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Visible-light induced photocatalytic mineralization of methylene green dye using $BaCrO_4$ photocatalyst

Brijesh Pare*[,1], Vijendra Singh Solanki[2], Premlata Gupta[2] & S B Jonnalgadda[3]

[1]Department of Chemistry, Laboratory of Photocatalysis,
Madhav Science P G College, Ujjain 456 010, India
[2]Department of Chemistry, ISLE, IPS Academy, Indore 452 012, India
[3]University of Kwazu-natal, Westville, Durban, South Africa
E-mail: brijeshpare2009@hotmail.com, vijendrasingh0018@gmail.com, premlatagupta03@yahoo.co.in

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The photocatalytic degradation of a hazardous methylene green dye solution has been reported. The effects of various parameters such as catalyst loading, *p*H, initial concentration of the dye, concentration of H_2O_2 and $K_2S_2O_8$, concentration of NaCl and Na_2CO_3, N_2 and O_2 bubbling, and intensity of light on decolourization have been investigated. The photocatalytic removal of methylene green dye and its degradation efficiency has been evaluated by determination of reduction in the chemical oxygen demand (COD) from 440 mg/L to 5 mg/L and increase in CO_2 values from 9 mg/L to 212 mg/L in 7 h. A decrease in *p*H and increase in conductivity of solution is observed with increase in the extent of mineralization. The extent of decolourization has been discussed in terms of the Langmuir-Hinshelwood model. The rate of decolourization of dye is recorded with respect to the change in the intensity of absorption peak in visible region. The prominent peak at λ_{max}, i.e., 650 nm decreases gradually and finally disappears indicating that the dye is decolourized. Similarly the peak in the UV region at 300 nm decreases with the passage of time, thereby confirming the complete mineralization of the dye.

Keywords: Advanced oxidation process, $BaCrO_4$, Degradation, Photocatalysis, Methylene green

Colour is one of the most obvious indicators of water pollution and the discharge of highly coloured effluents containing dyes can be damaging to the receiving bodies. Dyes concentration in wastewaters is usually lower than any other chemical found in these wastewaters, but due to their strong colour they are visible even at very low concentrations, thus causing serious aesthetic and pollution problems in wastewater disposal. Furthermore, dyes represent about 50% of the worldwide production and correspond to an important source of contamination considering that approximately 15% of the synthetic textile dyes are lost in waste streams during manufacturing or processing[1]. Presently, the perilous effects of organic dyes to the environment are a particular concern. Conventional treatment methods, adsorptions for instance, are not always adequate and/or appropriate to remove organic dyes from wastewater streams in a large scale. Adsorption is a nondestructive method, which simply transfers dyes from one medium to another. In recent years, many researchers are interested in applying the 'photocatalytic decomposition process' to degrade the hard-to-biodegrade organic pollutants in industrial wastewater before discharge into mainstream water bodies[2].

Recently, there has been considerable interest in the utilization of advanced oxidation processes (AOPs) for the complete destruction of dyes. Heterogeneous photocatalysis, one of the advanced oxidation processes (AOPs), is a cost-effective treatment method for the removal of toxic pollutants from industrial waste water showing to its ability to convert these into safer end products such as CO_2, H_2O, and mineral acids[3]. Among various semiconductor photocatalysts, ZnO, CdS, BiOCl, and TiO_2 has been a leading photocatalyst for the treatment of organic pollutants in water and air due to its chemical stability, low cost, and nontoxicity[4]. In the recent 20 years, ZnO and TiO_2 has been the photocatalyst that is most extensively studied, and the applications of ZnO and TiO_2 and its modification to photocatalytic degradation of dyes have been extensively reported. Most of these semiconductor photocatalysts have a band gap in the ultraviolet UV region, i.e., equivalent to or larger than 3.2 eV and promote photocatalysis upon illumination with UV radiation. The limited amount of UV light in the sun's spectra around 7% stands as a big obstacle in the direct use of solar energy for photocatalytic decomposition of organic and inorganic pollutants[5]. Therefore, it is very important to develop visible light-sensitive photocatalyst, which can efficiently utilize inexpensive visible light. Very few catalysts are active under visible light, but their efficiency is very low due to fast charge recombination. Hence attempts have been made to search newer photocatalyst or to reduce that recombination time. Among these photocatalyst, $BaCrO_4$ (called hashemite) with bandgap of 2.6 eV is an attractive candidate for photocatalysis[6].

The aim of the present study is investigated the photocatalytic decolourization of methylene green dye over semiconductive, $BaCrO_4$ under visible light irradiation. In our study, various parameters such as catalyst dose, dye concentration, concentration of H_2O_2 and $K_2S_2O_8$, concentration of NaCl and Na_2CO_3, *p*H of the solution, N_2 and O_2 bubbling, and intensity of light, that may affect the degradation of methylene green in the presence of $BaCrO_4$ suspensions were analyzed to obtain a more complete knowledge of $BaCrO_4$ photocatalytic efficiency.

Experimental Section

Photocatalytic decolorization experiments were carried out in a slurry type batch reactor having pyrex glass vessel of dimension of 7.5 cm × 6 cm (height × diameter). The pyrex glass vessel equipped with magnetic stirrer was surrounded by thermostatic water circulation arrangement to keep temperature in the range of 30±0.3°C. A magnetic stirrer was used to ensure uniform mixing of solution in vessel. Prior to irradiation the dispersions were magnetically stirred in dark for 15 min to ensure the establishment of adsorption/desorption equilibrium. The intensity of visible light was measured by a digital lux-meter (Lutron LX-101). *p*H was constantly monitored. Experiments were performed at room temperature, with a constant lamp power of 500 W and a fixed distance between the photoreactor and the lamp housing (50 cm). The spectra were taken with UV-vis spectrophotometer (Systronics - 166).

Irradiation experiment

The photocatalyst was added to 100 mL of dye solution and the suspension was irradiated under visible light. At specific time intervals, aliquot (3 mL) was withdrawn and centrifuged for 2 min at rate of 3500 rpm to remove the $BaCrO_4$ particles in order to assess the extent of decolourization photometrically. Then absorption spectra of the dye solutions were recorded and rate of decolourization was observed in terms of change in intensity at λ_{max} of the dye. The decolourization efficiency (%) has been calculated as:

$$\text{Decolourization efficiency (\%)} = \{(C_0 - C)/C_0\} \times 100$$

where C_0 is the initial concentration of dye and C is the concentration of dye after photoirradiation[7].

For determining free CO_2, 100 mL sample taken in a conical flask was titrated again 0.05 mol dm^{-3} NaOH, with a few drops of phenolphthalein as indicator. Free CO_2 was calculated as: CO_2 (mg/L) = [(A× M) of NaOH × 1000 × 44]/amt. of sample (mL), where A= mL of NaOH[8].

Results and Discussion

Effect of catalyst loading

The amount of catalyst affects the reaction rate by providing the surface for the adsorption as well as generating oxidative valence band holes and electrons[9]. To determine the effect of catalyst loading on the reaction rate, experiments were also conducted at catalyst loading from 100 mg/100 mL to 400 mg/100 mL. Figure 1 shows the rate of decolourization of the methylene green dye increased from 1.23×10^{-4} s^{-1} to 3.18×10^{-4} s^{-1} with increase in photocatalyst concentration from 50 mg/100 mL to 200 mg/100 mL. Further increase in catalyst concentration from 200 mg/100 mL to 350 mg/100 mL resulted in decrease in rate constant up to 1.76×10^{-4} s^{-1} of photocatalytic reaction. Rate constant has been found to be maximal at 200 mg/100 mL of photocatalyst concentration. The results of effect of amount of $BaCrO_4$ on the rate of decolourization revealed that the value of rate constant increased

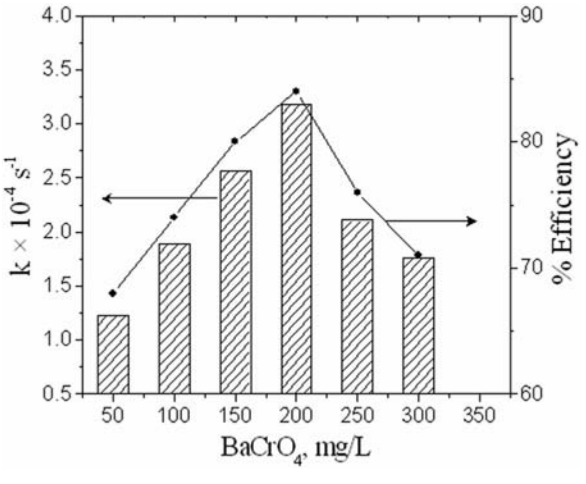

Fig 1 — Effect of catalyst loading: [MG] = 4.0×10^{-5} mol dm^{-3}, *p*H =11.0. Light intensity = 27×10^3 lux, Temperature = 30± 0.3°C.

with increase in the amount of $BaCrO_4$. This increase in the rate of decolourization might be attributed to an increase in the exposed surface area of semiconductor[10]. But after a certain limit, other factors came into play. At high concentrations, particles tend to aggregate which in turn reduced the interfacial area between the reaction solution and the photocatalyst. Thus, the number of active sites on the catalyst surface was decreased. The increase in opacity and light scattering by the particle might be the other reasons for the decrease in the decolourization rate at higher catalyst concentration[11].

Effect of substrate concentration

It was important both from mechanistic and from application point of view to study the dependence of photocatalytic reaction rate on the substrate concentration. It was noted that the degradation rate increased from 1.05×10^{-4} s^{-1} to 3.18×10^{-4} s^{-1} with the increase of dye concentration (from 1.0×10^{-5} mol dm^{-3} to 4.0×10^{-5} mol dm^{-3}) (Fig. 2). This increase was due to fact more dye molecules were available in photoactive volume for the photodegradation process. Further increase of the dye concentration led to a decrease in the degradation rate might be due to the fact that the color of the irradiating mixture became more and more intense which prevented the penetration of light to the surface of the catalyst. Hence, the generation of relative amount of $^{\bullet}OH$ radicals on the surface of the catalyst did not increase[12].

Effect of temperature

The influence of temperature was studied in the range 30-55°C. Rate constant was found to be increased from 3.18×10^{-4} s^{-1} to 3.70×10^{-4} s^{-1} with increase in temperature from 30-38°C. Further increase in temperature reduced the rate constant. Increased temperature tends to reduce electron-hole recombination[13]; however, an increase in temperature also decreases the solubility of oxygen in water[14]. The two above mentioned conflicting factors have been equipoised at 38°C.

Effect of *p*H

The *p*H value affects the oxidation of organic substances both directly and indirectly. Therefore, the role of initial *p*H on the degradation efficiency of methylene green was investigated in the *p*H range 4 to 13. It was observed that the degradation efficiency increased from 1.50×10^{-4} s^{-1} to 3.18×10^{-4} s^{-1} with increase in *p*H from 5.0 to 11.0. This observation can be explained on the basis that as the *p*H of solution increases, more OH^- ions are available. These OH^- ions will generate more $^{\bullet}OH$ radicals by combining with the positive holes of the semiconductor. These hydroxyl radicals are responsible for degradation of dye[15].

$$OH^-_{surface} + H^+ \; ^{\bullet}OH_{surface} \longrightarrow \qquad \text{... (1)}$$

On further increasing the pH value, the rate constant decreased up to 1.88×10^{-4} s^{-1}.

In the high basic medium, the rate of degradation was found to be decreased due to competition between the OH^- groups to attach to the active site of catalyst. The rate of attachment of OH^- groups thus decreased with a resultant decrease in formation of $^{\bullet}OH$ free radicals decreased[17] shown in (Fig. 3). The mode of formation of $^{\bullet}OH$ radical in acidic medium is different from the basic medium[16].

$$H_2O + h^+_{VB}\,^{\bullet} \longrightarrow OH + H^+ \qquad \text{... (2)}$$

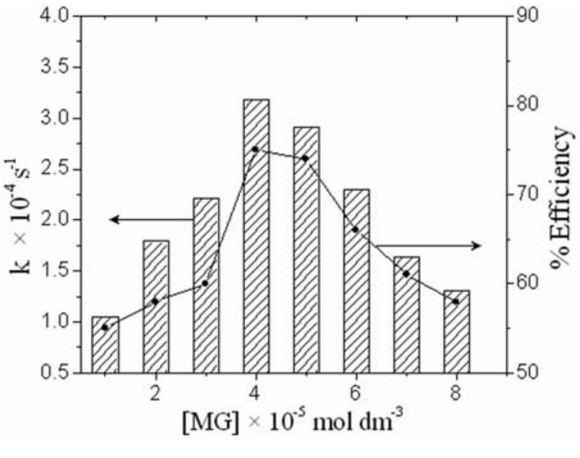

Fig. 2 — Effect of substrate concentration: $[BaCrO_4]$ = 200 mg/100 mL, *p*H = 11.0 Light intensity = 27×10^3 lux, Temperature = 30± 0.3°C.

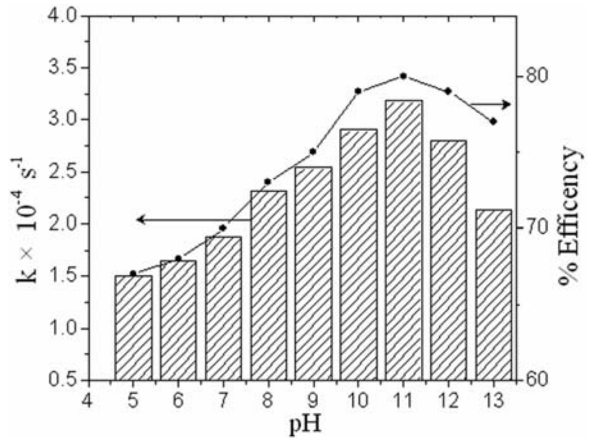

Fig. 3 — Effect of pH: [MG] = 4.0×10^{-5} mol dm^{-3}, $[BaCrO_4]$ = 200 mg/100 mL Light intensity = 27×10^3 lux, Temperature = 30± 0.3°C.

$$OH^{-}_{surface} + h^{+}_{VB}{}^{\bullet} \longrightarrow OH_{surface} \qquad \ldots (3)$$

Effect of H_2O_2 and $K_2S_2O_8$

Hydrogen peroxide has been widely known as a green oxidant due to the environmental friendly hydroxyl ($OH^{\bullet}$) radical produced during the reaction. The oxidant has a combined capacity as an oxidizing and reducing agent. It is used as an oxidizing agent to carry out bleaching in textile industries[17]. The values of rate constant increased from $3.18 \times 10^{-4}\ s^{-1}$ to $4.40 \times 10^{-4}\ s^{-1}$ with increase in oxidant concentration (from 1.0×10^{-4} mol dm^{-3} to 5.0×10^{-4} mol dm^{-3}). Further addition of H_2O_2 had a retarding effect on the degradation efficiency. This dual effect of H_2O_2 can be explained by the radical reaction mechanism. The added hydrogen peroxide inhibits the electron-hole recombination by accepting photogenerated electron from the conduction band of semiconductor and promotes charge separation and also forms $OH^{\bullet}$ radicals[18]. Production of additional hydroxyl radicals occurred when hydrogen peroxide was added through the following mechanisms:

Reaction with superoxide radical anion $O^{2\bullet-}$:

$$H_2O_2 + O^{2\bullet-} \longrightarrow HO^{\bullet} + HO^{-} + O_2 \qquad \ldots (4)$$

$$e^{-}_{CB} + H_2O_2 \longrightarrow HO^{\bullet} + OH^{-} \qquad \ldots (5)$$

Trapping of photogenerated electrons:

$$H_2O_2 + 2e^{-} \longrightarrow 2OH^{-} \qquad \ldots (6)$$

Self-decomposition by photolysis:

$$H_2O_2 + hv \longrightarrow 2HO^{\bullet} \qquad \ldots (7)$$

$$H_2O_2 + h^{+} \longrightarrow O_2 + 2H^{+} \qquad \ldots (8)$$

Excess H_2O_2 acts as hydroxyl radical or hole scavenger to form the perhydroxyl radical ($HO_2^{\bullet}$), which is a much weaker oxidant than hydroxyl radicals.

$$H_2O_2 + HO^{\bullet} \longrightarrow H_2O + {}^{\bullet}HO_2 \qquad \ldots (9)$$

$$HO_2 + HO^{\bullet} \longrightarrow H_2O + O_2 \qquad \ldots (10)$$

Similar to hydrogen peroxide, potassium peroxydisulphate or popularly known as persulphate is widely used in-situ in treatment of groundwater. It has recently gained large popularity due to its higher oxidizing capacity applicability in wider range of *p*H[19]. The values of rate constant increased from $3.18 \times 10^{-4}\ s^{-1}$ to $4.11 \times 10^{-4}\ s^{-1}$ with increase in oxidant concentration from 1.0×10^{-4} mol dm^{-3} to 5.0×10^{-4} mol dm^{-3}. Further addition of $K_2S_2O_8$ the rate of decolourization decreased up to $2.33 \times 10^{-4}\ s^{-1}$ (Fig. 4). Addition of persulphate to photocatalytic processes enhanced the decolourization rate by the following ways: (i) Persulphate ion scavenges the conduction band electron and promotes the charge separation and production of other oxidizing species namely sulphate radical anion [Eq. (11)].

$$S_2O_8^{2-} + e^{-}_{CB} \longrightarrow SO_4^{2-\bullet} + SO_4^{2-} \qquad \ldots (11)$$

(ii) $S_2O_8^{2-}$ can generate sulphate radical anion ($SO_4^{\bullet-}$) both thermally and photolytically in aqueous solution. This radical anion is a strong oxidant and participates in the degradation processes by the following ways:

$$SO_4^{\bullet-} + e^{-}_{(CB)} \longrightarrow SO_4^{2}- . \qquad \ldots (12)$$

$$SO_4^{\bullet-} + H_2O \longrightarrow SO_4^{2-} + {}^{\cdot}OH + H^{+} \qquad \ldots (13)$$

$$SO_4^{\bullet-} + MG \longrightarrow SO_4^{2-} + \text{dye intermediates} \qquad \ldots (14)$$

$$SO_4^{\bullet-} + \text{dye intermediates} \longrightarrow \text{mineralization} \qquad \ldots (15)$$

(iii) At high dosage of $S_2O_8^{2-}$ the inhibition of reaction occured might be due to the increase in concentration of SO_4^{2-} ion. The excess of SO_4^{2-} ion got adsorbed on the $BaCrO_4$ surface and reduced the catalytic activity. The adsorbed SO_4^{2-} ion also reacted with photogenerated holes [Eq. (16)] and with hydroxyl radicals [Eq. (17)].

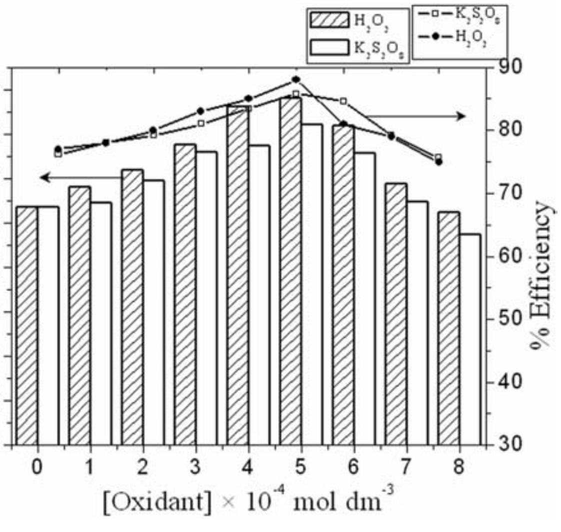

Fig. 4 — Effect of oxidant: [MG] = 4.0×10^{-5} mol dm^{-3}, *p*H =11.0 [$BaCrO_4$] = 200 mg/100 mL, Light intensity = 27×10^{3} lux Temperature = 30± 0.3°C.

$$SO_4 + h^+ \longrightarrow SO_4^{\bullet}- . \qquad ... (16)$$

$$SO_4^{2-} + {}^{\bullet}OH \longrightarrow SO_4^{\bullet -} + OH- \qquad ... (17)$$

Since $SO_4^{\bullet -}$ is less reactive than ${}^{\bullet}OH$ radical and h^+, the excess SO_4^{2-} reduced the photodegradation of the dye[20].

Effect of light intensity

Light intensity plays an important role in activating the suspended photocatalysts. The influence of light intensity on the rate of degradation has been examined at constant dye concentration (4.0 × 10^{-5} mol dm^{-3}) and catalyst loading (200 mg/100 mL). The rate constant values found to be increased from 1.90 × 10^{-4} s^{-1} to 4.66 × 10^{-4} s^{-1} on increasing light intensity from 12 × 10^3 lux to 56 × 10^3 lux. This is because at higher intensity electron hole separation competes with electron hole recombination and results high reaction rate[21].

Effect of Na_2CO_3 and NaCl

The waste water from dyeing operations normally contains considerable amount of carbonate ions as sodium carbonate is the common auxiliary chemical used in textile processing operations for adjusting the *p*H of the dye bath. Therefore it was important to study the influence of carbonate ion on the treatment efficiency. Sodium chloride also usually comes out in the effluent from textile mills as the dyeing process often requires high concentrations of sodium chloride for the transfer of dyestuff to the fabric. The study of the influence of NaCl is important in photocatalysis, because the NaCl might reduce reaction rates by poisoning the $BaCrO_4$ active sites or by scavenging radicals via the chloride ion[22]. The degradation percentage of the dye gradually decreased from 3.18 × 10^{-4} s^{-1} to 1.44 × 10^{-4} s^{-1} with increasing carbonate ion concentration. This is due to the hydroxyl scavenging property of carbonate ion, which can be accounted from the following [Eq. (18)].

$$OH + CO_3^{\,2-} \longrightarrow OH^- + CO_3^{\,2\bullet -} \qquad ... (18)$$

$$OH + HCO_3 \longrightarrow H_2O + CO_3^{\bullet} - \qquad ...(19)$$

Thus the free hydroxyl radical which is a primary source for the photocatalytic degradation decreases gradually with increase in the carbonate ion concentration resulting in the ultimate decrease in the percentage degradation of the dye significantly. Similarly, the results of the studies carried out with the addition of NaCl revealed that the degradation percentage of the dye decreased from 3.18 × 10^{-4} s^{-1} to 1.80 × 10^{-4} s^{-1} with increase in the amount of chloride ion. In the presence of NaCl the Cl^- ions migrate to the surface of $BaCrO_4$ and scavenge for h^+ and ${}^{\bullet}OH$.

$$Cl^- + OH^{\bullet} \longrightarrow Cl^{\bullet} + OH^- \qquad ... (20)$$

$$Cl^- + h^+ \longrightarrow Cl^{\bullet} \qquad ... (21)$$

$$Cl^{\bullet} + Cl^- \longrightarrow Cl_2^{\bullet -} \qquad ... (22)$$

$$Cl_2^{\bullet -} + dye \longrightarrow dye^{\bullet +} + 2Cl^- \qquad ... (23)$$

$$dye^{\bullet -} + O_2 \longrightarrow \text{oxidation product} \qquad ... (24)$$

The $Cl_2^{\bullet\,-}$ formed is capable of oxidizing the organic compounds, but at a lower rate than $OH^{\bullet}$ radicals. In the presence of O_2, $dye^{\bullet -}$ is further oxidized into lower molecular weight organics and carbon dioxide [23] as shown in [Eq. (24)].

Effect of bubbling of N_2 and O_2

Gases present in a real aqueous sample play an important role in the degradation of dissolved organic pollutants. The degradation of methylene green decreased from 3.18 × 10^{-4} s^{-1} to 2.40 × 10^{-4} s^{-1} by bubbling of pure N_2 but increased rapidly from 3.18 × 10^{-4} s^{-1} to 4.93 × 10^{-4} s^{-1} on bubbling oxygen through the dye solution (Fig. 5). Dissolved oxygen

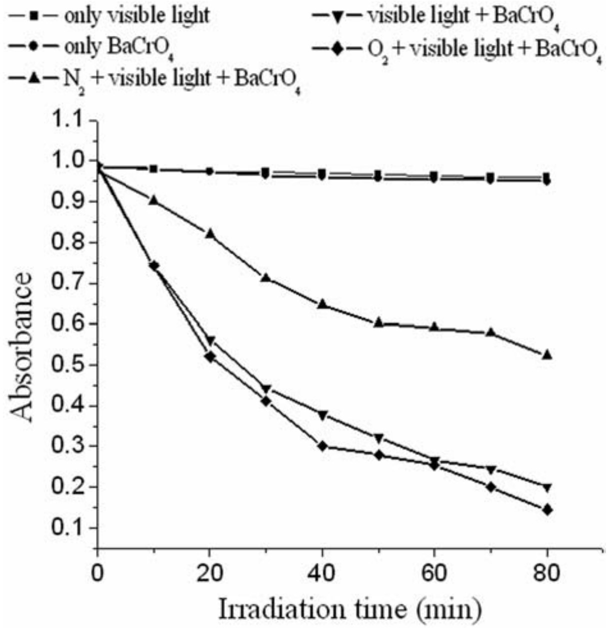

Fig. 5 — Decolorization of Methylene green under various photocatalytic systems: [MG] = 4.0 × 10^{-5} mol dm^{-3}, [$BaCrO_4$] = 200 mg/100 mL Light intensity = 27 × 10^3 lux, *p*H = 11.0, Temperature = 30± 0.3°C.

Table 1 — COD and free CO_2 measurement during photodegradation process: {[MG] = 4×10^{-5} mol dm^{-3}, [$BaCrO_4$] = 200 mg/100 mL, *p*H = 11.0, light intensity = 27×10^3 lux, temperature = 30± 0.3°C.}

Time (h)	COD (mg/L)	CO_2 (mg/L)	Efficiency (%)	NO_3^- (mg/L)	SO_4^{2-} (mg/L)	*p*H	Conductivity (mS/cm)
0	440	6.0	0	0	0	7.1	0.102
1	330	22.2	25	3.0	2.0	5.9	0.112
2	261	51.0	40	4.7	5.0	5.2	0.132
3	210	67.5	52	8.0	7.5	4.4	0.154
4	145	90.5	67	15.0	11.4	3.7	0.161
5	77	119	82	24.1	18.0	3.2	0.190
6	34	165	92	27.0	23.0	2.9	0.245
7	5	212	98	31.1	28.2	2.6	0.298

trapped the conduction band electron by forming superoxide ions ($O_2^{-\cdot}$) and thus preventing the electron-hole recombination and at the same time H_2O_2 was formed $HO^\bullet$ radicals from $O_2^{-\bullet}$(Ref.24).

No degradation was observed in the presence of only visible light. However, in the presence of $BaCrO_4$ without irradiation, a slight decrease in absorbance was observed which may be due the adsorption of the dye on to the surface of $BaCrO_4$.

$$O_2 + e^- \longrightarrow O_2^{-\bullet} \quad . \qquad \text{... (25)}$$

$$O_2^{\bullet -} + H_2O_2 \longrightarrow HO^\bullet + HO + O_2 \qquad \text{... (26)}$$

Spectral study

A typical time-dependent UV-vis spectrum of methylene green dye during photo irradiation with $BaCrO_4$ was observed. The rate of decolorization of dye was recorded with respect to the change in the intensity of absorption peak in visible region. The prominent peak at λ_{max}, i.e., 650 nm got decreased gradually and finally disappeared indicating that the dye got decolorized. Similarly the peak in the UV region at 300 nm got decreased with the passage of time, thereby confirming the complete mineralization of the dye.

Kinetic study

The photocatalytic degradation of methylene green dye followed pseudo first order kinetics. The detection was realized at 650 nm. The absorbance of methylene green dye decreased with an increase in irradiation time. The plot of log absorbance versus time followed pseudo first order kinetics with correlation co-efficient of 0.97, rate constant of 3.18×10^{-4} s^{-1} and half life time of 2.17×10^3 s.

Chemical oxygen demand (COD) and free CO_2 measurement during photo degradation process

The chemical oxygen demand test is widely used as an effective technique to measure the organic strength of wastewater. 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 methylene green dye solution. The open reflux method was applied for COD determination and the treated solution showed a significant decrease in the COD value of the initial colour solution from 440 to 5 mg/L while there was an increased in CO_2 values from 6 mg/L to 212 mg/L and inorganic ions. A decrease in *p*H and increase in concentrations of NO_3^- & SO_4^{2-} and conductivity of solution was also conformed the complete mineralization of methylene green (Table 1). The photodegradation efficiency was found to be 98.0%.

Conclusion

It has been observed that photocatalysis using $BaCrO_4$ as photocatalyst could be an effective technique for the degradation of methylene green dye in aqueous solutions. It is found that the solution *p*H, catalyst dosage, initial dye concentration, light intensity, presence of oxidants (H_2O_2 and $K_2S_2O_8$) and the presence of anions can affect the photocatalytic performance greatly. The reduction in the estimated COD value and increase in CO_2 value indicated the photodegradation of treated dye solution. Also the peaks in the UV region at got decreased with the passage of time, thereby confirming the complete mineralization of the dye. Methylene green dye was degraded about 98% under visible light over $BaCrO_4$ in 60 min. The degradation result could be related to the high surface area of the catalyst. The catalytic processes can be suitably and cost effectively employed for the removal of pollutants from wastewaters in a short period of time.

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