



VISIBLE LIGHT INDUCED DEGRADATION OF ACRIDINE ORANGE DYE OVER BaCrO₄ PHOTOCATALYST

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ABSTRACT

The photocatalysed degradation of acridine orange dye has been investigated in aqueous suspension of BaCrO₄ under variety of conditions using visible spectrophotometric analysis technique. The effect of different parameters such as effect of H₂O₂ and K₂S₂O₈, catalyst loading, dye concentration, effect of pH, effect of FeCl₃, effect of temperature, light intensity, electron acceptors such as NaCl and Na₂CO₃ on the rate of degradation of dye were studied. Decrease in chemical oxygen demand and increases in carbon dioxide indicate the complete mineralization of acridine orange in the presence of BaCrO₄. BaCrO₄ was found to be a potentially efficient photocatalyst for the visible light.

Key words: Visible light, Photocatalysis, BaCrO₄, Degradation, Acridine orange.

INTRODUCTION

The waste water generated by the textile and dyeing industry is rated as the most polluting among all the industrial sectors. The release of this wastewater without treatment into water stream is very dangerous, since most of the dyes are carcinogenic in nature and pose a serious threat to the environment¹. As a result, effective purification methods for eliminating of dye in water have been in urgent demand. The already existing methods like adsorption or biological treatment appear to have many drawbacks. In recent years advanced oxidation processes (AOPs)² have become popular for degradation of organic pollutants due to its effectiveness and safe nature. These processes are based on the production of [•]OH radicals (reduction potential E₀ = 2.8 V) and they attack unselectively most of the organic molecules for degradation³. The often used photocatalyst are TiO₂, ZnO, WO₃ and SrTiO₃ having band gap in UV region, larger than 3.2 eV⁴⁻⁵. UV being unsafe and expensive, use of visible light in its place has recently been undertaken by many workers. In the present study,

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we have used visible light induced photocatalysis using BaCrO_4 as photocatalyst that has band gap 2.6 eV^6 .

EXPERIMENTAL

Procedure

Acridine orange dye was obtained from Sigma-Aldrich. The photocatalyst BaCrO_4 was obtained from Qualigen fine chemicals, 99% pure with surface area of $10 \text{ m}^2/\text{gm}$. H_2O_2 (30% aqueous), FeCl_3 , NaCl and Na_2CO_3 were of analytical grade and used without further purification. All the solutions were prepared in double distilled water. The photocatalytic and photolytic experiments were carried out in a slurry type batch reactor having pyrex vessel of dimension of $7.5 \text{ cm} \times 6 \text{ cm}$ (height \times dia.). The pyrex glass vessel equipped with magnetic stirrer was surrounded by thermostatic water circulation arrangement to keep temperature in the range of $30 \pm 0.3^\circ\text{C}$. The irradiation was carried out using 500 W halogen lamps (Philips India) surrounded with aluminum reflectors in order to avoid loss of irradiation. During the photocatalytic experiment, after stirring for ten minute, the slurry composed of dye solution and catalyst was placed in dark for half an hour in the order to establish equilibrium between adsorption and desorption phenomenon dye molecule on the surface of photocatalyst. Now slurry containing aqueous dye solution and BaCrO_4 particles 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 at the rate of 3500 rpm to remove BaCrO_4 particles to assess the extent of decolorization spectrophotometrically. The intensity of visible radiation was measured by a digital lux-meter. pH was constantly monitored. COD and CO_2 was determined by the methods reported earlier. Performance efficiency was calculated as:

$$\% \text{ Efficiency} = \frac{C_0 - C}{C_0} \times 100$$

$$\text{COD or CO}_2 = \frac{C}{C_0}$$

where C and C_0 are initial and final dye concentration or COD or CO_2 for reaction time⁷.

Kinetics of dye disappearance

Langmuir-Hinshelwood pseudo-first order kinetics model can be utilized as follows -

$$\ln (C_0/C) = kt$$

Where C_0 , C , t and k are the initial dye concentration, dye concentration in decolorization time 't' and apparent rate constant (time^{-1}), respectively⁸.

The absorbance of acridine orange dye decreases with an increase in irradiation time, while in dark and during photolysis, no significant changes has been observed as shown in Fig. 3.

RESULTS AND DISCUSSION

Effect of catalyst

The photodegradation of the acridine orange has been studied at different amount of BaCrO_4 . With the increase in amount of photocatalyst the rate got enhanced from 100 mg to 250 mg and then the degradation rate decreased upto 350 mg. The increase in the reaction rate was due to the increase in active sites for the production of $\cdot\text{OH}$ radicals. The degradation reached maximum at optimal concentration of BaCrO_4 . Further increase in the photocatalyst amount resulted in the decrease in the degradation rate due to turbidity, which reduce the light transition through the solution, while below this optimum level it is assumed that the catalyst surface and adsorption of light by the catalyst are limited⁹.

Effect of pH

Experiments were conducted at different initial pH values varying from 5 to 13. The percent degradation of dye was increased with an increasing of pH up to 9 and further increase in pH got resulted into decrease in the degradation rate. The increase in rate of photocatalytic degradation may be due to the more availability OH^- ions in basic medium which would generate more $\cdot\text{OH}$ radicals by combining with holes, which are formed due to the electronic excitation. At higher pH the rate of degradation decreases due to competition between OH^- groups to attach to active site of catalyst¹⁰. At lower pH positively charged active sites on catalyst surface caused low concentration of positively charged dyes molecule on catalyst surface⁷.

Effect of electron acceptors and hole scavengers

H_2O_2 and $\text{K}_2\text{S}_2\text{O}_8$ plays crucial role in photodegradation of dyes. The photocatalytic degradation of acridine orange was conducted at different concentration of H_2O_2 and $\text{K}_2\text{S}_2\text{O}_8$. The result indicated the rate of degradation was increased with increasing concentration up to 9 and 7 mol dm^{-3} respectively but above this concentration, degradation efficiency was decreased. It could be explained by the scavenging reaction of $\cdot\text{OH}$ radical by the H_2O_2 . Indeed, the $\cdot\text{OH}$ radical can react with H_2O_2 leading to the generation of less reactive radical such as hydroperoxide ($\text{HO}_2\cdot$) or superoxide ($\text{O}_2\cdot$).

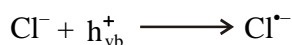
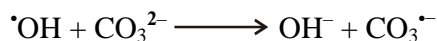


The $\cdot\text{OH}$ radicals preferentially attack the organic molecules at low H_2O_2 concentration, whereas at higher H_2O_2 concentration, there is a competitive reaction between the substrate and H_2O_2 ¹¹.

$\text{K}_2\text{S}_2\text{O}_8$ on the other hand, can also trap the photogenerated electron in conduction band resulting in formation of sulphate ion, a strong oxidizing agent. The decrease in rate of photodegradation above optimal concentration is due to the adsorption of the sulphate ions on the surface of the photocatalyst⁸.

Effect of NaCl and Na_2CO_3

Na_2CO_3 is mainly used in the dyeing bath in order to adjust the pH of the bath as it plays an important role in the fixing of the dye on the fabrics and in the fastness of the color and NaCl usually comes out in effluent along with sectional wastes in textile mills. Experiments were performed with Na_2CO_3 and NaCl, the rate of degradation was decreased with increasing carbonate and chloride ions. The decrease in the degradation of the dye in the presence of carbonate and chloride ions can be understood in the light of following hydroxyl scavenging reactions¹².



Effect of temperature

Influence of temperature was studied in the range 28 to 40°C. Rate constant was increased ($2.99 \times 10^{-4} \text{ s}^{-1}$ to $3.56 \times 10^{-4} \text{ s}^{-1}$) with the increase in temperature from 28-34°C. However further increase in temperature reduced the rate constant. Increase in temperature tend to reduce electron hole recombination, however an increase in temperature also decreases the solubility of oxygen in water¹³.

Effect of FeCl_3

The metal ions such as Fe^{3+} could be used as sensitizers during semiconductor photo catalytic degradation of organic pollutants. In present case, effect of FeCl_3 on the photodegradation of acridine orange has been studied by varying the concentration from $1.0 \times 10^{-6} \text{ mol dm}^{-3}$ to $13.0 \times 10^{-6} \text{ mol dm}^{-3}$. Addition of FeCl_3 causes an increase in rate constant

upto concentration $7.0 \times 10^{-6} \text{ mol dm}^{-3}$. Photoactivation of surface adsorbed complex ion ($\text{Fe}^{3+}\text{OH}^-$) resulted in the formation of $\text{Fe}^{2+}\text{OH}^-$ specie which injects electrons to the conduction band of BaCrO_4 . The rate of decolorization in case of FeCl_3 is also due to rapid scavenging of conduction band electrons by molecular oxygen leading to formation of superoxide and hydroperoxide radicals¹⁴⁻¹⁶.

However, above optimal concentration, rate constant was decreased on the addition of FeCl_3 . Higher concentration of FeCl_3 , eliminated the adsorption of cationic dye on the surface of BaCrO_4 and also inhibits the reaction rate by reducing the production of hydroxyl radicals^{17,14}.

Effect of dye concentration

The effect of dye concentration was investigated by varying the initial concentration from $1 \times 10^{-5} \text{ mol dm}^{-3}$ to $8 \times 10^{-3} \text{ mol dm}^{-3}$. The rate of degradation was found to increase up to a concentration $4 \times 10^{-5} \text{ mol dm}^{-3}$. This was due to the fact that more dye molecules was available in photoactive volume for the degradation processes. The rate of degradation was decreased with further increase in dye concentration. Above the optimal value due to excessive adsorption of dye on the catalyst surface hinders the competitive adsorption of OH^- ions and lowers the formation rate of hydroxyl radicals⁸.

COD and CO_2 measurement during dye degradation

COD values are related to the total concentration of organics in the solution¹³. After 7 hours of irradiation, COD values were decreased from 400 mg/L to 2 mg/L, while there was an increase in CO_2 values from 5.28 mg/L to 211.2 mg/L and inorganic ions.

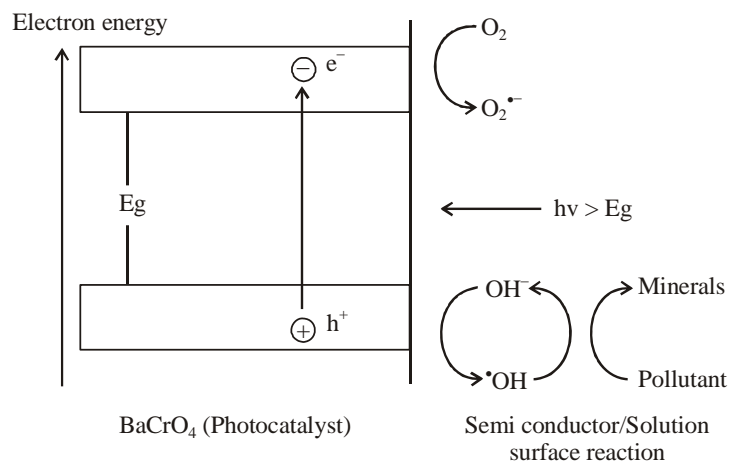


Fig. 1: Photocatalytic degradation of dye on the surface of the photocatalyst

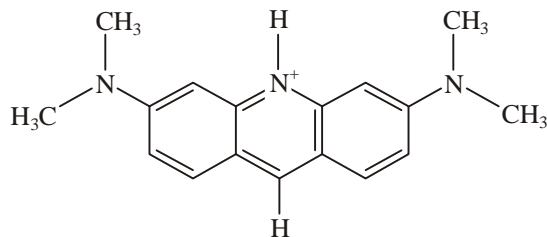


Fig. 2: Structure of dye

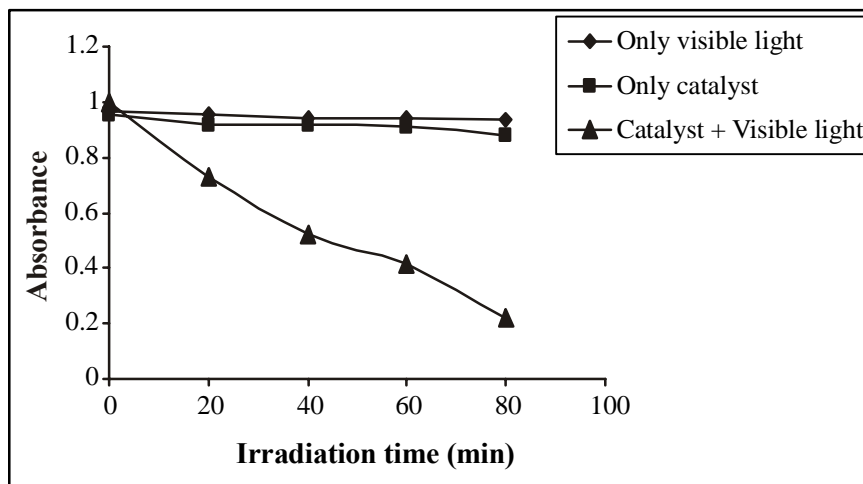
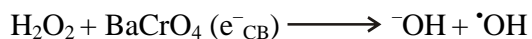
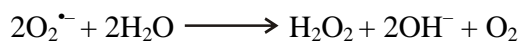
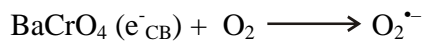
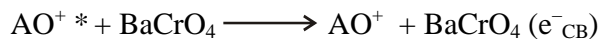
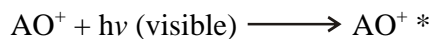
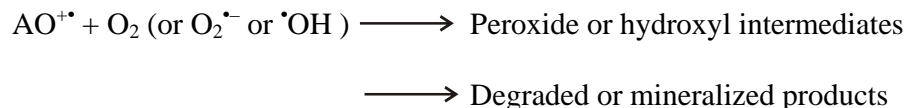


Fig. 3: Photocatalytic degradation of acridine orange dye only (♦) Visible light, (■) only BaCrO₄ (300 mg/100 mL) and (▲) Visible light + BaCrO₄.

MECHANISM

The mechanism of photosensitization approach for degradation of dye molecules on BaCrO₄ surface is shown as under:





The principle of photocatalytic degradation on the surface of the photocatalyst is shown in Fig. 1.

CONCLUSION

The photocatalytic activity of BaCrO₄ in photodegradation of acridine orange has been found to be quite efficient. The results of this research indicates that photodegradation of dye was considerably affected by various parameters such as catalyst loading, electron scavengers, pH, NaCl and Na₂CO₃, FeCl₃, substrate concentration. The degradation of dye was negligible when the reaction was carried out in the absence of photocatalyst and also in the absence of visible light. The value of COD and CO₂ confirmed the complete degradation of dye.

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