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Photooxidation treatment of wastewater containing malachite green dye using sono-photo-Fenton and photo-Fenton reagent: A comparative study

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ABSTRACT

The present study aims to investigate the degradation of malachite green (a textile dye, MG) using Advanced Fenton process (AFS) such as photo-Fenton and sono-photo-Fenton in homogeneous aqueous solution. The effect of different variables like the concentration of ferric ions (Fe^{3+}), concentration of dye, hydrogen peroxide (H_2O_2), pH and light intensity was evaluated. The progress of the sono-photochemical degradation was monitored spectrophotometrically. The optimum degradation conditions were determined experimentally. The results showed that the dye was completely oxidized and degraded into CO_2 and H_2O. Efficiency towards degradation of malachite green (MG) was enhanced when the photo-Fenton's process was coupled with ultrasound treatment. These results exemplified the advantages of combining ultra sound with photo-Fenton oxidation for recalcitrant compounds degradation. A suitable tentative mechanism for sono-photochemical degradation of MG by sono-photo Fenton's reaction has been proposed.

KEYWORDS: Sono-photo-Fenton, Fenton oxidation, malachite green, advanced oxidation process.

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INTRODUCTION

Various chemicals and dyes of complex structures are used for the different processes in the textile industries. Over the last few years, there is increasing concern regarding discharge of textile industrial wastewaters into either municipal sewerage system or directly into recipient water bodies because of its adverse effect on environment.[1-2] The presence of textile dyes in water bodies affects the photosynthetic activity, aesthetic appearance, makes water unfit for drinking and for the use of domestic and irrigation purposes.[3-5] Therefore the remediation of wastewaters polluted with these dyes, is a need indeed. There are several methods applicable for the reclamation of dyeing waste waters such as ozonation, membrane filtration, oxidation, photochemical, and adsorption etc.[6-9]

One of those dyes is, malachite green, a tri-aryl methane dye[10] which is widely used, easily available and cheap dye. Inspite of this it is classified as class III hazardous dye (W.H.O.) and is even banned in European countries but due to its effective colour and price, is being regularly used in India.[11, 12] The toxicity of this dye increases with exposure time, temperature and concentration. It can cause genotoxicity, histopathological and biochemical alterations in aquatic organisms and it has been reported to cause carcinogenesis, mutagenesis, chromosomal fractures.[13] Therefore it is necessary to employ new methods and treat malachite green contaminated wastewater before its discharge to the environment.

In this context, Advanced oxidation processes (AOPs) comprise a promising technology for the treatment of wastewaters such as photo catalysis, Fenton-based processes and ozonation.[14-17] AOPs generally means application of either advanced oxidation technologies using UV/O_3, O_3/H_2O_2, UV/H_2O_2 or the photo-Fenton reaction ($UV/H_2O_2/Fe^{2+}$ or Fe^{3+}) which generate highly reactive oxidants such as hydroxyl radicals. It is one of the strongest and nonselective oxidant and capable of quickly oxidizing a broad range of organic pollutants to harmless compounds like H_2O, CO_2 and inorganic salts. The degradation of malachite green was also observed time to time.[18] But the discharging limits determined by legislation, forcing the industries to develop more effective methods for the removal of these various organic recalcitrant contaminants, leading to intensive research and development of on-site treatment technologies for industrial waste water.

The Fenton's reagent alone or in combination has proven to be an effective way to degrade recalcitrant organic pollutants from industrial wastewaters.[19-21] The Fenton reaction was first observed by H. J. Fenton and is described as the enhanced oxidative power of H_2O_2 where iron is used as a catalyst under acidic conditions. The Fenton process is a relatively economical method since it requires no additional energy when compared to many other AOPs.[22] Furthermore, both iron and hydrogen peroxide are relatively cheap and safe. The Fenton process that takes place in presence of UV light or visible light is called the photo-Fenton process, which accelerates the degradation rate of organic pollutants.[23] Thus in recent years, attentions have been directed toward advanced Fenton Process[24] which is implemented for enhanced treatment ability and better energy efficiency such as sono-photo-Fenton process where the combination of sonochemistry and photo-Fenton chemistry has been investigated.[25-27]

In the Fenton process, highly reactive hydroxyl radical ($^{\bullet}OH$) is generated through the oxidation of Fe^{2+} to Fe^{3+} in presence of H_2O_2 in acidic media which initiates the Fenton reaction (I). In the dark, this reaction is stopped after complete conversion of Fe^{2+}–Fe^{3+} ions. The photo-Fenton process combines Fenton's reagent with light energy accelerates the degradation rate of organic pollutants. The reasons for the rate enhancement is the photo reduction of Fe^{3+} ions, enables another path for the regeneration of Fe^{2+} and produces new $^{\bullet}OH$ radicals with H_2O according to the following mechanism (II).

$$Fe^{2+} + H_2O_2 \longrightarrow Fe^{3+} + {}^{\bullet}OH + OH^{-} \qquad \text{….(I)}$$

$$Fe^{3+} + H_2O + h\nu \longrightarrow Fe^{2+} + {}^{\bullet}OH + H^{+} \qquad \text{….(II)}$$

The direct photolysis of H_2O_2 also generates $^{\bullet}OH$ radicals.

The main objective of this investigation was two-folded: (i) to verify the technical feasibility of treating MG using sono-photo-Fenton reaction with different parameters (ii) compared sono-photo-Fenton reaction with photo-Fenton and the results showed that the sono- photo-Fenton’s reagent is a better oxidizing reagent as compared to photo-Fenton’s reagent.

EXPERIMENTAL

Materials and Method

The entire reagents malachite green (MG) (Qualigens), $FeCl_3$ (CDH) and H_2O_2 (30%, Merck) used in the experiment were in analytical grade and were used without further purification. All the experiments were conducted at room temperature. All solutions were prepared in doubly distilled water. The concentrations of the solutions were 1.0×10^{-3} M and 5.0×10^{-3} M for MG and $FeCl_3$, respectively. These were used as stock solutions. Sono-photochemical degradation of malachite green was investigated by taking 30 mL of total reaction mixture consisting of dye solution, $FeCl_3$ solution and H_2O_2. The concentration of dye was kept as 2.67×10^{-4} M for sono-photo-Fenton (SPF) and 0.33×10^{-4} M for photo-Fenton (PF), of $FeCl_3$ was 6.67×10^{-4} M for sono-photo-Fenton and 6.67×10^{-4} M for photo-Fenton while H_2O_2 was 1.0 mL and 0.5 mL for sono-photo-Fenton and photo-Fenton, respectively, in the reaction mixture. The reaction mixture was exposed to the light (75.5 $mWcm^{-2}$) by a 200 W tungsten lamp (Sylvania Laxman). The light intensity was measured with a Suryamapi (CEL Model SM 201). In sono-photo-Fenton reaction, the reaction mixture was also exposed to the ultrasound (Systronics Ultrasonic Cleaner-392), with frequency 40.0 KHz. A water filter was used to cut off thermal radiations. pH of the solution was adjusted by the addition of previously standardized sulphuric acid and sodium hydroxide solutions and measured with a digital pH meter (Systronics Model 335). The necessary condition for the correct measurement of absorbance is that the solution must be free from any suspension. A G3 sintered glass crucible was used for filtration to obtain the desired accuracy in measurement of absorbance. λ_{max} of the dye was determined using an ultraviolet-visible spectrophotometer (Systronics Model 106). The kinetics of oxidation was observed at different parameters.

RESULT AND DISCUSSIONS

MG is named as [4-[[4-(dimethylamino)phenyl]-phenylmethylidene]cyclohexa-2,5-dien-1-ylidene]-dimethylazanium;chloride and other names are aniline green, basic green-4; diamond green-B; victoria green-B. Its molecular formula and molar mass are $C_{23}H_{25}ClN_2$ and 364.911 g/mol. Structure of MG is shown in Fig. 1.

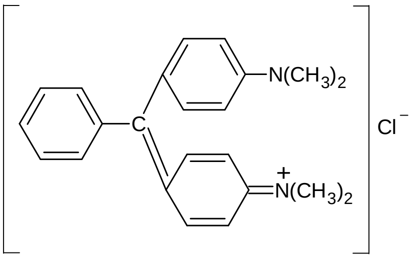

Fig. 1: Malachite Green

The sono-photo-Fenton and Fenton degradation of MG was observed at λ_{max} = 650nm. The results of a typical run are given in Table 1 and Fig. 2

Table 1: Typical run

Time (min)	Photo-Fenton		Sono-photo-Fenton	
	Absorbance (O.D.)	2 + log (O.D.)	Absorbance (O.D.)	2 + log (O.D.)
0.0	0.450	1.6532	0.954	1.9795
2.0	0.390	1.5910	0.765	1.8836
4.0	0.352	1.5465	0.594	1.7737
6.0	0.280	1.4471	0.395	1.5965
8.0	0.201	1.3031	0.265	1.4232
10.0	0.160	1.2041	0.174	1.2405
12.0	0.129	1.1105	0.095	0.9777
14.0	0.075	0.8750	0.043	0.6334
	$k = 2.14 \times 10^{-3}\ s^{-1}$		$k = 3.83 \times 10^{-3}\ s^{-1}$	

Table 1: **Photo-Fenton-**[MG] = 0.33×10^{-4} M, pH = 2.5, [Fe^{3+}] = 6.67×10^{-4} M, H_2O_2 = 0.5 mL, Light intensity = 75.5 mW cm^{-2}

Sono-Photo-Fenton- [MG] = 2.67×10^{-4} M, pH = 2.7, [Fe^{3+}] = 6.67×10^{-4} M, H_2O_2 = 1.0 mL, Light intensity = 75.5 $mWcm^{-2}$, Sonication = 40 KHz

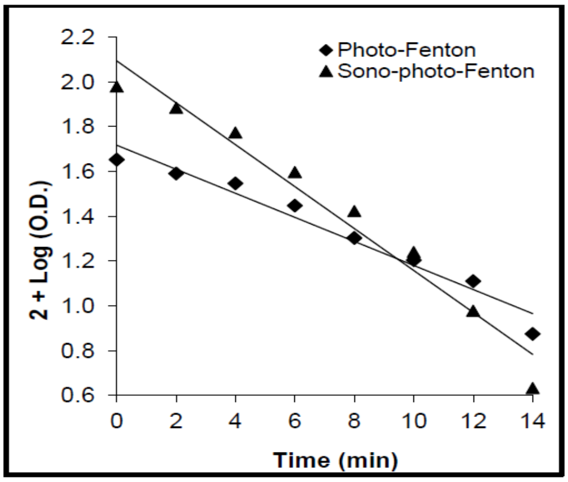

Fig. 2: A Typical Run. Photo-Fenton - [MG] = 0.33 x 10^{-4} M, pH = 2.5, [Fe^{3+}] = 6.67 x 10^{-4} M, H_2O_2 = 0.5 mL, Light intensity = 75.5 mW cm^{-2}; Sono-Photo-Fenton- [MG] = 2.67 x 10^{-4} M, pH = 2.7, [Fe^{3+}] = 6.67 x 10^{-4} M, H_2O_2 = 1.0 mL, Light intensity = 75.5 mWcm^{-2}, Sonication = 40.0 KHz

The results of a typical run are represented in table 1 and Fig. 2. It was observed that the absorbance of MG solution decreases with increasing time of irradiation; indicates that the dye is oxidized and consumed. A plot of log (Absorbance) against time was linear, shows that the oxidation process follows pseudo-first order kinetics. The rate constant k was calculated from the expression k = 2.303 x slope. The optimum rate constant for these reactions were determined as k = 2.14 x 10^{-3} s^{-1} for photo-Fenton reaction and k = 3.83 x 10^{-3} s^{-1} for sono-photo-Fenton reactions.

Effect of ph

The degradation of MG depends strongly on pH of the reaction medium. The effect of pH on the rate of degradation of MG was investigated in the pH range 2.0 to 2.7. The results are reported in Table 2.

Table 2: Effect of pH

pH	Photo-Fenton	Sono-Photo-Fenton
	k x 10^3 s^{-1}	k x 10^3 s^{-1}
2.0	0.19	2.61
2.1	0.36	2.70
2.2	0.54	2.87
2.3	0.74	3.06
2.4	1.09	3.28
2.5	2.14	3.44
2.6	1.25	3.59
2.7	0.97	3.83

Table:2 **Photo-Fenton-** [MG] = 0.33 x 10^{-4} M, [Fe^{3+}] = 6.67 x 10^{-4} M, H_2O_2 = 0.5 mL, Light intensity = 75.5 mW cm^{-2} **Sono-Photo-Fenton-** [MG] = 2.67 x 10^{-4} M, [Fe^{3+}] = 6.67 x 10^{-4} M, H_2O_2 = 1.0 mL, Light intensity = 75.5 mWcm^{-2}, Sonication = 40.0 KHz

The reaction rate increases with increasing pH up to 2.5 and 2.7 in photo-Fenton and sono-photo-Fenton reactions, respectively. The hydroxyl radicals are generated in two steps;

(i) in the reaction between Fe^{2+} ions with hydrogen peroxide,

$$Fe^{2+} + H_2O_2 \longrightarrow Fe^{3+} + OH^- + {}^{\bullet}OH \qquad \text{....(i)}$$

(ii) in photochemical reaction of Fe^{3+} ions and water.

$$Fe^{3+} + H_2O + h\nu \longrightarrow Fe^{2+} + {}^{\bullet}OH + H^+ \qquad \text{....(ii)}$$

The increase in pH of the medium favours the step (i) where OH^- ions are formed along with hydroxyl radicals, whereas protons are generated in step (ii). Thus, it may be concluded that the step (i) dominates over step (ii) at pH below 2.7 in SPF reaction. However, the retardation of the reaction above pH 2.7 in SPF reactions, suggests the dominance of step (ii) over step (i).

Effect of malachite green concentration

Effect of variation of dye concentration on the reaction rate was also studied by taking different concentrations of MG solutions. The results are given in Table 3.

Table 3: Effect of malachite green concentration

[MG] x 10^{-4} M	**Photo-Fenton**	**Sono-Photo-Fenton**
	k x 10^3 s^{-1}	**k x 10^3 s^{-1}**
0.33	2.14	1.43
0.67	1.95	2.14
1.00	1.81	2.38
1.33	1.64	2.68
1.67	1.49	3.06
2.00	1.25	3.25
2.33	0.96	3.39
2.67	0.80	3.83

Table: 3 **Photo-Fenton-** pH = 2.5, $[Fe^{3+}]$ = 6.67 x 10^{-4} M, H_2O_2 = 0.5 mL, Light intensity = 75.5 mWcm^{-2}

Sono-Photo-Fenton- pH = 2.7, $[Fe^{3+}]$ = 6.67 x 10^{-4} M, H_2O_2 = 1.0 mL, Light intensity = 75.5 mWcm^{-2}, Sonication = 40.0 KHz

The rate of degradation of the dye was found to increase with increasing concentration of MG up to 2.67 x 10^{-4} M in SPF but a decreasing trend up to 0.33 x 10^{-4} mol/L in PF reactions. On further increasing its concentration, a sudden decrease in the rate of degradation was observed in case of SPF reaction. This may be attributed to the fact that as the concentration of malachite green was increased, it may start acting as a filter for the incident light. The larger concentrations of the dye will not permit the desired light intensity to reach the dye molecules in the bulk of the solution.

Effect of ferric ion concentration

The effect of concentration of Fe^{3+} ions on the rate of degradation of MG was observed by keeping all other factors identical. The results are summarized in Table 4.

Table 4: Effect of ferric ion concentration

[Fe^{3+}] x 10^{-4} M	**Photo-Fenton**	**Sono-photo-Fenton**
	k x 10^3 s^{-1}	**k x 10^3 s^{-1}**
0.83	0.12	0.19
1.67	0.23	0.20
2.50	0.46	0.22
3.33	0.71	0.53
4.17	1.27	1.42
5.00	1.69	2.13
5.83	2.00	2.51
6.67	2.14	3.83

Table:4 **Photo-Fenton-** [MG] = 0.33 x 10^{-4} M, pH = 2.5, H_2O_2 = 0.5 mL, Light intensity = 75.5 mW cm^{-2}

Sono-Photo-Fenton- [MG] = 2.67 x 10^{-4} M, pH = 2.7, H_2O_2 = 1.0 mL, Light intensity = 75.5 $mWcm^{-2}$, Sonication = 40.0 KHz

It is clear from the data in the above table that in both these cases; sono-photodegradation and photo degradation of the dye, the rate of degradation increases on increasing the concentration of Fe^{3+} ions up to 6.67 x 10^{-4} M and 6.67 x 10^{-4} M for PF and SPF, respectively. This may be explained on the basis that with the increase in Fe^{3+} concentration, there will be enhanced generation of $^{\bullet}OH$ radicals and as a consequence, the rate of sono-photodegradation and photodegradation increases. As the concentration of Fe^{3+} was increased above its optimum concentration, the rate of the reactions (ii) and (iii) become very fast. In reaction (ii), hydroperoxyl radicals ($^{\bullet}OOH$) are generated, which consume more amounts of Fe^{3+} ions in PF but in SPF, an extra reaction (iv) also consume Fe^{3+} ions and hence, Fe^{3+} ions are less available for reaction (i) and as a result, less $^{\bullet}OH$ radicals are generated. Therefore, the rate of sono-photodegradation and photodegradation may also decrease.

$$Fe^{3+} + H_2O + h\nu \longrightarrow Fe^{+2} + {}^{\bullet}OH + H^+ \quad ....(i)$$

$$Fe^{3+} + H_2O_2 + h\nu \longrightarrow Fe^{2+} + HO_2^{\bullet} + H^+ \quad ....(ii)$$

$$Fe^{3+} + HO_2^{\bullet} \longrightarrow Fe^{2+} + O_2 + H^+ \quad ....(iii)$$

$$Fe^{3+} + H^{\bullet} \longrightarrow Fe^{2+} + H^+ \quad ....(iv)$$

Effect of amount of hydrogen peroxide

The effect of the amount of hydrogen peroxide on the sono-photodegradation and photodegradation of MG was also investigated. The results are reported in Table 5.

Table 5: Effect of amount of hydrogen peroxide

H_2O_2 (mL)	**Photo-Fenton**	**Sono-photo-Fenton**
	k x 10^3 s^{-1}	**k x 10^3 s^{-1}**

0.5	2.14	3.59
1.0	0.57	3.83
1.5	0.54	3.35
2.0	0.52	2.87
2.5	0.48	2.46
3.0	0.44	2.26
3.5	0.39	1.91
4.0	0.21	1.31

Table:5 **Photo-Fenton-** [MG] = 0.33 x 10^{-4} M, pH = 2.5, [Fe^{3+}] = 6.67 x 10^{-4} M, Light intensity = 75.5 mW cm^{-2} **Sono-Photo-Fenton-** [MG] = 2.67 x 10^{-4} M, pH = 2.7, [Fe^{3+}] = 6.67 x 10^{-4} M, Light intensity = 75.5 mWcm^{-2}, Sonication = 40.0 KHz

It was observed that the reaction rate increases on increasing the amount of H_2O_2, attaining an optimum value of H_2O_2 at 0.5 mL and 1.0 mL for PF and SPF reactions, respectively. Further increase in the concentration of H_2O_2 decreases the rate of reaction. It is because of the fact that as the amount of H_2O_2 was increased above its optimum value (0.5 mL for PF reaction) the rates of the reactions (v) and (vi) increase in PF system. Thereafter, the rate of degradation decreases on increasing the amount of hydrogen peroxide more than 1.0 mL and 0.5 mL for SPF and PF reaction, respectively. From eqn. (vii), $^{\bullet}OH$ radicals are consumed rapidly due to availability of more H_2O_2 molecules. From eqn. (v) and (vi), $^{\bullet}OOH$ radicals are generated in more amount. This $^{\bullet}OOH$ radical is utilized in eqn. (vii) and H^+ ions are produced. As a consequence, the rate of sono-photodegradation and photodegradation decreases.

$$Fe^{3+} + H_2O_2 + h\nu \longrightarrow Fe^{2+} + HO_2^{\bullet} + H^+ \qquad ....(v)$$

$$^{\cdot}OH + H_2O_2 \longrightarrow HO_2^{\bullet} + H_2O \qquad ....(vi)$$

$$Fe^{3+} + HO_2^{\bullet} \longrightarrow Fe^{2+} + O_2 + H^+ \qquad ....(vii)$$

Effect of light intensity

The effect of light intensity on the sono-photodegradation and photodegradation of MG was also investigated. The results obtained are reported in Table 6.

Table 6: Effect of light intensity

Light Intensity (mW cm^{-2})	**Photo-Fenton**	**Sono-photo-Fenton**
	k x 10^3 s^{-1}	**k x 10^3 s^{-1}**
27.7	0.29	1.71
30.6	0.52	2.20
34.6	0.70	2.43

39.6	0.81	2.59
45.6	0.99	2.91
53.2	1.52	3.23
62.9	1.53	3.64
75.5	2.14	3.83

Table: 6 **Photo-Fenton-** [MG] = 0.33×10^{-4} M, pH = 2.5, $[Fe^{3+}] = 6.67 \times 10^{-4}$ M, H_2O_2 = 0.5 mL, **Sono-Photo-Fenton-** [MG] = 2.67×10^{-4} M, pH = 2.7, $[Fe^{3+}] = 6.67 \times 10^{-4}$ M, H_2O_2 = 1.0 mL, Sonication = 40.0 KHz

Plots of the rate constant versus light intensity were found to be linear, which indicates that an increase in the light intensity increases the reaction rate. This may be attributed to the increased number of photons reacting with Fe^{3+} ions and, as a result, increased numbers of active species, the hydroxyl radicals are formed. Therefore, an overall increase in the rate of reaction was observed. However, higher intensities were avoided due to thermal effects.

Proposed mechanism

On the basis of experimental observations and the existing literature, a tentative mechanism has been proposed for sono-photodegradation of MG with the sono-photo-Fenton (SPF) reagent.

$$Fe^{3+} + H_2O + h\nu \xrightarrow{\qquad} Fe^{+2} + {}^{\bullet}OH + H^+ \qquad ....(1)$$

$$Fe^{3+} + H_2O_2 + h\nu \xrightarrow{\qquad} Fe^{2+} + HO_2^{\bullet} + H^+ \qquad ....(2)$$

$$Fe^{2+} + H_2O_2 \xrightarrow{\qquad} Fe^{3+} + {}^{\bullet}OH + OH^- \qquad ....(3)$$

$${}^{\bullet}OH + H_2O_2 \xrightarrow{\qquad} HO_2^{\bullet} + H_2O \qquad ....(4)$$

$${}^{\bullet}OH + {}^{\bullet}O_2H \xrightarrow{\qquad} H_2O + O_2 \qquad ....(5)$$

$$Fe^{2+} + {}^{\bullet}OH \xrightarrow{\qquad} Fe^{3+} + OH^- \qquad ....(6)$$

$$Fe^{3+} + HO_2^{\bullet} \xrightarrow{\qquad} Fe^{2+} + O_2 + H^+ \qquad ....(7)$$

$${}^{\bullet}OH + {}^{\bullet}OH \xrightarrow{\qquad} H_2O_2 \qquad ....(8)$$

By ultrasound:

$$H_2O \xrightarrow{\bullet)))} {}^{\bullet}OH + H^{\bullet} \qquad ....(9)$$

$$H^{\bullet} + H_2O_2 \xrightarrow{\qquad} {}^{\bullet}OH + H_2O \qquad ....(10)$$

$$Fe^{3+} + H^{\bullet} \xrightarrow{\qquad} Fe^{2+} + H^+ \qquad ....(11)$$

$$\text{Malachite green} + {}^{\cdot}OH \xrightarrow{\qquad} \text{Products} \qquad ....(12)$$

An aqueous solution of ferric ions on exposure to light decomposes water into a proton and ${}^{\bullet}OH$ radical and ferric ions are reduced to ferrous ions (1). The ferrous ions decompose H_2O_2 into hydroxide ion and hydroxyl radical, while ferrous ions undergo oxidation to ferric ions (3). Due to reaction of ferric ions with H_2O_2 in presence of light, $HO_2^{\bullet}$ radicals are also produced (2). The reaction of ${}^{\bullet}OH$ with H_2O_2 also produces $HO_2^{\bullet}$ radicals (4). Ferrous ions will undergo oxidation to ferric ions by addition of ${}^{\bullet}OH$ radicals, while ferric ions get reduced to ferrous ions by incorporation of $HO_2^{\bullet}$ radical and producing H^+ ions (6 and 7). $HO_2^{\bullet}$ radicals are highly unstable in water and undergo facile disproportionation rather than reacting slowly with dye molecules. The participation of hydroxyl radical as an active oxidizing species was confirmed by using a hydroxyl radical scavenger like propan-2-ol, where the rate of photodegradation was drastically reduced.

The $^{\bullet}OH$ radicals are consumed in five reactions (4, 5, 6, 7 and 11). They can induce dissociation of H_2O_2 into $HO_2^{\bullet}$ and water or they combine (dimerize) to form H_2O_2 molecules. They can also induce dissociation of $HO_2^{\bullet}$ into water and O_2 (5). Secondly, these may react with MG to give colorless degradation products. In SPF reaction, $^{\bullet}OH$ radicals are produced in two reactions (9 and 10). The ultrasonic wave can induce dissociation of H_2O into $^{\bullet}OH$ and $H^{\bullet}$, and $H^{\bullet}$ can induce dissociation of H_2O_2 into $^{\bullet}OH$ and water, and this extra generation of $^{\bullet}OH$ radicals enhances the rate of SPF of reaction. The results showed that the dye was completely oxidized and degraded into CO_2 and H_2O.

CONCLUSION

The study concluded that the Fenton process coupled with other UV/solar light is more efficient than the stand-alone Fenton process towards degradation of MG. The main advantage of using sono-photo-Fenton's and/or photo-Fenton's reagents is the regeneration of the consumed Fe^{2+} ions on illumination. Each Fe^{2+} ion can produce many $^{\bullet}OH$ radicals in contrast to the dark Fenton reaction. The process is a cyclic one. It means that the amount of ferrous salt required under SPF and PF conditions is very small as compared to Fenton conditions, where ferrous ions are to be added at regular intervals, otherwise, the reaction will stop after complete conversion of ferrous ions to ferric ions. This is important from industrial point of view because further separation of ferric ions is not required after wastewater treatment.

The investigations in the field of sono-photo-Fenton processes is still at a priliminary level for utilizing this green technology for remediation of pollutants from industrial waste water; however, looking to the encouraging experimental results in the present investigations, it can be suggested that sono-photo-Fenton processes have the desired potential to harness solar energy and degrade organic pollutants from water resources. Therefore, present investigation has opened a new avenue in the field of "Green Technologies" and still there are rooms to investigate these processes in detail to enhance their efficiency.

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