PHOTOCATALYTIC DEGRADATION OF ENVIRONMENTALLY HAZARDOUS CRYSTAL VIOLET DYE USING BISMUTH OXYCHLORIDE AS PHOTOCATALYST

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ABSTRACT

Photocatalytic degradation of crystal violet, a widely used industrial dye has been studied utilizing visible light and BiOCl as photocatalyst. This manuscript discusses the optimizing conditions for efficient photocatalytic degradation of crystal violet such as the effect of variation of pH, dye concentration, catalyst loading, light intensity and effect of addition of oxidants such as H_2O_2 & $K_2S_2O_8$ and salts such as Na_2CO_3 & NaCl. Experimental studies revealed the catalyst loading of 90 mg/100 mL as the optimal dose for the degradation of 2.5×10^{-5} mole dm^{-3} dye. The gradual reduction in the COD revealed its complete mineralization. Results demonstrated that BiOCl in the presence of visible irradiation can effectively degrade crystal violet dye.

**Key words**: Photocatalysis, Degradation, Visible light, BiOCl, Crystal violet

INTRODUCTION

Crystal violet (CV), a hexamethyl pararosaniline chloride dye (Fig. 1) is used in human and veterinary medicine as a biological stain and in various commercial textile processes as a dye. It's a recalcitrant molecule, therefore, poorly metabolized by microbes and consequently, it is long lived in a variety of environments. Moreover, it is a potent clastogen, possibly responsible for promoting tumor growth[1]. Many alternating processes aimed at removing crystal violet from wastewater have been investigated including chemical oxidation and reduction, physical precipitation and flocculation, advanced oxidation, reverse osmosis and biodegradation. Physicochemical processes merely transfer dyes from the liquid

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to the solid phase causing secondary pollution and requiring further treatment[2]. This led to the study of Advanced Oxidation Processes (AOPs) for the complete degradation. Further the heterogeneous photocatalysis which is emerging as an effective AOP has been in use recently[3]. These processes are based on the production of highly reactive hydroxyl radicals that oxidizes a broad range of organic pollutants quickly and non-selectively[4] and leads to total mineralization to CO_2, water and mineral acids[5]. When illuminated with uv/visible light source, these semiconductors generate electron/hole pairs, with electrons promoted to the conduction band and leaving positive holes in the valence band. The generated electron/hole pairs initiate a complex series of chemical reactions involving vestigial organic compounds adsorbed at the surface of the semiconductor that might result in the complete degradation of the adsorbates. Obviously, the formation of eco-friendly end products, as compared to the original pollutants, is an attractive feature of this process. In the view of using natural energy, solar energy, there is an urgent need to develop new types of photocatalysts responding to visible light irradiation[6].
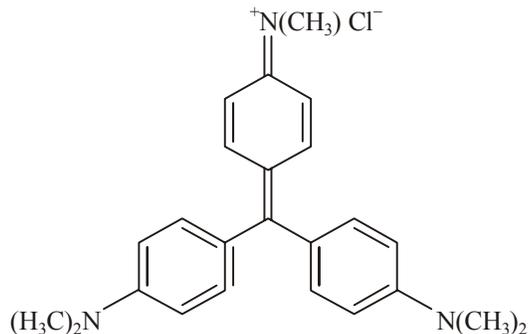
Fig. 1: Structure of dye ammonium, (4-(bis(p-(dimethylamino)phenyl) methylene)-2,5-cyclohexadiene-1-ylidine)dimethyl, chloride

Here we report a relatively new photocatalyst BiOCl with band gap of 3.5 eV, which showed a good response to visible light irradiation. Offlate BiOCl nanoparticles have been utilized efficiently in decomposing methyl orange under U.V. light[7]. However, literature survey revealed that, no attempt has been made for photocatalytic degradation of crystal violet dye with BiOCl under visible irradiation. Therefore, the present study.

EXPERIMENTAL

Crystal violet was obtained from Sigma-Aldrich Chemical Company. Photocatalyst BiOCl was obtained from the Merck Company. All solutions were prepared in doubly distilled water. Photocatalytic experiments were carried out with 50 mL of dye solution (2.5

x 10^{-5} mol dm^{-3}) using 45 mg of BiOCl photocatalyst under exposure to visible irradiation in a specially designed double-walled slurry type batch reactor vessel made up of Pyrex glass (7.5 cm height, 6 cm diameter) surrounded by thermostatic water circulation arrangement to keep the temperature in the range of $30 \pm 0.3^{\circ}C$. Irradiation was carried out using 500 W halogen lamp surrounded by aluminum reflector to avoid irradiation loss.

During photocatalytic experiment, after stirring for 10 min. slurry composed of dye solution and catalyst was placed in dark for 1/2 h in order to establish equilibrium between adsorption and desorption phenomenon of dye molecule on photocatalyst surface. Then slurry containing aqueous dye solution and BiOCl was stirred magnetically to ensure complete suspension of catalyst particle while exposing to visible light. At specific time intervals, aliquot (3 mL) was withdrawn and centrifuged for 2 min at 3500 rpm to remove BiOCl particles from aliquot to assess extent of decolourisation photometrically. Changes in absorption spectra were recorded at 588 nm on double-beam UV-Vis. spectrophotometer (Systronic Model No. 166). Intensity of visible radiation was measured by a digital lux-meter (Lutron LX-101). pH of solution was measured using a digital pH meter. The desired pH of the solution was adjusted by the addition of previously standardized 0.050M H_2SO_4 and 1.0M NaOH solutions. COD and CO_2 estimation were performed[8,9]. Performance efficiency was calculated as -

$$\% \text{ Efficiency} = \frac{C_o - C}{C_o} \text{ x } 100 \qquad \ldots(1)$$

where C and C_o are initial and final dye concentration or COD or CO_2 for reaction time t.

RESULTS AND DISCUSSION

An aliquot was taken from the reaction mixture at regular time interval and the absorbance was measured spectrophotometrically at λ_{max} value of 588 nm. The absorbance of the solution was found to decrease with increasing time, which indicates that the concentration of crystal violet dye decreased with increasing time of exposure.

Catalyst screening

To determine the effect of the catalyst loading, a series of experiments were carried out by varying the amount of catalyst from 20-80 mg/50 mL keeping other parameters constant. Degradation rate constant increased from 1.34 x 10^{-4} s^{-1} to 2.11 x 10^{-4} s^{-1} with increase in catalyst loading from 20 mg/50 mL to 45 mg/ 50 mL because with the increase in catalyst dosage, total active surface area and hence the availability of more active sites on catalyst surface increased, which enhanced the rate of formation of hydroxyl radicals and

superoxide radicals[5,10]. Further increase in catalyst amount (50-80 mg/50 mL) showed reduction in degradation rate constant from $2.11 \times 10^{-4}\,s^{-1}$ to $0.73 \times 10^{-4}\,s^{-1}$ because when the catalyst concentration was very high, after traveling a certain distance on an optical path, turbidity i.e. screening effect of excess catalyst particles impeded further penetration of light in the reactor. This is totally in agreement with reported studies for heterogeneous system[11].

Effect of pH

Discharged dyes effluent has different pH; therefore, it is necessary to study the role of pH values on degradation rate. Experiments were carried out at various pH values, ranging from 4 to 10 for constant dye concentration ($2.5 \times 10^{-5}\,mol\,dm^{-3}$) and catalyst loading (45 mg/50 mL). The reaction rate increased with increase in pH exhibiting maximum rate of degradation at pH 8. Crystal violet, a cationic dye, contains a positive ammonium center coupled with a chlorine anion, which makes the dye molecules positively charged. Therefore, at higher pH value about 8, the electrostatic attraction between the negatively charged active sites on the surface of BiOCl catalyst and positive dye molecule causes strong adsorption[12], but if the pH value is too high, crystal violet molecules change to a leuco compound. Under acidic conditions, the cationic dye crystal violet was difficult to adsorb on the BiOCl surface and hence, the photodegradation of crystal violet was very slow[13].
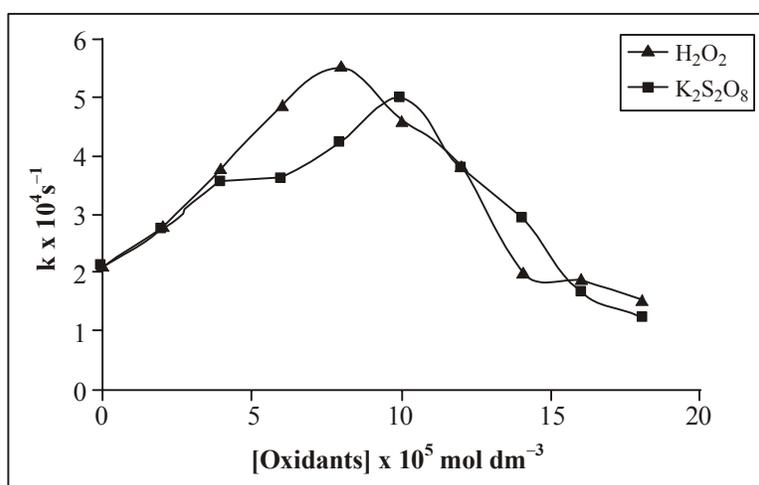
Effect of electron acceptors and hole scavengers

The rate of photocatalytic degradation of organic compounds significantly changed either in the presence of oxygen or by addition of hydrogen peroxide or potassium persulphate. The degradation rate has been studied at different hydrogen peroxide and potassium persulphate concentrations. The degradation rate of CV increased with increasing H_2O_2 and $K_2S_2O_8$ concentrations upto $10 \times 10^{-5}\,mol\,dm^{-3}$ but above this concentration range, the degradation rate was found to decrease (Fig. 2). At their respective low concentrations H_2O_2 and $K_2S_2O_8$ inhibits the electron-hole recombination and hence, accelerate the reaction by producing an extremely strong and non-selective oxidant ($E^o = +3.06V$) hydroxyl radical from scavenging the electrons and absorption of visible light by the following reactions:

$$H_2O_2 + BiOCl\,(e^-_{CB}) \longrightarrow {}^{\bullet}OH + {}^-OH \qquad\qquad ...(2)$$

$$H_2O_2 + h\nu \longrightarrow 2\,{}^{\bullet}OH \qquad\qquad ...(3)$$

$$S_2O_8{}^{2-} + e^-_{CB} \longrightarrow SO_4{}^{-\bullet} + SO_4{}^{2-} \qquad\qquad ...(4)$$

At an excess H_2O_2 concentration, H_2O_2 may start acting as hydroxyl radical and hole

scavenger, thereby decreasing the reaction rate. Similarly, the decrease in degradation rate at high $K_2S_2O_8$ concentration is due to the adsorption of sulphate ions formed during the reaction on the surface of BiOCl deactivating a section of photocatalyst.

$$H_2O_2 + {}^\bullet OH \longrightarrow HO_2^\bullet + H_2O \qquad \qquad ...(5)$$

$$HO_2^\bullet + {}^\bullet OH \longrightarrow H_2O + O_2 \qquad \qquad ...(6)$$

$$H_2O_2 + h_{VB}^+ \longrightarrow H^+ + HO_2^\bullet \qquad \qquad ...(7)$$

$$SO_4^{2-} + {}^\bullet OH \longrightarrow SO_4^{\bullet -} + {}^- OH \qquad \qquad ...(8)$$

$$SO_4^{2-} + h_{VB}^+ \longrightarrow SO_4^- \qquad \qquad ...(9)$$

Fig. 2: Effect of oxidants on photocatalytic degradation of CV [CV = 2.5 x 10^{-5} mole dm^{-3}, BiOCl = 90 mg/100 mL, Irradiation intensity = 25 x 10^3 lux, pH = 6.1]

Wastewater contains not only organic contaminants but also considerable amount of inorganic anions such as nitrate, sulfate, carbonate, etc. Hence, it is useful to study the influence of these ions on this photocatalytic process. Two possible influences of inorganic ions on the photocatalytic reaction are : (1) changing the ionic strength of reaction medium and (2) inhibition of catalytic activity of the photocatalyst. Increase in the concentration of Cl^- and CO_3^{2-} from 2.5 x 10^{-5} mol dm^{-3} to 15 x 10^{-5} mol dm^{-3} decreased the reaction rate from 2.11 x 10^{-4} s^{-1} to 0.43 x 10^{-4} s^{-1}. The inhibition effect of these ions is due to the reaction of these ions with holes and $^\bullet OH$. These ions may also block the active sites on the BiOCl surface; thus, deactivating the catalyst towards the crystal violet molecules. Although,

the generated radical anions has been shown to be an oxidant itself, but its oxidation potential is less positive than that of the hydroxyl radicals[14,15].

$$CO_3^{2-} + {}^{\bullet}OH \longrightarrow CO_3^{{\bullet}-} + {}^{-}OH \qquad \qquad ...(10)$$

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

Effect of substrate concentration

Effect of variation of dye concentration was studied by taking different concentrations of crystal violet from 0.5×10^{-5} mol dm^{-3} to 4.0×10^{-5} mol dm^{-3}. The photocatalytic degradation rate was found to increase from 1.3×10^{-4} s^{-1} to 2.11×10^{-4} s^{-1} with increasing concentration of dye upto 2.5×10^{-5} mol dm^{-3}. Further increasing the concentration beyond the limit decreased the degradation rate from 2.11×10^{-4} s^{-1} to 1.11×10^{-4} s^{-1} which is in agreement with reported studies[2,16].

Effect of light intensity

An almost linear behavior between light intensity and rate of reaction was observed. The rate of degradation increased with increase in radiation on the catalytic surface resulting in more hydroxyl radicals[17].

COD and CO_2 measurements

The reduction in the estimated COD values from 350 mg/L to 0 mg/L and increase in CO_2 values from 20 mg/L to 890 mg/L in 8 hours of illumination indicated the photocatalytic degradation of treated dye solution (Table 1).

Table 1: COD and CO_2 measurements for degradation of crystal violet dye. Crystal violet concentration : 2.5×10^{-5} mol dm^{-3}; Amount of BiOCl : 90 mg/100 mL; Irradiation intensity : 25×10^3 lux; pH : 6.1

Irradiation time (h)	COD (mg/L)	CO_2 (mg/L)	% Efficiency	pH
0	350	20	0	6.1
1	324	59	7	5.7
2	264	110	24	5.2
3	253	230	27	4.8

Irradiation time (h)	COD (mg/L)	CO_2 (mg/L)	% Efficiency	pH
4	205	398	41	4.3
5	149	440	57	4.0
6	63	560	82	3.8
7	19	750	94	3.5
8	0	890	100	3.1

Kinetics of photo degradation

The rate of heterogeneous photocatalytic degradation of dye has been described by Langmuir-Hinshelwood (L-H) model, which has the following mathematical formula[18].

$$\frac{-dC}{dt} = \frac{k_{L-H}K_{ad}C}{1+K_{ad}C} \qquad ...(12)$$

Where $k_{L\text{-}H}$ is the reaction rate constant, K_{ad} is the adsorption coefficient of dye on photocatalyst and C is the variable concentration at any time t. For pseudo-first order reaction $K_{ad}C$ is very small as compared to 1 in the denominator of Eq. (1). So for simplification, the denominator becomes 1. Integrating Eq. (1), we obtain –

$$\ln\left(\frac{C_o}{C}\right) = k_{L-H}K_{ad}\, t = kt \qquad ...(13)$$

Where C_o is the initial concentration and $k = k_{L\text{-}H}\, K_{ad}$ is the pseudo-first order reaction rate constant whose value is determined by the expression -

$$k = 2.303 \text{ x slope} \qquad ...(14)$$

The half lifetime $t_{1/2}$ can be calculated according to

$$t_{1/2} = 0.693/k \qquad ...(15)$$

plotting the natural logarithm of the ratio between the original concentration of crystal violet and the concentration after photocatalytic degradation [ln (C_o/C)] versus the corresponding irradiation time (min) yielded a linear relationship. Therefore, the photocatalytic degradation reaction of crystal violet by BiOCl belongs to the pseudo-first-order reaction kinetics. The rate constant is the slope of the straight line.
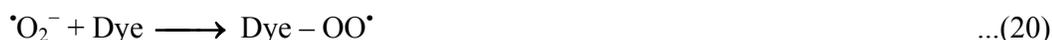
Mechanism

When a photon of visible light with energy greater than the band gap energy of BiOCl photocatalyst ($h\nu > Eg = 3.5$ eV) strikes its surface, an electron from its valence band (VB) jumps to the conduction band (CB) leaving behind a positively charged hole (h_{VB}^{+}). The negative charge is increased in the conduction band (e^{-}_{CB}) and photocatalytic active centres are formed on the surface of BiOCl particles according to equation:

$$BiOCl + h\nu \text{ (visible)} \longrightarrow BiOCl \ (e^{-}_{CB} + h_{VB}^{+}) \qquad ...(16)$$
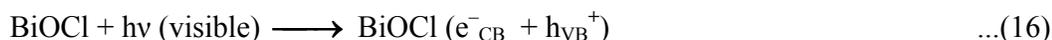
The valence band holes react with the chemisorbed H_2O molecules or ^{-}OH to form very reactive hydroxyl radicals, which subsequently react with dye molecules to cause their complete degradation.

$$H_2O \longrightarrow (H^{+} + {}^{-}OH) + BiOCl \ (h_{VB}^{+}) \longrightarrow H^{+} + {}^{\bullet}OH \qquad ...(17)$$
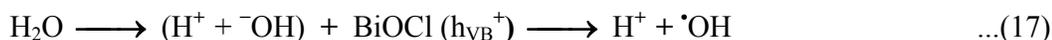
Alternatively, e^{-}_{CB} and h_{VB}^{+} can recombine on the surface of the particle within a few nanoseconds and the resulting energy is dissipated as heat. Furthermore, the e^{-}_{CB} and h_{VB}^{+} can be trapped in surface states where they may react with species adsorbed or close to the surface of the particle. The e^{-}_{CB} can react with an acceptor, such as dissolved O_2, which consequently is transformed into a superoxide radical anion ($O_2^{\bullet-}$) which leads to the formation of perhydroxyl radicals ($HO_2^{\bullet}$). The superoxide radical anion, in the presence of perhydroxyl radicals and organic scavenger, may form hydrogen peroxide or organic peroxides.

$$O_2 + BiOCl \ (e^{-}_{CB}) \longrightarrow {}^{\bullet}O_2^{-} + (H^{+} + {}^{-}OH) \longrightarrow HO_2^{\bullet} + {}^{-}OH \qquad ...(18)$$

$$^{\bullet}O_2^{-} + HO_2^{\bullet} + H^{+} \longrightarrow H_2O_2 + O_2 \qquad ...(19)$$

$$^{\bullet}O_2^{-} + Dye \longrightarrow Dye - OO^{\bullet} \qquad ...(20)$$

Electrons in the conduction band are also responsible for the production of hydroxyl radicals.

$$H_2O_2 + BiOCl \ (e^{-}_{CB}) \longrightarrow {}^{\bullet}OH + {}^{-}OH \qquad ...(21)$$

On the other hand, h_{VB}^{+}, could interact with donors, such as ^{-}OH and $HO_2^{\bullet}$, to form $^{\bullet}OH$ radicals, which is the primary cause of organic matter mineralization[4,11,18].

$$HO_2^{\bullet} + {}^{-}OH + BiOCl \ (h_{VB}^{+}) \longrightarrow {}^{\bullet}OH \qquad ...(22)$$

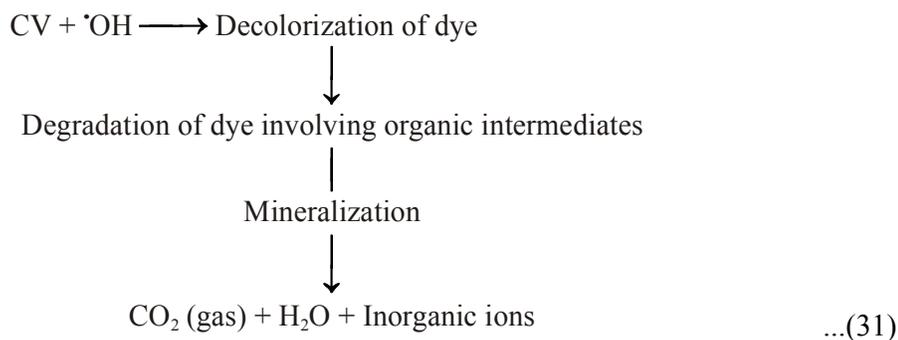$$^\bullet OH + Dye \longrightarrow \text{Degradation of the dye} \qquad \text{...(23)}$$

The main factor affecting the efficiency of BiOCl is the amount of $^\bullet OH$ radicals as described above. Therefore, any factor that supports the generation $^\bullet OH$ radicals will enhance the rate of photocatalytic degradation of crystal violet dye.

In second way, crystal violet (CV) absorbs radiations of suitable wavelength and goes to excited state. It then undergoes intersystem crossing (ISC) to the triplet state of the dye. This triplet state may donate its electrons to the semiconductor and the crystal violet becomes positively charged. The dissolved oxygen of the solution may pull an electron form the conduction band of semiconductor, thus regenerating the semiconductor and forming superoxide anion radical. The positively charged molecule of crystal violet will immediately react with hydroxyl ion to form $^\bullet OH$ radicals and these $^\bullet OH$ radicals will oxidize the crystal violet molecule into colorless product[16,17].

$$^1CV_0 \xrightarrow{\;hv\;} {}^1CV_1 \qquad \text{...(24)}$$

$$^1CV_1 \xrightarrow{\;ISC\;} {}^3CV_1 \qquad \text{...(25)}$$

$$^3CV_1 + BiOCl\,(h_{VB}^+) \longrightarrow CV^+ + (BiOCl)e^- \qquad \text{...(26)}$$

$$BiOCl\,(e^-_{CB}) + O_2 \longrightarrow BiOCl + O_2^{\bullet-} \qquad \text{...(27)}$$

$$CV^+ + {}^-OH \longrightarrow CV + {}^\bullet OH \qquad \text{...(28)}$$

$$CV + {}^\bullet OH \longrightarrow \text{Degradation products} \qquad \text{...(29)}$$

$$CV + {}^\bullet O_2^- \longrightarrow \text{Degradation products} \qquad \text{...(30)}$$

The mechanism of the photocatalytic degradation of dye is very complex in nature but it may be simplified as -

$$CV + {}^\bullet OH \longrightarrow \text{Decolorization of dye}$$
$$\downarrow$$
$$\text{Degradation of dye involving organic intermediates}$$
$$|$$
$$\text{Mineralization}$$
$$\downarrow$$
$$CO_2\,(gas) + H_2O + \text{Inorganic ions} \qquad \text{...(31)}$$

CONCLUSION

Photoassisted mineralization of CV can be effectivly carried out utilizing BiOCl with visible light. Carbonate and chloride ions have detrimental effect on the degradation rate. Catalyst loading and pH value of the solution have been found to be vital parameters. Synergetic action of H_2O_2 and $K_2S_2O_8$ has also been investigated. H_2O_2/BiOCl/Vis. process has been found to be most efficient for dye degradation. Under optimum reaction condition, for complete mineralization of CV (2.5×10^{-5} mol dm^{-3}), 8 hours of irradiation time was required. Decolourisation and mineralization are not simultaneous but tend to approach each other as time of irradiation is increased.

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