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PHOTOOXIDATION OF TOLUIDINE BLUE USING SULPHATE RADICAL ION AND HYDROXYL RADICAL GENERATED BY PEROXYDISULPHATE AND FERROUS ION

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ABSTRACT

This paper is focused on optimising the use of additional oxidants in the photooxidation of toluidine blue. Photochemical oxidation of toluidine blue was investigated using sulphate radical ion ($SO_4^{-\bullet}$) and hydroxyl radical ($HO^\bullet$) which was generated by Fe^{2+} and peroxydisulphate ions at normal temperature and pressure. The effect of operating variables like the concentration of ferrous ions, concentration of toluidine blue, pH, concentration of peroxydisulphate ion and light intensity on the rate of reaction was also observed. The progress of the reaction was monitored spectrophotometrically. The photooxidation of dye follows pseudo first order kinetics. The toluidine blue was completely oxidized into CO_2 and H_2O and maximum decolorization was achieved at the optimum conditions of the reaction time 30 min. A tentative mechanism for photooxidation of toluidine blue has been proposed.

Key words: Photooxidation, Ferrous ion, Peroxydisulphate ion, Toluidine blue.

INTRODUCTION

Organic dyes constitute one of the larger groups of pollutants in waste water released from textile industries. The discharge of highly colored wastewater into the ecosystem involves environmental problems like aesthetic pollution, perturbation of aquatic life and the high concentration of dyes has raised a serious environmental concern. Half-lives of commercial dyes in sunlight would generally be greater than 2000 h.[1] Due to stability and the large percentage of organic material present in modern textile dyes, biological treatment is ineffective for their degradation and discoloration[2-6]. Thus demands new eco-friendly methods to degrade the organic dyes. 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.

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In recent years, peroxydisulphate ion with metal ion has become a widely studied option in the advanced oxidative treatment of organic pollutants in waste water due to its ability to destroy a wide range of contaminants using solar or UV/Vis irradiation. 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 House[7]. Oxidation of malic acid and lactic acid by peroxydisulphate catalyzed by Cu(II) was investigated by Meyerstein[3] and Agrawal et al.[8,9] Photocatalytic decolorization of methylene blue in aqueous TiO_2 suspension has been reported by Lee et al.[10] while Soni et al.[11] suggested the photochemical oxidation of azure-B with sulphate radical ion ($SO_4^{-\bullet}$) and hydroxyl radical ($HO^\bullet$) generated by the conjunction of peroxydisulphate ion with ferric ion. To improve the removal performance is always of interest and the photochemical oxidant, $Fe^{2+}/S_2O_8^{-2}$ process[12], could be a good option for such a purpose. Peroxydisulphate ($S_2O_8^{-2}$) has been used widely in the petroleum industry for the treatment of hydraulic fluids or as a reaction initiator[13]. It has also been reported to be effective for degrading organics in hazardous waste-waters in acidic or basic media through direct chemical oxidation, where peroxydisulphate is used as a sacrificial reagent[14].

The aim of this study is to analyze the feasibility of discoloration and mineralization of toluidine blue dye using a new photooxidant, i.e. peroxydisulphate ion with ferrous ion.

EXPERIMENTAL

Toluidine blue (Reidel), ferrous sulphate (Merck) and potassium peroxydisulphate (S.D. fine) were used in present investigations. 100 mL stock solutions of toluidine blue, ferrous sulphate (1.0×10^{-3} M) and potassium peroxydisulphate (0.10 M) were prepared in doubly distilled water. The working solutions were prepared by the process of further dilution. The absorbance of the dye solution was measured with the help of a spectrophotometer (Systronics Model) and the intensity of light was measured by a solarimeter (Surya Mapi Model CEL 201) in the units of $mWcm^{-2}$. The pH of the solution was measured by a digital pH meter (Systronics Model 106).

A 200 W tungsten lamp (Philips) was used for irradiation purpose. A water filter was used to cut off thermal radiations. The desired pH of the solution was adjusted by the addition of previously standardized sulphuric acid and sodium hydroxide solutions.

RESULTS AND DISCUSSION

At regular time intervals an aliquot of 2.0 mL was taken out from the reaction mixture and the absorbance was measured at λ_{max} = 625 nm for toluidine blue. The structure of toluidine blue is given in Fig. 1.

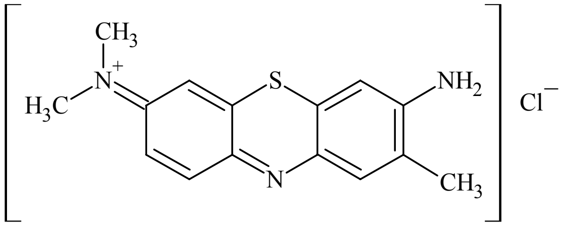

Fig. 1: Toluidine blue (Tolonium chloride)

It was observed that the optical density (O.D.) of the reaction mixture decreases with increasing time intervals showing thereby that the concentration of dye decreases with increasing time exposure. A plot of 2 + log O.D. 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 for this reaction determined was 11.51×10^{-4} s^{-1}. Results for typical run are given in Table 1 and represented graphically in Figure 2.

Table 1: A typical run

[Toluidine blue] = 0.33×10^{-4} M
pH = 3.0
[$S_2O_8^{-2}$] = 0.66×10^{-2} M
[Fe^{2+}] = 0.50×10^{-4} M
Light intensity = 70.0 $mWcm^{-2}$

Time (min.)	Absorbance (O.D.)	2 + log O.D.
0	0.40	1.60
5	0.30	1.47
10	0.20	1.30
15	0.14	1.14
20	0.10	1.00
25	0.07	0.84
30	0.05	0.69
		$k = 11.51 \times 10^{-4}$ s^{-1}

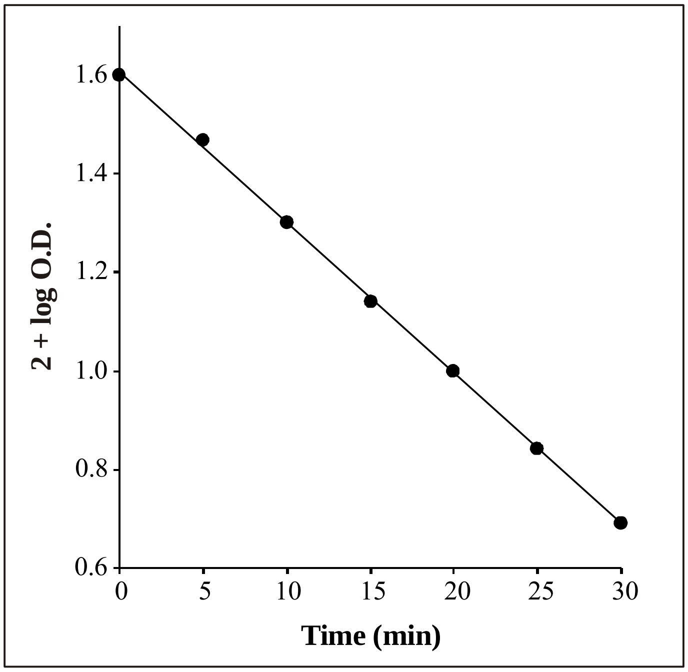

Fig. 2: A typical run

Effect of pH

The effect of pH on the rate of degradation of toluidine blue was investigated in the pH range (2.0 - 5.0). The results are reported in Table 2.

Table 2: Effect of pH

[Toluidine blue] = 0.33×10^{-4} M [$S_2O_8^{-2}$] = 0.66×10^{-2} M
[Fe^{2+}] = 0.50×10^{-4} M Light intensity = 70.0 $mWcm^{-2}$

pH	**$k \times 10^4$ (s^{-1})**
2.0	8.69
2.5	10.15
3.0	11.50
3.5	10.15
4.0	7.44
4.5	5.41
5.0	4.73

The rate of photochemical oxidation of toluidine blue was maximum at pH 3.0. 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 the optimum value of 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.

$$2\ SO_4^{-\bullet} + 2\ OH^- \longrightarrow 2\ SO_4^{-2} + H_2O_2$$

Effect of dye concentration

The effect of variation of the dye concentration on rate of reaction was also studied by taking different concentrations of dye. The photodegradation was studied in the range of 0.166×10^{-4} to 1.16×10^{-4} M for toluidine blue. The maximum rate was found at 0.33×10^{-4} M for the dye. The results are reported in Table 3.

Table 3: Effect of dye concentration

pH = 3.0
$[S_2O_8^{-2}] = 0.66 \times 10^{-2}$ M
$[Fe^{2+}] = 0.50 \times 10^{-4}$ M
Light intensity = 70.0 $mWcm^{-2}$

[Toluidine blue] × 10^5 M	k × 10^4 (s^{-1})
1.67	9.58
3.33	11.50
5.00	7.68
6.67	4.77
8.33	3.82
10.00	2.87
11.67	0.95

The rate of reaction 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 degradation decreases.

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.

Table 4: Effect of peroxydisulphate ion concentration

[Toluidine blue] = 0.33×10^{-4} M pH = 3.0
$[Fe^{2+}] = 0.50 \times 10^{-4}$ M Light intensity = 70.0 $mWcm^{-2}$

$[S_2O_8^{-2}] \times 10^2$ M	$k \times 10^4$ (s^{-1})
0.16	7.26
0.33	7.86
0.50	8.47
0.66	11.50
0.83	9.69
1.00	7.86

The results indicate that the rate of the reaction increases on the increase in the oxidant concentration upto 0.66×10^{-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 be formed by 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 toluidine 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[15-18].

Effect of ferrous ion concentration

The effect of concentration of Fe^{2+} ions was also studied by keeping all other factors identical. The photooxidation was studied in the range of 0.166×10^{-4} to 1.00×10^{-4} M for toluidine blue. The results are given in Table 5.

Table 5: Effect of ferrous ion concentration

[Toluidine blue] = 0.33×10^{-4} M pH = 3.0
[$S_2O_8^{-2}$] = 0.66×10^{-2} M Light intensity = 70.0 $mWcm^{-2}$

$[Fe^{2+}] \times 10^4$ M	$k \times 10^4$ (s^{-1})
0.16	9.37
0.33	9.79
0.50	11.50
0.66	8.52
0.83	7.24
1.00	5.53

It is clear from the data that the rate of degradation of dye increases on increasing the concentration of ferrous sulphate upto 0.50×10^{-4} M. 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 reaching the optimum value a reverse trend was obtained. This can be explained on the basis that on increasing the number of Fe^{2+} ions, it also reacts 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.

Effect of light intensity

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

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 attributed 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.

Table 6: Effect of light intensity

[Toluidine blue] = 0.33×10^{-4} M pH = 3.0
[$S_2O_8^{-2}$] = 0.66×10^{-2} M [Fe^{2+}] = 0.50×10^{-4} M

Light Intensity (mWcm^{-2})	$k \times 10^4$ (s^{-1})
10.0	0.98
20.0	1.97
30.0	3.51
40.0	4.26
50.0	5.92
60.0	8.55
70.0	11.50

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 degradation of the toluidine blue has been proposed as–

$$Fe^{2+} + S_2O_8^{-2} \longrightarrow Fe^{3+} + SO_4^{-\bullet} + SO_4^{-2}$$

$$TB + h\nu \longrightarrow TB^*$$

$$Fe^{3+} + MB^* \longrightarrow Fe^{2+} + MB^{+\bullet}$$

$$S_2O_8^{-2} + h\nu \longrightarrow 2\ SO_4^{-\bullet}$$

$$Fe^{2+} + SO_4^{-\bullet} \longrightarrow Fe^{3+} + SO_4^{-2}$$

$$SO_4^{-\bullet} + H_2O \longrightarrow HSO_4^{-} + HO^{\bullet}$$

$$Fe^{3+} + H_2O \longrightarrow Fe^{2+} + H^{+} + HO^{\bullet}$$

$$Fe^{2+} + H_2O_2 + H^{+} \longrightarrow Fe^{3+} + H_2O + HO^{\bullet}$$

$$HO^{\bullet} + HO^{\bullet} \longrightarrow H_2O_2$$

$$HO^{\bullet} + H_2O_2 \longrightarrow H_2O + HO_2^{\bullet}$$

$$TB^{+\bullet} + S_2O_8^{-2} \longrightarrow P + SO_4^{-\bullet} + SO_4^{-2} + 2H^+$$

$$HO^{\bullet} + TB \longrightarrow P + SO_4^{-2} + 2H^+$$

$$SO_4^{-\bullet} + TB^{+\bullet} \longrightarrow P + SO_4^{-2} + 2H^+$$

(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 pull an electron from excited dye molecule to yield dye cation radical and Fe^{2+} ions. 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 degradation 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).

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