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Fenton and Photo-Fenton Processes for the Degradation of Thiosalicylic Acid.

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ABSTRACT

The degradation of thiosalicylic 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 variation was studied. Photoproduct was characterized by physical, chemical and spectral methods. A tentative mechanism has been proposed with overall reaction.

Keywords: Photo –degradation, thiosalicylic acid, Fenton and photo-Fenton reagent

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INTRODUCTION

Thiosalicylic acid is used as an intermediate of dyes, insecticides, pharmaceutical, pesticides and other chemical compounds. Salicylic Acid and its derivatives are important for the preparation of other pharmaceutical products, dyes, food flavours and preservatives. Thiosalicylate is the moiety of thiomersal (an organomercurial) used as an antiseptic, antifungal and bacteriostatic. Due to the increasing use of these compounds in present time, traces of these compounds are passing to environment. 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.

Fenton reaction is an advanced oxidation technology that works through the generation of highly reactive hydroxyl radical (•OH) by the combination of Fe^{2+} and H_2O_2 [1,2]. Fenton reaction ($Fe^{2+} + H_2O_2$) which produces HO• and results in oxidation of the Fe^{2+} to Fe^{3+} [3].

Fenton's oxidation process has been successfully employed to treat landfill leachate [4], pesticides and phenolic contaminants [5], textile wastewater [6, 7], paper pulp wastewater [8] and single contaminants in aqueous solution [9].

EXPERIMENTAL

Thiosalicylic acid (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. Photo oxidation was carried out in Borosil glass wares and all the reactions were performed using dried equipments. 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.

Thiosalicylic acid (0.50 gm) was dissolved in methanol in a round bottom flask, solution of ferrous sulphate (4.0 ml, 0.1M), hydrogen peroxide (0.45 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 method. The concentration of various ingredients in the reaction mixture were thiosalicylic acid 3.2×10^{-2} M, H_2O_2 4.1×10^{-2} M, $FeSO_4$ 4.0×10^{-3} M and the pH of the solution was found to be 2.7.

The reaction mixture was irradiated with light source (Tungsten lamps, 2 X 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. Oxygen gas [2.01 min^{-1}] was continuously bubbled through the reaction mixture.

This served two purposes:

- Continuous stirring of the reaction mixture.
- 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 [10-12].

The control experiments were performed. The reaction was carried out in the presence of:

- Oxygen and light (no photo catalyst was added).
- Oxygen and photo catalyst (no exposure to light).
- 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. Those were 2.0×10^{-2} M, 2.6×10^{-2} M, 3.2×10^{-2} M, 3.8×10^{-2} M, 4.4×10^{-2} M and 5.0×10^{-2} M The % yield of photoproduct was 19.8, 22.2, 31.8, 29.6, 28.4 and 26.2

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, 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 . Those were 3.3 X 10^{-2} , 3.7 X 10^{-2} M, 4.1 X 10^{-2} M, 4.5 X 10^{-2} M, 4.9 X 10^{-2} M and 5.3 X 10^{-2} M. The % yield of photoproduct was 16.3, 20.4, 31.8, 30.2, 29.5 and 27.4

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. Those were 3.0 X 10^{-3} M, 3.5 X 10^{-3} M, 4.0 X 10^{-3} M, 4.5 X 10^{-3} M, 5.0 X 10^{-3} M and 5.5 X 10^{-3} M. The % yield of photoproduct was 18.6, 21.3, 31.8, 29.6, 27.4 and 24.2

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. pH were 2.1, 2.4, 2.7, 2.9, 3.1 and 3.3. The % yield of photoproduct was 19.4, 22.6, 31.8, 24.6, 20.2 and 17.4

These observations are showing that the rate of reaction increases up to a certain limit (2.7). 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 15.7, 19.1, 22.3 and 31.8. 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. Those were H_2O_2, $H_2O_2 + Fe^{2+}$, $H_2O_2 + UO_2^{2+}$ and $H_2O_2 + UO_2^{2+} + Fe^{2+}$. The % yield of photoproduct was 25.3, 31.8, 34.2 and 36.4

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.

RESULTS AND DISCUSSION

On the basis of spectral data, physical and chemical analysis the photoproduct was characterized as dithio-di(salicylic acid). The photoproduct dithio-di(salicylic acid) was separated as its amide derivative.

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.

The structure was further confirmed by quantitative elemental analysis of the photoproduct dithio-di(salicylic acid) formed:

	C	H	S
Found	-54.91 %	3.25 %	20.94 %
Calculated	54.89 %	3.29 %	20.93 %

The photo-Fenton process can be divided into the following stages [13,14] : the first step is the so-called Fenton reaction, in which ferrous ions (Fe^{2+}) are oxidized to ferric ions(Fe^{3+}) in acidic aqueous solution, as shown in Eq. (1), giving rise to hydroxyl radicals ($HO^{\bullet}$)

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

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

$$[Fe(OH)]^{2+} \xrightarrow{h\nu} Fe^{2+} + HO^{\bullet} \qquad (2)$$

The ferric species can also form complexes with the initial organic compounds and/or degradation products, leading to photo-reduction back to Fe^{2+} according to Eq. (3).

$$[Fe(OOC\text{-}R)]^{2+} \xrightarrow{h\nu} Fe^{2+} + R^{\bullet} + CO_2 \qquad (3)$$

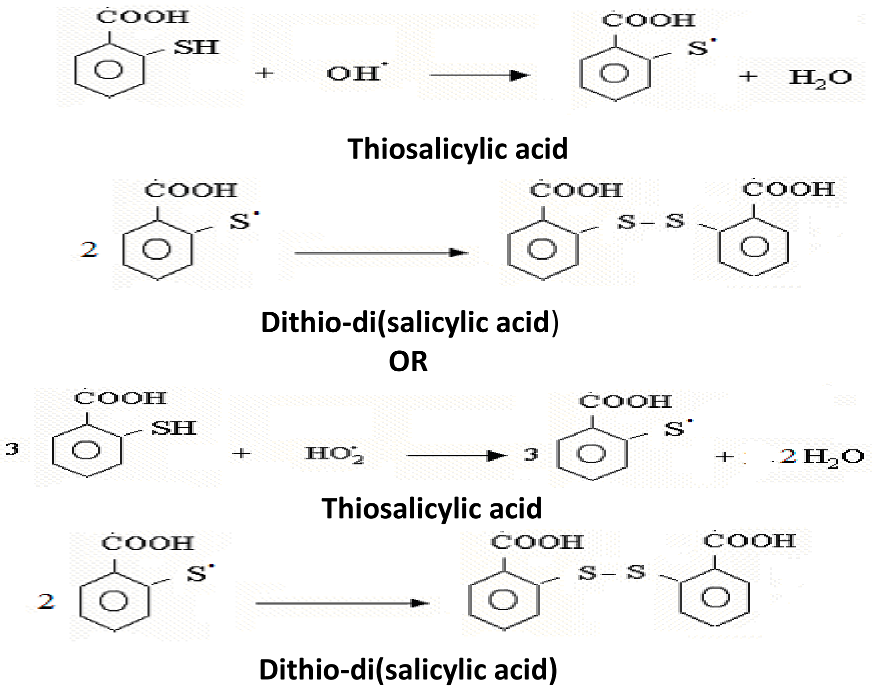
The generated hydroxyl radicals oxidize the target organic compounds (RH), shown in Eq. (4).

$$HO^{\bullet} + RH \longrightarrow H_2O + R^{\bullet} \qquad (4)$$

The efficiency of Fenton's process depends on H_2O_2 and Fe^{2+} concentrations and pH of the reaction [15-17]. The chemical reaction between two species is retarded due to conversion of Fe^{2+} ions to Fe^{3+} ions. Pignetallo [18] reported that illumination of Fe^{2+} - H_2O_2 system increases the rate of photochemical oxidation of a number of organic compounds. This increase in the oxidation or degradation on exposure may be due to photo reduction of Fe^{3+} ions to Fe^{2+} ions back thus making whole process cyclic in nature. The $OH^{\cdot}$ radical formed from the photolysis brings about a radical chain mechanism [18-21]. Hydroxyl radicals thus formed in the reaction mixture degrade the substrate thiosalicylic acid to form dithio-di(salicylic acid) as photoproduct. In fact, an excess of ferrous ions can provoke an inhibition of the photochemical degradation process, because, at these levels, The Fe^{2+} can compete with the organic compounds by the oxidant agents (hydroxyl radicals) [22] as indicated in Eq. (5)

$$Fe^{2+} + HO^{\bullet} \longrightarrow Fe^{3+} + OH^{-} \qquad (5)$$

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:



Thiosalicylic acid

Dithio-di(salicylic acid)

OR

Thiosalicylic acid

Dithio-di(salicylic acid)

Figure 1: Photo-degradation of Thiosalicylic Acid by Fenton Reagent

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