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A Comparative Study of Eco-Friendly Photochemical Oxidation of Gentian Violet Dye Using Singlet-Photo-Fenton with Photo-Fenton and Singlet-Oxygen Processes

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ABSTRACT*:* Singlet molecular oxygen ($^1O_2$) and hydroxyl radical ($^\bullet OH$) are highly reactive species. Singlet molecular oxygen is a nonradical and electrophilic molecule. It is different from diradical triplet molecular oxygen in its electronic arrangement. Singlet molecular oxygen has been used as an effective photooxidant for carrying out a number of chemical reactions. Singlet molecular oxygen with photo-Fenton reaction accelerates the rate of photochemical oxidation of gentian violet (GV). This study was conducted to assess the removal efficiency of GV by using different methods. The rate of photooxidation of dye in aqueous medium has been compared among the photo-Fenton in the presence of singlet molecular oxygen (Singlet-photo-Fenton process (SPF)), photo-Fenton process (PF), singlet oxygen process (SOP) and PF ($< 10^0C$), where the reaction was conducted at the temperature below 10^0C. The effect of different parameters like pH, the concentration of Fe^{3+} ions, concentration of gentian violet, amount of hydrogen peroxide, light intensity, etc. have been observed on the rate of reaction. The progress of the reaction was monitored spectrophotometrically and it follows pseudo-first order kinetics. A tentative mechanism has been proposed for the photochemical oxidation of dye.

Keywords: Singlet-photo-Fenton process; Fenton reaction; photo-Fenton reaction; singlet molecular oxygen; photochemical oxidation; gentian violet.

Introduction

Bright and fabulous coloration, attractive outlook and ever changing fashion have revolutionized the textile industry. In contrast to the front end production of beautiful fabrics, the backside discharge of waste water from textile industries containing a high concentration of dyes has raised a serious environmental concern. Different processes were developed to treat waste water from textile industry [1-3]; and these textile effluents have already been treated by various physical, chemical and biological methods [4,5].

In recent years, innovative technologies such as the Advanced Oxidation Processes (AOPs) have emerged to convert the dye present in waste water to harmless compounds. Some systems like Fenton, photo-Fenton, sono-photo-Fenton, UV/H_2O_2, UV/O_3, SOP, etc. are widely known and are in practical use also. Miralles-Cuevas et al. [6] compared some of them like UV/H_2O_2, UV/$S_2O_8^{2-}$, solar/Fe^{2+}/H_2O_2 and solar/ Fe^{2+}/$S_2O_8^{2-}$ at pilot plant scale for the elimination of micro contaminants in natural water.

The molecular orbital configuration for oxygen is KK $\sigma_{2s}2.\ \sigma^*_{2s}2.\ \sigma_{2pz}2.\ (\pi_{2px})^2.\ (\pi_{2py})^2.\ (\pi^*_{2px})^1.\ (\pi^*_{2py})^1.$ The last two valence electrons enter one each into the degenerated π^*_{2px} and π^*_{2py} pair of orbitals with parallel spins giving triple ground state $^3\Sigma_g^-$ which is represented as:

$$^3\Sigma_g^- : \underset{\pi^*2p_x}{\underline{\ \uparrow\ }}\quad \underset{\pi^*2p_y}{\underline{\ \uparrow\ }}$$

The two electronically excited states are $^1\Sigma_g$ and $^1\Delta_g$. The pairing of two electrons in one molecular orbital

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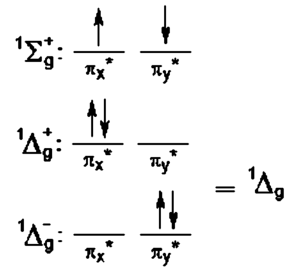
results in the $^1\Delta_g$ state. This is a doubly degenerated state ($^1\Delta_g^+$ and $^1\Delta_g^-$). The spin pairing in different orbitals results in the $^1\Sigma_g^+$ state. These states can be represented as:



A strong oxidizing agent, hydroxyl radical ($^{\bullet}OH$), generated by the singlet- photo-Fenton, singlet molecular oxygen, Fenton and photo-Fenton in water, is responsible for decolorization of dye. Fenton and photo-Fenton methods are very useful in degradation of organic contaminants.

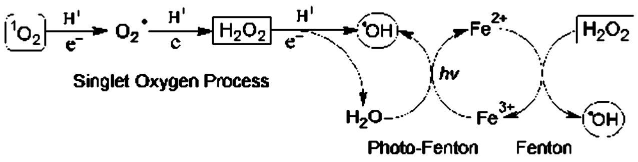


Fig. 1: Formation of hydroxyl radicals in Fenton, photo-Fenton and singlet oxygen process.

Kumar et al. [7,8] reported the use of photo-Fenton reagent for the photochemical bleaching of metanil yellow and fast green. Photo-Fenton oxidation of phenol with Fe(III)-tetra-4-carboxyphenylporphyrin/SiO_2 assisted with visible light was studied by Carlos et al. [9] while Velasquez et al. [10] studied the oxidative degradation of sulfathiazole by Fenton and photo-Fenton reactions.

Lima et al. [11] used an innovative static mixer photoreactor for degradation of antibiotics by homogeneous and heterogeneous photo-Fenton reactions. Such methods are very useful for the removal of persistent pollutants by combining zero valent iron (ZVI) reduction with photo-Fenton process [12]. Degradation of triclosan by photo-Fenton like oxidation was studied by Cokay and Oztamer [13] while Perez et al. [14] reported the effect of temperature and photo-Fenton absorption has been reported on the kinetics of micropollutants removal by solar photo-Fenton in raceway and pond reactor.

Singlet molecular oxygen has also been found to be an active oxidizing species for a number of biological compounds [15]. Minaev [16] explained many photochemical and spectral properties of dioxygen produced by the dye sensitization in solvents. Miyoshi and Tomita [17] investigated the reaction of singlet oxygen with 1,3-diphenylisobenzofuran in aqueous micellar solutions of sodium dodecyl sulfate and dodecyl trimethylammonium chloride using pyrene as a photosensitizer.

Arnold et al. [18] studied the photochemical fate of pharmaceutical compounds while Bhatnagar et al. [19,20] reported the photooxidation of some pharmaceutical drugs (thiopentone, phenytoin, bengyl penicillin and streptomycin) by singlet molecular oxygen. Capparelli et al. [21] carried out photooxidation of pterin in aqueous solution. Zhang et al. [22] highlighted the eosin-Y catalyzed photooxidation of triarylphosphines under visible light irradiation and aerobic conditions while Packer et al. [23] studied the effect of singlet molecular oxygen on naproxen, dichlofenac, ibuprofen and clofibric acid. Singlet molecular oxygen was used for the removal of 2-chlorophenol by Gryglik et al. [24].

Zampini et al. [25] synthesized the different silica-protoporphyrin IX(PpIX) nanocomposites synthesized to evaluate the dependence of singlet oxygen production and bacterial inactivation efficiency on the morphology of the nanomaterials. Chen et al. [26] designed and synthesized Pt/PCN-224(m) composites by integration of Pt nanocrystals and porphyrinic metal organic frameworks (MOFs), PCN-224(m). These composites exhibit excellent photocatalytic performance in the photooxidation of aromatic alcohols and singlet oxygen production.

The present work has been undertaken to done a comparative study on photooxidation of GV by singlet-photo-Fenton (SPF), PF, PF (< 10°C) and SOP. It was found that in singlet-photo-Fenton reaction, singlet molecular oxygen shows a synergistic effect on the rate of photochemical oxidation of dye by the photo-Fenton process. Thus, an enhancement in the rate of degradation of GV was observed.

II. METHOD AND MATERIALS

Gentian violet, $FeCl_3$ (CDH), H_2O_2 (30% Merck) and H_2SO_4 were used. PF, PF (< 10°C), SOP and SPF oxidative degradation of the dye were studied by using Fe^{3+} ions, H_2O_2 singlet molecular oxygen and visible light. 0.2039 g of dye was dissolved in 250 mL of doubly distilled water to give 2.0 × 10^{-3} ML^{-1} solution. 4.0552 g of anhydrous $FeCl_3$ was dissolved in 250 mL of doubly distilled water; the concentration of the solution was 0.1ML^{-1}. These were used as stock solutions. Degradation of GV dye was investigated taking 30 mL of the total reaction mixture consisting of a dye solution, $FeCl_3$ solution and H_2O_2. In the reaction mixture the concentration of dye for the SPF, PF, PF (< 10^0C) and SOP are 2.0 × 10^{-4}, 2.0 × 10^{-4}, 1.0 × 10^{-4} and 2.0 × 10^{-4} M respectively. The concentration of $FeCl_3$ for SPF, PF, PF (< 10^0C) are 0.67 × 10^{-4}, 0.50 × 10^{-4} and 1.0 × 10^{-4} M respectively. Similarly, H_2O_2 is used for SPF, PF, PF (< 10^0C) is 2.5, 2.5 and 3.5 mL, respectively. The reaction mixture was exposed to a 200 W tungsten lamp (Philips) (70.0 mW cm^{-2}). The light intensity was measured with a Suryamapi (CEL Model SM 201). Sunlight was used for higher light intensities. In the SPF and SOP, the air was continuously bubbled through the reaction mixture by an aerator to treat the reaction mixture with singlet molecular oxygen. A water filter was used to cut off thermal radiations.

pH of the solution was adjusted by the addition of standardized sulphuric acid and sodium hydroxide solutions, It was measured with a digital pH-meter (Eco tester pH 2; Oakton). A necessary condition for the correct measurement of absorbance is that the solution must be free from solids. λ_{max} of the dye was determined using a UV-vis spectrophotometer (Systronics Model-108). The structure of gentian violet given below in Fig. 2.

III. RESULTS AND DISCUSSION

All degradations of GV were observed at λ_{max} = 580 nm in processes. The results of a typical run are given in Table 1 and Fig. 3.

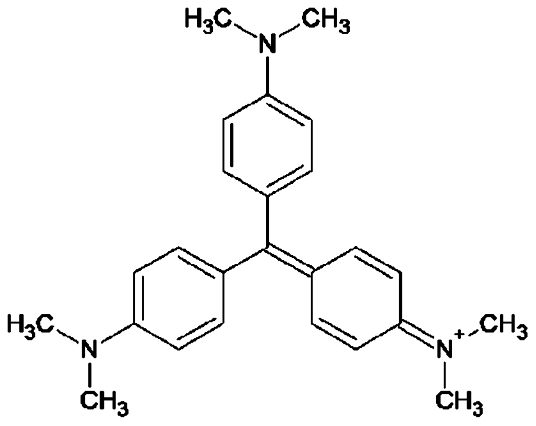


Fig. 2: Structure of gentian violet.

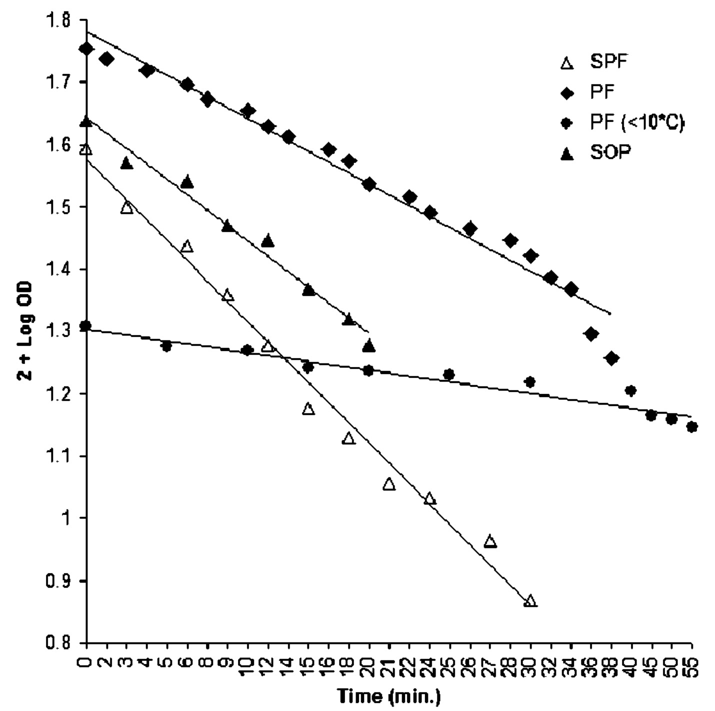


Fig. 3: Typical run

Table 1: Typical Run

Time (min.)	SPF		PF		PF (< 10^{0}C)		SOP	
	[GV] = 2.0 × 10^{-4} M pH = 3.8 [Fe^{3+}] = 0.67 × 10^{-4} M H_2O_2 = 2.5 mL Lig. Int.= 70.0 mW cm^{-2} k_1 = 90.05 × 10^{-5} s^{-1}		[GV] = 2.0 × 10^{-4} M pH = 4.2 [Fe^{3+}] = 0.50 × 10^{-4} M H_2O_2 = 2.5 mL Lig. Int. = 70.0 mW cm^{-2} k_2 = 44.34 × 10^{5} s^{-1}		[GV] = 2.0 × 10^{-4} M pH = 4.0 [Fe^{3+}] = 1.0 × 10^{-4} M H_2O_2 = 3.5 mL Lig. Int. = 70.0 mW cm^{-2} k_3 = 10.39 × 10^{-5} s^{-1}		[GV] = 2.0 × 10^{-4} M pH = 3.8 Lig. Int. = 70.0 mW cm^{-2} k_4 = 67.57 × 10^{-5} s^{-1}	
	OD	**2 + log A**	**OD**	**2 + log A**	**OD**	**2 + log A**	**OD**	**2 + log A**
0	0.394	1.595	0.567	1.754	0.203	1.307	0.435	1.638
2	-	-	0.546	1.737	-	-	-	-
3	0.316	1.500	-	-	-	-	0.373	1.572
4	-	-	0.523	1.719	-	-	-	-
5	-	-	-	-	0.189	1.276	-	-
6	0.274	1.438	0.496	1.695	-	-	0.348	1.542
8	-	-	0.472	1.674	-	-	-	-
9	0.229	1.360	-	-	-	-	0.295	1.469
10	-	-	0.451	1.654	0.186	1.269	-	-
12	0.190	1.279	0.427	1.630	-	-	0.279	1.446
14	-	-	0.411	1.614	-	-	-	-
15	0.150	1.176	-	-	0.174	1.241	0.234	1.369
16	-	-	0.390	1.591	-	-	-	-
18	0.135	1.130	0.374	1.573	-	-	0.209	1.320
20	-	-	0.344	1.537	0.172	1.236	0.190	1.279
21	0.114	1.057	-	-	-	-	-	-
22	-	-	0.327	1.515	-	-	-	-
24	0.108	1.033	0.310	1.491	-	-	-	-
25	-	-	-	-	0.170	1.230		
26	-	-	0.292	1.465	-	-	-	-
27	0.092	0.964	-	-	-	-	-	-
28	-	-	0.280	1.447	-	-	-	-
30	0.074	0.869	0.264	1.422	0.165	1.217	-	-
32	-	-	0.243	1.386	-	-	-	-
34	-	-	0.234	1.369	-	-	-	-
36	-	-	0.198	1.297	-	-	-	-
38	-	-	0.181	1.258	-	-	-	-
40	-	-	-	-	0.160	1.204	-	-
45	-	-	-	-	0.146	1.164	-	-
50	-	-	-	-	0.144	1.158	-	-
55	-	-	-	-	0.140	1.146	-	-

It was observed that the absorbance of GV solutions decreases with increasing time of irradiation; thus, indicating that the dye is degraded. A plot of 2 + log OD against time was linear, following the pseudo-first order kinetics. The rate constants k was calculated from the expression $k = 2.303 \times \text{slope}$. The optimum rate constants for SPF was $k_1 = 90.05 \times 10^{-5}\ s^{-1}$, for PF $k_2 = 44.34 \times 10^{-5}\ s^{-1}$, for PF (< 10^{0}C) $k_3 = 10.39 \times 10^{-5}\ s^{-1}$ and for SOP $k_4 = 67.57 \times 10^{-5}\ s^{-1}$.

Effect of pH

The effect of pH on the rate of degradation of GV was investigated in the pH range 3.2 to 4.5. The results are reported in Table 2. In all variation of pH, it was observed that with an increase in pH, the rate of photochemical degradation of dye increases, but with further increase after a certain pH, the rate of photochemical degradation was found to decrease. The reaction rate increases with increasing pH up to 3.8 in SPF and SOP and 4.0 in PF and PF (< 10^0C), and then decreases.

Table 2: Effect of pH: {**SPF:** [GV] = 2 × 10^{-4} M, [Fe^{3+}] = 0.67 × 10^{-4} M, H_2O_2 = 2.5 mL, Lig. Int. = 70.0 mW cm^{-2}; **PF:** [GV] = 2 × 10^{-4} M, Lig. Int.= 70.0 mW cm^{-2}, [Fe^{3+}] = 0.50 × 10^{-4} M, H_2O_2 = 2.5 mL; **PF (< 10^0C):** [GV] = 2 × 10^{4} M, [Fe^{3+}] = 1.0 × 10^{-4} M, H_2O_2 = 3.5 mL, Lig. Int.= 70.0 mW cm^{-2}; **SOP:** [GV] = 2 × 10^{-4} M, Lig. Int.= 70.0 mW cm^{-2}}

	SPF	PF	PF (< 10^0C)	SOP
	$\kappa \times 10^5\ s^{-1}$	$\kappa \times 10^5\ s^{-1}$	$\kappa \times 10^5\ s^{-1}$	$\kappa \times 10^5\ s^{-1}$
3.2	33.69	25.23	5.3	16.56
3.5	48.96	40.04	8.05	33.78
3.8	**90.05**	41.83	9.17	**67.57**
4.0	46.25	**44.34**	**10.39**	39.07
4.2	38.61	42.43	7.13	37.64
4.5	26.32	37.29	5.63	16.48

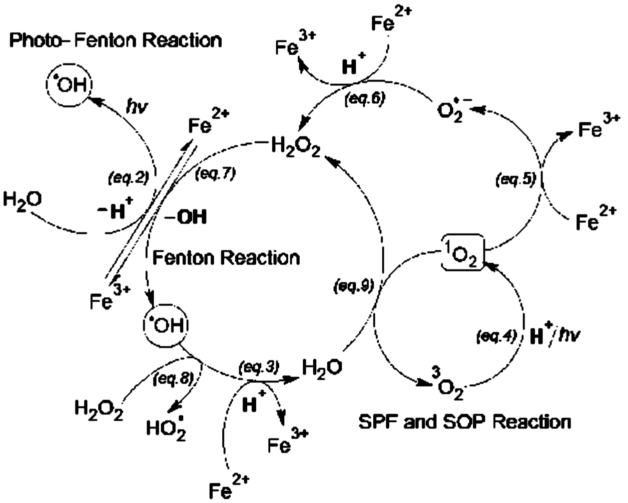


Fig. 4: Effect of pH on the singlet-photo-Fenton reaction of photochemical degradation of gentian violet.

The increase in pH of the medium favors eq. 2 where H^+ ions are formed along with •OH radicals. Here, the effect of common ion (H^+ ions) is decreased and therefore, the rate of this reaction is increased. These H^+ ions (formed in eq. 2) excite triplet molecular oxygen ($^3O_2$) into singlet molecular oxygen ($^1O_2$) (eq. 4). This singlet molecular oxygen accepts an electron from Fenton reaction (eq. 1) and these processes form superoxide radical anion ($O_2^{\bullet-}$) (eq. 5). This $O_2^{\bullet-}$ converted into H_2O_2 in presence of H^+ ion and electron from Fenton reaction (eq. 6). H_2O_2 is also generated through eq. 9. Both these reactions increase the rate of photochemical degradation.

$$Fe^{+2} + H_2O_2 \longrightarrow Fe^{+3} + {}^{\bullet}OH + OH^- + e^- \quad ....(eq.1)$$

After the optimum value, the concentration of H^+ ions decreases on further increasing pH. Therefore, the rates of reactions of eqs. 4-6 are decreased. These are cyclic reactions, and as the rate of these reactions decreases, the formation of H_2O_2 decreases. Ultimately, the rate of Fenton reaction (eq. 7) decreases. Simultaneously, H^+ ions react with •OH and electron form H_2O (eq. 3) and H_2O_2 react with •OH form $HO_2^{\bullet}$ (eq. 8) also decreases the rate of reaction. Both these factors retard the rate of photochemical degradation. The participation of different radicals in these variations may be explained by the following reactions.

Effect of Amount of Hydrogen Peroxide

The effect of the amount of hydrogen peroxide on the photochemical degradation of GV was also investigated. The effect of H_2O_2 in different variations SPF, PF and PF (< 10^0C) is shown in Table 3.

It was observed that the reaction rate increases on increasing the amount of H_2O_2, attaining an optimum value of H_2O_2 (2.5 mL) for the SPF and PF reactions. Thereafter, the rate of degradation decreases on increasing the amount of H_2O_2 above 2.5 mL. It can be explained on the basis that as the amount of H_2O_2 was increased more molecule are available for Fe^{2+} ions to react, which increases the number of •OH radicals. After the optimum value, rate of reaction was decreased. It is because of the fact that as the amount of H_2O_2 was increased rate of reactions of eq. 16 and the eq. 18 increase in the photo-Fenton reaction. According to equation eq. 16, •OH radicals are consumed rapidly due to more availability of H_2O_2 molecules and in eq. 18, $HO_2^{\bullet}$ radicals rapidly react with Fe^{3+} and form Fe^{2+}, O_2 and H^+ ion.

But in the SPF process, some additional cyclic reactions of singlet oxygen (eq. 10-13) also increases the rate of reaction, wherein H_2O_2 are generated and these reactions maintain the concentration of hydrogen peroxide.

It was also observed that the reaction rate decreases on increasing the amount of H_2O_2, attaining a minimum value of H_2O_2 (2.0 mL) for PF (< 10^0C) reaction. Thereafter, the rate of degradation increases on increasing the amount of H_2O_2 above 2.0 mL. It can be explained on the basis that the rate of reaction of Fe^{2+} with H_2O_2 (eq. 14) was very slow at low temperature. Due to the low temperature i.e. below 10^0C, the lifetime of •OH radical is increased and in Fenton reaction (eq. 14) the formation of ˙OH radicals also decreases.

Table 3: Effect of Amount of Hydrogen Peroxide: {**SPF:** [GV] = 2×10^{-4} M, [Fe^{3+}] = 0.67×10^{-4} M, pH = 3.8, Lig. Int. = 70.0 mW cm^{-2}; **PF:** [GV] = 2×10^{-4} M, Lig. Int.= 70.0 mW cm^{-2}, [Fe^{3+}] = 0.50×10^{-4} M, pH = 4.2; **PF (< 10⁰C):** [GV] = 2×10^{-4} M, [Fe^{3+}] = 1.0×10^{-4} M, pH = 4.0, Lig. Int.= 70.0 mW cm^{-2}}

H_2O_2(mL)	SPF	PF	PF(<10°c)
	$\kappa \times 10^5\ s^{-1}$	$\kappa \times 10^5\ s^{-1}$	$\kappa \times 10^5\ s^{-1}$
0.5	12.82	23.64	5.61
1.0	30.25	26.10	4.86
1.5	42.87	29.26	3.83
2.0	53.36	29.96	3.6
2.5	**90.05**	**44.34**	4.41
3.0	68.19	37.66	6.15
3.5	55.11	35.79	**10.39**

As the lifetime of ˙OH radical increases, it not only reacts with dye molecule, but it also reacts with proton (H^+) in presence of electron (eq. 17) and form a water molecule. The reaction of H_2O_2 with ˙OH radical (eq. 16) decreased the rate of reaction by consuming the active species ˙OH radical. As a consequence, the rate of PF (< 10⁰C) decreases. After the minimum value (2.0 mL), the rate of reaction of Fenton reaction (eq. 14) increases with increasing the amount of H_2O_2. Therefore, the rate of reaction was increased with increasing the amount of H_2O_2.

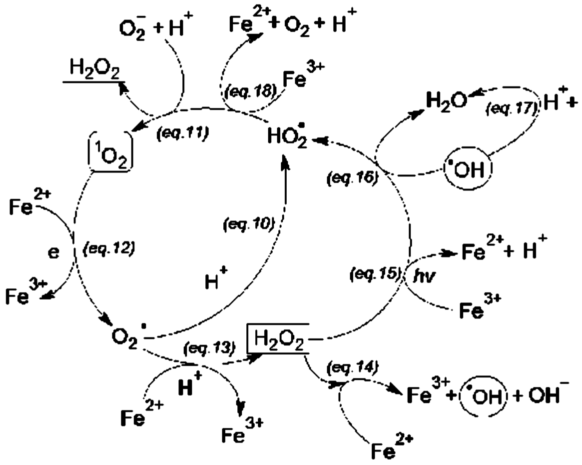


Fig. 5: Effect of amount of hydrogen peroxide on the photochemical degradation of gentian violet.

Effect of Dye Concentration

Effect of variation of dye concentration on the reaction rate was also studied by taking different concentrations of GV solutions. The results are given in Table 4.

Table 4: Effect of Dye Concentration: {**SPF:** H_2O_2 = 2.5 mL, [Fe^{3+}] = 0.67×10^{-4} M, pH = 3.8, Lig. Int = 70.0 mW cm^{-2}; **PF:** H_2O_2 = 2.5 mL, Lig. Int.= 70.0 mW cm^{-2}, [Fe^{3+}] = 0.50×10^{-4} M, pH = 4.2; **PF (< 10⁰C):** H_2O_2 = 3.5 mL, [Fe^{3+}] = 1.0×10^{-4} M, pH = 4.0, Lig. Int.= 70.0 mW cm^{-2}; **SOP:** pH = 3.8, Lig. Int.= 70.0 mW cm^{-2}}

[GV]×10⁴ M	SPF	PF	PF (< 10⁰C)	SOP
	$\kappa \times 10^5\ s^{-1}$	$\kappa \times 10^5\ s^{-1}$	$\kappa \times 10^5\ s^{-1}$	$\kappa \times 10^5\ s^{-1}$
1.00	25.91	31.79	**10.39**	18.11
1.33	55.44	34.02	8.04	23.62
1.67	68.59	36.59	6.51	45.53
2.00	**90.05**	**44.34**	4.43	**67.57**
2.33	63.33	37.59	1.2	13.37
2.67	49.78	31.41	0.64	4.06
3.00	43.07	26.63	0.63	3.77
3.33	36.02	22.05	0.19	2.86

The rate of dye degradation in all variations SPF, PF and for singlet molecular oxygen increases with increasing concentration of dye up to 2.0×10^{-4} M and in PF (< 10⁰C) up to 1.0×10^{-4} M. On further increasing its concentration, a sudden decrease in the rate of degradation was observed.

It may be attributed to the fact for the PF and PF (< 10⁰C), as the concentration of dye was increased, more dye molecules were available for excitation and hence, there was an increase in the rate of reaction. In SPF and SOP reactions, the concentration of dye was increased; more dye molecules were available for excitation followed by inter-system crossing.

$$Dye_o \xrightarrow{h\nu} {}^1_1Dye^{\bullet} \qquad \ldots(eq.19)$$

$$^1_1Dye^{\bullet} \xrightarrow{ISC} {}^3_1Dye^{\bullet} \qquad \ldots(eq.20)$$

$$^3O_2 + {}^3_1Dye^{\bullet} \longrightarrow {}^1_0Dye + {}^1O_2 + {}^1\Delta_g \text{ or } \Sigma_g \ldots(eq.21)$$

Hence, there was an increase in the rate. On further increasing the concentration of dye resulted in a decrease in the rate of reaction.

This may be explained on the basis that at higher concentrations the dye starts acting as an internal filter for the incident light and it does not permit the desired light intensity to reach the particles and the rate of photochemical degradation of dye decreases in all variations.

Effect of Ferric ion Concentration

The effect of concentration of Fe^{3+} ions on the rate of photochemical degradation of GV using PF, PF (< 10^0C) and SPF reactions was observed by keeping all other factors identical. The results are summarized in Table 5.

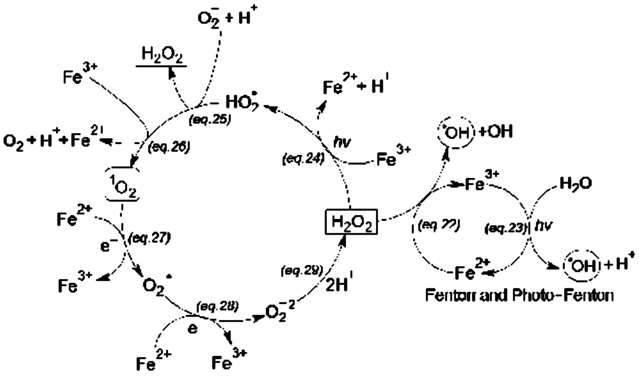


Fig. 6: Effect of Fe^{3+} ions on the singlet-photo-Fenton process of photochemical degradation of gentian violet.

It is clear from the data in the table that the rate of degradation increases with increasing the concentration of Fe^{3+} ions for SPF and PF up to 0.67×10^{-4} M, and for PF (< 10^0C) up to 1.0×10^{-4} M. This may be explained on the basis that with the increasing the Fe^{3+} concentration, there will be enhanced generation of $^{\bullet}OH$ radicals (eq. 22 and eq. 23); as a consequence, the rate of degradation of dye also increases. However, on increasing the concentration of Fe^{3+} ions further, the rate of the reactions was found to decrease. This is because of the fact that the concentration of Fe^{+3} was increased above its optimum concentration, the rate of reaction of $HO_2^{\bullet}$ with Fe^{+3} ion (eq. 26) becomes very fast, wherein a less reactive O_2 was generated, instead of (eq. 25) in which two reactive compounds $^1O_2$ and H_2O_2. At higher concentrations, Fe^{3+} ions also imparts a yellow color to the solution and at larger concentrations, it may act as a filter for the incident light.

Table 5: Effect of Ferric Ion Concentration: {SPF: [GV] = 2×10^{-4} M, H_2O_2 = 2.5 mL, pH = 3.8, Lig. Int. = 70.0 mW cm^{-2}; **PF:** [GV] = 2×10^{-4} M, Lig. Int.= 70.0 mW cm^{-2}, H_2O_2 = 2.5 mL, pH = 4.2; **PF (< 10^0C):** [GV] = 2×10^{-4} M, H_2O_2 = 3.5 mL, pH = 4.0, Lig. Int.= 70.0 mW cm^2}

$[Fe^{3+}] \times 10^4$ M	SPF	PF	PF (< 10^0C)
	$\kappa \times 10^5\ s^{-1}$	$\kappa \times 10^5\ s^{-1}$	$\kappa \times 10^5\ s^{-1}$
0.17	55.56	18.21	4.79
0.33	68.89	18.90	5.22
0.50	85.22	**44.34**	5.39
0.67	**90.05**	27.84	6.17
0.83	54.46	25.38	6.64
1.00	46.64	24.38	**10.39**

But in the SPF an extra path of cyclic reactions of singlet oxygen (eq. 24 to eq. 29) supports the PF reactions. Therefore, rates of cyclic reaction of singlet oxygen are also increased with increasing concentration of Fe^{3+} ions, and as a result, more H_2O_2 is generated. Therefore, the rate of reaction for photochemical oxidation of GV is higher than PF and PF (< 10^0C).

Effect of Light Intensity

The effect of light intensity on the SPF, PF, PF (< 10^0C) and SOP was also investigated. The results obtained are reported in Table 6.

Table 6: Effect of Light Intensity: {SPF: [GV] = 2×10^{-4} M, H_2O_2 = 2.5 mL, pH = 3.8, $[Fe^{3+}]$ = 0.67×10^{-4} M; **PF:** [GV] = 2×10^{-4} M, $[Fe^{3+}]$ = 0.67×10^{-4} M, H_2O_2 = 2.5 mL, pH = 4.2; **PF (< 10^0C):** [GV] = 2×10^{-4} M, H_2O_2 = 3.5 mL, pH = 4.0, $[Fe^{3+}]$ = 0.67×10^{-4} M; **SOP:** [GV] = 2×10^{-4} M, pH = 3.8}

Light Intensity (mW cm^{-2})	SPF	PF	PF (< 10^0C)	SOP
	$\kappa \times 10^5\ s^{-1}$	$\kappa \times 10^5\ s^{-1}$	$\kappa \times 10^5\ s^{-1}$	$\kappa \times 10^5\ s^{-1}$
8.2	29.9	19.90	2.23	14.44
15.6	39.25	25.88	2.33	21.92
22.1	41.11	25.91	4.08	23.33
31.4	56.08	29.99	4.21	24.75
39.2	61.24	34.34	5.18	26.72
45.3	81.36	35.10	6.01	30.91
57.5	83.35	36.21	6.03	51.41
70.0	**90.05**	**44.34**	**10.39**	**67.57**

Plots of the rate constant versus light intensity were in increasing order, 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 in SPF, PF, PF (< 10^0C) but in SOP, these photons react with dye molecules ($_0Dye$) and converts it into triplet excited dye molecule ($^3{}_1Dye\bullet$) via singlet excited dye molecule ($^1{}_1Dye\bullet$)(eq. 19-21), and as a result, increased numbers of active species, the hydroxyl radicals and singlet molecular oxygen ($^1O_2$) are formed. Therefore, an overall increase in the rate of reaction was observed.

Mechanism

On the basis of experimental observations and corroborating the existing literature, a tentative mechanism has been proposed for photochemical degradation of GV with SPF, PF, PF (< 10^0C) and SOP.

Dye Sensitization and Formation of Singlet Molecular Oxygen:

$${}^{1}_{0}\mathrm{Dye} \xrightarrow{h\nu} {}^{1}_{1}\mathrm{Dye}\bullet \qquad \ldots(\text{eq. } 19)$$

$${}^{1}_{1}\mathrm{Dye}\bullet \xrightarrow{\mathrm{ISC}} {}^{3}_{1}\mathrm{Dye}\bullet \qquad \ldots(\text{eq. } 20)$$

$${}^{3}O_2 + {}^{3}_{1}\mathrm{Dye} \longrightarrow {}^{1}_{0}\mathrm{Dye} + {}^{1}O_2 + {}^{1}\Delta_g \text{ or } \Sigma_g \quad \ldots(\text{eq. } 21)$$

Cyclic Reactions of Singlet-photo-fenton Reaction:

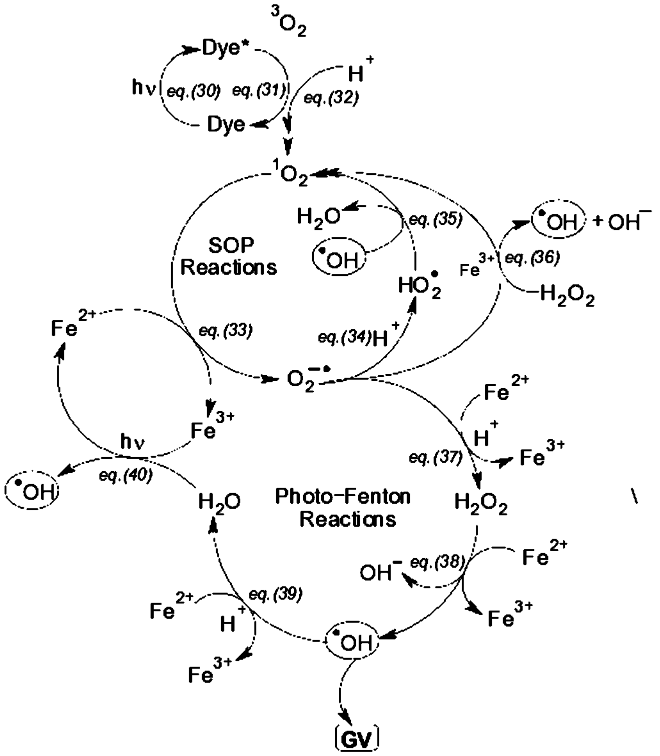


Fig. 7: Some cyclic reactions of SOP, PF, PF (< 10^0C) and SPF.

Some Other Important Reactions:

$$e^{2+} + H_2O_2 \longrightarrow Fe^{+3} + {}^{\bullet}OH + OH^- + e^- \quad \ldots(\text{eq. } 41)$$

$$Fe^{3+} + H_2O_2 + h\nu \longrightarrow Fe^{+2} + HO_2^{\bullet} + H^+ \ldots(\text{eq. } 42)$$

$${}^{\bullet}OH + H_2O_2 \longrightarrow H_2O + H^+ + O_2^{-\bullet} \quad \ldots(\text{eq. } 43)$$

$${}^{\bullet}OH + H_2O_2 \longrightarrow HO_2^{\bullet} + H_2O \quad \ldots(\text{eq. } 44)$$

$$HO_2^{\bullet} + O_2 + H^+ \longrightarrow {}^{1}O_2 + H_2O_2 \quad \ldots(\text{eq. } 45)$$

$$2\,{}^{1}O_2 + 2\,H_2O \longrightarrow {}^{3}O_2 + 2\,H_2O_2 \quad \ldots(\text{eq. } 46)$$

$${}^{3}O_2 + H^+ + e^- \longrightarrow O_2^{-\bullet} \quad \ldots(\text{eq. } 47)$$

$$H_2O_2 + H^+ + e^- \longrightarrow {}^{\bullet}OH + H_2O \quad \ldots(\text{eq. } 48)$$

$$O_2^{-\bullet} + e^- \longrightarrow O_2^{2-} \quad \ldots(\text{eq. } 49)$$

$$O_2^{2-} + 2\,H^+ \longrightarrow 2\,H_2O_2 \quad \ldots(\text{eq. } 50)$$

$$H_2O_2 + h\nu \longrightarrow 2\,{}^{\bullet}OH \quad \ldots(\text{eq. } 51)$$

$$2\,HO_2^{\bullet} \longrightarrow H_2O_2 + {}^{1}O_2 \quad \ldots(\text{eq. } 52)$$

GV absorbs radiation of a suitable wavelength and goes to the its first excited state. It then undergoes intersystem crossing (ISC) to the triplet excited state of the dye. This triplet state gives its energy to the triplet molecular oxygen and this becomes excited singlet molecular oxygen, and dyes molecule return to its singlet state (eq. 30-32).

This singlet molecular oxygen further under goes a cyclic reaction, where different reactive species are formed completing the reaction of SOP (eq. 33-35). In this SOP reaction, superoxide anion radical formed (eq. 33) react with H^+ ion and form another reactive species $HO_2^{\bullet}$ which helps to generate $^1O_2$ by reacting with $^{\bullet}$OH radical (eq. 35). The reactions of superoxide anion with the hydrogen peroxide provides even more strong oxidizing agent $^{\bullet}$OH and $^1O_2$; this Haber-Weiss cycle can be catalyzed by Fe^{3+} ions (eq. 36) [27].

$HO_2^{\bullet}$ radicals are highly unstable in water and undergo facile disproportion rather than reacting slowly with dye molecules. As well as formed superoxide anion radical ($O_2^{-\bullet}$) goes into another cyclic reaction. This radical reacts with H^+ and an electron to form H_2O_2 (eq. 37). It is a strong oxidizing agent, which plays an important role for dye degradation in photo-Fenton reaction. It generates $^{\bullet}$OH radical by reaction with the Fe^{2+} ion. It is very reactive oxidizing species and completes photo-oxidation reaction of dye. There are two possibilities for the consumption of $^{\bullet}$OH radicals, (i) either, it reacts with ferrous ions and oxidizing it to ferric ions and H_2O or (ii) it may react with GV to give the colourless degradation products. This is a cyclic photo-Fenton reaction, (eq. 37-40). In eqs. 43, 44 and 47 superoxide radical anion ($O_2^{-\bullet}$) and perhydroxyl radicals ($HO_2^{\bullet}$) are produced, which can effectively oxidize bio-substrates [28], there can also generate hydrogen peroxide and singlet excited oxygen upon dismutation (eq. 45 & 52) [29].

The main advantage of using photo-Fenton's reagent is the regeneration of the consumed Fe^{+2} ions, which can produce more $^{\bullet}$OH radicals to make this process cyclic in nature. Hence, the high rate of reaction of dye degradation in SPF can be easily explained on the basis that it is a synergetic effect of both the reactions, SOP and PF. Where, both these reactions generate hydroxyl radicals.

Therefore, in SPF, more hydroxyl radicals attack dye molecules to completely mineralize dye into CO_2 and H_2O.

IV. CONCLUSION

Ordinary water from industries, process house, etc. is accompanied by hazardous dye contents, which adds to environmental pollution. The present work provides a facile route for degradation process, i.e. singlet-photo-Fenton process. The photochemical degradation of gentian violet using singlet molecular oxygen, photo-Fenton reagent (PF), photo-Fenton reagent (PF) below 10^0C and singlet oxygen process (SOP) were compared. The result showed that singlet-photo-Fenton process is better photo oxidizing process as compared to the PF, PF(<10^0C) and SOP, because more $OH^{\cdot}$ radicals are formed comparatively to PF and SOP. The photochemical oxidation of dye by the singlet-photo-Fenton process is an eco-friendly route and the rate of the reaction may be increased which will make this process commercially viable.

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