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Research Article

PHOTO-ASSISTED DEGRADATION OF 3-MERCAPTOPROPIONIC ACID BY FENTON REAGENT

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ABSTRACT

Objectives: The main objective of the research were to develop an energy saver, cheaper eco-friendly method for removal of pollutants, because another process needing a large consumption of energy, time and produce harmful byproducts. This process may used to eliminate toxic and bio-resistant organic and inorganic pollutants through their transformation into harmless species. Thiol compounds are widely used in pharmaceuticals and agrochemicals. These chemicals has high risk bracket for human health diseases like, corrosive to skin, eyes, respiratory system, chemical burns, irritation, ulcers etc.

Methods: The Photo-assisted degradation of 3-Mercaptopropionic acid by Fenton reagent has been investigated. The effect of various reaction parameters such as conc. of substrate, conc. of H2O2, conc. of FeSO4, pH, polarity of solvent and catalyst variation on the rate of photocatalytic process has been studied.

Results: The control experiments were performed. The reaction was carried out in the presence of Fenton reagent, oxygen and light. Advanced oxidation processes (AOPs) have proved superiority over the conventional techniques like precipitation, flocculation, filtration, incineration or the biological pathways. These methods are based on the principle of generation of highly reactive hydroxyl radical, which is capable for destruction of pollutants. The Photoproduct 3,3’-dithiodipropionic acid was characterized by physical, chemical and spectral methods. A tentative mechanism has been proposed with overall reaction.

Conclusion: This research method is promising and eco-friendly for removal of pollutants from wastewater. The treated water may be used for daily purpose like irrigation and cleaning etc.

Keywords: Photosensitized oxidation, 3-Mercaptopropionic acid, Fenton and photo-Fenton reagent.

INTRODUCTION

3-Mercaptopropionic acid (MPA) is used in a variety of applications like intermediate for the manufacture of pharmaceuticals and agrochemicals, co-catalyst in the manufacture of bisphenol A, which is a key raw material in polycarbonate production. MPA enhances the process efficiency. MPA is used as chain transfer agent during polymerization of polycarboxylates, which are used in the building industry as superplasticizer in concrete. MPA esters are used as intermediates in the manufacture of tin heat-stabilizers for PVC. MPA can be used to esterify polyols resulting in polythiols which are used as cross-linking additives in coatings, adhesives, and sealants and as monomers to manufacture optical resins. They react rapidly with isocyanates, unsaturated monomers (thiol-ene reaction) and epoxies.

These traces may harm biota if they are not degraded. The improper handling of these toxic chemicals has a 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 health diseases like corrosive to skin, eyes, respiratory system, chemical burns, irritation, ulcers, etc.

Advanced oxidation processes (AOPs) have considerable potential for becoming feasible alternatives for the remediation of contaminated wastewater. AOPs are based on the generation of hydroxyl radical, which has a high oxidation potential, extraordinary reactive and unstable short-lived species that can attack on the organic contaminants [1-3]. 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 degradation of various industrial wastewaters including oil mill wastewater [4], refractory organics [5] explosives [6], a wide variety of dyes [7-9], pesticides [10], insecticides [11], surfactants [12] as well as many other substances.

METHODS

MPA (Merck, Germany), ferrous sulfate (Merck, India), hydrogen peroxide 30% (Merck, India), sulfuric 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 such as ethanol, acetone, and ethyl acetate. All melting points were recorded on Toshniwal melting point apparatus. The phmeasurements were done with the help of Systronics-327 Griph (digital) ph meter. An infrared (IR) spectrum was scanned on SCHIMADZU FTIR-8400S spectrophotometer. Elemental analysis was carried out using Carlo-Erba-1106 automatic analyzer.

MPA (0.7 ml) was dissolved in methanol in a round bottom flask, solution of ferrous sulfate (3.5 ml, 0.1 M), hydrogen peroxide (0.25 ml, 30%) and sulfuric acid (0.5 N) were added for maintaining ph. The 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 was MPA 6.59×10^{-2} 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 2.2.

The reaction mixture was irradiated with a 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. Oxygen gas (2.01/min) 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 thin layer chromatography (TLC), at every 2 hrs 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 hrs, two spots corresponding to the parent compound and photoproduct were observed. The reaction was allowed for completion (7 hrs). After the completion of photocatalytic reaction, the photoproduct was characterized by its usual chemical tests [13-15].

RESULTS AND DISCUSSION

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

It was observed that no photoproduct had formed in the first two cases, and the yield was very low in the third case. Hence, it is concluded that both light and photocatalyst are necessary for the photoreaction 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 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 photocatalytic reaction was studied using a variable amount of substrate. The results are summarized in Table 1.

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 the concentration of substrate, yield of photoproduct 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 a different concentration of H_2O_2. The results are summarized in Table 2.

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.

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 the 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 a scavenger.

Effect of pH variation

The effect of ph on the photo-oxidation was studied. The results are summarized in Table 4.

Table 1: Effect of substrate concentration

S. No.	Substrate	% Yield of photoproduct
1.	3.77×10^{-2} M	23.3
2.	4.71×10^{-2} M	26.4
3.	5.65×10^{-2} M	34.8
4.	6.59×10^{-2} M	39.7
5.	7.54×10^{-2} M	35.9
6.	8.48×10^{-2} M	33.4

Table 2: Effect of H_2O_2 concentration

S. No.	H_2O_2	% yield of photoproduct
1.	9.0×10^{-3} M	25.5
2.	13.5×10^{-3} M	28.7
3.	18.0×10^{-3} M	36.4
4.	22.5×10^{-3} M	39.7
5.	27.0×10^{-3} M	33.6
6.	31.5×10^{-3} M	29.4

Table 3: Effect of ferrous ion concentration

S. No.	Fe^{2+}	% Yield of photoproduct
1.	2.0×10^{-3} M	20.4
2.	2.5×10^{-3} M	28.6
3.	3.0×10^{-3} M	35.8
4.	3.5×10^{-3} M	39.7
5.	4.0×10^{-3} M	35.8
6.	4.5×10^{-3} M	30.7

Table 4: Effect of pH variation

S. No.	pH	% Yield of photoproduct
1.	1.6	28.7
2.	1.8	31.8
3.	2.0	36.6
4.	2.2	39.7
5.	2.4	35.9
6.	2.6	32.1

These observations are showing that the rate of reaction increases up to a certain limit (2.2). With the 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 the 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.

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.

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 IR spectrum shows the peak at 400-500/cm indicates the presence of disulfide (-S-S-) group. There is no absorption in region

2600-2500/cm (S-H stretching) confirms the absence of thiol (-SH) group in the photoproduct [16,17].

On the basis of the above, the following mechanism (Fig. 1) has been proposed for the photocatalytic reaction of MPA 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 a different path. Production of hydroxyl radical with this reagent triggers a chain of reaction in the following manner. Reaction (1) is the chain initiation step whereby the hydroxyl radical is generated. It has a high oxidation potential (2.8 V). If both Fe^{2+} and $OH^{\cdot}$ are in excess, reaction (2) will terminate the chain reaction. Production of hydroperoxyl radicals ($HO_2^{\cdot}$) in reaction (4) plays a role in the regeneration of Fe^{2+} ions (5). Regeneration of Fe^{2+} ions can also happen as shown in reaction (6). Superoxide radical ($O_2^{\cdot-}$) formed through reaction (7). It plays a greater role in the redox cycle of Fe^{2+} andFe^{3+} (reaction 8 and 9) [18-21].

(1) $Fe^{2+} + H_2O_2 \longrightarrow Fe^{3+} + OH^- + OH^{\bullet}$ k = 76 M/s

(2) $Fe^{2+} + OH^{\bullet} \longrightarrow Fe^{3+} + OH^-$ k = 3 × 10^8 M/s

(3) $OH^{\bullet} + OH^{\bullet} \longrightarrow H_2O_2$ k = 5.2 × 10^9 M/s

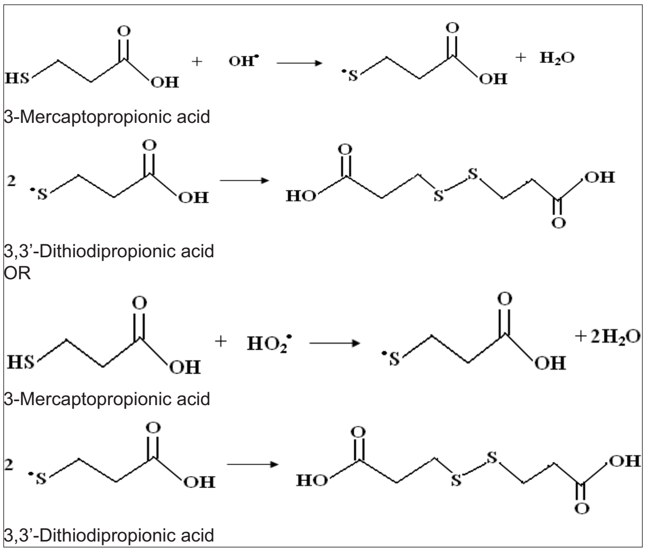

Fig. 1: Photo-oxidation of 3-Mercaptopropionic acid by Fenton reagent

Table 5: Effect of solvent polarity

S. No.	Solvent	% Yield of photoproduct
1.	Ethyl acetate	28.4
2.	Acetone	32.9
3.	Ethanol	37.5
4.	Methanol	39.7

Table 6: Effect of catalyst variation

S. No.	Catalyst	% Yield of photoproduct
1.	H_2O_2	27.7
2.	$H_2O_2+Fe^{2+}$	39.7
3.	$H_2O_2+UO_2^{2+}$	40.4
4.	$H_2O_2+UO_2^{2+}+Fe^{2+}$	42.2

(4) $OH^{\bullet} + H_2O_2 \longrightarrow HO_2^{\bullet} + H_2O$ k = 3.3 × 10^7 M/s

(5) $Fe^{3+} + HO_2^{\bullet} \longrightarrow Fe^{2+} + H^+ + O_2$ k = 3.3 × 10^5 M/s

(6) $Fe^{3+} + H_2O_2 \longrightarrow Fe^{2+} + HO_2^{\bullet} + H^+$ k = 0.01 M/s

(7) $HO_2^{\bullet} \longrightarrow O_2^{\bullet-} + H^+$ k = 1.58 × 10^5 M/s

(8) $Fe^{2+} + O_2^{\bullet-} \longrightarrow Fe^{3+} + O2$ k = 1.0 × 10^7 M/s

(9) $Fe^{3+} + O_2^{\bullet-} \longrightarrow Fe^{2+} + O_2$ k = 1.5 × 10^8 M/s

(10) $HO_2^{\bullet} + OH^{\bullet} \longrightarrow O_2 + H_2O_2$ k = 1.0 × 10^{10} M/s

Hydroxyl radicals thus formed in the reaction mixture degrade the substrate MPA to form 3, 3'-dithiodipropionic acid as photoproduct.

In this way, the substrate reacts with $OH^{\cdot}$ and/$HO_2^{\cdot}$ radicals to form the photoproduct. Overall reaction can be shown in Figure 1.

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