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Degradation of crystal violet using copper modified iron oxide as heterogeneous photo-fenton reagent

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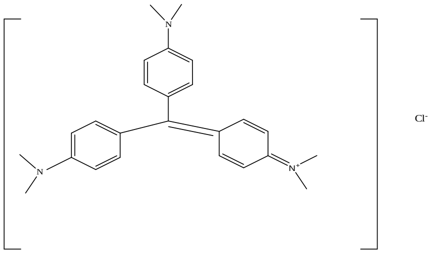
The heterogeneous photo-Fenton degradation of crystal violet under visible light has been investigated using copper modified iron oxide. The photocatalyst has been prepared by coprecipitation method. The rate of photocatalyic degradation of dye was monitored spectrophotometrically. It has been observed that photocatalytic degradation follows pseudo first order kinetics. The effect of various parameters like pH, concentration of dye, amount of photocatalyst, amount of H_2O_2 and light intensity on the rate of photo-Fenton degradation has also been observed. Photocatalyst has been characterized by IR spectroscopy, scanning electron microscopy and X-ray diffraction. Chemical Oxygen Demand (COD) of the reaction mixture before and after exposure was determined. A tentative mechanism for the photocatalytic degradation of crystal violet has also been proposed. Involvement of $^{\bullet}OH$ radicals has been confirmed by using isopropanol and butylated hydroxy toluene (BHT) as $^{\bullet}OH$ radical scavengers. It has been observed that rate of reaction is drastically reduced in the presence of these scavangers. Under similar conditions Fe_2O_3 has also been prepared. The efficiency of Fe_2O_3 and copper modified Fe_2O_3 has been compared for the photocatalytic degradation of crystal violet.



Structure of crystal violet

Keywords: Heterogeneous photo–Fenton reagent; Copper modified iron oxide; Crystal violet.

1. INTRODUCTION

Pollution of water caused by industries is a serious global problem all over the world and its remediation is a great challenge for scientists. Dye wastes represent one of the most problematic groups of pollutants because they can be easily identified by the human eye and are not easily destroyed. Dyes cause a severe threat to environment because of their low biodegradability[1]. Advanced oxidation methods (AOP) can be effective in their degradation as they can result in almost complete mineralization in a less expensive and easy way. AOPs are based on the generation of very reactive species such as hydroxyl radicals ($^{\bullet}OH$) which have a very strong oxidation potential second to fluorine. Hydroxyl radicals rapidly and non selectively oxidize a broad range of organic pollutants. Common AOPs involve photocatalytic, Fenton processes, photo-Fenton process, ozonation, photochemical and electrochemical oxidation. Photocatalytic process is well known method for wastewater treatment.

Photocatalytic degradation of dye effluents by titanium dioxide pillar pellets in aqueous solution has been observed by Li et al [2]. Photocatalytic degradation of brilliant red dye and textile wastewater has been investigated by Martins et al.[3]

The Fenton reagent consisting of H_2O_2 and Fe (II) is a strong oxidizing agent. In this reaction ferrous ion react with hydrogen peroxide and generate $^{\bullet}OH$ radicals which are the active species in oxidation of organic compounds [4]. Vlyssides et al. investigated small sewage treatment works using a Fenton oxidation method[5]. Degradation of phenol with Fenton like treatment by using heterogeneous modified iron oxide and hydrogen peroxide was studied by Lee et al.[6]

But the main drawback of the Fenton reaction is that the reaction becomes very slow after consumption of ferrous ions. This drawback of Fenton reaction can be overcome by the use of photo-Fenton reaction. The degradation of different organic pollutants by homogeneous photo-Fenton reagent has been known for over a century. In this reaction, the generated $^{\bullet}OH$ radicals decompose organic compounds to smaller end products. Gomati Devi et al. studied photodegradation of methyl red by advanced and homogeneous photo-Fenton's processes[7]. Homogeneous photo-Fenton degradation of 1,2,9,10-tetrachlorodecane in aqueous solution using hydrogen peroxide, iron and UV light has been observed by Morsi et al.[8] Punjabi et al. carried out photocatalytic degradation of phenol red and sunset yellow FCF using complexes of some transition metals and hydrogen peroxide. [9,10] In homogeneous photo-Fenton process the iron ions remain in water solution after catalytic reaction is over. This disadvantage of the homogeneous catalytic system can be overcome with the use of heterogeneous photo- Fenton catalytic system.

Photo-Fenton- and Photo-Fenton like degradation of a textile dyes by heterogeneous processes with Fe/ZSM-5 Zeolite has been observed by Duarte and Madiera[10]. Heterogeneous catalytic treatment of synthetic dyes in aqueous medium using Fenton and photo-assisted Fenton process has been studied by Soon and Hameed[11]. Martinez et al. studied heterogeneous photo-Fenton degradation of phenolic aqueous solutions over iron-containing SBA-15 catalyst [12]. Synthesis, characterization and visible light photo-Fenton catalytic activity of hydroxy Fe/Al intercalated montmorrilonite has been studied by Li et al. [13]

Feng et al. studied discoloration and mineralization of reactive red HE-3B by heterogeneous photo-Fenton reaction [14]. Highly active S-modified $ZnFe_2O_4$ heterogeneous catalyst and its photo-Fenton behavior under UV–visible irradiation was studied by Liu et al.[15] Heterogeneous photo-Fenton photodegradation of reactive brilliant orange X-GN over iron-pillared montmorillonite under visible irradiation was observed by Chen et al[16]. Plata et al. studied decomposition of 2-chlorophenol employing goethite as Fenton catalyst [17]. Yang et al. observed degradation of methylene blue by heterogeneous Fenton reaction using titanomagnetite at neutral pH values [18].

A study of catalytic behaviour of aromatic additives on the photo-Fenton degradation of phenol red was examined by Jain et al.[19] Degradation of bismark brown-R using copper loaded neutral alumina as heterogeneous photo-Fenton reagent has been studied by sharma et al.[20].

2. EXPERIMENTAL

2.1. Preparation of photocatalyst

In the present investigation, a modified iron oxide catalyst has been prepared in the following manner. 50g $FeSO_4.7H_2O$ was dissolved in 250 mL of water and 25 g of $CuSO_4.5H_2O$ was dissolved in 250 mL of water and both solutions were mixed. Then aqueous NaOH was added dropwise and the pH was adjusted to 9.0. The content was agitated for 40 mins. The precipitate was filtered, washed with water to ensure complete removal of the NaOH and sulphate ions (SO_4^{2-}) and air dried. The precipitate was kept in a muffle furnace at 400°C for 2 hours.

2.2. Characterization by SEM and FTIR

Scanning electron microscopy (Model-Leo 430 Cambridge) has been used to observe the morphological changes caused by loading of copper ions in Fe_2O_3. It has been observed that loading of copper ions lead to the formation of smaller and more regular particles of the catalyst. This factor has led to the increased surface area of the catalyst and therefore, increased rate of photo-Fenton degradation. The SEM photographs of pure and modified Fe_2O_3 are shown in Fig. 1 and 2, respectively.

The particle size of pure Fe_2O_3 and Cu–modified Fe_2O_3 was measured with the help of SEM and it was observed that the average particle size is 5µm and 40 µm, respectively.

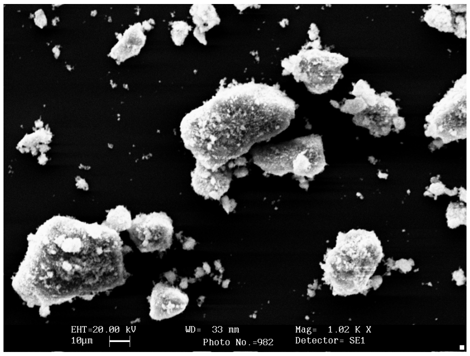


Fig. 1. pure Fe_2O_3.

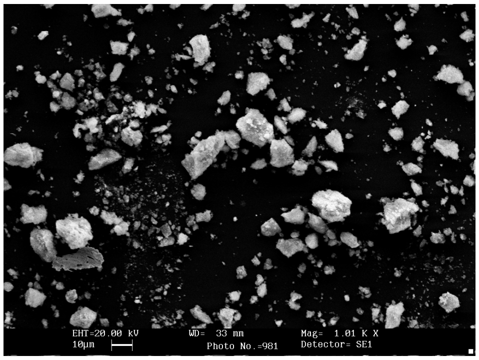


Fig. 2. Cu loaded Fe_2O_3.

2.3. FT-IR

A characteristic band at 459 cm^{-1} due to Fe-O stretching is present in the FT-IR of pure sample of Fe_2O_3 [21]. A band at 592 cm^{-1} due to Cu-O stretching is obtained in the FT-IR of Cu- modified Fe_2O_3 in addition to band due to Fe-O stretching. It clearly indicates that the loading of copper in Fe_2O_3 has taken place successfully.

2.4. Atomic absorption spectroscopy (AAS)

Stability of the catalyst was checked by Atomic Absorption Spectroscopy using ECTL 4129A atomic Absorption spectrophotometer. Even after one month leaching of copper ions from the catalyst was found to be negligible. Thus catalyst was found to posses good stability for its use as heterogeneous photo-Fenton like reagent under visible range.

2.5. X-Ray Diffraction studies

XRD diffraction patterns of the samples were recorded on 18 KW X-Ray diffractometer using Cu Kα radiation. Diffraction patterns were recorded over the 2θ range from 10° to 90 ° with a step size of 0.05°.

The Fig3 and 4 illustrates the indexed XRD patterns of the pure Fe_2O_3 and Cu modified Fe_2O_3, all the bragg reflections have been indexed in rhombohedral structure in the hexagonal setting. (Space group: R-3C No. 167)

The obtained value of the cell parameters for the pure Fe_2O_3: a = 5.035 (5) A°, c = 13.799 (17) A° are in very good agreement with reported standard values a = 5.035 A°, c = 13.748 A°. Relative changes in the peak position and peak intensity in the Cu modified Fe_2O_3 clearly indicates that Cu atoms are well incorporated in the Fe_2O_3 matrix. The obtained values of the cell parameters in Cu modified Fe_2O_3 are a= 5.059(5) A° and c = 13.8222(15) A°.

Thus the unit cell slightly expands relative to pure Fe_2O_3, which is consistent with the substitution of larger cation Cu^{2+} (0.72 A°) on the Fe^{3+} (0.64 A°) sites. The partial occupancy of the interstitial octahedral site would be expected to further increase in the expansion.

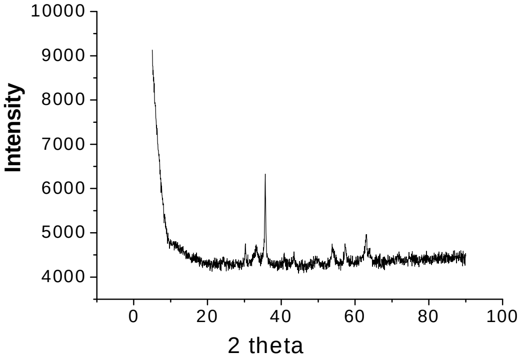


Fig. 3. XRD Patterns of pure Fe_2O_3.

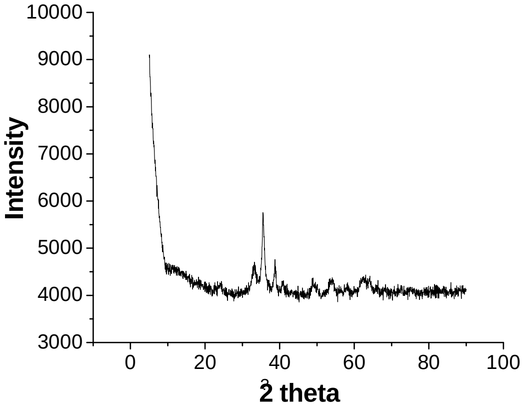


Fig. 4. XRD Patterns of Cu modified Fe_2O_3.

Stock solution of crystal violet (10^{-3} M Himedia) was prepared. Degradation of crystal violet was observed by taking 40.0 mL mixture of 1.75×10^{-5} M dye solution, 0.15 mL H_2O_2 (CBH, 30 % vol.) and 0.03 g Cu- modified Fe_2O_3. The reaction mixture was irradiated with a 200 W tungsten lamp (Philips). The intensity of light at various distances from the lamp was measured using a solarimeter (SM CEL 201). A water filter has been used to cut off thermal radiations. A digital pH meter (Model 232) was used to measure the pH of the reaction mixture. The pH of the solution was adjusted by the addition of previously standardized 0.1 N sulphuric acid and 0.1 N sodium hydroxide solution. The progress of the photo-Fenton degradation was monitored by measuring the absorbance of the reaction mixture at regular time intervals using UV visible spectrophotometer (Systronics Model 106). IR spectrum of Cu- modified and pure Fe_2O_3 has been obtained using 8400 S FTIR spectrophotometer. SEM pictures of the catalysts were obtained using Model- Leo 430 Cambridge. Different quality parameters for water has been determined by using water analyser Systronics Model 371.

3. RESULTS AND DISCUSSION

An aliquot of 3.0 mL was taken out from the reaction mixture at definite time intervals and the absorbance was measured at 590 nm. It was observed that the absorbance of the solution decreases with increasing time intervals, which indicates that the concentration of crystal violet decreases with increasing time of exposure. A plot of 2 + log A against time was linear and follows pseudo-first order kinetics. The rate constant was measured with the expression.

$$k = 2.303 \times \text{Slope} \qquad \dots (1)$$

The chemical oxygen demand of reaction mixture before and after treatment has been determined by redox method using ferrous ammonium sulphate and $KMnO_4$.

The photodegradation efficiency of the catalyst was calculated from the following expression:

$$\eta = \frac{COD_{before} - COD_{after}}{COD_{before}} \times 100$$

η = Photodegradation efficiency (%)
COD_{before} = COD of dye solution before illumination
COD_{after} = COD of dye solution after illumination

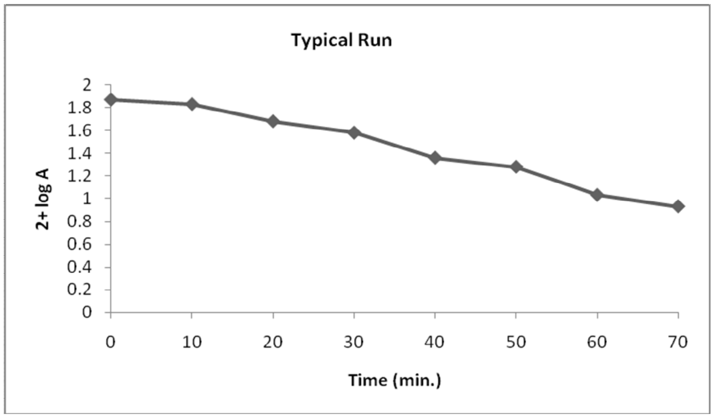


Fig. 5. A Typical run for photodegradation of Crystal violet.

Table 1. Typical run.

pH = 8.5 [Crystal violet] =1.75 x 10^{-5}M

Photocatalyst = 0.03 g H_2O_2 = 0.15 mL

Light intensity = 70 $mWcm^{-2}$

Time (min.)	**Absorbance (A)**	**2 + log A**
0	0 .748	1.87
10	0. 684	1.83
20	0. 481	1.68
30	0 .372	1.58
40	0. 234	1.36
50	0 .192	1.28
60	0.108	1.03
70	0 .087	0.93

k = 2.87 x 10^{-4} sec^{-1}

3.1. Effect of pH

The effect of pH on the rate of photo-Fenton degradation has been investigated in pH range 6.5-10.0. It has been observed that with an increase in pH, rate of reaction increases and after attaining the maximum value at pH 8.5, rate decreases with further increase in pH. The optimum value was obtained for pH 8.5. The increase in rate of degradation on increasing pH may be explained by the fact that larger numbers of hydroxyl ions are available at higher pH values. These $^{-}$OH ions will generate more $^{\bullet}$OH radicals resulting in higher rate of degradation of dye. But on increasing the pH above 8.5 degradation rate decreases due to the fact that dye does not remain in its cationic form because $^{-}$OH ions surround dye molecules at higher pH, therefore there is repulsion between dye molecules and negatively charged catalyst surface and so number of molecules approaching the catalyst surface also decreases. As a result, the rate of degradation decreases.

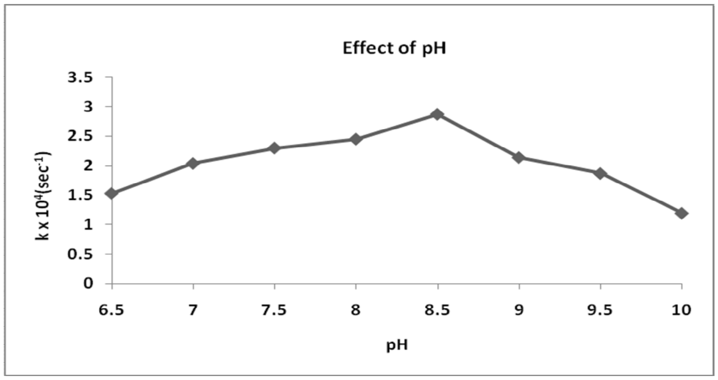


Fig. 6. Effect of pH.

Table 2. Effect of pH.

[Crystal violet] = 1.75 x 10^{-5}M
Photocatalyst = 0.03g H_2O_2 = 0.15 mL
Light intensity = 70 mWcm^{-2}

pH	**Rate constant (k x 10^4 sec^{-1})**
6.5	1.53
7.0	2.04
7.5	2.30
8.0	2.45
8.5	2.87
9.0	2.14
9.5	1.87
10.0	1.19

3.2. Effect of Concentration of Dye

The effect of variation of concentration of dye on the rate of photo-Fenton degradation has been observed in the range from 0.75 × 10^{-5} M – 2.50 × 10^{-5}M. It has been observed that the rate of degradation increases with increasing concentration of crystal violet up to 1.75 × 10^{-5} M. Further increase in concentration beyond 1.75 × 10^{-5} M decreases the rate of degradation. This may be explained on the basis that initially, on increasing the concentration of dye, the reaction rate increases as more molecules of dye are available for degradation. But further increase in concentration beyond 1.75 × 10^{-5} M causes retardation of reaction due to number of collisions among dye molecules increase whereas, collisions among dye and $^{\bullet}OH$ radicals decrease. As a consequence, rate of reaction is retarded.

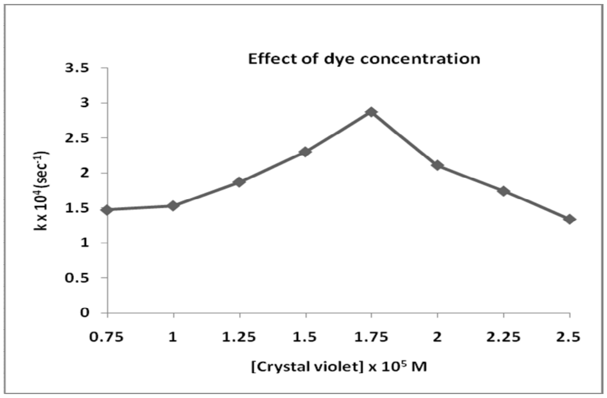


Fig. 7. Effect of dye concentration.

Table 3. Effect of Concentration of Dye.

pH = 8.5 Photocatalyst = 0.03g H_2O_2 = 0.15 mL
Light intensity = 70 $mWcm^{-2}$

[crystal violet x 10^{-5}]	**Rate constant (k x $10^4 sec^{-1}$)**
0.75	1.47
1.00	1.53
1.25	1.87
1.50	2.30
1.75	2.87
2.00	2.11
2.25	1.74
2.50	1.34

3.3. Effect of amount of photocatalyst

The effect of variation of amount of photocatalyst has also been observed on the rate of photo-Fenton degradation. As clear from the above data that with increase in the amount of catalyst, the rate of photo-Fenton reaction increases to a certain amount of catalyst (0.03 g), which may be regarded as a saturation point. Beyond this point, the rate of reaction decreases with increase in amount of catalyst. This may be explained by the fact that with the increase in the amount of catalyst, the surface area of catalyst will increase. Hence, the rise in the rate of reaction has been observed. But after a certain limiting amount of catalyst (0.03g), if the amount of photocatalyst was further increased, it would also increase the number of iron and copper ions and then there is a possibility of short circuiting between ferrous & ferric and cuprous & cupric ions. As a result, less number of hydroxyl radicals are formed and reaction rate is retarded.

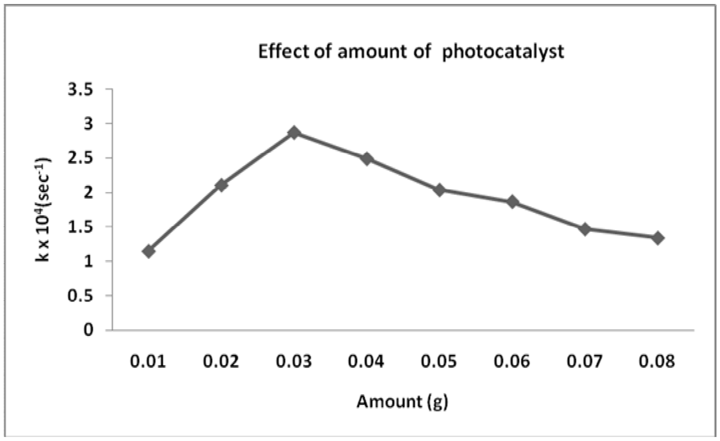


Fig. 8. Effect of amount of photocatalyst.

Table 4. Effect of amount of photocatalyst.

[Crystal violet] = 1.75×10^{-5}M
H_2O_2 = 0.15 mL pH = 8.5
Light intensity = 70 mWcm^{-2}

Amount (g)	**Rate constant ($k \times 10^4$ sec^{-1})**
0.01	1.15
0.02	2.11
0.03	2.87
0.04	2.49
0.05	2.04
0.06	1.87
0.07	1.47
0.08	1.34

3.4. Effect of H_2O_2

The effect of variation of amount of H_2O_2 on the photo-Fenton degradation of crystal violet has also been investigated in the range from 0.05 mL to 0.40 mL. It has been observed that initially upon increase of H_2O_2 from 0.05 mL – 0.15 mL, the rate of degradation increases. However, beyond 0.15 mL the rate of photo-Fenton degradation decreases. It may be attributed to the fact that $^{\bullet}OH$ radicals react with increasing amount of H_2O_2. The reaction generates hydroperoxy radicals ($HO_2^{\bullet}$) which are less powerful oxidizing agent as compared to $^{\bullet}OH$ radical.

$$H_2O_2 + HO^{\cdot} \rightarrow H_2O + HO_2^{\cdot} \qquad \ldots (2)$$

As a result, a decrease in rate of reaction has been observed beyond 0.15mL of H_2O_2

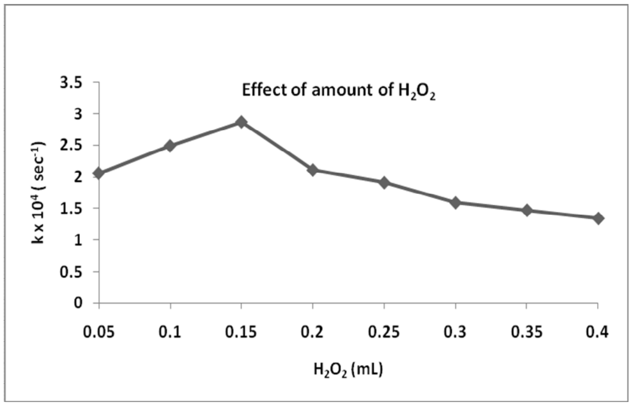


Fig. 9. Effect of amount of H_2O_2.

Table 5. Effect of H_2O_2.

[Crystal violet] =1.75 X 10^{-5} M pH = 8.5
Photocatalyst = 0.03g
Light intensity = 70 $mWcm^{-2}$

H_2O_2 (mL)	**Rate constant (k x 10^4 sec^{-1})**
0.05	2.06
0.10	2.49
0.15	2.87
0.20	2.11
0.25	1.91
0.30	1.59
0.35	1.47
0.40	1.34

3.5. Effect of Light Intensity

The data indicate that as we increase light intensity, the rate of reaction also increases and maximum rate has been found at 70.0 $mWcm^{-2}$. It may be explained on the basis that as light intensity was increased, the number of photons striking per unit area also increase, resulting into higher rate of degradation. Further increase in the light intensity beyond 70.0 $mWcm^{-2}$ results in a decrease in the rate of reaction. It may be probably due to thermal side reactions.

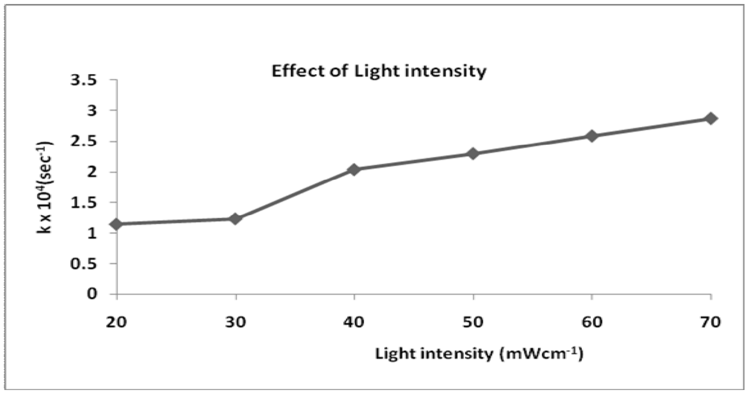


Fig. 10. Effect of light intensity.

Table 6. Effect of Light Intensity.

[Crystal violet] = 1.75×10^{-5} M
pH = 8.5 Photocatalyst = 0.03g
H_2O_2 = 0.15 mL

Light intensity(mW cm^{-2})	Rate constant ($k \times 10^4 sec^{-1}$)
20.0	1.15
30.0	1.24
40.0	2.04
50.0	2.30
60.0	2.59
70.0	2.87

3.6. Mechanism

On the basis of the experimental observations and corroborating the existing literature, a tentative mechanism has been proposed for the degradation of crystal violet by photo-Fenton reagent

$$Fe^{3+} + H_2O \xrightarrow{Visible\ light} Fe^{2+} + HO^{\bullet} + HO^{-} \qquad \ldots(3)$$

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO^{\bullet} + HO^{-} \qquad \ldots(4)$$

$$Cu^{2+} + H_2O \xrightarrow{Visible\ light} Cu^{+} + HO^{\bullet} + H^{+} \qquad \ldots(5)$$

$$Cu^{+} + H_2O_2 \rightarrow Cu^{2+} + HO^{\bullet} + HO^{-} \qquad \ldots (6)$$

The $^{\bullet}OH$ radical is non selective and strong oxidizing agent with high oxidation potential, which is relatively high as compared to common oxidizing agent like H_2O_2, O_3, O_2 etc. These $^{\bullet}OH$ radicals react with dye and degrade it into smaller products like CO_2, NO_3^- ions etc. These products have been identified by usual chemical tests.

$$^{1}[Dye] \xrightarrow{h\nu} {}^{1}[Dye]^{*} \qquad \ldots (7)$$

$$^{1}[Dye]^{*} \xrightarrow{ISC} {}^{3}[Dye]^{*} \qquad \ldots (8)$$

$$^{3}[Dye]^{*} + {}^{\bullet}OH \longrightarrow \text{Smaller products} \qquad \ldots (9)$$

The involvement of $^{\bullet}OH$ radicals in the reaction has been confirmed by carrying out the reaction in presence of $^{\bullet}OH$ radical scavenger, e.g., 2-propanol and butylated hydroxy toluene (BHT). In presence of 2-propanol and BHT, reaction rate has been found to be drastically reduced.

3.7. Quality parameters of water

Quality of water before and after photo-Fenton degadation has been tested by measuring some parameters

Various parameters studied	Before photo-Fenton degradation (Cu loaded Fe_2O_3)	After photo-Fenton degradation (Cu loaded Fe_2O_3)
COD (mg/L)	22	7
DO (ppm)	6.6	12.8
Conductivity(µS)	79	118
Salinity (ppt)	0.04	0.11
TDS (ppm)	49.7	78.3
pH	8.5	6.87

3.7.1. COD (Chemical Oxygen Demand)

Chemical oxygen demand of dye solution before and after illumination has been determined by redox method. COD of dye solution before and after exposure was found to be 22 mg/L and 7 mg/L, respectively. The photodegradation efficiency after 2 hours of illumination has been found to be 68 %.

3.7.2. Dissolved Oxygen

Dissolved oxygen analysis measures the amount of gaseous oxygen dissolved in an aqueous solution. Increase in dissolved oxygen after photo-Fenton degradation indicates mineralization of dye to a significant extent.

3.7.3. Conductivity

Conductivity as a summation parameter is a measure of the level of ion concentration of a solution. Conductivity parameter has been increased after the treatment because dye has been mineralized into ions like CO_3^{2-} , NO_3^-, SO_4^{2-} etc. Because of the same reason, total dissolved solids (TDS) and salinity of the dye solution has been found to increase after photo-Fenton degradation of dye.

3.7.4. pH

Before the treatment pH of reaction mixture is basic but after the degradation pH becomes neutral because dye particles are mineralized in significant extent.

4. CONCLUSION

Cu–modified Fe_2O_3 catalyst has been prepared by co- precipitation method, using ferrous sulphate and copper sulphate as precursors. The amount of photo-Fenton catalyst required (typically around 0.03 g in 40 mL) is much less than that usually used earlier. The effect of the amount of photo-Fenton catalyst, hydrogen peroxide, concentration of dye, pH of the reaction medium and light intensity were observed on rate of reactions. At optimal conditions, rate of degradation for crystal violet dye was found to be as $k = 2.87 \times 10^{-4}$. However, in presence of pure Fe_2O_3, rate of photo-Fenton degradation was to be 2.16×10^{-4} . During heterogeneous photo-Fenton process, $^{\bullet}OH$ radicals react with dye and degrade it into smaller products like H_2O, CO_2, NO_3^- ions etc.

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