VISIBLE LIGHT INDUCED PHOTOCATALYTIC DEGRADATION OF MALACHITE GREEN USING NANOSIZED BARIUM CHROMATE

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ABSTRACT

The photocatalytic degradation of malachite green was carried out in presence of nanosized barium chromate semiconducting powder used as a photocatalyst. The nanophotocatalyst was prepared by precipitation method and further characterized by XRD, SEM-EDS and FT-IR. The progress of the reaction was monitored spectrophotometrically. A tentative mechanism has been proposed where hydroxyl radical has been reported as an oxidizing agent for the photocatalytic degradation of the dye molecules. Some physicochemical parameters were studied, which also supported the mineralization of the dye solution.

Keywords: Photocatalytic degradation, Photocatalyst, Malachite green, Barium chromate.

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INTRODUCTION

Water pollution is one of the world's most burning issues of today. The different industries produced a huge amount of wastewater in developing countries. The release of dyes from different dying industries into the aquatic system creates a large amount of water pollution. The colored wastewaters containing dye pollutants create many environmental and health hazards. Different methods have been used for the removal of dyes from wastewater like chemical, physical and biological methods, but each method has its own advantages and disadvantages. Photocatalysis method may play an important role to solve this problem. It is also an eco-friendly and low-cost method to remove dyes from wastewater. Soltaninezhad and Aminifar¹ synthesized ZnO nanocrystalline photocatalyst and examined the photocatalytic activity of as-synthesized samples for the photodegradation of methylene blue while photodegradation of naphthol green B has been carried out by Ameta et al.² using antimony trisulphide semiconductor. Houas et al.³ used TiO₂/UV-based photocatalyst to study the photocatalytic degradation pathway of methylene blue in aqueous solution whereas photocatalytic degradation of an azo dye acid red 27 was studied by Shanthi and Kuzhalosai⁴ using nano ZnO photocatalyst. CdSe-TiO₂ photocatalyst was synthesized by Lim et al.⁵ using a facile solvothermal method and used for photocatalytic degradation of methylene blue under UV and visible light. Movahedi et al.⁶ compared the photocatalytic efficiency of ZnO and TiO₂ by photocatalytic bleaching of congo red dye.

Trabelsi et al.⁷ carried out the photocatalytic degradation of malachite green in a photoreactor using TiO₂/cellulosic fibre as photocatalyst whereas CdIn₂S₄ microspheres were synthesized by Xin et al.⁸ using a facile hydrothermal method at different temperatures ranging from 120 to 200°C and the photocatalytic activity of as-prepared CdIn₂S₄ products was examined on photodegradation of methyl orange under visible light irradiation. Abdollahi et al.⁹ investigated the photocatalytic degradation of p-cresol by ZnO under UV irradiation while Yang et al.¹⁰ synthesized H₃PW₁₂O₄₀/SiO₂ photocatalyst using a sol-gel method and sensitized by H₂O₂ and the photocatalytic degradation of rhodamine B were studied using the as-prepared sample in presence of simulated natural light irradiation.

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Kamel *et al.*¹¹ prepared porous MgO powder and tested for the decolorization of reactive orange 5 dye from aqueous solution in presence of H₂O₂ under UV radiation while Rose *et al.*¹² synthesized lanthanum chromium oxide using co-precipitation method and proper heating cycles and the as-synthesized catalyst was used for photocatalytic degradation of azure-B.

The photocatalytic mineralization of phenol has been carried out by Zhang *et al.*¹³ in presence of BiPO₄ photocatalyst under UV irradiation whereas Nihalani and co-workers¹⁴ used a new nanosized photocatalyst BaO₃TiO.SrO₃TiO for the photocatalytic degradation of commercially used dyes (malachite green, crystal violet) and eosin yellow respectively. Hu and Meng¹⁵ synthesized MoS₂/TiO₂ nanocomposite by a chemical method and characterized by EDS spectrum and HRTEM and the photocatalytic activity of as-synthesized MoS₂/TiO₂ nanocomposite was tested on the degradation of malachite green. Ag₃PO₄ nanoparticles/TiO₂ nanobelts heterostructures were synthesized by Liu *et al.*¹⁶ using co-precipitation method and the photocatalytic degradation of methyl orange was carried out using Ag₃PO₄/TiO₂ under UV irradiation while Gopalappa *et al.*¹⁷ prepared CaZnO₂ nanoparticles using solution combustion method and characterized by XRD and SEM. The photocatalytic decolorization of azo dye acid orange 7 (AO7) was investigated using as-synthesized powder under sunlight. Anasane and Ameta¹⁸ reported morphologies of nanostructured bismuth sulphide and Mn (II) doped bismuth sulphide nanoparticles and decolorization of methyl violet using as prepared doped bismuth sulphide while Ashok *et al.*¹⁹ reported hydrothermal synthesis of ultraviolet-visible light responsive ruthenium doped titania (RuXTi1-XO2) nanosheet and also investigated its effect on photocatalytic degradation of reactive red dyes. In the present study, nanosized barium chromate has been prepared and it was further used to investigate the photocatalytic degradation of malachite green. It has been observed that due to its yellow color, it was an efficient photocatalyst in the visible region.

EXPERIMENTAL

Materials and Methods

K₂CrO₄, BaCl₂, Malachite green, NaOH and H₂SO₄ (Himedia) were used as received.

The molecular formula of malachite green is C₂₃H₂₅ClN₂ and its molecular weight is 364.91 g mol⁻¹. Its chemical structure is given in Figure 1.

Fig. 1:- Chemical Structure of Malachite Green

Preparation of Nano-sized Barium Chromate Semiconductor

Nanosized barium chromate was prepared using K₂CrO₄ and BaCl₂ through precipitation method. 100 mL 5 % aqueous solution of BaCl₂ was mixed with 100 mL 5 % aqueous solution of K₂CrO₄ with constant stirring. The resulting precipitate of BaCrO₄ was allowed to settle down. The product was filtered, washed with doubly distilled water several times and dried at 60°C in an oven.

A stock solution of malachite green having the concentration of 1.0 × 10⁻³ M was prepared in double distilled water. This stock solution was further diluted as and when required. The absorbance of the malachite green solution was measured with the help of a spectrophotometer (Systronics Model 106) at λ_{max} = 620 nm. In the present work, the malachite green dye has been used as a model system to study the photocatalytic activity of barium chromate. The results of some control experiments showed that degradation of malachite green requires the presence of both light and the semiconductor BaCrO₄ and therefore, this reaction is a photocatalytic reaction in nature.

Characterization

XRD

X-ray diffraction studies of the sample were conducted using PANalytical, Singapore make, XPERT-PRO model with Cu K α radiation ($\lambda = 1.54060 \text{ \AA}$, $2\theta = 10$ to 80° with generator setting 40 mA, 45 kV). Diffraction pattern was taken over the 2θ range 10° - 70° . Figure-2 shows the XRD pattern of synthesized nano-particles of BaCrO $_4$. It was observed that all the diffraction peaks were similar to that of orthorhombic phase of BaCrO $_4$ (JCPDS-15-376, lattice constants, $a = 8.2026^\circ$, $b = 8.2026^\circ$, $c = 13.6302^\circ$ A).

The particle size of the synthesized barium chromate was calculated using Sherrer formula (Eq.-1) and it was found as 14.71 nm.

$$D = \frac{K\lambda}{\beta \cos\theta} \quad (1)$$

Where K is a constant, which depends on the shape of the crystal and its value is 0.9 assuming spherical shape; λ is the wavelength; D is the crystallite size; β is full width of half maxima (FWHM) value (calculated for the XRD pattern) and θ is Bragg's angle.

Fig. 2:- XRD of Barium Chromate Semiconductor

SEM-EDS Analysis

Scanning electron microscopy studies of the sample were conducted using JEOL, Japan make, 5610LV model. It was operated at 15 kV. SEM-EDS of barium chromate is given in Fig.-3.

Fig. 3:- SEM-EDS of Barium Chromate

SEM of the synthesized semiconductor indicates that particles are unevenly distributed in size and EDS gives clearly that the catalyst contains only barium, chromium and oxygen only and it does not have any impurity.

FT-IR

Fourier transform-infrared (FT-IR) spectroscopy of the sample was carried out on a Shimadzu, IR Affinity, using KBr disk method and it showed in Fig.-4.

Fig.-4: FT-IR of Barium Chromate

FT-IR spectra of BaCrO_4 nano-particles shows the characteristic absorption bands of chromate group located at 875, 894 and 952 cm^{-1} .

RESULTS AND DISCUSSION

A solution of 1.1×10^{-4} M of malachite green was prepared in double distilled water and 0.10 g of BaCrO_4 was added to it. The pH of the reaction mixture was adjusted to 9.0 with the help of previously standardized sodium hydroxide and sulphuric acid solutions. Then the solution was exposed to the light of a 200 W tungsten lamp. An aliquot of 2.0 mL was taken out from the reaction mixture and its absorbance was measured at 620 nm at regular time intervals.

Table-1: A typical run pH = 9.0, [Malachite green] = 1.1×10^{-4} M, BaCrO_4 = 0.10 g, Light intensity = 60.0 mWcm^{-2}

Time (min.)	Absorbance (A)	1 + log A
0.0	0.72	0.8573
5.0	0.62	0.7924
10.0	0.52	0.7160
15.0	0.45	0.6532
20.0	0.38	0.5798
25.0	0.32	0.5051
30.0	0.27	0.4314
35.0	0.23	0.3617
40.0	0.20	0.3010
45.0	0.17	0.2304
50.0	0.14	0.1461
Rate constant (k) = $5.50 \times 10^{-4} \text{ sec}^{-1}$		

It was observed that there was a decrease in the absorbance of the malachite green solution with increasing time of exposure. The typical run for the photocatalytic degradation of malachite green in presence of barium chromate semiconductor has been presented in Table-1 and graphically represented in Fig.-5.

A linear plot between $1 + \log A$ against time was obtained, which indicates that the photocatalytic degradation of malachite green follows pseudo-first order kinetics. The rate constant of this reaction was measured with the expression; $k = 2.303 \times \text{slope}$. Some of the factor affecting the rate of the reaction was studied to obtain optimum conditions for photocatalytic degradation of the dye.

Fig.-5: Typical Run for Degradation of Malachite Green

Effect of pH

The pH of the solution may affect the degradation of malachite green. The effect of pH on the rate of degradation of malachite green was studied in the pH range of 5.0 – 10.0. The results are summarized in Table-2.

Table-2: Effect of pH

[Malachite green] = 1.1×10^{-4} M, Light intensity = 60.0 mWcm⁻², BaCrO₄ = 0.10 g

pH	Rate Constant (k) $\times 10^4$ (sec ⁻¹)
5.0	0.13
5.5	0.19
6.0	0.34
6.5	0.81
7.0	2.30
7.5	3.11
8.0	3.67
8.5	4.33
9.0	5.50
9.5	4.57
10.0	3.35

It has been observed that there was an increase in the rate of photocatalytic degradation of malachite green with an increase in pH and it attained optimum value at pH 9.0. On further increasing pH, the rate of degradation was decreased. The increase in the rate of photocatalytic degradation may be due to more availability of the OH⁻ ions at higher pH values. OH⁻ ions will generate more •OH radicals by combining with the holes (h⁺) of semiconductor and these •OH radicals are considered responsible for the photocatalytic degradation. But after a certain value of pH i.e. 9.0, a further increase in pH of the medium decreased the rate of photocatalytic degradation. It may be due to the fact that malachite green does not

remain in its cationic form due to a greater concentration of OH^- ions and as such, the repulsion between the dye and negatively charged semiconductor surface increases. As a result, the reaction rate decreases.

Effect of Malachite Green Concentration

The effect of dye concentration on the rate of photocatalytic degradation was studied by taking different concentrations of malachite green. The results are summarized in table 3.

Table-3: Effect of Malachite Green Concentration
pH = 9.0, $\text{BaCrO}_4 = 0.10 \text{ g}$, Light intensity: 60.0 mWcm^{-2}

[Malachite green] $\times 10^4 \text{ M}$	Rate Constant (k) $\times 10^4 (\text{sec}^{-1})$
0.8	2.75
0.9	3.28
1.0	4.26
1.1	5.50
1.2	4.44
1.3	3.69
1.4	3.20

It was observed that the rate of photocatalytic degradation increased with increase in the concentration of malachite green up to $1.1 \times 10^{-4} \text{ M}$. This may be attributed to the fact that as the concentration of malachite green was increased, more dye molecules were available for excitation followed by intersystem crossing and energy transfer and hence, the rate of degradation was increased. There was a decrease in the rate of degradation with a further increase in the concentration above $1.1 \times 10^{-4} \text{ M}$. This may be attributed to the fact that the dye will start acting as a filter for the incident light and it will not permit the desired light intensity to reach the semiconducting particles, thus, decreasing the rate of photocatalytic degradation of the dye.

Effect of Amount of Photocatalyst

The amount of semiconductor may also affect the rate of degradation of dye and hence, different amounts of semiconductor barium chromate were taken. The results are summarized in Table 4.

Table-4: Effect of Amount of Photocatalyst
pH = 9.0, [Malachite green] = $1.1 \times 10^{-4} \text{ M}$, Light intensity = 60.0 mWcm^{-2}

$\text{BaCrO}_4 (\text{g})$	Rate Constant (k) $\times 10^4 (\text{sec}^{-1})$
0.02	2.66
0.04	3.16
0.06	3.84
0.08	4.42
0.10	5.50
0.12	5.48
0.14	5.50
0.16	5.48

It was observed that there was an increase in the rate of photocatalytic degradation with an increase in the amount of semiconductor up to 0.10 g, but after the amount 0.10 g of semiconductor, it becomes almost constant. This may be attributed to the fact that as the amount of semiconductor was increased, the exposed surface area of semiconductor also increased, but after a certain limit i.e. 0.10 g, if the amount of semiconductor was further increased, then there will be no increase in the exposed surface area of the photocatalyst. It may be considered like a saturation point; above which, any increase in the amount of semiconductor had negligible or no effect on the rate of photocatalytic degradation of dye, as an increase

in the amount of semiconductor after this saturation point would only increase the thickness of the layer at the bottom of the reaction vessel. This was confirmed by taking reaction vessels of different dimensions. The saturation point shifted to the higher range for larger vessels, while the reverse was true for smaller vessels.

Effect of Light Intensity

The variation in light intensity may also affect the rate of photocatalytic degradation. Hence, the distance between the light source and the exposed surface area was varied. The intensity of light at each distance was measured using Suryamapi (CEL Model SM201). The results are reported in Table-5.

Table-5: Effect of Light Intensity
pH = 9.0, [Malachite green] = 1.1×10^{-4} M, BaCrO₄ = 0.10 g

Light intensity (mWcm ⁻²)	Rate Constant (k) $\times 10^4$ (sec ⁻¹)
20.0	2.29
30.0	3.26
40.0	4.26
50.0	4.98
60.0	5.50
70.0	4.84
80.0	4.39

The results showed that degradation of dye was accelerated as the intensity of light was increased, because any increase in the light intensity will increase the number of photons striking per unit area of semiconductor powder. However, by increasing the intensity above 60.0 mWcm⁻², there was a little decrease in the rate. This may be due to some thermal reactions.

Mechanism

On the basis of the experimental observations, a tentative mechanism of photocatalytic degradation of malachite green has been proposed as follows:

Malachite green (MG) absorbs radiation of suitable wavelength giving rise to its excited first singlet state followed by intersystem crossing (ISC) to the triplet state. On the other hand, the semiconducting barium chromate also utilizes the incident light energy to excite its electron from the valence band to conducting band; thus, leaving behind a hole. This hole may abstract an electron from hydroxyl ions to generate hydroxyl radicals. These hydroxyl radicals will then oxidize the dye to its leuco form, which may ultimately degrade to harmless products.

The participation of $\cdot\text{OH}$ radicals as an active oxidizing species was confirmed by using hydroxyl radical scavengers (2-propanol), where the rate of degradation was drastically reduced.

Some of the physicochemical parameters were studied to confirm the mineralization of dye solution in harmless products so that it may be used for cleaning purpose after photocatalytic treatment.

pH of the dye solution was 4.45 before treatment and it was found almost neutral after photocatalytic degradation of the dye. TDS and conductance were also increased from 40 to 71 ppm and 28 to 88 μS ,

respectively in treated water. Dissolved oxygen (DO) analysis measures the amount of gaseous oxygen dissolved in an aqueous solution and in the present case it was increased from 6.7 to 7.9 ppm. Enhancement in pH, conductivity, TDS and DO confirms the mineralization of dye to a significant extent. The value of chemical oxygen demand (COD) shows the oxidizability of a substance and it is expressed as the equivalent amount in oxygen of an oxidizing reagent consumed by the substance under fixed laboratory conditions. The chemical oxygen demand of reaction mixture before and after treatment has been determined by redox method. The photodegradation efficiency of the catalyst was calculated from the following expression:

$$\eta = \frac{\text{COD}_{\text{before}} - \text{COD}_{\text{after}}}{\text{COD}_{\text{before}}} \times 100$$

η = Photodegradation efficiency (%),

$\text{COD}_{\text{before}}$ = COD of dye solution before illumination, and

$\text{COD}_{\text{after}}$ = COD of dye solution after illumination

In the present case, COD was decreased from 36 to 12 ppm, which is a notable change. The photodegradation efficiency after 4 hours of illumination has been found to be 73.22%.

Biological Oxygen Demand (BOD) is a measure of the oxygen used by microorganisms to decompose waste. BOD of the dye solution before and after treatment was decreased from 6.2 to 1.5 ppm, which shows that photocatalytic treatment increases the biodegradability.

Table-6: A Comparative Study for Some Physico-Chemical Parameters of Aqueous Solution of Malachite Green (Before and After Treatment)

Parameters	Before Treatment	After Treatment
pH	4.45	7.78
Conductance	28.0 μS	88.0 μS
TDS	40.0 ppm	71.0 ppm
DO	6.7 ppm	7.9 ppm
COD	54.9 ppm	14.7 ppm
BOD	6.2 ppm	1.5 ppm

CONCLUSION

Nanosized barium chromate photocatalyst was synthesized by precipitation method further characterized to know its morphology. It was used for the photocatalytic degradation of malachite green successfully. The results showed that dye was completely degraded using this photocatalyst and the use of the photocatalyst can be explored for the degradation of different pollutants.

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