PHOTO-FENTON AND FENTON PROCESSES FOR THE DEGRADATION OF 4-MERCAPTOBENZOIC ACID

DHARMENDRA KUMAR[*]

Department of Chemistry, M. S. J. Govt. College, BHARATPUR – 321001 (Raj.) INDIA

ABSTRACT

Fenton and Photo-Fenton processes are attractive alternate treatment method for to thiol compounds. The degradation of 4-mercaptobenzoic acid by Fenton and photo-Fenton processes was studied. The effect of various reaction parameters such as substrate, hydrogen peroxide, ferrous ion, pH, polarity of solvent and catalyst was studied. Photoproduct was characterized by physical, chemical and spectral methods. A tentative mechanism has been proposed with overall reaction.

Key words: Photodegradation, 4-Mercaptobenzoic acid, Fenton and photo-Fenton processes.

INTRODUCTION

4-Mercaptobenzoic acid is used as an intermediate for manufacturing synthetic organic compounds, pharmaceuticals, colorants and agrochemicals. Due to the increasing use of these compounds in present time may harm biota, if they are not degraded. The improper handling of these toxic chemicals has serious impacts like skin irritation, eye irritation, respiratory problems etc. to the workers. Advanced oxidation processes (AOP's) based on the chemistry of hydroxyl radicals ($^{\bullet}$OH) are currently used for destroying organic pollutants[1]. These radicals react in a nonselective way on organic compounds, leading finally to mineralized end products. Fenton's reagent is a system based on the generation of very reactive free radicals, especially hydroxyl radicals. Fenton's oxidation process has been successfully employed to treat phenol[2], textile wastewater[3], methylphenylglycine[4], recalcitrant industrial wastewater[5], wastewater from paper mill[6], organophosphorus pesticides from wastewater[7] etc.

EXPERIMENTAL

4-Mercaptobenzoic acid (Sigma-Aldrich, USA), ferrous sulphate (Merck, India), hydrogen peroxide 30% (Merck, India), sulphuric acid (Merck, India) and methanol (Rankem, India) were used. 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. Infra-Red spectrum was scanned on Schimadzu FTIR-8400S spectrophotometer. Elemental analysis was carried out using Carlo-Erba-1106 automatic analyzer.

_____

4-Mercaptobenzoic acid (0.03 g) was dissolved in methanol in a round bottom flask, solution of ferrous sulphate (3.5 mL, 0.1 M), hydrogen peroxide (0.25 mL, 30%) and sulphuric acid (0.5 N) were added for maintaining pH. 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 4-mercaptobenzoic acid 19.46×10^{-4} M, $FeSO_4$ 3.5×10^{-3} M, H_2O_2 22.5×10^{-3} M and the pH of the solution 2.2.

The reaction mixture was irradiated with light source (Tungsten lamps, 2×200 W, 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 hr interval. 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 hr, two spots corresponding to parent compound and photoproduct were observed. The reaction was allowed for completion (7 hr).

The rate of the oxidation depends on various parameters like substrate, H_2O_2, $FeSO_4$, pH, polarity of solvent and the catalyst variation. The results of these variations are as follows:

Effect of substrate concentration

The effect of concentration of substrate on photo catalytic reaction was studied using variable amount of substrate. These were 6.49×10^{-4} M, 12.97×10^{-4} M, 19.46×10^{-4} M, 25.94×10^{-4} M and 32.43×10^{-4} M. The % yield of photoproduct was 21.3, 25.3, 33.1, 30.5 and 27.7. It has been observed that as the concentration of substrate increases, the yield of photoproduct was found to increase, up to an optimum level. On further increase in concentration of substrate, yield of photo-product was decreased. It may be due to the fact that as the concentration of the substrate was increased, only a fraction of the light intensity will reach the catalyst surface.

Effect of hydrogen peroxide concentration

The effect of concentration of hydrogen peroxide on the yield of photoproduct was investigated using different concentration of H_2O_2. These were 13.5×10^{-3} M, 18.0×10^{-3} M, 22.5×10^{-3} M, 27.0×10^{-3} M and 31.5×10^{-3} M . The % yield of photoproduct was 20.5, 26.3, 33.1, 31.5 and 26.3.

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 adversely 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 were 2.5×10^{-3} M, 3.0×10^{-3} M, 3.5×10^{-3} M, 4.0×10^{-3} M, and 4.5×10^{-3} M. The % yield of photoproduct was 19.7, 25.4, 33.1, 30.5 and 29.4.

From above observations, it can be concluded that as the concentration of Fe^{2+} ions was increased the rate of reaction also increases, up to a certain limit. But after reaching on optimum level the efficiency decrease. This may be due to the formation of 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 photo-oxidation was studied. pH were 1.8, 2.0, 2.2, 2.4 and 2.6. The % yield of photoproduct was 21.6, 26.7, 33.1, 30.6 and 25.6. These observations show that the rate of reaction increases up to a certain limit (2.2). With further rise in pH, the yield of the photoproduct was decreased. The decrease in efficiency on the basic side was 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 was 27.4, 31.7, 33.1 and 38.6. It was observed that the rate of photo oxidation increased with the increase in the polarity of the solvent.

RESULTS AND DISCUSSION

The control experiments were also performed. The reaction was carried out in the presence of (i) Oxygen and light (no photo catalyst was added), (ii) Oxygen and photo catalyst (no exposure to light) and (iii) Light and photo catalyst (no oxygen was purged).

It was observed that no photoproduct formed in the first cases and the yield was very low in second and third case. So it is concluded that both light and photocatalyst are necessary for the photo reaction 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 was obtained. On the basis of spectral data, physical and chemical analysis, the photoproduct was characterized as 4,4'-dithiodibenzoic acid. The photoproduct 4,4'-dithiodibenzoic acid was separated as its amide derivative[8,9].

The I.R. spectrum shows the peak at 400-500 cm^{-1} indicating the presence of disulphide (-S-S-) group. There is no absorption in the region 2600-2500 cm^{-1} (S-H stretching) confirming the absence of thiol (-SH) group in the photoproduct[10,11].

The structure was further confirmed by quantitative elemental analysis of the photoproduct 4, 4'-dithiodibenzoic acid formed:

	C	H	S
Found	54.90%	3.25%	20.95%
Calculated	54.89%	3.29%	20.93%

On the basis of the above, the following mechanism (Fig. 1) has been proposed for the photocatalytic reaction of 4-mercaptobenzoic acid with Fenton reagent.

The photo-Fenton process can be divided into the following stages[12,13]; First step is the so-called Fenton reaction, in which ferrous ions are oxidised to ferric ions in acidic aqueous solution, as shown in Eq. (1), giving rise to hydroxyl radicals:

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

The ferric ions, represented by the complex $Fe(OH)^{2+}$, is reduced back to Fe^{2+} by UV-visible irradiation according to Eq. (2):

$$Fe(OH)^{2+} + h\nu \longrightarrow Fe^{2+} + OH^{\bullet} \ (\lambda < 450 \ nm) \qquad \ldots(2)$$
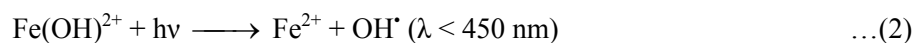
The ferric species can also form complex with the initial organic compound and/or degradation products, leading to photo-reduction back to Fe^{2+}, according to Eq. (3):

$$Fe(RCO_2)^{2+} + h\nu \longrightarrow Fe^{2+} + R^{\bullet} + CO_2 \ (\lambda < 500 \ nm) \qquad \ldots(3)$$
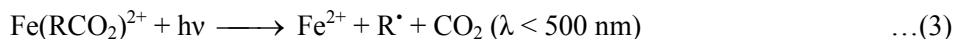
The $OH^{\bullet}$ species formed will then attack the organic substrates present in the wastewater. Nevertheless, numerous competitive reactions can also occur, namely, the following, which adversely affect the oxidation process:[14-16]
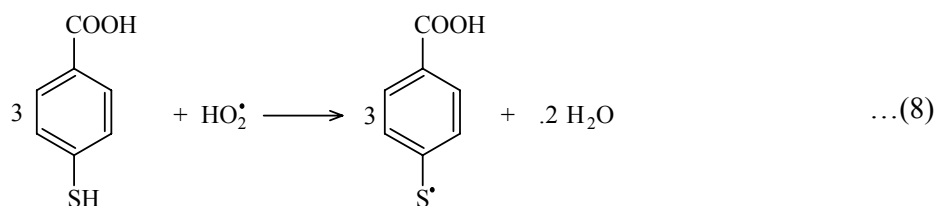
$$Fe^{2+} + OH^{\bullet} \longrightarrow Fe^{3+} + OH^{-} \qquad \ldots(4)$$

$$H_2O_2 + OH^{\bullet} \longrightarrow HO_2^{\bullet} + H_2O \qquad \ldots(5)$$

In this way the substrate reacts with $OH^{\bullet}$ and $/HO_2^{\bullet}$ radicals to form the photoproduct. Over all reaction can be written as follows:
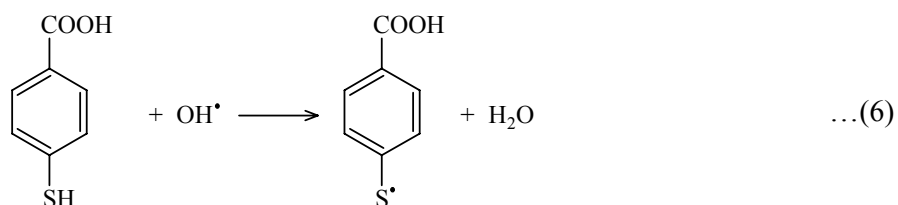
...(6)

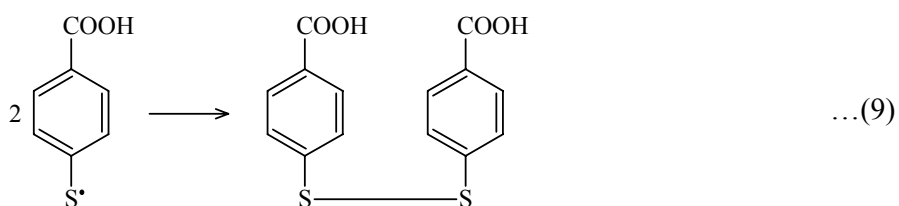4-Mercaptobenzoic acid

...(7)

4, 4' -Dithiodibenzoic acid

...(8)

4-Mercaptobenzoic acid

...(9)
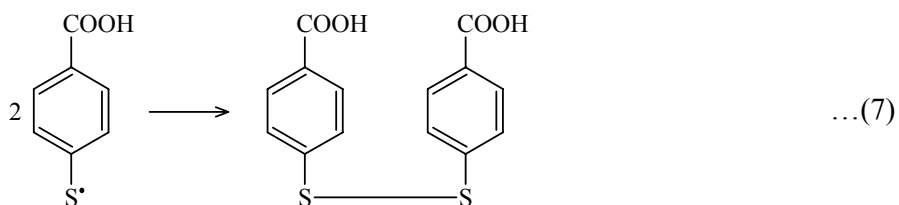
4, 4' - Dithiodibenzoic acid

Fig. 1: Degradation of 4-mercaptobenzoic acid by photo-Fenton processes

ACKNOWLEDGEMENT

REFERENCES

1.   M. A. Oturan, J. Electroanal. Chem., **507(1-2)**, 96-102 (2001).

2.   V. Kavitha and K. Palanivelu, Chemosphere, **55(9)**, 1235-1243 (2004).

3.   S. F. Kang, Chemosphere, **46**, 923-928 (2002).

4.   A. Serra, X. Domènech, E. Brillas and J. Peral, J. Environ. Monit., **13**, 167-174 (2011).

5.   H. Hansson, F. Kaczala, M. Marques and W. Hogland, Int. J. Photoenergy, doi: 10.1155/2012/531076 (2012).

6.   D. Hermosilla, N. Merayo, R. Ordóñez and A. Blanco, Waste Management, **32(6)**, 1236-1243 (2012).

7.   M. I. Badawy, M. Y. Ghaly and T. A. Gad-Allah, Desalination, **194(1-3)**, 166-175 (2006).

8.   N. K. Visnoi, Advanced Practical Organic Chemistry, 2nd Rev. Ed. Vikas Publishing Pvt. Ltd., New Delhi (2000).

9.   A. L. Vogel, Text Book of Practical Organic Chemistry, 4th Ed., ELBS Publishing, London (1978).

10.   R. M. Silverstein and F. X. Webster, Spectrometric Identification of Organic Compounds, John Wiley and Sons, Inc., 6th Ed. New York (1998).

11.   D. H. Williams and I. Fleming, Spectroscopic Methods in Organic Chemistry, 4th Ed. Tata Mc Graw Hill, New Delhi (1990).

12.   J. J. Pignatello, Environ. Sci. Technol., **26(5)**, 944-951 (1992).

13.   S. H. Bossmann, E. Oliveros, S. Gob, S. Siegwart, E. P. Dahlen, L. Payawan, M. Straub, M. Worner and A. M. Braun, J. Phys. Chem. A, **102(28)**, 5542-5550 (1998).

14.   F. Haber and J. Weiss, Proc. R. Soc. A, **147(861)**, 332-351 (1934).

15.   C. Walling, Acc. Chem. Res., **8(4)**, 125-131 (1975).

16.   Y. W. Kang and K. Y. Hwang, Water Res., **34(10)**, 2786-2790 (2000).