

BaCrO₄ assisted visible light induced advanced oxidation process for mineralizing Azur B

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The photocatalyst BaCrO₄ has been utilized to photocatalytically degrade Azur B in presence of visible light. The disappearance of the dye has been monitored spectrophotometrically, followed pseudo-first order kinetics, according to the Langmuir-Hinshelwood model. The total degradation of dye was tested by determining the chemical oxygen demand. To optimize the reaction condition, the effects of various parameters like amount of semiconductor, pH, light intensity, dye concentration, oxidants such as H₂O₂ and K₂S₂O₈, electron acceptors like NaCl and Na₂CO₃, on the rate of photodegradation have been investigated. Both NaCl and Na₂CO₃ are found to retard the rate of photocatalytic degradation, whereas increase in the initial concentration of both H₂O₂ and K₂S₂O₈ increases the degradation rate. The degradation efficiency was found to be the substantially high at around neutral pH values. The complete degradation of the dye has been confirmed using UV spectrum analysis. A pertinent mechanism for the photocatalytic degradation has also been proposed.

Keywords: Photochemistry, Photocatalysis, Degradation, Advanced oxidation process

Toxic and coloured effluents from industries have always been a matter of serious concern for the environment and consequently much attention has been drawn towards the removal of these harmful contaminants from wastewater¹. Dyes are difficult to decompose biologically as well as chemically. Physicochemical processes only transfer pollutant from one phase to another². Therefore, recently there has been considerable interest in the utilization of advanced oxidation process (AOPs) for the complete destruction of dyes. Efficiency AOPs are based on hydroxyl radicals which are the precursors to oxidize a broad range of organic pollutants fast and non-selectively. AOPs include photocatalysis systems such as a combination of semiconductor and light

and semiconductor and oxidants³. The hydroxyl radical species possesses a higher oxidation potential (2.80 V) as compared to other common oxidants like atomic oxygen (2.42 V), O₃ (2.07 V), H₂O₂ (1.78 V), hydroperoxy radicals (1.70 V) and chlorine dioxide (1.57 V). Often oxidants such as hydrogen peroxide, persulphate, ozone and Fenton reagent are also used in conjunction with UV/visible radiations to accelerate the rate of degradation of the pollutants. Thus, the hybrid AOPs which involve a combination of two or more techniques, aim to synergistically produce more hydroxyl radicals to effectively degrade the pollutants⁴.

Wide band gap metal oxide semiconductors photocatalysts such as TiO₂, ZnO, WO₃, SrTiO₃ and hematite-FeO₃² are attractive candidates for the removal of pollutants in water as they are capable of acting as catalyst upon exposure to light radiation to degrade the harmful organic contaminants into harmless mineral acids⁵. The development of new photocatalytic systems, which are active in a wide range of visible light, has become indispensable for the commercialization of photocatalysts⁶.

We report herein, a new, single phase BaCrO₄ material with *d*⁰ electronic configuration. BaCrO₄ with barite structure has so far been studied mainly for ecological system and photocatalytic H₂ generation from water⁷. The band gap⁸ of BaCrO₄ is 2.63 eV. BaCrO₄ (also called hashemite) is a naturally occurring chromate analog of barite. It has often been used as an oxidizing agent and as a catalyst for enhancing vapour-phase oxidation reactions⁹. Moreover, owing to its excellent photophysical and photocatalytic properties, barium chromate is a highly efficient photocatalyst, with a particularly marked response to visible-light irradiation⁷. Recently, BaCrO₄ has been reported in the case of visible light assisted photocatalytic degradation of methylene blue^{10,11}. Therefore, from the view point of utilization of a safe and cost effective photocatalyst in the visible region, BaCrO₄ has been considered for the present study.

Experimental

Azur B dye was obtained from CDH laboratory (India). The photocatalyst BaCrO₄ was obtained from Qualigen Fine Chemicals (99 % pure with surface

area of 10 m²/g) H₂O₂ (30 % aqueous), FeCl₃, NaCl and Na₂CO₃ were of analytical grade and used without further purification. All the solutions were prepared in doubly distilled water. The photocatalytic and photolytic experiments were carried out in a slurry type batch reactor having pyrex vessel of dimension of 7.5 cm × 6 cm (height × dia.). The pyrex glass vessel equipped with magnetic stirrer was surrounded by thermostatic water circulation arrangement to keep the temperature at 30±0.3 °C. The irradiation was carried out using 500 W halogen lamps (Philips India) surrounded with aluminum reflectors in order to avoid loss of irradiation.

The BaCrO₄ catalyst was stirred for half an hour in dark to establish equilibrium between adsorption and desorption phenomenon of dye molecule on the surface of photocatalyst. Reaction system was stirred magnetically with simultaneous exposure to visible light. At specific time intervals, aliquots (3 mL) were withdrawn and centrifuged at the rate of 3500 rpm. The changes in absorption spectra were recorded at λ_{max} on a Vis spectrophotometer (Systronics 166). The pH was constantly monitored and not adjusted unless otherwise stated. The COD and CO₂ estimation were performed by literature methods¹². The efficiency of the photocatalytic process was investigated as follows: % Efficiency = {(C₀ - C) / C₀} × 100; X COD = C / C₀, where C and C₀ are initial and final dye concentrations.

For determining free CO₂, 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 CO₂ was calculated as: CO₂ (mg/L) = [(A × M) of NaOH × 1000 × 44] / amt. of sample (ml), where A = ml titrant for sample, and M = Molarity of NaOH^{13,14}.

While working with BaCrO₄ as photocatalyst, the analysis of OH· radical formation under visible irradiation was done by fluorescence method using terephthalic acid. This reagent readily reacted with OH· radicals to produce highly fluorescent product, 2-hydroxyterephthalic acid¹⁵.

Results and discussion

The effect of catalyst loading on the selected dye was studied. The rate of degradation of the Azur B dye increased with the increase in catalyst concentration from 100 mg/ 100 mL to 250 mg/ 100 mL. Further increase in catalyst concentration resulted in decrease in rate constant of photocatalytic reaction. This indicates that beyond this optimum catalyst

concentration, other factors affect the degradation of dyes. At high concentrations, the particles aggregate, which in turn reduces the interfacial area between the reaction solution and the photocatalyst. Thus, the number of active sites on the catalyst surface is decreased. The increase in opacity and light scattering by the particle may be the other reasons for the decrease in the degradation rate at higher catalyst concentration^{16,17}.

In order to enhance the degradation efficiency of the organic molecules by the photocatalytic system, use of inorganic oxidants such as H₂O₂ and K₂S₂O₈ is quite prevalent. These oxidants often increase the quantum efficiency either by inhibiting electron-hole pair recombination through scavenging conduction band electrons at the surface of the photocatalyst, or, by offering additional oxygen atoms as an electron acceptor to form the superoxide radical ion (O₂^{·-})¹⁸. In the present investigation on increase in H₂O₂ concentration from 1.0 × 10⁻⁴ mol dm⁻³ to 5.0 × 10⁻⁴ mol dm⁻³, the rate constant values increased from 3.3 × 10⁻⁴ s⁻¹ to 4.1 × 10⁻⁴ s⁻¹. Further increase in H₂O₂ concentration resulted in decrease in degradation rate. Although H₂O₂ is a mild oxidant, after an increase in its concentration to an optimum level it started decreasing the photodegradation rate. This peculiar behavior might probably be due to the scavenging effect of H₂O₂ thus reducing the production of ·OH in the solution¹⁹.



Similar results have been obtained in the case of another oxidant, K₂S₂O₈. The degradation rate of Azur B was found to be maximal at 5.0 × 10⁻⁴ mol dm⁻³ of K₂S₂O₈. K₂S₂O₈ is reported to trap the photogenerated conduction band electron to produce sulphate ion with standard reduction potential = 2.6 eV. The decrease in rate of photodegradation above optimal concentration (5.0 × 10⁻⁵ mol dm⁻³) may be due to the adsorption of sulphate ions on surface of BaCrO₄ formed during the course of the reaction²⁰⁻²².

The effect of dye concentration on the degradation rate was studied at different concentrations of Azure B varying from 1.0 × 10⁻⁴ mol dm⁻³ to 7.0 × 10⁻⁴ mol dm⁻³. The rate constant (k) for the degradation of Azur B first increased with the increase in substrate concentration and reached highest efficiency at the concentration of 5.0 × 10⁻⁴ mol dm⁻³. This may be

explained on the basis of the fact that the reaction rate accelerates as more molecules of dye were available for oxidation²³. On further increase in the dye concentration beyond of $5.0 \times 10^{-4} \text{ mol dm}^{-3}$ the degradation rate was found to decreased. This phenomenon is quite expected in the case of heterogeneous systems. The decrease in degradation rate may be attributed to the following: (i) As dye concentration increased, number of photons reaching to the catalyst surface decreased, resulting in lesser number of catalyst molecules to undergo excitation, and hence, rate of formation of holes, hydroxyl radicals and supra oxide ($\text{O}^{\cdot-}$) ions decreased, decreasing the rate of degradation; (ii) since the catalyst surface area is fixed, with increase in concentration of dye the rate of degradation decreases because only a limited number of dye molecules can attach to the active site of catalyst. The remaining dye molecules remain in the solution until the earlier attached molecules are degraded; the number of active sites of catalyst also decreases due to less availability of photons for excitation of catalyst molecules; (iii) higher concentration, number of dye molecules are high and there will be more competition for attachment to active site of catalyst between dye molecules, resulting in reduction the rate of degradation²⁴.

Textile industries effluents invariably have a wide range of $p\text{H}$ values and the generation of hydroxyl radicals is also a function of $p\text{H}$. Thus, $p\text{H}$ plays an important role both in the characteristics of textile wastes and generation of hydroxyl radicals. Therefore, the present photodegradation process was examined at $p\text{H}$ values ranging from 4 to 10. Rate of degradation was very low at high acidic $p\text{H}$. When $p\text{H}$ of the reaction slurry was increased, rate of degradation also increased till the at $p\text{H}$ reached to 8.0. On further increasing the $p\text{H}$ value, the rate of degradation started decreasing. On increasing the $p\text{H}$ above 4, the increases in reaction rate may be due to the preferential adsorption of H^+ ions on the photocatalyst surface as compared to the cationic dye molecule. In the basic medium, the rate of degradation was found to decrease due to competition between the OH^- groups to attach to the active site of catalyst. The rate of attachment of OH^- groups thus decreases with a resultant decrease in formation of OH^{\cdot} free radicals decreased²⁵.

Dyeing is normally carried out in a neutral or slightly alkaline dye bath at or near boiling point with addition of either sodium chloride or sodium

carbonate. In view of this the effect of presence of NaCl and Na_2CO_3 was studied. The photocatalytic degradation rate decreased with the increase in Cl^- and CO_3^{2-} concentration from $1.0 \times 10^{-4} \text{ mol dm}^{-3}$ to $7.0 \times 10^{-4} \text{ mol dm}^{-3}$. The cause of inhibition may be the ability of these ions to act as hydroxyl radical (OH^{\cdot}) scavengers. The proposed mechanism of hydroxyl radical scavenging²⁶⁻²⁸ is given by Eqs (4) – (7).



The influence of light intensity on the rate of degradation has been studied at constant dye concentration ($5.0 \times 10^{-5} \text{ mol dm}^{-3}$) and catalyst loading (250 mg/100 mL). The rate constant values was found to increase from $1.53 \times 10^{-4} \text{ s}^{-1}$ to $2.34 \times 10^{-4} \text{ s}^{-1}$ on increasing the light intensity from $13 \times 10^3 \text{ lux}$ to $70 \times 10^3 \text{ lux}$. This is because at higher intensity, electron hole separation competes with electron hole recombination resulting in a high reaction rate^{29,30}.

Figure 1 shows a typical time-dependent UV–vis spectrum of Azur B dye during photoirradiation with BaCrO_4 . 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., 640 nm decreases gradually and finally disappears indicating that the dye has been decolorized. Similarly, the peak in the UV region at 288 nm decreases with time, thereby confirming the complete mineralization of the dye.

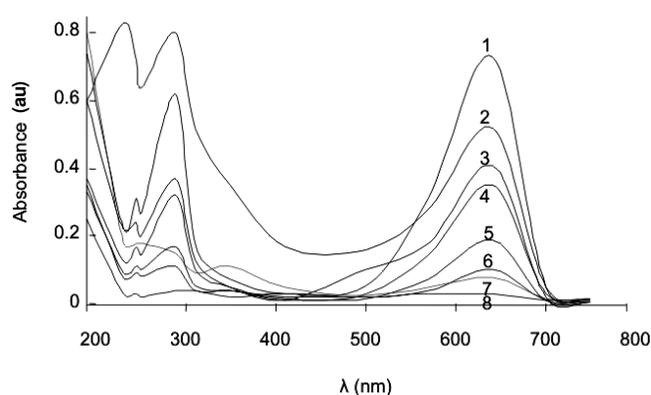


Fig. 1—Time dependent UV-visible absorption spectra depicting decolorization and complete degradation of Azur B using BaCrO_4 . [1, 0 min; 2, 10 min; 3, 20 min; 4, 30 min; 5, 40 min; 6, 50 min; 7, 60 min; 8, 70 min].

Both BaCrO_4 and visible light source are necessary for the photodegradation reaction to occur. A control experiment was conducted by irradiating the dye Azur B under only visible light in the presence of BaCrO_4 , with and without visible irradiation over a period of 90 min. 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 . However, on irradiating the dye with BaCrO_4 in aqueous slurry, about 95 % of the dye got decolorized within 90 min as shown in Fig. 2.

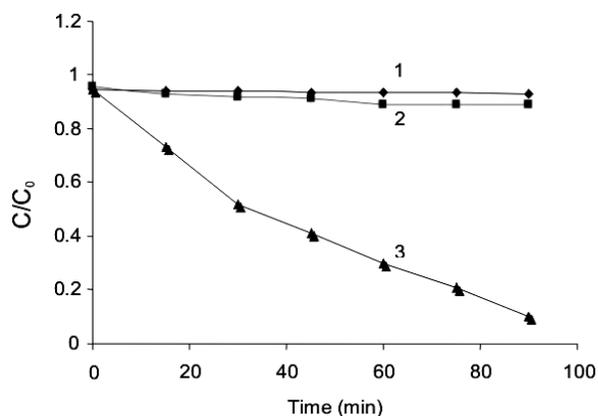
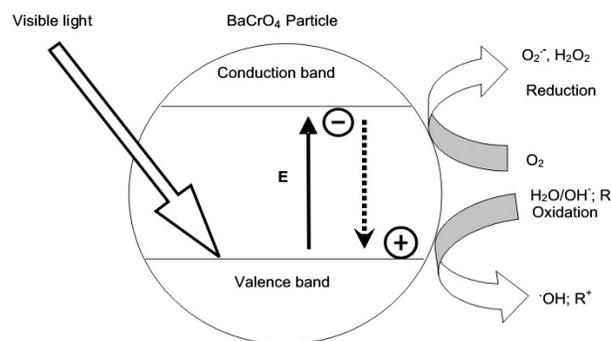


Fig. 2—Photocatalytic degradation of Azur B dye with: (1) (◆) only visible light; (2) (■) only BaCrO_4 (250 mg/ 100 ml); (3) (▲) visible light + BaCrO_4 .

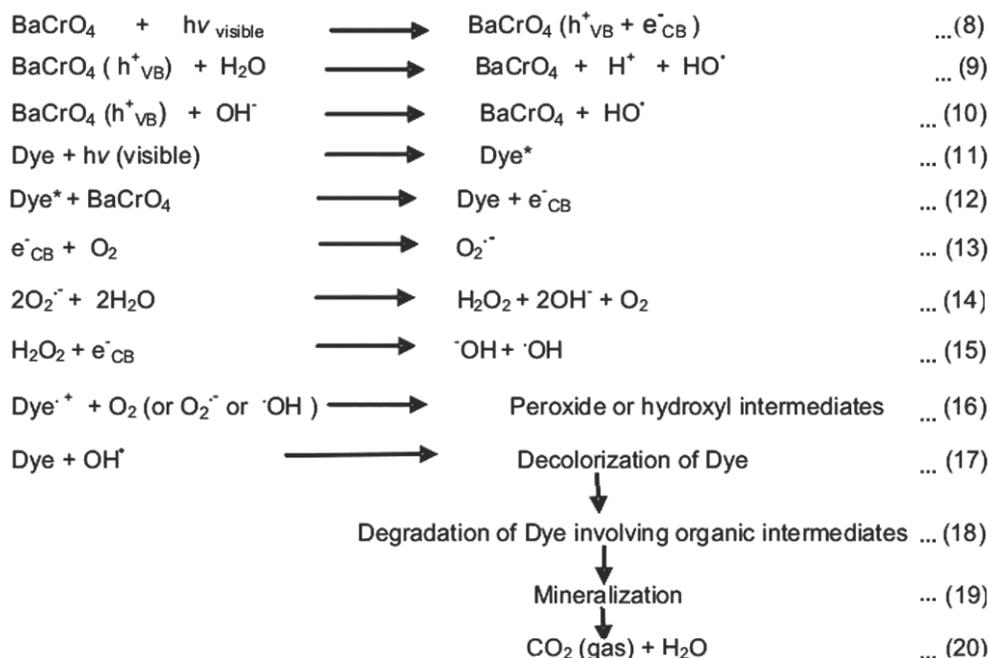
When photocatalyst BaCrO_4 was illuminated with visible radiation, electron/hole pairs with free electrons were produced in the nearby free conduction band leaving positive holes in valence band as depicted in Scheme 1.

The principle of photosensitized degradation on the semiconductor particle is illustrated in Scheme 1.

The holes at the BaCrO_4 valence band can oxidize the adsorbed water molecules and hydroxide radicals to produce hydroxyl radicals that are very strong oxidizing agents. Further, the dye molecule is itself known to act as a sensitizer therefore, on absorption of visible light they can transfer photogenerated electrons from the dye molecule to semiconductor^{31,32}. On the basis of the above mechanism of photosensitization for degrading dye molecules on BaCrO_4 surface may be best explained as given in Scheme 2.



Scheme 1



Scheme 2

Table 1—COD and CO₂ estimation at different intervals of time under optimum reaction conditions: {[Azur B] = 5 × 10⁻⁵ mol; [BaCrO₄] = 250 mg/100 ml; irradiation intensity = 27 × 10³ lux}

Time (h)	COD (mg/L)	CO ₂ (mg/L)	Efficiency (%)	pH	Cond. (mS/cm)
0	340	3.9	0	8.0	0.120
1	260	8.8	23	7.3	0.211
2	180	26.4	47	7.0	0.321
3	24	35.2	92	5.9	0.399
4	18	44	94	5.1	0.489
5	6	61.6	98	4.2	0.587

Photodegradation process is precursor to mineralization in most of the AOPs. COD and free CO₂ were determined to study the extent of mineralization of the organic molecule under consideration over BaCrO₄ suspension (Table 1). COD allows measurements of waste in terms of the total quantity of oxygen required for the degradation of organic matter to CO₂ and inorganic ions. After 5 hours of irradiation, COD values decreased from 260 mg/L to 6 mg/L, while there was an increase in CO₂ values. Decrease in pH and increase in conductivity of solution was observed with increase in the extent of degradation.

In the present study, a photocatalyst that works well in absence of UV has been obtained. The experimental findings revealed that BaCrO₄ is a suitable photocatalyst with visible irradiation for the removal of colored wastewater from textile industries. The photocatalytic efficiency of the process can be effectively improved utilizing oxidizing agents such as H₂O₂ and K₂S₂O₈, while the additives used during dyeing processes such as NaCl and Na₂CO₃ have been found to retard the rate of photocatalytic degradation. By pH optimization the process efficiency can be enhanced by manifolds. The COD values and UV spectra confirm the complete degradation of the dye Azur B. Hence, the photodegradation of dye employing artificial visible light with BaCrO₄ as photocatalyst has emerged as an effective and viable method.

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