

Biosynthesis, Characterization and Photocatalytic Activity of Copper/Copper Oxide Nanoparticles Produced Using Aqueous Extract of Lemongrass Leaf

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Abstract: The paper presents a green, simple and eco-friendly method to synthesize copper/copper oxide nanoparticles (Cu/CuO-NPs) from CuSO₄ solution using aqueous extract of lemongrass leaf as the reducing and capping agent. The influence of some factors such as the volume ratio of lemongrass leaf extract and CuSO₄ solution, pH and temperature to the synthesis of Cu/CuO-NPs were investigated. The results showed that the formation of stable Cu/CuO-NPs was rapid. CuSO₄ solution changed from light blue to yellowish green colour after adding aqueous extract of lemongrass leaf. The formation of Cu/CuO-NPs was confirmed by UV-Vis spectroscopy. In this research, transmission electron microscopy (TEM), energy dispersive X-ray (EDX) and X-ray diffraction (XRD) techniques were used to determine the morphology and crystalline phase of Cu/CuO-NPs. The obtained Cu/CuO-NPs were spherical, with the size ranging from 5.67 to 9.10 nm. The photocatalytic activity of the synthesized Cu/CuO-NPs was examined via degradation process of methylene blue under sunlight irradiation.

Keywords: Copper/Copper Oxide Nanoparticles, Lemongrass Leaf, Green Synthesis, Biosynthesis, Plant Extract

1. Introduction

Among the various metal/metal oxide nanoparticles, copper and copper oxide nanoparticles have wide applications as heat transfer systems, antimicrobial materials, gas sensors, catalysts, high temperature superconductors and solar cells [1-4]. The Cu and CuO nanoparticles can be synthesized by different methods such as vapor deposition, electrochemical reduction, solvothermal, sol-gel technique and chemical reduction of copper salts, but these methods are costly, high energy requirement and especially the use of toxic compounds limits their application [5, 6]. Hence the development of a reliable and environmental friendly biosynthesis approach for the synthesis of copper and copper oxide nanoparticles is important because of its eco-friendly products [7-31].

In this study, the copper/copper oxide nanoparticles were synthesized from CuSO₄ solution using aqueous extract of lemongrass leaf as a reducing agent. Synthesized Cu/CuO-NPs were applied to decompose methylene blue dye under sunlight irradiation.

2. Material and Methods

2.1. Preparation of Leaf Extract

Fresh leaves of lemongrass were collected from local places of Da Nang City, Viet Nam. A definite amount of leaves were cut into fine pieces and boiled with 100 mL of double distilled water at 80°C for t minutes. After the boiling process, the extract was filtered through Whatmann No.1 filter paper to obtain aqueous extract.

2.2. Phytochemical Analysis

The aqueous extract of lemongrass leaf was used for phytochemical analysis by standard phytochemical methods [32].

2.2.1. Test for Flavonoids

To 2 mL of extract, 1 mL of 2 N sodium hydroxide was added. The appearance of yellow color indicates the presence of flavonoids.

2.2.2. Test for Alkaloids

To 2 mL of extract, 2 mL of concentrated hydrochloric acid was added. Then few drops of Mayer's reagent were added. The appearance of green color or white precipitate indicates the presence of alkaloids.

2.2.3. Test for Terpenoids

2 mL of extract was treated with 2 mL of chloroform and 1 mL of conc. H_2SO_4 . The reddish brown color formation is observed.

2.2.4. The Chemical Composition of Lemongrass Essential Oils

The chemical composition of essential oils from aqueous extract of lemongrass was determined by GC-MS analysis using GC-MS7890B-5977B – Agilent instrumentation with a capillary column HP-5MS (30 m x 0.25 mm i.d. and 0.25 μ m film thickness). Helium gas was used as the carrier gas with a flow rate of 1.1 mL/min. Temperature program for the oven was from 40°C to 280°C at a rate of 5 min^{-1} with holding time of 1 to 10 min. Injector temperature was 270°C, and the injection volume was 1.0 μ L. The identification of components of the essential oil was based on the comparison of Kovat's retention indices and mass spectra that correspond with data (Adam, 1989) and mass spectra libraries (National Institute of Standards and Technology 98).

2.3. Synthesis of Copper/Copper Oxide Nanoparticles

For synthesis of Cu/CuO-NPs, a definite volume of lemongrass leaf extract was added to 50 mL of 1 mM $CuSO_4$ in 100 mL Erlenmeyer flasks. The formation of Cu/CuO-NPs was indicated by the change in the colour of the reaction mixture from light brown to pale green. The flasks were incubated for 24 hours at desired temperature. The influence of some factors such as the volume ratio of lemongrass leaf extract and $CuSO_4$ solution, pH, temperature to the synthesis of Cu/CuO-NPs were investigated.

2.4. UV-Vis Spectroscopy

The reduction of the Cu^{2+} ions by the supernatant of the aqueous extract of lemongrass leaf and the formation of copper/copper oxide nanoparticles were characterized by UV-visible spectroscopy.

2.5. Transmission Electron Microscopy (TEM), and Energy Dispersive X-ray Spectra (EDX) Analysis

Samples for transmission electron microscopy (TEM) analysis were prepared by drop coating biologically synthesized Cu/CuO-NPs solution onto carbon-coated copper TEM grids. TEM measurements and the EDX analysis were carried out using HRTEM Tecnai G2 F20.

2.6. XRD Measurement

Crystal phase identification of Cu/CuO-NPs was characterized by powder X-ray diffraction using a Panalytical X Pert PRO Diffractometer. The diffracted intensities were

recorded from 20°-80° 2 θ angles.

2.7. Photocatalytic Degradation of Dye

Photocatalytic degradation of methylene blue (MB) was carried out by using green synthesized Cu/CuO-NPs under solar light. About 5 mg of biosynthesized Cu/CuO-NPs was added to 100 mL of 10 ppm MB dye solution. A control experiment was carried out in a same manner without the addition of Cu/CuO-NPs. Before being exposed to irradiation, the reaction suspension was well mixed with a stirrer for 30 mins to obtain the equilibrium state of the working solution. Afterwards, the dispersion was put under the sunlight. The absorbance spectrum of the supernatant was subsequently measured using UV-Vis spectrophotometer. The effectiveness of the degradation process was calculated from the absorption intensity at 660 nm using the following equation (1):

$$MB \text{ degradation (\%)} = [(A_0 - A_t)/A_0] \times 100 \quad (1)$$

Where A_0 is the initial absorbance of MB solution and A_t is absorbance of the MB solution after t hours of exposure in solar irradiation.

3. Results and Discussion

3.1. The Optimal Conditions for the Extraction of Lemongrass Leaf

3.1.1. Effect of Extraction Time

The effect of extraction time of lemongrass leaf to the formation of Cu/CuO-NPs was investigated by varying the time for extraction at $t = 15, 30, 45, 60, 90$ minutes while fixing other parameters as: 20 gram lemongrass leaf /100 mL of distilled water; 5 mL aqueous extract of lemongrass leaf / 50 mL of 1 mM $CuSO_4$ solution; pH of the solution: 4.50.

The UV-Vis spectrum (Figure 1) shows changes in the absorbance of the Cu/CuO-NPs reaction mixture with the addition of lemongrass leaf extraction. Characteristic absorption maxima was observed at 420 - 460 nm for the yellowish green coloured Cu/CuO-NPs. The absorbance intensity of this maxima increases with the increase of the extraction time of lemongrass leaf from 15 minutes to 45 minutes, and reaches the highest absorption at an extraction time of 45 minutes.

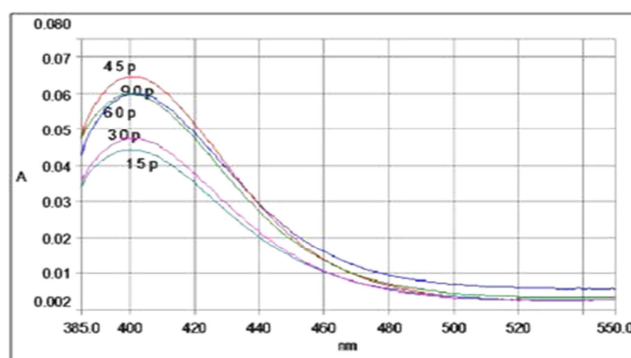


Figure 1. UV spectrum shows effect of extraction time of lemongrass leaf in the synthesis of Cu/CuO-NPs.

3.1.2. Effect of Solid / Liquid Ratio

The effect of lemongrass leaf weight/distilled water volume ratio was examined by varying the amount of lemongrass leaf from 10 g, 15 g, 20 g, 25 g to 30 g. The other parameters were fixed as described in 3.1.1, and the extraction times was 45 mins. The UV-Vis spectrum (Figure 2) of the Cu/CuO-NPs reaction mixture shows that the absorption at the maxima of 400 nm increases with the increase of lemongrass leaf weight and reaches the highest value at a ratio of 25 g of lemongrass leaf / 100 mL distilled water.

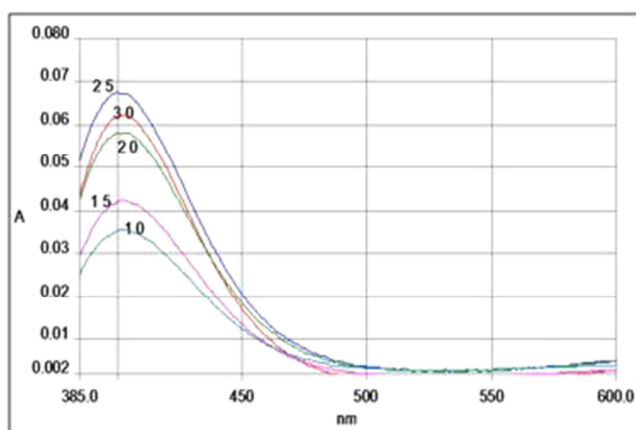


Figure 2. UV spectrum shows effect of the ratio of lemongrass leaf weight/distilled water volume in the synthesis of Cu/CuO-NPs.



3.3. The Factors That Affect the Synthesis of Copper/Copper Oxide Nanoparticles

3.3.1. The Effect of Mixing Ratio on the Formation of Cu/CuO-NPs

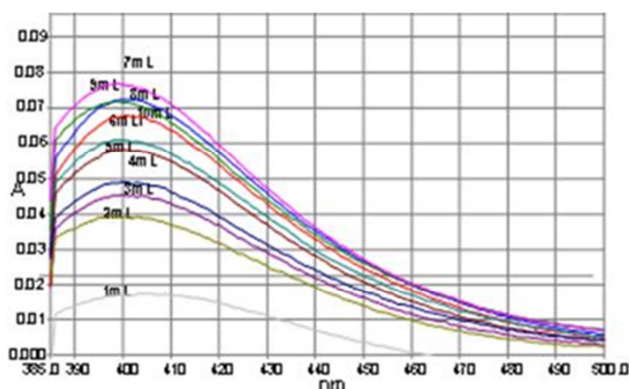


Figure 3. UV spectrum shows effect of mixing ratio of extract volume/ 1 mM CuSO₄ solution volume in the synthesis of Cu/CuO-NPs.

The effect of volume ratio between lemongrass leaf extract

3.2. GC-MS Characterization of Lemongrass Leaf Extract

The results of qualitative phytochemical analysis of the lemongrass leaf extract indicate the presence of flavonoids and terpenoids and the absence of alkaloids.

The chemical components and structure of main compounds of essential oils in aqueous extract of lemongrass leaf are given in Table 1.

Table 1. The structure of some main component essential oils in aqueous extract of lemongrass leaf.

Name	Chemical structure
β -Pinene	
(Ocimene) or 1,3,7-Octatriene, 3,7-dimethyl	
Isogeranial	
β -Citralor 2,6-Octadienal, 3,7-dimethyl (Z)	
α -Citralor 2,6-Octadienal, 3,7-dimethyl (E)	

The presence of flavonoids and terpenoids (Isogeranial, β -Citral and α -Citral) in aqueous lemongrass leaf extract is mainly responsible for the bio-reduction process.

The mechanism for the reducing of Cu^{2+} to form Cu/CuO nanoparticles can be suggested as the following reactions:

and CuSO₄ solution on the formation of Cu/CuO-NPs was studied by varying the extract volume added to 50 mL of 1 mM CuSO₄ solution from 1 mL to 7 mL. The UV-Vis spectrum of the resulting solution (Figure 3) shows that upon increasing the extraction volume, although the peak maxima doesn't change (around 415 - 420 nm), the peak intensity increases. And 7 mL of leaf extract was chosen as the optimal volume.

3.3.2. The Effect of Temperature on the Formation of Cu/CuO-NPs

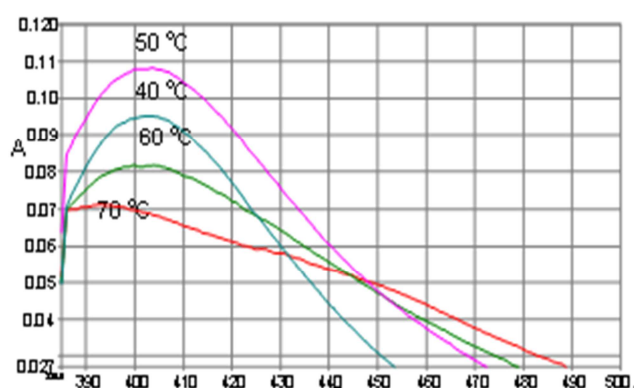


Figure 4. UV spectrum shows effect of temperature in the synthesis of Cu/CuO-NPs.

The UV-Vis spectrum (Figure 4) shows effect of temperature in the Cu/CuO-NPs synthesis. The obtained results of Figure 4 shows that when the temperature increases from 40°C to 50°C, the absorption intensity values increases and peaks at a temperature of 50°C. If temperature continue to rise, the absorption intensity decreases.

3.3.3. The Effect of pH on the Formation of Cu/CuO-NPs

pH also has a great effect on the formation of Cu/CuO-NPs. This effect was studied by varying the pH of 50 mL solution containing 1 mM CuSO₄ from 5 to 10 before adding 7 mL of lemongrass leaf extract. The UV-Vis spectrum of the final solution (Figure 5) shows that when pH increases from 5 to 9, the absorption intensity at maxima wavelength increases and peaks at pH value of 9. However, the intensity drops at pH = 10, which can be attributed to quick formation of Cu/CuO-NPs leading to a coagulation. Larger size of Cu/CuO-NPs results in the drop of absorption intensity.

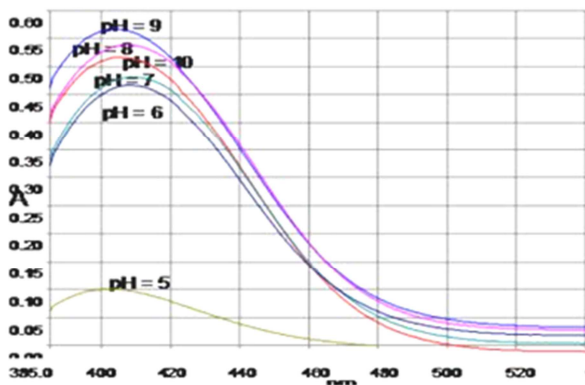


Figure 5. UV spectrum shows effect of pH on the formation of Cu/CuO-NPs.

3.4. TEM Analysis of Copper/Copper Oxide Nanoparticles

TEM technique was employed to visualize the size and shape of copper/copper oxide nanoparticles. TEM image of the produced Cu/CuO-NPs is shown in Figure 6. The formation of Cu/CuO-NPs as well as their morphological dimensions in the TEM study demonstrate that the average size is from 5.67 – 9.10 nm. The shapes of the Cu/CuO-NPs is proved to be spherical.

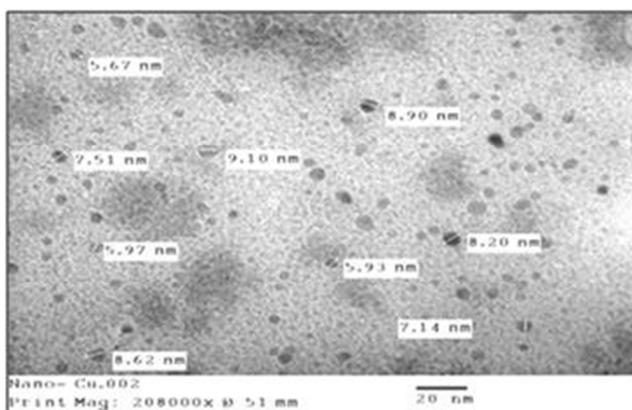


Figure 6. TEM micrograph of Cu/CuO-NPs synthesized by aqueous extract of lemongrass leaf.

3.5. EDX Analysis of Cu/CuO-NPs

EDX spectrum recorded from the Cu/CuO-NPs is shown in Figure 7.

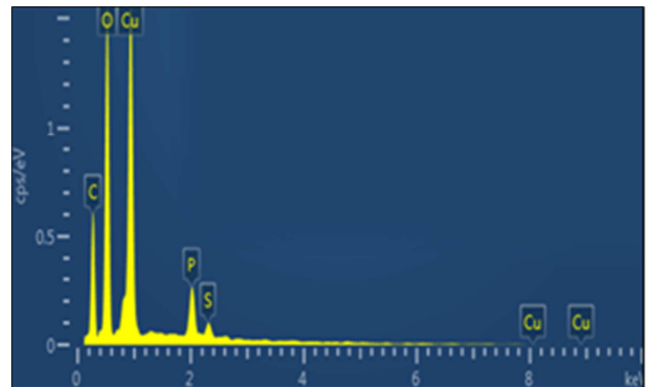


Figure 7. EDX micrograph of Cu/CuO-NPs synthesized by aqueous extract of lemongrass leaf.

The EDX spectrum clearly shows the peak of copper confirming that the Cu/CuO-NPs has been successfully synthesized.

3.6. XRD Analysis of Cu/CuO-NPs

Figure 8 shows the XRD pattern obtained for Cu/CuO-NPs synthesized by lemongrass leaf extract.

The diffraction peaks at $2\theta = 22.3^\circ$; 28.3° correspond to the {111}, {200} planes of Cu nanoparticles, and at $2\theta = 33.24^\circ$; 35.52° ; 53.72° correspond to the {110}, {-110}, {022} planes of CuO nanoparticles, respectively.

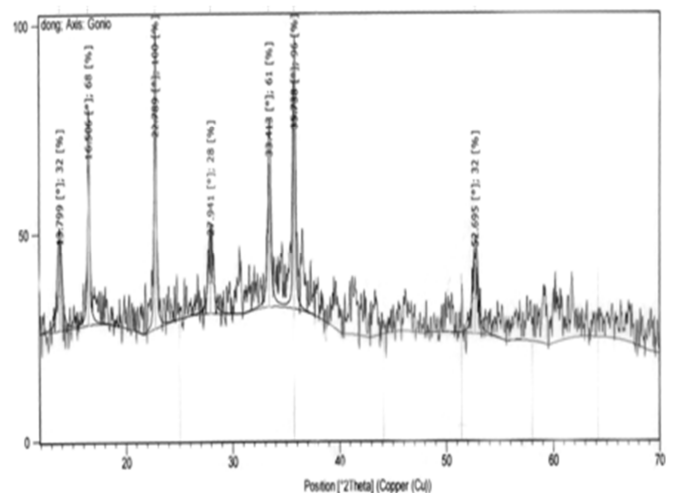


Figure 8. XRD pattern of Cu/CuO-NPs synthesized by aqueous extract of lemongrass leaf.

3.7. The Photocatalytic Activity of the Synthesized Cu/CuO-NPs

The photocatalytic activity of the synthesized Cu/CuO-NPs was examined on the degradation of MB under sunlight irradiation at 0 h, 1 h, 2 h, 3 h, 4 h, and 5 h of exposure time. Green synthesized Cu/CuO-NPs effectively degraded the dye

when nearly 80.71% of the dye was decomposed after 5 h of exposure time.

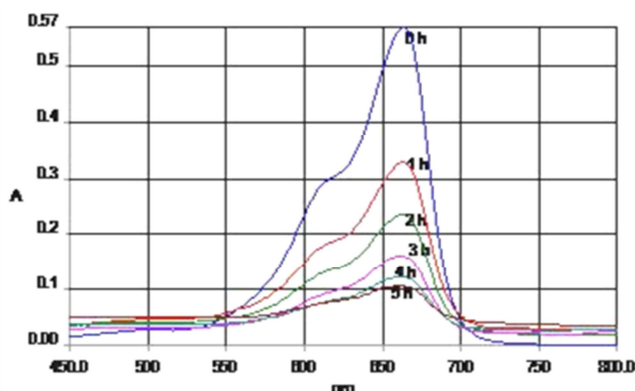
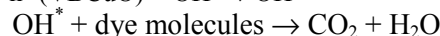
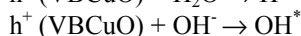
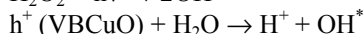
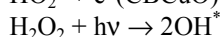
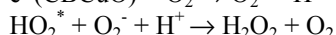
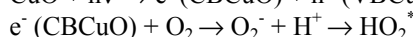


Figure 9. Degradation of MB in presence of Cu/CuO-NPs synthesized by aqueous extract of lemongrass leaf at 0 h, 1 h, 2 h, 3 h, 4 h, and 5 h of exposure time.

The possible mechanism of MB degradation under sunlight irradiation was proposed as follows (Wei, et al., 2013; Sharma and Sharma, 2012; Katwal, et al., 2015):



4. Conclusions

The reduction of Cu^{2+} ions by lemongrass leaf extract leading to the formation of Cu/CuO-NPs of fairly well-defined dimensions occurring in the optimal condition of 7 mL of extract /50 mL of 1 mM CuSO_4 , pH 9, $T = 50^\circ\text{C}$. The Cu/CuO-NPs were found to be in spherical shape with an average crystal size of 5.67 – 9.10 nm. The synthesis of Cu/CuO-NPs using green resources like lemongrass leaf extract is a better alternative route to chemical synthesis, since this green synthesis is pollutant free and eco-friendly. Green synthesized Cu/CuO-NPs effectively degraded the dye when nearly 80.71% of the dye was decomposed at 5 h of exposure time.

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