Role of copper Schiff-base complex for Photocatalytic degradation of methylene blue under visible irradiation

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Abstract: This study was focused on the application of Schiff-base metal complex as a catalyst for the photocatalytic degradation of methylene blue (MB), which was used as a model compound. The photocatalytic degradation has been considered to be an efficient process for the degradation of organic pollutants, which are present in the effluents released by industries. The photocatalytic bleaching of cationic dye methylene blue was carried out under visible irradiation using Cu(II) complex of N,N'-disalicylaldehyde-1,3-propanediimine (Salpd). Photocatalytic degradation of methylene blue was examined using various parameters such as effect of catalyst concentration, effect of dye concentration, effect of addition of H_2O_2, effect of different pH conditions (5, 7, 9, and 11) and effect of time of irradiation. It was found that the efficiency of decolorization process increases with increasing the concentration of H_2O_2 until it reached to its critical value. The results demonstrated that 60 mg/50ml of Cu-Salpd was found to be optimum dose for maximum degradation of MB. It was found that catalyst exhibited better catalytic activity for degradation at acidic pH. The time of decoloration increased with an increase in the initial dye concentration.

Keywords- **Metal complexes,Schiff base ligand L1,Salpd.**

1. Introduction

Water pollution can be defined as presence of harmful or objectionable material in sufficient quantity to measurably degrade water quality that affects living organisms. The main sources of water pollution are industrial effluents and human communities, which mainly caused the pollution of surface waters like seas [1], lakes and rivers. Dye is a common pollutant and contaminant compound that can be easily found in wastewater [2]. Many industries are using dyes to colour their products, and they use up vast volumes of water. The presence of small quantity of dyes in water is highly apparentand undesirable [3]. Dyes are mainly used in paper production, textile industries, leather tanning and food technology industries. The released of the major component of pollutants in wastewater into water sources from textile and other industries caused water quality including acidity BOD, turbidity, pH, temperature, alkalinity, COD, and colour. The released of those coloured wastewaters in the ecosystems causes humourlessenvironmental problems like eutrophication and aesthetic pollution and can begin hazardous by-products through hydrolysis, oxidation or some other chemical reactions in the wastewater phase [4, 5]. That is why the wastewater treatment is seductive to overcome this problem.

In the past years, advanced oxidation processes (AOPs) represent a powerful mean for water cleansing and for eliminating organic and inorganic pollutants from the wastewater. Many oxidation processes such as photo-Fenton, UV /TiO_2, UV/H_2O_2, UV /O_3 are presently employed for this purpose. AOPs involve the Photo- Fenton reaction as well as its modifications as well as H_2O_2/UV or ozonization [6-10]. In these processes, hydrogen peroxide is activated by dissolved iron or UV irradiation to produce high reactive species, which is hydroxyl free radical which oxidize organic dyes and generate oxidized products. The main drawbacks in Fenton-processes is that the Fenton's reagent can work only below acidic conditions (pH 2–4), and some dyes are not entirely decomposed [11, 12].

In current years, various heterogeneous degradation processes based on metal complexes have been grown. This is due to their unique benefit such as facile catalyst recovery from the solution, important decrease of material losses, and physical separation of active sites by dispersion on the supports and a cheap cost of the wastewater treatment. In the previous decade, attention has been focused on treatment technologies that lead to the complete devastation of the organic pollutants. Among these treatments advanced oxidation processes (AOPs) have come out as powerful remediation treatments to destroy stubbornpollutants in water. Among all the AOPs heterogeneous photocatalysis emerge as most promising treatment for the degradation of various dyes and industrial effluents at lab scale.

The Schiff-base metal complex possesses stable structure, peculiar electronic characteristic and space effect of complex precisely and easily by changing the ligand or metal ion [13-15]. The copper Schiff-base metal complex can act as catalyst. Currently, many copper Schiff-base complexes have been reported about the selective catalytic oxidation of various groups mainly in homogeneous reaction [16-18], but few research pays attention to the heterogeneous photocatalytic performance in water treatment of toxic organic pollutants under visible light [19]. Copper (II) complex systems have been apply for the degradation of lignin [20], polycyclic aromatic hydrocarbons [21] and synthetic dyes [20-23]. More interesting, it can form hydrophobic micro environment mimic enzyme catalytic properties and prevent the axial aggregation and degradation itself.

Another set of oxidation process makes use of transition metal ions mostly involving Cu in combination with ligand molecules for the breakdown of hydrogen peroxide and the resulting production of hydroxyl free radicals. The main advantage of such systems is the wide substrate specificity and its ability to perform at pH 3–9 [12, 23].

Here we have undertaken detailed study on photo degradation of Methylene blue dye which is a type of cationic dye having heterocyclic aromatic chemical compound with molecular formula $C_{16}H_{18}N_3SCl$. It was first prepared by German chemist Heinrich Caro (1834-1990). These groups enhance the solubility of dye in water due to their ionic characteristic [24]. This dye has many uses in chemistry and biology; for example; it can be used as a stain and as a medication. At room temperature it appears as a solid, odorless, dark green powder that produce a blue solution when dissolved in water. This dye has three molecules of water per unit in the hydrated form.
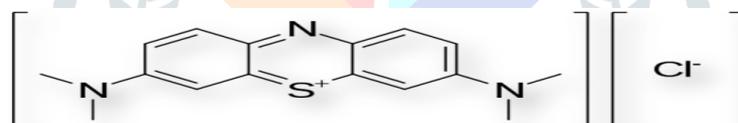
3, 7-bis (Dimethylamino)-phenothiazin-5-ium chloride

FigureNo.1 - Structural formula of methylene blue.

2. EXPERIMENTAL

2.1 Materials

Salicyldehyde and 1, 3-propanediamine was purchased at highest commercial quality from Sigma-Aldrich and used without further purification unless otherwise stated. Copper sulphate ($CuSO_4 \cdot 5H_2O$) were obtained from Himedia Company and are used as supplied. Solvent ethanol were distilled freshly, refluxed over appropriate drying agents following standard procedures and kept under vacuum. Hydrogen peroxide (H_2O_2) solution (30% stabilized for synthesis) was carried out in this work as a reagent. The solutions of H_2O_2 and dye were prepared in Millipore water. Methylene blue, procured from s.d. Fine was chosen as asimple model of a series of thiazin dyes largely used in the industry. Doubly distilled water was used throughout the investigation.

2.2 Synthesis

2.2.1 Synthesis ofSalpd ligand

The general method of preparation of Schiff bases is quite straightforward and consists of the condensation reaction of primary amines with an aldehyde precursor usually in alcoholic solution. The crystal structure is shown in Fig. 1. The yield of Salpd obtained in this manner was about 82%. The ligand was characterized by melting point & spectral analysis such as IR, ^{1}HNMR, ^{13}C,MS, UV-Vis. The results were: m.p;40ºC; ^{1}HNMR [δ 13.38 (s, 1H, OH), δ 8.47 (s, 1H, N=CH), δ 7.34-6.84 (m, 8H, Ar-H), δ 3.73-3.69 (t, 2H, N-CH$_2$), δ 2.12-2.05 (m, 2H, CH$_2$); IR; –CH=N at 1625 cm^{-1}; ^{13}C; –CH=N at 165.54 and 160.56; MS;m/z peak at 282. UV-Vis; two bands at 254 (π to π*) and 325 (n to π *) nm.

Scheme 1. Structure of Salpd ligand

2.2.2 Synthesis of Cu-Salpd complex

The Cu-Salpd complex was obtained by mixingCopper sulphate (CuSO$_4$·5H$_2$O) and ligand Salpd (1:1, molar ratio) in anhydrous ethanol solvent, upon addition the colour of the reaction mixture changes to green solution. The resultant mixture was then stirred at room temperature overnight. The solid formed during the stirring was collected through suction filtration. Thorough washing with ethanol followed by ether gave purified products. The yield of Cu-Salpd obtained in this manner was 67.6%. The UV-Vis spectra of metal complex shows a shifting of absorption spectra to higher wavelength beside an increase of peak to (n to π*) transition which confirms the co-ordination through azomethine nitrogen.

2.3 CHARACTERIZATION OF LIGAND

1. IR spectrum of Ligand, L1 N,N'-disalicylaldehyde-1,3-propanediimine, (Salpd)

Figure No. 2

The infrared spectrum of was recorded in KBr pellet for the ligand, L1 N,N'-disalicylaldehyde-1,3-propanediimine, (Salpd)as shown in Figure No. 2. The IR data ofligand shows a main characteristic peak of –CH=N at 1625 cm^{-1}. The IR data of free ligand L1 shows that the absorption peak at 3473 cm^{-1} was attributed to the υ$_{OH.}$

(II) NMR data of Ligand, L1 N,N'-disalicylaldehyde-1,3-propanediimine, (Salpd)

(a) ^{1}H NMR data of Ligand, L1 N,N'-disalicylaldehyde-1,3-propanediimine, (Salpd)

The ^{1}H NMR spectrum of Ligand, L1 was taken in DMSO as a solvent. The ^{1}H NMR data taken reveals the presence of -CH=N by the appearance of the singlet at 8.479 δ ppm due to one proton present in group, the presence of this peak shows that the formation of ligand takes place. The singlet peak at 13.38 δ ppm assigned to hydroxyl group. Multiplets attributed to two aromatic ring protons were recorded at 7.34-6.84 δ ppm. The triplet peak observed at 3.73-3.69 δ ppm assigned to N-CH$_2$. Multiplets in range 2.12-2.05 δ ppm attributed to methyl (-CH$_2$) group.

Figure No. 3

(b)^{13}C spectra ofLigand, L1N,N'-disalicylaldehyde-1,3-propanediimine, (Salpd)

Figure No. 4

The ^{13}C NMR of ligand shows a peak at 165.54 & 160.56 showing the presence of carbon atoms bonded with the nitrogen atom of –CH=N. The peak at 131.82, 131.21, 118.35, 118.19, and 116.26 shows the presence of aromatic carbon atoms. The peak at 56.23

showing the presence of carbon bonded with nitrogen of N-CH$_2$, where as peak at 31.40 confirms the presence of aliphatic carbon atoms.

(III) Mass spectrum of Ligand, L1 N,N'-disalicylaldehyde-1,3-propanediimine, (Salpd)

Figure No. 5

High resolution ionization mass spectrometry MS (ES$^+$) was used to identify the product by the evolution of molecular ion peak of ligand, L1 N,N'-disalicylaldehyde-1,3-propanediimine, (Salpd). The MS (ES$^+$) spectrum shows a peak at m/Z calculated at 282 and found exactly result at 282.

(IV) UV-Visible studies of Ligand, L1 N,N'-disalicylaldehyde-1,3-propanediimine, (Salpd)

The electronic spectrum of the free Schiff base ligand, L1 N,N'-disalicylaldehyde-1,3-propanediimine, (Salpd)showstwo absorption bands at 254 nm and 325 nm assigned for $\pi \rightarrow \pi^*$ (phenyl ring) and n$\rightarrow \pi^*$ (CH=N) transition as shown in Figure No. 6.
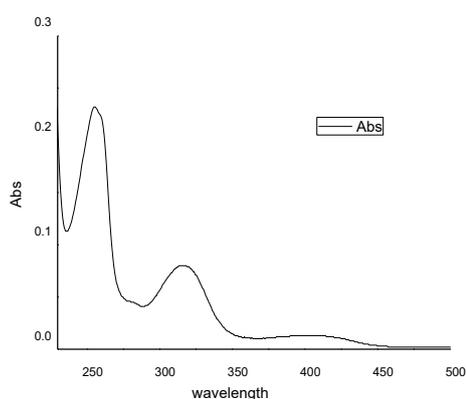
Figure No. 6
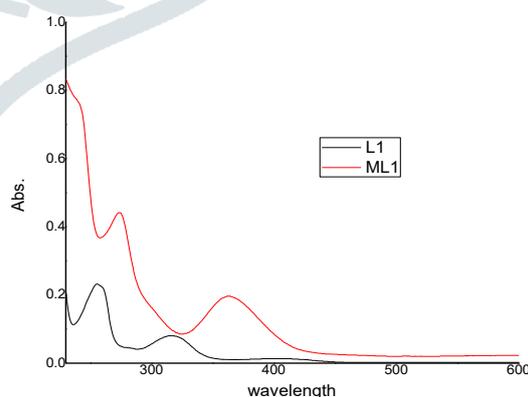
Figure No. 7

2.3.1 (I) UV-Visible studies of Cu-complex derived from the Ligand, L1 N,N'-disalicylaldehyde-1,3-propanediimine, (Salpd)

The UV-Vis spectrum of the ligands showed two bands at 254 and 325 nm which are assigned to π to π* and n to π* transitions, respectively. The UV-Vis spectra of 10^{-4}M of the metal complexes, Figure No. 7, display similar absorption spectra of the ligand which are shifted to higher wavelengths beside a increase of the peak to n to π* transition which are confirms the co-ordination through azomethine nitrogen. On the other hand, π to π* transition showed new band at 280nm due to complexation. Also the d-d transition in this complex may appear above 500nm but does not visible due to the low intensity of d-d transition [73].

2.4 Photocatalytic Activity

A photocatalytic activity of Schiff base metal complexes (MC) on the photo-degradation of methylene blue (MB) in water was examined with visible-light. A 200 W high pressure halogen lamp is a light source. The light source and the reaction mixture were kept $5cm^{-1}$ apart. It is well known that the adsorption and degradation of methylene blue in aqueous solution by the catalyst take place simultaneously.

2.5 Catalytic activity under visible light

2.5.1 Procedure

The photodegradation of methylene blue dye was examined by hydrophobic copper complexes under visible irradiation to identify complete decolorization and substantial mineralization of the dye. Effect of various experimental parameters such as time of irradiation, catalyst concentration (Cu-Salpd), substrate concentration (MB) and addition of H_2O_2 was examined at different experimental conditions. For that purpose the stock solution of MB of concentration 1.25×10^{-5} mol/L, different solutions of desired concentrations were prepared in Millipore water. The photodegradation experiments were carried out in photoreactor in which 20 ml of MB containing 0.20 g/L Cu-Salpd and appropriate H_2O_2 were put into a cylindrical glass bottle. The above solutions were placed in dark for 3h to achieve the adsorption and desorption-balance. To examine the effect of time of irradiation, photocatalytic degradation experiments were carried up the range of 3-7 hrs. The effect of catalyst concentration was studied by changing the amounts of Cu-Salpd. In order to examined the effect of substrate concentration; photocatalytic degradation experiments were carried out at optimized dye concentration. For each experiment, aliquot/solution was taken out after every one hour/30min with the help of syringe, which was then filtered through 0.3 μm, 12 mm diameter Millipore disc and analyzed for its concentration with UV-Visible spectrophotometer.

2.6 CHARACTERIZATION

2.6.1 UV-Visible Spectrophotometer-

UV-Visible spectrophotometer (Shimadzu UV 1800) was used to study the absorbance of synthesized catalyst .The rate of photodegradation of organic dye was monitored on UV-Vis spectrometer using photocatalysis on different time intervals. A spectrum was taken in the range of 190-800 nm. UV-Vis spectrum was recorded from SLIET, Longowal.

3. Heterogeneous photocatalytic degradation of dye methylene blue (MB) using Cu-Salpd complex

The photocatalytic activities of Cu-Salpd were tested by degradation of MB on different time intervals. Figure no. 8; showed the degradation kinetic curves. According to linear fitting of degradation of MB, the value of kinetic constant were $k = 4.6 \times 10^{-3}$ min^{-1}.It indicated that Cu-Salpd could activate H_2O_2 and degrade MB effectively under visible irradiation. The UV-Vis absorption spectra of MB in Vis/Cu-Salpd/H_2O_2 /MB system were shown in Figure no. 9. The maximum absorption 650 nm was reduced continuously in the reaction process, which demonstrated that conjugated ring of MB was destructed.
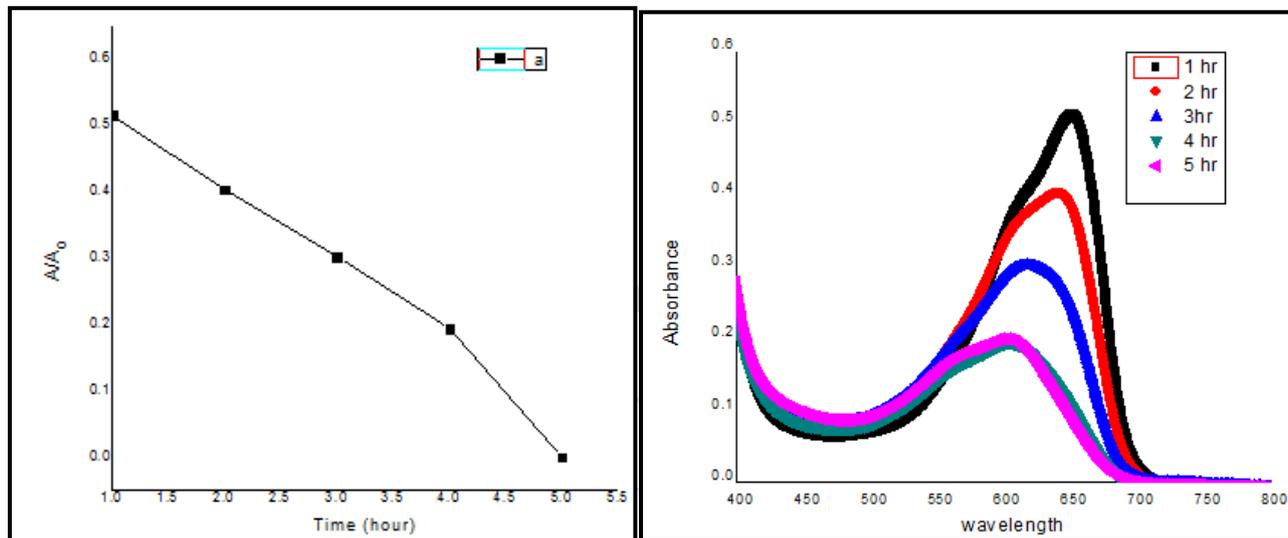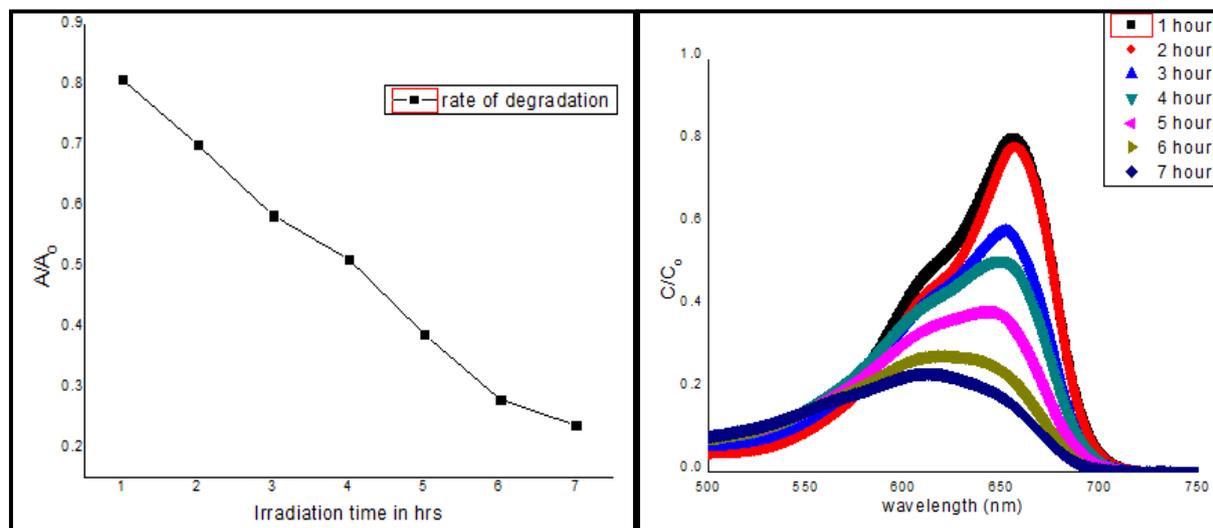

Fig no. 8– Degradation of MB under Vis/Cu-Salpd/H_2O_2 /MB   Fig no.9- UV-Vis absorptionspectra of MB inVis/Cu-Salpd/H_2O_2 /MB

[Cu-   Salpd] = 0.20g/L, [H_2O_2] = 1.50×10^{-3} mol/L, pH 7.0, [MB] = 1.25×10^{-5} mol/L.

MB was completely decolorized after 5 hour of visible irradiation. It showed that Cu-Salpd   can act as an effective catalyst and activateH_2O_2 to degrade cationic dye MB as shown below.

3.1 RESULTS AND DISCUSSION

The photo degradation of MB was carried out with AOP such as Vis/Cu-Salpd/H_2O_2 /MB for complete decolorization and substantial mineralization of the dye.

3.1.1 Optimization of various experimental parameters for treatment of real effluents.

(i) Effect of time of irradiation (ii) Effect of catalyst concentration (iii) Effect of substrate concentration (iv) Effect of addition of H_2O_2 (v) Effect of pH.

(i) Effect of time of irradiation

The effect of time of irradiation on photocatalytic degradation of MB was studied over the range of 3-7 hours. Obtained results show that maximum degradation of MB can be achieved in first 3 hours. The minimum time of irradiation for maximum degradation was found to be 6 hours. Beyond this, the rate of degradation of MB is almost constant. MB was completely decolorized after 7 hour of visible irradiation. The UV-Vis absorption spectra of MB system were shown in Figure No.11.The maximum absorption 650.50 nm was reduced continuously in the reaction process, which revealed that conjugated ring of MB was destructed.

Fig no.10 - Degradation of MB under visible light.   Fig no. 11- UV-Vis absorption spectra of MB.

(ii) Effect of Catalyst Concentration

The effect of catalyst concentration was examined by varying the amounts of Cu-Salpd ranging from 35 to 110 mg/50mL, in order to get the optimum catalyst concentration for the maximum photodegradation, which could save unnecessary use of excess of photocatalyst. For these studies the substrate concentration was kept constant (1.25×10^{-5} mol/L). Figure no. 34; show that the degradation efficiency increases up to 60mg/50mL of the dye solution, above which it   show reduction in degradation efficiency. Further increasing this dose, the substrate molecules available are notadequatefor adsorption by the increased number of Cu-Salpd particles. Hence the additional amount of catalyst is not involved in catalyst activities & the rate does not increase with an increase in the amount of catalyst. Also at high Cu-Salpd concentrations particles aggregate this decrease the interfacial area in between the reaction solution and the photocatalyst. Thus the numbers of active sites on the catalyst surface reduce. The extra addition of catalyst makes the solution more turbid and the decline in degradation efficiency may be due to the reduction in penetration of light with surplus amount of Cu-Salpd. In the present investigation 60 mg of Cu-Salpd in 50mL of dye solution was found to be optimized dose for maximum degradation of MB and could degrade the MB only in couple of hours.
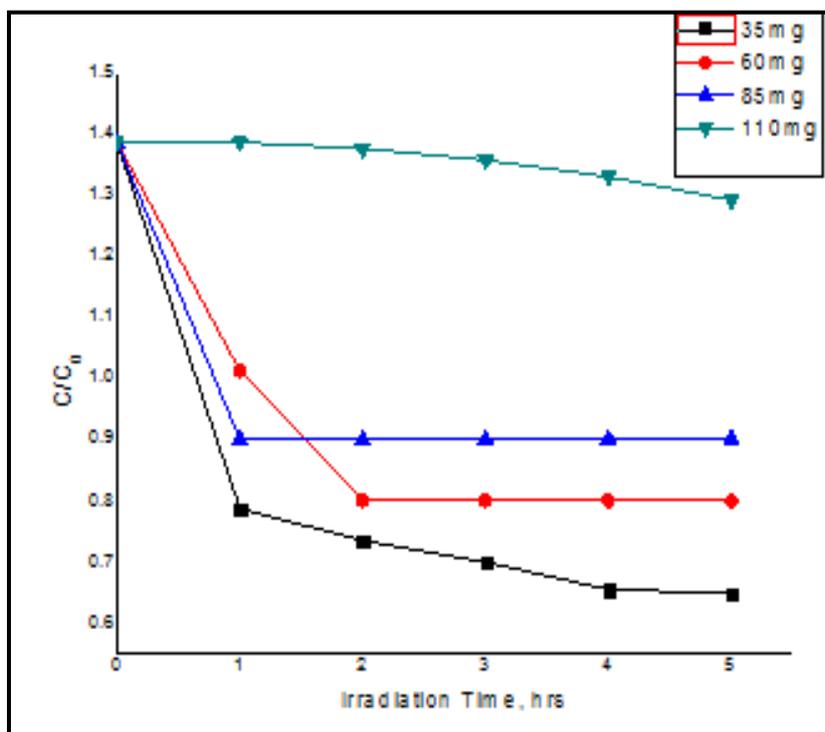
Figure No. 12- Optimization of Catalyst Concentration for the degradation of MB

(iii) Effect of Substrate Concentration

The effect of substrate concentration on degradation of MB dye was studied at different concentrations varying from 1×10^{-5} to 2.5×10^{-4} mol/L. Since the pollutant concentration is a very important parameter in water treatment. Experimental results are presented in Fig no.13, which shows that the degradation rate depends on the initial concentration of dye MB. It was found that rate of degradation increase with increasing the concentration of dye up to 2.5×10^{-5} mol/L. Beyond an increase in concentration of dye it reduces the rate of degradation. This may be explained on the basis that, on increasing the concentration of MB, the reaction rate increases as more molecules of the dye are available for degradation. Moreover, with an increase in dye concentration, the solution becomes more intense colored and the path length of photons entering the solution is decreased by that fewer photons reached the catalyst surface. Hence, the production of hydroxyl a radicals is reduced. Consequently, the photo degradation efficiency is reduced. Moreover, at the higher concentration, the number of collisions between MB (dye) molecules increases on other hand the number of collisions between dye molecules and OH^* free radical reduces. Table no. 1, showing data of slightvariation in optimized substrate concentration for photodegradation.

Time (hrs.) X-axis	0.00001 M Conc. A/A$_o$	0.000025 M Conc. A/A$_o$	0.00005 M Conc. A/A$_o$	0.000251 M Conc. A/A$_o$
0	3.3	3.3	3.3	3.3
1	0.248	1.452	0.512	3.300
2	0.144	1.326	0.476	3.250
3	0.108	1.301	0.445	3.185
4	0.099	1.272	0.436	3.140
5	0.052	1.100	0.425	3.117

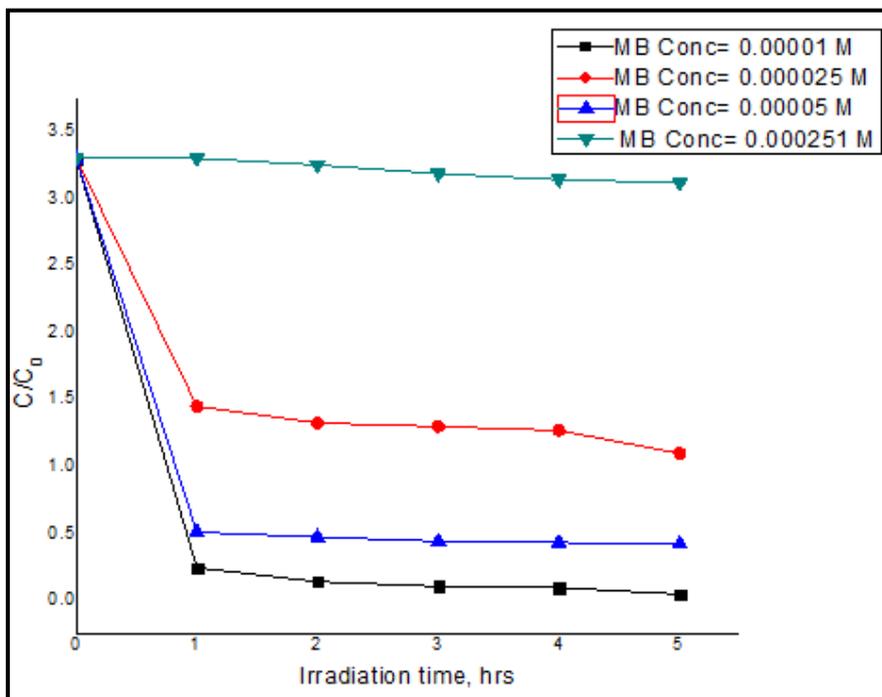Table No. 1 Data of optimization of substrate concentration for degradation

Figure No. 13- Optimization of Substrate Concentration for degradation of MB

As a result, the rate of reaction is retarded. Hence in the present investigation the optimum substrate concentration of MB was found to be 2.5×10^{-5} mol/L.

(iv) Effect of addition of H_2O_2

The effect of addition of H_2O_2 to the system with optimized catalyst concentration and optimized initial substrate concentration was studied by varying the amount of H_2O_2 ranging from 0.175 g/100ml to 0.475 g/100ml. Fig no.14, shows the variation in the photodegradation rate of MB for various amounts of H_2O_2. The highest rate of degradation was found for H_2O_2 = 0.272mg (8mM H_2O_2) and beyond this the rate of degradation of MB was not significant. The addition of H_2O_2 to the heterogeneous system increases the concentration of OH* radicals.
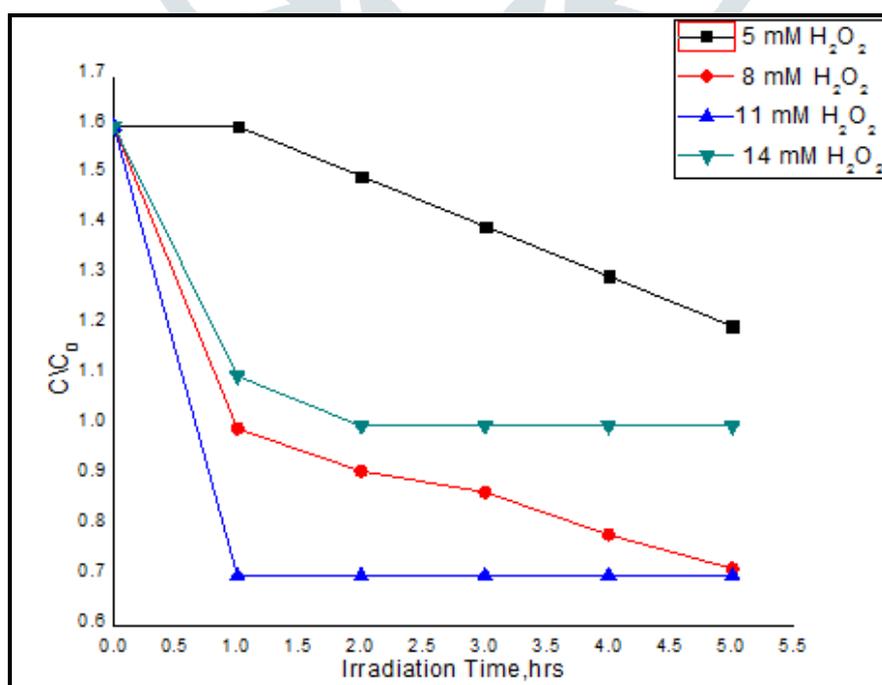

Figure No. 14 - Optimization of Concentration of H_2O_2

When H_2O_2 was added, maximum degradation was achieved in the first hour. Complete degradation was achieved in two hours. Thus in present investigation the optimized amount of H_2O_2 was found to be 0.274g/100mL. When the H_2O_2 concentration becomes high, the excess H_2O_2 consumes hydroxyl radicals and it performs like a hydroxyl radical scavengers.

(v) Effect of pH

To evaluate the effect of pH, the degradation of MB using Cu-Salpd and H_2O_2 was carried out under visible light irradiation at different pH values. The pH was adjusted by the addition of appropriate amounts of NaOH or H_2SO_4. When the pH value of the solution is increased from 5 to 7, it has been observed that up to pH 9 of the solution there was increase in degradation and decolorization as shown in Fig no. 10. Further increase in pH resulted in a decrease in the degradation and decolorization as shown in Fig no. 17.

Fig No. 15- Bleaching of MB after 240min at pH 9.   Fig No. 16- Decrease in decolorization of MB after 240min at pH 11.

 This may be due to the higher adsorption of MB dye on the surface of the catalyst taking place when the pH of the solution is above 9, which leads to inhibition of light penetration. This can also be explained on the basis of the influence of alkaline pH on the surface state of catalyst and generation of OH* free radical. The results indicated that catalyst exhibited better catalytic activity for degradation of MB at acidic pH than that at alkaline pH. In general, thephotochemical degradation depends strongly on the pH of the reaction medium. Under visible light irradiation, Cu-Salpd overcame the limit of pH and broadened the range of pH in the photocatalytic system.
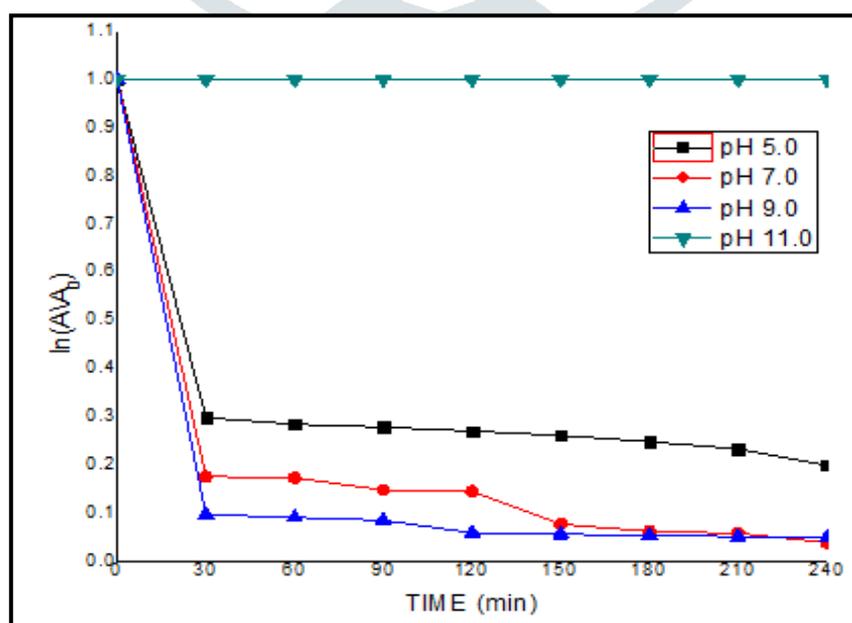

Figure No. 17- Effect of different pH on dye removal

Result revealed that as pH increased, the efficiency of catalyst for degrading dye decreased as well.Methylene blue was completely decolorized after 240min. under visible irradiation at pH 9.

6. Conclusions

1. The hydrophobic complex Cu-Salpd can be used as heterogeneous catalyst to degrade toxic organic dyes in aqueous system under visible light, Cu-Salpd can efficiently activate H_2O_2 to produce OH^*, which degraded organic pollutants effectively due to its highly oxidizing activity .

2. The results demonstrated that addition of hydrogen peroxide made the degradation much faster and can degrade the MB only in couple of hours until the dose reaches its critical value, beyond which the decolorization rate becomes independent of this dose as it begins to act as a scavenger for hydroxyl radicals. The optimum amount of H_2O_2 was found to be 0.274g/100mL.

3. The results revealed that that catalyst exhibited better catalytic activity for degradation of MB at acidic pH than that at alkaline pH.

4. Increasing the initial concentration of dye with a constant concentration of hydrogen peroxide increases the time of degradation. The optimum substrate concentration of MB was found to be 2.5 x 10^{-5} mol/L.

5. The results show that 60 mg of Cu-Salpd in 50mL of dye solution was found to be optimized dose for maximum degradation of MB.

6. The observations of these investigations clearly demonstrated the importance of choosing the optimum degradation parameters which are essential for any practical application of photocatalytic oxidation process for the complete degradation and may be extended to treat real industrial wastewater.

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