Photo Chemically Degradation of O-Aminophenol by Fenton Reagent

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ABSTRACT
Photo chemically degradation of o-aminophenol by Fenton reagent was studied. 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.

Keywords: Photo chemically degradation, o-aminophenol, Fenton and photo-Fenton reagent.

INTRODUCTION
Photo-Fenton process is used to eliminate toxic and bio-resistant organic and inorganic pollutants through their transformation into harmless species. Due to the increasing use of these organic compounds in present time, traces of these compounds passing to environment is unavoidable. These traces may harm biota if they are not degraded. The improper handling of these toxic chemicals has serious impact on the natural water bodies, land in the surrounding area, health and safety of workers. The contact with chemical puts them at the high risk bracket for contracting skin diseases like chemical burns, irritation, ulcers, respiratory problem and may also be carcinogenic due to photosensitizations and photodynamic damage.

The oxidation of organic substrates by iron (II) and hydrogen peroxide is called the “Fenton chemistry”, as it was first described by H.J.H. Fenton who first observed the oxidation of tartaric acid by H₂O₂ in the presence of ferrous iron ions. Alternatively, the name of “Fenton reaction” or “Fenton reagent” is often used. The Fenton reagent has been known for more than a century but its application as an oxidizing process for destroying hazardous organics was not applied until the late 1960s. After this time comprehensive investigations showed that the Fenton reagent is effective in treating various industrial wastewater components including aromatic amines, a wide variety of dyes, pesticides, surfactants, explosives as well as many other substances. As a result, the Fenton reagent has been applied to treat a variety of wastes such as those associated with the textile industry, chemical manufacturing, refinery and fuel terminals, engine and metal cleaning etc. The Fenton reagent can also effectively be used for the destruction of toxic wastes and non-biodegradable effluents to render them more suitable for secondary biological treatment. Moreover, the importance of Fenton chemistry has been long recognised among others in food chemistry and material ageing.

EXPERIMENTAL
o-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 Grifh (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.

o-Aminophenol (0.20 gm) was dissolved in methanol in a round bottom flask, solution of ferrous sulphate (3.5 ml, 0.1M), hydrogen peroxide (0.25 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 o-Aminophenol 18.3 X 10⁻³ M, FeSO₄ 3.5 X 10⁻³ M, H₂O₂ 22.5 X 10⁻³ M and the pH of the solution was found to be 2.4.

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 $9.2 \times 10^{-3}$ M, $13.8 \times 10^{-3}$ M, $18.3 \times 10^{-3}$ M, $22.9 \times 10^{-3}$ M and $27.5 \times 10^{-3}$ M. The % yield of photoproduct was 21.4, 26.3, 32.1, 31.6 and 28.5. 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 $13.5 \times 10^{-3}$ M, $18.0 \times 10^{-3}$ M, $22.5 \times 10^{-3}$ M, $27.0 \times 10^{-3}$ M and $31.5 \times 10^{-3}$ M. The % yield of photoproduct was 21.5, 25.2, 32.1, 30.8 and 27.3.

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 negatively affected. This may be due to auto-decomposition of $H_2O_2$ to oxygen and water and recombination of $OH^-$ radical.

Effect of ferrous ion concentration
The effect of $Fe^{2+}$ concentrations was studied using various concentrations of $Fe^{2+}$ ions, those were $2.5 \times 10^{-3}$ M, $3.0 \times 10^{-3}$ M, $3.5 \times 10^{-3}$ M, $4.0 \times 10^{-3}$ M, and $4.5 \times 10^{-3}$ M. The % yield of photoproduct was 20.8, 25.8, 32.1, 31.3 and 28.6.

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 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 $OH^-$ radical. In this case, $Fe^{2+}$ reacts with $OH^-$ radical as scavenger.

Effect of pH variation
The effect of pH on the photo oxidation was studied. pH were 2.0, 2.2, 2.4, 2.6 and 2.8. The % yield of photoproduct was 20.4, 27.6, 32.1, 29.6 and 26.7. These observations are showing that the rate of reaction increases up to a certain limit (2.6). 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 28.4, 30.7, 32.1 and 37.7. 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. 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, 4, 6-trinitrophenol derivative (recrystallized, M.P. 130 °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 1535 cm\(^{-1}\) and 1345 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) confirms the absence of NH\(_2\) group in the photoproduct.\(^{22,23}\)

The structure was further confirmed by quantitative elemental analysis of the photoproduct p-nitrophenol formed:

<table>
<thead>
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<th></th>
<th>C (%)</th>
<th>H (%)</th>
<th>N (%)</th>
</tr>
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<tbody>
<tr>
<td>Found</td>
<td>51.10</td>
<td>3.52</td>
<td>10.18</td>
</tr>
<tr>
<td>Calculated</td>
<td>51.31</td>
<td>3.62</td>
<td>10.07</td>
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On the basis of the above, the following mechanism (Fig.1) has been proposed for the photo catalytic reaction of p-aminophenol with Fenton reagent. The generally accepted mechanism for the Fenton process identifies the hydroxyl radical (OH) and hydroperoxy radical (HO\(_2\)) 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 the Fe\(^{3+}\), hydroxyl radical and the hydroxide ion.

The metal regeneration can follow different path. For Fe\(^{2+}\), the most accepted scheme is described in the following manner\(^{24}\):

\[
\begin{align*}
\text{Fe}^{2+} + \text{H}_2\text{O}_2 & \rightarrow \text{Fe}^{3+} + \text{OH}^- + \text{OH}^* \\
\text{Fe}^{3+} + \text{H}_2\text{O}_2 & \rightarrow \text{Fe}^{2+} + \text{HO}_2^* + \text{H}^+ \\
\text{Fe}^{2+} + \text{OH}^* & \rightarrow \text{Fe}^{3+} + \text{OH}^- \\
\text{OH}^* + \text{H}_2\text{O}_2 & \rightarrow \text{HO}_2^* + \text{H}_2\text{O} \\
\text{Fe}^{3+} + \text{HO}_2^* & \rightarrow \text{Fe}^{2+} + \text{H}^+ + \text{O}_2 \\
\text{Fe}^{3+} + \text{O}_2^* & \rightarrow \text{Fe}^{2+} + \text{O}_2 \\
\text{Fe}^{2+} + \text{HO}_2^* & \rightarrow \text{Fe}^{3+} + \text{HO}_2^- \\
\end{align*}
\]

Fenton reaction rates are strongly increased by irradiation with UV / visible light\(^{25,26}\) this type of photo assisted reaction is referred to as the photo-Fenton reaction.\(^{27}\) The positive effect of irradiation on the degradation rate is due to the photochemical regeneration of ferrous ions (Fe\(^{2+}\)) by photo-reduction of ferric ions (Fe\(^{3+}\)).

The new generated ferrous ions react with H\(_2\)O\(_2\) generating a second OH\(^*\) radical and ferric ions and the cycle continues. In these conditions, iron can be considered as a real catalyst.

\[
\begin{align*}
\text{OH}^- + 8\text{OH}^- & \rightarrow \text{NO}_2^- + 5\text{H}_2\text{O} + \frac{1}{2}\text{O}_2 \\
\end{align*}
\]

\[
\begin{align*}
\text{OH}^- + 2\text{HO}_2^* & \rightarrow \text{NO}_2^- + 2\text{H}_2\text{O} \\
\end{align*}
\]

**Fig.1:** Mechanism of photo chemically degradation of o-Aminophenol by Fenton reagent
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REFERENCES