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PHOTO-SENSITIZED OXIDATION OF 4-CHLOROTHIOPHENOL BY FENTON REAGENT

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ABSTRACT

Among advanced oxidation processes (AOPs), the photo chemically enhanced Fenton reaction may be effective for the treatment of industrial wastewater. The Photo-sensitized degradation of 4-Chlorothiophenol by Fenton reagent has been investigated. The effect of various reaction parameters such as substrate, H_2O_2, $FeSO_4$, pH, polarity of solvent and catalyst variation on the rate of photocatalytic process has been studied. Photoproduct was characterized by physical, chemical and spectral methods. A tentative mechanism has been proposed with overall reaction.

KEYWORDS: Photo - sensitized oxidation, 4-Chlorothiophenol, Fenton and photo-Fenton reagent.

INTRODUCTION

4- Chlorothiophenol is used as an intermediate for the manufacture of pharmaceuticals and pesticides. Pesticides have been ubiquitous solution for pest control in intensive agriculture since the 1950. As conventional biological wastewater treatments cannot effectively dispose of many of pesticides and other pollutants.[1] Advanced oxidation processes (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 pesticide contaminant.[2,3] Fenton reagent (Fe^{2+}/H_2O_2) and photo-Fenton ($Fe^{2+}/ H_2O_2/$ UV) methods have proved to be effective and economical AOP methods used for the detoxification and degradation of many organic compounds.[4,5] Fenton reagent has been found to be effective in treating various industrial wastewaters including surfactants,[6] refractory organics[7] explosives,[8] a wide variety of dyes,[9-11] pesticides,[12] insecticides,[13] oil mill waste water[14] as well as many other substances.

MATERIAL AND METHODS

4-Chlorothiophenol (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.

4-Chlorothiophenol (0.05gm) 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 4-chlorothiophenol 3.46×10^{-3} M, $FeSO_4$ 3.5×10^{-3} M, H_2O_2 22.5×10^{-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. Oxygen gas [2.01 min^{-1}] was continuously bubbled through the reaction mixture.

This served two purposes:

I. Continuous stirring of the reaction mixture.

II. Availability of oxygen.

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). After the completion of photo catalytic reaction, the photoproduct was characterized by its usual chemical tests.[15-17]

RESULTS AND DISCUSSION

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).
(iii) Light and photo catalyst (no oxygen was purged).

It was observed that no photoproduct had formed in the first two cases and the yield was very low in 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 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. The results are summarized in table 1:

Table - 1: Effect of substrate concentration

Sr. No.	[Substrate]	% Yield of Photoproduct
1.	1.38×10^{-3} M	21.4
2.	2.07×10^{-3} M	25.7
3.	2.77×10^{-3} M	33.3
4.	3.46×10^{-3} M	37.4
5.	4.15×10^{-3} M	34.3
6.	4.84×10^{-3} M	31.7

It was 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, it may start acting like a filter for the incident light. Hence, on increasing the concentration of substrate, only a fraction of the light intensity will reach the catalyst surface and thus; a decrease in the photocatalytic oxidation of substrate was observed.

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. The results are summarized in table 2:

Table - 2: Effect of H_2O_2 concentration

Sr. No.	$[H_2O_2]$	% yield of photoproduct
1.	9.0×10^{-3} M	22.8
2.	13.5×10^{-3} M	26.5
3.	18.0×10^{-3} M	35.8
4.	22.5×10^{-3} M	37.4
5.	27.0×10^{-3} M	32.9
6.	31.5×10^{-3} M	28.5

As the concentration of hydrogen peroxide was increased, the yield of photoproduct also increases. This is explained by the effect of the additional production of $OH^{\cdot}$ radical. 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. The results are summarized in table 3:

Table - 3: Effect of ferrous ion concentration

Sr. No.	$[Fe^{2+}]$	% Yield of Photoproduct
1.	2.0×10^{-3} M	18.5
2.	2.5×10^{-3} M	26.7
3.	3.0×10^{-3} M	33.9
4.	3.5×10^{-3} M	37.4
5.	4.0×10^{-3} M	31.3
6.	4.5×10^{-3} M	28.2

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. The results are summarized in table 4:

Table - 4: Effect of pH variation

Sr. No.	[pH]	% Yield of Photoproduct
1.	1.4	24.7
2.	1.6	28.9
3.	1.8	33.2
4.	2.0	37.4
5.	2.2	28.4
6.	2.4	23.5

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 results are summarized in table 5:

Table - 5: Effect of solvent polarity

Sr. No.	[Solvent]	% Yield of Photoproduct
1.	Ethyl acetate	25.4
2.	Acetone	29.3
3.	Ethanol	33.8
4.	Methanol	37.4

It was observed that the rate of photo oxidation increased with the increase in the polarity of the solvent.

Effect of catalyst variation

The effect of catalyst variation on the photo oxidation was studied. The results are summarized in table 6:

Table - 6: Effect of catalyst variation

Sr. No.	[Catalyst]	% Yield of Photoproduct
1.	H_2O_2	24.6
2.	$H_2O_2 + Fe^{2+}$	37.4
3.	$H_2O_2 + UO_2^{2+}$	38.1
4.	$H_2O_2 + UO_2^{2+} + Fe^{2+}$	39.8

It was observed that when Fe^{2+} ions of Fenton reagent replaced by uranyl ions [UO_2^{2+}], the percentage yield of photoproduct was increased. It may be due to the formation of more hydroxyl free radical which oxidizes the available organic matter.

The I.R. spectrum shows the peak at 400-500 cm^{-1} indicates the presence of disulphide (-S-S- group. There is no absorption in region 2600-2500 cm^{-1} (S-H stretching) confirms the absence of thiol (-SH) group in the photoproduct.[18,19]

On the basis of the above, the following mechanism (Fig.1) has been proposed for the photo catalytic reaction of 4-chlorothiophenol with Fenton reagent. 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[20]:

$$Fe^{2+} + H_2O_2 \longrightarrow Fe^{3+} + OH^{-} + OH^{\bullet}$$

$$Fe^{3+} + H_2O_2 \longrightarrow Fe^{2+} + HO_2^{\bullet} + H^{+}$$

$$Fe^{2+} + OH^{\bullet} \longrightarrow Fe^{3+} + OH^{-}$$

$$OH^{\bullet} + H_2O_2 \longrightarrow HO_2^{\bullet} + H_2O$$

$$Fe^{3+} + HO_2^{\bullet} \longrightarrow Fe^{2+} + H^{+} + O_2$$

$$Fe^{3+} + O_2^{\bullet -} \longrightarrow Fe^{2+} + O_2$$

$$Fe^{2+} + HO_2^{\bullet} \longrightarrow Fe^{3+} + HO_2^{-}$$

Fenton reaction rates are strongly increased by irradiation with UV / visible light.[21,22] This type of photo assisted reaction is referred to as the photo-Fenton reaction. 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+}).

Hydroxyl radicals thus formed in the reaction mixture degrade the substrate 4-chlorothiophenol to form 4,4'-dithio-di(chlorobenzene) as photoproduct.

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:

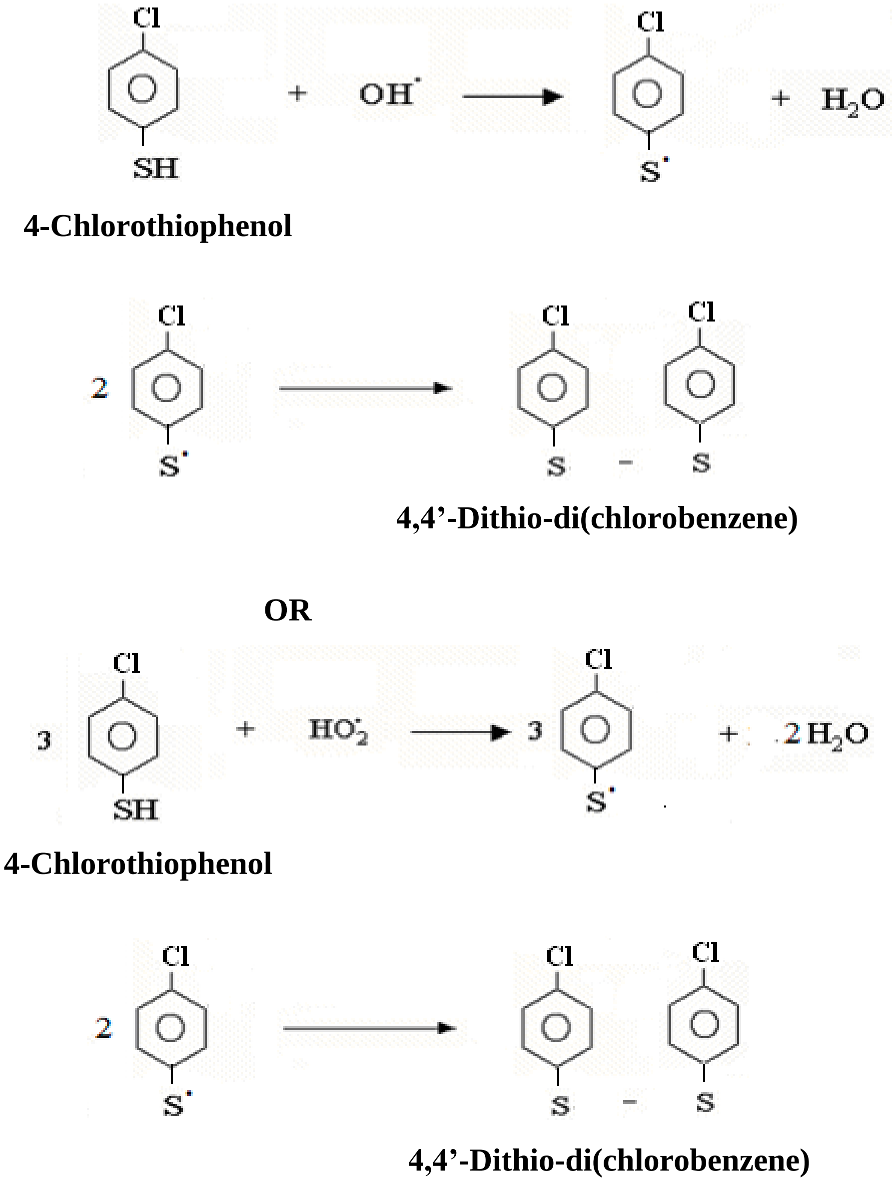

Fig. 1: Photo-oxidation of 4- Chlorothiophenol by Fenton reagent

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