Original Research Paper

Decolorization and Mineralization of Hazardous Brilliant Cresyl Blue Dye Using Visible Light and TiO$_2$ as Photocatalyst

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ABSTRACT

Photocatalytic degradation of Brilliant Cresyl Blue has been examined in TiO$_2$ dispersions under visible light. The degradation kinetics was studied under different conditions such as substrate and photocatalyst concentration, reaction pH, addition of oxidants and temperature. The degradation rates proved to be strongly influenced by these parameters. As a result, it was found that the efficiency of the process strongly depends on the working conditions. The highest degradation rate of BCB was obtained at optimum parameters such as dosage of TiO$_2$ (150 mg/100 mL), pH (11.00) and dye concentration 5.0×10^{-5} mol dm^{-3}. The degradation of dye was also investigated under sunlight. The photocatalyst TiO$_2$ was found to be more efficient for the degradation of BCB dye. Complete COD reduction was observed in 8 h of irradiation time. CO$_2$ and NO$_3^-$ ions were identified as final mineralization products.

INTRODUCTION

Paper, rubber, cosmetics, leather, ink, dyeing, plastic and textile industries use colour for dyeing their products and thus use a huge amount of water which results in the production of dye-containing wastewater with hazardous effects on the environment. Dye containing wastewater produces a huge amount of polluted effluents that are normally discharged in the surface water bodies and groundwater aquifers. This wastewater causes damage to the ecological system of receiving surface water capacity and a certain lot of disturbance to the groundwater resources (Iqbal et al. 2007). TiO$_2$ photocatalytic degradation technique has large capability for wastewater treatment. Among the new methods of coloured wastewater treatment, TiO$_2$ photocatalysis based on the generation of very reactive species such as hydroxyl radicals has been proposed to oxidize quickly a broad range of organic pollutants (Sano et al. 2008). This technique can be used for the decomposition of organic and inorganic compounds and removal of dyes (Hoffman et al. 1995). The TiO$_2$ semiconductor has been reported to be the most promising photocatalyst because of its low cost, non toxicity and relatively high efficiency and the possibility of using sunlight as a source of irradiation (Alex et al. 2005). Titanium dioxide shows its unique photocatalytic activity as an excellent choice of photocatalysis application. How to improve the photocatalytic activity of TiO$_2$ in the visible region is the main focus of the recent TiO$_2$ photocatalysis research. Many efforts have been made to achieve the utilization of visible light for TiO$_2$ material such transitional metal ion doping, non metal element doping and dye sensitization. Dye sensitization photocatalysis begins with the light absorption of dye and a subsequent electron transfer from the excited dye to the conduction band of TiO$_2$ and thereby the formation of dye radical cation and reactive oxygen species would lead to the degradation of the dye (Tariq et al. 2009). The main objective of this work is to study the mineralization of BCB dye by using TiO$_2$ in the presence of artificial radiations. The effect of concentrations of H$_2$O$_2$, K$_2$S$_2$O$_8$, NaCl, Na$_2$CO$_3$ in the degradation of BCB dye was studied. Several other parameters such as initial dye concentration, amount of TiO$_2$, solution pH and temperature were studied. The destruction of aromatic ring and mineralization of dye was confirmed by the estimation of COD, CO$_2$, NO$_3^-$ ion and UV-visible spectral analysis.

MATERIALS AND METHODS

Reagents: Titanium dioxide (Loba Chemie) and Brilliant Cresyl Blue. Double distilled water was used throughout the study to prepare the solution. The catalyst and dyes were used without further purification.

Photo reactor and light source: A 500-W halogen lamp was used as the light source. The photocatalytic reaction was carried out in a batch reactor with dimension of 7.5 × 6.0 cm (height × diameter) provided with an external water

flow jacket connected to a thermostatic bath and able to maintain the temperature in the range of 25-30°C.

Procedure: For the irradiation experiment 100mL aqueous solution of the dye of desired concentration was taken in the photoreactor and the solution was stirred and bubbled with air for at least 10 min in the dark to establish the adsorption equilibrium. Aliquots were taken at 10 min time intervals and centrifuged to separate the catalyst from the solution. The solution was then analysed spectrometrically. A visible spectrophotometer was used for measuring the absorbance of the reaction mixture. The intensity of light was measured by digital lux meter (Lutron LX-101). The pH of the solution was measured using a digital pH meter. The desired pH of the solution was adjusted by the addition of previously standardized sulphuric acid and sodium hydroxide solution. To quantify the extent of mineralization of mixture, COD was measured at regular time intervals using the closed reflux titrimetric method.

RESULTS AND DISCUSSION

Effect of initial dye concentration variation: The effect of different initial dye concentration was investigated in suspensions containing 150mg/100mL TiO_2 at constant pH 11.0. An increase in the rate constant from $1.03 \times 10^{-4} s^{-1}$ to $2.57 \times 10^{-4} s^{-1}$ with increase in dye concentration from 1.0×10^{-5} mol dm^{-3} to 5.0×10^{-5} mol dm^{-3}. Thereafter, rate constant values decreased to $1.57 \times 10^{-4} s^{-1}$ with increased dye concentration 7.0×10^{-5} mol dm^{-3}. Rate constant values have been found to be maximal at dye concentration of 5.0×10^{-5} mol dm^{-3} (Fig. 1). It is reported that, as the initial concentration of the dye increases, the degradation efficiency reduces. The possible reason suggested for this decrease is that, as the initial concentration of the dye got increased more dye molecules got adsorbed onto the surface of TiO_2. But the adsorbed dye molecules are not degraded immediately because the intensity of the light and the catalyst amount remain constant and also the light penetration is less (Neppolian et al. 2002). On increasing the dye concentration, the solution gets more intense coloured and the path length of photons entering the solution got decreased, thereby fewer photons reached the catalyst surface. Hence, the production of hydroxyl and superoxide radicals got limited, therefore the photodegradation efficiency reduced (Subramani et al. 2007).

Effect of amount of catalyst variation: The effect of TiO_2 loading on the photo degradation rate has been examined by varying its amount from 50mg to 350mg/100mL in the reaction solution. Rate constant values increased from $1.03 \times 10^{-4} s^{-1}$ to $2.37 \times 10^{-4} s^{-1}$ with the increase in catalyst loading from 50mg to 150mg/100mL. Further, rate constant values decreased to $1.11 \times 10^{-4} s^{-1}$ with the increased catalyst

loading (350mg/100mL). Rate constant value has been found to be maximal at 150mg/100mL of catalyst loading (Fig. 2). Photocatalytic degradation efficiency increased with an increase in catalysts mass. This behaviour might be due to an increase in the amount of active site on surface of TiO_2 particles. After the optimum amount of TiO_2, the activity of photocatalytic decolorization decreased with increase of catalyst concentration. Because higher loading of catalyst also causes increase in turbidity of the solution, which reduces the light penetration in photoactive volume (Murugandham et al. 2004). Hence photoactive volume shrinks and aggregations of TiO_2 particles causing decrease in the number of surface active sites.

Effect of solution pH: The photocatalyic degradation efficiency got greatly influenced by pH changes. The effect of pH on the photocatalytic reaction could be mainly explained by the surface charge of TiO_2. Point of zero change, (pzc) of TiO_2 is 6.8. Upon changing the pH, the surface hydroxyl group could undergo protonation and deprotonation according to the following reactions.

$$TiOH + H^+ \rightleftharpoons TiOH_2^+ \qquad \qquad ...(1)$$

$$TiOH + OH^- \rightleftharpoons TiO^- + H_2O \qquad ...(2)$$
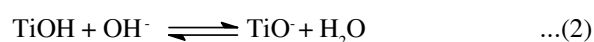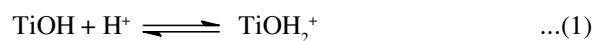
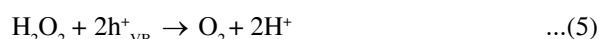The TiO_2 surface is positively charged in acidic media (pH < 6.8), whereas it is negatively charged under alkaline conditions (pH > 6.8). Since brilliant cresyl blue dye is cationic dye, in the acidic pH there was a poor adsorption. The decrease in pH value causes decrease in the reaction rate. At higher pH more dye molecules would adsorb on to the catalyst surface which resulted into high decolorization efficiency due to electrostatic attraction of the negatively charged TiO_2 with the cationic dye. The photocatalytic degradation reactions were conducted at different pH value varying from 5.0 to 13.0 and dye concentration 5.0×10^{-5} mol dm^{-3} at catalyst loading of 150mg/100mL (Fig. 3). The photocatalytic degradation of brilliant cresyl blue has been found to be maximum at pH 11.0. In the present observation, it could be presumed that the main reaction was presented by the hydroxyl radical attack. After optimal pH value, when pH further increased, the rate of reaction found to be decreased because at high pH values the hydroxyl radicals are so rapidly scavenged that they do not have the opportunity to react with dye (Galindo et al. 2000).

Effect of H_2O_2 and $K_2S_2O_8$: The degradation rate has been studied at different H_2O_2 and $K_2S_2O_8$ concentrations. The degradation rate increased with increasing H_2O_2 concentrations from 2.0×10^{-6} mol dm^{-3} to 8.0×10^{-6} mol dm^{-3}. The reaction rate increased for H_2O_2 from $3.49 \times 10^{-4} s^{-1}$ to $4.56 \times 10^{-4} s^{-1}$ (Fig. 4). This was because, H_2O_2 inhabited the electron-hole recombination and hence, accelerates the reaction
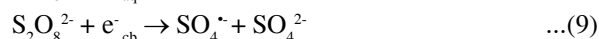
by producing an extremely strong and non-selective oxidant hydroxyl radical from scavenging the electrons and absorption of visible light by the following reactions:
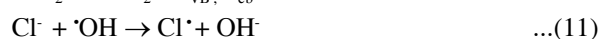
$$H_2O_2 + TiO_2\,(e^-CB) \rightarrow \,^{\bullet}OH + OH^- \qquad ...(3)$$

$$H_2O_2 + h\nu \rightarrow 2\,^{\bullet}OH \qquad ...(4)$$
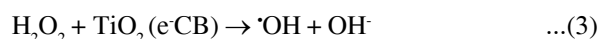
Further increase in concentration of H_2O_2 beyond optimal concentration, resulted into the decrease in rate constant, because at an excess H_2O_2 concentration, it might start acting as hydroxyl radical and hole scavenger.

$$H_2O_2 + 2h^+{}_{VB} \rightarrow O_2 + 2H^+ \qquad ...(5)$$

$$H_2O_2 + \,^{\bullet}OH \rightarrow HO_2^{\bullet} + H_2O \qquad ...(6)$$

$$HO_2^{\bullet} + \,^{\bullet}OH \rightarrow H_2O + O_2 \qquad ...(7)$$

With increase in $K_2S_2O_8$ concentration from 2.0×10^{-6} mol dm^{-3} to 8.0×10^{-6} mol dm^{-3}, rate constant increased from $3.33 \times 10^{-4}\,s^{-1}$ to $4.87 \times 10^{-4}\,s^{-1}$. At optimal amount of $K_2S_2O_8$, the rate of degradation has been found to be $4.87 \times 10^{-4}\,s^{-1}$. $K_2S_2O_8$ has always been found to be a beneficial oxidizing agent in photocatalytic detoxification due to generation of $SO_4^{\bullet-}$ radicals (Tang et al. 1997).

$$S_2O_8^{2-} + e^-{}_{aq} \rightarrow SO_4^{\bullet-} + SO_4^{2-} \qquad ...(8)$$

$$S_2O_8^{2-} + e^-{}_{cb} \rightarrow SO_4^{\bullet-} + SO_4^{2-} \qquad ...(9)$$

Effect of NaCl and Na_2CO_3: Sodium chloride usually comes out in the effluent along with wastewater. Therefore, rate of degradation in presence of Cl^- ions has been studied by change in concentration of Cl^- ions from 2.0×10^{-6} mol dm^{-3} to 14.0×10^{-6} mol dm^{-3} that resulted into reduction of rate constant from $2.95 \times 10^{-4}\,s^{-1}$ to $1.42 \times 10^{-4}\,s^{-1}$. The decrease in the degradation of dye in the presence of chloride ion might be due to the hole scavenging properties of chloride ion.

$$TiO_2 \rightarrow TiO_2\,(h^+{}_{VB},\,e^-{}_{cb}) \qquad ...(10)$$

$$Cl^- + \,^{\bullet}OH \rightarrow Cl^{\bullet} + OH^- \qquad ...(11)$$

$$Cl^- + h^+{}_{VB} \rightarrow Cl^{\bullet} \qquad ...(12)$$

$$Cl^{\bullet} + Cl^- \rightarrow Cl_2^{-\bullet} \qquad ...(13)$$

Similarly, sodium carbonate is mainly used in the dyeing bath in order to adjust the pH of the bath as it plays an important role in fixing of dye on the fabrics and in the fastness of colour. Therefore, the wastewater from the dyeing operation will contain considerable amount of carbonate ion (Pare et al. 2008). With an increase in the amount of carbonate ion from 2.0×10^{-6} mol dm^{-3} to 14.0×10^{-6} mol dm^{-3} resulted into reduction of rate constant from $2.99 \times 10^{-4}\,s^{-1}$ to $1.34 \times 10^{-4}\,s^{-1}$ (Fig. 5). The inhibition in the degradation of dye is due to the hydroxyl scavenging property of carbonate ions, which can be accounted from the following equation.

$$^{\bullet}OH + CO_3^{2-} \rightarrow OH^- + CO_3^{\bullet-} \qquad ...(14)$$

$$^{\bullet}OH + HCO_3^- \rightarrow H_2O + CO_3^{\bullet-} \qquad ...(15)$$
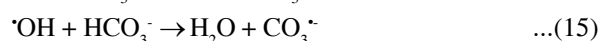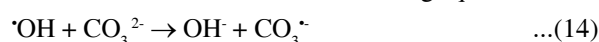
Effect of temperature: The photocatalytic degradation was studied at various temperatures in the range 30°C to 55°C (Fig. 6). The values show the semiconductor photocatalysis is usually not very temperature dependent (Walter et al. 1995). Increase in temperature led to decrease in the rate of degradation. This gradual decrease in the reaction rate values could be attributed to the following reasons: the adsorption rate decreased with increasing temperature because the adsorption is a heat releasing process, increase in reaction temperature tend to increase electron-hole recombination and with increase in temperature the solubility of oxygen in water decreased (Soares et al. 2008).

COD and CO_2 measurements during mineralization process: The chemical oxygen demand test is widely used as an effective technique to measure the organic strength of waste water. The test allows the measurement of waste in terms of the total quantity of oxygen required for the oxidation of organic matter to CO_2 and water. In the present work, results of chemical oxygen demand were taken as one of the parameters to judge the feasibility of the photochemical process for the degradation of BCB dye solution. The COD of the dye solution was estimated before and after treatment (Chen et al. 1993). The reduction in the COD values and increase in CO_2 values of the treated dye solution indicated the mineralization of the dye molecules along with the colour removal. The reduction in the estimated COD value from 312mg/L to 12mg/L and increased CO_2 value from 11mg/L to 143mg/L in 8 h of illumination indicated the photodegradation of treated dye solution (Table 1). A decrease in pH of solution has also been observed with increase in the extent of mineralization.

UV- Vis spectral analysis during mineralization: The UV-Vis absorption spectra of BCB was studied at different times of irradiation. BCB is phenoxazine dye in which the chromophore part of molecular structure contains phenoxazine group. The changes in the absorption spectra of BCB solution during the photocatalytic degradation at different irradiation times are presented in Fig. 7, both in the UV and visible region. Its λmax is 495 nm. The decrease of absorption peaks actually indicated a rapid decoloration and deg-

Table 1: COD and CO_2 measurements during photodegradation process: [BCB] = 5.0×10^{-5} mol dm^{-3}, TiO_2 =150 mg/ 100 mL, pH = 11.0 Light intensity = 14×10^3 lux, Temperature = 30 ± 0.3 ºC.

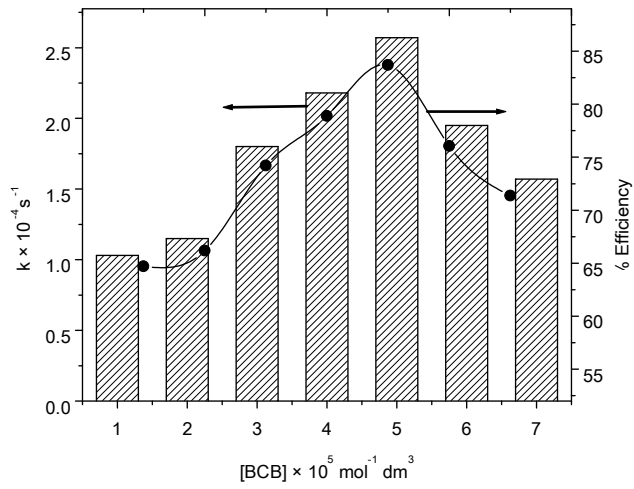| Irradiation time (h)	COD (mg/L)	CO_2 (mg/L)	Efficiency (%)	NO_3^- (mg/L)	pH
0	312	112	0	0	11.0
2	188	147	39	4	9.0
4	32	154	89	9	5.2
6	16	187	94	16	3.8
8	12	209	96	24	2.1

David Swami et al.

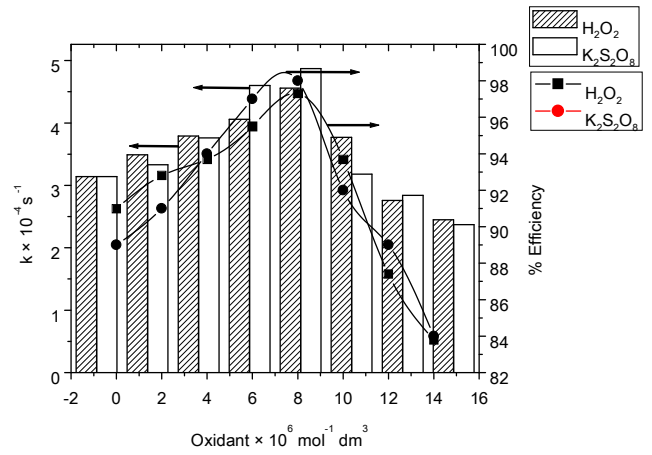Fig.1: Effect of initial dye concentration variation.

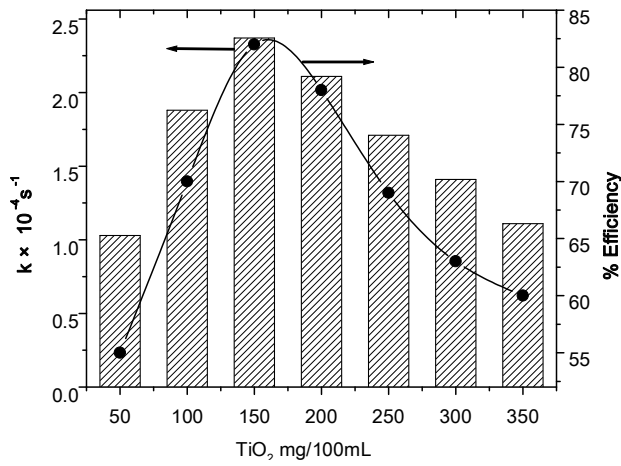Fig. 4: Effect of oxidant: H_2O_2 and $K_2S_2O_8$.

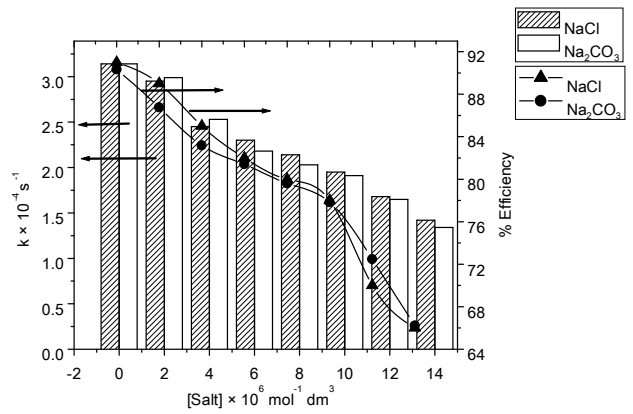Fig. 2: Effect of amount of catalyst variation.

Fig. 5: Effect of Salt: NaCl and Na_2CO_3
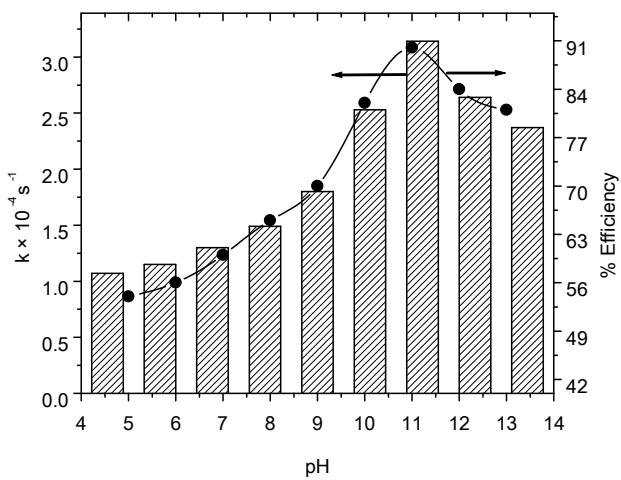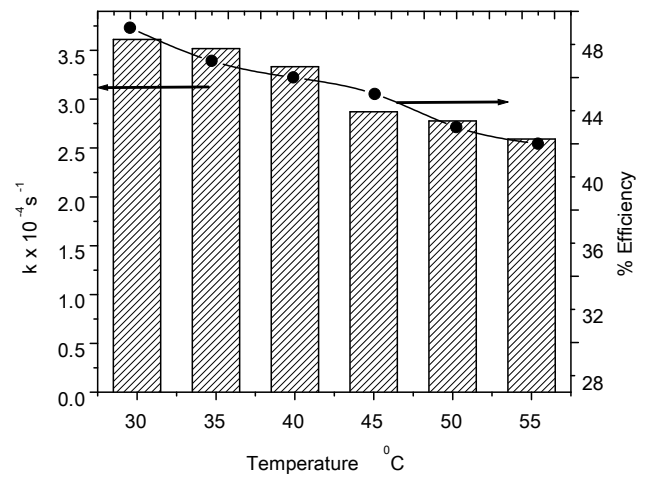

Fig. 3: Effect of solution pH.

Fig. 6: Effect of temperature.
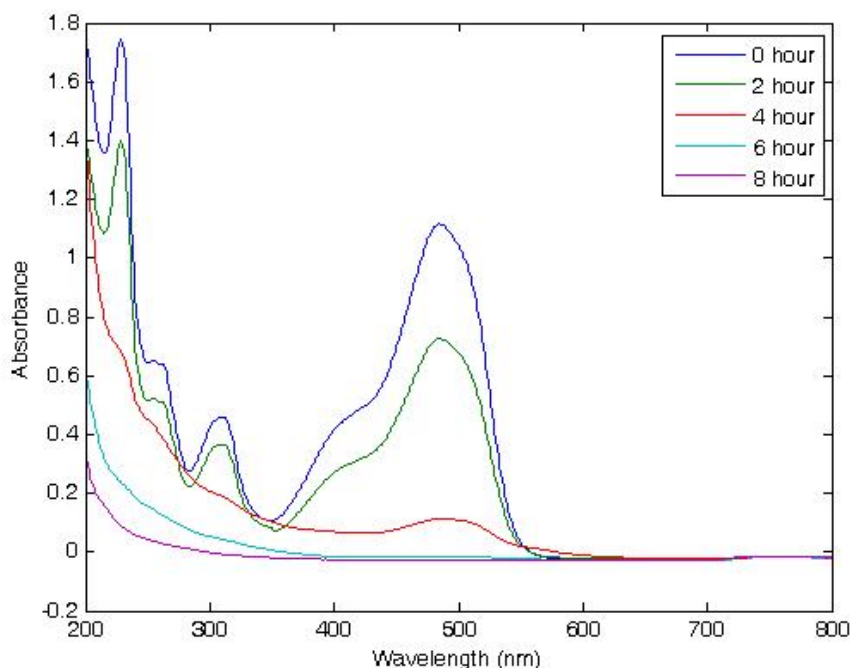
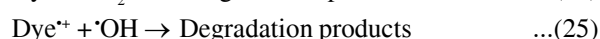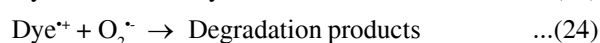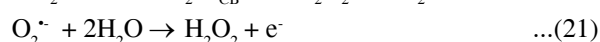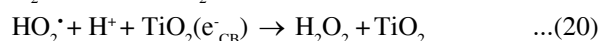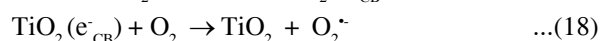Fig. 7: UV-Vis spectrum of Brilliant Cresyl Blue: [BCB] = 5.0×10^{-5} mol dm^{-3}, TiO$_2$ =150 mg/100 mL, pH = 11.0,
Light intensity = 14×10^3 lux, Temperature = 30 ± 0.3°C.

radation of BCB dye (Nishimote et al. 1985). The nearly perfect disappearance of peaks in UV region reveals that BCB dye is eliminated in presence of TiO$_2$ after 8 h of irradiation (Evgenidou et al. 2005).

Mechanism of BCB degradation: Organic pollutants like dyestuffs have the ability to absorb visible light. When dye molecules are adsorbed onto the surfaces of TiO$_2$, their translational mobility is considerably reduced and it extends the range of excitation energies of the semiconductors TiO$_2$ into visible region. The visible light excites the dye molecules adsorbed on TiO$_2$ and subsequently inject electrons to conduction band (CB) of TiO$_2$. While the CB acts as a mediator for transferring electrons from the dye molecule to substrate electron acceptors on TiO$_2$ surface, the valance band (VB) remains unaffected in a typical photosensitization (Akar et al. 2009). The conduction band electron of TiO$_2$ is scavenged by O$_2$ molecule to form O$_2^{\cdot-}$ or more active radicals such as $^{\cdot}$OH. These active oxygen species attack the cationic dye radical or dye molecule, leading to degradation followed by mineralization of organic pollutant. Photosensitized degradation of organic dyes has been carried out on TiO$_2$, where the organic dye serves as both a sensitizer and a substrate to be degraded (Sun et al. 2002). Such type of electron transfer mechanism has been called as photosensitizing oxidation. The mechanism of dye degradation under visible light irradiation can be described as eq. 16-25 (Chen et al. 2010).

$$Dye + h\nu \text{ (visible)} \rightarrow Dye^* \qquad ...(16)$$

$$Dye^* + TiO_2 \rightarrow Dye^{\cdot+} + TiO_2(e^-_{CB}) \qquad ...(17)$$

$$TiO_2(e^-_{CB}) + O_2 \rightarrow TiO_2 + O_2^{\cdot-} \qquad ...(18)$$

$$O_2^{\cdot-} + H^+ \rightarrow HO_2^{\cdot} \qquad ...(19)$$

$$HO_2^{\cdot} + H^+ + TiO_2(e^-_{CB}) \rightarrow H_2O_2 + TiO_2 \qquad ...(20)$$

$$O_2^{\cdot-} + 2H_2O \rightarrow H_2O_2 + e^- \qquad ...(21)$$

$$H_2O_2 + TiO_2(e^-_{CB}) \rightarrow {}^{\cdot}OH + OH^- + TiO_2 \qquad ...(22)$$

$$Dye^{\cdot+} + OH^- \rightarrow Dye + {}^{\cdot}OH \qquad ...(23)$$

$$Dye^{\cdot+} + O_2^{\cdot-} \rightarrow \text{Degradation products} \qquad ...(24)$$

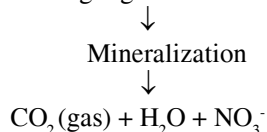$$Dye^{\cdot+} + {}^{\cdot}OH \rightarrow \text{Degradation products} \qquad ...(25)$$
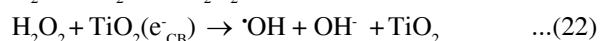
This process of dye sensitization has an advantage in degradation of organic pollutants with visible light. Photosensitizing mechanism will help to improve the overall efficiency and make the photocatalytic degradation of textile dyes using solar light more feasible (Zhao et al. 1995). The mechanism of TiO$_2$ photocatalysis is of very complex nature. Cationic dye radicals interact with O$_2^{\cdot-}$, HO$_2^{\cdot}$ or $^{\cdot}$OH species to generate intermediates ultimately leading to the generation of degradation products. Hydroxyl radical ($^{\cdot}$OH) being very strong oxidizing agent (standard oxidation potential 2.8 eV) mineralizes dye to end products.

$$BCB (BCB^{+\cdot}) + {}^{\cdot}OH \rightarrow \text{Decolorization of dye}$$
$$\downarrow$$
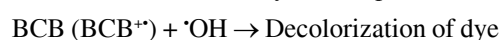
Degradation of dye involving organic intermediates
↓
Mineralization
↓
CO_2 (gas) + H_2O + NO_3^-

As the degradation process proceeds with illumination of many unstable intermediate species, which finally mineralized into CO_2, H_2O and NO_3^-. A decrease in COD and increase in CO_2 also confirmed the complete mineralization of dye. Significant amount of NO_3^- was also released during the mineralization of dye. Complete disappearance of peaks in UV-Vis region indicates the absence of any organic moiety.

CONCLUSION

This study confirms that TiO_2 photocatalytic degradation technique is an efficient process for decolorization and mineralization of BCB dye. The photodegradation process is highly pH dependent. The result showed that BCB dye underwent massive degradation in alkaline pH. The addition of oxidants such as H_2O_2 and $S_2O_8^{2-}$ increased the photocatalytic activity significantly. The presence of NaCl and Na_2CO_3 led to inhibition of the photodegradation process. UV visible spectra and estimated COD, evolution of CO_2 and formation of NO_3^- ions confirmed the mineralization of dyes during photocatalytic degradation.

ACKNOWLEDGEMENT

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