Photocatalytic and Antimicrobial Activities of Phytofabricated Copper (II) Oxide Nanoparticles by Using Leaves Extract of *Tamarindus Indica* L.

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Abstract

A simple, eco-friendly green synthesis of copper (II) oxide nanoparticles (CuO NPs) using leaves extract of *Tamarindus indica* L. was reported. Synthesized CuO NPs was characterized by XRD, TEM, SEM and FT IR. XRD spectrum showed the monoclinic crystalline nature of the synthesized CuO NPs and its particle size was 19.9 nm. FTIR spectrum confirmed the presence of Cu–O functional groups showing the characteristic peaks of CuO NPs at 511 and 434 cm^{-1} . Photocatalytic activity of CuO NPs was investigated by congo red and indigo carmine dyes solutions under sun light. Within 90 min, dye solutions degraded by CuO NPs were 86.46 % for congo red and 63.26 % for indigo carmine. Highest degradation percentage was attained for congo red (76.87 %) compared to indigo carmine (72.67 %) using dosage of 0.25 g CuO NPs. CuO NPs responded high antimicrobial activity on *Staphylococcus aureus, Bacillus pumilus, Candida albicans* and *Escherichia coli* but mild activity on *Bacillus subtilis* and *Pseudomonas aeruginosa*.

Keywords: copper (II) oxide nanoparticles, congo red, indigo carmine, photocatalytic activity, antimicrobial activity

Introduction

The use of plant extracts for the synthesis of nanoparticles is a gradually-evolving research area known as green synthesis of nanoparticles (NPs) (Das *et al*., 2013). In green synthesis of metal nanoparticles, a suitable and non-toxic natural product, as well as an eco-friendly solvent system should be necessary (Iravani *et al*., 2011). Material scientists have focused on green routes for the synthesis and production of nanoparticles (Sanka *et al*., 2014). CuO NPs have attracted huge attention due to its antimicrobial, catalytic, electrical, sensing, and optical properties (Sharmila *et al*., 2016). Green synthesis refers to the synthesis of nanoparticles using naturally obtainable reducing agents like plant extracts, polysaccharides, micro-organism like fungus and bacteria, etc. Among various metal oxides, transition metal oxides are the most technologically advanced and economically attractive. CuO NPs are of interest because it is simple, high stability, relatively more cost effective than other metals such as gold and silver, stable over a wide range of pH and high temperature resistance. CuO NPs is one of the metal oxides which were found to be extremely useful in wide variety of applications due to their uniqueness. CuO NPs were extensively utilized as antimicrobial agent (Ren *et al*., 2009), photocatalyst (Katwal *et al*., 2015), solar cells (Kidowaki *et al*., 2012), lithium ion battery (Thi *et al*., 2014) and gas sensor (Zhang *et al*., 2011). The main aim of this study is to synthesize CuO NPs via green route using *Tamarindus indica* leaves extract.

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Materials and Methods

Samples Collection

The *Tamarindus Indica* L. (Ma-gyi) leaves were collected from Leindaw village, Meiktila Township, Mandalay Region.

Preparation of CuO NPs

CuO NPs were synthesized by dropwise addition of 50 mL 0.5 M copper(II) nitrate solution into 25 mL of extracts sample solution in a 250 mL beaker and then mixed thoroughly by a magnetic stirrer at 60 ºC. The deep blue colour of solution changed to dark green and it was heated at 80 ºC. The dried sample was then collected and calcined in a muffle furnace at 500 ºC for 1 h. A black coloured powder was obtained and it was carefully collected and packed for characterization purposes.

Characterization Techniques

The crystalline structure and phase purity of the synthesized CuO NPs were examined by using X-ray diffractometer (Rigaku Co., Tokyo, Japan) using Cu Kα (λ=1.54056 Ȧ) radiation in a scattering range (2θ) of 10° to 70° at an accelerating voltage of 40 kV. The morphologies of CuO NPs were characterized by scanning electron microscopy (SEM, JEOL-JSM-5610 LV, Japan) at Universities' Research Center, Yangon and transmission electron microscopy (TEM, JEOL TEM-3010) with an accelerating voltage of 100 kV at State Key Laboratory, College of Science, Beijing University of Chemical Technology, China. The crystallite sizes of CuO NPs were calculated by using Image J software programme. FT IR spectrum of CuO NPs was recorded on a FT IR spectrometer (FT IR-8400 SHIMADZU, Japan).

Study on the Photocatalytic Activity of CuO NPs

Photocatalytic degradation of dyes solutions (congo red and indigo carmine) was studied. Effect of contact time and dosage of CuO NPs were studied by spectrophotometer at 496 nm for congo red and 610 nm for indigo carmine. Firstly, 50 mL of 25 ppm congo red solution and 0.25 g of prepared CuO NPs were separately added into six 250 mL capacity of clean and dry conical flasks. These solutions were stirred for 30 min in dark for equilibrium of adsorption and desorption processes of congo red with CuO NPs. After stirring, the conical flasks were placed in sun light. After every 30 min under sun light the conical flasks were taken out and filtered off the filtrate. And then the absorbance values of filtrates were measured at 496 nm by using a spectrophotometer. In the same way, the same procedure was carried out for the degradation of indigo carmine and the absorbance was measured at 610 nm. To study the effect of dosage of CuO NPs, the same procedure was employed using 0.05, 0.10, 0.15, 0.20, 0.25, 0.30 and 0.35 g of CuO NPs while other factors kept constant.

Antimicrobial activity of CuO NP

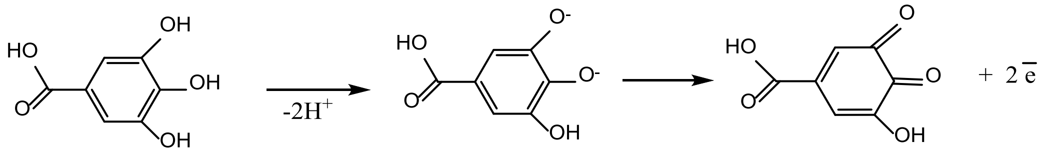
Antimicrobial activity of CuO NPs was investigated on six microorganisms such as *Bacillus subtilis, Staphylococcus aureus, Pseudomonas aeruginosa, Bacillus pumilus, Candida albicans* and *Escherichia coli* by using agar well diffusion method.

Results and Discussion

Mechanism for the Bioreduction of Cu^{2+} to CuO Nanoparticles

T.indica leaves contains polyphenolic compounds, for example gallic acid. These phenolic compounds have high reducing ability and they involve in bioreduction of Cu^{2+} solution. These phenolic compounds act as reducing as well as capping agents (Sharma *et al*., 2015). The proposed mechanism for the bioreduction process is shown as follows:

$$Cu(NO_3)_2 \longrightarrow Cu^{2+} + 2NO_3^-$$



Gallic Acid (Phenolic Form)

Quinone Form

$$2\,Cu^{2+} + 4\bar{e} + \frac{1}{2}O_2 \longrightarrow Cu_2O \text{ (reduction)}$$

$$Cu_2O + \frac{1}{2}O_2 \text{ (air)} \longrightarrow 2CuO \text{ (oxidation)}$$

Characterization of CuO NPs by XRD Analysis

Copper (II) oxide nanoparticles obtained by using leaves extract of *T.indica* were characterized by X-ray diffraction analysis. X-ray diffraction pattern of the prepared CuO NPs at 500 ^{o}C is shown in Figure 1. The XRD pattern shows no impurity peaks. Prominent diffraction peaks of CuO were observed at 2θ values of 35.308^{o} and 38.518^{o} using leaves extract corresponding to the Miller indices of $(\bar{1}11)$ and (111). CuO NPs were indexed as monoclinic with axial lengths of a=4.7093 Å , b=3.4557 Å and c=5.1307 Å and axial angles of $\alpha = \gamma = 90^{o}$ and $\beta = 99.59^{o}$.

The average crystallite size of CuO NPs was calculated from full width at half maximum (FWHM) using Scherrer equation according to the following formula:

$$\tau = \frac{0.9\,\lambda}{\beta \cos\theta}$$

where τ is the crystallite size (nm), λ is the diffraction wavelength (0.154056 nm for Cu Kα radiation), θ is the diffraction angle (degree) and β is the full width at half maximum (FWHM) for the diffraction peak (radian). The crystallite size of CuO NPs by using *T.indica* leaves extract obtained at 500 ^{o}C was 19.9 nm.

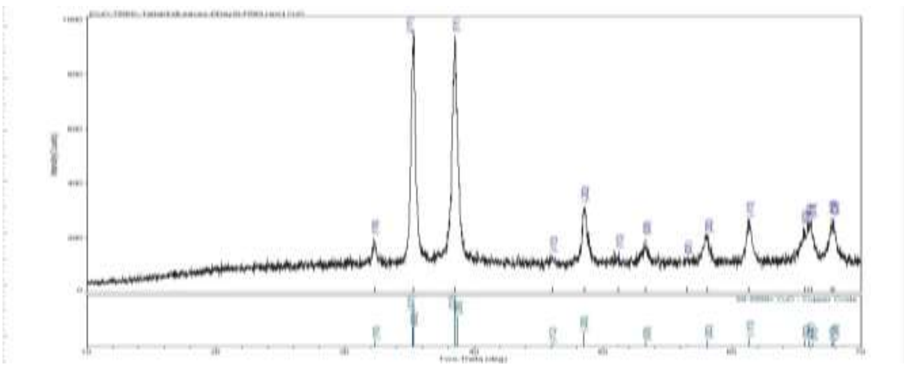
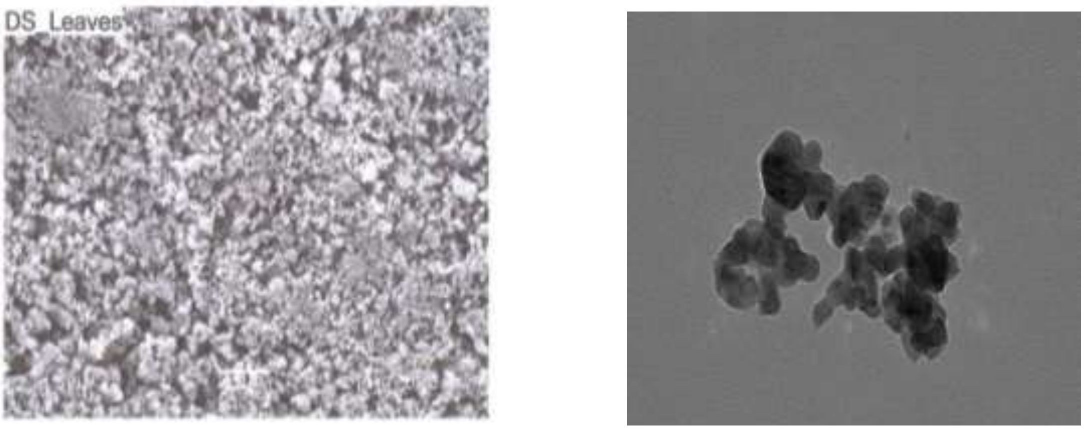


Figure 1. X ray diffractogram of CuO NPs by using *T. indica* leaves extract

Characterization of Prepared CuO NPs by SEM and TEM

SEM and TEM image of synthesized CuO NPs by using leaves extract are shown in Figure 2. SEM analysis showed that a large number of quasi-spherical nanoparticles in CuO NPs. Using TEM analysis, both the size and shape of the synthesized nanoparticles were observed. The average size of CuO nanoparticles by using leaves of *T. indica* found was 21.2 nm. The size was not much different from that obtained by X-ray diffraction analysis.



(a) (b)

Figure 2. (a) SEM image and (b) TEM image of CuO by using leaves extract and of *T. indica*

Characterization of CuO NPs by FT IR Analysis

Figure 3 shows the FT IR spectrum of CuO NPs. The absorption peaks at 511 and 434 cm^{-1} in FT IR spectrum of CuO NPs were the characteristic vibrations of Cu-O stretching vibration. The absorption peaks in the range of 430-606 cm^{-1} were attributed to the vibration of Cu-O stretching (Alizadeh-Gheshlaghi *et al*., 2012) and the presence of these peaks indicated the formation of CuO NPs.

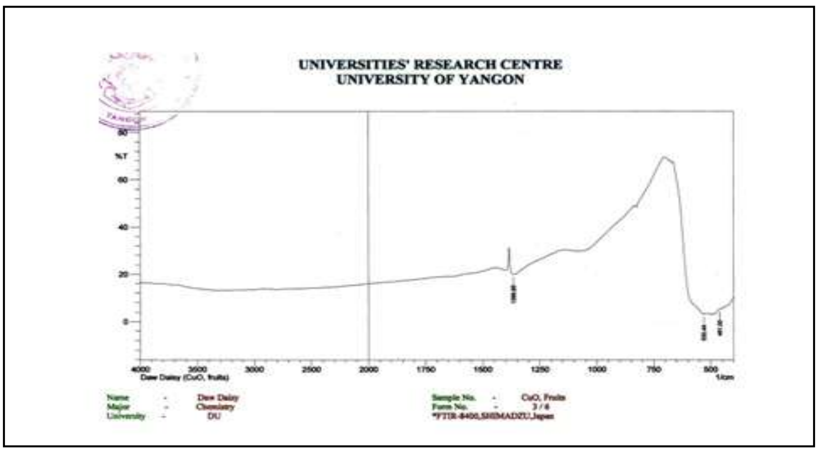


Figure 3. FT IR spectrum of CuO by using leaves extract of *T. indica*

Photocatalytic Degradation Activity of CuO NPs

The photocatalytic degradation experiments were conducted by varying the contact time ranging from 30 to 180 min with 30 min interval. Degradation percent of congo red and indigo carmine dyes solutions increased as duration of the contact time increased until 90 min. However, beyond 90 min negligible changes were observed. So, 90 min was chosen to study the effect of dosages of CuO NPs. Within 90 min 86.46 % for congo red dye and 63.26 % for indigo carmine dye were degraded by CuO NPs. Degradation percents of congo red and indigo carmine dyes using prepared CuO NPs with different dosages (0.05-0.35 g) were studied under sun light. It was indicated that as the dosages of the sample increased from 0.05 to 0.25 g, degradation of dyes increased due to the increase of the availability of total surface. However, decrease in degradation percent of each dye was observed at higher dosages. These may be due to the enhancement of light reflectance by the catalyst and decrease in light penetration. According to the results, 0.25 g dose of CuO NPs was the best dosages for degradation of dyes. These results are shown in Figures 4 and 5.

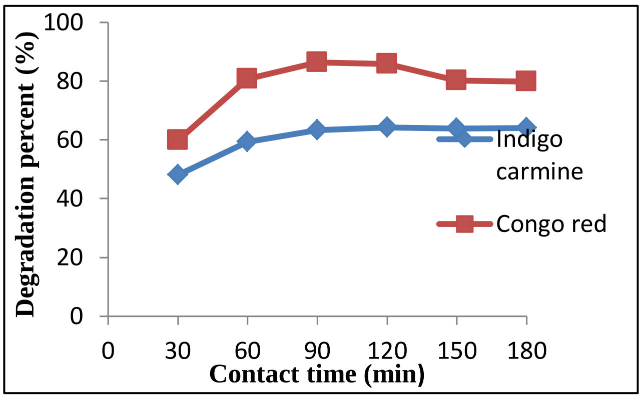


Figure 4: Degradation percen tage of dyes solutions as a function of contact times

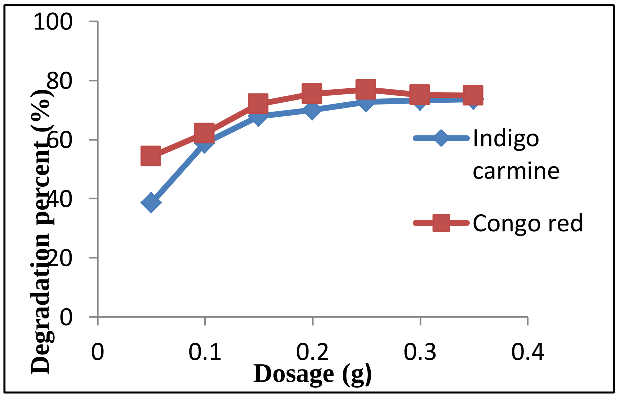


Figure 5: Degradation percentage of dyes solutions as a function of dosages

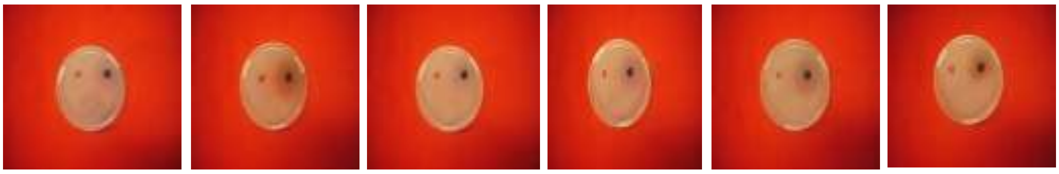
Antimicrobial Activity of CuO NPs

The antimicrobial activity of CuO NPs was also investigated against six microorganisms. From the inhibition zone diameter results, CuO NPs were shown better inhibition activity against *S. aureus, B. pumilus, C. albicans and E. coli* compared to *B. subtilis* and *P. aeruginosa.* (Figure 6 and Table 1).

Table 1. Antimicrobial Activity of CuO NPs Against Different Microorganisms by Agar Well Diffusion Method

Inhibition Zone Diameter (mm)					
B. subtilis	*S. aureus*	*P. aeruginosa*	*B. pumilus*	*C. albicans*	*E. coli*
13 (+)	22 (+++)	14 (+)	20(+++)	20 (+++)	20 (+++)

Diameter of agar well = 10 mm; 15 mm ~ 19 mm = ++ (medium activity);
10 mm ~ 14 mm = + (low activity); 20 mm above = +++ (high activity)



B. subtilis *S. aureus* *P. aeruginos* *B. pumilus* *C. albicans* *E. coli*

Figure 6. Antimicrobial activity of CuO NPs on six microorganisms

Conclusion

CuO NPs were successfully synthesized by a green synthesis method using leaves extract of *T. indica*. The synthesized CuO-NPs were characterized using XRD, TEM and FTIR. XRD data showed that pure monoclinic crystallite structure of CuO nanoparticles was formed. The average crystallite size was found to be 19.9 nm which was not much different from 21.2 nm by TEM analysis. The presence of characteristic vibration of Cu-O in the range of 430-606 cm^{-1} was confirmed by FT IR analysis. The green synthesized CuO NPs showed good catalytic activity in the degradation of organic dyes like congo red and indigo carmine.

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