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Photochemical degradation of azure-b with sulphate radical ion generated by peroxydisulphate ion with cupric ion

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Abstract

In this paper, the photochemical degradation of azure-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 120 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 2.8×10^{-5} , 4.1×10^{-4} and 3.6×10^{-4} M, respectively and light intensity 62.9 mWcm^{-2} . The value for the reaction rate constants have been determined and found to be $3.20 \times 10^{-4} \text{ s}^{-1}$. 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($\text{S}_2\text{O}_8^{2-}$); Azure-b.

1. 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. Dye bath 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 focussed 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.

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Different processes were developed to treat waste water from textile industry.[1-3] 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, TiO₂ 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[4] and Ball et al.[5] 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).[6-8] Photocatalytic decolorization of methylene blue in aqueous TiO₂ suspension has been reported by Lee et al.[9] while Abassi and Razzaghi[10] 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[11] using CeCuO₃ as photocatalyst. The oxidation of methylene blue was carried out by Dutta et al.[12] using photo-Fenton reagent while the oxidation of reactive blue-19 dye with UV/H₂O₂ was also carried out by Rezaee et al.[13] Various physical, chemical and biological methods and advanced oxidation processes have been used for the treatment of textile effluents or industrial waste.[14-16] 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 TiO₂ and Fe²⁺ 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 dyes with sulphate radical ion (SO₄^{•-}) and hydroxyle radical (HO[•]) generated by S₂O₈²⁻ / Fe³⁺.

2. Materials and Methods

Azure-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 mWcm². 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.

3. Result and Discussion

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

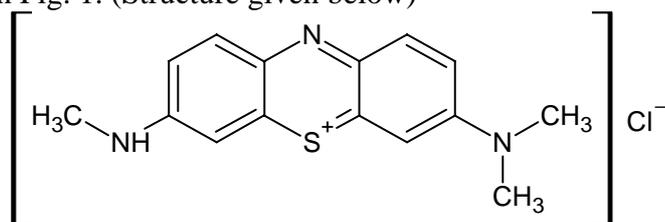


Fig. 1. Azure-B.

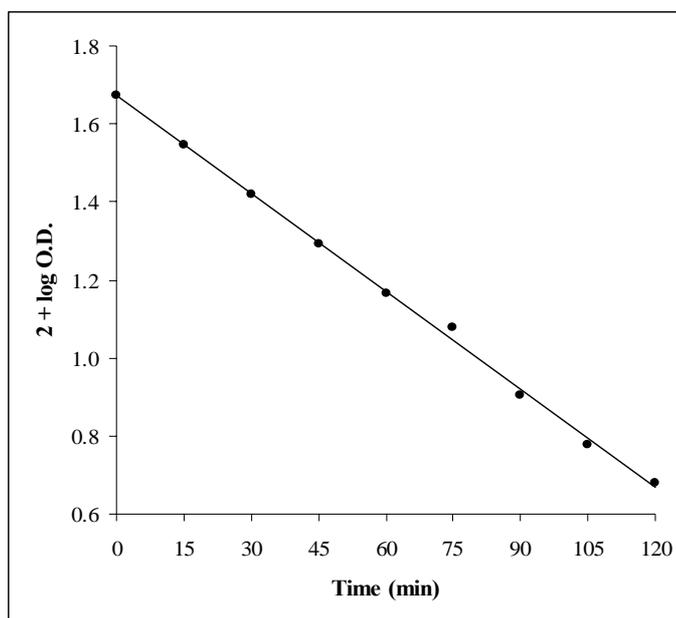
At regular time intervals, an aliquot of 2.0 mL was taken out from the reaction mixture. The optical density (O.D.) of the reaction mixture was decreases with increasing time intervals showing thereby that the concentration of dye decreases with increasing time exposure. A plot of $2 + \log \text{OD}$ 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.

pH = 4.5		[Azure B] = $3.3 \times 10^{-5} \text{ M}$
[S ₂ O ₈ ²⁻] = $3.6 \times 10^{-4} \text{ M}$		[Cu ²⁺] = $4.1 \times 10^{-4} \text{ M}$
Light intensity = 62.9 mWcm ²		
Time (min)	Optical density (O.D.)	2 + log O.D.
0	0.470	1.672
15	0.352	1.546
30	0.262	1.418
45	0.196	1.293
60	0.146	1.166
75	0.199	1.079
90	0.080	0.903
105	0.059	0.778
120	0.048	0.679

$$k = 3.20 \times 10^{-4} \text{ s}^{-1}$$

**Fig. 2.** A typical run for photochemical oxidation of azure b.

3.1. Effect of pH

The pH of the solution is expected to affect the photochemical reaction of azure b, and hence, photochemical reaction of azure b was investigated in the pH range (2.0 – 5.5). The results are represented in Table 2.

The rate of photooxidation of azure b increases on increasing the pH of the reaction mixture. On increasing pH further above 4.5, the rate of photooxidation of dye decreases. This may be attributed to the facts that 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 $S_2O_8^{2-}$ ions increase, which is utilized in oxidation. Cu^{2+} ions play an important role in oxidizing excited dye to its cation radical. 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 increases and these OH^- ions may react with sulphate anion radical ($SO_4^{\bullet-}$) to give SO_4^{2-} . 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.

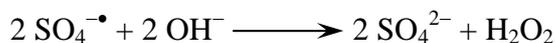


Table 2
Effect of pH.

[Azure B] = 3.3×10^{-5} M		[$S_2O_8^{2-}$] = 3.6×10^{-4} M	
[Cu^{2+}] = 4.1×10^{-4} M		Light intensity = 62.9 mWcm ²	
pH		$k \times 10^4 s^{-1}$	
2.0		0.73	
2.5		1.07	
3.0		2.11	
3.5		2.31	
4.0		2.76	
4.5		3.20	
5.0		2.84	
5.5		2.68	

3.2. Effect of dye concentration

The effect of variation of dye concentration on rate of photooxidation was also studied by taking different concentrations of dye. Photooxidation of azure b was studied in the range of 2.0×10^{-5} to 6.6×10^{-5} M. The maximum rate was found at 3.3×10^{-5} M for the dye. The results are represented in Table 3.

Table 3
Effect of dye concentration.

pH = 4.5		[$S_2O_8^{2-}$] = 3.6×10^{-4} M	
[Cu^{2+}] = 4.1×10^{-4} M		Light intensity = 62.9 mWcm ²	
[Azure-B] $\times 10^5$ M		$k \times 10^4 s^{-1}$	
2.0		1.46	
2.2		1.99	
2.5		2.34	
2.8		2.89	
3.3		3.20	
4.0		2.88	
5.0		2.54	
6.6		1.94	

The rate of oxidation 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 3.3×10^{-5} M, the reaction rate of photochemical oxidation of azure b decreases. This is probably due to the fact that after 3.3×10^{-5} M 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.

3.3. Effect of peroxydisulphate ion concentration

The effect of variation of $S_2O_8^{2-}$ ions concentration on rate of the reaction was observed by taking different concentrations of $S_2O_8^{2-}$ ions. Photooxidation of azure b was studied in the range of 0.3×10^{-4} to 5.0×10^{-4} M. The maximum rate was found at 3.6×10^{-4} M for the dye. The results are represented in Table 4.

Table 4
Effect of peroxydisulphate ion concentration

[Azure B] = 3.3×10^{-5} M		pH = 4.5	
[Cu ²⁺] = 4.1×10^{-4} M		Light intensity = 62.9 mWcm ²	
[S ₂ O ₈ ²⁻] × 10 ⁴ M		k × 10 ⁴ s ⁻¹	
0.3		0.65	
1.0		1.28	
1.6		2.35	
2.3		2.57	
3.0		3.00	
3.6		3.20	
4.3		2.62	
5.0		2.39	

The results indicate that the rate of the reaction increases on the increase in the oxidant concentration upto 3.6×10^{-4} 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 sulphate ion and HO[•], and as a result, the activity of these ions is decreased. The less reactive H₂O₂ can be formed by the recombination of hydroxyl radicals. H₂O₂ is a known quencher of HO[•] radical. Therefore, the rate increment of azure b photooxidative decolorization is slightly slowed down at higher S₂O₈²⁻ 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 azure b at higher S₂O₈²⁻ dosages are still expected. The finding was in agreement with literature reports where optimal concentration of S₂O₈²⁻ would result in higher photooxidative removal efficiency [20-23].

3.4 Effect of cupric ion concentration

The effect of increasing concentration of Cu²⁺ ions was also studied by keeping all other factors identical. Photooxidation of azure b was studied in the range of 0.9×10^{-4} to 6.5×10^{-4} M. The maximum rate was found at 4.1×10^{-4} M for the dye. The results are presented in Table 5.

Table 5
Effect of cupric ion concentration

pH = 4.5 [S ₂ O ₈ ²⁻] = 3.6 × 10 ⁻⁴ M		[Azure B] = 3.3 × 10 ⁻⁵ M Light intensity = 62.9 mWcm ²
[Cu ²⁺] × 10 ⁴ M	k × 10 ⁴ s ⁻¹	
0.9	2.48	
1.7	2.70	
2.5	2.97	
3.3	3.12	
4.1	3.20	
4.9	2.64	
5.7	2.58	
6.5	2.33	

3.5. Effect of light intensity

The effect of light intensity on the photodegradation of azure b was also observed. The results are presented 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 Cu⁺ ions and as a result, there is an increase in the number of active species, the S₂O₈²⁻ and SO₄^{•-} radical ions and corresponding increase in the rate of reaction. However, higher intensities were avoided due to thermal effects.

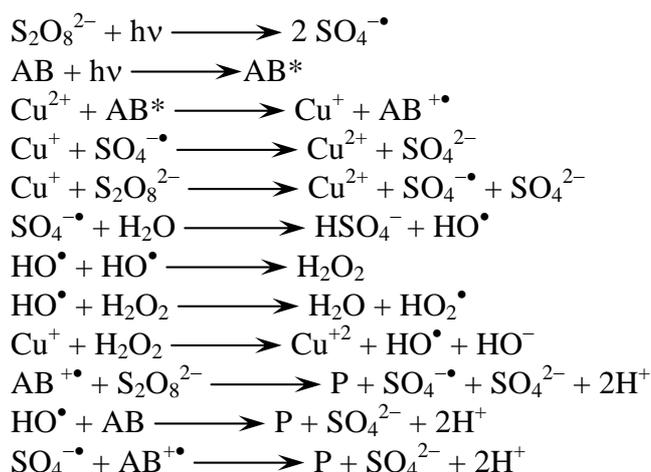
Table 6
Effect of light intensity

pH = 4.5 [S ₂ O ₈ ²⁻] = 3.6 × 10 ⁻⁴ M		[Azure B] = 3.3 × 10 ⁻⁵ M [Cu ²⁺] = 4.1 × 10 ⁻⁴ M
Light Intensity (mWcm ²)	k × 10 ⁴ s ⁻¹	
27.7	0.64	
30.6	0.99	
34.6	1.29	
39.6	2.21	
45.6	2.44	
53.3	2.98	
62.9	3.20	

3.6. Mechanism

Peroxydisulphate is a strong two electron oxidant and it has also been used for metal ion catalyzed oxidation of various substrates. On the basis of experimental observations, a tentative

mechanism for metal ion catalyzed photochemical oxidation of azure b dye has also been proposed as:



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

Decolorization of azure b is reasonable, since as the concentration of S₂O₈²⁻ is increased, more sulphate and HO[•] radicals are available to attack the aromatic rings of azure b and rate of reaction increases. However, at higher S₂O₈²⁻ dosages, excessive generated hydroxyl radicals would be recombined to form less reactive H₂O₂ and the Fenton's reaction also produces hydroxyl radicals by interaction of H₂O₂ with Cu⁺.

In the initial step, dye is excited by absorbing radiations of suitable wavelength. Cu²⁺ ions pull an electron from excited dye molecule to yield dye cation radical (AB^{•+}) and Cu⁺ ions. 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. The dye cation radical also reacts with peroxydisulphate ions giving sulphate ion, sulphate anion radical, protons and the degraded products of the dye. Cu⁺ 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 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 values (strong acidic medium), as evident from experimental observations.

4. Conclusions

The results of this study demonstrate that Cu²⁺/S₂O₈²⁻ process could efficiently optimize the photooxidative decolorization of azure b. Under optimum conditions of the process parameters, high color removal was obtained for the dye solution containing azure b. 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.

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References

- [1] L.J. Sojka, T. Koprowski, W. Machnowski, H.H. Knudsen, *Desalination* 119 (1998) 1-9.
- [2] H. Barlas, T. Akgun, *Resenius Environ. Bull.* 9(9-10) (2000) 597-602.
- [3] G. Ciardelli, G. Capannelli, A. Bottino, *Water Sci. Technol.* 44(5) (2001) 61-70.
- [4] D.A. House, *Chem. Revs.* 62 (1962) 185-203.
- [5] D.L. Ball, M.M. Gutchfield, J.O. Edwards, *J. Org. Chem.* 25 (1960) 1599-1611.
- [6] D. Meyerstein, *J. Inorg. Nucl. Chem.* 43 (1981) 401-402.
- [7] S.C. Agrawal, G. Chandra, S.K. Jha, *J. Inorg. Nucl. Chem.* 41 (1979) 99-902.
- [8] S.C. Agrawal, L.K. Saxena, *J. Inorg. Nucl. Chem.* 42 (1980) 932-935.
- [9] B.N. Lee, W.D. Liaw, J.C. Lou, *Environ. Eng. Sci.* 16 (1999) 165-175.
- [10] M. Abassi, N. Razzaghi Asl, *J. Iran. Chem. Res.*, 2 (2009) 221-230.
- [11] I. Bhati, A. Kumar, S.C. Ameta, *J. Iran. Chem. Res.*, 3 (2010) 211-217.
- [12] K. Dutta, S. Mukhopadhyay, S. Bhattacharjee, B. Chau, *J. Hazard. Mater.* 84 (2001) 57-71.
- [13] A. Rezaee, M.T. Ghaneian, S.J. Hashemian, G. Moussavi, A. Khavanin, G. Ghanizadeh, *J. Appl. Sci.* 8(6) (2008) 1108-1112.
- [14] F. Cicek, D. Ozer, A. Ozer, *J. Hazard. Mater.* 146 (2007) 408-416.
- [15] N.A. Daneshvar, Aleboyesh, A.R. Khataee, *Chemosphere* 59 (2005) 761-767.
- [16] A. Gemeay, G. El-Ghrabawy, A. Zaki, *Dyes Pigm.* 73 (2007) 90-97.
- [17] I. Fatimah, P.R. Shukla, F. Kooli, *J. Appl. Sci.* 9(20) (2009) 3715-3722.
- [18] H. Gabriel, J. Hong, *Res. J. Appl. Sci.* 3(3) (2008) 216-224.
- [19] J. Soni, A. Kumar, A. Saifee, K. Intodia, *Bull. Catal. Soc. India* 7 (2010) 64-67.
- [20] T.K. Lau, W. Chu, N.J.D. Graham, *Environ. Sci. Technol.* 41 (2007) 613-619.
- [21] P.M.D. Gara, G.N. Bosio, M.C. Gonzalez, D.O. Martire, *Int. J. Chem. Kinet.* 40 (2007) 19-24.
- [22] D. Salari, A. Niaei, S. Aber, M.H. Rasoulifard, *J. Hazard. Mater.* 166 (2009) 61-66.
- [23] A.R. Khataee, O. Mirzajani, *Desalination* 251(1-3) (2010) 64-69.