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Biosynthesis of Copper Oxide Nanoparticles Using Bitter Leaf Extract and Photodegradation Effect on Methylene Blue Dye

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Abstract
A copper oxide nanoparticles was synthesized using bitter leaf extract via hydrothermal technique. The catalyst was applied for the degradation of methyl blue under UV light irradiation. The catalysts were characterized for its physicochemical, optical, and structural properties using XRD, UV-visible, SEM, TEM and FT-IR spectroscopic techniques. Photocatalysis of the methyl orange dye indicates degradation after 1h reaction, while the addition of the copper oxide nanoparticles resulted in the decolouration of the dye to 65%. The efficiency of the catalyst was attributed to the nanoparticle morphology, low band gap, and small crystallite size of the catalyst used

Keywords: Photocatalysis, Nanoparticles, Synthesis, Spectroscopy, Calcination.

Introduction
Many chemicals are utilized in the dying process, including acids, alkalis, surface active substances, and salts. Processes in production including dyeing, washing, etc. produce large quantities of wastewater polluted with various chemicals. Synthetic dyes are the substances of the highest concern, being relatively stable compounds and difficult to degrade in wastewater treatment plants based on physical, chemical or/and biological treatment. Various systems of advanced oxidation were employed for the decomposition of organic dyes, 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) (Munter, 2001). Dye pollution in wastewater has widely existed in many fields such as textile industry (Bizani *et al*., 2006). Thus, many strategies were applied to decolorize the textile wastewater and degrade organic dye including adsorption, chemical oxidation and active sludge biochemical processes (Malwal and Gopinath, 2015). However, the dyes couldn't be degraded thoroughly with those traditional ways and might cause new waste treatments. Nowadays heterogeneous photocatalysis as a simple, low-cost and advanced oxidation technology has been successfully used to oxidize many organic pollutants in aqueous systems (Zhao *et al.*, 2016).TiO_2, as one of the most potential and promising photocatalytic materials, has been widely used due to its cost-efficiency, high stability and low toxicity (Chang *et al.,* 2017). Unfortunately, naked TiO_2 particles possess poor reusability and may lead to secondary pollution (Yu *et al.*, 2003) Therefore, some carriers with large surface area are applied to TiO_2 loading for achieving efficient photocatalysis (Asahi *et al*,.2014). Copper doping has been less explored compared to other transition metals mentioned above. Also, it appears from the limited literature reports available on copper doping that the doped catalysts have been tested only in the UV or near-UV range of radiation (Choi, and Kang, 2007). Biodegradability studies on dyestuffs have shown that azo dyes are rarely biodegradable under aerobic conditions, large quantities of the dye and its metabolites being sorbed by bioflocs in the sludge (Pagga, and Brown, 1986). Nevertheless, biotreatment of textile effluents containing azo dyes and their hydrolysis products can be a cost-effective alternative when the effluents are pretreated chemically prior to treatment in the biological unit (Sheu, *et al.,* 1996). In this work, copper (II) complex was synthesized and calcined at 700 ^{O}C for 2 hours leading to the formation of nanoparticle. The obtained nanoparticle was successfully tested as catalyst for the decolouration of methyl blue as a model dye pollutant. The

physicochemical properties of the catalyst were investigated by XRD, SEM, TEM, and FTIR. The reaction was conducted under UV irradiation for about 1 h.

Materials and Methods

Synthesis of Schiff base ligand

About 1.07 ML (10.00mmol) of salicylaldehyde was measured and refluxed with 1.10g (10.00mmol) of 4-Bromoaniline in ethanol for about 2 hours to obtain an 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 (Garba *et al*., 2021)

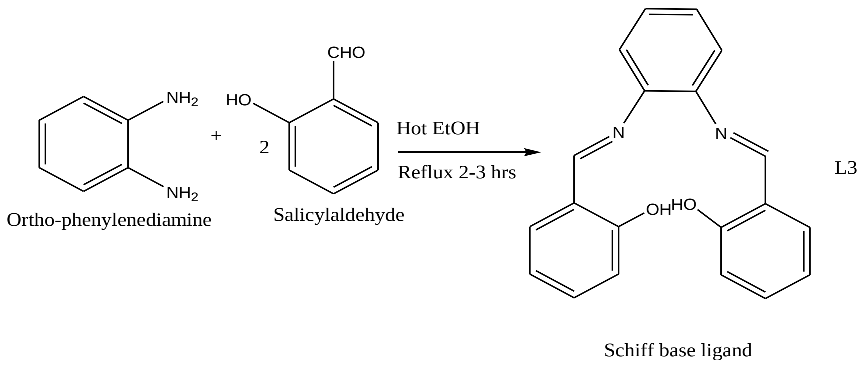

Figure 1: Synthesis of Schiff base ligand

Synthesis of Copper (II) complex

A copper acetate monohydrate $Cu(OAc)_2.H_2O$, (0.123 g, 0.617 mmol) was completely dissolved in ethanol (10 mL) and ethanolic solution of the synthesized ligand (0.30 g, 1.23 mmol) was added drop-wise with vigorous stirring. A green precipitated of the product (86.9%) was form which was suction filtered, washed with ethanol and dried in a desiccator (Ali *et al* ., 2016).

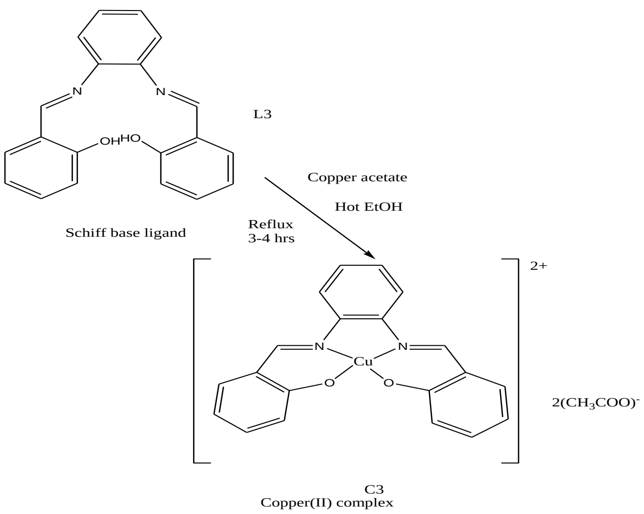

Figure 2: Synthesis of copper complex

Preparation of Bitter Leaf Extract

The fresh leaves of *bitter leaf* was obtained from a Mubi market in Mubi North Local Government Area of Adamawa State. The collected fresh leaves were washed thoroughly with deionized water to remove dirt particles if any adsorbed on the surface of the leaves. The washed leaves were then air-dried at room temperature. The cleaned and dried leaves were ground into fine powder using an electrical blender followed by sieving using a 20 mesh sieve. In order to prepare a flavonoid-rich extract, 2 g of the dried leaf powder was extracted with 200 mL deionized water in a Soxhlet apparatus for 6 hours. The aqueous leaf extract was then stored at 5°C for further use (Jayakumari *et al*., 2019)

Synthesis of copper oxide nanoparticles

The copper complex was synthesized and calcined at 700 °C for about 2 hour under air atmosphere leading to copper oxide nanopartices and mixed with 2ml extracts of bitter leaf. The mixture obtained was then structurally determined and characterized by some spectroscopic methods such as: XRD, TEM, SEM and FT-IR (Jayakumari *et al*., 2019)

Optimization of Copper oxide NPs

The biosynthesis of CuO NPs was carried out at different volumes of leaf extract (1, 2, 3, 4 mL) at pH 8 and room temperature. The pH of the reaction was varied by adding 0.1 NaOH to achieve the pH of the solution 8, 9, 10 and 11, accordingly. The reaction temperature was optimized by conducting the experiment at three different temperatures, namely, at room temperature, 60°C and 80°C. Finally, the reaction time was recorded up to the saturation time. The entire optimization process of biosynthesis CuO NPs was monitored by UV-Vis spectroscopy. After completion of the optimization experiment, the colloidal solution was centrifuged at 14800 rpm for 20 min. The obtained precipitate was washed with double distilled water, and dried and kept in a desiccator for further use (Jayakumari *et al*., 2019)

Photocatalytic Study

The photocatalytic degradation experiment was carried out by adding 0.1 g of samples into 100 ml of 20 ppm MB dye solution. The suspension was subjected to UV irradiation for 3 hours. The UV light source was provided by an UV bench lamp (302 nm, 230V ~ 50 Hz). The aqueous suspension was magnetically stirred throughout the experiment. At every 10 minutes of time intervals 3 ml of aliquot was taken out using syringe and then filtered through 0.45 μm Millipore syringe filter paper. The absorption spectra were recorded via UV-Vis spectrophotometer (Perkin Elmer Lambda 35 UV-Vis) and the percentage of MB degradation was calculated using the formula as adopted by Garba *et al.*, (2021) below;

Degradation (%) = C_0-C_t x 100%

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

Preparation of 20 ppm MB solution

About 20 ppm of MB was irradiated using UV lamp for about 2 hours to check the effect of light on the solution before introducing the catalyst. About 2 ml of the sample was taken at 10 minutes interval and tested using UV-Vis spectrophotometer.

Reusability Test

The used copper oxide nanoparticles were washed with distilled water several times and applied for the decomposition of MB again. The photocatalytic efficiency of MB removal was still 100% efficiency after five times degradation process which shows that copper complex nanoparticle has a better recycling performance for the decolouration of methylene blue. (Handy *et al*., 2020).

Results and Discussions

Photodegradation of methylene blue using UV-vis spectroscopy

UV-vis spectroscopy was explore for the optical properties of copper (II) complex nanoparticles and adsorption spectra for the samples are shown below. The peaks are evidence in wavelength range between 240-300nm which confirmed the synthesis of nanoparticles and the result obtained are in agreement with the literature (Jayakumari *et al*., 2019)

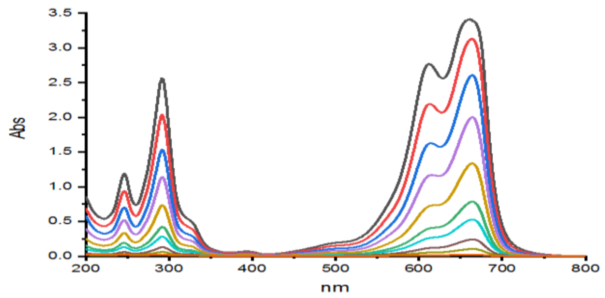

Figure 3: Photodegradation of methylene blue using copper oxide nanoparticles.

Morphology of the copper complex nanoparticle.

Agglomeration and large grains formation were observed in the SEM images (Figure 4 &5) 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 nanoparticles. The SEM image also confirmed the nanostructure behaviour of the particles (Khanm *et al.*, 2017). The TEM results (Figure 6) depicted that synthesized particles were FCC in accordance with XRD results. The TEM results also indicates the formation of spherical copper complex nanoparticles. XRD revealed the monoclinic single phase structure (Khanm *et al.*, 2017).

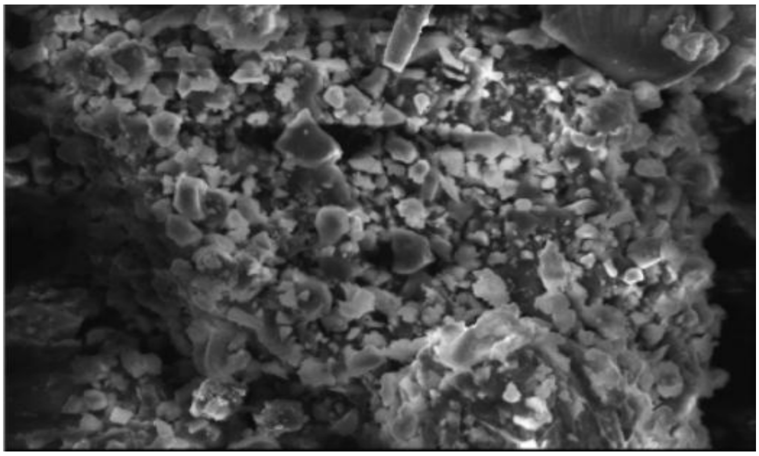

Figure 4: SEM image of copper oxide nanoparticles at magnification of 10 µm.

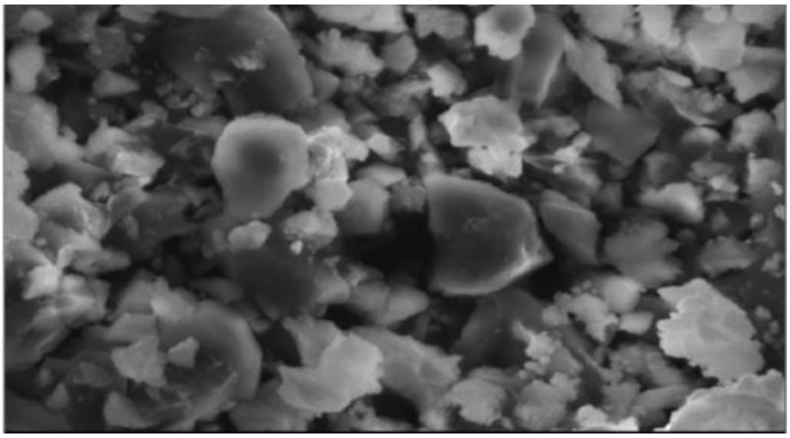

Figure 5: SEM image of copper oxide nanoparticle at magnification of 5µm.

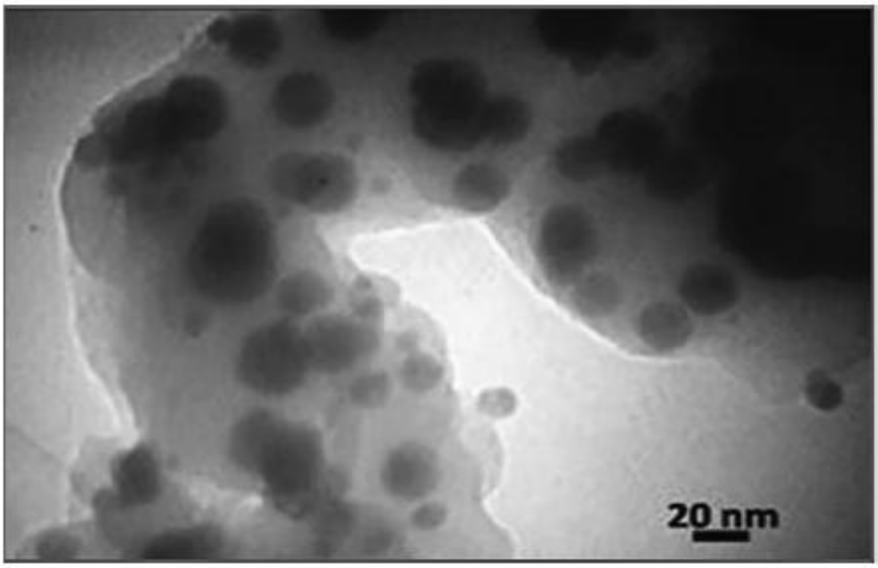

Figure 6: TEM image of copper oxide nanoparticles at magnification of 20µm.

XRD analysis

The XRD analysis (Figure 7) showed intense peaks at 35.45^{o}, 35.55^{o}, 38.74^{o}, 38.93^{o}, 48.74^{o}, 51.38^{o}, 58.30^{o}, 61.56^{o} and 65.84^{o}, which correspond to (-011), (002), (110), (202), (-202), (202), (202), (113), (-022) and (113) respectively. The observed diffraction reflections were comparable with other literature data as shown by Nordin and Shamsuddin, (2019). All diffraction peaks could be indexed as the typical monoclinic structure and no extra diffraction peaks of other phases were observed (Li *et al*., 2017).

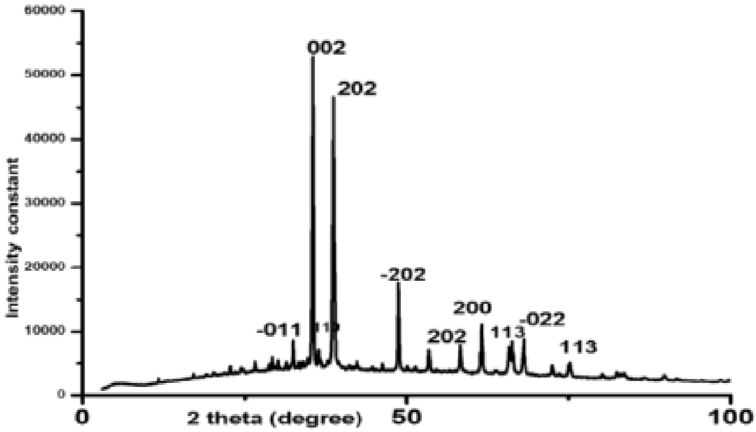

Figure 7: XRD spectrum of the copper oxide nanoparticle.

FT-IR spectra analysis of the copper oxide nanoparticles

The infrared band of synthesized nanoparticles Table 1 and Figure 8, show the appearance of frequency at 3433 cm^{-1} was due to N-H stretching of amines. The band at 2921 cm^{-1} was allocated 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 result obtained in the study was found to be in complete agreement with the reviewed literatures (Khanm *et al.*, 2017)

Table 1. Significant FT-IR data for the copper (II) oxide nanoparticle

Functional groups	Frequency (cm^{-1})
N-H	3433
C-H	2921
C=N	1632
C-O	1327

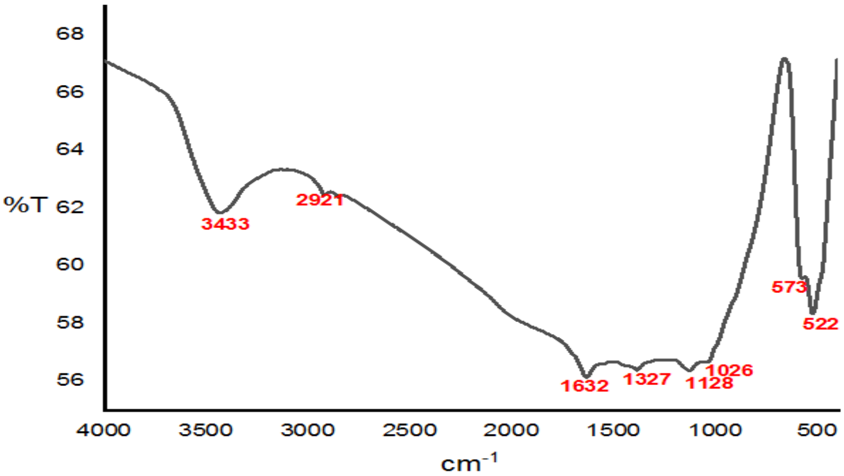

Figure 8: FT-IR spectrum of the copper (II) complex nanoparticles.

Conclusion

A copper oxide nanoparticles was successfully synthesized using bitter leaf extract via hydrothermal technique. The catalyst obtained was used for the degradation of methyl blue under UV light irradiation. The catalysts were characterized for its physicochemical, optical, and structural properties using XRD, UV-visible, SEM, TEM and FT-IR spectroscopic techniques. Photocatalysis of the methyl orange dye indicates degradation after about 1h reaction time, while the addition of the copper oxide nanoparticles resulted in the decolouration of the dye to 65%. The efficiency of the catalyst was attributed to the nanoparticle morphology, low band gap, and small crystallite size of the catalyst. Recyclability of the catalyst proves that the catalyst was active and can be recycle without significant decrease in the degradations performance.

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