

## Photocatalytic Route for Reduction of Color and Chemical Oxygen Demand from Dye-Containing Wastewater

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### Abstract

The color and chemical oxygen demand arising from Acid Blue I, Rhodamine B and textile industry wastewater containing vinyl sulphone-based reactive dye are treated using  $\text{TiO}_2$ /UV technique. Color is found to be removed substantially during first one hour of irradiation of Acid Blue I and Rhodamine B systems. The rate of color removal from textile dyeing industry wastewater in an order of magnitude lower than that of Acid Blue I and Rhodamine B. Simultaneously, the overall COD removal efficiencies under aerated condition are found to be 60% for Acid Blue I/  $\text{TiO}_2$  in 2 hours, 90 % for Rhodamine B/ $\text{TiO}_2$  in 4-5 hours and 45 % for wastewater/  $\text{TiO}_2$  in 3 $\frac{1}{2}$  hours. The supplied air is found to enhance rate of color and COD removals. The results suggested that some stable intermediates are formed during photooxidation of these dyes and the photocatalytic degradation of reactive dye containing wastewater is relatively slower.

### Introduction

Dye-house effluents contain significant quantities of dissolved organic dyes. They are often colored and have high COD. Due to complex nature of the dyes wastewater becomes bio-resistant. Discharge of colored effluent in to surface water bodies is highly unacceptable and unethical. Conventionally, color as well as COD from wastewater is removed by the application of biological and physiochemical methods, but the need for long contact times, use of high chemical doses and entailing regeneration and sludge management problems act as a seed for further advanced research for solving these problems. The new advancements include, ozonation, electrochemical oxidation and photocatalytic oxidation. The present paper deals with the photocatalytic route ( $\text{TiO}_2$ /UV) for color and chemical oxygen demand (COD) removal from aqueous solutions containing synthetic dyes, namely Acid Blue I and Rhodamine B. The study was also extended to wastewater from a textile-dyeing unit. Titanium dioxide is capable of generating powerful oxidants such as hydroxyl and superoxides radicals when suspended in aqueous medium and irradiated with UV-light. The oxidizing power of UV-illuminated  $\text{TiO}_2$  suspensions has been successfully exploited for the photocatalytic degradation of various organic compounds present in water/ air environment (Ollis 1985, Ibusuki, *et al.* 1993, Rao and Dubey 1997, Rao and Dubey 1998 and Dhodapakar, *et al.* 1999).



## Materials and Methods

Titanium dioxide ( $\text{TiO}_2$ ) used in the experimentation was obtained from British Drug House (BDH, Mumbai). The  $\text{TiO}_2$  is pure anatase with mean particle size of  $0.34 \mu\text{m}$ . The dyes used were:

1. Acid Blue I (commercial name – Patent Blue VS) supplied by Amar Dye Chem Ltd. Kalyan
2. Basic Violet 10 (commercial name – Rhodamine B) procured from E. Merck (Germany)

Both the dyes contain the same chromophoric group i.e. p-quinoid (Structure is shown in Fig. 1). However, Acid Blue I is acidic whereas Rhodamine B is basic in nature. Distilled water was used for preparing aqueous solutions of appropriate concentration of these dyes. In addition, textile industrial wastewater containing vinyl sulfone based Remazol type dye was also used.

A typical photooxidation experiment includes exposing the aqueous dye solution containing a certain amount of  $\text{TiO}_2$  catalyst powder in suspension to UV light. The catalyst containing dye solution was taken in to 500 ml capacity glass reactor and a 125 W high-pressure Hg-arc lamp housed in a borosilicate thimble was inserted into the reactor. Cold water was circulated through borosilicate sleeve in order to control excessive heating of reaction liquid from lamp source. The reaction mixture was magnetically stirred throughout the experiment. The experiments were conducted both in the absence and presence of externally supplied air. Air was bubbled using an aquarium pump. Samples of color and COD determination were collected periodically. Prior to these determinations, the catalyst powder was removed from the aqueous samples by filtering through membrane filter ( $0.22 \mu\text{m}$ ). Spectrophotometric measurements were carried out in the range of 200 – 700 nm using double beam Perkin Elmer  $\lambda$  900 Spectrophotometer. The reduction in the color band intensity was determined from the time-overlaid spectra. On the other hand, diminution in COD was also determined following standard procedure, APHA-AWWA-WPCF 1989.

## Results and Discussion

The UV-VIS absorption spectra for Acid Blue I, Rhodamine B and wastewater from textile dyeing unit are shown in Fig. 2. The decrease in the intensity of the color band of Acid Blue I ( $\lambda_{\text{max}} = 638 \text{ nm}$ ,  $\epsilon = 0.59 \times 10^5 \text{ M}^{-1}$ ), Rhodamine B ( $\lambda_{\text{max}} = 551 \text{ nm}$ ,  $\epsilon = 0.89 \times 10^5 \text{ M}^{-1}$ ) and textile dyeing unit wastewater ( $\lambda_{\text{max}} = 661 \text{ nm}$ ) is depicted in Fig. 3 a-c. The influence of aerating the suspensions on the color band reduction is also illustrated in these figures. The color of these dyes quickly decreased during the first 1-hour irradiation period under photocatalytic conditions. The initial rate of color removal (in absorption units, a.u.) in each case was deduced from linear regression and  $R^2 > 0.9$  is regarded as indication of best fit. The initial rate of color reduction for the case of Acid Blue I is  $0.107 \text{ a.u./min}$  (with aeration) and  $0.106 \text{ a.u./min}$  (without aeration)

## Photocatalytic Oxidation

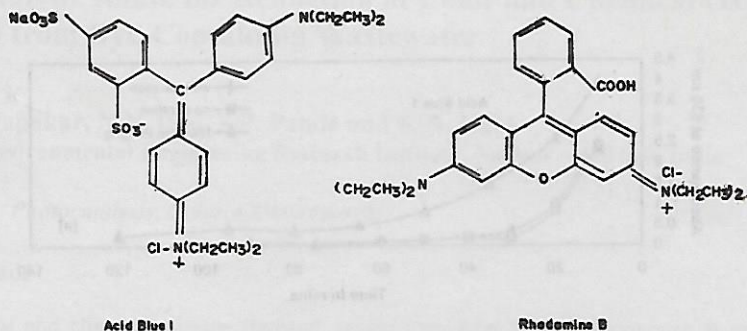


Fig. 1: Structure of Acid Blue I and Rhodamine B

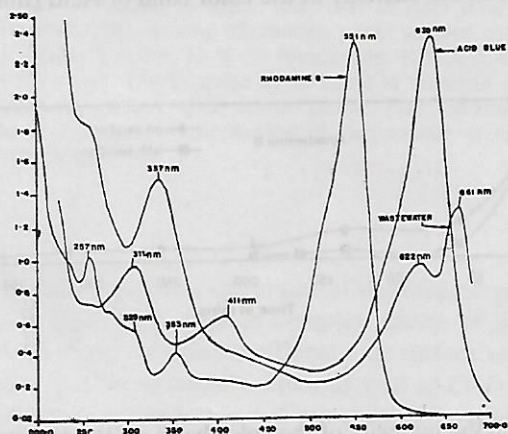
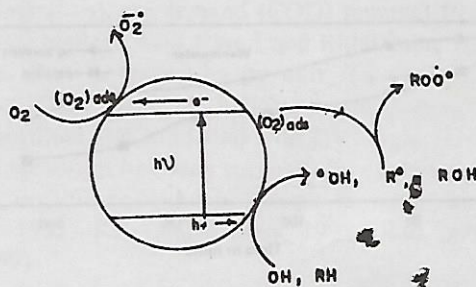


Fig. 2: UV – VIS absorption spectra of Acid Blue I, Rhodamine B and Textile dyeing unit wastewater



Scheme 1: Tentative pathway showing participation of oxygen, formation of hydroxyl and organo-radicals



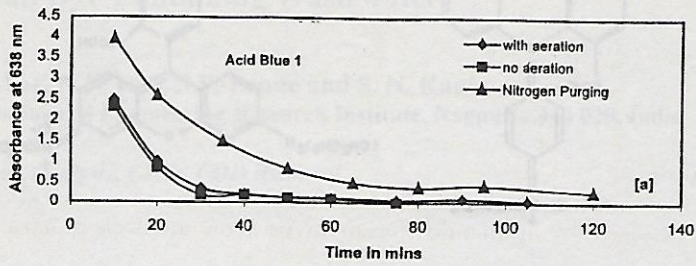


Fig. 3 (a): Decrease in the intensity of the color band of Acid Blue I at 638 nm

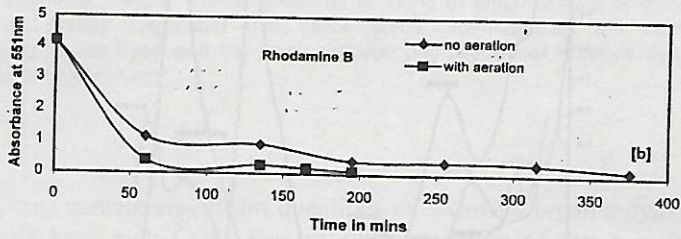


Fig. 3 (b): Decrease in the intensity of the color band of Rhodamine B at 551 nm

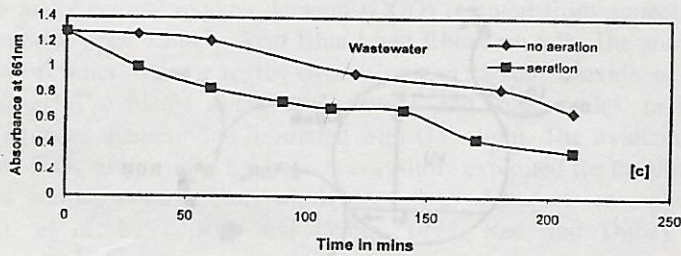


Fig. 3 (c): Decrease in the intensity of the color band of Textile dyeing unit wastewater at 661 nm

## Photocatalytic Oxidation

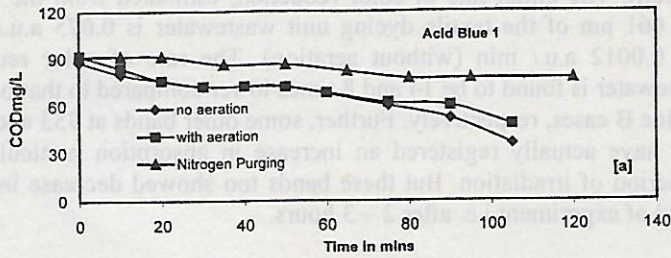


Fig. 4 (a): COD reduction from Acid Blue I

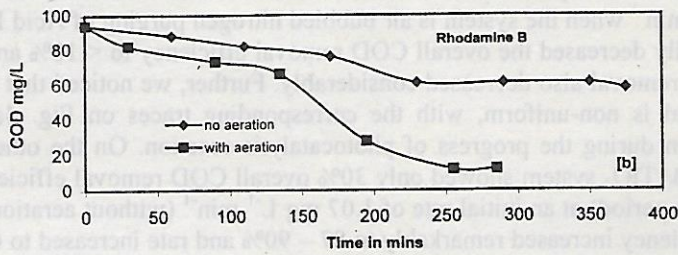


Fig. 4 (b): COD reduction from Rhodamine B

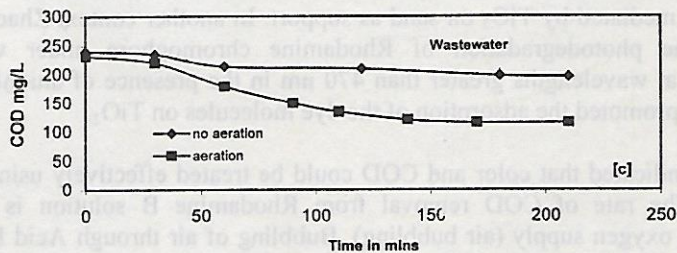


Fig. 4 (c): COD reduction from Textile dyeing unit wastewater



and for the case of Rhodamine B, it is 0.06 a.u./ min (with aeration) and 0.05 a.u./min (without aeration). The initial rate of color reduction, estimated from the decrease of color band at 661 nm of the textile dyeing unit wastewater is 0.075 a.u./ min (with aeration) and 0.0012 a.u./ min (without aeration). The rate of color removal from industrial wastewater is found to be 14 and 8 times lower compared to that of Acid Blue I and Rhodamine B cases, respectively. Further, some other bands at 353 and 329 nm of Rhodamine B have actually registered an increase in absorption particularly during intermediate period of irradiation. But these bands too showed decrease in absorption towards the end of experiment i.e. after 2 – 3 hours.

Fig. 4 (a – c) depict the removal of COD from Acid Blue – I and Rhodamine B containing solutions as well as textile dyeing industry wastewater under the photocatalytic conditions. These figures illustrate the effect of aeration on the COD removal kinetics also. The Acid Blue I /  $\text{TiO}_2$  system has shown 60% overall COD removal efficiency without external supply of oxygen during 2 hours irradiation period. The initial rate of COD removal in this case is  $0.60\text{-mg L}^{-1}\text{min}^{-1}$ . Although, the overall COD removal efficiency decreased to 50%, the initial rate of COD removal increased to  $0.68\text{ mg L}^{-1}\text{ min}^{-1}$  when the system is air bubbled nitrogen purging of Acid Blue I/  $\text{TiO}_2$  system actually decreased the overall COD removal efficiency to  $< 10\%$  and the initial rate of COD removal also decreased considerably. Further, we noticed that the trend of COD removal is non-uniform, with the corresponding traces on Fig. 4a exhibiting plateau region during the progress of photocatalytic reaction. On the other hand, the Rhodamine B/  $\text{TiO}_2$  system showed only 30% overall COD removal efficiency (during 4<sup>th</sup> irradiation period) at an initial rate of  $1.07\text{ mg L}^{-1}\text{ min}^{-1}$  (without aeration). With the aeration efficiency increased remarkably to 87 – 90% and rate increased to  $0.195\text{ mg L}^{-1}\text{ min}^{-1}$ . Textile dye-waste/  $\text{TiO}_2$  system showed an overall COD efficiency of 45 – 50 % during 3 ½ hour irradiation period, with an initial rate of  $0.43\text{ mg L}^{-1}\text{ min}^{-1}$  (without aeration) and  $0.96\text{ mg L}^{-1}\text{ min}^{-1}$  (with aeration). Once again the trend of COD removal is non-uniform and the corresponding plot showed plateau towards the end of the reaction period. In relation to our studies, Matthews, 1991 reported on the transformation of Rhodamine B its partial mineralization under artificial UV light and sunlight UV mediated by  $\text{TiO}_2$  on sand as support. In another context Zhao *et al.* 1998 examined the photodegradation of Rhodamine chromophore under visible light illumination at wavelengths greater than 470 nm in the presence of anionic surfactant that actually promoted the adsorption of the dye molecules on  $\text{TiO}_2$ .

The results indicated that color and COD could be treated effectively using  $\text{TiO}_2$ / UV technique. The rate of COD removal from Rhodamine B solution is remarkably enhanced by oxygen supply (air bubbling). Bubbling of air through Acid Blue I/  $\text{TiO}_2$  system resulted in only moderate increase in COD removal rate. Although same chromophoric group, p- quinoid is present in both the dyes, the difference in color removal rates between Acid Blue – I and Rhodamine B cases can be attributed to the other structural dissimilarities between these dyes. The Acid Blue I dye molecule contains  $\text{SO}_3^- \text{Na}^+$  group and Rhodamine B has – COOH group. The position of these groups in the dye molecules could substantially influence adsorption of these dyes on



TiO<sub>2</sub>. Particularly in view of the initial pH which is 4.9 for Rhodamine B system and 6.7 for Acid Blue I system, the adsorption of Acid Blue dye is more preferred. The -COOH group is a poorer functionality for adsorption. Indeed, Rhodamine B adsorbed very less (2-5%) on TiO<sub>2</sub> catalyst. Further, the observed rise in absorption of 411 and 311 nm bands in Acid Blue I and 441, 353 and 329 nm bands in Rhodamine B during the photocatalytic experiments may be due to the formation of some intermediates with their absorption overlapping with that of the native dye molecules.

The present study revealed that the oxygen supply favorably affects the COD removal efficiency for Acid Blue I and Rhodamine B with TiO<sub>2</sub>. This finding is also supported by previous studies made by Rao and Dubey 1997, Schwitzgebel *et al.* 1995 and Kesselman *et al.* 1994. Molecular oxygen has been shown to scavenge photoelectrons transforming it self into superoxide radicals (Schwitzgebel *et al.*, 1995). The superoxide radicals participate in the oxidation of organic molecules in addition to the photogenerated hydroxyl radicals. This process appears to play a major role in enhancing the COD removal from Rhodamine B/ TiO<sub>2</sub> system. Since the state of affair until photogeneration of hydroxyl radicals and photoelectron scavenging by molecular oxygen is the same in both the cases, some stable intermediates may have formed during the reaction of COD removal from these systems due to which the corresponding plots displayed plateaus. The tentative pathway showing the participation of oxygen is shown in Scheme --I. Oxygen scavenges photoelectrons that accumulate at conduction band and form superoxide radicals. The photogenerated holes (h<sup>+</sup>) and / or hydroxyl radicals at valence band react with organic molecules (RH) and generate organo radicals (R<sup>\*</sup>). The absorbed oxygen and freshly formed organo radicals on the surface readily react to give organoperoxy radicals (ROO<sup>\*</sup>) opening up oxygen mediated route of photooxidation. Alternatively, the superoxide radicals could also cause substantial oxidation of dye molecules.

## Conclusion

The color and COD in wastewater imparted by the dissolved organic dyes can be treated using TiO<sub>2</sub>/ UV technique. Both Acid Blue I and Rhodamine B showed dissimilar color reduction kinetics although the same chromophoric group, p-quinoid is present in both the dyes. Although COD can be removed from both Acid Blue I/ TiO<sub>2</sub> and Rhodamine B/ TiO<sub>2</sub> systems, the rate of removal of COD from the latter is remarkably enhanced by external oxygen supply. Finally, The TiO<sub>2</sub>/ UV technique may also be applied to treat color and COD from the textile dyeing unit waste water.

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