

# TAMARINDUS INDICA MEDIATED SYNTHESIS OF COPPER (II) OXIDE NANOPARTICLES AND STUDY ON ITS PHOTOCATALYTIC DEGRADATION OF ALIZARIN AND MALACHITE GREEN DYES

Daisy<sup>1</sup>, Ni Ni Sein<sup>2</sup>, Daw Hla Ngwe<sup>3</sup>

## Abstract

The present study deals with the synthesis of copper(II) oxide nanoparticles (CuO NPs) by using aqueous solution of copper(II) nitrate and leaves extracts of *Tamarindus indica* L. (Ma-Gyi). Characterizations of the CuO NPs were made by Thermogravimetric-Differential Thermal Analysis (TG-DTA), X-ray diffraction (XRD), Fourier Transform Infrared spectroscopy (FT IR), Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM). CuO nanoparticles were indexed as monoclinic with average crystallite size of 19.9 nm. The presence of characteristic vibration of Cu-O in the range of 430-606 cm<sup>-1</sup> was confirmed by FT IR analysis. Photocatalytic degradation of alizarin and malachite green dyes by CuO NPs under sunlight was conducted. Highest degradation percentages of alizarin and malachite green were attained at 0.3 g dosage of CuO NPs for 120 min. Treatment of wastewater from textile dye factory with the CuO NPs was performed and 99.13 % of the colour was removed after 8 days.

**Keywords:** *Tamarindus indica* L., copper(II) oxide nanoparticles, photocatalytic degradation, alizarin, malachite green

## Introduction

There are several methods for production of CuO NPs such as chemical, physical and biological processes (Chatterjee *et al.*, 2012; Nasrollahzadeh and Sajadi 2015). For example, proton irradiation as physical method and vacuum vapour deposition employed for a wide range of metallic NPs synthesis (Ray *et al.*, 2009; Chin *et al.*, 2010). However, these methods have several disadvantages since the costs of these methods are higher, the use of toxic chemicals and thus, not environmentally friendly. Therefore, eco-friendly synthesis is essential for production of nanoparticles using biological systems (Lin *et al.*, 2011; Honary *et al.*, 2012). 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, the difficult task is to find a suitable and non-toxic natural product, as well as an eco-friendly solvent system (Iravani, 2011). Many researchers have focused on green routes for the synthesis and production of nanoparticles (Sankar *et al.*, 2014).

Organic dyes are extensively used for various industrial applications including textile dyeing, photographic, coating and photochemical industries (Shaabani *et al.*, 2014). The presence of these pollutants in the natural environment, particularly in the water surface should be prohibited. Hence, there is a clear need for the development of innovative techniques for the collection, treatment, and storage of water, and the implementation of eco-friendly technology for the effective remediation of water pollutants is highly dedicated. This has inspired the development of photocatalysis, a “catalytic reaction which involves the production of a catalyst by absorption of light” for the treatment of contaminated water. The pollutants can be effectively removed from wastewater by the photocatalytic process using semiconductor photocatalysts like CuO (Narasaiah *et al.*, 2017).

---

<sup>1</sup> Lecturer, Department of Chemistry, Dagon University

<sup>2</sup> Dr, Professor (Retired), Department of Chemistry, University of Yangon

<sup>3</sup> Dr, Professor and Head (Retired), Department of Chemistry, University of Yangon

The aim of this study is the use of environmentally friendly leaf extracts of *Tamarindus indica* L. for the preparation of CuO NPs and to study its photocatalytic activity on degradation of organic dye pollutants.

## Materials and Methods

### Sample Collection and Sample Preparation

The sample of *Tamarindus indica* L. leaves was collected from Leindaw village, Meiktila Township, Mandalay Region and identified at Department of Botany, Dagon University. The samples were dried under the laboratory condition at room temperature. The dried samples were ground into powder by using grinding machine. The powdered samples were separately stored in air-tight containers.

### Preparation of CuO NPs

Leaves extract of *T. indica* was prepared by adding 150 mL of deionized water to 20 g of sample in 250 mL beakers followed by heating the mixtures at 80 °C for 30 min. Then, the mixture was cooled at room temperature and filtered to obtain leaves extract of *T. indica*. Next, 50 mL of 0.5 M copper(II) nitrate solution was slowly added into 25 mL of leaves extract of *T. indica* in a 250 mL beaker with constant stirring by a magnetic stirrer at 60 °C. The colour of solution changed from deep blue to dark green and it was heated at 80 °C. The heated sample was then calcined in a muffle furnace at 500 °C for 1h. The resulting black coloured powder (CuO NPs) was formed.

### Characterization of CuO Nanoparticles

TG-DTA (DTG-60H) Thermal Analyzer, SHIMADZU, Japan was employed for investigation of the thermal property of the prepared sample before calcination. The prepared CuO NPs were analysed by using X-ray diffractometer (Rigaku Co., Tokyo, Japan) using Cu K $\alpha$  ( $\lambda=1.54056$  Å) radiation in a scattering range ( $2\theta$ ) of 10° to 70° at an accelerating voltage of 40 kV. The morphology 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. Fourier Transform Infrared (FT IR) spectrum of CuO NPs was recorded on a FT IR spectrometer (FT IR-8400 SHIMADZU, Japan).

### Investigation on Photocatalytic Activity of CuO NPs

To study the effect of contact time on degradation of alizarin the following procedure was employed. Briefly, 50 mL of 25 ppm alizarin solution and 0.3 g of prepared CuO NPs were added into 250 mL capacity of clean and dry conical flasks. These solutions were stirred for 15 min in dark for equilibrium of adsorption and desorption processes of alizarin with CuO NPs. After stirring, the conical flasks were placed in sunlight. After every 30 min under sunlight the conical flasks were taken out and centrifuged and decanted. The absorbance values of decantates were measured at 518 nm by using a spectrophotometer. The same procedure was carried out for the degradation study of malachite green and the absorbance values were measured at 617 nm.

To study the effect of dosage of CuO NPs on degradation of alizarin and malachite green dyes, the above mentioned 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.

To study the effect of initial concentrations of alizarin and malachite green dyes, the above mentioned procedure was employed using different concentrations of 15, 25, 35, 45, 55 and 65 ppm while other factors kept constant.

### **Application of Prepared CuO NPs for Colour Removal of Wastewater Effluent from Textile Factory**

Wastewater sample (100 mL each) and prepared CuO NPs (0.5 g each) were added into 250 mL capacity of clean and dry conical flasks. These solutions were stirred for 15 min in dark for equilibrium of adsorption and desorption process of wastewater with nanoparticles. After stirring, the conical flasks were placed in sunlight. After 2 days, 4 days, 6 days and 8 days, the conical flask were taken out and centrifuged and decanted. And then the absorbance values of decantates were measured at 520 nm (wavelength of the maximum absorption of this wastewater) by using a spectrophotometer.

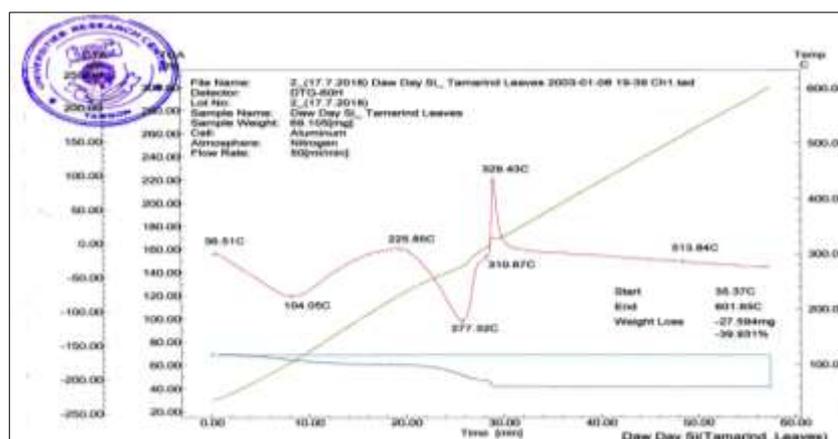
## **Results and Discussion**

### **Thermogravimetric- Differential Thermal Analysis**

Thermal analysis of CuO NPs obtained before calcination was carried out. Figure 1 shows the TG-DTA thermogram of CuO NPs obtained by using leaves extract of *T. indica* and its thermal data are shown in Table 1. The first endothermic peak was due to the removal of physically sorbed water. The second endothermic peak was due to removal of chemisorbed water. The exothermic peak appeared at 329.43 °C due to conversion of Cu<sub>2</sub>O to CuO (Xu *et al.*, 2004). It was observed that CuO NPs were almost thermally stable beyond 400 °C. Thus, according to thermal analysis data the calcination of the residue was calcined at 500 °C to obtain CuO NPs.

### **XRD Analysis**

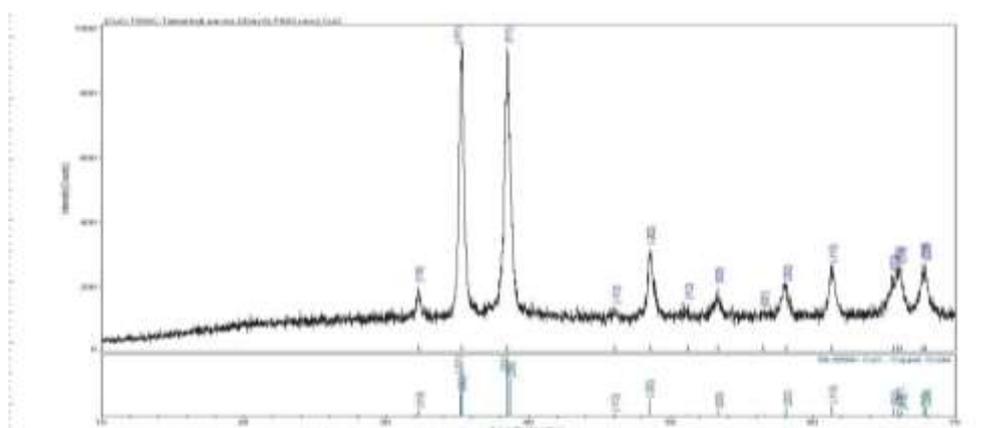
CuO NPs prepared by using leaves extract of *T. indica* was characterized by X-ray diffraction analysis. Figure 2 shows the X-ray diffractogram of CuO NPs calcined at 500 °C. Phase identification by X-ray analysis showed only single phase of CuO. The peaks were well-matched with the standard CuO (89-5899 > CuO). No impurity peaks were observed in the diffractogram. Characteristic diffraction peaks of CuO appeared at 2θ values of 35.308° and 38.518° corresponding to the Miller indices of ( $\bar{1}11$ ) and (111), respectively. CuO NPs were indexed as the monoclinic structure with a = 4.7093 Å, b = 3.4557 Å and c = 5.1307 Å. The average crystallite size was calculated by Scherrer equation and found to be 19.9 nm (Table 2).



**Figure 1** TG-DTA thermogram of the CuO residue by using leaves extracts of *T. indica* at 500 °C

**Table 1** TG-DTA Data of the Prepared CuO NPs by Using Leaves Extract of *T. indica*

No.	Temperature range (°C)	Break in temperature (°C)	Weight loss (%)	Nature of peak	Remark
1	36.51-230	104.05	12.886	Endothermic	Desorption of physically sorbed water molecules
2	230-310	277.32	19.934	Endothermic	Removal of chemisorbed water
3	310-350	329.43	6.639	Exothermic	Conversion of Cu <sub>2</sub> O to CuO
4	350-601	-	0.047		Thermally stable



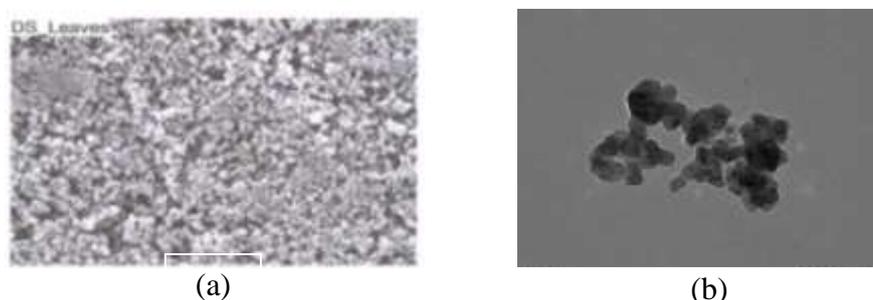
**Figure 2** X ray diffractogram of the prepared CuO NPs by using leaves extract of *T. indica*

**Table 2** Lattice Constant, Interaxial angle, Crystal Structure and size of the Prepared CuO NPs by Using Leaves Extract of *T. indica* at 500 °C

No.	Lattice constant Axial length (Å)	Interaxial angle (°)	Crystal structure	Average crystallite size (nm)
1	a=4.7093 b=3.4557 c=5.1307	$\alpha, \gamma=90$ $\beta=99.59$	Monoclinic	19.9

## Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM) Analysis

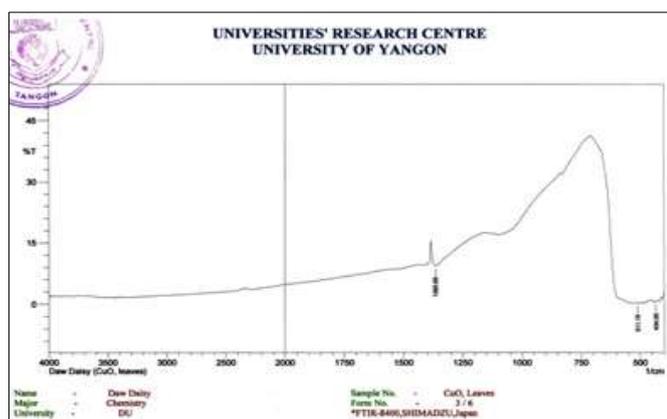
SEM and TEM images of prepared CuO nanoparticles by using leaves extract is depicted in Figure 3. A large number of quasi-spherical nanoparticles were observed in SEM image of CuO NPs as shown in Figure 3(a). Furthermore, elongated shapes of CuO NPs were seen in TEM image as depicted in Figure 3(b). It confirmed the monoclinic structure of CuO NPs given by X-ray diffraction analysis. The average crystallite size obtained from TEM was found to be 21.2 nm which was not much different from that calculated from X-ray data.



**Figure 3** (a) SEM image and (b) TEM image of CuO NPs by using leaves extract of *T. indica*

## Fourier Transform Infrared Analysis

Figure 4 shows FT IR spectrum of CuO NPs. The absorption peaks appeared at  $434\text{ cm}^{-1}$  and  $511\text{ cm}^{-1}$  were between  $430\text{-}606\text{ cm}^{-1}$ , the characteristic range of Cu-O stretching vibration (Alizadeh-Gheshlaghi *et al.*, 2012).



**Figure 4** FT IR spectrum of the prepared CuO NPs prepared by using leaves extract of *T. indica*

## Photocatalytic Degradation Activity of CuO NPs

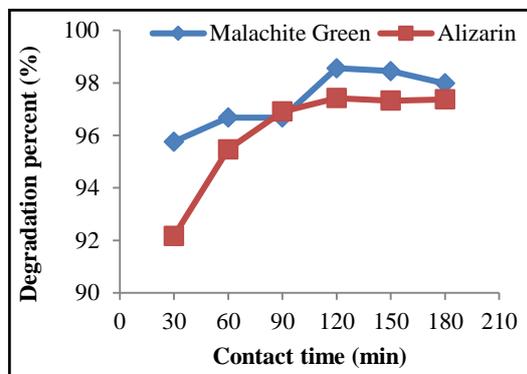
### Effect of contact time

The photocatalytic degradation experiments were conducted under sunlight by varying the contact time ranging from 30 to 180 min with 30 min interval. After 30 min of contact time, degradation percentage of alizarin was 92.17 % and that of malachite green was 95.76 % (Table 3 and Figure 5). Degradation percentages of alizarin and malachite green dyes solutions increased as the contact time was increased until 120 min at which 97.42 % of alizarin and 98.56 % of malachite dye solutions were degraded. However, beyond 120 min slight changes were observed. The photocatalytic degradation phenomena can be described as follows. First, CuO NPs comes in contact with sunlight, creating a photo-generated electron and a hole (Ijaz *et al.*, 2017). The photo-

generated electron reacts with oxygen molecule to form superoxide free radical in the second step. Next, the hole reacts with water and hydroxyl ions to produce highly mercurial hydroxyl radicals. These superoxide free radicals and hydroxyl free radicals degraded the organic dyes and decolourized it. As the time was increased, the surface active sites of CuO NPs was gradually occupied by dye molecules and reached a saturation point. Consequently, less number of surface active sites were available for further adsorption, and followed by photodegradation which was a relatively slow process.

**Table 3 Degradation Percent of Dyes by CuO Nanoparticles with Different Contact Times**

No	Contact time (min)	Degradation percent (%)	
		Alizarin	Malachite green
1	30	92.17	95.76
2	60	95.47	96.68
3	90	96.91	96.68
4	120	97.42	98.56
5	150	97.32	98.45
6	180	97.37	97.98



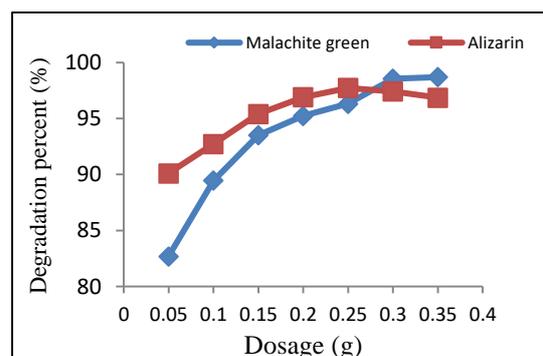
**Figure 5** Degradation percentage of dyes solutions as a function contact time

#### Effect of dosage of CuO NPs

Degradation percentages of alizarin and malachite green dyes using prepared CuO NPs with different dosages (0.05-0.35 g) were studied under sunlight. It was indicated that as the dosage of the sample was increased from 0.05 to 0.3 g, degradation of alizarin increased from 90.11 % to 97.42 % and that of malachite green from 82.69 % to 98.56 % (Table 4 and Figure 6). With the increment of the CuO NPs photocatalyst amount, the quantity of active sites increases on the catalyst surface bringing about the adsorption of more dye particles. Thus, the photocatalytic degradation increased. Further increase of CuO NPs to 0.35 g, degradation percentage of alizarin was found to decrease (96.86 %). After a certain level of catalyst, the degradation percentage decreases because dye molecules are not available for adsorption on active sites of the photocatalyst (Pamecha *et al.*, 2016). This reduces the site density for surface holes and electrons and additional catalyst particles, therefore, are not involved in the catalytic activity. Change in degradation percentage of malachite green using 0.035 g CuO NPs was negligible.

**Table 4 Degradation Percentage of Dyes by CuO Nanoparticles with Different Dosage**

No	Dosage(g)	Degradation percent (%)	
		Alizarin	Malachite green
1	0.05	90.11	82.69
2	0.10	92.73	89.47
3	0.15	95.41	93.51
4	0.20	96.91	95.24
5	0.25	97.73	96.32
6	0.30	97.42	98.56
7	0.35	96.86	98.70



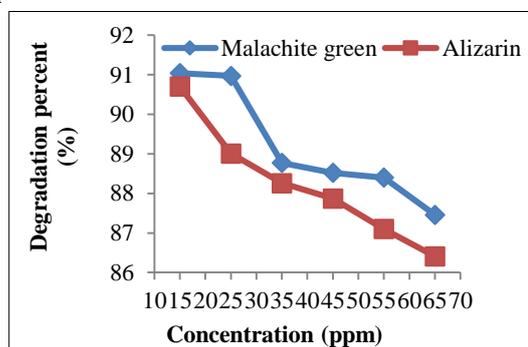
**Figure 6** Degradation percentage of dyes solutions as a function of dosage of CuO NPs

### Effect of initial concentration of dye solutions

A series of alizarin and malachite green solutions with different concentrations (15 ppm, 25 ppm, 35 ppm, 45 ppm, 55 ppm and 65 ppm) were used to observe the effect of initial dye concentration on the degradation. For 15 ppm concentration of alizarin and malachite green dyes, the degradation percentages were 90.70 % and 91.04 %, respectively (Table 5 and Figure 7). It was observed that the degradation percentages decreased gradually with increasing concentration of dyes. When the initial concentration of the dyes reached 65 ppm, 86.41 % and 87.46 % of alizarin and malachite, respectively, were degraded by CuO NPs obtained from leaves extract of *T.indica*. It is generally noted that increase in dye concentration leads to decrease in the degradation percent. The degradation percent relates to the probability of hydroxyl radicals (OH<sup>•</sup>) formation on the catalyst surface and to the probability of these hydroxyl radicals reacting with dye molecules. Increasing the concentration of dye while keeping the photocatalyst CuO NPs constant, the catalyst surface gets saturated. Simultaneously intense colour of the dye does not permit light to reach photocatalyst (Pamecha *et al.*, 2016). The generation of hydroxyl radicals on the surface of catalyst is reduced at high dye concentrations, since the active sites are covered by dye molecules. As a result the degradation percentages decreased.

**Table 5 Degradation Percentage of Dyes by CuO NP s with Different Initial Concentration**

No	Concentration (ppm)	Degradation Percent (%)	
		Alizarin	Malachite green
1	15	90.70	91.04
2	25	89.01	90.97
3	35	88.26	88.77
4	45	87.87	88.52
5	55	87.10	88.40
6	65	86.41	87.46



**Figure 7** Degradation percentage of dyes solutions as a function of concentration

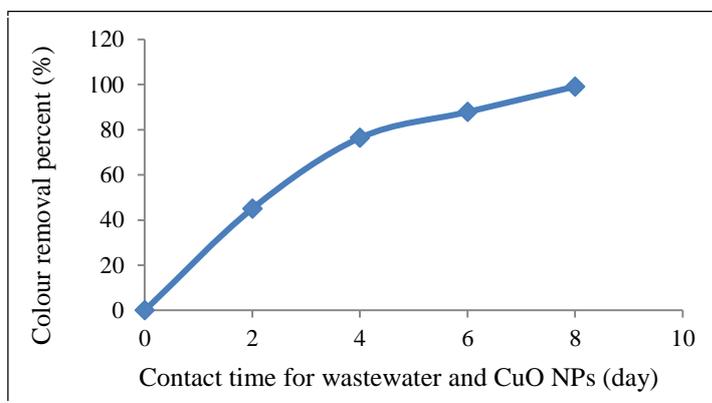
### Application of Prepared CuO NPs for Colour Removal of Wastewater

Wastewater from a textile dye factory (South Okkalapa Township) was firstly determined for its wavelength of maximum absorption and found to be 520 nm. The colour of the effluent from textile dye was reddish brown. After treatment of the wastewater with CuO NPs prepared from leaves extract of *T.indica* for 2 days, 45.07 % of wastewater were decolourized (Table 6 and Figure 8). The percentage of decolourization was observed to be gradually increased and after 4 days, the decolourization percentage was 76.42 %. Increase in decolourization percentage was not noticeable after treatment with CuO NPs for 8 days, i.e., 99.13 %. In this study, higher decolourization percentage of CuO nanoparticles for the treatment of dye effluent was observed.

**Table 6 Colour Removal Percentages of Wastewater for Treatment with CuO NPs**

No.	Time of treatment (Day)	Absorbance at 520 nm*	Colour removal percent (%)
1	0	2.290	0.00
2	2	1.258	45.07
3	4	0.540	76.42
4	6	0.278	87.86
5	8	0.020	99.13

\* $\lambda_{\max}$  of wastewater = 520 nm



**Figure 8** Colour removal percent of wastewater as a function of contact time with CuO nanoparticles

### Conclusion

In this study a simple, eco-friendly and efficient preparation of CuO NPs by using leaves extracts of *T. indica* was reported. Aqueous extracts of *T. indica* leaves has been used as reducing agent and also as a capping agent in the CuO NPs preparation. Thermal analysis of CuO nanoparticles showed that CuO was almost thermally stable beyond 400 °C. The XRD analysis confirmed the crystalline nature of CuO NPs with monoclinic structure and the average crystallite sizes from leaves extracts was found to be 19.9 nm. SEM image showed a large number of quasi-spherical nanoparticles with dense agglomerates. By TEM analysis CuO NPs showed elongated shape and its crystallite size was 21.2 nm. The presence of characteristic vibration of Cu-O in the range of 430-606  $\text{cm}^{-1}$  was confirmed by FT IR analysis. The green synthesized CuO NPs showed good photocatalytic activity in the degradation of organic dyes like alizarin and malachite green. Highest degradation percentages of alizarin and malachite green were attained at 0.3 g dosage of CuO and contact time of 120 min. CuO NPs could degrade 99.13 % of the organic dye of the wastewater effluent from the textile factory. The significant catalytic performance of CuO NPs is due to their high surface to volume ratio providing more active sites of the reactant molecules to interact. The photocatalytic results conclude that the prepared CuO nanoparticles have high efficiency to degrade organic dyes under sunlight and thus, they can find applications in textile industry and water treatment plants.

### Acknowledgement

The authors would like to express their profound gratitude to the Department of Higher Education, Ministry of Education, Yangon, Myanmar, for provision of opportunity to do this research and Myanmar Academy of Arts and Science for allowing to present this paper.

## References

- Alizadeh-Gheshlaghi, E., Shaabani, B., Khodayari, A., Azizian-Kalandaragh, Y. and Rahimi, R. (2012). "Investigation of the Catalytic Activity of Nano-sized CuO, Co<sub>3</sub>O<sub>4</sub> and CuCo<sub>2</sub>O<sub>4</sub> Powders on Thermal Decomposition of Ammonium Perchlorate". *Powder Techno*, vol. 217, pp. 330–339
- Chatterjee, A. K., Sarkar, R. K., Chattopadhyay, A. P., Aich, P., Chakraborty, R. and Basu, T. (2012). "A Simple Robust Method for Synthesis of Metallic Copper Nanoparticles of High Antibacterial Potency against *E. coli*". *Nanotechnology*, vol. 23(8), pp. 1-11
- Chin, H. S., Cheong, K. Y. and Razak, K. A. (2010). "Review on Oxides of Antimony Nanoparticles: Synthesis, Properties, and Applications". *J Mater Sci*, vol. 45(22), pp. 5993-6008
- Das, S. K., Khan, M. M. R., Parandhaman, T., Laffir, F., Guha, A. K., Sekaran, G. and Mandal, A. B. (2013). "Nano-Silica Fabricated with Silver Nanoparticles: Antifouling Adsorbent for Efficient Dye Removal, Effective Water Disinfection and Biofouling Control". *Nanoscale*, vol. 5(12), pp. 5549-5560
- Honary, S., Barabadi, H., Gharaei-Fathabad, E. and Naghibi, F. (2012). "Green Synthesis of Copper Oxide Nanoparticles Using *Penicillium aurantiogriseum*, *Penicillium citrinum* and *Penicillium waksmanii*". *Dig. J Nanomater Biostruct*, vol. 7(3), pp. 999-1005
- Ijaz, F., Shahid, S., Khan, S. A., Ahmad, W. and Zaman, S. (2017). "Green synthesis of Copper Oxide Nanoparticles using *Abutilon indicum* Leaf Extract: Antimicrobial, Antioxidant and Photocatalytic Dye Degradation Activities". *Tropical Journal of Pharmaceutical Research*, vol. 16(4), pp. 743-753
- Iravani, S. (2011). "Green Synthesis of Metal Nanoparticles Using Plants". *Green Chem*, vol. 13(10), pp. 2638-2650
- Lin, X., Wu, M., Wu, D., Kuga, S., Endo, T. and Huang, Y. (2011). "Platinum Nanoparticles Using Wood Nanomaterials: Eco-Friendly Synthesis, Shape Control and Catalytic Activity for p-Nitrophenol Reduction". *Green Chem*, vol. 13(2), pp. 283-287
- Narasaiah, P., Mandal, B. K. and Sarada, N. C. (2017). "Biosynthesis of Copper Oxide Nanoparticles from *Drypetes sepriaria* Leaf Extract and Their Catalytic Activity to Dye Degradation". *Materials Science and Engineering*, vol. 263, pp. 1-9
- Nasrollahzadeh, M. and Sajadi, S. M. (2015). "Green Synthesis of Copper Nanoparticles Using *Ginkgo biloba* L. Leaf Extract and their Catalytic Activity for the Huisgen [3+ 2] Cycloaddition of Azides and Alkynes at Room Temperature". *J Colloid Interface Sci*, vol. 457, pp. 141-147
- Pamecha, K., Mehta, V. and Kabra, B. V. (2016). "Photocatalytic Degradation of Commercial Textile Azo Dye Reactive Blue 160 by Heterogeneous Photocatalysis". *Adv. Appl.Sci.Res*, vol. 7(3), pp. 95-101
- Ray, S. C., Saha, A., Jana, N. R. and Sarkar, R. (2009). "Fluorescent Carbon Nanoparticles: Synthesis, Characterization, and Bioimaging Application". *J Phys Chem C*, vol. 113(43), pp. 18546-18551
- Sankar, R., Manikandan, P., Malarvizhi, V., Fathima, T., Shivashangari, K. S. and Ravikumar, V. (2014). "Green Synthesis of Colloidal Copper Oxide Nanoparticles Using *Carica Papaya* and its Application in Photocatalytic Dye Degradation". *Spectrochim Acta Mol Biomol Spectrosc*, vol. 121, pp. 746-750
- Shaabani, B., Alizadeh-Gheshlaghi, E., Azizian-Kalandaragh, Y. and Khodayari, A. (2014). "Preparation of CuO Nanopowders and Their Catalytic Activity in Photodegradation of Rhodamine-B". *Advanced Powder Technology*, vol. 25(3), pp. 1043-1052
- Xu, C. H., Woo, C. H. and Shi, S. Q. (2004). "Formation of CuO Nanowires on Cu Foil". *Chemical Physics Letters*, vol. 399(1), pp. 62-66