

Undoped, single phase barite BaCrO₄ photocatalyst for the degradation of methylene blue under visible light

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Received 26 February 2009;
re-revised and accepted 23 December 2009

The photoassisted degradation of a phenothiazine dye, methylene blue, has been examined in aqueous dispersions under visible irradiation at wavelengths greater than 400 nm with BaCrO₄ and bare TiO₂. Spectral changes during the photocatalytic degradation of methylene blue suggest that the de-methylation is an initiation process of photocatalysis reaction followed by ring opening and finally mineralisation into mineral acid and water. Comparative study shows that BaCrO₄ is a better photocatalyst than bare TiO₂ under visible light irradiation. COD analysis suggests that the degradation of methylene blue is due to photocatalysis and not due to any other reason. Catalytic poisoning is observed for both the photocatalysts.

Keywords: Photocatalysis, Degradations, Dyes, Phenothiazines, Barite, Titania, Methylene blue, Organic pollutants

IPC Code: Int. Cl.⁹ B01J21/00; C09B

Today's highly industrialized environment is charged with a multitude of potentially toxic agents, inorganic as well as organic. It is thus of interest to develop novel and cost-effective technologies to treat polluted water. Dye pollutants from the textile and photographic industry are a principal source of environmental contamination. Textile dyes are of environmental interest because of their widespread use, potential to form toxic aromatic amines and low removal rate during aerobic waste treatment. Colour removal from textile waste water has been a matter of considerable interest during the last two decades, not only because of the potential toxicity of certain dyes but also due to their visibility in receiving waters. Estimates indicate that approximately 15% of the synthetic textiles dyes used flow into waste streams during the manufacturing or processing operations. Furthermore, some azo dyes, their precursors and a

number of their reaction products are carcinogenic. Therefore, the treatment of effluents containing these compounds are important for the protection of natural water. Indeed, dyes are designed to have a good fastness under typical usage conditions and thus, are resistant to microbial attack. Therefore, these waste waters cannot be treated easily and require expensive methods.

Chemical oxidation methods (advanced oxidation technology) are capable of almost complete mineralisation of organic pollutants and are effective for a wide range of pollutants as compared to other conventional methods. It is difficult to successfully treat dye wastewater using traditional biological process. Dyes are indeed refractory to microbial degradation because of their substitutional groups such as azo, nitro or sulpho group. In recent years there has been active interest in finding better ways to degrade these recalcitrant compounds. Over the last 30 years, the studies on semiconductor photocatalysts for clean hydrogen energy production and environment decontamination have attracted much interest¹⁻⁴. From the viewpoint of utilization of solar energy, extensive research has been carried out on visible light sensitive photocatalysts⁵⁻⁸. In an attempt to develop visible light sensitive photocatalysts, researchers have tried some anion-substituted metal oxide semiconductors⁹⁻¹⁵ as well as some transition metal-doped metal oxides semiconductors¹⁶⁻²¹ which are used for the degradation of dyes. More recently, there are reports on single phase metal oxides that are active under visible light for photocatalytic applications. Such samples usually contain metal ion having nd^0 valence configuration and sometimes nd^{10} or ns^2 valence configuration. Generally, single phase photocatalysts are more stable than doped photocatalysts. On the other hand, these compounds possess fewer defects and electron holes recombination centers, which would be more effective for carrier separation and migration and thus be a better photocatalyst. Though many visible light sensitive photocatalyst have been developed, there are very few materials that can remove organic contaminants in aqueous and in air media. The development of visible light responsive photocatalyst is necessary in order to utilize the solar energy effectively.

We report herein, a new single phase BaCrO_4 material with d^0 valence electronic configuration instead of doped material which shows response to visible light irradiation and acts as a photocatalyst to eliminate hazardous dyes. Methylene blue has been selected a refractory model compound in this oxidation process. BaCrO_4 with barite structure has been studied mainly for its effect on the ecological system and photocatalytic H_2 generation from water²²⁻²⁴. However, the photocatalytic property for degradation of organic pollutants has not been reported. The photocatalytic degradation of methylene blue has been reported herein.

Experimental

All chemicals used in this study were of AR grade. Doubly distilled water was used for the preparation of all solutions required for the experiment. BaCrO_4 and TiO_2 (100% anatase) were supplied by Qualigen Fine Chemicals. Structure of BaCrO_4 sample was confirmed by X-ray powder diffraction. The average surface of both powder samples is about $20 \text{ m}^2/\text{g}$.

Photolysis of aqueous solution of methylene blue, 100 mg of BaCrO_4 and/or bare TiO_2 was carried out in a circular glass reactor (designed and fabricated in our laboratory). The pH of the resultant mixture solution was 5.6. Halogen lamp (40W/230V/36D, Phillips, Essential) was used as the visible light source. During the photolysis, air was bubbled through the solution continuously as a source of oxygen. Aliquots of the reaction mixture were withdrawn and the suspensions were filtered through $0.2 \mu\text{m}$ millipore discs prior to quantitative determination of methylene blue spectrophotometrically using UV-visible spectrophotometer (Shimadzu UV-1800).

Chemical oxygen demand (COD) measurements were carried out using standard method²⁵. Samples of the reaction mixture were taken at different time intervals and microfiltered through a hydrophilic membrane (Millipore). The organic matter was oxidized by potassium dichromate under energetic conditions. The temperature of the solution was raised to $170 \text{ }^\circ\text{C}$ over 2 hours. The excess of potassium dichromate was measured out by Mohr salt titration. COD was calculated from the expression,

$$\text{COD (mg O}_2/\text{L)} = 8000 \times (V_{(\text{MS})\text{blank}} - V_{(\text{MS})\text{sample}}) \times N_{(\text{MS})}/V_0$$

where $V_{(\text{MS})\text{blank}}$ and $V_{(\text{MS})\text{sample}}$ are the volumes of standard Mohr salt solution used for the blank and

sample respectively, $N_{(\text{MS})}$ is the normality of Mohr salt solution, and V_0 is the volume of the sample.

Results & discussion

The crystal structure of BaCrO_4 was determined by powder X-ray diffraction and photocatalyst powder was found to be of single phase. BaCrO_4 has a barite structure, and shows orthorhombic symmetry with space group Pbnm. The band gap was determined to be 2.63 eV for BaCrO_4 , indicating that BaCrO_4 semiconductors can be excited by visible light irradiation.

Temporal spectral changes in the concentration of methylene blue were monitored by examining the variations in maximal absorption in UV-visible spectra at 655 and 300 nm. Typically, methylene blue solutions display maximal absorption at 668 and 309 nm. Under the present experimental conditions, maximal absorption occurs at 655 and 300 nm. Hence, the absorption bands at 655 and 300 nm were selected to monitor the temporal concentration changes of methylene blue in aqueous suspensions during the photocatalysis reaction by using BaCrO_4 as a photocatalyst and visible light. Temporal spectral changes during the degradation of methylene blue are shown in Fig. 1. During the course of photocatalytic degradation of methylene blue, the band at 655 nm shifts considerably towards the blue region. Blue shift of absorption band may be due to the N-dealkylation reaction. Similar results of N-dealkylation of methylene blue during "photodynamic therapy" studies using visible light irradiation have been

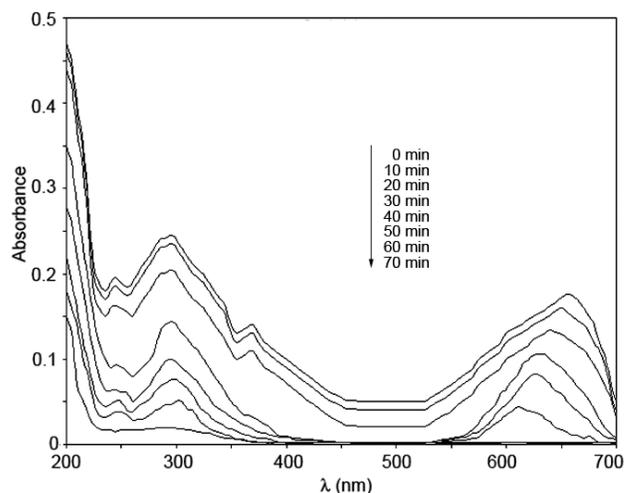


Fig. 1 – Temporal spectral changes of methylene blue in aqueous suspensions of BaCrO_4 as photocatalyst and visible light irradiations. [BaCrO_4 as photocatalyst: 100 mg; initial conc. of methylene blue: $1 \times 10^{-4} \text{ mol/L}$; visible light; pH of solution: 5.6].

reported earlier²⁶. N-dealkylation of dyes containing auxochromic alkylamine groups plays an important role in photocatalytic degradation. The color of methylene blue solutions becomes less intense (hypsochromic shift) when all auxochromic groups (methyl or alkylamine) are degraded.

Spectral changes show the degradation of methylene blue by BaCrO_4 as a photocatalyst. To verify if BaCrO_4 can be a better photocatalyst than standard photocatalyst, P-25 Degussa TiO_2 , degradation of methylene blue by BaCrO_4 as a photocatalyst was compared with that of bare TiO_2 . The photocatalytic degradation efficiency shown in Fig. 2 clearly indicates that BaCrO_4 is a better photocatalyst than bare TiO_2 under visible light irradiation. It is also observed that the bare titanium dioxide does not act as a photocatalyst after 60 min of reaction time. To understand why the degradation reaction stopped after the 60 min of reaction time when bare TiO_2 was used as a photocatalyst for the degradation of methylene blue, the reaction mixture was investigated by spectrophotometric analysis. The spectrum of reaction mixture after 60 min does not show any visible light absorption. On the basis of spectral analysis of reaction mixture, we assume that no chromophores remain in the solution after 60 min of reaction time, (which can sensitize the titanium dioxide under visible region, wavelength greater than 400 nm) and hence the reaction gets terminated. It is assumed that when BaCrO_4 is used as a photocatalyst

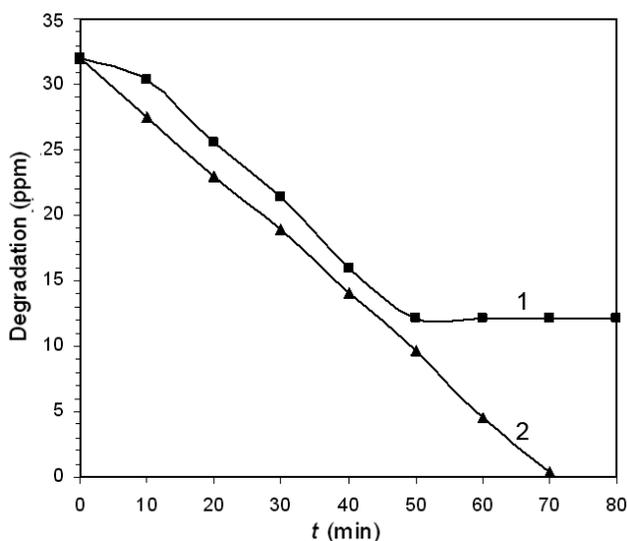


Fig. 2 – Comparison of methylene blue degradation by the two photocatalysts. [BaCrO_4 /bare TiO_2 : 100 mg; initial conc. of methylene blue: 1×10^{-4} mol/L; visible light; pH of solution: 5.6. 1, TiO_2 ; 2, BaCrO_4].

for the degradation of methylene blue, it is truly photocatalytic while when bare TiO_2 used as a photocatalyst the degradation of methylene blue is sensitized degradation reported earlier in literature.

The COD of the dye solutions was measured after the degradation, in order to verify whether the dye actually degraded by photocatalytic reactions or the disappearance of color was due to some other effect. To determine the reduction of COD of the dye solution, initial COD and COD at different time intervals were measured in both cases (Fig. 3). It is clear that the photocatalytic pathway was followed by degradation of dye during the course of the reaction in the case of BaCrO_4 as photocatalyst. From spectrophotometric analysis, 99% conversion was observed but according to the COD analysis only 71.4% conversion was observed within 80 min of reaction time when BaCrO_4 was the photocatalyst. Similarly, in the case of bare TiO_2 when used as a photocatalyst, 63% conversion was observed spectrophotometrically while 48.8% conversion of COD was observed within 80 min of reaction time. These results indicate that some reaction intermediates, which were colorless, are formed during the reaction which takes more time to degrade. This type of difference has also been reported earlier for the degradation of phenol by $\text{UV}/\text{H}_2\text{O}_2$ ²⁷.

Nitric acid is formed when N-containing compounds undergo photocatalytic degradation. The nitric acid accumulates on the surface of photocatalyst and as a result, there is poisoning of catalyst²⁸. Hence,

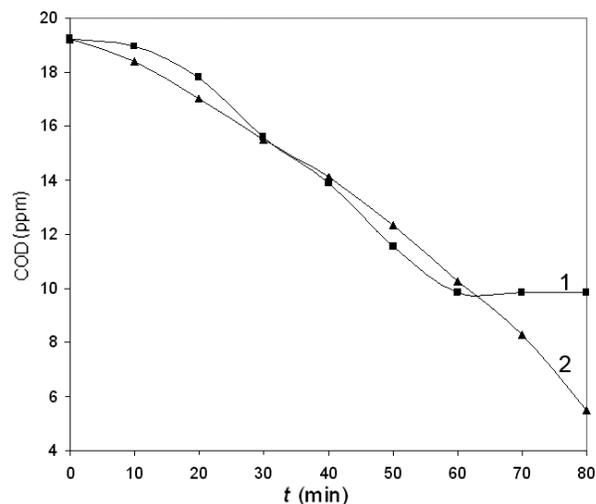


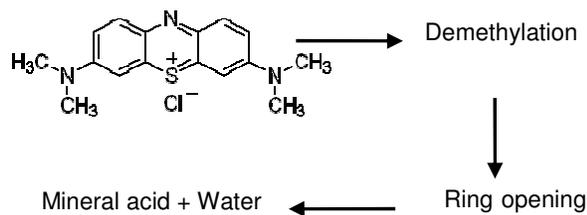
Fig. 3 – COD removal in presence of BaCrO_4 and bare TiO_2 . [BaCrO_4 /bare TiO_2 : 100 mg; initial conc. of methylene blue: 1×10^{-4} mol/L; visible light; pH of solution: 5.6. 1, TiO_2 ; 2, BaCrO_4].

in order to study the catalytic poisoning during the photocatalytic degradation of methylene blue, we have investigated the degradation of methylene blue using bare TiO_2 as well as BaCrO_4 as a photocatalyst which was used for the first run. Photocatalytic degradation efficiency after the first run decreased for both the photocatalysts. In the case of BaCrO_4 , 64% degradation of dye was observed for first run which decreased to 51% after the second run. In the case of bare TiO_2 , 60% degradation of dye was observed for first run which decreased to 48% after the second run. Similar results were obtained for the successive runs. From the above observation it is concluded that the nitric acid that was formed during the photocatalytic degradation of nitrogen-containing material was adsorbed on the surface of photocatalyst and decreases the H_2O sites, and hence the $\cdot\text{OH}$ radical production.

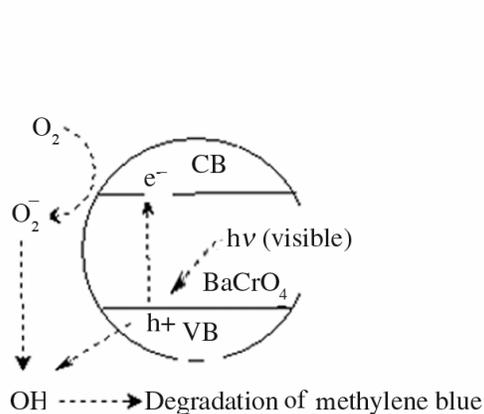
Based on the above data we propose a scheme for the degradation of methylene blue when BaCrO_4 is used as a photocatalyst (Scheme 1).

On the basis of above results the degradation of methylene blue on BaCrO_4 and TiO_2 is diagrammatically represented in Scheme 2.

In the case of TiO_2 as a photocatalyst, methylene blue absorbs the light and get excited. The excited



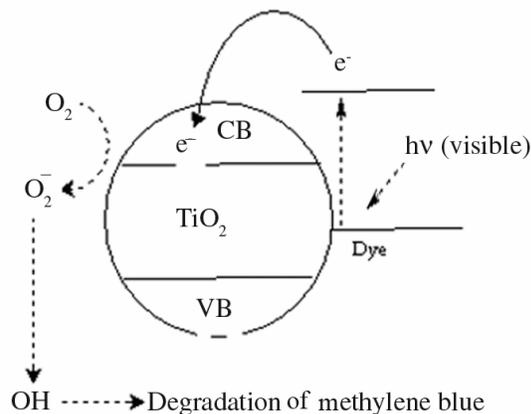
Scheme 1



A: Truly photocatalytic degradation

dyes transfer the electron to the conduction band of TiO_2 , which are transferred on the surface of the TiO_2 and subsequent chemical reaction occurs which leads to the degradation of methylene blue. We rule out the direct excitation of TiO_2 because visible light source is used for irradiation having wavelength greater than 400 nm which is not sufficient for the excitation. In the case of BaCrO_4 , the band gap is 2.64 eV indicating that it can be excited under visible light irradiation. When it is used as a photocatalyst the excitation of valence band electron to conduction band of the material takes place. The excited electron gets transferred to the surface and subsequent chemical reaction occurs which leads to the degradation of methylene blue. In this case we do not rule out the sensitized degradation path along with the photocatalytic pathways. However, when chromophores get degraded the reaction is not stopped as in the case of BaCrO_4 indicating that the photocatalytic degradation pathway is dominant along with the possibility of sensitized degradation. In the case of TiO_2 , sensitized degradation is the dominant pathway.

The above data show that BaCrO_4 powder exhibits better photocatalytic properties than the bare TiO_2 under visible light irradiation. The degradation efficiency is also better in the case of BaCrO_4 than the bare TiO_2 . In the presence of BaCrO_4 , the degradation of methylene blue is truly photocatalytic while in presence of bare TiO_2 the degradation of methylene blue is photosensitized. The use of BaCrO_4 is more economical than Pt doped TiO_2 because Pt is very costly. Therefore, BaCrO_4 is a more effective and economical photocatalyst than unmodified TiO_2 .



B: Photosensitized degradation

Scheme 2

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