

Photooxidation of Pyronin B with Sulphate Radical Ion and Hydroxyl Radicals Generated by Peroxydisulphate Ion with Cupric Ion

Dr. Bindu Kataria (Lecturer)

Department of Chemistry, S.M.B Govt PG College, Nathdwara [Rajasthan], India

ABSTRACT

In this paper, the photochemical degradation of Pyronin B by $\text{Cu}^{2+}/\text{S}_2\text{O}_8^{2-}$ process has been presented. Cu^{2+} as photocatalyst and $\text{S}_2\text{O}_8^{2-}$ ion as photooxidant used in this process. At extremely low concentrations, cupric ion showed true catalytic activity in the overall process. The influence of various parameters on the performance of the treatment process has been considered, such as pH, concentration of peroxydisulphate ion ($\text{S}_2\text{O}_8^{2-}$), concentration of Cu^{2+} ion, concentration of methylene blue and effect of light intensity etc. were observed. The progress of the photochemical oxidation was monitored spectrophotometrically. The results showed that the dye was completely oxidized and maximum decolorization efficiency was achieved at the optimum conditions of the reaction time 135 min. The optimum conditions of initial dye, Cu^{2+} ion, initial peroxydisulphate ion ($\text{S}_2\text{O}_8^{2-}$) concentration for photooxidation were determined to be 5.0×10^{-5} , 2.3×10^{-4} and 4.9×10^{-4} M, respectively and light intensity 62.9 mWcm^{-2} . The value for the reaction rate constants have been determined and found to be $3.61 \times 10^{-4} \text{ s}^{-1}$. Overall photochemical oxidation of methylene blue was observed to follow first-order kinetics.

A suitable tentative mechanism for photochemical oxidation of methylene blue has been proposed.

Keywords: Photochemical oxidation; Cupric ion(Cu^{2+}); Peroxydisulphate ion($\text{S}_2\text{O}_8^{2-}$); Pyronin B.

I. Introduction

The textile industry has been condemned as being one of the world's worst offenders in terms of pollution because it requires a great amount of chemical and water. Textile mills discharge millions of gallons of effluent each year, full of chemicals such as dyes and others, which are significant causes of environmental degradation and human illnesses. Dyebath effluents may contain heavy metals, ammonia, alkali salts, toxic solids and large amounts of pigments - many of which are toxic. The stability and non-biodegradability of dyes causes major problems in its treatment and thus demands new ecofriendly methods. Recently, there has been a 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.

Study was conducted on the Aqueous Degradation of Butylated Hydroxyanisole by UV/ ($\text{S}_2\text{O}_8^{2-}$), and generation of weaker oxidants or radicals which results in a slower degradation of the BHA [1]. Other stream of experiments indicated that on the sulfate radical-mediated photo-oxidation of humic substances with organic matter extracted from vermicompost (VC) was studied by flash-photolysis, shown encouraging results on oxidation [2]. The photooxidative decolorization of C.I. Basic Yellow 2 (BY2), was investigated using UV radiation in the presence of peroxydisulfate ($\text{S}_2\text{O}_8^{2-}$), in a rectangular photoreactor at experimental condition. ($\text{S}_2\text{O}_8^{2-}$) and UV-light showed negligible effect when they were used independently [3], Khataee et al studies that photooxidative decolorization rate was affected by the operational parameters such as the reaction time, UV light intensity and initial concentrations of peroxydisulfate and Basic Blue 3 [4].

Different processes were developed to treat waste water from textile industry.[5-7] There has been considerable research focus in last few decades on development of various techniques to treat dye waste water. Among various tertiary treatment methods, Advanced Oxidation Treatment (AOT) techniques has been found to promising to convert the dye present in waste water to harmless compounds.

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 also 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 [8] and Ball et al.[9] reported the kinetics and mechanism of oxidation of 2-propanol by peroxydisulphate. Oxidation of malic acid and lactic acid by peroxydisulphate catalyzed by Cu (II).[10-12]

Photocatalytic decolorization of methylene blue in aqueous TiO₂ suspension has been reported by Lee et al.[13] while Abassi and Razzaghi[14] suggested the removal of hazardous reactive blue-19 dye from aqueous solutions by agricultural waste. Degradation of the some dyes like fast green and yellowish orange was also observed by Bhati[15] using CeCuO₃ as photocatalyst. The oxidation of methylene blue was carried out by Dutta et al. [16] using photo-Fenton reagent while the oxidation of reactive blue-19 dye with UV/H₂O₂ was also carried out by Rezaee et al. [17] Various physical, chemical and biological methods and advanced oxidation processes have been used for the treatment of textile effluents or industrial waste.[18-20] 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.[21] under a combined photocatalytic and Fenton based oxidation in the presence of TiO₂ and Fe²⁺ and the decoloration of the reactive blue dye KN-R was also investigated by Gabriel and Hong [22] using Fenton and UV/Fenton processes. Soni et al.[23] suggested the photochemical oxidation of dyes with sulphate radicalion (SO₄^{•-}) and hydroxyle radical (HO[•]) generated by S₂O₈²⁻ / Fe³⁺.

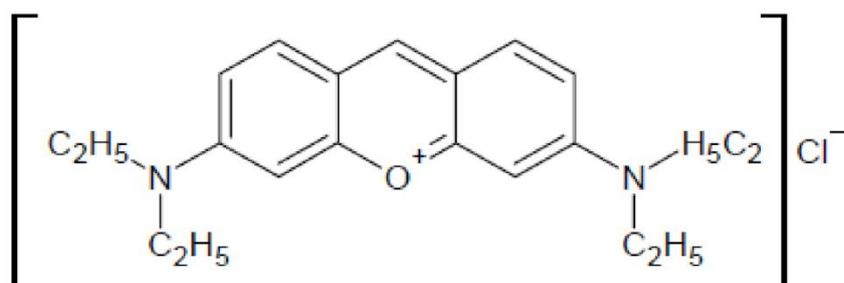
II. Materials & Methods

Pyronin B (Reidel), copper 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.

III. Results and discussion

The photocatalytic degradation of pyronine B was observed at $\lambda_{\text{max}} = 650$ nm. The results for a typical run are given in Fig. 1. (Structure given below)



(Fig 1: Pyronine B)

At regular time intervals, an aliquot of 2.0 mL was taken out from the reaction mixture. The optical density (O.D.) of the reaction mixture was decreases with increasing time intervals showing thereby that the concentration of dye decreases with increasing time exposure. A plot of $2 + \log \text{OD}$ versus time was linear and follows pseudo-first order kinetics. The rate constant was determined by the expression: $k = 2.303 \times \text{slope}$. The rate constant (k) for this reaction was determined $3.20 \times 10^{-4} \text{ s}^{-1}$. The results of a typical run are given in Table 1 and Fig. 2.

TABLE 1
A TYPICAL RUN

[Pyronin-B] = 5.0×10^{-5} M pH = 4.5
[S₂O₈²⁻] = 4.9×10^{-4} M [Cu²⁺] = 2.3×10^{-4} M Light intensity = 62.9 mWcm⁻²

Time (min)	Optical Density (O.D.)	2 + log O.D.
0	0.279	1.45
15	0.199	1.30
30	0.159	1.20
45	0.109	1.04
60	0.776	0.89
75	0.060	0.78
90	0.040	0.60
105	0.028	0.48
120	0.020	0.30
135	0.015	0.19

$$k = 3.61 \times 10^{-4} \text{ s}^{-1}$$

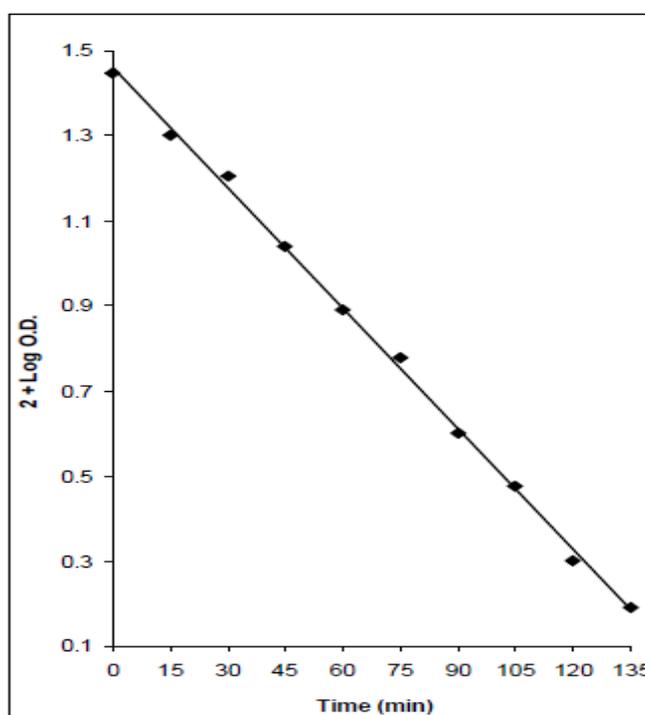


Fig. 2 : A Typical Run

3.1 EFFECT OF pH

The effect of pH on the rate of degradation of pyronin-B was investigated in the pH range (2.0 – 5.5). The results are reported in Table 2.0 and graphically represented in Figure 3.

The rate of photooxidation of pyronin-B increases on increasing the pH of the reaction mixture. On increasing pH further above 4.5, the rate of photooxidation of dye decreases.

TABLE 2
EFFECT OF pH

[Pyronin-B] = 5.0×10^{-5} M

[S₂O₈²⁻] = 2.3×10^{-4} M

[Cu²⁺] = 4.9×10^{-4} M

Light intensity = 62.9 mWcm⁻²

pH	k x 10 ⁴ s ⁻¹
2.0	1.53
2.5	1.66
3.0	1.98
3.5	2.44
4.0	2.62
4.5	3.61
5.0	2.07
5.5	1.66

This may be explained on the basis that at lower pH value, (i.e. in presence of high concentration of hydrogen ion) the photooxidation of dye is relatively slow. As the pH increases the number of S₂O₈²⁻ ions increases, which are utilized in oxidation. Cu²⁺ ions play an important role in oxidizing excited dye to its cation radical (PyB⁺). After attaining the maximum rate at particular pH 4.5, it starts decreasing. It may be explained on the basis that with increase in pH, OH⁻ ions increase and these OH⁻ ions may react with sulphate anion radical (SO₄^{•-}) to give SO₄²⁻. 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.

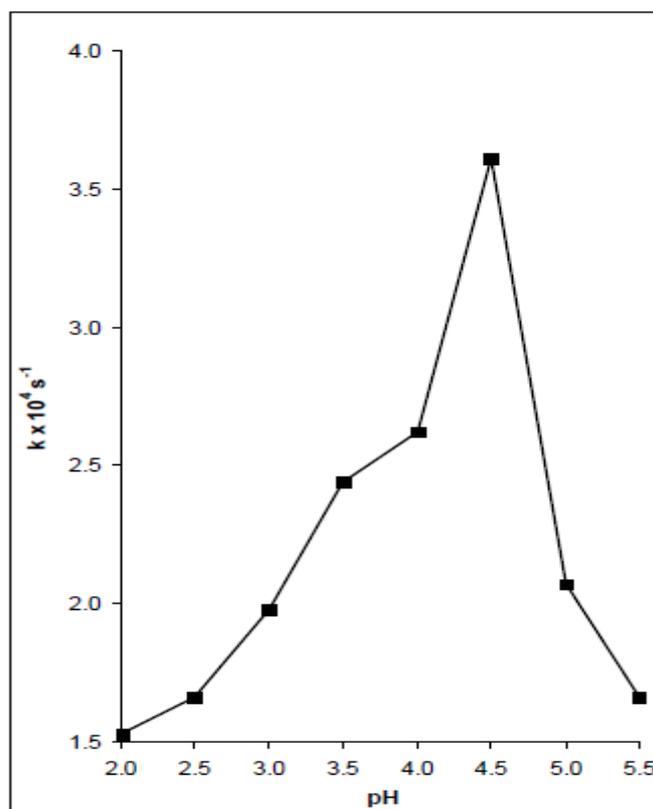


Fig. 3 Effect of pH

3.2 EFFECT OF PYRONIN-B CONCENTRATION

The effect of variation of dye concentration on rate of photooxidation was also studied by taking different concentrations of dye. Photooxidation of pyronin-B was studied in the range of 2.0×10^{-5} to 10.0×10^{-5} M. The maximum rate was found at 5.0×10^{-5} M for pyronin-B. The results are tabulated in Table 3 and graphically represented in Figure 4

TABLE 3
EFFECT OF PYRONIN-B CONCENTRATION

$$\text{pH} = 4.5[\text{S}_2\text{O}_8^{2-}] = 2.3 \times 10^{-4} \text{ M}$$

$$[\text{Cu}^{2+}] = 4.9 \times 10^{-4} \text{ M} \quad \text{Light intensity} = 62.9 \text{ mWcm}^{-2}$$

[Pyronin-B] x 10 ⁵ M	k x 10 ⁴ s ⁻¹
2.0	0.61
2.2	0.65
2.5	0.75
2.8	1.23
3.3	1.63
4.0	2.61
5.0	3.61
6.6	3.42
10.0	2.93

The rate of oxidation was found to increase with increasing concentration of pyronin-B. 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 5.0×10^{-5} M, the reaction rate of photochemical oxidation of pyronin-B decreases. This is probably due to the fact that after 5.0×10^{-5} M concentration of pyronin-B, 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.

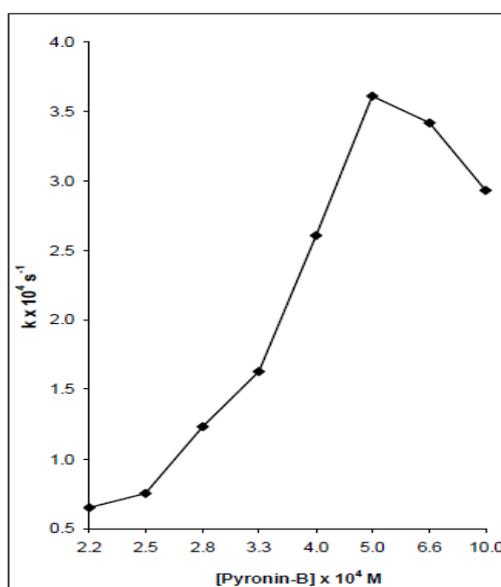


Fig. 4: Effect of Pyronin-B Concentration

3.3 EFFECT OF PEROXYDISULPHATE ION CONCENTRATION

The effect of variation of concentration of $S_2O_8^{2-}$ ions on the rate of the reaction was observed by taking different concentrations of $S_2O_8^{2-}$ ions. The results are summarized in the Table 4 and graphically represented in Figure 5

TABLE 4
EFFECT OF PEROXYDISULPHATE ION CONCENTRATION

[Pyronin-B] = 5.0×10^{-5} M

pH = 4.5

[Cu^{2+}] = 4.9×10^{-4} M

Light intensity = 62.9 mWcm^{-2}

[$S_2O_8^{2-}$] x 10^4 M	k x 10^4 s $^{-1}$
0.3	0.94
1.0	1.13
1.6	1.39
2.3	3.61
3.0	2.53
3.6	1.93
4.3	1.74
5.0	0.90

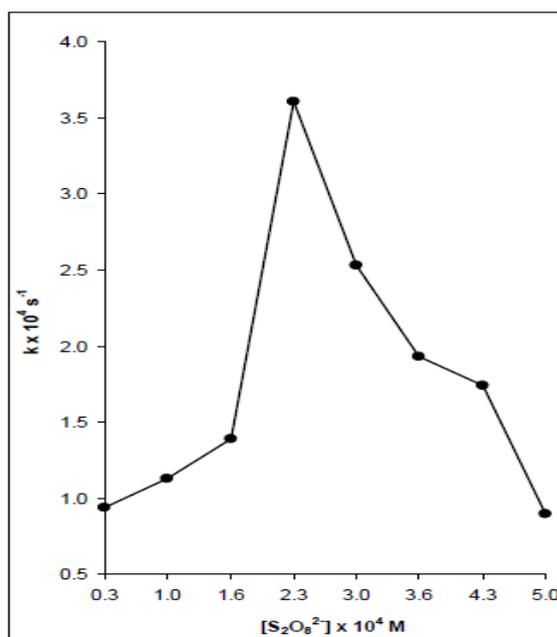


Fig. 5: Effect of Peroxydisulphate Ion Concentration

The results which have been summarized in the Table 4 indicate that the rate of reaction increases on the increase in the peroxydisulphate ion concentration upto 2.3×10^{-4} M because more peroxydisulphate ions are available for oxidation. As the concentration of $S_2O_8^{2-}$ is increased, $S_2O_8^{2-}$ is excited by absorbing radiations of suitable wavelength and forms two moles of sulphate ion radicals. More $S_2O_8^{2-}$, $SO_4^{\cdot-}$ and HO^{\cdot} radicals are available to attack the aromatic rings of pyronin-B and rate of reaction increases. The optimal concentration of $S_2O_8^{2-}$ would result in higher photooxidative removal efficiency.

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 pyronin-B 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.¹⁻⁴

3.4 EFFECT OF CUPRIC ION CONCENTRATION

The effect of increasing concentration of Cu^{2+} ions was also studied by keeping all other factors identical. The results are tabulated in Table 4 and graphically represented in Figure 5. On the basis of above data it is clear that the rate of photochemical oxidation of dye increases on increasing the concentration of Cu^{2+} ions. This may be due to increase in the number of cupric ions, which convert excited dye molecule to its cation radical (PyB^+), which then undergoes degradation. Cu^+ ions will also react with $S_2O_8^{2-}$ and H_2O_2 , converting them into sulphate anion radical and HO^{\cdot} . Thereafter, sulphate anion radical and HO^{\cdot} react with pyronin-B and oxidize it. But after reaching the optimum value ($4.9 \times 10^{-4} M$) a reverse trend was obtained. This can be explained on the basis that on increasing the number of Cu^+ ions, they also reacts with sulphate anion radical ($SO_4^{\cdot-}$), which are reduced to sulphate ion (SO_4^{2-}). So at higher concentration of the Cu^+ ions, the rate of photochemical oxidation decreases.

TABLE 5

EFFECT OF CUPRIC ION CONCENTRATION

[Pyronin-B] = $5.0 \times 10^{-5} M$

[$S_2O_8^{2-}$] = $2.3 \times 10^{-4} M$

pH = 4.5 Light intensity = $62.9 mWcm^{-2}$

[Cu^{2+}] x $10^4 M$	k x $10^4 s^{-1}$
0.9	1.63
1.7	1.63
2.5	1.67
3.3	1.72
4.1	2.23
4.9	3.61
5.7	3.16
6.5	2.61

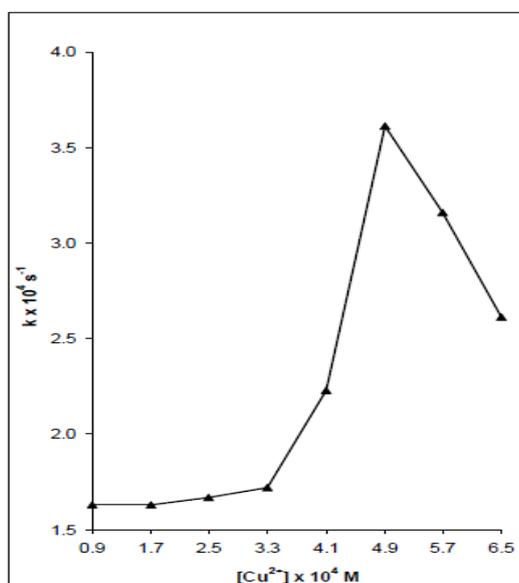


Fig. 6 : Effect of Copper (II) Ion Concentration

3.5 EFFECT OF LIGHT INTENSITY

The effect of light intensity on the photodegradation of pyronin-B was also observed. The results obtained are reported in Table 6 and graphically presented in Figure 7.

An increasing 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 $S_2O_8^{2-}$ ions and pyronin-B, as a result, there is an increase in the number of active species (PyB^{*+} and $SO_4^{\cdot-}$) which are responsible for increase in the rate of reaction. However, higher intensities were avoided due to thermal effects.

TABLE 6
EFFECT OF LIGHT INTENSITY
pH = 4.5

[Pyronin-B] = 5.0×10^{-5} M

[$S_2O_8^{2-}$] = 4.9×10^{-4} M [Cu^{2+}] = 2.3×10^{-4} M

Light Intensity ($mWcm^{-2}$)	$k \times 10^4 s^{-1}$
27.7	1.18
30.6	1.37
34.6	1.48
39.6	1.74
45.6	2.09
53.3	3.02
62.9	3.61

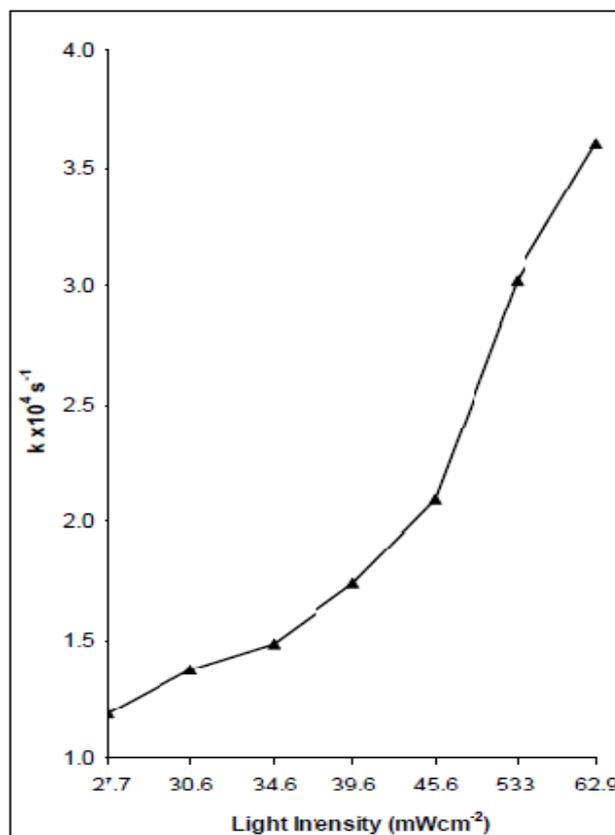
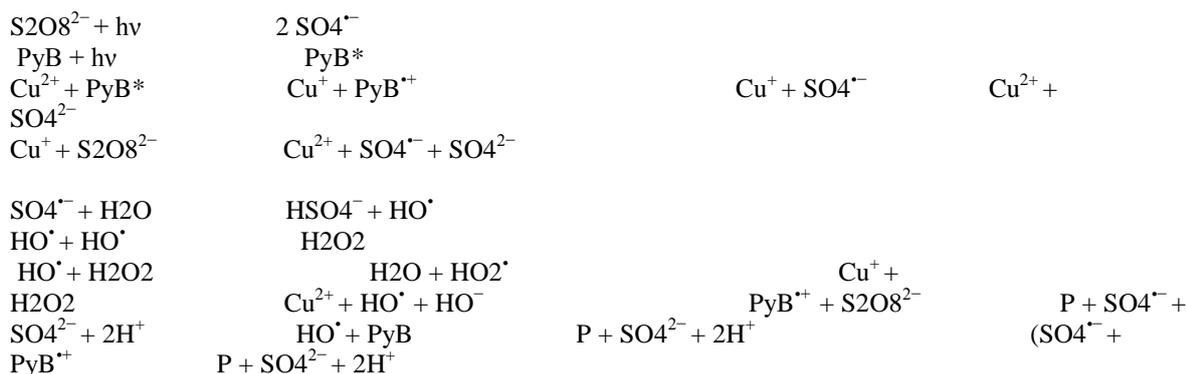


Fig. 7: Effect of Light Intensity

3.6 MECHANISM

On the basis of experimental observations, a tentative mechanism for metal ion catalyzed photochemical oxidation of pyronin-B (PyB) dye has also been proposed as –



Here P = gaseous products like CO₂, H₂O, etc.

In the initial step, dye is excited by absorbing radiations of suitable wavelength and S₂O₈²⁻ forms two moles of sulphate ion radicals. Cu²⁺ ions pull an electron from excited dye molecule to yield dye cation radical (PyB^{·+}) and Cu⁺ ions. As the concentration of S₂O₈²⁻ is increased, it attacks the aromatic rings of dye cation radical (PyB^{·+}) and it converts dye cation radical (PyB^{·+}) into product and forms SO₄^{·-} with SO₄²⁻. Cu⁺ transfers its electron to peroxydisulphate ion and hence, Cu⁺ is oxidized to Cu²⁺ and peroxydisulphate ion is broken into sulphate ion and sulphate anion radical. Cu⁺ ions will also react with sulphate anion radical, converting it into sulphate ions. SO₄^{·-} reacts with a molecule of water and forms HSO₄⁻ and HO[·].

In the final step, hydroxyl radical and sulphate anion radical reacts with dye or dye cation radical to give sulphate ion and products.

The production and use of aromatic dyes for printing operation have resulted in environmental pollution. Their presence in waterways has an ecological and health hazard. Development of Mⁿ⁺/S₂O₈²⁻ processes is of great importance in order to remove these dyes. Mⁿ⁺/S₂O₈²⁻ processes occupy an important place in environmental-protection technologies. They are effectively used in water purification from harmful dyes to human health and environment. Degradation of dyes by Cu²⁺/S₂O₈²⁻ as oxidizing agent may open new avenues for the treatment of wastewater from dyeing, printing and textile industries.

IV. Conclusion:

The results of this study demonstrate that Cu²⁺/S₂O₈²⁻ process could efficiently optimize the photooxidative decolorization of pyronin-B. Under optimum conditions of the process parameters, high color removal was obtained for the dye solutions. The results showed that the addition of proper amount of S₂O₈²⁻ and Cu²⁺ ions could improve the photooxidative decolorization efficiency. Effect of experimental parameters on the decolorization efficiency of Cu²⁺/S₂O₈²⁻ process was established.

References:

- [1]. Tim K. Lau, Wei Chu, and Nigel J. D. Graham, *Environ. Sci. Technol.*, 41, 2, (2007), 613–619
- [2]. M.D. Gara, G.N. Bosio, M.C. Gonzalez, and D.O. Martire, *Int. J. Chem. Kinet.*, 40, 1, (2008) 9–24
- [3]. D. Salari, A. Niaei, S. Aber and M.H. Rasoulifard, *J. Hazard. Mater.*, 166 (2009) 61–66
- [4]. A.R. Khataee and O. Mirzajani, *Desalination*, 251(1-3) (2010) 64-69.
- [5]. L.J. Sojka, T. Koprowski, W. Machnowski, H.H. Knudsen, *Desalination* 19 (1998) 1-9.
- [6]. H. Barlas, T. Akgun, *Resenius Environ. Bull.* 9(9-10) (2000) 597-602.
- [7]. G. Ciardelli, G. Capannelli, A. Bottino, *Water Sci. Technol.* 44(5) (2001) 61-70.
- [8]. D.A. House, *Chem. Revs.* 62 (1962) 185-203.
- [9]. D.L. Ball, M.M. Gutchfield, J.O. Edwards, *J. Org. Chem.* 25 (1960) 1599-1611.
- [10]. D. Meyerstein, *J. Inorg. Nucl. Chem.* 43 (1981) 401-402.
- [11]. S.C. Agrawal, G. Chandra, S.K. Jha, *J. Inorg. Nucl. Chem.* 41 (1979) 99-902.
- [12]. S.C. Agrawal, L.K. Saxena, *J. Inorg. Nucl. Chem.* 42 (1980) 932-935.
- [13]. B.N. Lee, W.D. Liaw, J.C. Lou, *Environ. Eng. Sci.* 16 (1999) 165-175.
- [14]. M. Abassi, N. Razzaghi Asl, *J. Iran. Chem. Res.*, 2 (2009) 221-230.