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Photocatalytic Degradation of Methylene Blue Dye over Copper(II) Complex Nanoparticle Catalyst

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Abstract— A novel copper(II) complex nanoparticles catalyst was synthesized via precipitation and calcination. The catalyst was applied for the degradation of methylene blue under UV light irradiation. The catalyst was characterized for its physicochemical and structural properties by XRD, SEM, TEM and FT-IR spectroscopic techniques. XRD studies revealed that the particles were monoclinic single phase crystalline structure, the morphology of the nanostructure was confirmed by SEM while the TEM studies revealed that the particles were FCC. FTIR spectra showed the presence of diverse vibrational functional groups. Photolysis of the methylene blue dye indicates no degradation after 1 hour reaction, while the addition of the copper(II) complex nanoparticles catalyst resulted in the decolouration of the dye by ~94%. The efficiency of the catalyst was attributed to the nanoparticle's morphology.

Keywords: ***Catalysis, Nanoparticlesg, Photodegradation, Synthesis.***

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I. INTRODUCTION

Many chemicals have been used, surface active substances, and salts, in the process of dyeing. Production procedures, namely dyeing, cleaning, etc., create vast volumes of wastewater contaminated with various substances. Synthetic dyes, being reasonably stable compounds and challenging to degrade in wastewater treatment plants based on physical, chemical or/and biological treatment, are the substances of the great relevance. Various advanced oxidation systems, including ozone (O_3) at pH > 8.5; O_3 and hydrogen peroxide (O_3 + H_2O_2); O_3 and catalyst; Fenton system (H_2O_2 + Fe^{2+}); O_3 and UV; H_2O_2 and UV; O_3, H_2O_2 and UV; photo-Fenton system; and photocatalytic oxidation (TiO_2 + UV) have been used for decomposition of organic dyes [1]. Wastewater dye contamination has been widespread in several areas, such as the textile industry [2]. Several methods were then used to decolorize textile waste water and degrade organic colouring, namely adsorption, chemical oxidation and biochemical processes of active sludge [3]. In those conventional approaches, however, the dyes could not be fully degraded and could cause new waste treatments. Heterogeneous photocatalysis has been successfully used presently as an easy, low-cost and advanced oxidation technology to oxidize several organic contaminants in aqueous systems [4]. TiO_2 has been commonly used as one of the most prospective and promising photocatalytic materials because of its cost-effectiveness, high stability and low toxicity [5]. Wide surface area are however used to load TiO_2 to facilitate successful photocatalysis [6]. Roughly equivalent with other transition metals outlined above, copper(II) complex nanoparticles seem to be less examined. Biodegradability studies on azo dyes have already shown that under anaerobic environment, azo dyes are rarely biodegradable, with large quantities of the dye and its metabolites identified by bioflocs in the sludge [7-8]. However, biotreatment of textile effluents including azo dyes and their hydrolysis results may be a cost-effective option if the effluents are chemically pretreated in the biological unit prior to care [9]. In this work, copper(II) complex nanoparticles were synthesized using precipitation method and calcined at 700 ^{O}C for 2 hours leading to the formation of nanoparticles. The obtained nanoparticles were successfully tested as photocatalyst for the decolouration of methylene blue as a model dye pollutant. The

physicochemical properties of the catalyst was investigated by XRD, SEM, TEM, and FTIR. The reaction was conducted under UV irradiation for 1 h at a wavelength of λ_{max} of 291 and 663 nm.

II. MATERIALS AND METHODS

A. Materials

All materials are of analytical grades. The chemicals used are salicylaldehyde ($C_7H_6O_2$, 98% purity) produced by Sigma-Aldrich, copper acetate monohydrate ($Cu(CO_2CH_3)_2.H_2O$, 98% purity) produced by Sigma-Aldrich and ortho-phenylenediamine ($C_6H_8N_2$, 99.5% purity produced by Sigma-Aldrich.

B. Methodology

1. Synthesis of Schiff base ligand

Salicylaldehyde (1.07 mL, 10.00 mmol) was refluxed with ortho-phenylenediamine (1.10 g, 10.00 mmol) in ethanol for 2 hours to obtain and orange solution. The solution was reduced under suction to form an orange precipitate. The precipitate was filtered under suction, washed with ethanol and recrystallized from ethanol. It was dried over silica gel in desiccator [10]. The schematic representation of the synthesis procedure is represented in Fig. 1.

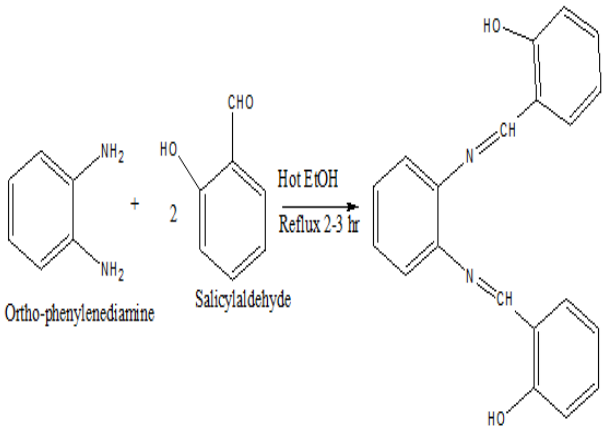

Figure 1 Schematic synthesis of Schiff base ligand.

2. Synthesis of Copper (II) complex nanoparticles.

Copper(II)complex was synthesized following a procedure adopted from [10].Typically, 50 mL hot ethanolic solution of Schiff base ligand (3.16 g, 0.01 mol) and 50 mL hot ethanolic solution of copper acetate monohydrate (1.71 g, 0.01 mol) was mixed. The pH was adjusted by adding few drops of dilute ammonium hydroxide solution which led to the precipitate of the solid chelate. The mixture was refluxed for 3 hours under constant stirring to obtain precipitate and then was washed until the colour turned clear. The synthesized complex was calcined at 700 °C for 2 hours under air atmosphere leading to nanosized copper complex. The synthesized Copper(II) complex nanoparticles was characterized by XRD, TEM, SEM and FT-IR spectroscopic methods. The schematic diagram for the synthesis of copper(II) complex are shown in Fig. 2.

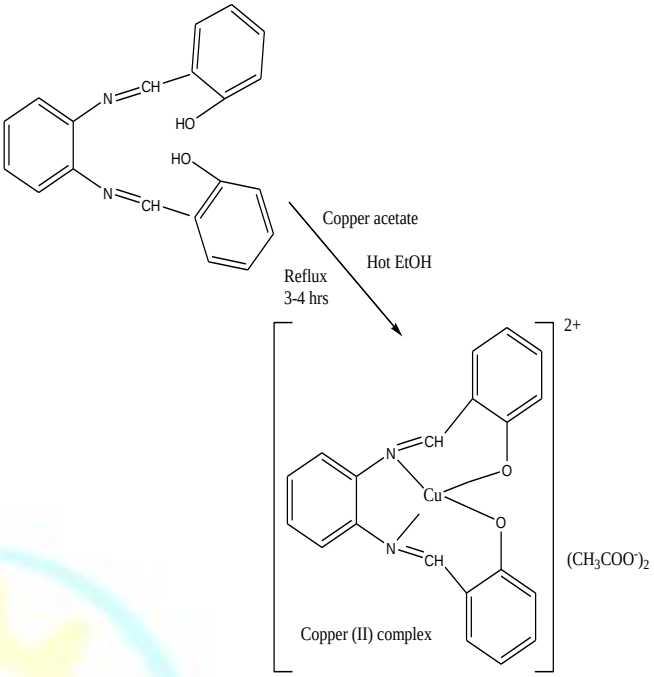

Figure 2 Synthesis of copper (II) complex.

C. Photocatalytic Study

By mixing 0.1 g of samples to 100 ml of 20 ppm methylene blue dye solution, the photocatalytic degradation procedure was conducted. The suspension was exposed for 1 hour to UV irradiation. The UV light source was given by a 0.6 mW/cm2 strength UV bench lamp (365 nm, 230V ~ 50 Hz). Throughout the experiment, the aqueous suspension was magnetically stirred. 3 mL of aliquot was removed using a syringe after every 10 minutes of time intervals and then filtered through a 0.45 µm Millipore filter syringe. Then absorption spectra were recorded via UV-Visible spectrophotometer (Perkin Elmer Lambda 1600FT-IR) and the percentage of MB degradation was calculated using the formula in Eqn. 1.

$$\text{Degradation (\%)} = C_o - C_t / C_o \times 100\% \quad (1)$$

Where C_0 is the initial absorption of dye and C_t is the absorption of dye after the reaction at *t* time.

1. Calibration curve for MB solution

1000 ppm stock solution of methylene blue was prepared by dissolving 0.1 g of the substance in 100 mL volumetric flask with distilled water. Then using dilution formula; 5, 10, 15, 25, and 30 ppm was prepared using the dilution formula (Eqn. 2). The absorbance was measured by using UV-Visible spectrophotometer.

$$M_1 \times V_1 = M_2 \times V_2 \quad (2)$$

2. Preparation of 20 ppm MB solution

1000 ppm stock solution of methylene blue was prepared by dissolving 0.1 g of the substance in 100 mL volumetric

flask with distilled water. Then 20 ppm was prepared from the solution using the dilution formula (Eqn. 2).

3. Photolysis

In order to verify the effect of light on the solution before the catalyst was applied, the methylene blue solution (20 ppm) was irradiated using a UV lamp for 1 hour. Every 10 minutes, 2 mL of the sample was taken and assessed using the UV-Visible spectrophotometer.

III. RESULTS AND DISCUSSIONS

A. XRD analysis

Phase structure and crystallinity of the Cu(II) complex nanoparticles was analyzed by XRD. Fig. 3 indicates the XRD analysis having intense peaks at 35.45°, 35.55°, 38.74°, 38.93°, 48.74°, 51.38°, 58.30°, 61.56° and 65.84°, which relate to (-011), (002), (110), (202), (-202), (202), (202), (113), (-022) and (113), respectively. The observed diffraction reflections were comparable with other literature data [11]. All diffraction peaks could be indexed as the typical monoclinic crystal structure with $P2_1/_C$ space group, and no extra diffraction peaks of other phases were observed [12]. This shows that the materials in monocrystalline.

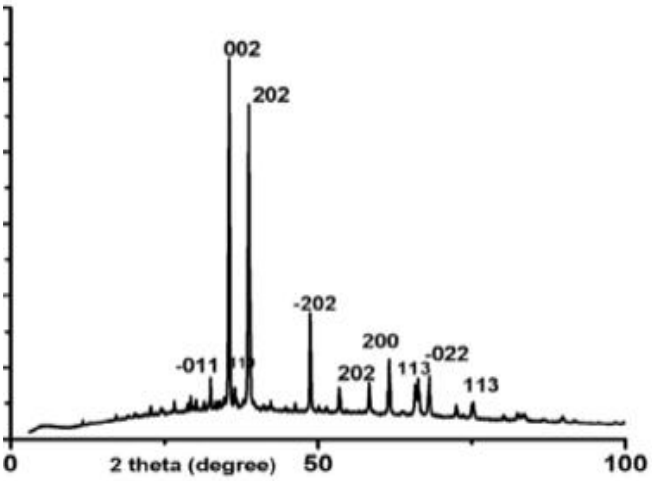

Figure 3 XRD spectrum of the copper complex nanoparticle.

B. SEM and TEM analysis

Morphology of the synthesized nanoparticles was analyzed by SEM and TEM techniques. Fig. 4 shows the SEM micrographs of Cu(II) complex nanoparticles. It can be clearly observed that agglomeration and large grains formation were formed in the SEM images and the image also revealed that few spherical shaped particles are also present. Some nanoparticles are quite separated from each other and agglomeration formations are due to the oxidation of metal nanoparticle. The SEM image also confirmed the nanostructure behavior of the particles [13]. The TEM results (Fig. 5) depicted that synthesized particles were FCC in accordance with XRD results. The TEM results also clearly indicates the formation of spherical copper complex nanoparticles as shown in SEM images. XRD revealed the monoclinic single-phase structure [13].

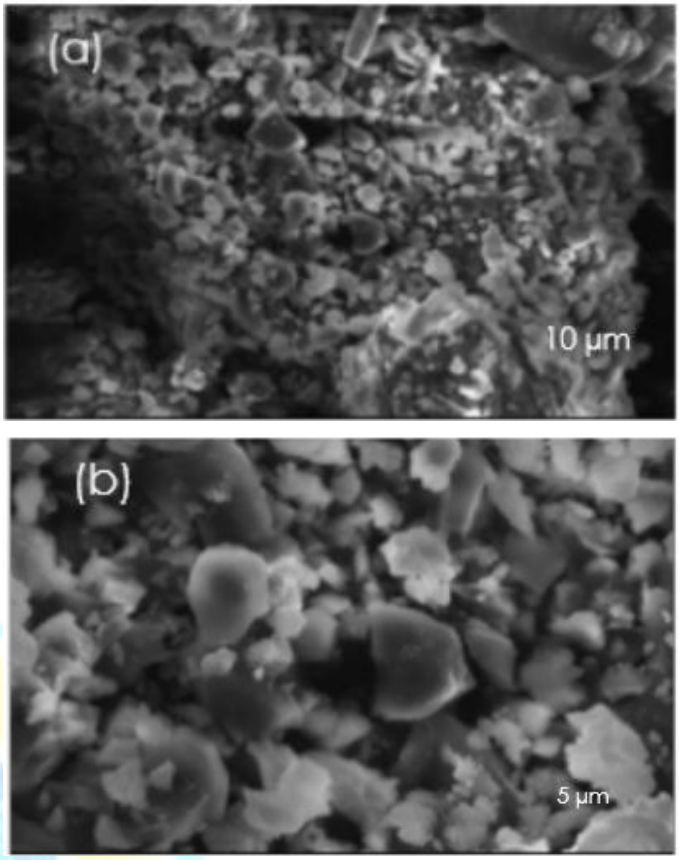

Figure 4 SEM image of copper complex nanoparticle at (a) magnification of 10 µm and (b) magnification of 5 µm

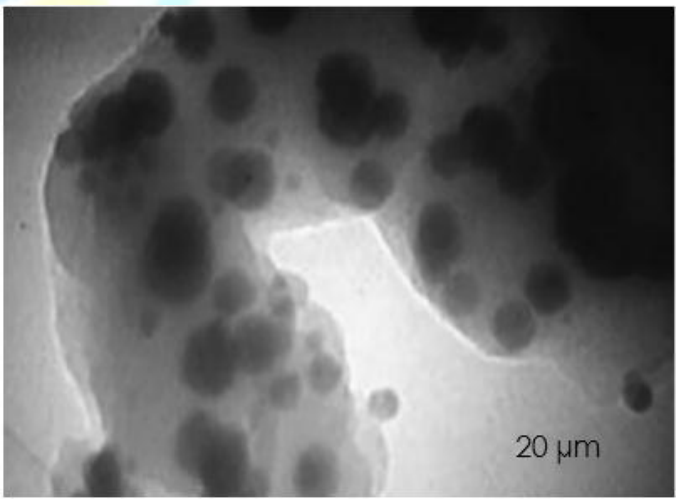

Figure 5 TEM image of copper complex nanoparticle at magnification of 20µm.

C. FT-IR spectral analysis

FTIR analysis was conducted to investigate the functional group of the synthesized material at wavelength of 4000 to 400 cm^{-1}. Fig. 6 revealed the spectra of the Cu(II) complex nanoparticles. The IR band at 3433 cm^{-1} was due to OH stretching of hydroxyl group. The band at 2921 cm^{-1} was attributed to C–H group. The stretching vibration at 1632 cm^{-1} and 1327 cm^{-1} was assigned to C=N and C–O groups, respectively. The band at 573 and 522 cm-1 confirmed the

presence of Cu–N and Cu–O, respectively. Similar result was reported by [13]. The functional group assignment is tabulated in Table1.

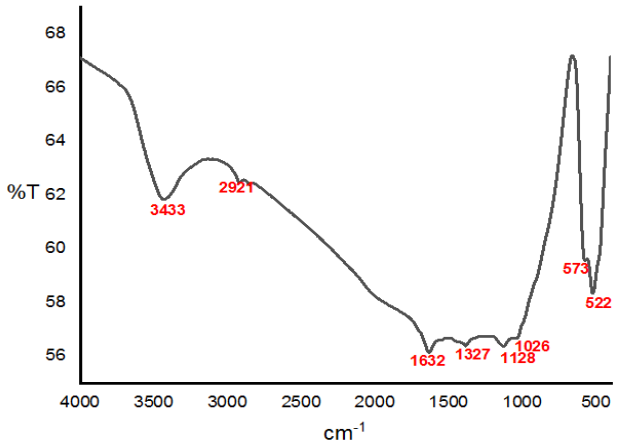

Figure 6. FT-IR spectrum of the copper(II) complex nanoparticles.

D. Photodegradation activity of Copper(II) complex nanoparticles

UV-visible spectroscopy was employed for the optical properties of copper(II) complex nanoparticles and adsorption spectra for the samples are shown in Fig. 7. Through the observation of characteristic absorption bands of MB at about 291 and 663 nm, the distinct dye concentration was monitored. As the illustration from Fig 7a, with the time of irradiation, the diverse dye absorption spectra gradually reduced. In photocatalytic process, it is easy to observe the discoloration of dye with physical eyes. Fig. 8 reveals the change of dye solution against the time of irradiation C_t/C_o diagram (in which the C_o represents the initial dye solution concentration, and the C_t represents the dye concentration dye concentration at any designated time). The calculation results display that the percent of degradation for MB is 96.4%, indicating an efficient decoloration in 60 min. The performance is attributed to higher production of OH• radicals which degrade the pollutant at the catalyst surface.

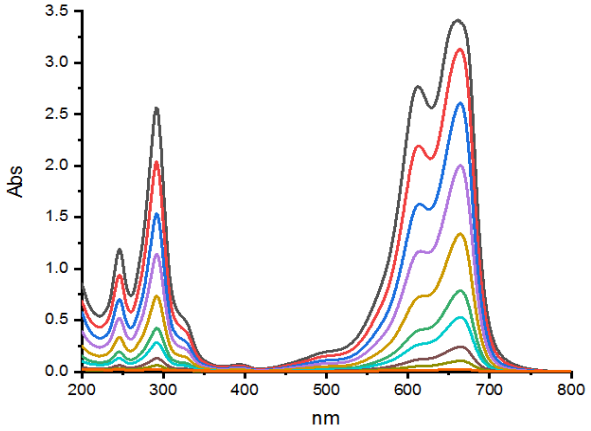

Figure 7. Photodegradation of methylene blue using copper complex nanoparticles.

Table I Significant FT-IR data for the copper (II) complex nanoparticle.

Functional Groups	*Frequency*
OH	3433
C-H	2921
C=N	1632
C-O	1327
Cu-N	573
Cu-O	522

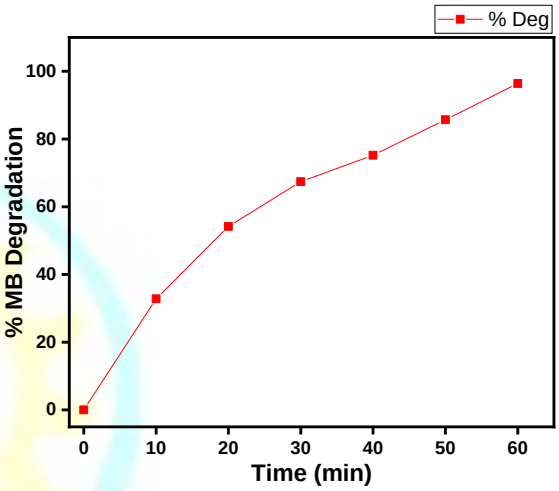

Figure 8. % Degradation of MB dye over Cu (II) complex.

IV. CONCLUSION

Copper(II) complex nanoparticles was successfully synthesized via 2 step process by precipitation method and calcination. The compound was used as photocatalyst for the decoloration of methylene blue (MB) in aqueous medium. The nanoparticles was characterized by XRD, SEM, TEM, and FTIR. Results indicated that the material contains Cu ion, and the morphology of the particles is in spherical shape. The catalytic activity of the complex shows excellent degradation of methylene blue in 60 min and the percentage degradation was calculated and found to be 94.6% which revealed that the catalyst was efficient for the degradation of methylene blue dye and other organic wastewater pollutants.

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CONFLICT OF INTEREST

Authors declared that there is no conflict of interest in them.

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