Est. 1984

ORIENTAL JOURNAL OF CHEMISTRY

An International Open Free Access, Peer Reviewed Research Journal

www.orientjchem.org

ISSN: 0970-020 X
CODEN: OJCHEG
2011, Vol. 27, No. (3):
Pg. 1179-1184

Photochemical Treatment of Amido Black - 10B Waste Water by Photo-Fenton Reagent

MUKESH KUMAR, RICHA TIWARI[1], KRISHNA SHARMA, OM PRAKASH SHARMA and MOHAN KUMAR SHARMA*

*Department of Chemistry, M. S. J. Govt. P. G. College, Bharatpur, Rajasthan - 321 001 (India).
[1]Department of Chemistry, University College of Science, Sukhadia University, Udaipur, Rajasthan - 313 002 (India).
*Corresponding author: E-mail: mukesh-pgt-chem@yahoo.in, richatiwari06@gmail.com

(Received: April 29, 2011; Accepted: May 30, 2011)

ABSTRACT

Oxidation of pollutants in waste water by photo-Fenton reaction has proven an eco- friendly and economical method. Oxidation of amido black – 10B, (an acid dye of azo series) using photo-Fenton reagent was investigated under ambient conditions. The effect of different parameters like the concentration of ferric ion, amido black- 10B and hydrogen peroxide, pH, light intensity etc. on the reaction rate has been observed. A tentative mechanism for the degradation of amido black-10B by photo-Fenton has been proposed.

Key words: Photochemical degradation, Photo-Fenton, Amido black-10B, Advanced oxidation process (AOPs).

INTRODUCTION

The world is facing the challenge of purification of water resources. Recent progress in chemical water treatment has lead to the development of the purification methods, which includes chemical, photochemical, sonochemical or radiolytic techniques for the chemical degradation of pollutants[1]. Recently, advanced oxidation processes (AOPs) have been developed to oxidize the organic compound into CO_2, H_2O and inorganic ions, or biodegradable compounds[2]. Some system e.g. UV-H_2O_2 and UV-O_3 are widely known and are in practical use also[3-4]. Fenton (H_2O_2/Fe^{2+}) and photo-Fenton (UV/H_2O_2/ Fe^{2+}) methods have proved to be effective and economical AOP methods used for the detoxification and degradation of many organic compounds[5]. It is proved that dye decolourisation is accelerated by the combination of UV irradiation and Fenton's process because it produced •OH radicals directly[6]. (Esq. 1-3).

$$H_2O_2 + h\nu \rightarrow 2{\bullet}OH \qquad ...(1)$$

$$\bullet OH + \text{dye} \rightarrow \text{dye intermediate} \qquad ...(2)$$

$$\bullet OH + \text{dye intermediate} \rightarrow CO_2 + H_2O + MP$$
$$(MP = \text{mineralization products}) \qquad ...(3)$$

Chen and Zhu[7] catalytically degraded orange–II by UV-Fenton with hydroxyl-Fe-pillared-bentonite in water. Degradation of rose bengal dye in aqueous medium using the heterogeneous photo-Fenton process has been assessed by Sharma *et al*[8]. Research studies using Fenton's reagent have demonstrated its ability to oxidize phenols[9,10], pesticides[11], surfactants[12], aromatics[13,14], dyes [15] and polychlorinated biphenyls (PCBs)[16].

MATERIAL AND METHODS

Amido black-10B (SDS), $FeCl_3$ (CDH) and H_2O_2 (30%, Merck), were used in the present investigation. The dye solution of amido black- 10B was prepared in doubly distilled water. The photochemical degradation of amido black-10B was studied in the presence of Fe^{+3} ions, H_2O_2 and light. 0.06165 g of amido black- 10B was dissolved in 100 mL of doubly distilled water (1.0×10^{-3}) M and 0.081105 g of anhydrous $FeCl_3$ was dissolved in 500 mL of doubly distilled water so that the concentration of the $FeCl_3$ solution was 1.0×10^{-3} M. These were used as stock solutions. The photochemical degradation of amido black- 10B was studied taking 28 mL of dye solution (2.67×10^{-4} M) and 1.0mL of $FeCl_3$ solution (1.0×10^{-3}). The reaction mixture was exposed to light (intensity 58.17mW Cm^{-2}). A 200-watt tungsten lamp (Philips) was used for irradiation purpose. Sunlight was used for higher intensities of light. The intensity of light at various distances was measured by solarimeter CEL model 211.

A water filter was used to cut off thermal radiations. The pH of the solution was measured by a digital pH meter (Systronics). The desired pH of the solution was adjusted by the addition of previously standardized H_2SO_4 and NaOH solutions. The necessary condition for the correct measurement of optical density is that the solution must be free from suspension. Centrifuge machine (Remi-1258) and Whatman filter paper was used to remove the suspension but both were not found suitable. Thus, G-3 sintered glass crucible was used for filtration to obtain the desire accuracy in measurement of optical density at different time intervals, whereas λ_{max} of the dye was determined with the help of Ultraviolet - Visible recording spectrophotometer (Double beam UV-VIS Spectro photo meter UV 570 4SS).

RESULT AND DISCUSSION

The photochemical degradation of amido black- 10B was observed at $\lambda_{max\ P\%}$ 617.8 nm. The results for a typical run are graphically represented in fig.1, it was observed that optical density of amido black- 10B solution decreases with the increases in the time of irradiation; thus, indicating that amido black- 10B is consumed on irradiation. A plot of 2+ logOD against time was linear and it followed-first order kinetics. The rate constant was measured with expression k = 2.303 × slope. The Optimum rate constant for this reaction was determined as $k = 44.22\times10^{-3}$.

Effect of pH

The effect of pH on photo catalytic degradation was also investigated. The results are reported in Table 1 and are graphically presented in Fig. 2.

The effect of pH on the rate of degradation of amido black- 10B was investigated in the pH range of 1.0 to 4.5.The photochemical degradation depends strongly on the pH of the reaction medium as it is evident from Fig.2 that the range of photochemical degradation of amido black- 10B increases with increase in pH up to 2.5 and then the rate of reaction decreases with increasing pH.

OH^- ions will generate more •OH radicals by combining with the hole of the semiconductor and these •OH are considered responsible for the photo catalytic bleaching. After a certain pH value, more OH^- ions in the bulk will retard the approach of the dye molecules towards the semiconductor surface in the desired time limit due to the decrease in the movement of the large dye molecules. This will result in a decrease in the rate of photo catalytic bleaching of amido black- 10B

Effect of Amido Black- 10B Concentration

Effect of variation of dye concentration on rate of reaction was also studied by taking different concentrations of amido black- 10B solution. The results are given in Fig, 3. The rate of photochemical degradation was found to increase with increasing concentration of amido black- 10B (up to 2.67 × 10

Progress of the Photo catalytic reaction

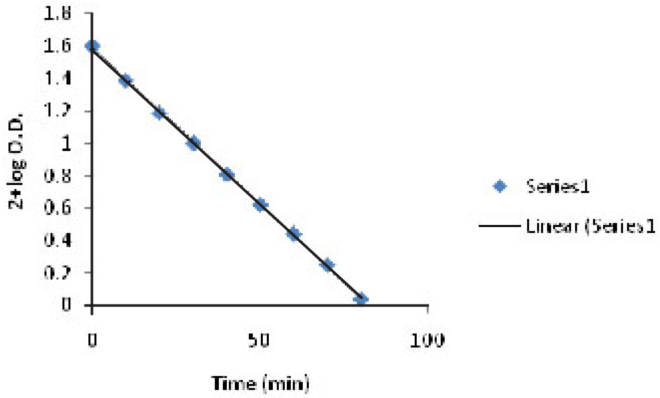

Fig. 1: A typical run [amido black- 10B] = (2.67×10^{-5} M); pH = 2.5 [Fe^{+3}] = 5.3×10^{-5} M ; H_2O_2 = 4mL ;light intensity = 58.17 $mWcm^{-2}$

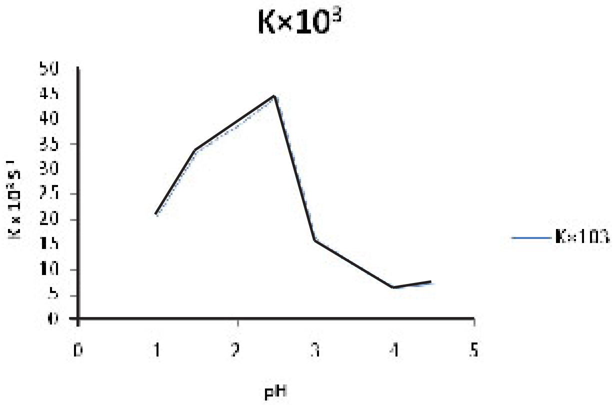

Fig. 2: Effect of pH [amido black 10-B]= (2.67×10^{-5}M); H_2O_2 = 4.0 mL; [Fe^{+3}]= 5.3×10^{-5} M; Light intensity =58.17 $mWcm^{-2}$

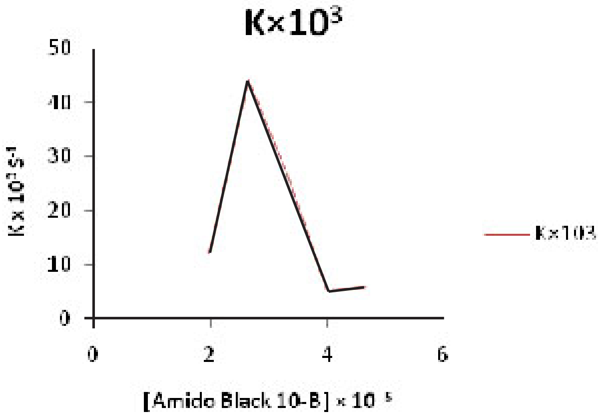

Fig.3 Effect of amido black-10B Concentration pH =2.5; H_2O_2 =4.0mL; Fe^{+3} =5.3×10^{-5} M; Light intensity =58.17 $mWcm^{-2}$

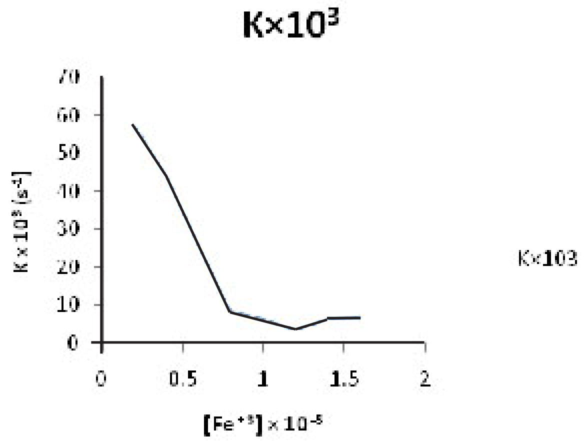

Fig. 4: Effect of ferric ion Concentration [amido black-10B] =2.67×10^{-5}M; pH =2.5;H_2O_2 =4.0mL ; light intensity = 58.17 mWcm^{-2}

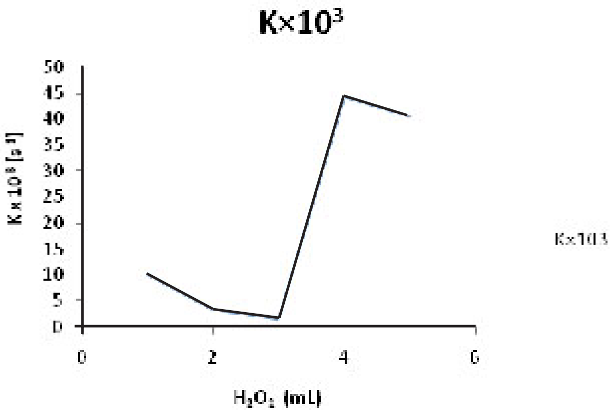

Fig. 5: Effect of hydrogen per oxide [amido black 10-B] = (2.67 × 10^{-5}M); pH =2.5; Fe $^{+3}$ =5.3×10^{-5}; light intensity = 58.17 mWCm^{-2}

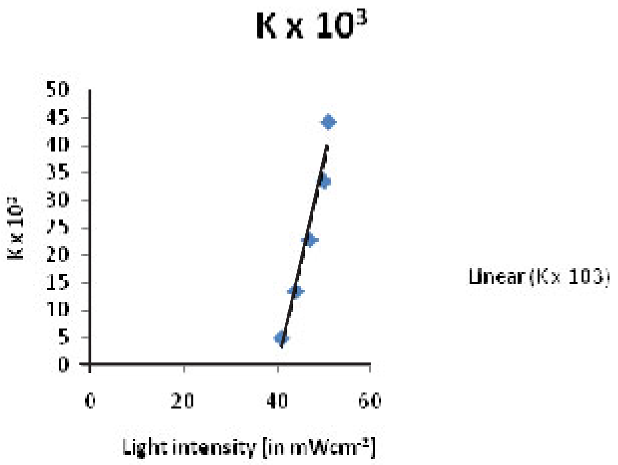

Fig. 6: Effect of light intensity [amido black 10-B] = (2.67 × 10^{-5}M); pH =2.5; Fe $^{+3}$ =5.3×10^{-5}; H_2O_2 =4.0 Ml

$^{-5}$M). This may be attributed to the fact that as the concentration of amido black- 10B was increased, more dye molecule were available for the excitation followed by inner system crossing and hence, there was an increase in the rate. On increasing the concentration above 2.67 × 10 $^{-5}$, the reaction rate was found to decrease. It may be attributed to the fact that as the concentration of amido black- 10B was increased, it started acting like a filter for the incident light, whereas its larger intensity to reach the dye molecule in the bulk of the solution and thus, a decrease in the rate of photochemical bleaching of amido black- 10B was observed. Fig. 3.

Effect of ferric ion concentration

The effect of concentration of Fe^{+3} ions on the rate of photochemical degradation of amido black- 10B was observed by keeping all other factors constant. **Fig.4**

The results are presented in Fig.4. It is clear that the rate of photo degradation increases on increasing concentration of Fe^{+3} ions up to 5.3×10^{-6} M, while a reverse trend was observed beyond this limit. This may be explained on the basis that on increasing the Fe^{+3} ions in the reaction mixture, the concentration of Fe^{+2} ions also increases, which is accompanied by enhanced generation of the active species $^{\cdot}OH$ radicals and as a consequence, the rate of photo degradation also increases. However, on increasing the concentration of Fe^{+3} ions further, the rate of the reaction was found to decrease. This is because of the fact that the Fe^{+3} ions imparts a yellow colour to the solution and at larger concentrations, it may also act as a filter for the incident light. As the concentration of Fe^{+3} was increased above its optimum concentration, the rate of the reaction of [Eq. (2)] and [Eq.(6)] (see mechanism) become very fast. Now in [Eq.(2)] hydro per oxyl radicals ($^{\cdot}OOH$) are generated, hence, Fe^{+3}ions are now less available [Eq.(1)] and as a consequence less $^{\cdot}OH$ radicals are generated and the rate of photo degradation also decreases.

Effect of hydrogen peroxide

The effect of amount of hydrogen peroxide on photo degradation of amido black- 10B was also investigated. The results are presented in Fig.5. It was observed that the rate of reaction increases on increasing the amount of H_2O_2 and it attained an optimum value at H_2O_2 = 4mL. Thereafter, the rate of degradation decreases on increasing the amount of the hydrogen peroxide above 4mL.

This can be explained on the basis that more H_2O_2 molecules are available for Fe^{+2} ions to react, which increases the number of $^{\cdot}OH$ radicals. Therefore, the rate of reaction also increases. On further increasing the amount of H_2O_2 more than 4mL, the rate of reaction was found to decrease. It is because of the fact that as the amount of H_2O_2 was increased along its optimum condition (4mL) the rates of the reaction [Eq.(2)] and [Eq.(4)]become fast and $^{\cdot}OH$ radicals are consumed rapidly [Eq.(4)] due to more availability of H_2O_2 molecules. From [Eq.(2)] and [Eq.(4)], ($^{\cdot}OOH$) radicals generated in more amount. This ($^{\cdot}OOH$) radical is utilized [Eq.(6)] and H^+ ions are produced. The production of H^+ ions is confirmed by a slight decrease in pH of the reaction mixture at the end of reaction. As a consequence, the rate of photo degradation decreases. Fig.5

Effect of light intensity

The effect of light intensity on the photo degradation of amido black- 10B was also observed. The results obtained are given in Fig. 6. A linear plot was obtained 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^{+3} ions and as a result, there is an increase in the number of active species, the hydroxyl radicals and corresponding increase in the rate of reaction. Fig.6

Mechanism

On the basis of experimental observations and corroborating the existing literature, a tentative mechanism has been proposed for photo degradation of amido black- 10B with photo-Fenton reagent.

$$Fe^{+3} + H_2O + h\nu \rightarrow Fe^{+2} + {}^{\cdot}OH + H^+ \quad ...(1)$$
$$Fe^{+3} + H_2O_2 + h\nu \rightarrow Fe^{+2} + {}^{\cdot}O_2H + H^+ \quad ...(2)$$
$$Fe^{+2} + H_2O_2 \rightarrow Fe^{+3} + {}^{\cdot}OH + OH^- \quad ...(3)$$
$${}^{\cdot}OH + H_2O_2 \rightarrow {}^{\cdot}O_2H + H_2O \quad ...(4)$$
$$Fe^{+2} + {}^{\cdot}OH \rightarrow Fe^{+3} + OH^- \quad ...(5)$$
$$Fe^{+3} + {}^{\cdot}O_2H \rightarrow Fe^{+2} + O_2 + H^+ \quad ...(6)$$
$${}^{\cdot}OH + {}^{\cdot}OH \rightarrow H_2O_2 \quad ...(7)$$
$$\text{amido black- 10B} + {}^{\cdot}OH \rightarrow \text{Product} \quad ...(8)$$

When the aqueous solution of ferric ion expose to light which, dissociates water into a proton and ·OH radical also, ferric ions are reduced to ferrous ions. These ferrous ions will decompose H_2O_2 into hydroxyl ion and hydroxyl radical, while ferrous ions undergo oxidation to ferric ions. The ferric ions generates (·OOH) radical due to dissociation of H_2O_2 in presence of light. The incorporation of ·OH with H_2O_2 also produces (·OOH) radicals. Ferrous ions will undergo oxidation to ferric ions by addition of ·OH radicals. While ferric ions get reduced to ferrous ions by incorporation of (·OOH) radical and producing H^+ ion. (·OOH) Radicals are highly unstable rather than reacting slow with dye molecules. The participation of hydroxyl radical as an active oxidizing was confirmed by using hydroxyl radical scavenger like isopropanol, where the rate of photo degradation was drastically reduced.

Now there are two possibilities for the consumption of ·OH radicals. First hydroxyl radicals may dissociate H_2O_2 molecules and secondly, it may react with amido black- 10B to give the colourless degradation products.

CONCLUSION

Photo-Fenton reaction is capable of oxidizing dyes like amido black- 10B into colourless degradation products. The present work opens an eco-friendly method by heterogenizing the homogenous photo-Fenton system to achieve a stable and efficient photo-Fenton catalyst for wastewater treatments. The treated waste water may be used for cooling, cleaning, waste land irrigation etc. which is not possible otherwise coloured water**.**

ACKNOWLDGEMENTS

Author wish to thank Prof. Suresh C. Ameta, Sukhadiya University,Udaipur for their guidance in this present research**.**

REFERENCES

1. Huston, P.; Pignatello J. *Water Res*. **33**: 1238 (1999).
2. Nogueira, R.F.P.; Silva M.R.A.; Trov´o, A.G. *Solar Ener*. **79**: 384 (2005).
3. Kearney, P. C.; Zang, Q.; Ruth, J. M. *ACS Sym Ser*. **259**: 195 (1984).
4. Hanger, D.G.; *Innovative Hazard Wastes Treat. Tech. Ser.* **2**: 143 (1990).
5. Lin, J. G.; Ma, Y. S. *J. of Env. Eng*. **126**: 130 (2000).
6. Xiang, X.; Zheng, H.; *Chongqing Jianzhu Univ*. **26**: 126 (2004).
7. Chen, J.; Zhu, L. *Chemosphere*. **65**: 1249 (2006).
8. Arora, R.; Chanderia, K.; Punjabi, P. B.; Sharma, V. K.; *J. Chem. Pharm. Res*. **2**: 627 (2010).
9. Kiwi, J.; Pulgarin, C.; Peringer, P.; *Appl. Catal. B: Environ*. **3**: 335 (1994).
10. Kwon, B.; Lee, D.; Kang, N.; Yoon, J. *Water Res*. **33**: 2110 (1999).
11. Huston, P.; Pignatello, J.; *Water Res*. **33**: 1238 (1999).
12. Lin, S.; Lin, C.; Leu, H. *Water Res*. **33**: 1735 (1999).
13. Chen, R.; Pignatello, J.; *Environ. Sci. Technol*. **31**: 2399 (1997).
14. Casero, I.; Sicilia, D.; Subio, S.; Perez-Bendito, D. *Water Res*. **31**: 1985 (1997).
15. Li, Y. S.; Liu, C. C.; Fang, Y. Y. *J. Environ. Sci. Health*. **34**: 1205 (1999).
16. Sedlak, D.; Andrin, A. *Environ. Sci. Technol*. **25**: 1419 (1991).