Iron Catalyzed Photo-oxidation Of Azure-A with Peroxydisulfate Ion

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ABSTRACT

Oxidation by Photocatalised reactions is proven and economically feasible process for destruction of a variety of hazardous pollutants in wastewater. We report herein the oxidation of azure-A, a basic dye of thiazine series using a photocatalised reaction and potassium peroxydisulfate as photo oxidant and ferrous sulphate as photocatalyst at normal laboratory temperature and at atmospheric pressure. The effects of different parameters like the concentrations of dye, Fe^{2+} and $S_2O_8^{-2}$ ions, pH of the solution, light intensity etc. were observed and discussed. The progress of the photochemical oxidation was monitored spectrophotometrically. The optimum reaction conditions were experimentally determined. The photochemical oxidation of dye follows pseudo–first order kinetics. The result showed that the azure-A was completely oxidized and degraded into CO_2 and H_2O. A suitable tentative mechanism for photochemical bleaching of azure-A by photocatalised reaction has been proposed.

Keywords: Photochemical oxidation, ferrous sulphate, potassium peroxydisulfate, Azure-A.

INTRODUCTION

Dyes have been used for over 5000 years. Synthetic dyes quickly replaced the traditional natural dyes due to their low cost, their vast range of new colors and their better properties upon the dyed materials. However, 1000 of synthetic dyes are raising concerns due to their negative environmental effects. Synthetic dyes are the major water contaminants.[1,2] The color is objectionable aesthetically and it also reduces light penetration into the water thereby decreasing the efficiency of photosynthesis in aquatic plants hence impacting on their growth and development.[3] Furthermore, their presence in drinking water constitutes a potential human health hazard.[4]

Recently, developed techniques include the so called Advanced Oxidation Process (AOPs). AOPs are designed to oxidize organic compounds into CO_2, H_2O and inorganic ions, or biodegradable compounds and to facilitate oxidation process involving hydroxyl radicals.[5] Generation of the hydroxyl radical has been accomplished with the following technologies: ultraviolet (UV) irradiation[6], ozonation[7], ozonation in combination with UV or hydrogen peroxide[8], Fenton reagent oxidation[9], photocatalysis with titanium dioxide in combination with UV and oxygen.[10]

Oxidation of various substrates by peroxydisulfate ion is known to occur through several schemes. Jonnalagadda et al.[11] reported the one electron transfer by the direct reaction between the oxidant and reductant. Two successive reaction steps of the one electron transfer from the reductant has been reported by Wilmarth et al.[12] A kinetic and mechanistic study on the oxidation of indole–3 acetic acid by peroxydisulfate was presented by Kalyanasundharam et al.[13] The photooxidation of vitamine E (tochopherol) in the presence of peroxydisulfate in aqueous solution at neutral pH has been carried out in a quantum yield reactor using a high pressure mercury vapour lamp.[14] Nishida et al.[15] reported the light induced electron transfer oxidation reaction of ethylenediamine tetra acetate by peroxydisulfate in presence of aqueous tris [2,2–bipyridine ruthenium (II) ion].

Peroxydisulfate has also been used as an oxidizing agent for paracetamol and sulpha drugs by Murad et al.[16] and Gupta.[17] Perez-ruiz et al.[18] reported the photodegration of phenosafranine and neutral red in the presence of iron (III) as photocatalyst. Aarthi et al.[19] photocatalytic degraded the azure (A and B) and sudan (III & IV) dyes using nano TiO_2 as photocatalyst. Azure-A was also photocatalytic degraded using carbon doped zinc oxide[20] and n-doped zinc oxide.[21] Recently, Meena, et al.[22] developed photocatalyst immobilized resin dowex-11 and used to degrade the textile dyes ponceau-S and sudan–IV. Panwar et al.[23] used zirconium phosphate as a photocatalyst for the photobleaching of tolonium chloride dye. Photodestruction and COD removal of toxic dye erioglaucine using TiO_2-UV process was studied by Jain and Sikarwar.[24]

EXPERIMENTAL

MATERIALS AND METHODS

Azure-A is an organic compound with the chemical formula $C_{14}H_{14}ClN_3S$ (Figure 1). It is a light blue to dark blue dye. It is used for screening test for mucopolysaccharides. It is also known as Giemsa stain, Azure-A chloride and dimethylthionine. It was used as received and its structure is shown in figure 1.

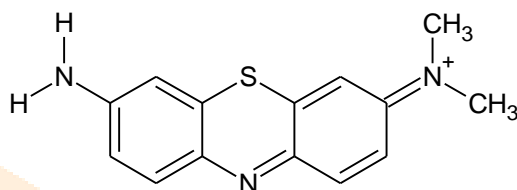|	
IUPAC name	(7-Amino-8-methyl-phenothiazin-3-ylidene)-dimethyl-ammoniumchloride
Molecular formula	$C_{14}H_{14}ClN_3S$
Molecular weight	291.80 g·mol−1
Appearance	Green to dark brown powder
Solubility	Water

Figure 1: A Structure of azure-A

The dye solution of azure-A was prepared in doubly distilled water. 0.029181 g of azure-A was dissolved in 100.0 mL doubly distilled water, so the concentration of azure-A was 1.0×10^{-3} M. It was used as a stock solution. The absorbance of the dye solution was determined with the help of spectrophotometer at $\lambda_{max} = 620$ nm. 0.027802 g of ferrous sulphate was dissolved in 100.0 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 peroxydisulfate was prepared a fresh just before use by dissolving 2.7031 g potassium peroxydisulfate in 100.0 mL doubly distilled water so that concentration of solution was 0.10 M.

Photocatalised oxidation of azure-A was studied by taking 30.0 mL reaction mixture containing 0.66×10^{-4} M dye solution, 0.83×10^{-2} M peroxydisulfate and 0.83×10^{-4} M ferrous sulphate solution in a 100.0 mL beaker and then this reaction mixture was exposed to light (light intensity = 70.0 mWcm^{-2}). The pH was adjusted at 3.5. 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 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.

RESULT AND DISCUSSION

The photochemical degradation of azure-A was observed at $\lambda_{max} = 620$ nm. The results for a typical run are given in Table 1 and Figure 2.

An aliquot of 2.0 mL was taken out from the reaction mixture at regular time intervals. It was observed that optical density (OD) of reaction mixture decreases with increasing time intervals showing thereby that the concentration of dye decreases with increasing time exposure. A plot of 2 + log OD versus time was linear and follows pseudo-first order kinetics. The rate constant was determined by the following expression: $k = 2.303 \times$ slope. The rate constant (k) for this reaction was determined as 8.82×10^{-4} s^{-1} .Results for typical run is given in Table 1.

Table 1: Typical Run

[Azure-A] = 0.66×10^{-4} M	pH = 3.5
[$S_2O_8^{2-}$] = 0.83×10^{-2} M	[Fe^{2+}] = 0.83×10^{-4} M
Light intensity = 70.0 mWcm^{-2}	

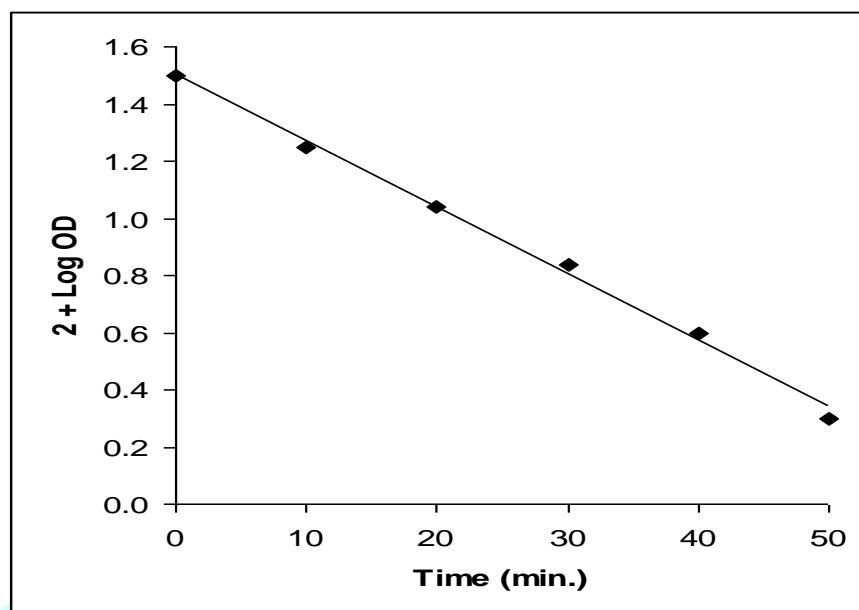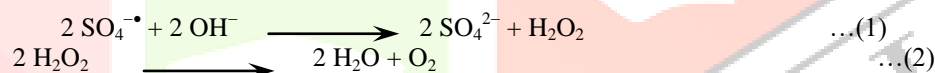| Time (min.)	Log O.D.	2 + log O.D.
0.0	0.32	1.50
10.0	0.18	1.25
20.0	0.11	1.04
30.0	0.07	0.84
40.0	0.04	0.60
50.0	0.02	0.30
$k = 8.82 \times 10^{-4}$ s^{-1}		

Figure 2: A Typical Run

Effect of pH

The effect of pH was studied up to pH 2.5 to 5.0 for azure-A. The rate of reaction for azure-A was maximum at pH 3.5. It was observed that the rate of reaction increases on increasing pH of the reaction mixture. This may be attributed to the fact that as the pH increases the number of $S_2O_8^{2-}$ ion increase, which are utilized in oxidation of Fe^{+2} to Fe^{+3} ions, which 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, OH^- ions increases as pH increases and these OH^- ions may react with sulphate anion radical ($SO_4^{-\bullet}$) to give sulphate ion (SO_4^{2-}). Sulphate anion radical is also considered one of the active oxidizing species and its removal from reaction mixture at higher pH will retard the rate of reaction.

$$2\,SO_4^{-\bullet} + 2\,OH^- \longrightarrow 2\,SO_4^{2-} + H_2O_2 \quad\quad\quad …(1)$$
$$2\,H_2O_2 \longrightarrow 2\,H_2O + O_2 \quad\quad\quad …(2)$$

At pH > 5.0 for azure-A some turbidity appeared and measurement of optical density becomes difficult and therefore, the effect of pH was studied up to pH 2.5 to 5.0. The results are reported in Table 2.

Table 2: Effect of pH

[Azure-A] = 0.66×10^{-4} M   [$S_2O_8^{2-}$] = 0.83×10^{-2} M
[Fe^{2+}] = 0.83×10^{-4} M   Light intensity = 70.0 mWcm^{-2}

pH	$k \times 10^4$ s^{-1}
2.5	5.29
3.0	7.07
3.5	**8.82**
4.0	7.07
4.5	6.17
5.0	4.79

Effect of dye concentration

Effect of variation of dye concentration on rate of bleaching was also studied by taking different concentrations of dye. The photo degradation was studied in the range of 0.16×10^{-4} M to 1.16×10^{-4} M. The maximum rate was found at 0.66×10^{-4} M. The results are reported in Table 3.

The rate of photooxidation was found to increase with increasing concentration of dye. This may be explained on the basis that on increasing the concentration of dye, the reaction rate increases as 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 molecules 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 bleaching decreases.

Table 3: Effect of azure-A dye concentration

pH = 3.5 $[S_2O_8{}^{2-}] = 0.83 \times 10^{-2}$ M

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

[Azure-A] $\times 10^4$ M	k $\times 10^4$ s^{-1}
0.16	4.39
0.33	6.17
0.50	7.07
0.66	**8.82**
0.83	8.22
1.00	7.94
1.16	6.91

Effect of peroxydisulfate ion concentration

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

The results indicate that rate of the reaction increases on the increase in the oxidant concentration upto 0.83×10^{-2} M, because more peroxydisulfate 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 these ions and as a result, the activity of these ions was decreased.

Table 4: Effect of peroxydisulfate ion concentration

$[Azure-A] = 0.66 \times 10^{-4}$ M   pH = 3.5

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

$[S_2O_8{}^{2-}] \times 10^2$ M	k $\times 10^4$ s^{-1}
0.50	6.989
0.66	7.655
0.83	**8.820**
1.00	6.989
1.16	5.658
1.33	4.992

Effect of ferrous ion concentration

The effect of increasing concentration of Fe^{2+} ions was also studied by keeping all other factors identical. The result indicates that the rate of the reaction of azure-A increases on the increase in the photocatalyst concentration upto 0.83×10^{-4} M. The results are given in Table 5.

Table 5: Effect of ferrous ion concentration

$[Azure-A] = 0.66 \times 10^{-4}$ M   pH = 3.5

$[S_2O_8{}^{2-}] = 0.83 \times 10^{-2}$ M   [Light intensity = 70.0 mWcm^{-2}

[Fe^{2+}] $\times 10^4$ M	k $\times 10^4$ s^{-1}
0.166	6.24
0.33	6.65
0.50	7.29
0.66	7.80
0.83	**8.82**
1.00	7.29
1.16	6.65

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 peroxydisulfate ions. These Fe^{3+} ions convert excited dye molecule to its cation radical, which then undergoes degradation.

Effect of light intensity

The effect of light intensity on the photodegradation of azure-A was also observed. The results obtained are reported in Table 6.
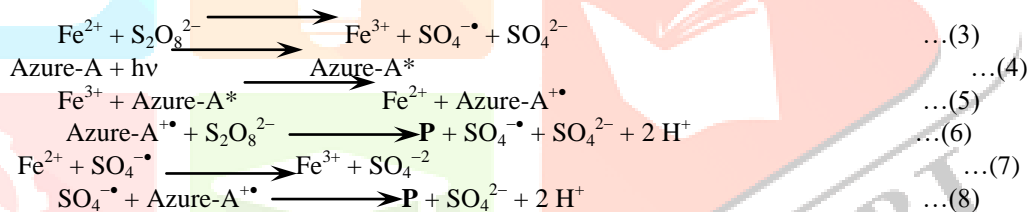
Table 6: Effect of light intensity

| [Azure-A] = 0.66×10^{-4} M | pH = 3.5 |
| [$S_2O_8^{2-}$] = 0.83×10^{-2} M | [Fe^{2+}] = 0.83×10^{-4} M |

Light Intensity (mWcm^{-2})	$k \times 10^4$ s^{-1}
10.0	2.68
20.0	3.07
30.0	3.45
40.0	5.75
50.0	6.80
60.0	7.67
70.0	**8.82**

A linear plot between the rate constant and light intensity indicates that an increase in the light intensity increases the rate of reaction. This may be duo 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.

Mechanism

Peroxydisulfate 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 also been proposed as –

$$Fe^{2+} + S_2O_8^{2-} \longrightarrow Fe^{3+} + SO_4^{-\bullet} + SO_4^{2-} \qquad \ldots(3)$$

$$Azure\text{-}A + h\nu \longrightarrow Azure\text{-}A^* \qquad \ldots(4)$$

$$Fe^{3+} + Azure\text{-}A^* \longrightarrow Fe^{2+} + Azure\text{-}A^{+\bullet} \qquad \ldots(5)$$

$$Azure\text{-}A^{+\bullet} + S_2O_8^{2-} \longrightarrow P + SO_4^{-\bullet} + SO_4^{2-} + 2\,H^+ \qquad \ldots(6)$$

$$Fe^{2+} + SO_4^{-\bullet} \longrightarrow Fe^{3+} + SO_4^{-2} \qquad \ldots(7)$$

$$SO_4^{-\bullet} + Azure\text{-}A^{+\bullet} \longrightarrow P + SO_4^{2-} + 2\,H^+ \qquad \ldots(8)$$

Where **P** = gaseous products like CO_2, H_2O, etc.

In the initial step, Fe^{2+} transfers its electron to peroxydisulfate ion and hence, Fe^{2+} is oxidized to Fe^{3+} and peroxydisulfate ion is broken into sulphate ion and sulphate anion radical. (eq. 3). Fe^{3+} ion pulls an electron from excited dye molecule to yield dye cation radical and Fe^{2+} ion (eq. 5). The dye cation radical also reacts with peroxydisulfate ions giving sulphate ion, sulphate anion radical ($SO_4^{-\bullet}$), protons and the degraded products of the dye (eq. 6). Fe^{2+} ion will also react with sulphate anion radical, converting it into sulphate ions (eq. 7). In next step, sulphate anion radical reacts with dye cation radical to give sulphate ion and products (eq. 8). 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.

The oxidative bleaching of dyes by peroxydisulfate 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).

References

1. Brown, D.; Hitz, H. R.; Schafer, L. *Chemosphere* **1981,** *10*, 215.
2. Vaidya, A. A.; Datya, K. V. *Colourage* **1982,** *14*, 3.
3. AL-Degs, Y.; Khraisheh, M. A. M.; Allen, S. J.; Ahmad, M. N. *Water Res.* **2000,** *34*, 927.
4. Boeningo, M. *Washington DC, U.S Gov. Printing Off; DNHS(NIOSH) Publication,* **1994,** 80.

5. Nogueira, R. F. P.; Silva, M. R. A.; Trovo, A. G. *Solar Energy* **2005,** *79*, 384.
6. Legrini, O.; Oliveros, E.; Braun, A. M. *Chem. Rev.* **1983,** *93*, 671.
7. Hapeman, C. J.; Anderson, B. G.; Torrents, A.; Acher, A. *J. Agric. Food Chem.* **1997,** *45*, 1006.
8. Staehelin, S.; Hoigne, J. *Environ. Sci. Technol.* **1982,** *16*, 676.
9. Howsawkeng, J.; Watts, G. J.; Washington, D. L.; Teel, A. L.; Hess, T. F.; Crawford, R. L. *Environ. Sci.Technol.* **2001,** *35*, 2961.
10. Gimenez, J.; Curco, D.; Marco, P. *Water Sci. Technol.* **1997,** *35*, 207.
11. Jonnalagadda, S. B.; Choudhary, V.; Bhattacharya, A. K. *J. Chem. Soc. Perkin Trans.* **1983,** *2,* 849.
12. Wilmarth, W. K.; Haim, A.; *Edwards J. O. (Ed) Interscience, New York. N. Y.* **1962,** *194.*
13. Kalyanasundharam, S.; Chandramohan, G.; Suresh, M.; Anbazhagan, V.; Lavanya, S.; Rehganathan, R. *Inter. J. Chem. Kinetics* **2005,** *37(6)*, 355.
14. Swaraga, M. S.; Adinarayana, M. *Indian J. Chem. Sec. A, Inorganic, Physical, Theoretical and Analytical Chemistry* **2004,** *43(2),* 303.
15. Nishida, S.; Kimura, M. *Bull. Chem. Soc. Japan.* **1987,** *60(7),* 2367.
16. Helaleh, M. I. H.; Korenaga, T.; Abu-nameh, E. S. M.; Jamhour, R. M. A. Q. *Pharm. Acta. Helv.* **1999,** *73(5),* 255.
17. Gupta, V. K. *Thermochim. Acta.* **1983,** *69(3),* 389.
18. Ruiz, T. P.; Lozano, C. M.; Tomas, V. *Microchemica Acta* **1985,** *85(1-2),* 103.
19. Aarthi, T.; Narahari, P.; Madras, G. *J. Hazard. Mater.* **2007,** *149(3),* 725.
20. Rao, P.; Tak, P.; Benjamin, S. *Sci. Revs. Chem. Commun.* **2016,** *6(2)*, 19.
21. Rathore, P.; Ameta, R.; Sharma, S. *J. Text. Sci. Technol.* **2015,** *1,* 118.
22. Meena, R. C.; Pachwarya, R. B.; Meena, V. K.; Arya, S. *Am. J. Env. Sci.* **2009,** *5(3),* 444.
23. Panwar, O. P.; Kumar, A.; Ameta, R.; Ameta, S. C. *Macedonian Journal of Chemistry and Chemical Engineering* **2008,** *27(2),* 133.
24. Jain, R.; Sikarwar, S. *Inter. J. Phys. Sci.* **2008,** *3(12),* 299.