Synthesis of Metal Complex for Photocatalytic Degradation of Dyes under Visible Light Irradiation

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Abstract. In the present work, Schiff base ligand has been synthesized from synthesized dialdehyde and primary amine. The synthesized ligand and its copper metal complex were characterized by melting point & spectral analysis such as IR, 1H NMR, 13C and GC-MS. In the presence of H2O2 as an oxidising agent the photocatalytic performance of the complex was assessed by the photodegradation of dyes. By carrying spectrophotometrically on irradiation of visible light using Cu(II) metal complex of Schiff base ligand the photocatalytic degradation of Naphthol Blue Black dye (NBB), Rhodamine B (RB) and Methylene Blue (MB) dyes was carried out. The photocatalytic degradation of NBB, RB and MB dyes was carried out with reference to effect of time. The results revealed that Cu-complex of Schiff base ligand is consistent for photocatalysis of these dyes for treatment of authentic effluents. The results show that the optimal dose for maximal degradation of these dyes was found to be 5 mgL⁻¹ of the Cu(II) metal complex. The % degradation of NBB, RB and MB were found to be 55%, 50% and 80% in the visible light irradiation. The % degradation of MB dye was greater as compare to other two dyes. The order of % degradation of three dyes by copper metal complex was found as MB > NBB > RB

1. Introduction
Water pollution is a big environmental and social issue all across world. It has reached to the critical point now. According to the national environment engineering research institute (NEERI), Nagpur, it has been noted that around 70 per cent of the river water has been polluted to a great extent. Developments in industrial and agriculture sector have resulted in generation of large amount of waste water containing toxic pollutants. Organic dyes are one of the large groups of pollutants which are released from textile industrial waste water. Different generic methods like chemical, biological and physical are being survey and employed however they have their own disadvantage as the physical methods like reverse osmosis, adsorption on activated carbon etc. do not lead to complete mineralization, rather they simply displace the pollutants from one phase to another phase bring about secondary pollution [1]. Biological treatment methods have proved to be ineffective not only due to the resistance of azo dyes to aerobic degradation but also due to the composition aromatic amines which are carcinogenic [2]. To overcome the weak points in the existing research treatment techniques and development in creative technologies during the last decade have shown that Advanced oxidation processes (AOPs) have been applied for water cleansing effectively. The most promising advanced oxidation processes (AOPs) are
photocatalytic degradation as it is cheap and less time consuming [3]. These processes involve the generation and subsequent reaction by using the mixture of powerful UV light and oxidizing agent to create OH⁻ hydroxyl free radical [4,5]. There are currently many oxidation processes, which including photo-Fenton, UV/TiO₂, UV/H₂O₂, UV/O₃, used for this purpose. AOPs include the Photo-Fenton reaction as well as its modifications and H₂O₂/UV or ozonization [6-10]. Fenton’s reagent can function only under acidic conditions (pH 2-4), and some dyes are not fully decomposed [11,12]. From all AOPs heterogeneous photocatalysis emerges as the most promising treatment for the degradation of different dyes and industrial effluents on a laboratory scale [13-18].

The Schiff-base metal complexes can also act as catalyst in many oxidation processes to remove industrial effluents [19]. The Schiff-base metal complex has a stable structure, unique electronic functionality and the spatial effect of the complex precisely and easily through the alteration of the ligand or metal ion [20-22]. A number of Schiff-based copper complexes have currently been published for the selective catalytic oxidation of various groups, mainly in homogeneous reactions [23-25], but few studies have focused on the photocatalytic degradation of toxic organic pollutants in water treatment under visible light irradiation [26]. Complex copper (II) systems of various metal ions have been used to degrade lignin [27], polycyclic aromatic hydrocarbons [28] and synthetic dyes [26-29]. It can create a hydrophobic micro-environment, mimic the catalytic properties of the enzyme, and prevent axial aggregation and degradation itself. The key benefit of such systems is the large specificity of the substrate and its capacity to perform at pH 3-9 [25,26]. Therefore considering the potential of Cu(II) complex in photocatalysis concerning the degradation of three organic dyes under visible light irradiation for environmental remediation, Cu(II) complex of ligand, 2,2’-(ethane-1, 2-diylbis(oxy))diphenol (EDBD) has been synthesized and applied its catalytic application in photodegradation of three dyes emphasizing on the influence of degradation time on its catalytic activity has been investigated in the present study.

2. Materials and Methods
Copper metal salt is obtained from Himedia-Company and is used as supplied. Salicylaldehyde, 2-aminophenol, Naphthol Blue Black and Rhodamine B were purchased from Sigma-Aldrich at the highest commercial quality and used, unless otherwise specified, without further purification. Solvents such as methanol and ethanol were freshly distilled, refluxed over suitable drying agents following standard practices and kept under vacuum. The solution of hydrogen peroxide (H₂O₂) (30%) was carried out as a reagent in this work. In Millipore water, the solution of H₂O₂ and dye were prepared. Doubly distilled water was used all through the examination. Infrared spectrum of the ligand and metal complex was recorded in the 4000-400 cm⁻¹ region (KBr pellets) on a FT-Infra-red spectrophotometer model RZX (Perkin Elmer). ¹H and ¹³C NMR analysis were recorded in DMSO on FT-NMR Cryo-magnet spectrometer 400 MHz (Bruker). Mass spectrometric analysis was carried on a Shimadzu GC-MS QP 2010 Ultra in EI mode.

2.1 Synthesis of 2, 2’-(ethane-1, 2-diylbis(oxy))dibenzaldehyde (EDD)
The synthetic procedure for EDD was adopted as reported in the literature [30] as shown in (Figure 1). Salicylaldehyde (0.61g, 5mmol) was dissolved in 20 ml DMF, and potassium carbonate (1.73g, 12.5mmol) was added. The mixture was stirred at room temperature, and then 1, 2-dibromo ethane (0.51g, 2.5mmol) was added
drop-wise. Then, the reaction mixture was stirred under reflux for 6h. The resulting mixture was partitioned between water and ethyl acetate then the ethyl acetate layer was collected, concentrated under reduced pressure and then subjected to silica gel 100-200 mesh column chromatography using 1 ratio 9 hexane-ethylacetate as the eluent to afford compound (1.07g, 75%) in pure form.

![Synthesis of 2, 2'-((ethane-1,2-diylbis(oxy))dibenzaldehyde (EDD)](image)

2.2 Synthesis of ligand 2,2'-((1Z,1'Z)-(((ethane-1,2-diylbis(oxy))bis(2,1-phenylene))bis(methanylylidene))bis(azanylylidene))diphenol (EDBD)

To the solution of 0.0008 moles (0.22 gm) of dialdehyde (EDD) in 20 ml of absolute ethanol, the appropriate solution of pure 2-aminophenol 0.0016 moles (0.174 gm) in 20 ml of absolute ethanol were allowed to refluxed for six hours as shown in (Figure 2). The solid formed after stirring was collected by suction filtration. Recrystallization from hot ethanol furnished the required product in pure form.

![Synthesis of ligand2,2'-((1Z,1'Z)-(((ethane-1,2-diylbis(oxy))bis(2,1-phenylene))bis(methanylylidene))bis(azanylylidene))diphenol (EDBD)](image)

2.3 Synthesis of Copper metal complex of ligand EDBD

The synthesis of copper metal complex of ligand EDBD is shown in (Figure 3). To a solution of appropriate ligand (0.001 moles) in ethanol (10 ml), the solution of metal acetate salt (0.001 moles) in ethanol (10 ml) was added drop wise with the help of dropping funnel, upon addition the color of the reaction mixture is changed. The resultant mixture was then refluxed for 4-5 hrs. The solvent was then evaporated by using rotary evaporator and solid product obtained in round bottom flask.
2.4 Photocatalytic Activity

Photo-catalytic dye degradation was performed spectrophotometrically on visible light irradiation using Cu(II) complex of ligand (EDBD) on NBB, RB and MB dyes in water. It is well known that NBB, RB and MB dyes are adsorbed and degraded simultaneously by the catalyst in an aqueous solution. In order to identify complete decolorization and significant mineralization of the dyes, photodegradation of NBB, RB and MB dye was examined regularly by the copper complex under visible light irradiation. Effect of time of irradiation with catalyst concentration Cu(II)(EDBD), was examined during the experimental conditions. For this reason, concentrations of $1.25 \times 10^{-5}$ mol/L of stock solution of NBB, RB and MB dyes were prepared in Millipore water. Photodegradation experiments were performed in a photoreactor in which 50 mL of three dyes containing 5 mg Cu(II)(EDBD) and an appropriate quantity of H$_2$O$_2$ (0.1 mL) were placed in a cylindrical glass container. To achieve the adsorption and desorption balance, the above solutions were put in the dark for 1 h. Photocatalytic degradation experiments were performed in the range of 10-50 minutes to analyze the impact of the irradiation period. After every 10 minutes, aliquot/solution was taken out for each experiment with the help of a syringe, which was then filtered through a 0.22 μm, 12 mm diameter millipore disc and analyzed with a UV spectrophotometer for its concentration. The rate of photodegradation of organic dyes was monitored using a photocatalyst on a UV-Visible spectrometer at different time intervals. A spectrum in the range of 400-800 nm was taken. Cu(II)(EDBD) photocatalytic activities were studied at different time intervals with degradation of NBB, RB and MB dyes.

The photocatalytic activity of Schiff base metal complex Cu(II)(L) on the photo-degradation of NBB, RB and MB dyes in water was examined under visible light. A high pressure visible lamp is used as a light source. The light source and the reaction mixture were held 5cm$^{-1}$ apart.

The percentage of dye degradation was computed by utilizing the following equation:

$$\text{Dye degradation (\%)} = \left[\frac{[A_0 - A]}{A_0}\right] \times 100$$  \hspace{1cm} (1)

where $A_0$ and $A$ are the initial and final concentration of the dye.

The chemical kinetics of dye degradation can be described as follows by the pseudo first order reaction:

$$\ln \left(\frac{c}{c_0}\right) = k_{o_{irr}}t$$  \hspace{1cm} (2)

Here, $c_0$ is the initial concentration of dye at $t = 0$ min, $c$ is the concentration of dye at a time $t$ and $k$ is the rate constant. A plot of $\ln \left(\frac{c}{c_0}\right)$ vs irradiation time $t$, gives a linear relationship.
3. Results and Discussion

The physical and analytical information of ligand and its metal complex is given in Table 1. The synthesized compounds are stable to air and moisture. The yield of the complex is lower than the yield of ligand. The real reason might be due to the steric hindrance. The metal complex is insoluble in organic solvents yet is dissolvable in DMF and DMSO.

| Compound          | Color        | Yield (%) | M.P (°C) |
|-------------------|--------------|-----------|----------|
| Ligand (EDBD)     | Brown yellow | 70        | 163      |
| Cu(II) (EDBD)     | Dark green   | 64        | 221      |

3.1 IR Spectrum of ligand EDBD

The infrared spectrum of ligand EDBD was recorded in KBr pellet as shown in (Figure 4). The ligand, EDBD in IR data shows a principal characteristic peak of –CH=N at 1618 cm⁻¹. The absorption peak at 3405 cm⁻¹ was attributed to the νOH of free ligand.

![Fig. 4 IR Spectrum of ligand EDBD](image)

3.2 IR Spectrum of Cu-complex derived from ligand EDBD

The IR data of the complex when studied shows a shifting of the peak from 1618 cm⁻¹ to 1597 cm⁻¹ as shown in (Figure 5). The absorption peak at 3405 cm⁻¹ was attributed to the νOH of free ligand and after complexation this peak was shifted to lower frequency at 3285 cm⁻¹. This shifting of peaks towards the lower frequency is because of the coordination of nitrogen and phenolic -OH bond with metal ion. This confirms the coordination of the metal ion with ligand in metal complex.
3.3 $^1$H NMR Spectrum of ligand EDBD
The $^1$H NMR spectrum of ligand, EDBD (Figure 6) was taken in DMSO as a solvent. The $^1$H NMR data taken reveals that the peak at 8.89 δ ppm is due to -OH aryloxy hydrogen and the presence of -CH=N is confirmed by the appearance of signal at 8.21 δ ppm. This peak shows that the formation of ligand took place. Multiplets from 8.21-6.67 δ ppm are attributed to aromatic ring protons and the singlet observed at 4.55 δ ppm to bridged O-CH$_2$ functionality.

3.4 $^{13}$C Spectrum of ligand EDBD
The $^{13}$C NMR of ligand shown in (Figure 7) reveals a peak at 68.10 showing the presence of aliphatic carbon bonded with oxygen of O-CH$_2$ and 139.01 confirms the presence of carbon atoms bonded with the nitrogen atom of -CH=N. The peaks at 133.32 to 113.92 show the presence of aromatic carbon atoms where as peak at 151.52 assigned to aromatic carbon atom bonded with nitrogen. The peak at 158.98 shows the presence of carbon bonded with phenolic, -OH group.
3.5 Mass Spectrum of ligand EDBD

High resolution ionization mass spectrometry (EI+)MS was used to identify the product by the evolution of molecular ion peak of ligand EDBD. The (EI+)MS spectrum shows a peak at m/Z calculated at 452 and found exactly result at 452 shown in (Figure 8).

3.6 Photocatalytic degradation of dyes by using Cu(II)(L) under Visible Light Irradiation

In the range of 50 minutes, the effect of irradiation time on photocatalytic degradation of dyes was studied, as shown in (Figure 9, 11 and 13). The results obtained show that it is possible to achieve maximum degradation of dyes in 30-40 minutes. The minimum irradiation time for maximum degradation was found to be 50 minutes. In addition, the rate of dyes degradation is nearly constant. The % degradation of NBB, RB and MB were found to be 55%, 50% and 80% in the visible light irradiation for 50 min.
Fig. 9 Photodegradation of NBB dye under Visible/Cu-EDBD/H₂O₂/NBB dye
[Cu-EDBD] = 5mg, [H₂O₂] = 0.1 mL, pH 7.0, [NBB] = 1.25 × 10⁻⁵ mol/L

The result also reveals that Cu(II)(EDBD) could activate H₂O₂ and degrade dyes effectively under visible light irradiation. The value of k in case of NBB, RB and MB are 0.00705 min⁻¹, 0.01193 min⁻¹ and 0.02205 min⁻¹. The absorption spectra of NBB dye in Visible/Cu-EDBD/H₂O₂/NBB dye system were shown in (Figure 10). The maximum absorption 618.00 nm was reduced continuously in the reaction process, which demonstrated that conjugated ring of NBB dye was destroyed.

In the same case of RB dye (Figure 12) and in MB dye (Figure 14), the maximum absorption 530.00 nm and 660.00 nm was diminished continuously during the reaction progress, finally leads to the destruction of the conjugated ring system of the dyes.

Fig. 10 Absorption spectra of NBB dye under Visible/Cu-EDBD/H₂O₂/NBB dye

Fig. 11 Photodegradation of RB dye under Visible/Cu-EDBD/H₂O₂/RB dye
[Cu-EDBD] = 5mg, [H₂O₂] = 0.1 mL, pH 7.0, [RB] = 1.25 × 10⁻⁵ mol/L

Fig. 12 Absorption spectra of RB dye under Visible/Cu-EDBD/H₂O₂/RB dye
4. Conclusion

Cu(II)(EDBD) can be used as heterogeneous catalyst to degrade toxic organic dyes in aqueous system under visible light, Cu(II)(EDBD) can efficiently activate H₂O₂ to produce OH•, which degraded organic pollutants effectively due to its highly oxidizing activity. The results demonstrated that addition of hydrogen peroxide made the degradation much faster and can degrade the three dyes and each dye degrade only in 50 minutes 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 results show that 5mg/50 ml Cu(II)(EDBD) in NBB, RB and MB dyes solution was found to be optimized dose for maximum degradation of these dyes. The photocatalytic degradation of these dyes indicates that when the time of irradiation increases the percent degradation increases and reaches a maximum for 50 minutes irradiation. With increase of time more and more light energy falls on the catalyst surfaces which increases the formation of photo excited species and enhances the photocatalytic activity. The % degradation of NBB, RB and MB were found to be 55%, 50% and 80% in the visible light irradiation. The order of % degradation of three dyes by copper complex was MB > NBB > RB. The observations of these investigations clearly demonstrated the importance of choosing the optimum degradation with time which is essential for any practical application of photocatalytic oxidation process for the complete degradation and may be extended to treat real industrial waste water.

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