DECOLORIZATION AND MINERALIZATION OF HAZARDOUS BRILLIANT CRESYL BLUE DYE UTILIZING VISIBLE LIGHT AND TiO$_2$ AS PHOTOCATALYST

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ABSTRACT

Photocatalytic degradation of Brilliant cresyl blue (BCB) has been examined in TiO$_2$ dispersions under visible light. The degradations 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 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.

Key words: Brilliant cresyl blue, TiO$_2$, Visible light, Degradation, Parameters, COD, Mineralization.

INTRODUCTION

Paper, rubber, cosmetics, leather, ink, dyeing, plastic and textile industries use color for dyeing their products and thus use as huge amount of water which results in the production of dye-containing wastewater with hazardous effects on the environment. Dye containing wastewater produces huge amount of polluted effluents that are normally discharged on the surface water bodies and ground water aquifers. This wastewater causes damages to the ecological system of receiving surface water capacity and certain a lot of disturbance to the ground water resources[1]. TiO$_2$ photocatalytic degradation technique has large capability for wastewater treatment. Among the new methods of colorful wastewater

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tretment TiO_2 photocatalysis based on the generation of very reactive species such as hydroxyl radicals have been proposed to oxidize quickly and none selectiviely a broad range of organic polutants[2]. This technique can be utilized for the decomposition of organic and inorganic compounds and removal of dyes[3]. 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[4]. Titanium dioxide shows its unique photocatalytic activity at 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 the degradation of the dye[5]. The main objective of this work was to study the mineralization of BCB dye by using TiO_2 in the presence of artificial radiations. The effects of concentrations of H_2O_2, $K_2S_2O_8$, $NaCl$, Na_2CO_3 in the degradation of BCB dye were studied. Several other parameters such as initial dye concentration, amount of TiO_2, solution pH, 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.

EXPERIMENTAL

Reagents

Titanium dioxide (Loba Chemie) and Brilliant cresyl blue (Loba Chemie) were used. Titanium dioxide is mainly anatase (80%). All other chemicals used were of analytical grade. 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 x 6.0 cm (height x 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 irradiation experiment 100 mL 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 analyzed spectrometrically. A visible spectrophotometer (Systronic Model No. 116) 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 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 150 mg/100 mL TiO_2 at constant pH 11.0. An increase in the rate constant from 1.03×10^{-4} s^{-1} to 2.57×10^{-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 1.57×10^{-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}. It is reported that as the initial concentration of the dye increases, the degradation efficiency reduces[6,7].
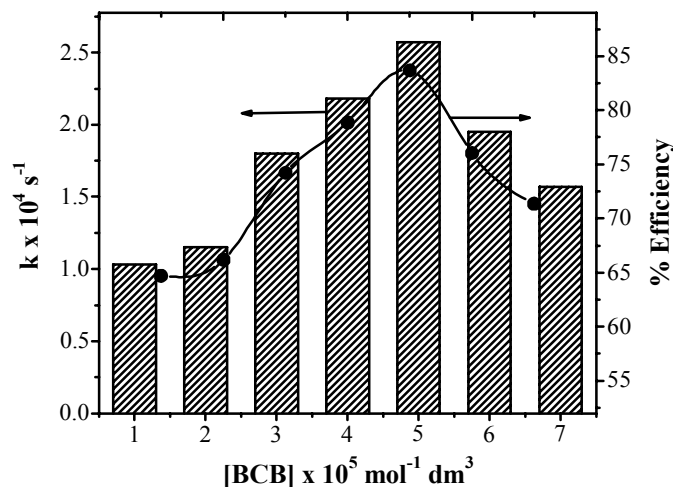

Fig. 1: Effect of initial dye concentration variation

The possible reason suggested for this decrease that as the initial concentration of the dye was increased, more dye molecules were 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. On increasing the dye concentration, the solution gets more intense colored 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[8].

Effect of amount of catalyst variation

The effect of TiO_2 loading on the photodegradation rate has been examined by varying its amount from 50 mg to 350 mg/100 mL 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 50 mg to 150 mg/100 mL. Further, rate constant values decreased to $1.11 \times 10^{-4}\,s^{-1}$ with the increased catalyst loading (350 mg/100 mL). Rate constant value has been found to be maximal at 150 mg/100 mL of catalyst loading. Phtcatalytic degradation efficiency increased with an increase in catalysts mass. This behavior 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 reduced the light penetration in photoactive volume[9]. Hence photoactive volume shrinks and aggregations of TiO_2 particle causing decrease in the number of surface active sites.
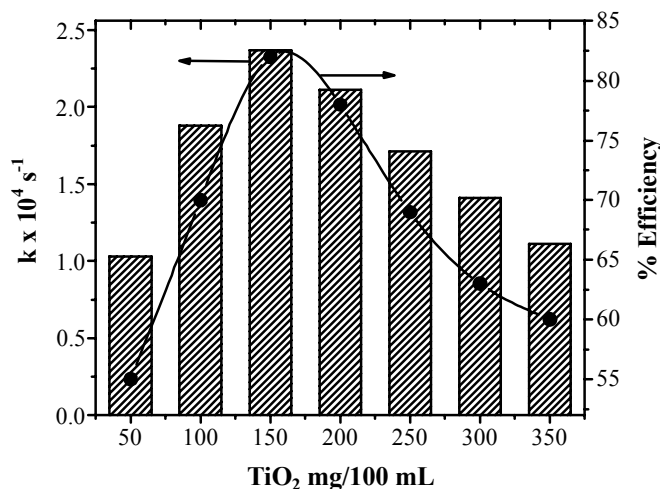

Fig. 2: Effect of amount of catalyst variation

Effect of solution pH

The photocatalyic degradation efficiency was 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 deprotation according to the following reactions[10].

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

$$TiOH + OH^- \rightleftharpoons TiO^- + H_2O \qquad\qquad …(2)$$
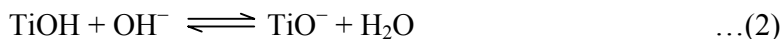
The TiO_2 surface is positively charged in acidic media (pH < 6.8), where as it is negatively charged under alkaline conditions (pH > 6.8). Since brilliant cresyl blue dye is cationic dye, in the acidic pH there was a poor adsorption. The decrease in pH value causes decrease in the reaction rate. At 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 varied from 5.0 to 13.0 and dye concentration 5.0×10^{-5} mol dm^{-3} at catalyst loading of 150 mg/100 mL (Fig. 3). The photocatalytic degradation of brilliant cresyl blue has been found to be maximal 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[11].
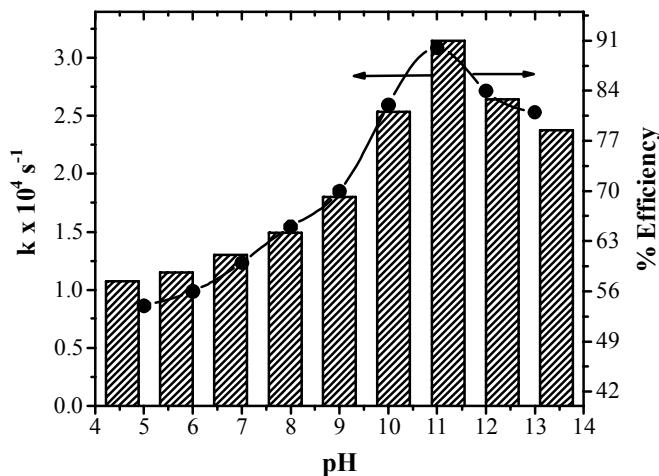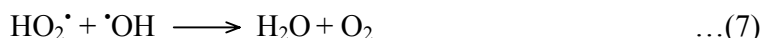

Fig. 3: Effect of solution pH

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 3.49×10^{-4} s^{-1} to 4.56×10^{-4} s^{-1}. 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:

$$H_2O_2 + TiO_2\,(e^-_{CB}) \longrightarrow {}^{\bullet}OH + OH^- \qquad ...(3)$$

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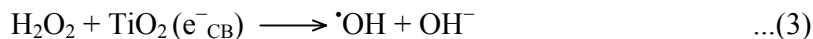
Further increase in concentration of H_2O_2 beyond optimal concentration, resulted into the decrease in rate constant because at an excess H_2O_2 concentration, it might start acting as hydroxyl radical and hole scavenger.

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

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

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

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 3.33×10^{-4} s^{-1} to 4.87×10^{-4} s^{-1}. At optimal amount of $K_2S_2O_8$, the rate of degradation has been found to be 4.87×10^{-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[12].

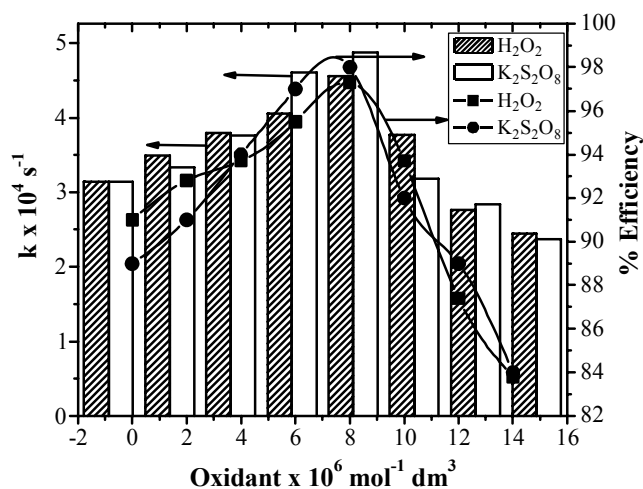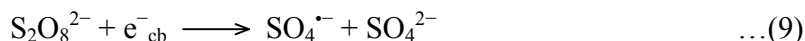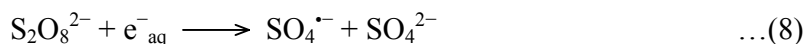$$S_2O_8^{2-} + e^-_{aq} \longrightarrow SO_4^{\bullet-} + SO_4^{2-} \qquad ...(8)$$

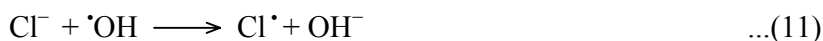$$S_2O_8^{2-} + e^-_{cb} \longrightarrow SO_4^{\bullet-} + SO_4^{2-} \qquad ...(9)$$

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

Effect of NaCl and Na$_2$CO$_3$

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 2.95×10^{-4} s^{-1} to 1.42×10^{-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.

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

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

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

$$Cl^{\bullet} + Cl^- \longrightarrow Cl_2^{-\bullet} \qquad\qquad …(13)$$

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 color. Therefore the wastewater from the dyeing operation will contain considerable amount of carbonate ion[13]. 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 2.99×10^{-4} s^{-1} to 1.34×10^{-4} s^{-1}. 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.
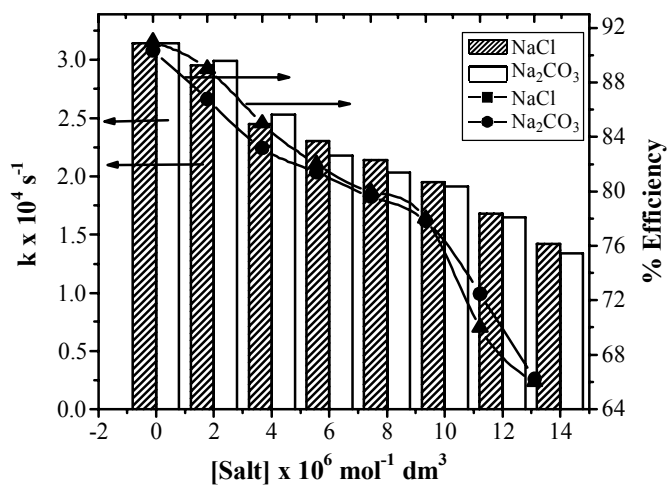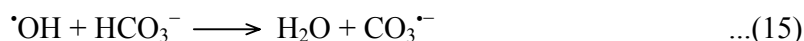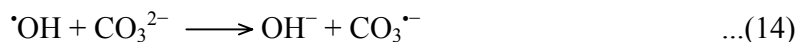
$$^{\bullet}OH + CO_3^{2-} \longrightarrow OH^- + CO_3^{\bullet-} \qquad\qquad ...(14)$$

$$^{\bullet}OH + HCO_3^- \longrightarrow H_2O + CO_3^{\bullet-} \qquad\qquad ...(15)$$

Fig. 5: Effect of Salt: NaCl and Na$_2$CO$_3$

Effect of temperature

The photocatalytic degradation was studied at various temperatures in the range 30°C to 55°C. The values in Fig. 6 show the semiconductor photocatalysis is usually not very temperature dependent[14]. Increase in temperature led to decrease 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[15].
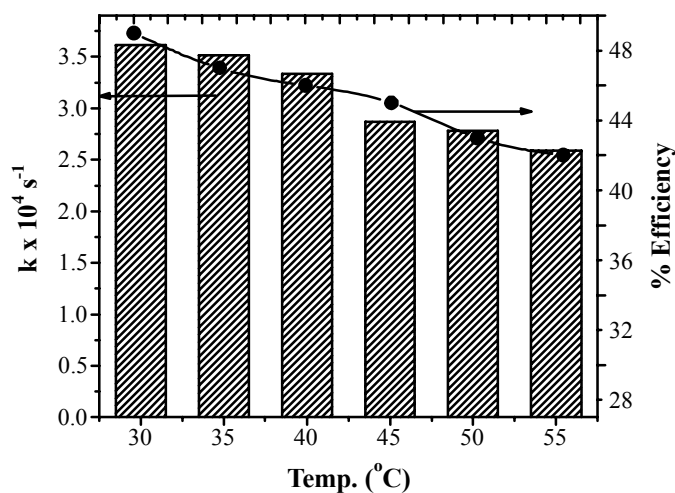

Fig. 6: Effect of temperature

Effect of N₂ and O₂ purging

Dissolved N_2 and O_2 gases played significant role in the degradation of dissolved organic pollutants. It was observed that photodegradation efficiency was severely retarded by bubbling pure nitrogen (decrease in rate constant from 3.14×10^{-4} s^{-1} to 1.34×10^{-4} s^{-1}) but the photodegradation efficiency increased rapidly with increasing oxygen flow increases in rate constant from 3.14×10^{-4} s^{-1} to 4.98×10^{-4} s^{-1}. According to the photocatalytic mechanism the surface redox reactions are initiated by photogenerated electrons and holes start the photocatalytic degradation of organics. If the surface chemical reactions of conduction band (CB) electron were blocked by N_2 purging, the valence band (VB) holes would had a tendency to be consumed by the accumulated electrons via the electron-hole recombination inside the catalyst; hence, the photocatalytic degradation process would be significantly suppressed. Dissolved oxygen in the solution plays an important role by trapping the conduction band electrons forming superoxide ions ($O_2^{-\bullet}$) and thus preventing

the electron-hole recombination ($O_2 + e^- \ O_2^{-\bullet}$) and superoxide radical anion further reacts with the hydrogen ion to form a hydroxyl radical which in turn increases the degradation rate[16].
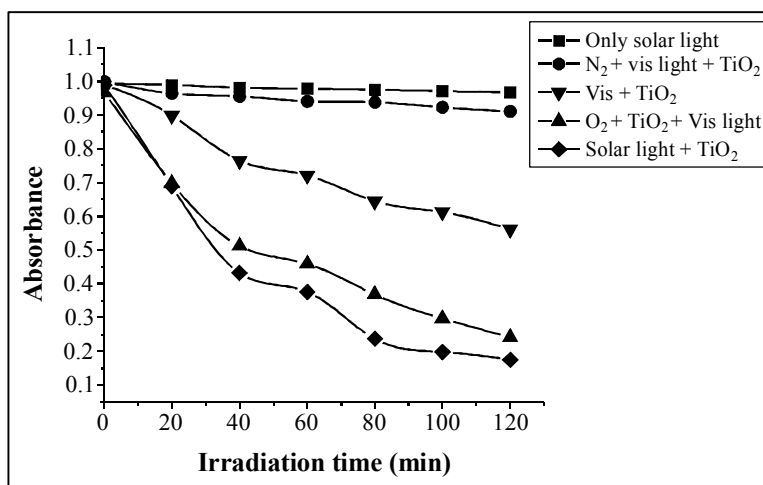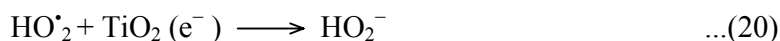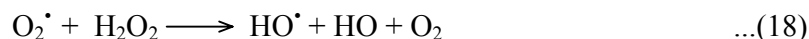
$$O_2 + e^- \longrightarrow O_2^{-\bullet} \qquad \qquad ...(16)$$

$$H_2O_2 + TiO_2(e^-) \longrightarrow HO^\bullet + HO \qquad \qquad ...(17)$$

$$O_2^\bullet + H_2O_2 \longrightarrow HO^\bullet + HO + O_2 \qquad \qquad ...(18)$$

$$O_2^\bullet + H^+ \longrightarrow HO^\bullet_2 \qquad \qquad ...(19)$$

$$HO^\bullet_2 + TiO_2(e^-) \longrightarrow HO_2^- \qquad \qquad ...(20)$$

$$HO_2^- + H^+ \longrightarrow H_2O_2 \qquad \qquad ...(21)$$

$$2\,HO^\bullet_2 \longrightarrow O_2 + H_2O_2 \qquad \qquad ...(22)$$

Fig. 7: Declorization of Brilliant cresyl blue under various systems

[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 ± 0.3ºC.

Effect of solar light

The natural sunlight irradiation was performed on a sunny day. Aqueous solution of BCB and TiO$_2$ was exposed to sunlight. The degradation of dye proceeded much more rapidly in the presence of solar light. Estimated rate constant value has been found to be

$k = 5.10 \times 10^{-4}$ s^{-1}. When artificial visible light was used the rate of degradation was found less than solar light ($k = 3.14 \times 10^{-4}$ s^{-1}). Blank experiments were also carried out under sunlight in absence of photocatalyst but no observable loss of dye was seen. Though sunlight has optimum energy for photocatalytic excitation and for the degradation of textile dyes, it could be a safe and cost effective source. Moreover there is no material deterioration in case where sunlight is used as a radiation source. Since intense sunlight is available throughout the year in tropical country like India; it could be effectively used for the photocatalytic degradation of pollutants in waste water from the industrial point of view[17,18].

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 parameter 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[19]. 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 color removal[20]. The reduction in the estimated COD value from 312 mg/L to 12 mg/L and increased CO$_2$ value from 11 mg/L to 143 mg/L in 8 h of illumination indicated the photodegradation of treated dye solution. A decrease in pH of solution has also been observed with increase in the extent of mineralization.

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.

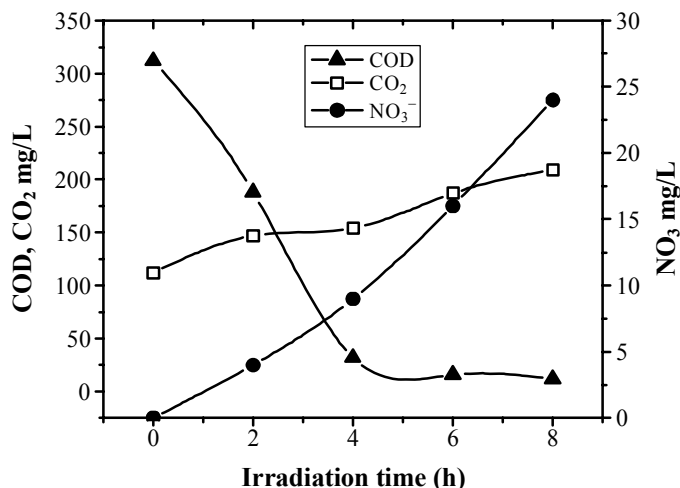| Irradiation time (h)	COD (mg/L)	CO$_2$ (mg/L)	Efficiency (%)	NO$_3^-$ (mg/L)	pH
0	312	112	0	0	11.0
2	188	147	39	4	9.0
4	32	154	89	9	5.2
6	16	187	94	16	3.8
8	12	209	96	24	2.1

Fig. 8: COD and CO$_2$ measurements and formation of NO$_3^-$ during photodegradation process 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 ºC.

UV- Vis spectral analysis during mineralization

The UV-Vis absorption spectra of BCB were 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. 9 both in the UV and visible region. Its λ_{max} is 495 nm. The decrease of absorption peaks actually indicated a rapid decoloration and degradation of BCB dye[21]. 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[22].

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[8]. 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[23].
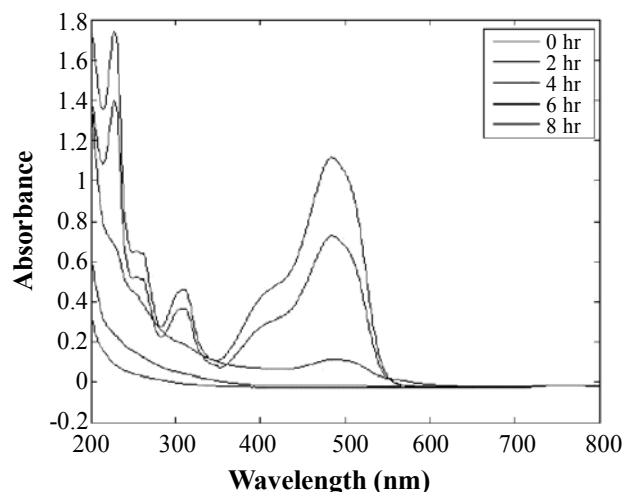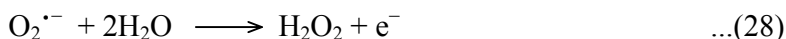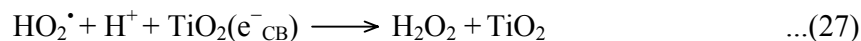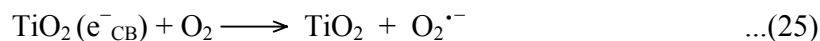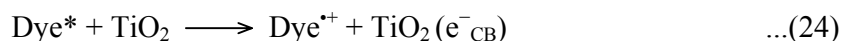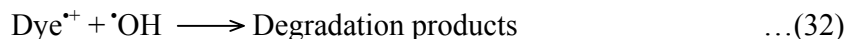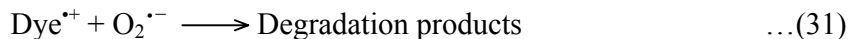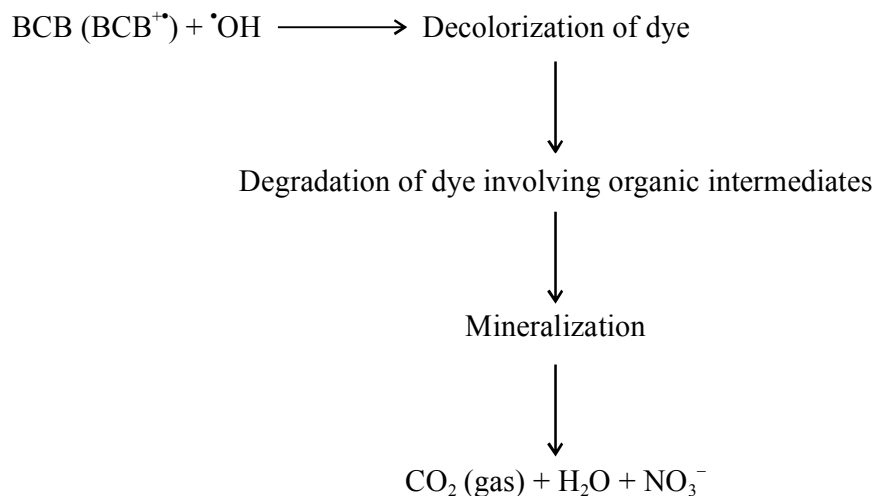
Fig. 9: UV-Vis spectrum of Brilliant cresyl blue

[BCB] = 5.O × 10^{-5} mol dm^{-3}, TiO_2 = 150 mg/100 mL, pH = 11.0
Light intensity = 14 × 10^3 lux, Temperature = 30 ± 0.3^{o}C

The conduction band electron of TiO_2 is scavenged by O_2 molecule to form $O_2^{•-}$ or more active radicals such as $^•OH$, 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[24]. Such type of electron transfer mechanism has been called a "photosensitizing oxidation". The mechanism of dye degradation under visible light irradiation can be described as Eq. 23-32.[25]

$$Dye + h\nu \; (visible) \longrightarrow Dye^* \qquad \qquad ...(23)$$

$$Dye^* + TiO_2 \longrightarrow Dye^{•+} + TiO_2 \, (e^-_{CB}) \qquad \qquad ...(24)$$

$$TiO_2 \, (e^-_{CB}) + O_2 \longrightarrow TiO_2 \; + \; O_2^{•-} \qquad \qquad ...(25)$$

$$O_2^{•-} \; + H^+ \longrightarrow HO_2^{•} \qquad \qquad ...(26)$$

$$HO_2^{•} + H^+ + TiO_2(e^-_{CB}) \longrightarrow H_2O_2 + TiO_2 \qquad \qquad ...(27)$$

$$O_2^{•-} \; + 2H_2O \longrightarrow H_2O_2 + e^- \qquad \qquad ...(28)$$

$$H_2O_2 + TiO_2(e^-_{CB}) \longrightarrow \, ^•OH + OH^- + TiO_2 \qquad \qquad ...(29)$$

$$Dye^{•+} + OH^- \longrightarrow Dye + \, ^•OH \qquad \qquad ...(30)$$

$$Dye^{\bullet+} + O_2^{\bullet-} \longrightarrow Degradation\ products \qquad \qquad …(31)$$

$$Dye^{\bullet+} + {}^{\bullet}OH \longrightarrow Degradation\ products \qquad \qquad …(32)$$

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[26]. The mechanism of TiO_2 photocatalysis is of very complex nature. Cationic dye radicals interact with $O_2^{\bullet-}$, $HO_2^{\bullet}$ or ${}^{\bullet}OH$ species to generate intermediates ultimately lead to the generation of degradation products. Hydroxyl radical (${}^{\bullet}OH$) being very strong oxidizing agent (standard oxidation potential 2.8 eV) mineralizes dye to end product.

$$BCB\ (BCB^{+\bullet}) + {}^{\bullet}OH \longrightarrow Decolorization\ of\ dye$$

$$\downarrow$$

Degradation of dye involving organic intermediates

$$\downarrow$$

Mineralization

$$\downarrow$$

$$CO_2\ (gas) + H_2O + NO_3^-$$

As the degradation process precedes 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^- 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 $S_2O_8^{2-}$ increase 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.

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