

Photo-Fenton Reagent Oxidation of *m*-Aminophenol

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Abstract: Advanced oxidation technologies particularly Fenton and Photo-Fenton oxidation processes which rely on the generation of very reactive oxidizing agents, i.e. free radicals such as the hydroxyl radical (OH) are found effective owing to their high oxidation potential (+2.80 eV) in aqueous solution. These processes can adequately increase the biodegradability and remove toxicity of the wastewater prior to biological treatment. Photo-Fenton reagent oxidation of *m*-aminophenol was studied in present research paper. The effect of various reaction parameters such as substrate, hydrogen peroxide, ferrous ion, 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: Advanced oxidation processes, Photo-Fenton oxidation, *m*-aminophenol Fenton

Introduction:

A wide range of organic compounds is detected in industrial and municipal wastewater. Some of these compounds pose severe problems in biological treatment systems due to their resistance to biodegradation or/and toxic effects on microbial processes. As a result, the use of alternative treatment technologies, aiming to mineralize or transform refractory molecules into others which could be further biodegraded, is a matter of great concern. Among them, advanced oxidation processes (AOPs) have already been used for the treatment of wastewater containing harmful chemicals. It is also used as pretreatment methods in order to reduce the concentrations of toxic organic compounds that inhibit biological wastewater treatment processes^{1,2}.

The main mechanism of AOPs function is the generation of highly reactive free radicals. Hydroxyl radicals (OH) are effective in destroying organic chemicals because they are reactive electrophiles (electron preferring) that react rapidly and nonselectively with nearly all electron-rich organic compounds.

The Fenton's reagent has proven to be an effective way to degrade organic pollutants³⁻⁵ and it has been used for the treatment of a wide variety of industrial wastewaters⁶⁻⁸. The Fenton process is a relatively economical method since it has no energy requirements compared to many other AOP. Additionally, both iron and hydrogen peroxide are relatively cheap and safe. The mechanisms that take place in the Fenton process are well-known and the conventional Fenton process may be positively assisted by the application of UV-light¹⁰.

Experimental:

m-Aminophenol (Merck, Germany), ferrous sulphate (Merck, India), hydrogen peroxide 30% (Merck, India), sulphuric acid (Merck, India) and methanol (Rankem, India) were used to prepare 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.

m-Aminophenol (0.20 gm) was dissolved in methanol in a round bottom flask, solution of ferrous sulphate (2.5 ml, 0.1M), hydrogen peroxide (0.20 ml, 30%) and sulphuric acid (0.5N) 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 *m*-Aminophenol 18.3×10^{-3} M, FeSO_4 2.5×10^{-3} M, H_2O_2 18.0×10^{-3} M and the pH of the solution was found to be 2.0.

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 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, those were 9.2×10^{-3} M, 13.8×10^{-3} M, 18.3×10^{-3} M, 22.9×10^{-3} M and 27.5×10^{-3} M. The % yield of photoproduct was 20.7, 25.6, 31.4, 30.4 and 27.2. 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 , those were 9.0×10^{-3} M, 13.5×10^{-3} M, 18.0×10^{-3} M, 22.5×10^{-3} M and 27.0×10^{-3} M. The % yield of photoproduct was 19.4, 24.7, 31.4, 30.6 and 26.8.

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 OH^\cdot radical.

Effect of ferrous ion concentration:

The effect of Fe^{2+} concentrations was studied using various concentrations of Fe^{2+} ions, those were 1.5×10^{-3} M, 2.0×10^{-3} M, 2.5×10^{-3} M, 3.0×10^{-3} M, and 3.5×10^{-3} M. The % yield of photoproduct was 20.8, 25.8, 31.4, 29.6 and 25.3.

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 on 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 OH^\cdot radical. In this case, Fe^{2+} reacts with OH^\cdot radical as scavenger.

Effect of pH variation:

The effect of pH on the photo oxidation was studied. pH were 1.6, 1.8, 2.0, 2.2 and 2.4. The % yield of photoproduct was 21.6, 28.6, 31.4, 28.5 and 25.9.

These observations are showing that the rate of reaction increases up to a certain limit (2.0). With further rise in pH, the yield of the photoproduct is decreased. The drop in efficiency on the basic side 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; those were Ethyl acetate, Acetone, Ethanol and Methanol. The % yield of photoproduct was 27.4, 29.8, 31.4 and 34.9. It was observed that the rate of photo oxidation increased with the increase in the polarity of the solvent.

Results and Discussion:

After the completion of photo catalytic reaction, the photoproduct was characterized by its usual chemical tests^{11,12}. The chemical tests were (i) Nitrogen was found to be present. (ii) Black precipitates with Milliken Barker test confirm the presence of $-NO_2$ group. (iii) The photoproduct *o*-nitrophenol was separated as its 2, 6-dibromo derivative (recrystallized, M.P. $141^\circ C$)

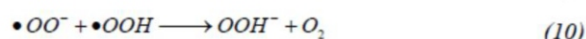
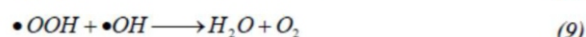
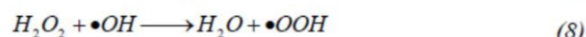
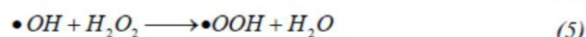
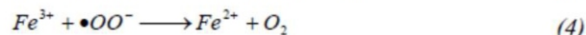
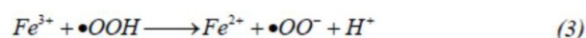
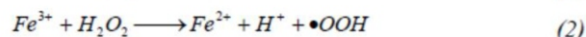
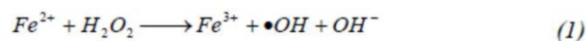
The control experiments were performed. The

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 had formed in the first cases and the yield was very low in second and third case. So it is concluded that both light and photo catalyst are necessary for the photo reaction and oxygen increases the rate of reaction. Involvement of free radicals has been confirmed by adding acryl amide in the reaction mixture where a resinous mass is obtained.

The I.R. spectrum shows the peak at 1540 cm^{-1} and 1350 cm^{-1} which confirms the presence of NO_2 group. There is no absorption in region $3500-3300\text{ cm}^{-1}$ (N-H stretching) and $1640-1560\text{ cm}^{-1}$ and 800 cm^{-1} (N-H bending) confirms the absence of NH_2 group in the photoproduct.^{13,14}

On the basis of the above, the following mechanism (Fig.1) has been proposed for the photo catalytic reaction of *m*-aminophenol with Fenton reagent. Fenton's reagent is homogenous catalytic oxidation process using a mixture of hydrogen peroxide and ferrous ions in an acidic environment. The metal regeneration can follow different path¹⁵⁻¹⁷.



The new generated ferrous ions react with H_2O_2 generating a second OH radical and ferric ions and the cycle continues. In these conditions, iron can be considered as a real catalyst¹⁸.

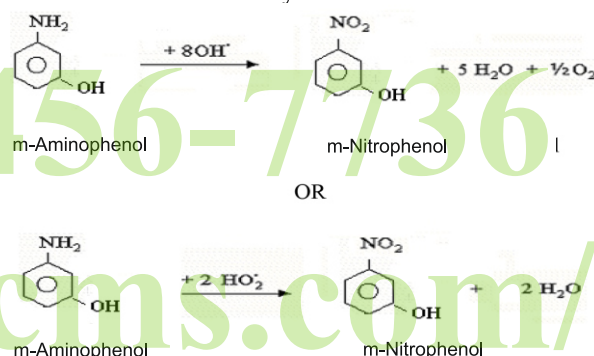


Fig.1: Mechanism of photo-Fenton oxidation of *m*-Aminophenol by Fenton reagent

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