

Use of Barium Chromate as Photo catalyst for Degradation of Methyl Violet 10B

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Abstract:

Water pollution is the one of the major problem. It is a big problem faced by everyone all over the world. In solving the problem of water pollution, important role is played by photocatalysis process. In the present study, barium chromate powder has been used as a photocatalyst for degradation of Methyl violet 10B dye. The rate of decomposition was optimum with different parameters like pH (9.0), concentration of dye (4.0×10^{-4} M), amount of photocatalyst (0.14 g) and intensity of light (40.0 mWcm^{-2}). The rate constant obtained was $k = 3.63 \times 10^{-4} \text{ sec}^{-1}$. The reaction proceeds through oxidation by hydroxyl radical as confirmed by radical scavenger, 2-propanol.

Keywords: Barium Chromate, Photocatalyst, Methyl Violet 10B, AOPs, Water pollution

Introduction:

Vargas et al.¹ used uncalcined Cu/Al LDH as adsorbent and photocatalyst in the adsorption and subsequent photodegradation of methyl violet 2B dye. The results showed that the dye was adsorbed on the LDH surface. Photocatalytic activity was evaluated in the Methyl violet 2B dye photodegradation process.

Bhattacharjee et al.² developed green synthesis of TiO₂ nanoparticles by microwave heating method using 1:1, 1:2 and 1:3 different ratios of water and glycerol, wherein glycerol acts as a good complexing as well as capping agent. This method resulted in the formation of spherical SnO₂ nanoparticles with an average diameter ~8-30 nm. The photocatalytic activity of as-synthesized SnO₂ NPs was evaluated for the degradation of toxic dye methyl violet 6B under the sunlight.

Sirajuddin et al.³ fabricated *Gum acacia* based nanocomposite ion exchanger using simple sol-gel method. The GA/CeMoPO₄ showed better ion exchange capacity of 1.04 meq g⁻¹ in comparison to its inorganic counterpart GA/CeMoPO₄ (0.65 meq/g⁻¹). The photocatalytic nature of GA/CeMoPO₄ and CeMoPO₄ was investigated using methyl violet as test dye. The GA/CeMoPO₄ showed 86% of methyl violet photodegradation in 2 h of illumination.

Sharma et al.⁴ synthesized zero valent iron @guar gum crosslinked soya lecithin nanocomposite hydrogel (Fe⁰@GG-cl-SY NCH) via ultrasonication method. It was utilized for

the photodegradation of methyl violet from aqueous solution. 81% degradation of methyl violet was observed within 120 min in the presence of H_2O_2 and $Fe^0@GG-cl-SY$ NCH.

Jeyasubramanian et al.⁵ prepared zinc oxide nanoparticles by precipitation method. ZnO NPs were obtained by the calcination of zinc oxalate powder precipitated from a reaction mixture containing zinc acetate and ammonium oxalate. Complete degradation of methyl violet was achieved exposing the suspension containing sonicated ZnO NPs in an aqueous medium in 60–80 min.

Saeed et al.⁶ prepared titanium oxide decorated with palladium (TiO_2/Pd) and platinum (TiO_2/Pt) nanoparticles via an incipient wetness method. The photodegradation study revealed that the TiO_2/Pd and TiO_2/Pt nanoparticles degraded 95 and 78% of methyl violet within 20 min, respectively. Photodegradation of methyl violet dye using ZnO nanorods was also carried out Punithavathy et al.⁷

ZnO nanorods were synthesized by Richard et al.⁸ and photocatalytic degradation of methyl violet was studied using these nanorods. It was revealed that rate depends highly on the morphology of the nanorods.

Use of barium chromate in photocatalytic degradation of eosin yellow and azure A was made by Gupta et al.^{9,10} Visible light induced photocatalytic degradation of malachite green using nanosized barium chromate was proposed by Prajapati et al.¹¹ Kapoor et al.¹² also studied the degradation of Evans blue using multi-walled carbon nanotubes (MWCNTs) – barium chromate composite. The photocatalytic degradation of Congo red using nano-sized barium chromate catalyst was investigated by Ameta et al.¹³

Materials and method:

Barium chromate was synthesized and characterized as done earlier by Goswami et al¹⁴

Photocatalytic degradation:

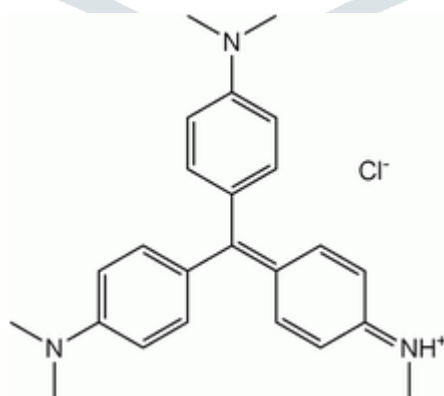


Fig. 1: Structure of methyl violet 10B

A stock solution of methyl violet 10B (1.0×10^{-3} M) was prepared by dissolving 0.0407 g of dye in 100 mL doubly distilled water. This stock solution was further diluted. The absorbance of methyl violet 10B solution was determined with the help of a spectrophotometer at $\lambda_{max} = 540$ nm. The photocatalytic degradation of methyl violet 10B dye was studied after addition of 0.1 g of photocatalyst $BaCrO_4$ in 40 mL

dye solution (4.0×10^{-5} M). The reaction mixture was exposed to visible light and irradiated with a 200 W tungsten lamp. Absorbance of solution was measured with the help of a spectrophotometer (Systronics Model 106) at regular time intervals. A digital pH meter was used to measure pH of the solution. pH of the dye solutions was adjusted by addition of previously standardized 0.1 N sulphuric acid and 0.1 N sodium hydroxide solutions. Control experiments were carried out to confirm that the degradation of methyl violet 10B is photocatalytic in nature.

Results and discussion

A graph was plotted between $\log A$ v/s time, which was a straight line showing that photocatalytic degradation of methyl violet 10 B followed pseudo-first order kinetics. The rate constant for degradation of dye was calculated by the following expression –

$$k = 2.303 \times \text{slope} \quad \dots(1)$$

A typical run has been reported for the photocatalytic degradation of methyl violet 10B using photocatalyst BaCrO_4 , where all the parameters were kept constant (Table 1 and Fig. 2). These constant parameters were obtained, when the degradation of the dye was found optimum.

Typical run:

pH = 9.0

Semiconductor = 0.14 g

[Methyl violet 10B] = 4.0×10^{-4} M

Light intensity = 40.0 mWcm^{-2}

Table 1 Typical run

Time (min)	Absorbance (A)	1 + log A
0	0.878	0.94349
15	0.682	0.83378
30	0.509	0.70672
45	0.359	0.55509
60	0.272	0.43457
75	0.198	0.29667
90	0.124	0.09342
Rate constant k		$3.63 \times 10^{-4} \text{ sec}^{-1}$

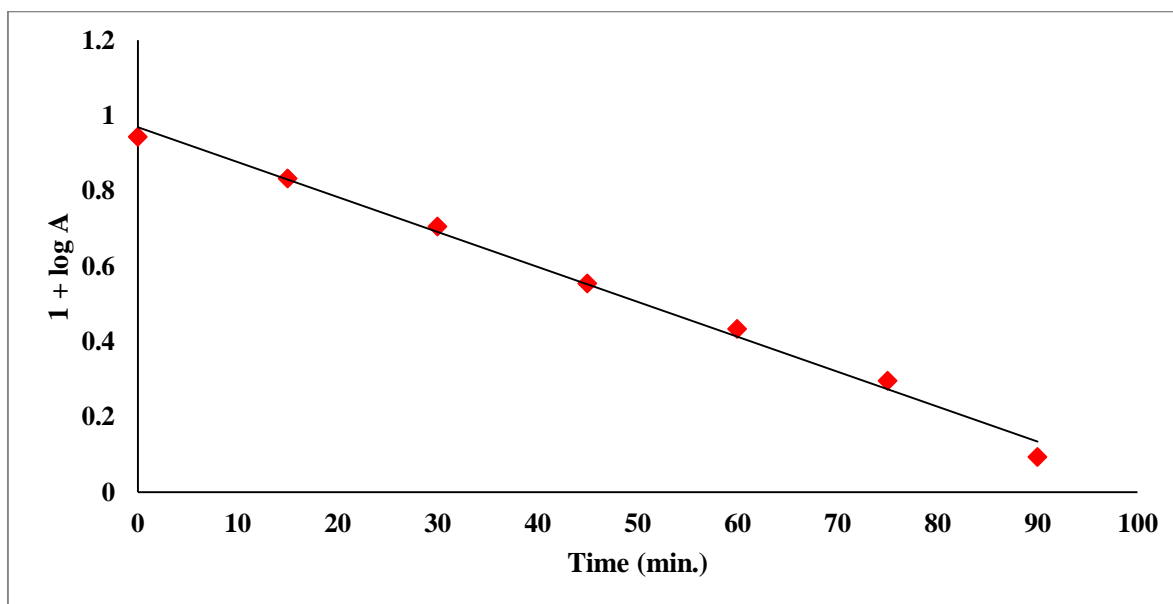


Fig. 2: Typical run

Effect of parameters:

pH variation: The effect of variation of pH was studied in the range 5.0-10.0. The results presented in Table 2. It was observed that the rate increases with an increase in pH up to 9.0, but the rate of degradation decreases with a further increase in pH. A decrease in the rate of photocatalytic degradation of methyl violet 10B is photocatalytic nature.

[Methyl violet 10B] = 4.0×10^{-4} M

Light intensity = 40.0 mWcm^{-2}

Semiconductor = 0.14 g

Table 2: pH Variation

pH	Rate constant (k) $\times 10^4$ (sec^{-1})
5.0	1.35
5.5	1.67
6.0	1.92
6.5	2.13
7.0	2.46
7.5	2.81
8.0	3.10

8.5	3.45
9.0	3.63
9.5	3.15
10.0	2.58

Dye concentration variation: The effect of dye concentration on the photocatalytic degradation of methyl violet 10B was observed in the range of 2.0×10^{-4} to 4.8×10^{-4} M and presented in Table 3. As the concentration of the dye was increased, it was observed that the dye degradation increases but after optimum condition 4.0×10^{-4} M, the photocatalytic degradation showed a declining behaviour. It is due to the fact that as the concentration of dye was increased further, dye molecules start acting as filter for the incident light at higher concentration and they do not allow the desired light intensity to reach the semiconducting particles and thus, resulted in decrease in the rate of the photocatalytic degradation.

Table 3 Dye concentration variation

pH = 9.0

Semiconductor = 0.14 g

Light intensity = 40.0 mWcm^{-2}

[Methyl violet 10B] x 10^4 M	Rate constant (<i>k</i>) x 10^4 (sec ⁻¹)
2.0	1.35
2.4	1.42
2.8	1.54
3.2	2.48
3.5	3.23
4.0	3.63
4.4	2.75
4.8	2.13

Amount variation: The effect of variation of the amount of catalyst on the rate of dye degradation has been studied in the range from 0.02 to 0.18 g. The results of variation of rate constant with photocatalyst are represented in Table 4. It was observed that as the amount of photocatalyst was increased, the rate of photocatalytic activity also increases. The rate of degradation was found to be optimum at 0.14 g of the semiconductor because the exposed surface area was also increased, but after this limit, when the amount of semiconductor was increased further; there was no increase in the exposed surface area of the photocatalyst, but multilayers are formed making $e^- - h^+$ combination easier. Thus, a decrease in rate of degradation was observed.

Table 4: Amount variation of photocatalyst

pH = 9.0

[Methyl Violet 10B] = 4.0×10^{-4} M

Light intensity = 40.0 mWcm^{-2}

Amount (g)	Rate constant (k) $\times 10^{-4}$ (sec^{-1})
0.02	1.95
0.04	2.48
0.06	2.69
0.08	2.75
0.1	2.84
0.12	3.03
0.14	3.63
0.16	3.45
0.18	3.23

Light intensity variation: The distance between the light source and exposed surface area of photocatalyst was varied to change the intensity of light. The effect of light intensity on the photocatalytic degradation was observed from 20.0 to 70.0 mWcm^{-2} . Rate constants with different light intensity are represented in Table 5. It was observed that photocatalytic degradation of methyl violet 10B was more on increasing the intensity of light as the number of photons striking per unit area of photocatalyst surface per unit time will also increase. The maximum rate was observed at 40.0 mWcm^{-2} for degradation of methyl violet 10B. However, at higher light intensities, some thermal side reactions may also start and hence, the rate of photocatalytic degradation was slightly decreased on increasing the intensity of light further.

Table 5 Amount of photocatalyst

pH = 9.0

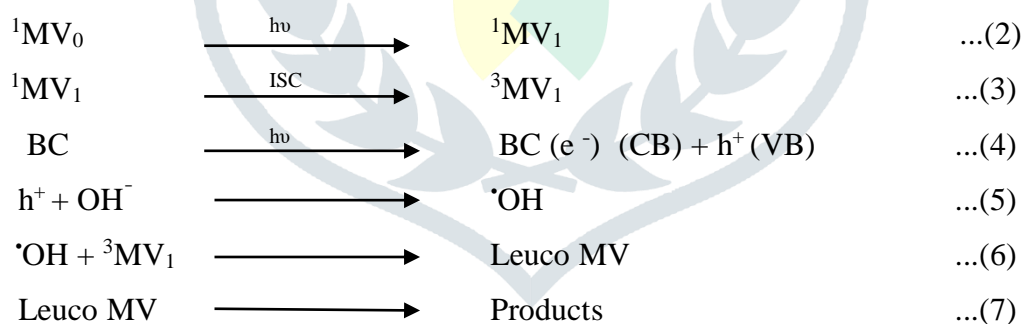
[Methyl violet 10B] = 4.0×10^{-4} M

Semiconductor = 0.14 g

Light intensity (mWcm^{-2})	Rate constant (k) $\times (10^4 \text{ sec}^{-1})$
20	3.22
30	3.54
40	3.63
50	3.46
60	3.18
70	2.94

Mechanism:

$\bullet\text{OH}$ radical participates as an active oxidizing species and this was confirmed by using hydroxyl radical scavenger (2-propanol), where the rate of degradation was decreased significantly. On the basis of the observations, a tentative mechanism for photocatalytic degradation of methyl violet 10B may be proposed as –



Methyl violet 10B (MV) absorbs radiation of suitable wavelength and it is excited to its first excited singlet state followed by intersystem crossing (ISC) to triplet state. On the other hand, the photocatalyst barium chromate (BC) also utilizes the incident light energy to excite its electron from valence band to conduction band; thus, leaving behind a hole. Hole will abstract an electron from OH^- ion to generate $\bullet\text{OH}$ radicals. These radicals will react with methyl violet 10B to convert it into its leuco form, which is unstable and ultimately, it will degrade to smaller products.

Conclusion:

In the present work, a ternary semiconductor i.e. BaCrO₄ has been successfully as a photocatalyst for degradation of methyl violet 10B, which suggests its possible use for removal of a variety of industrial effluents in future. The experimental results indicated that degradation efficiency of methyl violet 10B was optimum at pH (9.0), dye concentration (4.0×10^{-4} M), amount of semiconductor (0.14 g) and light intensity (40.0 mWcm⁻²). The present investigation revealed that barium chromate semiconductor showed better photocatalytic activity.

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References:

1. Vargas, A.G. Lima, E. Ortega, G. A. U. Tolentino, M. A. O. and Rodríguez, E. E. 2016. Adsorption and subsequent partial photodegradation of methyl violet 2B on Cu/Al layered double hydroxides. *Applied Surface Science*, 363, 372–380.
2. Bhattacharjee, A. Ahmaruzzaman, M. Devi, T. B. and Nath, J. 2015. Photodegradation of methyl violet 6B and methylene blue using tin-oxide nanoparticles (synthesized via a green route). *Journal of Photochemistry and Photobiology A Chemistry*, 325: 116–124.
3. Sirajuddin, Gupta, V. Sharma, G. Kumar A. Stadler, F.J. and Inamuddin. 2019. Preparation and characterization of gum acacia/Ce(IV)MoPO₄ nanocomposite ion exchanger for photocatalytic degradation of methyl violet dye. *Journal of Inorganic and Organometallic Polymers and Materials*, 29(4): 1171-1183.
4. Sharma, G. Kumar, A. Sharma, S. Al-Muhtaseb, A. H. Naushad, M. Ghfar, A. A. Ahamad, T. and Stadler, F.J. 2019. Fabrication and characterization of novel Fe⁰@Guar gum-crosslinked-soya lecithin nanocomposite hydrogel for photocatalytic degradation of methyl violet dye. *Separation and Purification Technology*, 211: 895-908.
5. Jeyasubramanian, K., Hikku, G. S. and Sharma, K. 2015. Photo-catalytic degradation of methyl violet dye using zinc oxide nano particles prepared by a novel precipitation method and its anti-bacterial activities, *Journal of Water Process Engineering*, 8: 35-44.
6. Saeed, K. Khan, I. Gul, T. and Sadiq, M. 2017. Efficient photodegradation of methyl violet dye using TiO₂/Pt and TiO₂/Pd photocatalysts, *Applied Water Science*, 7(7): 3841-3848.
7. Punithavathy, I. K. Jothibas, M. Praveen, P. and Richard, P. 2017. Photodegradation of methyl violet dye using ZnO nanorods., *Journal of Materials Science:Material in Electronics*, 28(3): 2494-2501.

8. Richard, J. P. Punithavathy, I. K. Jeyakumar. Johnson, S. Jothibas, M. and Praveen, P. 2017. Effect of morphology in the photocatalytic degradation of methyl violet dye using ZnO nanorods., *Journal of Materials Science: Materials in Electronics*. 28(5): 4025–4034.
9. Gupta, S. Soni, D. Ameta, R. and Benjamin, S. 2015. Use of barium chromate in photocatalytic degradation of eosin yellow, *Chemical Science Transactions*, 4(3): 851-857.
10. Gupta, S. Tak, P. Ameta, R. and Benjamin, S. 2013. Use of barium chromate semiconducting powder in photocatalytic degradation of azure A, *Journal of Advanced Chemical Sciences*, 1(2): 38-40.
11. Prajapati, D. I. Sharma, H. and Ameta, R. 2018. Visible light induced photocatalytic degradation of malachite green using nanosized barium chromate, *Rasayan Journal of Chemistry*, 11(3): 1311-1319.
12. Kapoor, N. Ameta, R. and Ameta, S. C. 2019. Degradation of evans blue using multi-walled carbon nanotubes (MWCNTs) barium chromate composite, *Journal of Nanoscience and Technology*, 5(2): 662-665.
13. Prajapati, D. I. Ameta, R. Punjabi, P. B. and Benjamin, S. 2019. Investigation of photocatalytic degradation of congo red by using nano-sized barium chromate catalyst, *Journal of Water Pollution & Purification of Research*, 2(2): 14-22.
14. Goswami, H. Ameta, S.C. and Soni, D. 2019. Use of barium chromate as photocatalyst for degradation of basic fuchsine, *Research Journal of Chemistry & Environment* (Communicated).

