

## Research Article

# Silver(I) Catalyzed Photochemical Oxidation of Methylene Blue and Safranin-O by Peroxydisulphate: A Green Chemical Approach

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In the present investigation, a comparative study of silver(I) catalysed photochemical oxidation of methylene blue (MB) and safranin-O (SO) by peroxydisulphate has been reported. The effect of different parameters, such as pH, concentration of peroxydisulphate, silver nitrate, and light intensity, on the reaction rate has been observed. The progress of the photochemical oxidation was monitored spectrophotometrically. The optimum conditions for photochemical oxidation were achieved. The dyes were completely oxidized and degraded into CO<sub>2</sub> and H<sub>2</sub>O. A tentative mechanism for silver(I) catalyzed photochemical oxidation of these dyes by peroxydisulphate has also been proposed.

## 1. Introduction

The nature has provided us a clean and green environment, but due to multifarious activities of human beings, it is being polluted with time. Water, which is an essential requirement for the life of man and many organisms, is being polluted as a result of numerous anthropological activities. Chemicals, food and beverage, textiles, pesticides and insecticides, dyeing and printing industries, and so forth are amongst main industries causing water pollution. Polluted water has detrimental effects on animals, plants life, and humans. Principal sources of water pollution are the dye based industries, where waste water is colored. This colored effluent of dyeing industries is toxic in nature. Therefore, removal of these toxic substances seems necessary. A number of attempts have been made for removal of toxic substances from polluted water by different methods like adsorption, thermal dehydration, chemical transformations, and so forth, but out of these, photocatalysis technology seems to be the most promising technique, as it is considered as a green technology.

Heterogeneous photocatalytic treatment of simulated dye house effluents using novel TiO<sub>2</sub> catalyst has been reported [1, 2]. Jonnalagadda et al. [3] observed the photodegradation of methyl orange in methanolic solution under both UV and visible radiations in the presence of Fe<sup>+2</sup>/H<sub>2</sub>O<sub>2</sub>. Oxidation of various substrates by peroxydisulphate ion is known to occur through several schemes: (i) a two-electron transfer by the direct reaction between the reductant and oxidant [4]; (ii) two successive reaction steps of one electron transfer from the reductant [5]; and (iii) a reaction initiated by the thermal decomposition of peroxydisulphate with no direct reaction between the reducing substrate and sulphate ion radical [6]. Here, the silver ion may react with persulfate ion to generate sulphate anion radical, which further reacts with silver ion to give sulphate ions. Sulphate anion radical may also react with dye to give the decomposition product or there is also a possibility of thermal decomposition of peroxydisulphate.

A kinetic and mechanistic study on the oxidation of indole-3-acetic acid by peroxydisulphate has been reported by Kalyanasundharam et al. [7]. The photooxidation of

vitamin E ( *$\alpha$ -tocopherol*) in the presence of peroxydisulphate in aqueous solution at neutral pH has been carried out using a high pressure mercury vapour lamp [8]. The rate of photocatalytic oxidation increases with increase in concentration of vitamin E, peroxydisulphate, and light intensity. Peroxydisulphate has also been used as an oxidizing agent for removal of paracetamol and sulfa drugs [9, 10]. Nishida and Kimura [11] carried out light induced electron transfer oxidation reaction of ethylenediamine tetraacetate by peroxydisulphate induced by visible light and in presence of aqueous tris [2,2-bipyridine ruthenium(II)] ion. The catalytic reduction of peroxydisulphate with different organic compounds has been used to determine the micro amount of silver, iron, and vanadium [12]. Preparation of highly efficient Ag/C catalyst by electrodecomposition method and its use in controlling microorganisms in water has been reported by Kumar et al. [13]. Takaki et al. [14] reported the photocatalytic oxidation of alkane with dioxygen by visible light using copper(II) and iron(II) chlorides. Peroxidative oxidation of benzene and mesitylene by vanadium catalysts has been studied by Reis et al. [15].

Cobalt mediated activation of peroxymonosulfate and sulphate radical on phenolic compounds was observed by Anipsitakis et al. [16]. Synthesis and characterization of Ag/MCM-41 and its catalytic performance for liquid phase oxidation of cyclohexane were investigated by Zhao et al. [17]. Yang et al. [18] investigated the oxidative degradation of diethyl phthalate by photochemically enhanced Fenton reaction. 4-alkyl or aryl substituted derivatives of 1,4-dihydropyridine were readily oxidized by urea nitrate. This oxidation reaction was also affected by peroxydisulphate in presence of cobalt(II) [19]. Photocatalytic reaction by Fe(III)-citrate complex and its effect on the photodegradation of atrazine in aqueous solution was observed by Ou et al. [20]. Pretzer et al. [21] reported the effect of Pt oxidation state and concentration on the photocatalytic removal of aqueous ammonia with Pt-modified titania. Sharma et al. [22] reported ferrate enhanced photocatalytic oxidation of pollutants in aqueous TiO<sub>2</sub> suspensions.

Ward et al. [23] have studied a range of Bi-TUD-1 silicas in conjunction with H<sub>2</sub>O<sub>2</sub> to mediate the photochemical oxidation of methylene blue whereas El-Kemary et al. [24] have carried out comparative study for photodegradation of safranin-O using nanoparticles TiO<sub>2</sub> and Ag-TiO<sub>2</sub>. Ember et al. [25] have developed new routes for clean oxidation of nonbiodegradable organic dyes. They have used Mn(II) salts that form efficient in situ catalysts for the activation of H<sub>2</sub>O<sub>2</sub> in the oxidation of orange II under mild reaction conditions while Cheng et al. [26] have reported the degradation of organic dyes with simple copper(II) ions as the catalyst in the HCO<sub>3</sub><sup>-</sup> solution using H<sub>2</sub>O<sub>2</sub> as the oxidant. They have efficiently decolorized some dyes such as orange II, methyl orange, methyl red, and toluidine blue. Although researchers have used potassium peroxydisulphate as an oxidant; however, no attention has been paid on the silver ion catalysed oxidation of dyes by peroxydisulphate. Therefore, the present work was planned for silver(I) catalyzed photochemical oxidation of methylene blue and safranin-O by peroxydisulphate.

## 2. Results and Discussion

Solutions of methylene blue (Reidel) and safranin-O (S.D. Fine), silver nitrate (Merck), and potassium peroxydisulphate (S.D. Fine) were prepared in double distilled water. The photocatalytic oxidations of dyes were studied in presence of silver nitrate and peroxydisulphate.

0.0374 g and 0.0350 g of MB and SO dyes, respectively, were dissolved separately in 100.0 mL double distilled water to prepare their stock solutions. The absorbance of these dye solutions was determined with the help of spectrophotometer (Systronics Model 106) at  $\lambda_{\max}$  = 665 nm and 510 nm for MB and SO, respectively. 0.1698 g of silver nitrate was dissolved in 100.0 mL double distilled water to obtain a stock solution of  $1.0 \times 10^{-2}$  mol dm<sup>-3</sup> concentration. The working solution was prepared by further dilution. Standard solution of potassium peroxydisulphate was prepared freshly just before use, by dissolving 0.2703 g potassium peroxydisulphate in 100.0 mL distilled water for  $1.0 \times 10^{-2}$  mol dm<sup>-3</sup> concentration of solution.

Photocatalytic oxidation of MB was studied by taking 25.0 mL reaction mixture containing  $1.2 \times 10^{-5}$  mol dm<sup>-3</sup> dye solution,  $2.0 \times 10^{-3}$  mol dm<sup>-3</sup> peroxydisulphate, and  $6.0 \times 10^{-5}$  mol dm<sup>-3</sup> silver nitrate solution in a 100 mL beaker and then this solution was exposed to light (light intensity = 60.0 mW cm<sup>-2</sup>). The pH was adjusted to 5.0. Similarly, photocatalytic oxidation of SO was studied by taking 25.0 mL reaction mixture containing  $3.0 \times 10^{-5}$  mol dm<sup>-3</sup> dye solution,  $3.6 \times 10^{-3}$  mol dm<sup>-3</sup> peroxydisulphate, and  $6.0 \times 10^{-5}$  mol dm<sup>-3</sup> silver nitrate solution in 100 mL beaker. This solution was exposed to light (light intensity = 60.0 mW cm<sup>-2</sup>). The pH was adjusted to 4.5. 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 mW cm<sup>-2</sup>. A water filter was used to cut off thermal radiations. The pH of the solution was measured by 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.

An aliquot of 2.0 mL was taken out from the reaction mixture at regular time intervals and the absorbance was measured spectrophotometrically at  $\lambda_{\max}$  = 665 nm and 510 nm for MB and SO, respectively. It was observed that the absorbance (*A*) of the dye solutions decreases with increasing time showing the progress of the dyes degradation. A plot of  $1 + \log A$  versus time was found linear, which shows that the rate follows pseudo-first-order kinetics. The rate constant was measured by the following expression: rate constant (*k*) =  $2.303 \times \text{slope}$ .

The effect of different rate affecting parameters like pH, concentration of peroxydisulphate, dye and silver nitrate, and light intensity on the rate of oxidation was studied. The data of typical runs were obtained using the optimum conditions of different parameters for silver(I) catalyzed photochemical oxidation of methylene blue and safranin-O by peroxydisulphate. The results for typical run are given in Table 1.

TABLE 1: Typical run.

Methylene blue		Safranin-O	
Time/min	1 + log A	Time/min	1 + log A
0.0	0.949	0.0	0.953
15.0	0.856	10.0	0.859
30.0	0.796	20.0	0.796
45.0	0.707	30.0	0.679
60.0	0.645	40.0	0.621
75.0	0.546	50.0	0.550
90.0	0.513	60.0	0.482
105.0	0.410	70.0	0.418

For methylene blue; pH = 5.0; [Methylene Blue] =  $1.2 \times 10^{-5}$  mol dm<sup>-3</sup>; [S<sub>2</sub>O<sub>8</sub><sup>2-</sup>] =  $2.0 \times 10^{-3}$  mol dm<sup>-3</sup>; [AgNO<sub>3</sub>] =  $6.0 \times 10^{-5}$  mol dm<sup>-3</sup>; light intensity = 60.0 mW cm<sup>-2</sup>; rate constant (*k*) =  $2.11 \times 10^{-4}$  sec<sup>-1</sup>. For safranin-O; pH = 4.5; [Safranin-O] =  $3.0 \times 10^{-5}$  mol dm<sup>-3</sup>; [S<sub>2</sub>O<sub>8</sub><sup>2-</sup>] =  $3.6 \times 10^{-3}$  mol dm<sup>-3</sup>; [AgNO<sub>3</sub>] =  $6.0 \times 10^{-5}$  mol dm<sup>-3</sup>; light intensity = 60.0 mW cm<sup>-2</sup>; rate constant (*k*) =  $3.07 \times 10^{-4}$  sec<sup>-1</sup>.

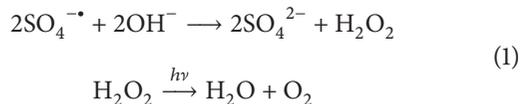
TABLE 2: Effect of pH.

pH	Methylene blue <i>k</i> × 10 <sup>4</sup> /sec <sup>-1</sup>	Safranin-O <i>k</i> × 10 <sup>4</sup> /sec <sup>-1</sup>
3.0	0.85	2.10
3.5	1.04	2.34
4.0	1.32	2.53
4.5	1.71	3.07
5.0	2.11	2.41
5.5	1.86	2.36
6.0	1.70	2.30

For methylene blue, [Methylene Blue] =  $1.2 \times 10^{-5}$  M; [S<sub>2</sub>O<sub>8</sub><sup>2-</sup>] =  $2.0 \times 10^{-3}$  mol dm<sup>-3</sup>; [AgNO<sub>3</sub>] =  $6.0 \times 10^{-5}$  mol dm<sup>-3</sup>; light intensity = 60.0 mW cm<sup>-2</sup>. For safranin-O, [Safranin-O] =  $3.0 \times 10^{-5}$  mol dm<sup>-3</sup>; [S<sub>2</sub>O<sub>8</sub><sup>2-</sup>] =  $3.6 \times 10^{-3}$  M; [AgNO<sub>3</sub>] =  $6.0 \times 10^{-5}$  mol dm<sup>-3</sup>; light intensity = 60.0 mW cm<sup>-2</sup>.

**2.1. Effect of pH.** The pH of the solution is likely to affect the degradation of MB and SO and hence, the effect of pH on the rates of degradation of MB and SO was investigated in the pH range 3.0–6.0. The results are reported in Table 2.

The rates of photocatalytic oxidation of MB and SO were at maximum 5.0 and 4.5, respectively. It was observed that initially the rate of photochemical oxidation was increased and on increasing the pH of the reaction mixture, it decreases. This may be attributed to the fact that as the pH was increased, the number of S<sub>2</sub>O<sub>8</sub><sup>2-</sup> ions also increases. These ions are utilized in oxidation of Ag<sup>+</sup> to Ag<sup>2+</sup> ions, which play an important role in oxidizing excited dye to its cation radical. After attaining the maximum rate at particular pH, rate starts decreasing. It may be explained on the basis that number of <sup>-</sup>OH ions increases as pH was increased and these <sup>-</sup>OH ions may react with sulphate anion radical to give sulphate ion. Sulphate anion radical is considered as one of the active oxidizing species and its removal from reaction mixture at higher pH will affect the rate of reaction adversely:



At pH > 6.0 for both dyes (MB and SO), some turbidity appeared in the reaction mixture and hence, measurement of absorbance becomes difficult as well as erroneous and therefore, the effect of pH was studied up to 6.0 for both the dyes.

**2.2. Effect of Peroxydisulphate Concentration.** The peroxydisulphate concentration also affects the oxidation of MB and SO dyes and hence, the effect of variation of peroxydisulphate concentration on the rates of photochemical oxidation was studied by taking different concentrations of peroxydisulphate. The results obtained are summarized in Table 3.

The data show that the rates of photochemical oxidation of MB and SO dyes were increased on increasing the peroxydisulphate concentration. It may be due to the fact that as the concentration of potassium peroxydisulphate increases, the concentration of S<sub>2</sub>O<sub>8</sub><sup>2-</sup> ions also increases, which, in turn, increases the rate of oxidation of Ag<sup>+</sup> to Ag<sup>2+</sup> ion. Ag<sup>2+</sup> ion oxidizes dye molecules to its radical cation, which in turn was degraded into the smaller products by reacting with ions through a sequence of reactions.

**2.3. Effect of Dyes Concentration.** Effect of variation of dyes concentration on rate of photochemical oxidation was studied by taking different concentrations of dyes. The reaction was studied in the range of  $0.4 \times 10^{-5}$  mol dm<sup>-3</sup> to  $1.4 \times 10^{-5}$  mol dm<sup>-3</sup> and  $1.0 \times 10^{-5}$  mol dm<sup>-3</sup> to  $6.0 \times 10^{-5}$  mol dm<sup>-3</sup> for MB and SO system, respectively. The maximum rates were obtained at  $1.2 \times 10^{-5}$  mol dm<sup>-3</sup> and  $3.0 \times 10^{-5}$  mol dm<sup>-3</sup> for MB and SO, respectively. The results are reported in Table 4.

The oxidation rates were found to increase with increasing concentration of dye. This may be explained on the basis that on increasing the concentration of dye, the reaction rates were increased as more molecules of dyes were available for degradation. However, on increasing the concentration beyond certain limits, the reaction rates were decreased. This may be attributed to the fact that after optimum conditions the dye will start acting as an internal filter for the incident light and it will not permit the desired light intensity to reach the dye molecules in the bulk of the solution; thus, a decrease in the rates of degradation of dyes was observed.

**2.4. Effect of Silver Nitrate Concentration.** Effect of varying concentrations of silver nitrate was also studied by keeping all other factors identical. The results are given in Table 5.

It is clear from data that the rates of photochemical oxidations of MB and SO were increased on increasing the concentration of silver nitrate. This may be due to increase in number of Ag(I) ions, which are oxidized to Ag(II) ions on reaction with peroxydisulphate ions. These Ag(II) ions will convert excited dyes molecule to their cation radical, which then undergoes degradation.

**2.5. Effect of Light Intensity.** The effect of variation of light intensity on rate of reaction was also investigated and the observations are reported in Table 6.

TABLE 3: Effect of peroxydisulphate concentration.

Methylene blue		Safranin-O	
$[\text{S}_2\text{O}_8^{2-}] \times 10^3/\text{M}$	$k \times 10^4/\text{sec}^{-1}$	$[\text{S}_2\text{O}_8^{2-}] \times 10^3/\text{M}$	$k \times 10^4/\text{sec}^{-1}$
0.4	0.23	2.0	1.98
0.8	0.50	2.4	2.18
1.2	1.12	2.8	2.30
1.6	1.68	3.2	2.59
2.0	2.11	3.6	3.07

For methylene blue, pH = 5.0; [Methylene Blue] =  $1.2 \times 10^{-5}$  mol dm<sup>-3</sup>; [AgNO<sub>3</sub>] =  $6.0 \times 10^{-5}$  mol dm<sup>-3</sup>; light intensity = 60.0 mW cm<sup>-2</sup>. For safranin-O, pH = 4.5; [Safranin-O] =  $3.0 \times 10^{-5}$  mol dm<sup>-3</sup>; [AgNO<sub>3</sub>] =  $6.0 \times 10^{-5}$  mol dm<sup>-3</sup>; light intensity = 60.0 mW cm<sup>-2</sup>.

TABLE 4: Effect of dye concentration.

[Methylene Blue] × 10 <sup>5</sup> /M	$k \times 10^4/\text{sec}^{-1}$	[Safranin-O] × 10 <sup>5</sup> /M	$k \times 10^4/\text{sec}^{-1}$
0.4	0.80	1.0	2.41
0.6	1.19	2.0	2.68
0.8	1.42	3.0	3.07
1.0	1.83	4.0	2.56
1.2	2.11	5.0	2.45
1.4	1.86	6.0	2.30

For methylene blue, pH = 5.0; [S<sub>2</sub>O<sub>8</sub><sup>2-</sup>] =  $2.0 \times 10^{-3}$  mol dm<sup>-3</sup>; [AgNO<sub>3</sub>] =  $6.0 \times 10^{-5}$  mol dm<sup>-3</sup>; light intensity = 60.0 mW cm<sup>-2</sup>. For safranin-O, pH = 4.5; [S<sub>2</sub>O<sub>8</sub><sup>2-</sup>] =  $3.6 \times 10^{-3}$  mol dm<sup>-3</sup>; [AgNO<sub>3</sub>] =  $6.0 \times 10^{-5}$  mol dm<sup>-3</sup>; light intensity = 60.0 mW cm<sup>-2</sup>.

TABLE 5: Effect of silver nitrate concentration.

[AgNO <sub>3</sub> ] × 10 <sup>5</sup> /M	Methylene blue $k \times 10^4/\text{sec}^{-1}$	Safranin-O $k \times 10^4/\text{sec}^{-1}$
1.0	1.01	1.07
2.0	1.20	1.88
3.0	1.42	2.06
4.0	1.68	2.14
5.0	1.90	2.25
6.0	2.11	3.07

For methylene blue, pH = 5.0; [Methylene Blue] =  $1.2 \times 10^{-5}$  mol dm<sup>-3</sup>; [S<sub>2</sub>O<sub>8</sub><sup>2-</sup>] =  $2.0 \times 10^{-3}$  mol dm<sup>-3</sup>; light intensity = 60.0 mW cm<sup>-2</sup>. For safranin-O; pH = 4.5; [Safranin-O] =  $3.0 \times 10^{-5}$  mol dm<sup>-3</sup>; [S<sub>2</sub>O<sub>8</sub><sup>2-</sup>] =  $3.6 \times 10^{-3}$  mol dm<sup>-3</sup>; light intensity = 60.0 mW cm<sup>-2</sup>.

TABLE 6: Effect of light intensity.

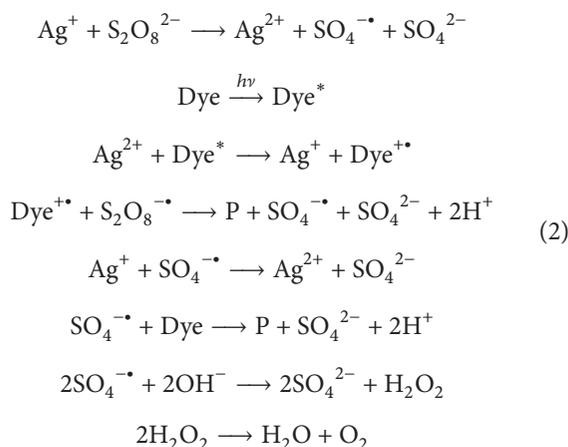
Light intensity/mW cm <sup>-2</sup>	Methylene blue $k \times 10^4/\text{sec}^{-1}$	Safranin-O $k \times 10^4/\text{sec}^{-1}$
20.0	0.56	2.51
30.0	0.75	2.79
40.0	1.12	2.98
50.0	1.53	3.07
60.0	2.11	3.45
70.0	1.90	3.10

For methylene blue, pH = 5.0; [Methylene Blue] =  $1.2 \times 10^{-5}$  mol dm<sup>-3</sup>; [S<sub>2</sub>O<sub>8</sub><sup>2-</sup>] =  $2.0 \times 10^{-3}$  mol dm<sup>-3</sup>; [AgNO<sub>3</sub>] =  $6.0 \times 10^{-5}$  mol dm<sup>-3</sup>. For safranin-O, pH = 4.5; [Safranin-O] =  $3.0 \times 10^{-5}$  mol dm<sup>-3</sup>; [S<sub>2</sub>O<sub>8</sub><sup>2-</sup>] =  $3.6 \times 10^{-3}$  mol dm<sup>-3</sup>; [AgNO<sub>3</sub>] =  $6.0 \times 10^{-5}$  mol dm<sup>-3</sup>.

The data indicate that on increasing the light intensity an increase in the rate of reactions was observed and the maxima were found at 60.0 mW cm<sup>-2</sup> for both dyes. This may be due

to the fact that an increase in light intensity will increase the number of photons striking per unit area of the reaction mixture in the beaker and as a result rates of reactions were increased. However, further increase in light intensity beyond 60.0 mW cm<sup>-2</sup> causes retardation of reaction. It may be due to some thermal side reactions.

2.6. *Mechanism.* Peroxydisulphate is a strong two-electron oxidant and it works well in many chemical processes. This oxidant has also been used for metal ion catalyzed oxidation of various substrates. On the basis of experimental observations, a tentative mechanism for Ag ion catalyzed photochemical oxidation of dyes MB and SO has been proposed, which is



where P = smaller products like CO<sub>2</sub> and H<sub>2</sub>O.

In the initial step, Ag(I) transfers its electron to peroxydisulphate ion and hence Ag(I) is oxidized to Ag(II) and

peroxydisulphate ion is broken into sulphate ion and sulphate anion radical. The dye is excited by absorbing radiations of suitable wavelength. Ag(II) ion pulls an electron from excited dye molecule to yield dye cation radical and Ag(I) ion. The dye cation radical also reacts with peroxydisulphate ions giving sulphate ion, sulphate anion radical, protons, and the degradation products of the dye. Ag(I) ion 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 as the final oxidation products was 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 value (strong acidic medium), as evident from experimental observations. On the other hand, the sulphate anion radical may react with  $^-\text{OH}$  ions (at higher pH) to give sulphate ions and hydrogen peroxide. Hydrogen peroxide is rapidly decomposed to water and oxygen in presence of light. However, hydrogen peroxide may also degrade the dye but sulphate anion radical is comparatively a stronger oxidant and its removal from the reaction mixture will result into corresponding decrease in the degradation rate of dyes.

### 3. Conclusion

The photochemical oxidative degradation of dyes by peroxydisulphate can be enhanced by the addition of metal ions like silver ions, which act as electron donor and/or acceptor, as it has variable oxidation states of +1 and +2. Such reaction may also be utilized for the treatment of effluents from textile, dyeing, and printing industries parallel to advanced oxidation processes (AOPs).

### Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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