© 2015 IJSRST | Volume 1 | Issue 2 | Print ISSN: 2395-6011 | Online ISSN: 2395-602X
Themed Section: Scienceand Technology

Ferrous Ion Catalyzed Photooxidation of Methylene Blue with Peroxydisulphate Ion

Jyoti Soni[1], Anil Chohadia[2], Narendra Nirwan[3], Kumud Intodia[4]
[1]Department of Chemistry, S. M. B. Government P. G. College, Nathdwara, Rajasthan,India
[2]Department of Chemistry, M. P. Government P. G. College, Chittorgarh, Rajasthan,India
[3]Department of Chemistry, S. D. Government College, Beawer, Rajasthan,India
[4]Department of Chemistry, Meera Girls Government P. G. College, Udaipur, Rajasthan,India

ABSTRACT

Photooxidation of dyes is a new concern among researchers since it offers an attractive method for decolorization of dyes and breaks them into simple products. Photochemical oxidation of methylene blue (MB) was investigated in presence of Fe^{2+} and peroxydisulphate ions at normal temperature and pressure. The effect of operating variables like the concentration of ferrous ions, concentration of methylene blue, pH, and concentration of peroxydisulphate ion and light intensity on the rate of reaction was also observed. The progress of the reaction was monitored spectrophotometrically. The photochemical oxidation of dye follows pseudo first order kinetics. The results showed that the methylene blue was completely oxidized and degraded into CO_2 and H_2O. A suitable tentative mechanism for photochemical oxidation of methylene blue has been proposed.

Keywords: Photochemical oxidation, ferrous ion, peroxydisulphate ion, methylene blue (MB).

I. INTRODUCTION

Bright and fabulous coloration, attractive outlook and ever changing fashion have revolutionized the textile industry which has been whole heartedly catering the need of current generation. In contrast to the front end production of beautiful fabrics, the backside discharge of waste water from many textile industries containing high concentration of dyes has raised a serious environmental concern. The stability and non-biodegradability of dyes causes major problems in its treatment and thus demands new ecofriendly methods. In last two decades, there has been considerable research focused on the development of various techniques to treat dye waste water. Among various treatment methods, Advanced Oxidation Treatment (AOT) techniques have been found to be promising to convert the dye present in waste water to harmless compounds. The homogeneous AOPs employingperoxydisulfate[1,2] and UV/ peroxydisulfate[3] have been found to be very effective in degrading dyes and pollutants.

Advanced oxidation treatment techniques such as Fenton and modified Fenton based treatment system, TiO_2 photocatalysis, ozonation, wet air oxidation have been found to be quite effective in treatment of waste water from dye industries. The peroxydisulphate ion is a powerful two electron oxidizing agent with a redox potential of –2.01 volts. Oxidation reactions of the inorganic and organic substrates have been reviewed by

IJSRST184178 | Received: 02 June 2015 | Accepted: 29 June 2015 | May-June 2015 [(1)2: 132-139]

House.[4] The kinetics and mechanism of oxidation of 2-propanol by peroxydisulphate has been reported by Ball et al.[5] Oxidation of malic acid and lactic acid by peroxydisulphate catalyzed by Cu(II) was investigated by Meyerstein[6] and Agrawal et al.[7,8] Photocatalytic decolorization of methylene blue in aqueous TiO_2 suspension has been reported by Lee et al.[9] while Spadaro et al.[10] observed the degradation of p-aminoazobenzene and p-hydroxyazobenzene using TiO_2 as a photocatalyst. Degradation of the same dye was also observed by Krishnan[11] using various heat treated TiO_2 as the catalyst. Oxidation of methylene blue was carried out by Dutta et al.[12] using photo-Fenton reagent. The oxidation of reactive blue-19 dye with UV/H_2O_2 was also carried out by Rezaee et al.[13] Various physical, chemical and biological methods have been used for the treatment of these textile effluents by Cicek et al.[14] and Daneshvar et al.[15] while Gemeay et al.[16] suggested the use of advanced oxidation processes both in industrial preparation and in the treatment of industrial waste water. These processes are used for degrading and removing color from dye baths, which allow wastewater for reuse. Methyl orange dye degradation was investigated by Fatimah et al.[17] under a combined photocatalytic and Fenton based oxidation in the presence of TiO_2 and Fe^{2+} and the decoloration of the reactive blue dye KN-R was also investigated by Gabriel and Hong[18] using Fenton and UV/Fenton processes. Soni et al.[19] suggested the photochemical oxidation of azure-B with sulphate radical ion ($SO_4^{-\bullet}$) and hydroxyle radical ($HO^\bullet$) generated by the conjunction of peroxydisulphate ion with ferric ion. Oxidative degradation of propachlor by ferrous and copper ion activated persulfate was suggested by Liu et al.[20] while Zhao et al.[21] investigated the 1,4-dioxane degradation efficiency and rate during persulfate oxidation at different temperatures, with and without Fe^{2+} addition, also considering the effect of pH and persulfate concentration on the oxidation of 1,4-dioxane.

II. EXPERIMENTAL

2.1 Materials And Methods

Methylene Blue (Reidel), ferrous sulphate (Merck) and potassium peroxydisulphate (S.D. Fine) were used in present investigations. All the solutions were prepared in doubly distilled water. The photocatalysed oxidation of dye was studied in the presence of ferrous sulphate. 0.0319 g of methylene blue (MB) was dissolved in 100 mL doubly distilled water, so the concentration of MB was 1.0×10^{-3} M. It was used as a stock solution. The absorbance of the dye solution was measured with the help of a spectrophotometer (Systronics Model) at $\lambda_{max} =$ 665 nm. 0.0278 g of ferrous sulphate was dissolved in 100 mL doubly distilled water so that a stock solution of 1.0×10^{-3} M concentration was obtained. The working solutions were prepared by the process of further dilution. Standard solution of potassium peroxydisulphate was prepared a fresh just before use by dissolving 2.7031 g of potassium peroxydisulphate in 100 mL doubly distilled water so that the concentration of solution was 0.1 M.

Photocatalised bleaching of MB was studied by taking 30.0 mL reaction mixture containing 5.00×10^{-5} M dye, 0.83×10^{-2} M peroxydisulphate and 0.50×10^{-4} M ferrous sulphate solutions in a 100 mL beaker and then this reaction mixture was exposed to light (light intensity = 70.0 mW cm^{-2}). The pH was adjusted at 2.7.

A 200 W tungsten lamp (Philips) was used for irradiation purpose. The intensity of light was measured with the help of a solarimeter (Surya Mapi Model CEL 201) in the units of mWcm^{-2}. A water filter was used to cut off thermal radiations. The pH of the solution was measured by a digital pH meter (Systronics Model 106). The desired pH of the solution was adjusted by the addition of previously standardized sulphuric acid and sodium hydroxide solutions.

2.2 Result And Discussion

An aliquot of 2.0 mL was taken out from the reaction mixture at regular time intervals and the absorbance was measured at λ_{max} = 665 nm for MB.

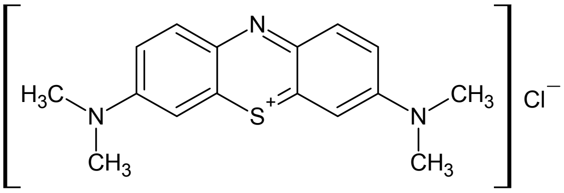

Figure 1. A structure of methylene blue (MB)

The structure of MB is given in Figure 1. It was observed that the optical density (OD) of the reaction mixture decreases with increasing time intervals showing thereby that the concentration of dye decreases with increasing time exposure. A plot of 1 + log OD versus time was linear and follows pseudo-first order kinetics. The rate constant was determined by the expression: $k = 2.303 \times$ slope. The rate constant (k) for this reaction was determined 2.41×10^{-4} s^{-1}. Results for typical run are given in Table 1 and Figure 2.

Table 1. A typical run

pH = 2.7 | [Methylene Blue] = 5.00×10^{-5} M

[$S_2O_8^{-2}$] = 0.83×10^{-2} M | [Fe^{+2})] = 0.50×10^{-4} M

Light intensity = 70.0 mWcm^{-2}

Time (min)	Absorbance (OD)	1 + log OD
0	0.797	0.901
10	0.695	0.842
20	0.608	0.783
30	0.509	0.707
40	0.432	0.635
50	0.370	0.568
60	0.330	0.518
70	0.283	0.452
80	0.253	0.403
90	0.217	0.336
100	0.186	0.269
		$k = 2.41 \times 10^{-4}$ s^{-1}

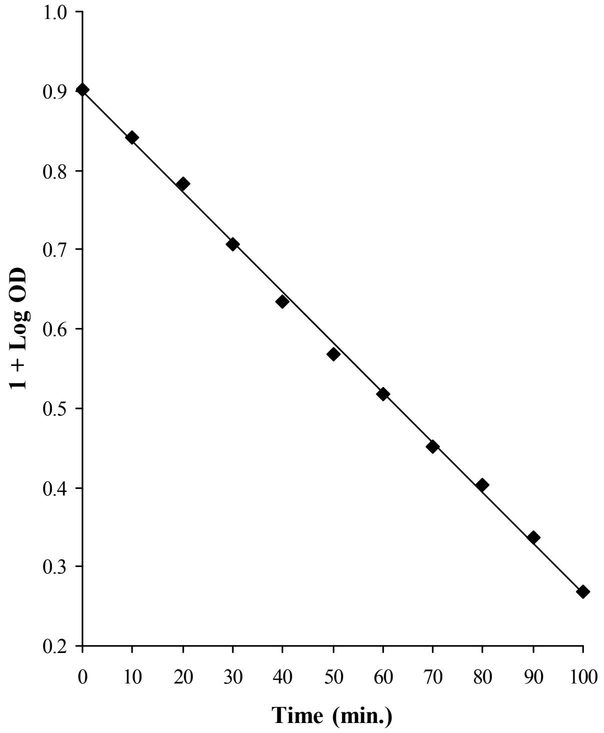

Figure 2. A typical run

2.2.1 Effect of pH

The rate of photochemical oxidation of MB was maximum at pH 2.7. It was observed that rate of oxidation increases on increasing the pH of the reaction mixture. This may be attributed to the fact that as the pH increases the number of $S_2O_8^{2-}$ ions increase, which is utilized in oxidation of Fe^{2+} to Fe^{3+} ions. Fe^{3+}ions play an important role in oxidizing excited dye to its cation radical. After attaining the maximum rate at particular pH, it starts decreasing. It may be explained on the basis that with increase in pH, OH^- ions increases and these OH^- ions may react with sulphate anion radical to give sulphate ion. Sulphate anion radical is also considered as one of the active oxidizing species and its removal from reaction mixture at higher pH will retard the rate of reaction.

$$2SO_4^{-\bullet} + 2\,OH^- \longrightarrow 2SO_4^{2-} + H_2O_2 \quad \ldots(1)$$

$$2\,H_2O_2 \longrightarrow 2\,H_2O + O_2 \quad \ldots(2)$$

At pH > 3.7 some turbidity appeared and measurement of optical density becomes difficult and therefore, the effect of pH was studied in the range 2.3 to 3.7 and the results are summarized in Table 2.

Table 2. Effect of pH

[Methylene Blue] = 5.00×10^{-5} M $[S_2O_8^{-2}] = 0.83 \times 10^{-2}$ M
Light intensity = 70.0 mWcm^{-2} $[Fe^{+2}] = 0.50 \times 10^{-4}$ M

pH	$k \times 10^4\ s^{-1}$
2.3	2.05
2.5	2.29
2.7	**2.41**
2.9	2.23
3.1	1.95
3.3	1.88
3.5	1.75
3.7	1.66

2.2.2 Effect of Dye Concentration

The effect of variation of the dye concentration on rate of bleaching was also studied by taking different concentrations of dye. The photodegradation was studied in the range of 1.67×10^{-5} to 11.67×10^{-5} M for MB. The maximum rate was found at 5.00×10^{-5} M for MB. The results are reported in Table 3.

The rate of bleaching was found to increase with increasing concentration of dye. This may be explained on the basis that on increasing the concentration of dye, more molecules of dye are available for excitation. However, on increasing the concentration beyond certain limits, the reaction rate decreases. This is probably due to the fact that after certain limiting concentration of dye, the dye molecules present in the upper layer of the solution will absorb a major portion of light. This will prevent the incident light to reach the dye molecule in the bulk of the solution. The high concentration of dye will act as a filter for the incident light and hence, at higher concentration of the dye, the rate of photochemical bleaching decreases.

Table 3. Effect of Dye Concentration

pH = 2.7 $[S_2O_8^{2-}] = 0.83 \times 10^{-2}$ M
$[Fe^{+2})] = 0.50 \times 10^{-4}$ M Light intensity = 70.0 mWcm^{-2}

[Methylene Blue] × 10^5 M	k × 10^4 s^{-1}
1.67	1.24
3.33	1.57
5.00	**2.41**
6.67	1.48
8.33	0.93
10.00	0.46
11.67	0.34

2.2.3 Effect of peroxydisulphate ion concentration

The effect of variation of peroxydisulphate ion concentration on rate of the reaction was observed by taking different concentrations of peroxydisulphate ion. The results are summarized in Table 4.

The results indicate that the rate of the reaction increases on the increase in the oxidant concentration upto 0.83×10^{-2} M because more peroxydisulphate ions are available for the oxidation. On further increasing the concentration of the oxidant, a reverse trend was obtained. The decrease in the rate of the reaction may be due to the hindrance in the movement of $HO^{\bullet}$ and sulphate ion and as a result, the activity of these ions is decreased. The less reactive H_2O_2 can beformedby the recombination of hydroxyl radicals. H_2O_2 is a known quencher of $HO^{\bullet}$ radical. Therefore, the rate increment of methylene blue photooxidative decolorization is slightly slowed down at higher $S_2O_8^{2-}$ dosages. However, such a recombination effect of the radical is likely not very effective due to the low steady-state concentrations of the radicals; higher decay rates of methylene blue at higher $S_2O_8^{2-}$ dosages are still expected. The finding was in agreement with literature reports where optimal concentration of $S_2O_8^{2-}$ would result in higher photooxidative removal efficiency.[22-25]

Table 4. Effect of peroxydisulphate ion concentration

pH = 2.7 [Methylene Blue] = 5.00×10^{-5} M
$[Fe^{2+}]$ = 0.50×10^{-4} M Light intensity = 70.0 mWcm^{-2}

$[S_2O_8^{2-}] \times 10^2$ M	k × 10^4 s^{-1}
0.33	1.73
0.50	1.91
0.67	2.09
0.83	**2.41**
1.00	1.91
1.16	1.46

2.2.4 Effect of ferrous ion concentration

The effect of increasing concentration of Fe^{2+} ions was also studied by keeping all other factors identical. The results are given in Table 5.

It is clear from the data that the rate of bleaching of dye increases on increasing the concentration of ferrous sulphate. This may be due to increase in number of Fe^{2+} ions, which are oxidized to Fe^{3+} ions on reaction with peroxydisulphate ions. These Fe^{3+}

ions convert excited dye molecule to its cation radical, which then undergoes degradation. But after a certain limit i.e., $[Fe^{2+}] = 0.50 \times 10^{-4}$ M, a reverse trend was obtained. This can be explain on the basis that on increasing the number of Fe^{+2} ions, it also react with sulphate ion radical ($SO_4^{-\bullet}$), which are reduced to sulphate ion (SO_4^{2-}). So at higher concentration of the Fe^{2+} ions, the rate of photochemical oxidation decreases.

Table 5. Effect of ferrous ion concentration

pH = 2.7	[Methylene Blue] = 5.00×10^{-5} M
$[S_2O_8^{2-}] = 0.83 \times 10^{-2}$ M	Light intensity = 70.0 $mWcm^{-2}$
$[Fe^{2+}] \times 10^4$ M	**$k \times 10^4\ s^{-1}$**
0.16	0.94
0.33	1.46
0.50	2.41
0.67	1.46
0.83	1.20
1.00	0.70

2.2.5 Effect of light intensity

The effect of light intensity on the photodegradation of MB was also observed. The results are reported in Table 6.

Table 6. Effect of light intensity

pH = 2.7	[Methylene Blue] = 5.00×10^{-5} M
$[Fe^{2+}] = 0.50 \times 10^{-4}$ M	$[S_2O_8^{2-}] = 0.83 \times 10^{-2}$ M
Light Intensity ($mWcm^{-2}$)	**$k \times 10^4\ s^{-1}$**
10.0	1.20
20.0	1.31
30.0	1.55
40.0	1.73
50.0	2.04
60.0	2.18
70.0	**2.41**

A linear plot was observed between the rate constant and light intensity, which indicates that an increase in the light intensity increases the rate of reaction. This may be due to the increased number of photons reacting with Fe^{2+} ions and as a result, there is an increase in the number of active species, the $S_2O_8^{2-}$ and $SO_4^{-\bullet}$ radical ions and corresponding increase in the rate of reaction. However, higher intensities were avoided due to thermal effects.

3.Mechanism

Peroxydisulphate is a strong two electron oxidant and it works as a good oxidant for many chemical processes. On the basis of experimental observations, a tentative mechanism for Fe^{2+} catalyzed photochemical bleaching of the dye has been proposed as–

$Fe^{2+} + S_2O_8^{2-} \longrightarrow Fe^{3+} + SO_4^{-\bullet} + SO_4^{2-}$ …(3)
$MB + h\nu \longrightarrow MB^*$ …(4)
$Fe^{3+} + MB^* \longrightarrow Fe^{2+} + MB^{+\bullet}$ …(5)
$S_2O_8^{2-} + h\nu \longrightarrow 2\ SO_4^{-\bullet}$ …(6)
$Fe^{2+} + SO_4^{-\bullet} \longrightarrow Fe^{3+} + SO_4^{2-}$ …(7)
$SO_4^{-\bullet} + H_2O \longrightarrow HSO_4^- + HO^\bullet$ …(8)
$Fe^{3+} + H_2O \longrightarrow Fe^{2+} + H^+ + HO^\bullet$ …(9)
$Fe^{2+} + H_2O_2 + H^+ \longrightarrow Fe^{3+} + H_2O + HO^\bullet$ …(10)
$HO^\bullet + HO^\bullet \longrightarrow H_2O_2$ …(11)
$HO^\bullet + H_2O_2 \longrightarrow H_2O + HO_2^\bullet$ …(12)
$MB^{+\bullet} + S_2O_8^{2-} \longrightarrow P + SO_4^{-\bullet} + SO_4^{2-} + 2H^+$ …(13)
$HO^\bullet + MB \longrightarrow P + SO_4^{2-} + 2H^+$ …(14)
$SO_4^{-\bullet} + MB^{+\bullet} \longrightarrow P + SO_4^{2-} + 2H^+$ …(15)
(Here P = gaseous products like CO_2, H_2O, etc)

In the initial step, Fe^{2+} transfer its electron to peroxydisulphate ion and hence, Fe^{2+} ions are oxidized to Fe^{3+} and peroxydisulphate ion is broken into sulphate ion and sulphate anion radical. Fe^{3+} ions pulls an electron from excited dye molecule to yield dye cation radical and Fe^{2+} ion. The dye cation radical also reacts with peroxydisulphate ions giving sulphate ion, sulphate anion radical, protons and the degraded products of the dye. Fe^{2+} ions will also react with sulphate anion radical, converting it into sulphate ions. In next step, sulphate anion radical reacts with dye cation radical to give sulphate ion and products. The presence of sulphate ions and carbon dioxide were detected by their usual tests. The release of protons in two steps increases the acidity of the reaction medium and the reaction rate decreases at lower pH values (strong acidic medium), as evident from experimental observations.

The oxidative bleaching of dyes by peroxydisulphate can be enhanced by the addition of metal ion like ferrous ions which act as electron donor and/or acceptor as it has variable oxidation states of +2 and +3. Such reactions may also be utilized for the treatment of effluents from textile, dyeing and printing industries parallel to advanced oxidation processes (AOPs).

III. CONCLUSIONS

The aim of this study is to analyze the feasibility of discoloration and mineralization of methylene blue using a new photochemical oxidation process and the results of this study shows that $Fe^{3+}/S_2O_8^{2-}$ process could efficiently optimize the photooxidative decolorization of methylene blue. Under optimum conditions of the process parameters, high color removal was obtained for the dye solution containing methylene blue. The results showed that the addition of proper amount of $S_2O_8^{2-}$ and Fe^{3+} ions could improve the photooxidative decolorization efficiency. Effect of experimental parameters on the decolorization efficiency of $Fe^{3+}/S_2O_8^{2-}$ process was established and the rate constant *k* for dye degradation was also studied at optimum conditions.

IV. ACKNOWLEDGEMENT

Authors are thankful to Principal, S. M. B. Govt. P.G. College, Nathdwara for providing necessary laboratory facilities and to Prof. Suresh C. Ameta for valuable critical discussions.

V. REFERENCES

[1]. Xu, X. R.; Li, X. Z. Sep. Puri. Technol. 2010, 72, 105.

[2]. Zhang, H.; Zhang, J.; Zhang, C.; Liu, F.; Zhang, D. Ultrason. Sonochem. 2009, 16, 325.

[3]. Wang, P.; Yang, S.; Shan, L.; Niu, R.; Shao, X. J. Environ. Sci. 2011, 23, 1799.

[4]. House, D. A. Chem. Revs. 1962, 62, 185.

[5]. Ball, D. L.; Gutchfield, M. M.; Edwards, J. O. J. Org. Chem. 1960, 25, 1599.

[6]. Meyerstein, D.; J. Inorg. Nucl. Chem. 1981, 43, 401.

[7]. Agrawal, S. C.; Chandra, G.; Jha, S. K. J. Inorg. Nucl. Chem. 1979, 41, 899.

[8]. Agrawal, S. C.; Saxena, L. K. J. Inorg. Nucl. Chem. 1980, 42, 932.

[9]. Lee, B. N.; Liaw, W. D.; Lou, J. C. Environ. Eng. Sci. 1999, 16, 165.

[10]. Spadaro, J. T.; Isabelle, L.; Renganathan, U. Environ. Sci. Technol. 1994, 28, 1389.

[11]. Krishnan, G. M.; Gomathi, D. L. J. Photochem. Photobiol. 1999, 121A, 141.

[12]. Dutta, K.; Mukhopadhyay, S.; Bhattacharjee, S.; Chau, B. J. Hazard. Mater. 2001, 84, 57.

[13]. Rezaee, A.; Ghaneian, M. T.; Hashemian, S. J.; Moussavi, G.; Khavanin, A.; Ghanizadeh, G. J. Appl. Sci. 2008, 8(6), 1108.

[14]. Cicek, F.; Ozer, D.; Ozer, A. J. Hazard. Mater. 2007, 146, 408.

[15]. Daneshvar, N. A.; Aleboyesh; Khataee, A. R. Chemosphere 2005, 59, 761.

[16]. Gemeay, A.; El-Ghrabawy, G.; Zaki, A. Dyes Pigm. 2007, 73, 90.

[17]. Fatimah, I.; Shukla, P. R.; Kooli, F. J. Appl. Sci. 2009, 9(20), 3715.

[18]. Gabriel, H. J. Hong, Res. J. Appl. Sci.2008, 3(3), 216.

[19]. Soni, J.; Kumar, A.; Saifee, A.; Intodia, K. Bull. Catal. Soc. India 2010, 7, 64.

[20]. Liu, C. S.; Shin, K.; Sun, C. X.; Wang, F. Sci. Toatal Environ. 2012, 416, 507.

[21]. Zhao, L.; Hau, H.; Fujii, A.; Hosomi, M.; Li, F. Environ. Sci. Pollut. Res. Int. 2014, 21(12), 7457.

[22]. Lau, T. K.; Chu, W.; Graham, N. J. D. Environ. Sci. Technol. 2007, 41, 613.

[23]. Gara, P. M. D.; Bosio, G. N.; Gonzalez, M. C.; Martire, D. O. Int. J. Chem. Kinet. 2007, 40, 19.

[24]. Salari, D.; Niaei, A.; Aber, S.; Rasoulifard, M. H. J. Hazard. Mater. 2009, 166, 61.

[25]. Khataee, A. R.; Mirzajani, O. Desalination 2010, 251(1-3), 64.