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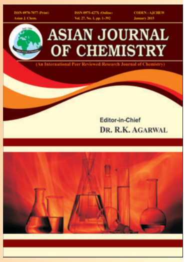

Green Synthesis of Cupric Oxide Nanoparticles Using Water Extract of *Murrya koenigi* and its Photocatalytic Activity

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Green synthesis of cupric oxide nanoparticles has been carried out from copper sulphate pentahydrate using the water extract of *Murrya koenigi*. The components present in the water extract react with copper sulphate pentahydrate to form an intermediate, which upon calcination at 300 ºC resulted in the formation of cupric oxide. The synthesized nanoparticles were spherical in shape and about 33-40 nm in size. X-Ray diffraction pattern confirmed the crystalline nature of cupric oxide. The green-synthesized cupric oxide nanoparticles possess excellent photocatalytic activity with about 80 % dye degradation in 10 min from initial concentration of 50 ppm.

Keywords: *Murrya koenigi*, Cupric oxide nanoparticles, Photocatalytic activity.

INTRODUCTION

It is well recognized that the nanoparticles possess better properties than their bulk counterparts. The specific surface area of particles is inversely proportional to the particle size. Hence the rates of interfacial processes are enhanced with the use of nanoparticles owing to their higher surface area. Thus nanoparticles are better catalysts and adsorbents. The requirement for nanomaterials is ever-increasing with intended applications in various fields of science and technology[1]. Cupric oxide is one of the metal oxide nanomaterials of interest for use in nanofluids[2], catalysis[3, 4], photocatalytic degradation[5], biosensor[6], gas sensor[7], *etc*. Cupric oxide nanostructures can be synthesized from a variety of precursors such as cupric sulphate[8,9], cupric chloride[10], cupric acetate[11], *etc*. Various acids and bases are used to convert these precursors to cupric oxide nanoparticles.

Green synthesis of nanomaterials has attracted plenty of attention in the literature. Green synthesis of silver nanoparticles has been widely reported with more than 700 publications since 2010 as extracted from the SCOPUS database. However, the green synthesis of cupric oxide has only been recently attempted as evident from few publications on this subject[12-14]. Extracts of plants that have medicinal value are widely used during green synthesis[15]. It is believed that few ingredients in plant extracts that have medicinal value are incorporated during the synthesis of nanoparticles. *Murrya koenigi,* commonly known as 'curry leaf' is one of the herbal plants and belongs to the family of *Rutaceue*. These plants are most used as flavoring agent to improve the food quality and possess medicinal values[16]. The extract of *Murrya koenigi* contains several compounds that are used for treatment of diarrhoea[17], dysentery, hepatoprotective effect[18], insect bites[19], *etc*., while the same can be used as stimulant. Other medicinal uses include their use for carminative, hypotensive, hypoglycaemic[20], antiinflammatory[21], anticancer[22], antiperiodic and antimicrobial activities[23].

The present work reports the synthesis of cupric oxide nanoparticles using the water-extract of *Murrya koenigi*. With respect to the use of green-synthesized CuO nanoparticles for environmental applications, the adsorption and photocatalytic activity of green-synthesized CuO nanoparticles have been evaluated both under sunlight (for activity in visible spectrum) and under intense ultraviolet radiation.

EXPERIMENTAL

Copper sulphate pentahydrate ($CuSO_4{\cdot}5H_2O$) was purchased from Merck laboratories, India limited. *Murrya koenigi* leaves were procured from local market. Water obtained through Millipore water purification system was used for the preparation of extract.

Preparation and characterization of water extract of *Murrya koenigi*: In a typical experiment, about 1 kg of *Murrya koenigi* leaves were washed and cut into small pieces and boiled in about 1 L of de-ionized water for 15 min. The temperature of mixture during extraction was maintained at 80 ºC. The liquid-solid mixture obtained after extraction was cooled and filtered using Whatmann filter paper 1 to recover the extract. The extract was stored in containers for use during subsequent experiments.

A part of the water extract was lyophilized to prepare a dry powder of the extract. This powder was dissolved in ethanol and subjected to GC-MS analysis (Clarus 500, Perkin Elmer, USA).

Preparation of nanoparticles: Several experiments were carried out with concentration of copper sulphate pentahydrate solution, quantity of extract, rate of addition of extract and calcinations temperature as variables. The experimental procedure and conditions for satisfactory synthesis of nanoparticles are as follows:

About 2.4 g of copper sulphate pentahydrate was dissolved in 100 mL of de-ionized water. 100 mL of water extract of *Murrya koenigi* was added drop-wise to the copper sulphate solution, with continuous mixing using a magnetic stirrer. The solution was left undisturbed overnight. The solid particles were recovered by centrifugation at 7000 rpm for 10 min. After washing the pellet with deionized water, the same was dried, crushed in a pestle and mortar to form fine powders. The powders were then calcined at 300 ºC for about 1 h.

Characterization of nanoparticles: The morphology of synthesized nanoparticles was studied using a Field Emission Scanning Electron Microscope (JSM 6701F, JEOL, Japan) at an acceleration voltage of 3 kV. The samples were placed on the stub and coated with gold for imaging. A powder X-ray diffractometer (D8 Focus, Bruker, USA) was used to determine the crystalline phases present in the sample. The elemental composition of the sample was determined using a X-ray fluorescence spectrometer (S8 Tiger, Bruker, Germany) using 1.54 Å X-ray tube. The zeta potential of dispersion of synthesized powder in water was determined using a zeta sizer (Nano-ZS, Malvern Instruments, UK). Chemical nature of synthesized nanoparticles was analyzed using FTIR analysis (Spectrum One, Perkin Elmer, USA).

Photocatalytic activity: A 50 ppm solution of Reactive black dye in water was taken as the initial sample for studies on photocatalytic activity and its absorbance was measured at 580 nm. 50 mg of synthesized particles were added to 50 ppm dye solution and ultrasonicated for about 15 min. The dye solution along with nanoparticles was kept under sunlight for about 1 h. Upon separating the nanoparticles from the dye-nanoparticles mixture through centrifugation, the absorbance of supernatant was measured at 580 nm to determine the concentration of dye and the percentage degradation of dye.

A photocatalytic reactor (Model IWQ1, SAIC India Ltd., India) was used to study the photocatalytic activity of nanoparticles under ultraviolet radiation. The addition of 50 mg of nanoparticles to 50 ppm dye solution was followed by ultrasonication for 15 min and exposure to ultraviolet radiation (254 nm). Dye-nanoparticles mixture were sampled at regular intervals of time, centrifuged and absorbance of supernatant measured at 580 nm.

RESULTS AND DISCUSSION

GC-MS spectra of extract: The GC-MS spectra of ethanol extract of *Murrya koenigi* is shown in Fig. 1. The major compounds identified are 1-methyl-pyrrolidine-2-carboxylic acid (60.70 %), phytol (12.77 %), octadecanoic acid (7.09 %) and 3,7,11,15-tetramethyl-2-hexadecen-1-ol (4.96 %). The elements present in the extract, as listed from compounds identified from GC-MS spectra are carbon, hydrogen, oxygen and nitrogen.

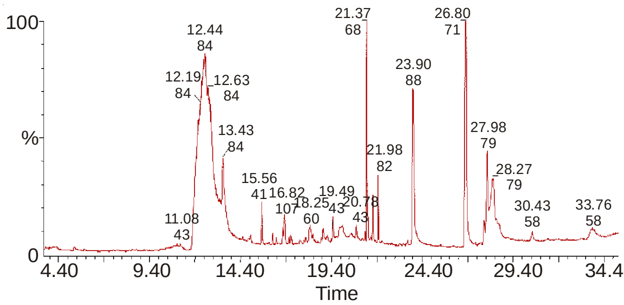

Fig. 1. GCMS spectra for curry leaf extract

Morphological features of the product: The morphological features of the product are shown in the scanning electron micrograph (Fig. 2). It is evident from Fig. 2 that the product contains a major share of nanostructures, nearly spherical in shape and measuring in the size range of 33-40 nm. Few bigger particles are also observed in the micrograph, which indicates the scope for further optimization of reaction conditions.

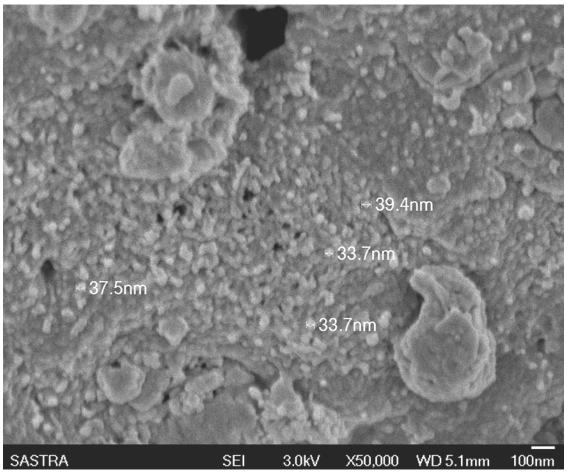

Fig. 2. SEM analysis of cupric oxide nanoparticles

Elemental composition and crystallinity: The composition of the synthesized product, as analyzed by the oxide mode of X-ray fluorescence spectrometer, reveals cupric oxide (CuO) as the major component of the product.

The powder X-ray diffractogram, shown in Fig. 3, reveals the formation of crystalline cupric oxide. The '2θ' values corresponding to peaks in X-ray diffraction pattern of synthesized product match very well with those of monoclinic CuO (JCPDS No. 801268), confirming its formation in the product. Organic acids are known to react with copper sulphate leading to formation of copper acetates. The presence of organic acids in the water extract of *Murrya koenigi*, are potential reaction partners for copper sulphate leading to formation of copper acetates. The decomposition temperature of copper acetate is about 200 ºC. It may be recalled that the precipitate obtained from the reaction between cupric sulphate and water extract

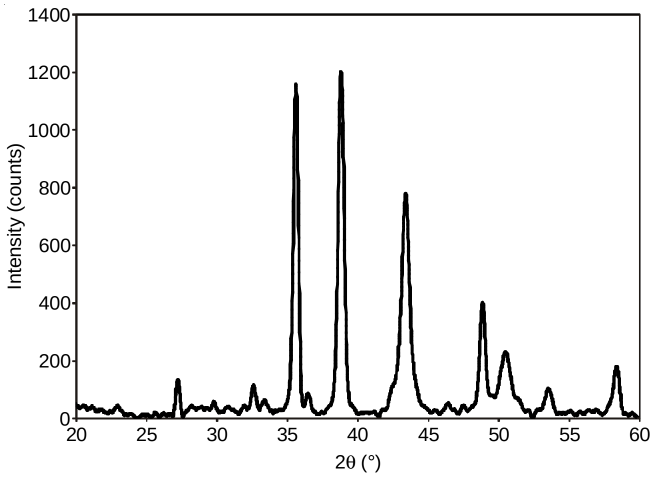

Fig. 3. XRD analysis of cupric oxide nanoparticles

of *Murrya koenigi* was calcined at 300 °C for the formation of product. The weight loss during calcination was about 31 %, which corresponds reasonably with the weight difference associated with the decomposition of cupric acetate to cupric oxide. Hence, it is hypothesized tha the cupric oxide has been formed due to decomposition of cupric acetate and formed by the reaction with carboxylic acids present in water extract of *Murrya koenigi* and cupric sulphate.

Zeta potential: When nanoparticles are dispersed in water, they tend to aggregate due to van der Waal's forces of attraction. However, if the particles acquire charge upon dispersion, the aggregation may be prevented if the electrostatic repulsive forces overcome attractive van der Waal's forces. Zeta potential is considered as a measure of charges on the nanoparticles' surface, the higher magnitude of which improves dispersion stability of nanoparticles.

The zeta potential of CuO nanoparticles dispersed in water was found to be -20.6 ± 4.74 mV (Fig. 4) at the pH of 6.8. The negative value of zeta potential may be attributed to the formation of hydroxyl groups on the particles' surface upon dispersion in water. Upon increasing the pH, the adsorption of hydroxyl groups on particles' surface is promoted leading to increase in zeta potential. Hence the cupric oxide nanoparticles prepared using water extract of *Murrya koenigi* can be dispersed in water with relative ease, suggesting its application for preparation of nanofluids.

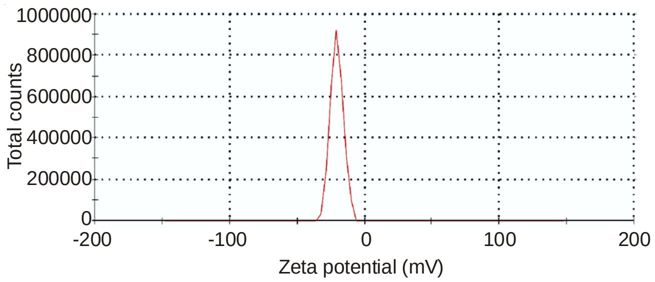

Fig. 4. Zeta size analysis of copper oxide nanoparticles

FTIR analysis: The FTIR spectra of the synthesized nanoparticles (Fig. 5) shows absorption bands characteristics of several functional groups. A band at 510 cm^{-1} corresponds to Cu-O bond. The band at 3788 cm^{-1} belongs to phenol and alcohol and bands around 3408, 2920 and 1622 cm^{-1} confirms the presence of carboxylic, nitro and aromatic groups respectively. Presence of these functional groups may be attributed to the organic contents from the leaf extract.

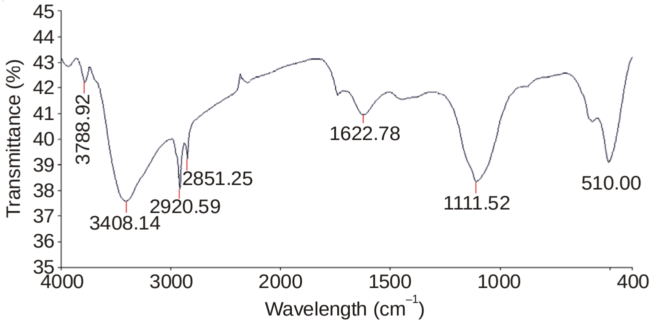

Fig. 5. FTIR spectrum of synthesized CuO nanoparticles using water extract of curry leaf

Photocatalytic activity: The variation of dye concentration with time during the photocatalytic (ultraviolet) degradation of reactive black solution is shown in Fig. 6. It is evident that the dye concentration decreases with time, with 90 % degradation achieved in 40 min. The dye degradation is rapid during the initial period of degradation, as 80 % of reduction in dye concentration was obtained within 10 min itself. The higher initial rate of degradation is predominantly attributed to the higher concentration of dye during the initial 10 min of degradation. The photocatalytic degradation may be assumed to consisting of two steps: (i) transport of dye molecules from the liquid bulk to the surface of photocatalyst or nanoparticles and (ii) degradation of dye molecule on the nanoparticle surface. At higher dye concentrations, the rate of dye transport from the liquid bulk to the catalyst surface is higher, leading to rapid degradation. The rapid degradation is accompanied by decrease in dye concentration in the liquid bulk, which in turn decreases the driving force for the mass transfer of dye from the bulk to the particle surface.

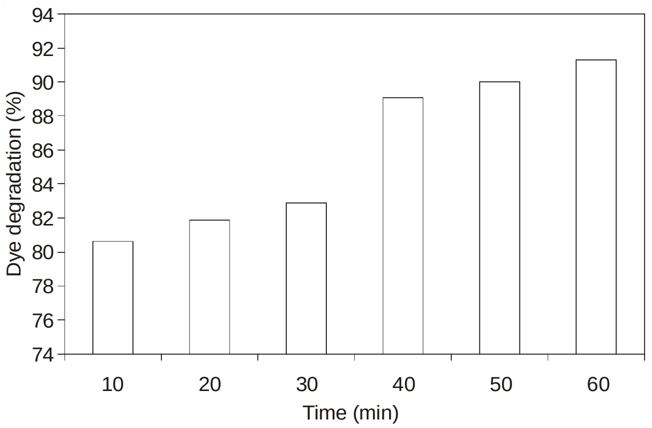

Fig. 6. Dye degradation efficiency of copper oxide nanoparticles

Hence the rate of dye transport becomes the rate controlling step with increase in time of exposure to dye solution to UV radiation. This is an implicit confirmation of the efficacy of green-synthesized cupric oxide as photocatalysts. The high activity may also be attributed to enhanced particle-liquid interaction due to smaller particle size and higher surface area[24-30].

Conclusion

A procedure for green synthesis of spherical, cupric oxide nanoparticles from copper sulphate pentahydrate using *Murrya koenigi* has been developed. The controlled rate of addition of water extract of *Murrya koenigi* to copper sulphate pentahydrate solution enabled the conversion of copper sulphate to copper acetate, which was subsequently calcined at 300 ºC to prepare cupric oxide nanoparticles. The green-synthesized nanoparticles have shown excellent photocatalytic and antimicrobial activities. The size control, crystallanity of the product along with photocatalytic activities achieved makes this green synthesis a valuable method for preparation of cupric oxide nanoparticles. The green synthesis can be scaled up to prepare cupric oxide nanoparticles in large quantities for their use in other fields of application.

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REFERENCES

1. R. Dhanya, K.S. Suganthi and K.S. Rajan, *Asian J. Chem.*, **26**, 4273 (2014).
2. K. Rohini Priya, K.S. Suganthi and K.S. Rajan, *Int. J. Heat Mass Transf.*, **55**, 4734 (2012).
3. R. Srivastava, M.U. AnuPrathap and R. Kore, *Colloids Surf. A*, **392**, 271 (2011).
4. N. Mittapelly, K. Mukkanti and B.R. Reguri, *Asian J. Chem.*, **25**, 483 (2013).
5. R. Sankar, P. Manikandan, V. Malarvizhi, T. Fathima, K.S. Shivashangari and V. Ravikumar, *Spectrochim. Acta A*, **121**, 746 (2014).
6. L. Hong, A.-L. Liu, G.-W. Li, W. Chen and X.-H. Lin, *Biosens. Bioelectron.*, **43**, 1 (2013).
7. C. Yang, X. Su, J. Wang, X. Cao, S. Wang and L. Zhang, *Sens. Actuators B*, **185**, 159 (2013).
8. K. Gopalakrishnan, C. Ramesh, V. Ragunathan and M. Thamilselvan, *Dig. J. Nanomet. Biostruct.*, **7**, 833 (2012).
9. J. Xu, C. Yao and Y. Wei, *Asian J. Chem.*, **22**, 6537 (2010).
10. K. Phiwdang, S. Suphankij, W. Mekprasart and W. Pecharapa, *Energy Procedia*, **34**, 740 (2013).
11. M. Ahamed, H.A. Alhadlaq, M.A.M. Khan, P. Karuppiah and N.A. Al-Dhabi, *J. Nanomater.*, **2014**, 1 (2014).
12. V.V.T. Padil and M. Cernik, *Int. J. Nanomedicine*, **8**, 889 (2013).
13. R. Sivaraj, P.K.S.M. Rahman, P. Rajiv, S. Narendhran and R. Venckatesh, *Spectrochim. Acta A*, **129**, 255 (2014).
14. S. Gunalan, R. Sivaraj and R. Venckatesh, *Spectrochim. Acta A*, **97**, 1140 (2012).
15. L.J.M. Rao, K. Ramalakshmi, B.B. Borse and B. Raghavan, *Food Chem.*, **100**, 742 (2007).
16. M.B. Ningappa, B.L. Dhananjaya, R. Dinesha, R. Harsha and L. Srinivas, *Food Chem.*, **118**, 747 (2010).
17. P. Sharma, G. Vidyasagar, A. Bhandari, S. Singh, U. Bhadoriya, S. Ghule and N. Dubey, *Asian Pac. J. Trop. Dis.*, **2**, 230 (2012).
18. S. Sathaye, Y. Bagul, S. Gupta, H. Kaur and R. Redkar, *Exp. Toxicol. Pathol.*, **63**, 587 (2011).
19. S. Arivoli and S. Tennyson, *Asian J. Exp. Biol. Sci.*, **2**, 721 (2011).
20. A.N. Kesari, R.K. Gupta and G. Watal, *J. Ethnopharmacol.*, **97**, 247 (2005).
21. S. Gupta, M. George and V. Garg, *J. Adv. Pharm. Technol. Res.*, **1**, 68 (2010).
22. A. Ghasemzadeh, H.Z.E. Jaafar, A. Rahmat and T. Devarajan, *Evid. Based Complement. Alternat. Med.*, **2014**, 1 (2014).
23. M. Malwal and R. Sarin, *J. Indian Nat. Prod. Res.*, **2**, 48 (2011).
24. K.S. Rajan, S.N. Srivastava, B. Pitchumani and V. Surendiran, *Int. J. Therm. Sci.*, **49**, 182 (2010).
25. K.S. Rajan, S.N. Srivastava, B. Pitchumani and K. Dhasandhan, *Appl. Therm. Eng.*, **28**, 1932 (2008).
26. K.S. Rajan, K. Dhasandhan, S.N. Srivastava and B. Pitchumani, *Int. J. Heat Mass Transf.*, **51**, 2801 (2008).
27. K.S. Rajan, S.N. Srivastava, B. Pitchumani and B. Mohanty, *Appl. Therm. Eng.*, **27**, 1345 (2007).
28. K.S. Rajan, B. Pitchumani, S.N. Srivastava and B. Mohanty, *Int. J. Heat Mass Transf.*, **50**, 967 (2007).
29. A. Jain, B. Mohanty, B. Pitchumani and K.S. Rajan, *J. Heat Transf.*, **128**, 761 (2006).
30. K.S. Rajan, S.N. Srivastava, B. Pitchumani and B. Mohanty, *Int. Commun. Heat Mass Transf.*, **33**, 1234 (2006).