

A Comparative Study of Photocatalytic Degradation of Methylene Blue in Presence of some Transition Metal Complexes and Hydrogen Peroxide

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Abstract : Advanced methods are in demand for removal of persistent organic pollutants from waste water and ground water. Photocatalysis can be a useful tool in the treatment of some recalcitrant and toxic pollutants. In fact, it is being applied today in several industrial processes. Photocatalytic degradation of methylene blue (MB) by thiocyanate complexes of iron (III), copper (II) and cobalt (II) and hydrogen peroxide was reported. The effect of different parameters, such as pH, concentration of the complexes and dye, amount of H₂O₂ and light intensity on the rate of photocatalytic degradation of MB was investigated. The disappearance of organic molecule was observed spectrophotometrically and it follows first-order kinetics. A tentative mechanism for the degradation of dye has also been proposed.

Keywords: Photocatalytic degradation; methylene blue; metal complexes; hydrogen peroxide.

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Introduction

Water is a basic requirement for all living beings. Population increase and industrialization led to water pollution. One of the pollutants of water is the dye effluents from various textile industries. In an industrialized world the issue of degradation of pollutants has become very serious from ecological point of view. Textiles, tannery, paper, pulp and printing industries are the biggest polluters of the environment. The effluents from these industries are highly colored, complex and toxic. Several methods of treatment of effluents have been employed from time to time, the most common of which are chemical precipitation and biological methods. However, these methods suffer from many disadvantages like chemical handling, sludge disposal and long term biodegradation.

Colored solution containing dyes from industrial effluents may cause skin cancer due to photosensitization and photodynamic damage. On the contrary, bleached dye solution is non-toxic and harmless. Secondly, water containing colored dye is of no use, but if this colored solution is bleached to give colorless water, then it may be used for washing, cooling, irrigation and cleaning

purposes. Therefore, removal of these toxic substances from waste water is necessary. A number of methods have been used to remove these dyes from polluted water like adsorption, chemical transformation etc., but photocatalytic degradation seems to be the most promising technique, since it is of low cost and less time consuming.

Photochemical degradation of dyes employing Fenton reagent provides a method for the treatment of waste water containing dyes effluents. Fenton reaction involves the formation of hydroxyl and perhydroxyl radicals. Fenton reagent is an established reagent for degradation of dyes but the main demerit of the reagent is that the reaction stops after complete consumption of Fe²⁺ ions, whereas, in photo-Fenton reaction, Fe²⁺ ions are regenerated from Fe³⁺ ions in the presence of light. This makes the process cyclic in nature and photochemical degradation proceeds smoothly.

Recently, several reports on the photocatalytic degradation of dyes and organic pollutants have been published. Legrini *et al.* [1] reported the photochemical process for water treatment. Jain *et al.* [2] investigated the

photocatalytic removal of hazardous dye cyanosine from industrial waste using titanium dioxide. Rehman *et al.* [3] studied the degradation of commercial textile dye by Fenton's reagent under xenon beam irradiation in aqueous medium. Photochemical reaction between rose bengal and benzophenone was given by Kataria *et al.* [4]. ALzaydien *et al.* [5] reported the adsorption of methylene blue from aqueous solution onto a low – cost natural joraianian Tripoli. Chen *et al.* [6] investigated the photo-Fenton degradation of malachite green catalyzed by aromatic compounds under visible light irradiation. Xie *et al.* [7] studied the photoassisted degradation of dyes in the presence of Fe^{3+} and H_2O_2 under visible irradiation. Photocatalytic degradation of direct Yellow 12 dye using UV/ TiO_2 in a shallow pond slurry reactor was studied by Toor *et al.* [8]. Bandala *et al.* [9] reported the degradation of 2,4-dichlorophenoxyacetic acid (2,4-D) using cobalt-peroxymonosulphate in Fenton-like process. Comparative photocatalytic studies of degradation of a cationic and an anionic dye was done by Hasnat *et al.* [10]. Duarte *et al.* [11] observed the Fenton-like degradation of azo-dye Orange II catalyzed by transition metals on carbon aerogels. Garcia *et al.* [12] investigated the comparative study of the degradation of real textile effluents by photocatalytic reactions involving UV/ $\text{TiO}_2/\text{H}_2\text{O}_2$ and UV/ $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ systems. Photodegradation of acid red 114 dissolved using a Photo-Fenton process with TiO_2 was carried out by Lee *et al.* [13].

Methylene blue was selected as a model compound for the present study because large intravenous doses of methylene blue produces nausea, abdominal and precordial pain, dizziness, headache, profuse swelling, sweating and mental confusion. Many scientist bleached this dye by various processes, but no attention has been paid to the photocatalytic degradation of methylene blue in presence of metal complexes such as $[\text{Fe}(\text{SCN})]^{2+}$, $[\text{Cu}(\text{SCN})]^+$, $[\text{Co}(\text{SCN})]^+$ and H_2O_2 . A comparative study of these complexes on photocatalytic degradation of methylene blue is reported. The method is very effective and economical and it has the additional advantage of a very fast degradation rate.

Experimental details

The photochemical degradation of methylene blue (REIDEL) was studied in the presence of a transition metal complex, i.e., $[\text{Fe}(\text{SCN})]^{2+}$, $[\text{Cu}(\text{SCN})]^+$ or $[\text{Co}(\text{SCN})]^+$, H_2O_2 and light. A stock solution of methylene blue (1.0×10^{-3} M) was prepared in doubly distilled water. The Complex $[\text{Fe}(\text{SCN})]^{2+}$ was prepared by mixing FeCl_3 (1.0×10^{-3} M, Himedia) and KSCN (1.0×10^{-3} M, Himedia) in a 1:1 ratio. The $[\text{Cu}(\text{SCN})]^+$ and $[\text{Co}(\text{SCN})]^+$ complexes were prepared in a similar manner. H_2O_2 (30%, Merck) was a commercial product and was used as received. The reaction mixture containing dye (10^{-5} M), complex (10^{-6} M) and hydrogen peroxide was exposed to light for a certain duration depending on the complex used. A 200 W tungsten lamp (Philips) was used for the irradiation. The intensity of the light at various distances was measured by a "Suryamapi" (CEL Model 201). The pH of the solution was measured using a digital pH meter (Systronics Model 335). The desired pH of the solution was adjusted by the addition of previously standardised 0.050 M sulphuric acid and 1.0 M sodium hydroxide solutions. A visible spectrophotometer (Systronics Model 106) was used for measuring the absorbance of the reaction mixture at regular time intervals.

Results and Discussion

An aliquot of 3.0 mL was taken out from the reaction mixture at regular time intervals and the absorbance was measured spectrophotometrically at $\lambda_{\text{max}} = 665$ nm. It was observed that the absorbance of the solution decreases with increasing time intervals, which indicates that the concentration of methylene blue decreases with increasing time of exposure. A plot of $2 + \log A$ versus time was linear and follows pseudo-first order kinetics. The rate constant was calculated using the following expression: $k = 2.303 \times \text{Slope}$

The data for this typical run are given in Table 1.

For iron complex/ H_2O_2 system, the reaction proceeded in two stages. The first stage was an induction period [14], in which radicals were generated, whereas the major degradation of the dye occurred in the second step, as shown by the sharp decrease in the absorbance.

TABLE-1
Typical Run

Time [min.]	[Fe(SCN)] ²⁺ / H ₂ O ₂ System [Methylene Blue]= 0.87×10 ⁻⁵ M H ₂ O ₂ = 0.2 ml Complex = 4.37×10 ⁻⁶ M Light Intensity = 60 mw cm ⁻² pH = 3.0		[Cu(SCN)] ⁺ / H ₂ O ₂ System [Methylene Blue]= 1.0×10 ⁻⁵ M H ₂ O ₂ = 0.3 ml Complex = 4.37×10 ⁻⁶ M Light Intensity = 70 mw cm ⁻² pH = 8.5		[Co(SCN)] ⁺ / H ₂ O ₂ System [Methylene Blue]= 1.0×10 ⁻⁵ M H ₂ O ₂ = 0.3 ml Complex = 4.37×10 ⁻⁶ M Light Intensity = 60 mw cm ⁻² pH = 8.0	
	Absorbance (A)	2 + log A	Absorbance (A)	2 + log A	Absorbance (A)	2 + log A
0.0	0.661	1.8202	0.490	1.6902	0.490	1.6902
5.0	0.631	1.8000	0.427	1.6304	0.437	1.6405
10.0	0.603	1.7803	0.381	1.5809	0.399	1.6010
15.0	0.590	1.7709	0.340	1.5315	0.398	1.5999
20.0	0.525	1.7202	0.300	1.4771	0.347	1.5403
25.0	0.500	1.6990	0.258	1.4116	0.339	1.5302
30.0	0.448	1.6513	0.224	1.3502	0.332	1.5211
35.0	0.408	1.6107	0.199	1.2989	0.324	1.5105
40.0	0.364	1.5611	0.187	1.2718	0.317	1.5011
45.0	0.324	1.5105	0.159	1.2014	0.302	1.4800
50.0	0.302	1.4800	0.135	1.1303	0.289	1.4609
55.0	0.252	1.4014	0.126	1.0212	0.270	1.4314
60.0			0.105	1.0040		
	k ₁ =1.92×10 ⁻⁴ (s ⁻¹) k ₂ =5.76×10 ⁻⁴ (s ⁻¹)		k=6.91×10 ⁻⁴ (s ⁻¹)		k=9.98×10 ⁻⁴ (s ⁻¹)	

1. Effect of pH

The effect of pH on photocatalytic degradation was investigated in the pH range 1.5 – 4.5, 5.5 – 8.5, and 4.5 – 8.0 for iron, copper and cobalt complexes, respectively. The results are reported in Table 2.

The Photochemical degradation of methylene blue was maximum at pH 3.0, 8.5 and 8.0 for iron, copper and cobalt complexes, respectively. The photochemical degradation depends strongly on the pH of the reaction medium. In case of iron complex, it was observed that the rate of degradation of dye increased on decreasing pH from 4.5 to 3.0. This may be due to dominance of

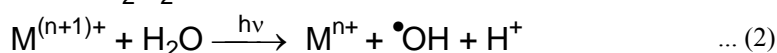
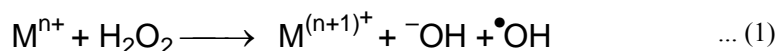
eq. (1) over eq. (2), where OH⁻ ions are generated. These OH⁻ ions are removed by increasing H⁺ ion concentration on decreasing pH. This will facilitate the eq. (1) forming more •OH radicals, which will be utilized for oxidative degradation of methylene blue as well as thiocyanate radical. On decreasing the pH further i.e. below 3.0, the reaction rate decreases again. It may be attributed to the fact that eq. (2) starts dominating over eq. (1) as Fe(OH)₃ is less soluble than Fe(OH)₂ and generation of •OH radicals by eq. (2) is retarded at lower pH than 3.0 [15].

TABLE – 2
Effect of pH

pH	[Fe(SCN)] ²⁺ / H ₂ O ₂ System [Methylene Blue]= 0.87×10 ⁻⁵ M H ₂ O ₂ = 0.3 mL Complex = 8.75×10 ⁻⁶ M Light Intensity = 60 mW cm ⁻²		[Cu(SCN)] ⁺ / H ₂ O ₂ System [Methylene Blue]= 1.0×10 ⁻⁵ M H ₂ O ₂ = 0.3 mL Complex = 8.75×10 ⁻⁶ M Light Intensity = 70 mW cm ⁻²		[Co(SCN)] ⁺ / H ₂ O ₂ System [Methylene Blue]= 1.0×10 ⁻⁵ M H ₂ O ₂ = 0.3 mL Complex = 8.75×10 ⁻⁶ M Light Intensity = 60 mW cm ⁻²	
	k ₁ ×10 ⁴ (s ⁻¹)	k ₂ ×10 ⁴ (s ⁻¹)	k × 10 ⁴ (s ⁻¹)		k × 10 ⁴ (s ⁻¹)	
1.5	0.85	0.49	–		–	
2.0	0.99	0.81	–		–	
2.5	1.50	3.45	–		–	
3.0	1.92	5.76	–		–	
3.5	1.00	2.03	–		–	
4.0	0.80	0.93	–		–	
4.5	0.72	0.85	–		0.66	
5.0	–	–	–		0.80	
5.5	–	–	0.98		0.93	
6.0	–	–	1.32		1.06	
6.5	–	–	1.38		1.86	
7.0	–	–	2.03		5.32	
7.5	–	–	2.88		7.32	
8.0	–	–	5.76		9.98	
8.5	–	–	6.91		–	

In the case of copper and cobalt complexes, reaction proceeds faster in basic medium. This may be due to dominance of eq. (2) over eq. (1), for copper complex and cobalt complex system, respectively, where H⁺ ions are generated. These H⁺ ions are removed by increasing OH⁻ concentration on increasing pH. This will facilitate eq. (2), for copper complex and cobalt complex system, respectively forming more •OH

increases continuously up to 0.7 mL H₂O₂ in the case of cobalt complex systems respectively. This may be explained on the basis that increasing the amount of H₂O₂ will provide more •OH radicals responsible for oxidative degradation of methylene blue. But after a fixed amount of H₂O₂ (0.2 and 0.3 mL) further increase in amount of H₂O₂ will produce more •OH ion along with •OH radicals and as a result, the pH of the medium



radicals, which will be utilized for oxidative degradation of methylene blue as well as thiocyanate radical.

It was not possible to measure the reaction rate for pH above 8.5 and 8.0 for copper and cobalt complex systems, respectively due to formation of some colloidal particles in the reaction mixture.

2. Effect of hydrogen peroxide

The effect of amount of H₂O₂ on the rate of photocatalytic degradation of methylene blue was also investigated. The results are reported in Table 3. The photochemical degradation of methylene blue was maximum at 0.2 mL and 0.3 mL for iron and copper complexes, but the rate

increases, resulting in a decrease in the rate of degradation in case of iron and copper complex.

A different kind of behaviour in [Co(SCN)]⁺/H₂O₂/methylene blue system was observed. In this case a continuous increase in the rate of degradation of methylene blue was observed on increasing the amount of H₂O₂ from 0.0 to 0.7 mL. It may be attributed to the fact that eq. (2) dominance over eq. (1) therefore, the H⁺ ions which are generated, are removed by increasing OH⁻ concentration on increasing amount of H₂O₂. This will facilitate the eq. (2), forming more •OH radicals, and due to this, rate of reaction increases on increasing the amount of H₂O₂.

TABLE-3
Effect of H₂O₂

H ₂ O ₂ [mL]	[Fe(SCN)] ²⁺ / H ₂ O ₂ System [Methylene Blue]= 0.87×10 ⁻⁵ M Complex = 8.75×10 ⁻⁶ M Light Intensity = 60 mW cm ⁻² pH = 3.0		[Cu(SCN)] ⁺ / H ₂ O ₂ System [Methylene Blue]= 1.0×10 ⁻⁵ M Complex = 8.75×10 ⁻⁶ M Light Intensity = 70 mW cm ⁻² pH = 8.5		[Co(SCN)] ⁺ / H ₂ O ₂ System [Methylene Blue]= 1.0×10 ⁻⁵ M Complex = 8.75×10 ⁻⁶ M Light Intensity = 60 mW cm ⁻² pH = 8.0	
	k ₁ ×10 ⁴ (s ⁻¹)	k ₂ ×10 ⁴ (s ⁻¹)	k × 10 ⁴ (s ⁻¹)		k × 10 ⁴ (s ⁻¹)	
0.0	0.35	1.10	2.05		1.17	
0.1	0.50	1.73	3.41		8.22	
0.2	1.92	5.76	6.14		8.81	
0.3	1.51	4.94	6.91		9.98	
0.4	1.10	4.52	5.12		10.57	
0.5	0.98	3.28	4.38		11.15	
0.6	0.75	3.16	3.84		16.44	
0.7	0.60	3.00	3.41		17.05	

3. Effect of concentration of complexes

The effect of concentration of complexes on the rate of photocatalytic degradation of methylene blue was observed by keeping all other factors identical. The results are reported in Table 4.

It is clear from the data that the rate of photocatalytic degradation increases on increasing concentration of complexes. The rates were determined upto the concentration 8.75 × 10⁻⁶ M for all the three systems, because beyond

this limit the rates were extremely fast and it was not possible to record the observation correctly due to experimental limitations. This trend may be explained on the basis that on increasing the concentration of complexes more molecules of complexes were available to take part in reaction. This results in an enhanced generation of the •OH radicals and as a consequence the rate of photocatalytic degradation of dye also increases.

TABLE-4
Effect of complex concentration

Complex con.×10 ⁶ M	[Fe(SCN)] ²⁺ / H ₂ O ₂ System [Methylene Blue]= 0.87×10 ⁻⁵ M H ₂ O ₂ = 0.2 mL Light Intensity = 60 mW cm ⁻² pH = 3.0		[Cu(SCN)] ⁺ / H ₂ O ₂ System [Methylene Blue]= 1.0×10 ⁻⁵ M H ₂ O ₂ = 0.3 mL Light Intensity = 70 mW cm ⁻² pH = 8.5		[Co(SCN)] ⁺ / H ₂ O ₂ System [Methylene Blue]= 1.0×10 ⁻⁵ M H ₂ O ₂ = 0.3 mL Light Intensity = 60 mW cm ⁻² pH = 8.0	
	k ₁ ×10 ⁴ (s ⁻¹)	k ₂ ×10 ⁴ (s ⁻¹)	k × 10 ⁴ (s ⁻¹)		k × 10 ⁴ (s ⁻¹)	
0.00	0.25	0.33	0.92		1.28	
1.25	0.31	1.12	1.95		6.07	
2.25	0.49	2.16	3.24		6.33	
3.75	0.61	2.88	3.89		6.51	
5.00	0.95	3.35	4.42		6.94	
6.25	1.15	4.57	5.40		7.37	
7.50	1.70	5.40	6.08		7.81	
8.75	1.92	5.76	6.91		9.98	

TABLE-5
Effect of dye concentration

[Methylene Blue] × 10 ⁵ M	[Fe(SCN)] ²⁺ / H ₂ O ₂ System H ₂ O ₂ = 0.2 mL Complex = 8.75×10 ⁻⁶ M Light Intensity = 60 mW cm ⁻² pH = 3.0		[Cu(SCN)] ⁺ / H ₂ O ₂ System H ₂ O ₂ = 0.3 mL Complex = 8.75×10 ⁻⁶ M Light Intensity = 70 mW cm ⁻² pH = 8.5		[Co(SCN)] ⁺ / H ₂ O ₂ System H ₂ O ₂ = 0.3 mL Complex = 8.75×10 ⁻⁶ M Light Intensity = 60 mW cm ⁻² pH = 8.0	
	k ₁ ×10 ⁴ (s ⁻¹)	k ₂ ×10 ⁴ (s ⁻¹)	k × 10 ⁴ (s ⁻¹)		k × 10 ⁴ (s ⁻¹)	
0.50	–	–	6.14		–	
0.62	0.65	2.97	–		–	
0.75	1.01	3.48	6.52		7.48	
0.87	1.92	5.76	–		–	
1.00	1.15	2.38	6.91		9.98	
1.12	1.00	2.21	–		–	
1.25	0.85	2.09	4.61		8.32	
1.37	0.62	1.76	–		–	
1.50	0.45	1.00	4.22		7.48	
1.75	–	–	3.99		5.82	
2.00	–	–	3.84		5.41	
2.25	–	–	3.76		4.57	
2.50	–	–	–		3.65	

4. Effect of methylene blue concentration

The effect of methylene blue concentration on the rate of photochemical degradation was observed and the results are given in Table 5. The rate of degradation was found to increase with increasing concentration of methylene blue upto 0.87×10⁻⁵ M, 1.00×10⁻⁵ M and 1.00×10⁻⁵ M for [Fe(SCN)]²⁺, [Cu(SCN)]⁺ and [Co(SCN)]⁺ complexes, respectively. Further increase in concentration beyond these limits decreases the rate of degradation. This may be explained on the basis that on increasing the concentration of methylene blue, the reaction rate increases as more molecules of dyes were available for degradation, but further increase in concentration after certain limit causes retardation of reaction. It is because at the higher concentration, the dye molecules themselves act as filter for incident light, thus proper intensity of the light does not reach the molecules present in the interior of the reaction mixture, which results in decrease in rate of degradation. Moreover, at the higher concentration the number of collisions between dye molecules increases whereas, collision

between dye and •OH radicals decreases. As a consequence, rate of reaction is retarded.

Unfavorable steric orientation is also one of the major factors for the decrease of the rate of reaction [16, 17].

5. Effect of light intensity

The effect of light intensity on the photocatalytic degradation of methylene blue was investigated. The results are reported in Table 6.

The data indicate that an increase in the light intensity, increases the rate of reaction and maximum rates for iron, copper and cobalt complexes systems have been found at 60.0 mw cm⁻², 70.0 mw cm⁻² and 60.0 mw cm⁻² respectively. This may be explained on the basis that as the light intensity was increased, the number of photons striking per unit area also increased, resulting into a higher rate of degradation.

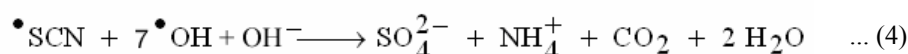
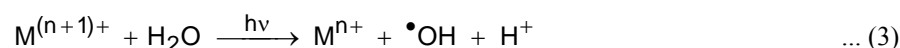
Further increase in the light intensity beyond this limit results in decrease in the rate of reaction.

TABLE-6
Effect of light intensity

Light intensity mW cm ⁻²	[Fe(SCN)] ²⁺ / H ₂ O ₂ System [Methylene Blue]= 0.87×10 ⁻⁵ M H ₂ O ₂ = 0.2 mL Complex = 8.75×10 ⁻⁶ M pH = 3.0		[Cu(SCN)] ⁺ / H ₂ O ₂ System [Methylene Blue] = 1.0×10 ⁻⁵ M H ₂ O ₂ = 0.3 mL Complex = 8.75×10 ⁻⁶ M pH = 8.5		[Co(SCN)] ⁺ / H ₂ O ₂ System [Methylene Blue]= 1.0×10 ⁻⁵ M H ₂ O ₂ = 0.3 mL Complex = 8.75×10 ⁻⁶ M pH = 8.0	
	k ₁ ×10 ⁴ (s ⁻¹)	k ₂ ×10 ⁴ (s ⁻¹)	k × 10 ⁴ (s ⁻¹)		k × 10 ⁴ (s ⁻¹)	
10.0	0.50	1.91	3.00		4.68	
20.0	0.75	2.30	5.11		5.63	
30.0	0.99	3.54	5.41		7.17	
40.0	1.25	3.84	5.71		7.80	
50.0	1.75	5.12	6.01		8.12	
60.0	1.92	5.76	6.31		9.98	
70.0	1.65	4.61	6.91		7.80	
80.0	1.45	3.84	4.80		6.86	

Mechanism

Based on the basis of the experimental observations and information in the existing literature a tentative mechanism has been proposed for the degradation of methylene blue in the presence of iron and copper complexes, H₂O₂ and light [18].



(Here M stands for iron and copper)

The above proposed mechanism is applicable for both iron and copper complexes.

In case of cobalt complex, following mechanism has been proposed.

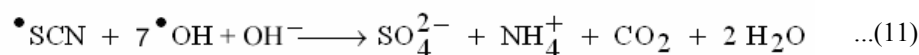
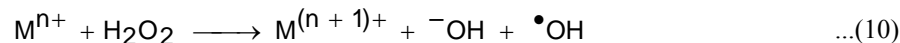
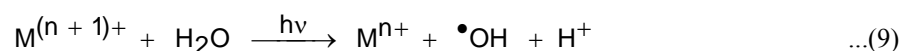
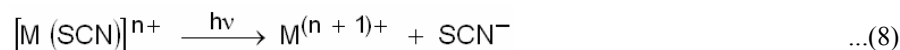




Photo-Fenton reaction is one of the examples of classical photocatalytic process in homogeneous system that involves H_2O_2 - iron (III) - visible radiations. The thiocyanate complex of Fe^{3+} gives Fe^{2+} and thiocyanate radical on exposure to light. Fe^{2+} ion decomposes hydrogen peroxide into $\bullet\text{OH}$ radical, OH^- ion and itself oxidized to Fe^{3+} ions. Fe^{3+} ion decompose water photochemically to give $\bullet\text{OH}$ radical and Fe^{2+} ions. Thiocyanate radical and dye are decomposed by hydroxyl radicals to simpler ions/molecules like sulphates ion and ammonium ions, carbon dioxide, water etc. Similar explanation applies for degradation of methylene blue by copper complex / H_2O_2 .

The mechanism for photocatalytic degradation of dye by cobalt complex differs from the mechanism for iron and copper complexes. In the case of cobalt complex, thiocyanate ion is involved, whereas in case of iron and copper complexes thiocyanate radical is formed. The release of thiocyanate ion from its cobalt complex was ascertained by its spot- test [19], however, the negative spot test of thiocyanate ion in the case of iron and copper complexes indicated that SCN^\bullet radicals are released in these reactions and not SCN^- ions.

Conclusion

The rate of photocatalytic degradation of methylene blue is enhanced by metal complexes. The increasing order of the rate with different metal complexes and Photo-Fenton reagent is as follows –



The hydroxyl radicals degrade the methylene blue. The participation of $\bullet\text{OH}$ radicals as an active oxidizing species was confirmed by using hydroxyl radical scavengers, like 2-propanol, where the rate of photodegradation was drastically reduced.

Further, this method has the more advantage over other methods, in that it does not add to further pollution. The active oxidizing species, the hydroxyl radicals, will dimerise to give hydrogen peroxide, which may degrade ultimately to water and oxygen.

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