PHOTOCATALYTIC DEGRADATION OF METHYLENE BLUE OVER FERRIC TUNGSTATE

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ABSTRACT

Photocatalytic degradation of methylene blue over ferric tungstate in presence of light has been carried out. The progress of the reaction was monitored spectrophotometrically. The effect of some parameters affecting the rate of reaction, such as pH, dye concentration, amount of semiconductor, light intensity, etc. has been studied. Kinetic studies show that this reaction follows pseudo-first order kinetics. A tentative mechanism for photocatalytic degradation of methylene blue has also been proposed.

INTRODUCTION

Water pollution is one the world wide problem, which is directly affecting living organisms. Effluents of various industries discharged directly or indirectly into water sources without any prior treatment for removal of harmful or dangerous compounds, create water pollution. There is a wide variety of water pollutants, which includes by products & wastage of industries, factories, organic matter, pathogens etc. Water pollution is a burning problem all over the globe, which requires some eco-friendly methods for its purification.

Researchers have developed some methods for wastewater treatment like adsorbents, electrolyte decomposition, ion exchange method, biological methods etc. These treatment methods are not suitable at large scale due to high cost and therefore, some alternative methods are required, which are reliable as well as green chemical in nature. Photocatalysis provides an eco-friendly pathway for degradation of many organic pollutants. This technique is considered as a promising technology for wastewater treatment.

Houas et al.[1] investigated TiO_2/UV based photocatalytic degradation of methylene blue in aqueous heterogeneous suspensions. Removal of the color of dyes and complete mineralization of carbon, nitrogen and sulfur heteroatoms into CO_2, NH_4^+, NO_3^- and SO_4^{2-}, respectively has also been studied by them. Rajeshwar et al.[2] focused on the heterogeneous photocatalytic treatment of organic dyes present in air and water. They have used TiO_2, ZnO, CdS, WO_3 and Fe_2O_3 for decolorizing and decomposing the organic dye

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to mineralized products. Abe[3] carried out photocatalytic and photoelectrochemical (PEC) water splitting using semiconductor materials. His research work was focused on the development of new co-catalysts for production of efficient H_2 or O_2. Tuite and Kelly[4] examined the effect of light-induced reactions of methylene blue and phenothiazinium dyes on the biological substrates. They observed that proteins, lipids, biological membranes, organelles, viruses, bacteria, mammalian cells and carcinomas were induced by the phenothiazinium dye.

Lachheb et al.[5] studied photocatalytic degradation of anthraquinonic (alizarin S), azoic (crocein orange G, methyl red), congo red, heteropolyaromatic (methylene blue) dyes in TiO_2/UV aqueous suspensions. They have performed decolorization and detoxification, particularly in textile industries. Garg et al.[6] have used pretreated Indian Rosewood (*Dalbergia sissoo*) sawdust with formaldehyde and sulphuric acid for removal of methylene blue dye from simulated wastewater. Devipriya and Yesodharan[7] have performed complete photocatalytic mineralization of pesticides to harmless products. Daneshvar et al.[8] compared the degradation of acid red 14 (AR14) in the presence and absence of UV light using photocatalyst ZnO. They observed that the amount of H_2O_2 also affect the photodegradation of dye.

Kansal et al.[9] carried out photocatalytic degradation of methyl orange and rhodamine 6G employing heterogeneous photocatalytic process. Photocatalytic activity of various semiconductors such as titanium dioxide, zinc oxide, stannic oxide, zinc sulphide and cadmium sulphide was investigated by them. Vaishnave et al.[10] studied effective decolorization and degradation of methylene blue dye by using photo-Fenton and sono-photo-Fenton processes. It was found that sono-photo-Fenton processes was more efficient as compared to photo-Fenton.

The sunlight mediated photocatalytic degradation of rhodamine B dye was studied by Byrappa et al.[11] using hydrothermally prepared ZnO. The reaction scheme for the photocatalytic degradation of RB dye was –

$$ZnO + h\nu \rightarrow ZnO* \qquad\qquad ...(1)$$

$$ZnO* + H_2O \rightarrow ZnO* + H^+ + •OH \qquad\qquad ...(2)$$

$$•OH + Dye\ molecule \rightarrow Intermediates \rightarrow CO_2 + H_2O + Mineral\ salts \qquad …(3)$$

Gandhi et al.[12] degradated methylene blue using coprecipitated sulphide photocatalyst. This coprecipitated semiconductor CoS-ZnS (in 1 : 10 mole ratios) was prepared by coprecipitation and used for photodegradation of methylene blue while Ameta et al.[13] used semiconducting iron (III) oxide as a photocatalyst for bleaching of methylene blue, crystal violet and malachite green dyes.

Bhati et al.[14] synthesized $CeCr_2O_5$ nanoparticles by microwave method for the decolorization of yellowish orange and fast green dyes, the common water effluents of textile industries. Shimizu et al.[15] carried out the degradation of methylene blue by the irradiation of ultrasound onto TiO_2 in aqueous solution. They observed that the addition of H_2O_2 had an effect on the methylene blue degradation, but the system containing Al_2O_3 was unaffected.

EXPERIMENTAL

Preparation of ferric tungstate

Solution A was prepared by dissolving 70 g ferrous ammonium sulphate in 1 Liter of doubly distilled water. 20 g of urea and few drops of dilute H_2SO_4 was added to this solution. On the other hand, solution B was prepared by dissolving 18 g of sodium tungstate in 1 Liter doubly distilled water. 20 mL of hydrogen peroxide was added to this solution. Thereafter, solutions A and B were mixed and warmed at 60°C for 1 hour. The product obtained was washed with hot distilled water three times. The product was

filtered and dried in oven at 100°C for 7-10 hours. It was calcined in a muffle furnace at 500°C for 4 hours. Ferric tungstate was obtained in the form of brownish black crystalline powder. This semiconductor was used as a photocatalyst for the degradation of methylene blue dye.
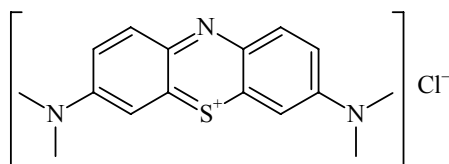
Structure of methylene blue

Stock solution of methylene blue dye (1 x 10^{-3} M) was prepared in doubly distilled water. It was further diluted as and when required. The photocatalytic degradation of methylene blue dye was studied after addition of 0.06 g of ferric tungstate in 50 mL dye solution (1 x 10^{-5} M). A 200W tungsten lamp was used for irradiation (50.0 W cm^{-2} light intensity). Irrdiation was carried out in glass vessel (Pyrex. 100 mL). A solarimeter (Suryamapi CEL 201) was used for the measurement of light intensities. Water filter was used to cut thermal effect. A digital pH meter (Systronic Model 335) was used to measure pH of the dye solutions. pH of the dye solutions were adjusted by addition of previously standardized 0.1 N sulphuric acid and 0.1 N sodium hydroxide solution. UV-Visible spectrometer (Systronic Model 106) was used to measure absorbance (A) of the dye solution at regular time intervals. Controlled experiments were also carried out to confirm that the degradation of methylene blue by ferric tungstate was photocatalytic in nature.

RESULTS AND DISCUSSION

Degradation of methylene blue was observed at λ = 660 nm. A graph plotted between log Absorbance v/s time was a straight line, which shows that photocatalytic degradation of methylene blue follows pseudo-first order kinetics. The rate constant for degradation of dye was calculated by the following expression –

$$k = 2.303 \text{ x slope} \qquad \qquad …(4)$$

Table 1: Typical run

pH = 9.5   [Methylene blue] = 1.10 x 10^{-5} M
Ferric tungstate = 0.06 g   Light intensity = 50.0 mWcm^{-2}

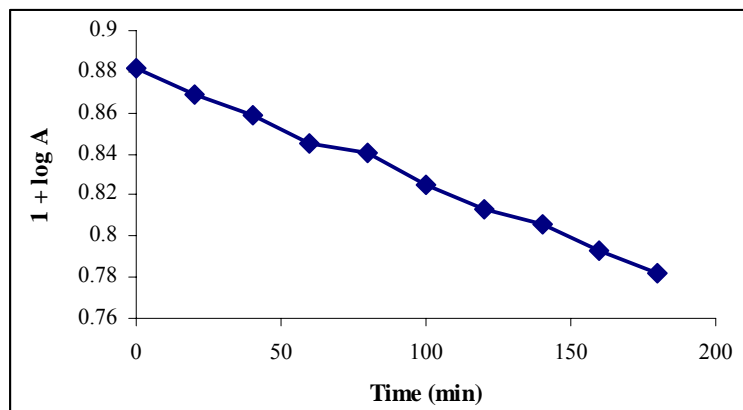| Time	Absorbance (A)	1 + log A
0.0	0.761	0.8814
20.0	0.740	0.8692
40.0	0.722	0.8585
60.0	0.700	0.8451
80.0	0.692	0.8401
100.0	0.669	0.8254
120.0	0.650	0.8129
140.0	0.640	0.8062
160.0	0.621	0.7931
180.0	0.605	0.7818
		k = 2.11 x 10^{-5} sec^{-1}

Fig. 1: Typical run

Effect of pH

The effect of pH on photocatalytic degradation was investigated at different pH and the results are given in Table 2 and Figure 2. The reaction rates were determined in the pH range 6.0–10.5 and the photocatalytic degradation of methylene blue was found maximum at pH 9.5.

It has been observed that with an increase in pH, the rate of photocatalytic degradation of dye increases from 6.0 to 9.5. On further increasing the pH above 9.5 resulted into a decrease in the rate of photocatalytic degradation. This observation can be explained on the basis that as the pH of the solution was increased, more $O_2^{-\bullet}$ radicals are generated by abstraction of an electron by dissolved oxygen, which are considered responsible for reduction of dye molecules. After a certain pH value, more $O_2^{-\bullet}$ will make the surface of semiconductor negatively charged and it restricts the approach of neutral dye molecules towards the semiconductor surface. This will result into a decrease in the rate of photocatalytic degradation of dyes.

Table 2: Effect of pH

[Methylene blue] = 1.10×10^{-5} M   Ferric tungstate = 0.06 g
Light intensity = 50.0 mWCm^{-2}

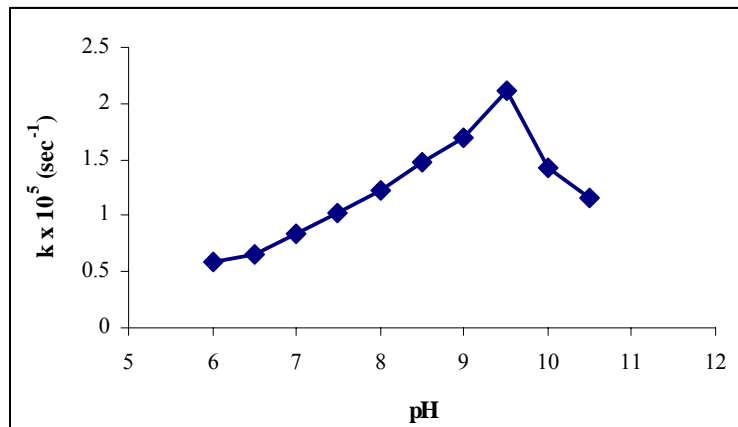| pH	$k \times 10^5$ (sec^{-1})
6.0	0.58
6.5	0.66
7.0	0.84
7.5	1.03
8.0	1.22
8.5	1.48
9.0	1.70
9.5	**2.11**
10.0	1.42
10.5	1.16

Fig. 2: Effect of pH

Effect of methylene blue concentration

Effect of variation of dye concentration was also studied by taking different concentrations of dye i.e. 0.5×10^{-5} M-1.4×10^{-5} M. The results are tabulated in Table 3 and represented in Figure 3. From the observed data, it is evident that the rate of photocatalytic degradation increases with increasing concentration of the dye. The rate constant was found optimum at 1.1×10^{-5} M. It was decreased on further increasing the dye concentration.

This may be attributed to the fact that as the concentration of dyes was increased, more dyes molecules were available for excitation followed by inter system crossing and hence, there was an increase in the rate. The rate of photocatalytic degradation was found to decrease with an increase in the concentration of dye further. Here, the dye molecules starts acting as filter for the incident light and they do not permit the desired light intensity to reach the semiconducting particles and thus, results in decrease in the rate of the photocatalytic degradation of dye.

Table 3: Effect of methylene blue concentration

pH = 9.5   Ferric tungstate = 0.06 g

Light intensity = 50.0 mWCm^{-2}

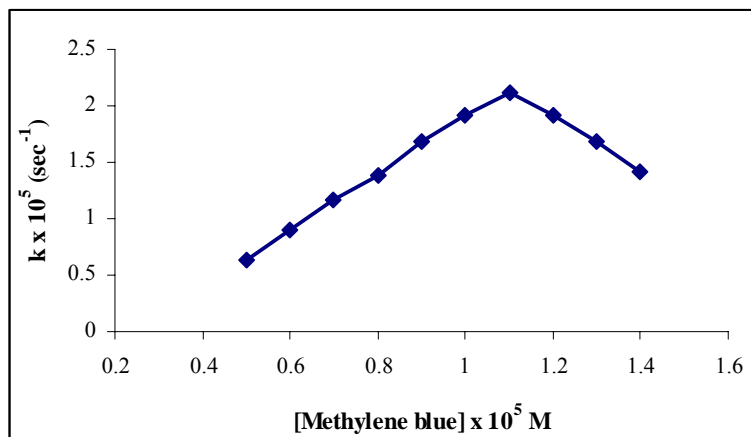| [Methylene blue] x 10^5 M	k x 10^5 (sec^{-1})
0.50	0.63
0.60	0.90
0.70	1.17
0.80	1.39
0.90	1.69
1.00	1.92
1.10	**2.11**
1.20	1.91
1.30	1.69
1.40	1.42

Fig. 3: Effect of methylene blue concentration

Effect of amount of ferric tungstate

The amount of semiconductor also affects the process of dye degradation. Different amounts of photocatalyst were used (0.02 to 0.11 g) and the results are given in Table 4 and Figure 4.

It has been observed that as the amount of semiconductor was increased, the rate of photodegradation of dye increases but ultimately, the reaction rate become virtually constant after a certain amount (0.06 g) of the semiconductor. This may be due to the fact that as the amount of semiconductor was increased, the exposed surface area also increases, but after a certain limit, if the amount of semiconductor was further increased; 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 has negligible or no effect on the rate of photocatalytic degradation of dye, as any increase in the amount of semiconductor after this saturation point will only increase the thickness of the layer at the bottom of the vessel. It was observed that the saturation point was increased on using vessels of higher dimensions.

Table 4: Effect of amount of ferric tungstate

pH = 9.5   [Methylene blue] = 1.10×10^{-5} M

Light intensity = 50.0 $mWCm^{-2}$

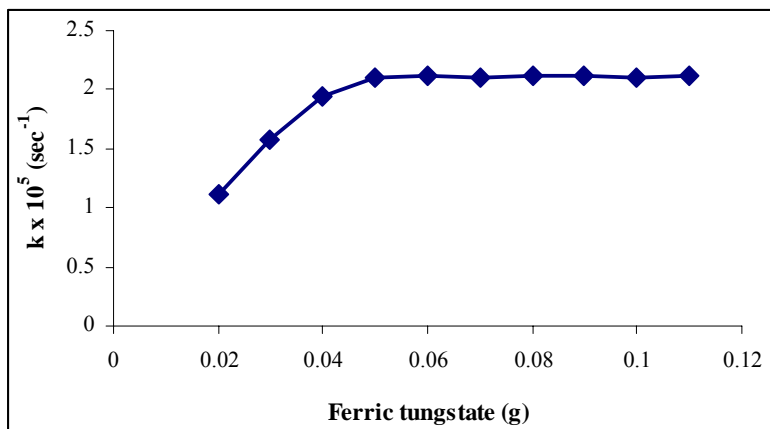| Ferric tungstate (g)	$k \times 10^5$ (sec^{-1})
0.02	1.11
0.03	1.57
0.04	1.95
0.05	2.10
0.06	**2.11**
0.07	2.10
0.08	2.12
0.09	2.11
0.10	2.10
0.11	2.11

Fig. 4: Effect of amount of ferric tungstate

Effect of light intensity

The effect of the variation of light intensity on the rate was also investigated and the observations are reported in the Table 5 and Figure 5.

Table 5: Effect of light intensity

pH = 9.5   [Methylene blue] = 1.10×10^{-5} M

Ferric tungstate = 0.06 g

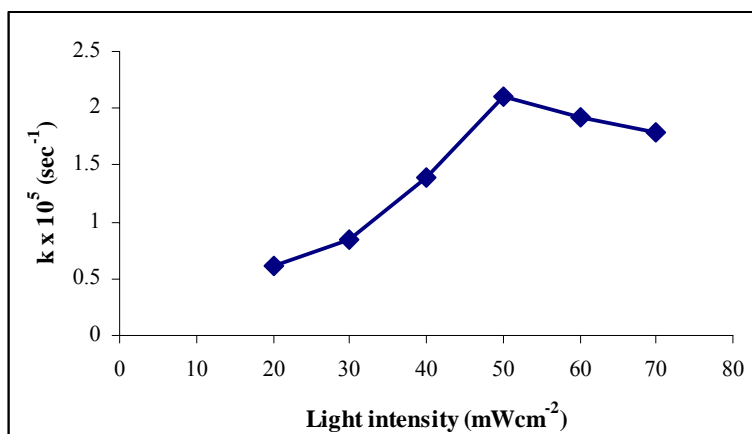| Light intensity (mWcm^{-2})	k x 10^5 (sec^{-1})
20.0	0.61
30.0	0.85
40.0	1.39
50.0	**2.11**
60.0	1.92
70.0	1.78

Fig. 5: Effect of light intensity

The results indicate that degradation rate of methylene blue was enhanced as the intensity of light was increased. It was found maximum at 50.0 mWcm^{-2} and the rate was retarded on further increasing the light intensity. It may be attributed to the fact that an increase in the light intensity will increase the number of photons striking per unit area of semiconductor powder. The rate is decreased, when the light intensity is increased further from 50.0 mWcm^{-2}, may be due to thermal reactions.

Mechanism

On the basis of the observations, a tentative mechanism for photocatalytic degradation of methylene blue may be proposed as –

$$^{1}MB_0 \xrightarrow{\;h\nu\;} {}^{1}MB_1 \qquad \qquad \ldots(5)$$

$$^{1}MB_1 \xrightarrow{\;ISC\;} {}^{3}MB_1 \qquad \qquad \ldots(6)$$

$$SC \xrightarrow{\;h\nu\;} e^- (CB) + h^+ (VB) \qquad \qquad \ldots(7)$$

$$e^- + O_2 \longrightarrow O_2^{-\bullet} \qquad \qquad ...(8)$$

$$O_2^{-\bullet} + {}^{3}MB_1 \longrightarrow Leuco\ MB + O_2 \qquad \qquad \ldots(9)$$

$$Leuco\ MB \longrightarrow Products \qquad \qquad \ldots(10)$$

Methylene blue (MB) 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 semiconducting ferric tungstate also utilized the incident light energy to excite its electron from valence band to conduction band; thus, leaving behind a hole. The dissolved oxygen accepts electron of semiconductor and is converted into oxygen anion radical. In the next step, the dye molecule in triplet state takes electron from oxygen anion radical and reduced to its leuco form, which further degrades into harmless products. The hydroxyl radicals do not participate in the photodegradation of dye as the reaction rate was not appreciably retarded in presence of hydroxyl radical scavengers; isopropanol.

REFERENCES

1. A. Houas, H. Lachheb, M. Ksibi, E. Elaloui, C. Guillard and J. M. Hermann, Photocatalytic Degradation Pathway of Methylene Blue in Water, Appl. Catal. B: Environ., **31(2)**, 145-157 (2001).

2. K. Rajeshwar, M. E. Osugi, W. Chanmanee, C. R. Chenthamarakshan, M. V. B. Zanoni, P. Kajitvichyanukul and R. K. Ayer, Heterogeneous Photocatalytic Treatment of Organic Dyes in Air and Aqueous Media, J. Photochem. Photobiol. C, **9(4)**, 171-192 (2008).

3. R. Abe, Recent Progress on Photocatalytic and Photoelectrochemical Water Splitting under Visible Light Irradiation, J. Photochem. Photobiol. C, **11(4)**, 179-209 (2010).

4. E. M. Tuite and J. M. Kelly, New Trends in Photobiology: Photochemical Interactions of Methylene Blue and Analogues with DNA and other Biological Substrates, J. Photochem. Photobiol. B, **21(2-3)**, 103-124 (1993).

5.   H. Lachheb, E. Puzenat, A. Houas, M. Ksibi, E. Elaloui, C. Guillard and J.-M. Herrmann, Photocatalytic Degradation of Various Types of Dyes (Alizarin S, Crocein Orange G, Methyl Red, Congo Red, Methylene Blue) in water by UV-Irradiated Titania, Appl. Catal. B: Environ., **39(1)**, 75-90 (2002).

6.   V. K. Garg, M. Amita, R. Kumar and R. Gupta, Basic Dye (Methylene Blue) Removal from Simulated Wastewater by Adsorption using Indian Rosewood Sawdust: A Timber Industry Waste, Dyes and Pigments, **63(3)**, 243-250 (2004).

7.   S. Devipriya and S. Yesodharan, Photocatalytic Degradation of Pesticide Contaminants in Water, Sol. Energy Mater. Sol. Cells, **86(3)**, 309-348 (2005).

8.   N. Daneshvar, D. Salari and A. R. Khataee, Photocatalytic Degradation of Azo Dye Acid Red 14 in Water on ZnO as an Alternative Catalyst to TiO_2, J. Photochem. Photobiol. A, **162(2-3)**, 317-322 (2004).

9.   S. K. Kansal, M. Singh and D. Sud, Studies on Photodegradation of Two Commercial Dyes in Aqueous Phase using Different Photocatalysts, J. Hazard. Mater., **141(3)**, 581-590 (2007).

10. P. Vaishnave, G. Ameta, A. Kumara, S. Sharma and Suresh C. Ameta, Sono-photo-Fenton and Photo-Fenton Degradation of Methylene Blue : A Comparative Study, J. Indian Chem. Soc., **88**, 397-403 (2011).

11. K. Byrappa, A. K. Subramani, S. Ananda, K. M. L. Rai, R. Dinesh and M. Yoshimura, Photocatalytic Degradation of Rhodamine B Dye using Hydrothermally Synthesized ZnO, Bull. Mater. Sci., **29(5)**, 433-438 (2006).

12. N. Gandhi, V. Sharma, A. Khant and R. C. Khandelwal, Preparation and Use of CoS-ZnS (1 : 10) in Photodegradation of Methylene Blue, Int. J. Chem. Sci., **8(3)**, 1924-1932 (2010).

13. R. Ameta, J. Vardia, P. B. Punjabi and Suresh. C. Ameta, Use of Semiconducting Iron (III) Oxide in Photocatalytic Bleaching of some Dyes, Indian J. Chem. Tech., **13**, 114-118 (2006).

14. I. Bhati, J. Sharma, A. Ameta and S. C. Ameta, Synthesis and Characterization of Nanosized $CeCr_2O_5$ and its use as a Photocatalyst, Int. J. Chem. Sci., **9(4)**, 1787-1796 (2011).

15. N. Shimizu, C. Ogino, M. F. Dadjour and T. Murata, Sonocatalytic Degradation of Methylene Blue with TiO_2 Pellets in Water, Ultrason. Sonochem., **14(2)**, 184-90 (2007).