

Degradation of azo dye Sudan 1 by Photo Fenton Process

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Abstract: Fenton and photo-Fenton reagent is used to eliminate toxic and bio-resistant organic and inorganic pollutants through their transformation into harmless species. The oxidation is based on the generation of hydroxyl radicals that is considered as advanced oxidation processes (AOPS). Hydroxyl radicals are extraordinarily reactive and unstable species that attack most of the organic pollutants. The attack by hydroxyl radical, in the presence of oxygen, initiates a oxidative reactions leading to degradation. Photo-catalytic degradation of azo dye Sudan 1 by Fenton reagent has been studied. The effect of different reaction parameters such as concentration of dyes, hydrogen peroxide, ferrous ion, pH and intensity of light were studied. The progress of the reaction was observed by spectroscopy. Photoproduct was characterized by physical, chemical and spectral methods. A tentative mechanism has been proposed with overall reaction.

Key words: Photo-degradation, Azo dye Sudan 1, Photo Fenton reagent.

Introduction:

Dyes are present in many spheres of our everyday life and their application are continuously growing, e.g., in textile industry, in leather tanning industry, in paper production, in food technology, in agricultural research, inks, varnishes and in hair colorings etc. Dyes make our world beautiful, but they bring pollution. Wastewater from textile industry is one of the major sources of pollutants in to the environment. Wastewater from textile industry is one of the major sources of pollutants in to the environment. Azo dyes contribute to about 80% of all used dyes. The degradation of azo dyes is difficult due to their complex structure and recalcitrant nature.

Fenton and photo-Fenton reagent is used to eliminate toxic and bio-resistant organic and inorganic pollutants through their transformation into harmless species. The oxidation is based on the generation of hydroxyl radicals that is considered as advanced oxidation processes (AOPS). Hydroxyl radicals are extraordinarily reactive and unstable species that attack most of the organic pollutants¹.

The attack by hydroxyl radical, in the presence of oxygen, initiates a oxidative reactions leading to degradation. The Oxidation ability of the Fenton mixtures can be greatly enhanced via UV irradiation and production rate of hydroxyl radicals can be enhanced by the rebirth of ferrous ions².

Fenton's oxidation process has been successfully employed to treat landfill leachate³, pesticides and phenolic contaminants⁴, textile wastewater⁵, paper pulp wastewater⁷ and single contaminants in aqueous solution⁸.

Sudan 1 (CI Solvent Yellow 14 and Solvent Orange R) is typically classified as an azo dye. It is an intensely orange-red solid that is added to colourise waxes, oil, petrol, solvents and polishes, colouring for cotton refuse. Sudan I has also been adopted for colouring various foodstuffs, especially curry powder and chili powder although the use of Sudan I in foods is now banned in many countries, because Sudan I is genotoxic and carcinogenicity to humans.

The chemical structure of sudan1 is as follow:

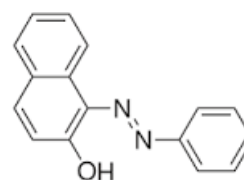


Fig. 1: Structure of dye Sudan 1

Experimental:

Material:

The stock solution of sudan1 (2.5×10^{-3} M) and ferrous sulphate (1.0×10^{-3} M) were prepared in doubly distilled water. The desired pH of the solution was adjusted by the addition of standardized H_2SO_4 and NaOH solution. All laboratory reagents were of analytical grade.

Procedure and analysis:

The reaction mixture was prepared by taking 1.5 ml of sudan 1 (2.5×10^{-3} M), 3.0 ml of ferrous sulphate (1.0×10^{-3} M), 1.5 ml of Hydrogen peroxide (30%) in a round bottom flask. The total volume of the reaction mixture was made 100 ml by adding doubly distilled water. The concentration of various ingredients in the reaction mixture was $[\text{Dye}] = 3.75 \times 10^{-5}$ M, $[\text{FeSO}_4] = 3.0 \times 10^{-5}$ M, $\text{H}_2\text{O}_2 = 1.5$ ml and the pH = 2.6.

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 pH of the solution was measures by pH meter (Systronics 106). The intensity of visible radiation measured by digital lux meter (Lutron Lx -1108). The progress of the reaction was measured as absorbance

by spectrophotometer (Systronics- 166) at different time intervals.

Results and Discussions:

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 added).

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.

The photo degradation of sudan 1 was observed at 418 nm. On irradiation it was observed that optical density decreases with increase in time, indicating that the dye is irradiated. A graph between $2 + \log \text{O.D.}$ and exposure time has been plotted. The straight linearity of graph indicates that photo bleaching of dyes follow first order kinetics. The rate constant k was measured with the expression- $k = 2.303 \times \text{slop}$

A typical has been presented in table 1 and graphically presented in Fig. 1.

Table 1: Typical run of photo-degradation of sudan 1

[Sudan 1] = $3.75 \times 10^{-5} \text{ M}$, $[\text{Fe}^{2+}] = 3.0 \times 10^{-5} \text{ M}$, $\text{H}_2\text{O}_2 = 1.5 \text{ ml}$ pH = 2.6, Light Intensity = 60 mWcm²

Time (min.)	Optical Density (O.D.)	$2 + \log \text{O.D.}$
0	0.419	1.6222
30	0.399	1.6009
60	0.378	1.5775
90	0.356	1.5575
120	0.342	1.5340
150	0.325	1.5119
180	0.298	1.4742

$k = 3.16 \times 10^{-5} \text{ sec}^{-1}$

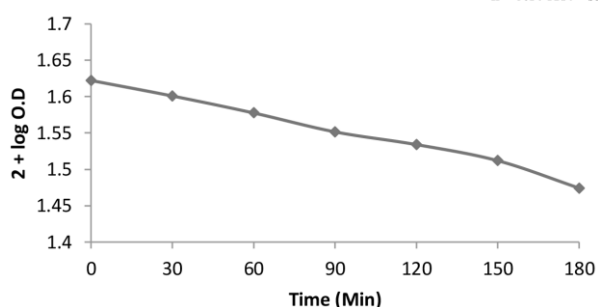


Fig. 1: Typical run for photodegradation of sudan 1

The rate of the degradation depends on various parameters like conc. of dye, amount of H_2O_2 , conc. of FeSO_4 , pH and intensity of light. The results of these variations are as follows:

Effect of dye concentration:

The effect of concentration of substrate on photo catalytic reaction was studied using variable conc. of dye. The results are graphically presented in Fig.2

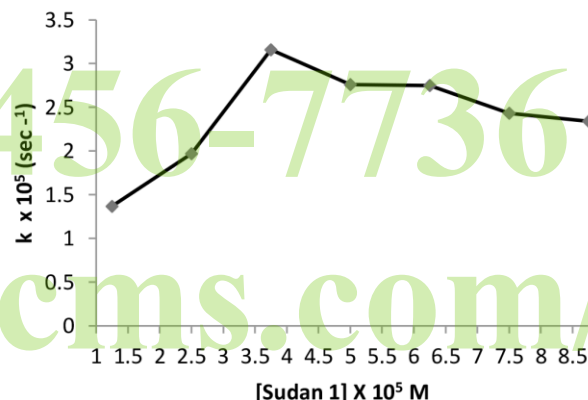


Fig.2: Effect of Sudan 1 concentration

$[\text{Fe}^{2+}] = 3.0 \times 10^{-5} \text{ M}$, $\text{H}_2\text{O}_2 = 1.5 \text{ ml}$, pH = 2.6, Light Intensity = 60 mWcm²

It has been observed that as the concentration of dye increases, the rate of photo – degradation was also found to increase, up to an optimum level ($3.75 \times 10^{-5} \text{ M}$). On further increasing in concentration of dye a sudden decrease in the degradation was observed. It may be due to the fact that on increasing the conc. of dye, more molecules are available for excitation and degradation. On further increasing the conc. of dye above $3.75 \times 10^{-5} \text{ M}$, the rate of reaction was found to decrease. It may be due to as the conc. of dye was increased after optimum level, 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 degradation of dye was observed.

Effect of hydrogen peroxide concentration:

The effect of concentration of hydrogen peroxide on the photo-degradation of dye was investigated using different concentration of H_2O_2 . The results are presented in Fig.3

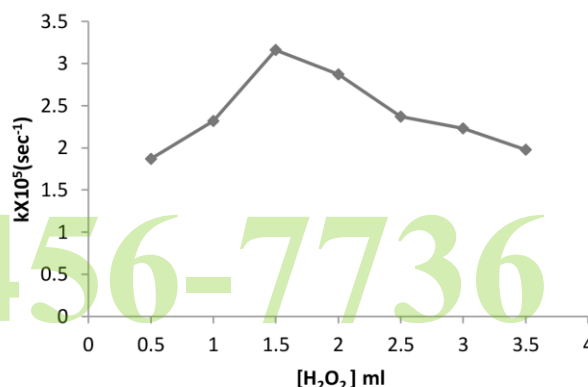


Fig.3: Effect of H_2O_2

[Sudan 1] = $3.75 \times 10^{-5} \text{ M}$, $[\text{Fe}^{2+}] = 3.0 \times 10^{-5} \text{ M}$, pH = 2.6, Light Intensity = 60 mWcm²

It was observed that the rate of degradation increases on increasing the amount of H_2O_2 upto 1.5 ml. On

further increasing the amount of H_2O_2 , the rate of degradation was decreased. 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 and scavenging nature of hydroxyl radical.

Effect of ferrous ion concentration:

Keeping all factors constant, the effect of Fe^{2+} concentrations on the rate of photo degradation of Sudan 1 was studied. The results are graphically presented in Fig. 4.

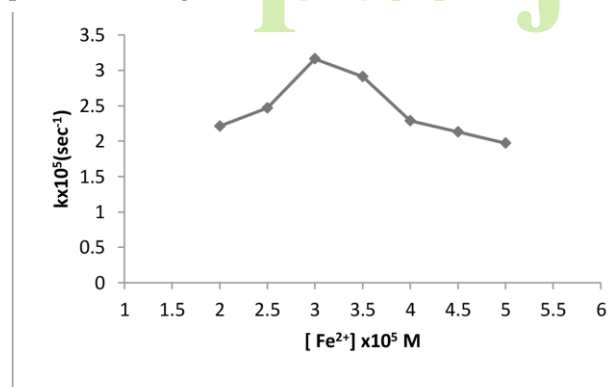


Fig.4: Effect of Fe^{2+} ion Conc.

[Sudan 1] = $3.75 \times 10^{-5} \text{ M}$; $\text{H}_2\text{O}_2 = 1.5 \text{ ml}$; $\text{pH} = 2.6$; Light Intensity = 60 mWcm^{-2}

From above observations it can be concluded that as the rate of photodegradation increases on increasing the concentration of Fe^{2+} ions upto a certain limit $3.0 \times 10^{-5} \text{ M}$. But after reaching on optimum level the efficiency decrease. This may be due to that on increasing the Fe^{2+} ions in the reaction mixture is accompanied by enhanced generation of unstable and reactive species OH^\cdot radical. However on further increasing in conc. of Fe^{2+} ion, which increases the 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 photodegradation of dye was studied. The results are graphically presented in Fig.5.

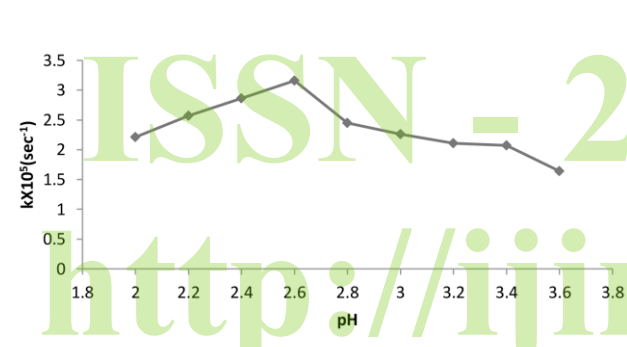


Fig. 5: Effect of pH

[Sudan 1] = $3.75 \times 10^{-5} \text{ M}$; $[\text{Fe}^{2+}] = 3.0 \times 10^{-5} \text{ M}$; $\text{H}_2\text{O}_2 = 1.5 \text{ ml}$; Light Intensity = 60 mWcm^{-2}

These observations are showing that the rate of reaction increases up to a certain limit (2.6). With further rise in pH, the rate of the photodegradation 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 Intensity of light:

The effect of light intensity on the photodegradation of Sudan 1 was studied. The results are graphically presented in Fig.6.

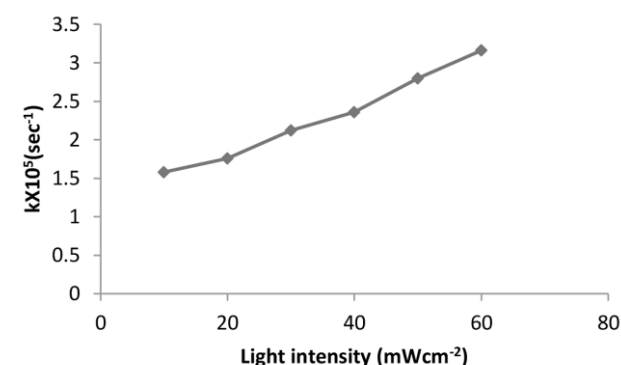
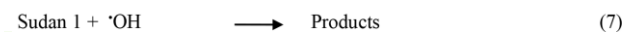
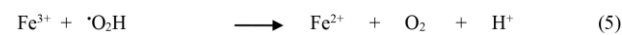
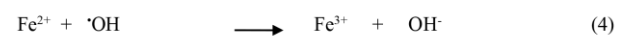
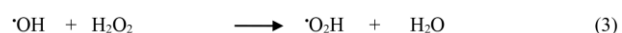
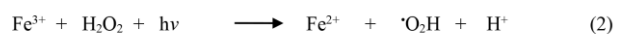


Fig. 5: Effect of pH

[Sudan 1] = $3.75 \times 10^{-5} \text{ M}$; $[\text{Fe}^{2+}] = 3.0 \times 10^{-5} \text{ M}$; $\text{H}_2\text{O}_2 = 1.5 \text{ ml}$; Light Intensity = 60 mWcm^{-2}

Mechanism:

On the basis of the above, the following mechanism has been proposed for the photo-degradation of sudan 1 with Fenton reagent.



The generally accepted mechanism for the Fenton process identifies the hydroxyl radical (OH^\cdot) and hydroperoxy radical (HO_2^\cdot) as the active oxidizing intermediate in the system. HO_2^\cdot radicals are highly unstable in water and undergo facile disproportionation rather than reacting slowly with the dye molecules. The participation of the OH^\cdot radical as an active oxidizing species was confirmed using the hydroxyl radical scavenger, 2-propanol, drastically reduced rate of degradation. 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 ion⁹. Fenton reaction rates are strongly increased by irradiation with UV / visible light^{10,11}. 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+}).

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References:

1. Fenton HJH. Oxidation of tartaric acid in presence of iron. J Chem Soc 1894; 65:899.
2. Ruppert G, Bauer R, Heisler G. UV- O_3 , UV - H_2O_2 , UV - TiO_2 and the photo-Fenton reaction- comparison of advanced oxidation processes for waste water treatment. Chemosphere 1994; 28 (8): 1447-1454.
3. Deng Y, Englehardt J D. Treatment of landfill leachate by the Fenton process. water res 2006 ; 40 (20): 3683-94.
4. Rasul M G, Brown R, Hashib M A. Influence of parameters on the heterogeneous photocatalytic degradation of pesticides and phenolic contaminants in wastewater: A short review. J Environ Manage 2011; 92 (3): 311-30.
5. Perez M, Torrades F, Domenech X, Peral J. Fenton and photo-Fenton oxidation of textile effluents. Water Res 2002; 36(11): 2703-2710.
6. Kang S F, Liao C H, Chen M C. Pre-oxidation and coagulation of textile wastewater by the Fenton Process. Chemosphere 2002; 46(6): 923-928.
7. Perez M, Torrades F, Hortal JAG, Domenech X, Peral J. Removal of organic contaminants in paper pulp treatment effluents under Fenton and photo-Fenton conditions. Appl Catal B: Environmental 2002; 36(1): 63-74.
8. Oturan M A, Oturan N, Lahitte C, Trevin S. Production of hydroxy radicals by electrochemically assisted Fenton's reagent Application to the mineralization of an organic micropollutant pentachlorophenol. J Electroanal Chem 2001; 507(1-2): 96-102.
9. Sychev AY, Isak VG. Iron compounds and the mechanism of the homogenous catalysis of the activation of O_3 and H_2O_2 and of the activation of organic substrates. Russian Chemical Reviews 1995; 64 (12): 1105.
10. Sun Y F, Pignatello J J. Photochemical reactions involved in the total mineralization of 2,4-D by iron (3+)/hydrogen peroxide/UV. Environ Sci Technol 1993; 27 (2): 304-310.