significantly attend the dye degradation. The study shows utilized  $TiO_2$  was nanosized and porous in nature by SEM. The maximum degradation efficiency of dye achieved with the concentration of UV +H<sub>2</sub>O<sub>2</sub>+TiO<sub>2</sub>. The removal efficiency of Indigo caramine dye was found to be 80.6%.

## Acknowledgement

Author is gratefully acknowledged to the Director, SICART, Vallabh Vidyanagar for SEM analysis . Thanks are also due to Dr.Z.Benzo, IVIC, Caracas, Venezuala for useful discussions. Author is also thankful to the Principal G.T.P. College, Nandurbar for providing necessary laboratory facilities.

## REFERENCES

[1] C.L. Hsueh, Y.H. Huang, C.C. Wang, C.Y. Chen, *Chemosphere* 2005, 58,1409–1414.

[2] C. Baiocchi, M.C. Brussino, E. Pramauro, A.B. Prevot, L. Palmisano, G. Marci, *Int. J. Mass Spectrom.* **2002**, 214 247–256.

[3] S.Y. Kim, J.Y. An, B.W. Kim, Dyes Pigments, 2008, 76, 256–263.

[4] A.P.P. Cione, M.G. Neumann, F. Gessner, J. Colloid Interf. Sci. 1998, 198, 106–112.

[5] C. Namasivayam, D.J.S.E. Arasai, *Chemosphere* **1997**, 34, 401–417.

[6] A. Mittal, A. Malviya, D. Kaur, J. Mittal, L. Kurup, J. Hazard. Mater. 2007, 148, 229–240.

[7] B. Mounir, M.N. Pons, O. Zahraa, A. Yaacoubi, A. Benhammou, J. Hazard. Mater. 2007, 148, 513–520.

[8] G.M. Colonna, T. Caronna, B.Marcandalli, Dyes Pigments 1999, 41,211–220.

[9] I.A. Salem, M.S. El-Maazawi, *Chemosphere* **2000**, 41 ,1173–1180.

[10] N. Daneshvar, A.R. Khataee, A.R. Amani Ghadim, M.H. Rasoulifard, J. Hazard. Mater. 2007, 148, 566–572.

[11] N. Mohan, N. Balasubramanian, C. Ahmed Basha, J. Hazard. Mater. 2007, 147,644–651.

[12] C.T.Wang, Q.H. He, P. He, Environ. Sci. Technol. 2006, 29,65–67 (in Chinese).

[13] C.T.Wang, Q.Wang, Q.H. He, Z.F. Zhou, Dyestuffs Coloration 2006, 43, 49–55.

[14] L.S. Shi, H.M. Zhu, Y.Y. Dong, Y.Y. Li, J.Shandong Univ. (Eng. Sci.) 2006, 36,91-95.