*Int. J. Chem. Sci.: 9(3), 2011, 1415-1420*
*ISSN 0972-768X*
*www.sadgurupublications.com*

# PHOTOCHEMICAL OXIDATION OF *p*-AMINOPHENOL BY FENTON REAGENT

**DHARMENDRA KUMAR**

Department of Chemistry, M. S. J. Government College, BHARATPUR – 321 001 (Raj.) INDIA

## ABSTRACT

Photochemical degradation of *p*-aminophenol by Fenton reagent was studied. The effect of various parameters such as substrate, $H_2O_2$, $FeSO_4$, pH, polarity of solvent and catalyst variation was studied. Photoproduct was characterized by physical, chemical and spectral methods. A tentative mechanism has been proposed with overall reaction.

**Key words**: Photochemical degradation, *p*-Aminophenol, Fenton, photo-Fenton.

## INTRODUCTION

Advances in waste water treatment has lead to the development of Advanced Oxidation Processes (AOPs). These processes employ chemical, photochemical and sonochemical techniques to bring about chemical degradation of ground, surface and wastewaters containing non-biodegradable organic pollutants[1-3]. AOPs are based on the generation of hydroxyl radical, which has a high oxidation potential, extraordinary reactive and unstable species that can attack of the organic contaminant[4]. Fenton reagent ($Fe^{2+}/H_2O_2$) and photo-Fenton ($Fe^{2+}$/ $H_2O_2$/ UV) method have proved to be effective and economical AOP methods used for the detoxification and degradation of many organic compounds[5,6].

Research studies using Fenton's reagent have demonstrated its ability to oxidize Mordant red 73 azo dye[7], Orange II azo-dye [8], pulp mill effluent[9], 1,2-dichloroethane[10], phenol[11], natural organic matter[12] etc.,

## EXPERIMENTAL

*p*-Aminophenol (Merck, Germany), ferrous sulphate, hydrogen peroxide 30% and sulphuric acid (all from Merck, India) and methanol (Rankem, India) were used to prepare

*Author for correspondence; E-mail: dk_kanwat@yahoo.com

all the solutions. Besides methanol, the rate of reaction was also studied in solvents like ethanol, acetone and ethyl acetate. All melting points were recorded on Toshniwal melting point apparatus. The pH measurements were done with the help of Systronics-327 Griph (digital) pH meter. An Infra-red spectrum was scanned on Schimadzu FTIR-8400S spectrophotometer. Elemental analysis was carried out using Carlo-Erba-1106 automatic analyzer.

*p*-Aminophenol (0.15 g) was dissolved in methanol in a round bottom flask, solution of ferrous sulphate (3.0 mL, 0.1M), hydrogen peroxide (0.25 mL, 30%) and sulphuric acid (0.5N) were added and pH was maintained. Total volume of the reaction mixture was made 100 mL by adding methanol. All the chemicals used in the investigation were purified according to the recommended methods. The concentration of various ingredients in the reaction mixture were *p*-aminophenol $1.38 \times 10^{-2}$ M, $FeSO_4$ $3.0 \times 10^{-3}$ M, $H_2O_2$ $2.25 \times 10^{-2}$ M and the pH of the solution was 2.6.

The reaction mixture was irradiated with light source (Tungsten lamps, 2 x 200W, Philips) at a distance of 30 cm from the reaction vessel. A water filter (15 cm thick) was placed between light source and the reaction vessel to cut off thermal radiations.

The progress of the reaction was observed with the help of TLC, at every 2 h interval and the product was identified by its usual tests. In initial stages of reaction, only a single spot corresponding to parent compound was observed when the TLC plate was placed in iodine chamber. After 4 h two spots corresponding to parent compound and photoproduct were observed. The reaction was allowed for completion (7 h).

The rate of the oxidation depends on various parameters like concentration of substrate, $H_2O_2$ & $FeSO_4$, pH, polarity of solvent and the catalyst.

## Effect of substrate concentration

The effect of concentration of substrate on photo-Fenton reaction was studied using variable concentrations of substrate, these were $4.5 \times 10^{-3}$ M, $9.2 \times 10^{-3}$ M, $13.8 \times 10^{-3}$ M, $18.6 \times 10^{-3}$ M and $23.3 \times 10^{-3}$ M . The % yield of photoproduct was 25.7, 30.1, 36.2, 35.3 and 33.7, respectively. It has been observed that as the concentration of substrate was increased, the yield of photoproduct was found to increase, up to an optimum level. On further increase in concentration of substrate, yield of photoproduct was decreased. It may be due to the fact that as the concentration of the substrate was increased, more molecules will participate in reaction but after a particular concentration, the substrate molecule will hinder its own movement.

## Effect of hydrogen peroxide concentration

The effect of concentration of hydrogen peroxide on the yield of photoproduct was investigated using different concentrations of $H_2O_2$. These were 13.5 x $10^{-3}$ M, 18.0 x $10^{-3}$ M, 22.5 x $10^{-3}$ M, 27.0 x $10^{-3}$ M and 31.5 x $10^{-3}$ M. The % yield of photoproduct was 23.4, 29.8, 36.2, 35.7 and 34.5, respectively.

As the concentration of hydrogen peroxide was increased, the yield of photoproduct also increases. However, above a certain $H_2O_2$ concentration, the reaction rate levels off and is negatively affected. This may be due to auto-decomposition of $H_2O_2$ to oxygen and water and recombination of $^{\bullet}OH$ radical.

## Effect of ferrous ion concentration

The effect of $Fe^{2+}$ concentrations was studied using various concentrations of $Fe^{2+}$ ions. These are 2.0 x $10^{-3}$ M, 2.5 x $10^{-3}$ M, 3.0 x $10^{-3}$ M, 3.5 x $10^{-3}$ M and 4.0 x $10^{-3}$ M. The % yield of photoproduct was 27.8, 31.1, 36.2, 33.8 and 30.3, respectively.

From above observations, it can be concluded that as the concentration of $Fe^{2+}$ ions is increased, the rate of reaction also increases, up to a certain limit. But after reaching an optimum level, the efficiency decrease. This may be due to the increase of a brown turbidity that hinders the absorption of the light required for the photo-Fenton process or by the recombination of $^{\bullet}OH$ radical. In this case, $Fe^{2+}$ reacts with $^{\bullet}OH$ radical as scavenger.

## Effect of pH variation

The effect of pH on the photooxidation was also studied. pH of the solutions were kept 2.0, 2.3, 2.6, 2.9 and 3.2. The % yield of photoproduct was 29.6, 32.8, 36.2, 34.1 and 32.7, respectively.

These observations show that the rate of reaction increases up to a certain limit of pH (2.6). With further rise in pH, the yield of the photoproduct is decreased. The drop in efficiency at higher pH is attributed to the transition of iron from a hydrated ferrous ion to a colloidal ferric species. In this form, iron catalytically decomposes the $H_2O_2$ into oxygen and water, without forming hydroxyl radical.

## Effect of polarity of solvent

The effect of polarity of solvent was observed using a wide range of solvents with different polarity. These are ethyl acetate, acetone, ethanol and methanol. The % yield of photoproduct in these solvents was 26.4, 32.1, 34.5 and 36.2, respectively. It was observed that the rate of photooxidation increased with the increase in the polarity of the solvent.

## RESULTS AND DISCUSSION

After the completion of photooxidation reaction, the photoproduct was characterized by its usual chemical tests[13,14]. The chemical tests were (i) Nitrogen was found to be present. (ii) Black precipitates with Mulliken-Barker test confirm the presence of $–NO_2$ group. (iii) The photoproduct *p*-nitrophenol was separated as its 2,4,6-trinitrophenol derivative (recrystallized, M.P. 126$^o$C)

The control experiments were also performed. The reaction was carried out in the presence of (i) light (no $Fe^{2+}/H_2O_2$ was added), (ii) $Fe^{2+}$ and $H_2O_2$ (no exposure to light) and (iii) Light, $Fe^{2+}$ and $H_2O_2$).

It was observed that no photoproduct was formed in the first case and the yield was very low in second but reasonably good in third case. So it is concluded that light, $Fe^{2+}$ and $H_2O_2$ are all necessary for the photoreaction and oxygen increases the rate of reaction. Involvement of free radicals has been confirmed by adding acrylamide in the reaction mixture, where a resinous mass is obtained.

The I.R. spectrum shows the peak at 1530 and 1350 $cm^{-1}$ which confirms the presence of $NO_2$ group. There is no absorption in region 3500-3300 $cm^{-1}$ (N-H stretching) and 1640-1560 $cm^{-1}$ and 800 $cm^{-1}$ (N-H bending). It confirms the absence of $NH_2$ group in the photoproduct.[15,16].

The structure was further confirmed by quantitative elemental analysis of the photoproduct formed (*p*-nitrophenol).

| | **C** | **H** | **N** |
|---|---|---|---|
| Found | 51.83 % | 3.58 % | 10.12 % |
| Calculated | 51.31 % | 3.62 % | 10.07 % |

On the basis of the above, the following mechanism (Fig. 1) has been proposed for the photooxidation reaction of *p*-aminophenol with Fenton reagent. The generally accepted mechanism for the Fenton process identifies the hydroxyl radical ($^{\bullet}OH$) and hydroperoxy radical ($HO_2^{\bullet}$) as the active oxidizing intermediate in the system. According to this mechanism, the combination of ferrous iron and hydrogen peroxide induces a series of chain reactions initiated by the degradation of peroxide to give $Fe^{3+}$, hydroxyl radical and the hydroxide ion (Reaction 1). Ferric ion reacts with water in presence of light to regenerate ferrous ion producing sidewise $^{\bullet}OH$ radial (Reaction 2).

$$Fe^{2+} + H_2O_2 \longrightarrow Fe^{3+} + OH^{-} + {}^{\bullet}OH \quad \ldots(1)$$

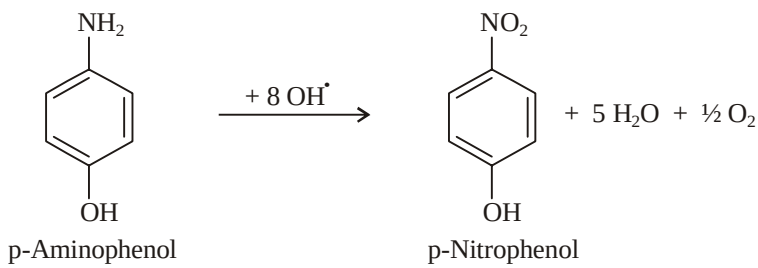
$$Fe^{3+} + H_2O \xrightarrow{h\nu} Fe^{2+} + {}^{\bullet}OH + H^{+} \quad \ldots(2)$$

Hydrogen peroxide decomposes catalytically by Fe (III) and generates hydroperoxy radicals and $Fe^{2+}$ (Reactions 3 and 4).

$$Fe^{3+} + H_2O_2 \longrightarrow H^{+} + [Fe\text{-}HO_2]^{2+} \quad \ldots(3)$$

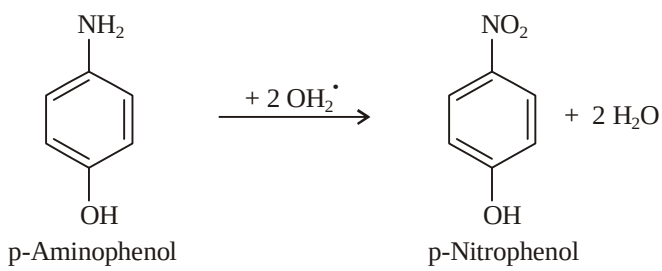
$$[Fe\text{-}HO_2]^{2+} \longrightarrow HO_2^{\bullet} + Fe^{2+} \quad \ldots(4)$$

The hydroxyl radical and hydroperoxy radical reacts with substrate to give the product respectively by reactions (4) and (6). The ${}^{\bullet}OH$ radical formed from the photolysis brings about a radical chain mechanism[17-19].




…(5)

or




…(6)

**Fig. 1: Mechanism of photochemical oxidation of p-aminophenol by a Fenton reagent**

## ACKNOWLEDGEMENT

The author is thankful to U.G.C. Central Regional Office, Bhopal for providing Minor Research Project.

## REFERENCES


1. O. Legrini, E. Oliveros and A. M. Braun, Chem. Rev., **93**, 671 (1993).
2. R. Venkatadri and R. W. Peters, Hazard, Waste Hazard Mater., **10(2)**, 107 (1993).
3. K. Rajeshwar, Chem. Ind., **6**, 454 (1996).
4. W. H. Glage, J. W. Kang and D. H. Chapin, Ozone Sci. Engg., **9(4)**, 335 (1987).
5. A. Y Sychev and V. G Isak, Russ. Chem. Rev., **64(12)**, 1105 (1995).
6. B. C. Faust and J. Hoigne, Atmos. Environ., **24A(1)**, 79 (1990).
7. T. M. Elmorsi, Y. M. Riyad, Z. H. Mohamed and H. M. Abd. El. Bary, J. Hazard Mater., **174** (1-3), 352 (2010).
8. T. Maezono, M. Tokumura, M. Sekine and Y. Kawase, Chemosphere., **82(10)**, 1422 (2011).
9. E. C. Catalkaya and F. Kargi, J. Hazard Mater., **139(2)**, 244 (2007).
10. M. Vilve, S. Vilhunen, M. Vepsäläinen, T. A. Kurniawan, N. Lehtonen, H. Isomäki and M. Sillanpää, Environ. Sci. Pollut. Res. Int., **17(4)**, 875 (2010).
11. K. Hanna, T. Kone and C. Ruby, Environ. Sci. Pollut. Res. Int., **17(1)**, 124 (2010).
12. A. Matilainen and M. Sillanpää , Chemosphere, **80(4)**, 351 (2010).
13. N. K. Visnoi**,** Advanced Practical Organic Chemistry, 2nd Rev. Ed., Vikas Publishing Pvt. Ltd., New Delhi, (2000).
14. A. L. Vogel**,** Text Book of Practical Organic Chemistry, 4th Ed., ELBS Publishing, London (1978).
15. R. M. Silverstein and F. X. Webster, Spectrometric Identification of Organic Compounds, John Willey and Sons, Inc., 6th Ed., New York (1998).
16. D. H. Williams and I. Fleming**,** Spectroscopic Methods in Organic Chemistry, 4th Ed. Tata McGraw Hill, New Delhi (1990).
17. A. Y. Sychev and V. G. Isak**,** Russ. Chem. Rev., **64(12)**, 1105 (1995).
18. J. D. Laat and H. Gallard**,** Environ. Sci. Technol., **33**, 2726 (1999).
19. H. Gallard and J. De Laat**,** Water Res., **34(12)**, 3107 (2000).


*Revised : 05.06.2011* *Accepted : 10.06.2011*