INTRODUCTION

Metal complexes of Schiff base have played a vital role in the development of coordination chemistry. For living systems, as copper is a fundamental metal, it plays a diverse role in cellular functional chemistry. It also has the capability to catalyse oxidation reduction chemistry and has potential applications for catalytic processes in living organisms that involve electron transfer reactions or activation of some antimicrobial substances. Copper complexes also found to exhibit antineoplastic activity, antibacterial and antifungal and anticancer activity. In the present paper, we report the synthesis and characterization of Copper (II) metal complexes using amino acid as a ligand and with their applications as antibacterial and antifungal agents. The synthesis of CuO nanoparticles with the same have also been carried out. The synthesized CuO nanoparticles from the same synthesized complex were then prepared by using precipitation method. The synthesized CuO nanoparticles were then characterized by FTIR and SEM techniques. Photocatalytic degradation of Rhodamine B dye was carried out at basic pH by using the same synthesized CuO nanoparticles.

ABSTRACT

When glycine (amino acid) reacts with salicylaldehyde in basic medium, it results in the synthesis of Schiff base, which was confirmed by TLC technique. Then Stable Cu (II) metal complex was synthesized by using the same Schiff base as a ligand. Various techniques viz., FTIR, Elemental analysis and TGA have been used to characterize the synthesized complex. The conductance was measured in DMF solvent on Equiptronics Conductivity meter (EQ-664A). The synthesized Cu (II) metal complex were evaluated for Antimicrobial activity against Staphylococcus aureus, *Escherichia coli* and *Bacillus subtilis*. The Copper nanoparticles from the same synthesized complex were then prepared by using precipitation method. The synthesized CuO nanoparticles were then characterized by FTIR and SEM techniques. Photocatalytic degradation of Rhodamine B dye was carried out at basic pH by using the same synthesized CuO nanoparticles.

INTRODUCTION

Metal complexes of Schiff base have played a vital role in the development of coordination chemistry. For living systems, as copper is a fundamental metal, it plays a diverse role in cellular functional chemistry. It also has the capability to catalyse oxidation reduction chemistry and has potential applications for catalytic processes in living organisms that involve electron transfer reactions or activation of some antimicrobial substances. Copper complexes also found to exhibit antineoplastic activity, antibacterial and antifungal and anticancer activity. In the present paper, we report the synthesis and characterization of Copper (II) metal complexes using amino acid as a ligand and with their applications as antibacterial and antifungal agents. The synthesis of CuO nanoparticles with the same have also been carried out. The synthesized CuO nanoparticles are further used for the degradation of Rhodamine B dye.

Experimental

**Materials:** All chemicals and reagents used were of the analytical grade (AR). Solvent like ethanol and methanol wherever used were distilled and purified according to standard procedures. Silica gel was purchased from Sigma Aldrich. Double distilled water was used throughout the experiment.

**Methods:** Synthesis of Ligand: The ligand was synthesized by reacting equimolar quantities of glycine and salicylaldehyde. By dissolving glycine (0.5 g) in ethanol and salicylaldehyde (1.0 g). 50% Sodium hydroxide solution was added drop wise to the above solution to make the reaction medium basic. This reaction mixture was refluxed for 7 hours at 50°C with continuous stirring (Figure 1). The success of the reaction was monitored by thin layer chromatographic (TLC) tests. The material was cooled and solvent was removed by rotary evaporator. The synthesized ligand was filtered, washed with ethanol and dried in desiccator.

**Synthesis of complex:** The Schiff base (ligand) and metal acetates (Cu) were reacted in (1:2) molar ratio in order to form the series of metal complexes. The metal acetates were dissolved in toluene separately and ligand was dissolved in ethanol. Both the solutions were reacted in a 250 ml reaction flask. The material inside the round bottom flask was refluxed at 50°C for 6–7 h. The progress of the reaction was monitored by using TLC tests. After the completion of the reaction, the material was cooled and solvent was removed by using rotary evaporator (Figure 2). The precipitated product was washed with solvent and dried after filtration.

**Key Words:**
Ligand, TLC, nanoparticles, Antimicrobial activity, Rhodamine B, dye degradation.
Characterization of Synthesized Cu (II) metal Complexes

The solubility of the synthesized metal compounds depends on various factors such as pH, other ion’s presence, oxidation state of the metal, etc. The synthesized metal complex was found to be soluble in ethanol, methanol and DMSO. The synthesized metal complex was characterized by following methods:

**Molar conductivity:** Systronic conductivity bridge instrument was used to measure the molar conductance of the synthesized metal complex using DMSO solvent (10^-3 M). The molar conductivity of the complex was found to be 10 mho cm^-2 mol^-1, indicating the non-electrolytic nature of the complex in DMSO.

**Elemental Analysis**

<table>
<thead>
<tr>
<th>Elements</th>
<th>C</th>
<th>H</th>
<th>O</th>
<th>N</th>
<th>Zn</th>
<th>Empirical unit</th>
<th>% Yield complex</th>
<th>M.P.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Theoretic al %</td>
<td>51.73</td>
<td>3.35</td>
<td>22.99</td>
<td>6.70</td>
<td>15.21</td>
<td>C_{18}H_{13}O_{6}N_{2}Cu</td>
<td>69.04%</td>
<td>240°C</td>
</tr>
<tr>
<td>Practical %</td>
<td>50.22</td>
<td>3.12</td>
<td>21.95</td>
<td>6.14</td>
<td>15.16</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**FTIR Spectrum**

Perkin-Elmer instrument in KBr pallets was used to record the IR spectra of the complex in the range of 4000-400 cm^-1. A broad signal at 3442 cm^-1 indicates the presence of the –OH group in the formation of the coordination complex and suggest the presence of water in its structure (Figure 5). The medium intensity band at 1407-1586 cm^-1 is due to the aromatic (C=C) vibrations. The band around 1152-1248 cm^-1 indicating coordination through oxygen of (C-O) group. Two absorption bands at 753 cm^-1 and 855 cm^-1 in the spectrum of the Cu (II) complex were observed which can be due to the stretching vibrations of copper-oxygen bonds, namely C=O→Cu and HO→Cu. The (M-O) band was observed in the complexes around 680 cm^-1.

**Thermo gravimetric Analysis (TGA):** TGA analysis of metal complex was carried out in nitrogen atmosphere in the range of 10-500°C on Rigaku Thermo Plus-8120 TG-DTA instrument with a heating rate of 10°C min^-1. Thermo gravimetric (TG) weight loss curves for the complex shows (Figure 6) two well-defined steps at 240°C (Loss of water molecule) and 350°C (54.26%) together with another steps at 490°C (6.58%), totalling 79.23% weight loss.
Applications of Synthesized Copper complex: Antimicrobial Activities

Antimicrobial Screening. In vitro antimicrobial screening. The studies of antimicrobial activities (i.e. antibacterial and antifungal) was performed by the agar cup method\textsuperscript{9,10}. Nutrient agar growth media was prepared according to the procedures in the laboratory only. The metal complexes shows significant effects on biological activities.

**Antibacterial activity**: The synthesized Cu (II) metal complex was tested against gram-positive (Staphylococcus aureus), gram-negative (Escherichia coli) and Bacillus subtilis pathogenic bacteria at a concentration of 100 μg disc\textsuperscript{-1}. In this method, bacterial culture suspensions are inoculated on the surface of assay agar medium (base layer). The holes were used as a reservoir for compound or antibiotics. The sample containing copper complex solution in DMSO, to be tested present in the reservoir come into contact with inoculated medium and after overnight incubation at 37°C, the plates were observed for the zone of inhibition surrounding the reservoir. The zone of inhibition is the clear area around the reservoir, showing the inhibition of the microorganism by the diffused substances through the agar (Figure 7). The diameter of the clear zone around the reservoir (zone of inhibition) was measured. However, if the sample to be tested is ineffective, then no zone of inhibition will develop (Figure 8).

![Antibacterial screening using Cu metal complex](image1.png)

**Fig. 7**: Antibacterial screening using Cu metal complex

**Antifungal Screening**: Two pathogenic fungi i.e. Candida albicans and Aspergillus niger were screened by using Tube Dilution Method for the study of antifungal activity of copper metal complex (Figure 9). The DMSO solution (300 ppm) of the synthesized metal complex (0.1 mL) was mixed with 5 mL of Sabouraud broth test tube, autoclaved it for 15 minutes, then kept on a rotary shaker and incubated at room temperature for 24 hours. The optical density (OD) of the solution was recorded using spectrophotometer at 530 nm with inoculated Sabouraud broth as a blank and on the basis of optical density the percentage growth of the fungus was calculated. The results are given in Figure 10 and 11.

![Antifungal Screening](image2.png)

**Fig. 9**: Antifungal Screening

![Fungi: A. niger](image3.png)

**Fig. 10**: Fungi: A. niger

![Fungi: C. albicans](image4.png)

**Fig. 11**: Fungi: C. albicans

**Synthesis of CuO nanoparticles**\textsuperscript{3}: Copper oxide (CuO) nanoparticles were synthesized by aqueous precipitation method where copper acetate is used as a precursor and NaOH as a stabilizing agent. A mixture of copper acetate (0.02 mol) solution and 1 ml glacial acetic acid is taken in a round bottom flask and heated to 70-80°C with constant stirring. NaOH (0.5g) is added to the mixture to adjust the pH up to 6-7. The black precipitate is formed which is centrifuged and washed 3-4 times with deionized water. The obtained precipitate was dried in air for 24 h. A large amount of CuO nanoparticles were obtained easily.

**Characterization of CuO nanoparticles**: The synthesized CuO nanoparticles were characterized by FTIR Spectroscopy and SEM techniques. The FTIR spectra of copper oxide nanoparticles were recorded on Perkin-Elmer spectrum on FT-IR spectrometer over the wave number range of 4000–400 cm\textsuperscript{-1}.
at a scanning rate of 4 cm/min. The bands around at 454 cm$^{-1}$ and 605 cm$^{-1}$, can be assigned to the vibrations of Cu-O bonds. The broad absorption peak at around 3416 cm$^{-1}$ is caused by the adsorbed water molecules. This analysis confirmed the presence of metal-oxygen bonding in these nanoparticles (Figure 12).

Scanning electron microscope (SEM) is used to study the surface morphology of the copper oxide nanoparticles. The SEM images of CuO nanoparticles are shown in (Figure 13). The size determination of CuO nanoparticles was done on JEOL-JSM-6360 Scanning Electron Microscope (SEM) in the SAIF, IIT, Bombay. SEM images indicate that the obtained Copper oxide (CuO) nanoparticles are highly crystalline. The microgram appears to be diffused and shows uneven morphology.

Application of Synthesized CuO nanoparticles in the degradation of Rhodamine B Dye:

Rhodamine B stock solution was prepared by dissolving 0.0048g of dye in 100 mL of double distilled water (1.0X $10^{-5}$ M). Now 1.0 mL from the same prepared Rhodamine B solution was taken in a beaker and 24.0 mL of double distilled water was added. Now 0.12 g of solid CuO (0.015 M) nanoparticle was added in the same beaker. The mixture thus obtained was stirred for two hours at acidic pH using digital pH meter Equip Tronics (EQ-614 A). Now the reaction mixture was exposed to light by using 150 W tungsten lamp (Philips) for irradiation at regular time intervals (i.e. 0 min to 150 min). The $\lambda_{max}$ was found to be 550 nm by using UV spectrophotometer. The results for typical run are given in Figure 14.

**Table 2.0: Effect of Time on Rhodamine B Degradation with CuO nanoparticles**

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>Absorbance ($A_0$)</th>
<th>%X</th>
<th>%D</th>
</tr>
</thead>
<tbody>
<tr>
<td>00</td>
<td>1.927</td>
<td>100.00</td>
<td>0.00</td>
</tr>
<tr>
<td>10</td>
<td>1.834</td>
<td>95.17</td>
<td>4.82</td>
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<td>1.721</td>
<td>89.30</td>
<td>10.69</td>
</tr>
<tr>
<td>30</td>
<td>1.701</td>
<td>82.87</td>
<td>11.72</td>
</tr>
<tr>
<td>40</td>
<td>1.623</td>
<td>84.22</td>
<td>15.77</td>
</tr>
<tr>
<td>50</td>
<td>1.567</td>
<td>81.31</td>
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<tr>
<td>60</td>
<td>1.426</td>
<td>74.00</td>
<td>25.99</td>
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<tr>
<td>70</td>
<td>1.309</td>
<td>67.92</td>
<td>32.07</td>
</tr>
<tr>
<td>80</td>
<td>1.289</td>
<td>66.89</td>
<td>33.10</td>
</tr>
<tr>
<td>90</td>
<td>0.957</td>
<td>49.66</td>
<td>50.33</td>
</tr>
<tr>
<td>100</td>
<td>0.812</td>
<td>41.13</td>
<td>57.86</td>
</tr>
<tr>
<td>110</td>
<td>0.769</td>
<td>39.90</td>
<td>60.09</td>
</tr>
<tr>
<td>120</td>
<td>0.543</td>
<td>28.17</td>
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<td>130</td>
<td>0.448</td>
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<tr>
<td>140</td>
<td>0.131</td>
<td>6.79</td>
<td>93.20</td>
</tr>
<tr>
<td>150</td>
<td>0.131</td>
<td>6.79</td>
<td>93.20</td>
</tr>
</tbody>
</table>

**CONCLUSIONS**

The synthesis of copper metal complex by using Schiff base was confirmed by FTIR, Elemental analysis and TGA techniques. The antimicrobial activity of the synthesized copper complex shows that the complex is useful as an antibacterial and antifungal agent. The synthesis of copper oxide nanoparticles was confirmed by FTIR and SEM techniques. The CuO nanoparticles are successfully used for the degradation of Rhodamine B dye.
Acknowledgement

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