Biological and chemical synthesis of CuO nanoparticles: A comparative study for yield attributes and characterization

Gupta Akshita, Tandon Moksh and Kaur Anupreet*
Department of Biotechnology, University Institute of Engineering and Technology, Panjab University, Chandigarh, INDIA
*anupreet410@gmail.com

Abstract

The interest in Copper oxide (CuO) nanoparticles has seen an upsurge due to its wide range of applications including chemical sensors, biomedical use, ceramic resistors, high-tech superconductors, fish industries, paint industries and many more. Conventional chemical method uses many toxic chemicals hence the biological method was developed. This work is mainly concentrated on the comparative study of CuO nanoparticles using two different synthesis methodologies namely chemical and biological. The green CuO nanoparticles were synthesized from Mentha spicata (common name: spearmint) plant leaf extract. Subsequently, CuO nanoparticles were also synthesized via chemical preparation method. The synthesized CuO nanoparticles were characterized by UV-Vis analysis, Fourier Transform Infrared analysis (FTIR) and X-ray diffraction analysis (XRD) analysis.

Since, the biological method uses natural extract for the synthesis, it can be suggested that biosynthesized CuO nanoparticles are more cost effective and environmentally benign upon comparison with chemically synthesized CuO nanoparticles.

Keywords: CuO nanoparticles, FTIR, yield attributes, XRD, UV-vis spectroscopy, green synthesis, cost effective.

Introduction

Nowadays most of the industries in the world are diverting their attention to nanotechnology because of numerous advantages offered by nano-technological advancements applicable to various sectors. Nanotechnology has emerged to be a worth-full field dealing in size ranging from 1-100nm holding diverse applications in physics, medicine, electronics and cosmetics[1]. Among various types of nanoparticles, metallic nanoparticles are considered to have the greatest importance. CuO, TiO_2, SiO_2 and ZnO are just a few examples of metallic nanoparticles.

The metallic nanoparticles have been studied because they possess high specific surface area, high fraction of surface atoms and unique physicochemical characteristics including catalytic activity, optical properties, electronic properties, antimicrobial properties and magnetic properties[2,3]. Metallic nanoparticles synthesis can be achieved via physical method, chemical method and biological method also called as green synthesis. Metal oxide nanoparticles are synthesized by chemical method that includes chemical reduction, sono-chemical, solvo-thermal reduction, electrochemical techniques.[4] The synthesis of nano sized metal copper particles with controlled morphologies and sizes can be achieved by using chemical reduction of copper salts.[5]

In the present scenario, researchers are readily turning to green synthesis approach for the production of nanoparticles. Green synthesis corresponds to the use of plant extract for the creation of nanoparticles with minimum release of hazardous chemicals. Green synthesis has thus turned out to be an eco-friendly and cost effective method for the production of desired nano-material[6,7]. Metallic nanoparticles are commonly synthesized by chemical approach which involves exposure to harsh chemicals[7]. This method is equally efficient but there is a need of an ecological approach for the production of more stable and less harmful nano material as mentioned in figure 1. In the green synthesis method, the plant extract is mixed with a precursor chemical resulting into the production of a desired nano material. Thus, utilization of harmful chemicals can be minimized.

Nanomaterials based on metal oxides have aroused great interest because of many unique properties related to nanoscale particle size[8]. Oxides of transition metal elements are an imperative class of semiconductors which find applications in solar energy processing, magnetic storage media, electronics, catalysis and so on[9].CuO is a p type semiconductor possessing a band gap of approximately 1.3 eV[10]. Of the metal oxides, CuO nanomaterials are of particular interest because of their versatility as catalysts[11].

The present work is mainly concerned with the comparisons made on copper oxide nanoparticles (CuO) synthesized by chemical as well as green synthesis approach using the plant extract of *Mentha spicata*. Copper oxide nanoparticles are said to possess antimicrobial activity, super thermal conductivity, photocatalytic properties and high stability. The plant is a readily available species and is being used from centuries for its various benefits like high levels of antioxidants, relieve symptoms of indigestion, nausea and gas, may help in reducing blood sugar and stress. Copper oxide nanoparticles thus formed by these two approaches have been compared for their yield as obtained from two methodologies, physical characteristics and characterization by XRD, FTIR and UV-Vis spectroscopy techniques.

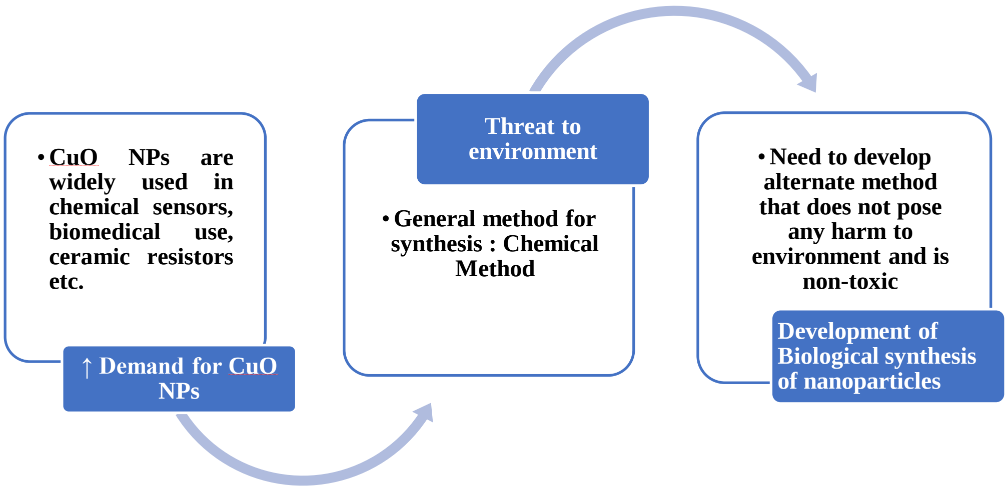

Figure 1: Development of alternate to the chemical method since it involves exposure to harsh chemicals.

Material and Methods

Materials: Leaves of *Mentha spicata* were collected from a nursery nearby the campus UIET, Panjab University, Chandigarh. Fehling solution A and B were purchased from Sisco Research Laboratories. Sodium hydroxide (NaOH) and copper sulfate ($CuSO_4$) were purchased from Sigma. Ethanol was bought from Oswal Scientific; Methanol HPLC Grade was purchased from LabSol Scientific.

Preparation of leaf extract: Fresh leaves of *Mentha spicata* were washed with deionized water several times and air dried. After the leaves were air dried, about 20g were boiled with 80 mL of deionized water for about 30 minutes. This extract was filtered through whatmann filter paper (grade II) which was further centrifuged to remove any traces of residue. The supernatant collected was used for synthesis of nanoparticles.

Biosynthesis of CuO-NPs: The bio-reduction of copper sulfate to copper oxide nanoparticles was carried out by various biomolecules present in leaf extract that act as reducing agent to $CuSO_4$(1). About 40 mL of leaf extract was added to 10ml of copper sulfate solution (Fehling solution A + Fehling solution B) with continuous stirring at boiling temperature.

The reaction was carried out till the color of the reaction mixture changed from greenish blue to brick red which took about 2.5 h. Several washings were given to the precipitates with distilled water and a final wash with ethanol. Obtained pellets were left in oven overnight and the dried pellets were stored for further use.

Chemical synthesis of CuO-NPs: Copper oxide nanoparticles were prepared using copper sulfate and sodium hydroxide as precursor via co-precipitation method[12]. 1M of copper sulfate was prepared in distilled water. Once the copper sulfate gets dissolved completely, 2M NaOH was added into the solution with continuous stirring. The reaction was carried for about two hours with continuous stirring. The solution was allowed to settle overnight. The supernatant solution was carefully discarded. The precipitates collected were washed with distilled water several times and were oven dried overnight.

Characterization of CuO-NPs: The characterization of synthesized nanoparticles was performed in SAIF/CIL Panjab University, Chandigarh The optical properties of copper oxide nanoparticles (CuO-NPs) were studied by UV-spectroscopy with wavelength ranging from 200nm to 800nm. UV-Vis spectroscopy was carried out at room temperature with methanol as blank. The structural behavior and the size of nanoparticles were determined by X-ray diffraction (XRD). The X-ray diffraction was carried at angle starting from 0°to 50°. Various functional groups present were detected by the use of Fourier Transform Infrared Spectroscopy (FTIR).

Results and Discussion

The synthesized nanoparticles by both the routes were further investigated for various aspects like their yield, optical properties, structural behavior, size and different functional groups present.

Yield and physical parameters: The synthesis process via both the routes was carried out in triplicate. Both the biologically synthesized and chemically synthesized nanoparticles were compared for their percentage yield. When the particles were dried, the yield of the samples was calculated and compared. The formula used to calculate the yield is mentioned below:

$$\%\,yield = \frac{\text{Synthesized amount}}{\text{Theoretical amount}} \times 100$$

The biologically synthesized nanoparticles gave an average yield of about 80% whereas chemically synthesized gave a average yield of 72%. This difference on yield could be because of the chemically synthesized NPs released less CuO compared to the green route[13].This clearly indicates that the improved yields can be achieved when nanoparticles were biologically synthesized nanoparticles than they were chemically synthesized, hence are more cost efficient.

The synthesized nanoparticles by both the routes were compared for some physical parameters which are mentioned in table 1.

UV-Spectroscopy: The results obtained from UV-Visible spectroscopy analysis of the CuO nanoparticles are presented in figure 2. Figure 2(a) depicts that the chemically synthesized nanoparticles show an absorption peak near 350nm in the UV-region, which is in accordance with results presented by Muthuvel A et al.[10] Figure 2(b) shows that the spectrum of biologically synthesized absorption peak appears around 280nm, the peak was slightly shifted towards the shorter wavelength[7]. The probable reason for the shift of absorption spectra is the difference in color of both the particles and this change is mainly due to presence of various biomolecules in plant extract.

Fourier Transform Infra-Red Spectroscopy: The FTIR technique was used to identify and estimate the potential biomolecules responsible for capping and stabilizing the CuO nanoparticles. The FTIR analysis of the nanoparticles synthesized by two different routes i.e. chemical and biological is shown in figure 3. The peaks in the spectrum originate from the various chemicals and extract that were used to synthesize these particles and FTIR is done to identify the molecules used to synthesize the particles. The CuO nanoparticles synthesized via biological method have sharp and more peaks of functional groups than the chemically synthesized particles which have blunt and comparatively less peaks; this is mainly due to presence of more functional groups in biologically synthesized nanoparticles because it uses plant extract as precursor.

Figure 3(s) shows the FTIR spectra of chemically synthesized CuO NPs. The major functional groups detected through FTIR in chemically synthesized nanoparticles sample were alkyl halides, alcohols, hydroxyl, C-C-O stretching and CH bending. The FTIR spectra of biologically synthesized nanoparticles are depicted in figure 3(b). The FTIR spectra of nanoparticles corresponding to biological method showed the presence of alcohol, alkanes, aromatic compounds, phenyl, alkenes, cytosine and C-O deoxyribose stretching[14]. The probable reason for this could the presence of biomolecules in plant extract which was used to biologically synthesize CuO nanoparticles.

X-Ray Diffraction: The XRD pattern demonstrates the orientation and crystalline nature of CuO nanoparticles. XRD patterns for chemically and biologically synthesized nanoparticles have been shown in figure 4. Both the samples were found out to be monoclinical crystalline in nature[15].

Average crystallite size of the particles was calculated by Debye-Scherer's formula:

$$s = \frac{0.9\,\lambda}{W\cos\theta}$$

where λ= X-Ray wavelength used; θ = Bragg's Angle; W= Half of the peak height

Table 1
Various physical parameters compared for both the routes

Parameters	Biological route	Chemical route
Source	$CuSO_4$	$CuSO_4$
Reducing agent	Natural leaf extract of *mentha spicata*	NaOH
Temperature	Boiling temperature	Room temperature
Nature	Crystalline	Crystalline
Time	2.5 hours(appx)	2 hours (appx)

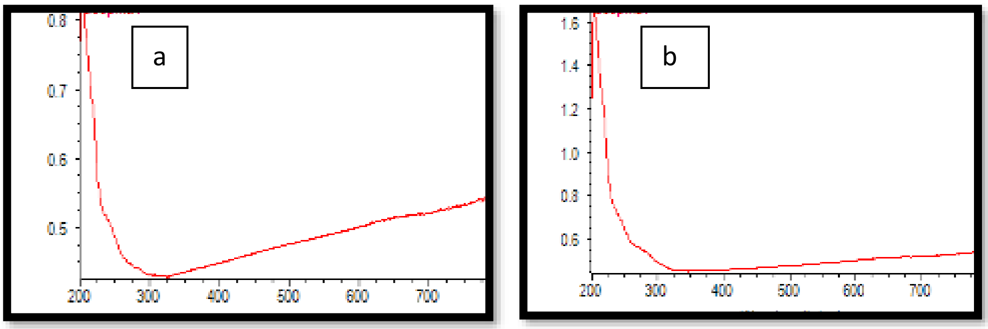

Figure 2: UV-analysis of the synthesized samples (a) Chemically-synthesized (b) Biologically-synthesized CuO nanoparticles

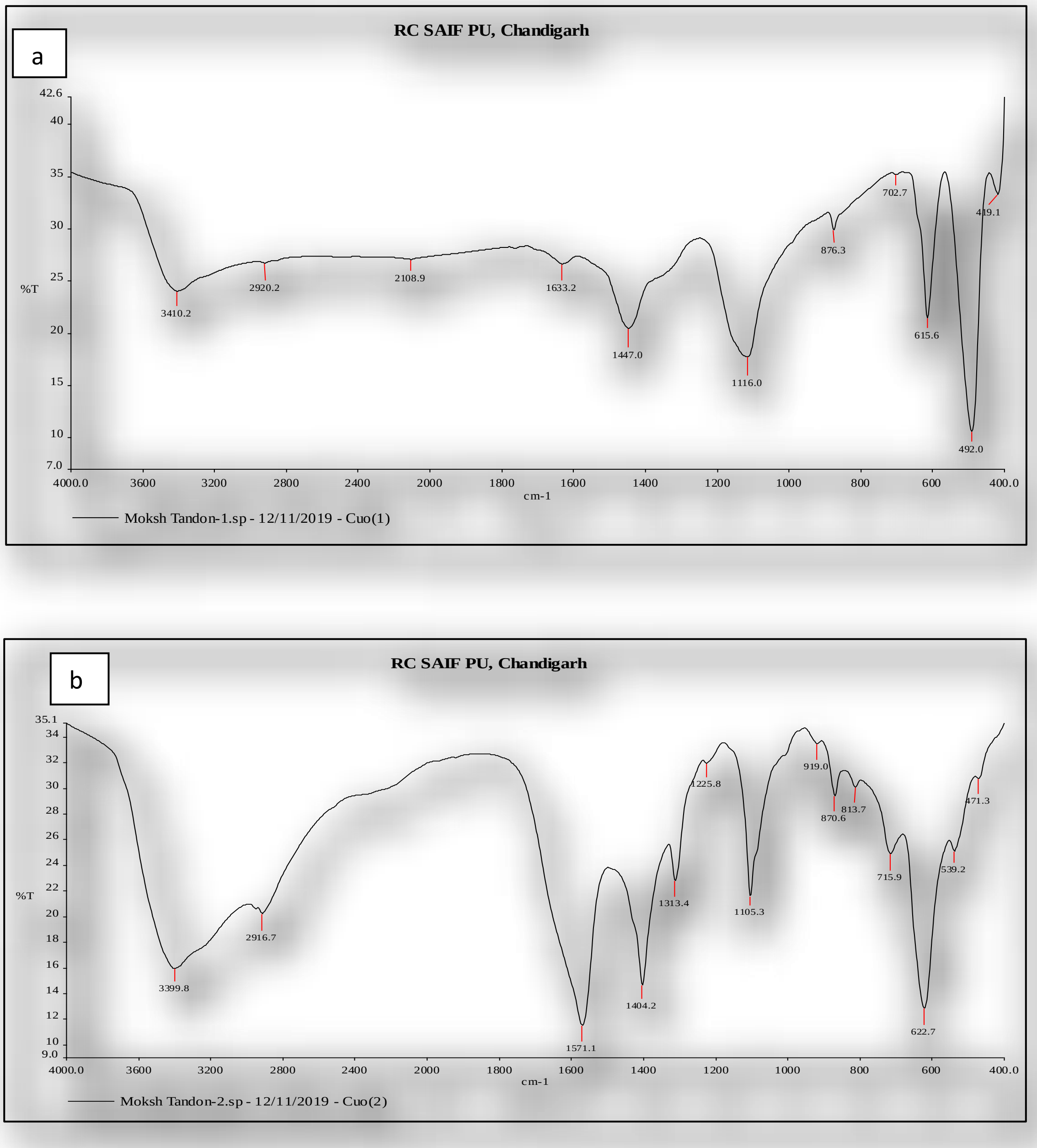

Figure 3: FTIR analysis of (a) chemically synthesized; (b) biologically synthesized CuO nanoparticles

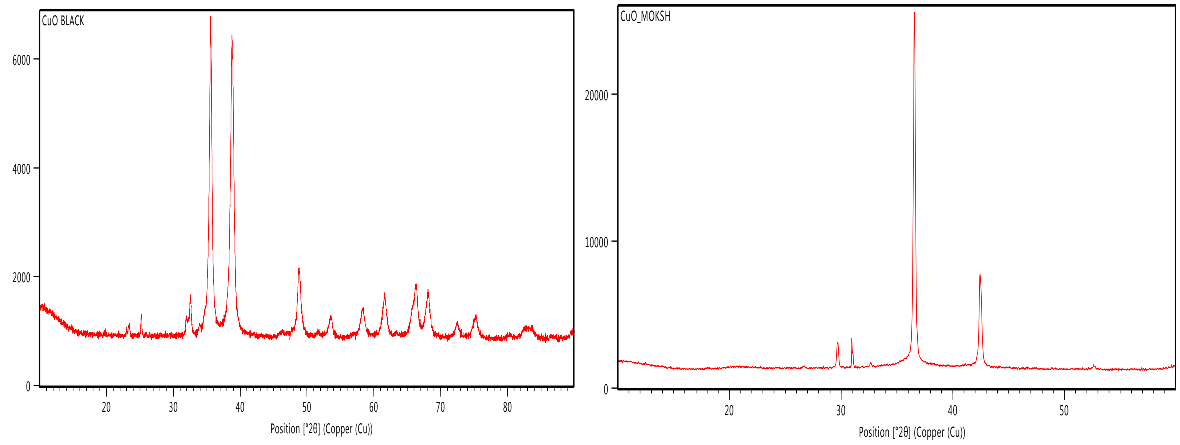

Figure 4: XRD pattern of chemically (left)and biologically (right) synthesized nanoparticles

The crystallite size of chemically synthesized nanoparticles was found to be around 63nm whereas that of naturally synthesized nanoparticles came out to be 92 nm. The chemically synthesized nanoparticles show various peaks due to the noise disturbances in background while carrying out the process of XRD.

Conclusion and Future perspective

The study acclaims that CuO nanoparticles have been successfully synthesized by both conventional chemical method as well as novel plant extract based synthesis method. It was established that the percentage yield of CuO nanoparticles as achieved by greener method was higher compared to its counterpart achieved via chemical method.

All characteristic studies are based on XRD, FTIR and UV-Visible results have confirmed the formation of CuO nanoparticles. Hence, M*entha spicata* can be suggested as a potential source of production for CuO NPs. Green synthesis is definitely an emerging technique for the synthesis of sustainable nanoparticles being environmentally benign, cost effective and less tedious owing to its less workup.

The synthesized nanoparticles can be used for various applications like drug delivery, treating waste water, checking its antimicrobial efficiency against pathogenic microbes and many more. Nanotechnology is a vast field to be explored and finds application in various industries. Hence the applications of the synthesized nanoparticles do not limit to the above mentioned applications. Further, these nanoparticles can be explored for various other applications.

References

1. Sharma D., Thakur N., Vashistt J. and Bisht G.S., Antibacterial evaluation of cuprous oxide nanoparticles synthesized using leaf extract of callistemon viminalis, *Indian J Pharm Educ Res.* **(2018)**

2. Jamdagni P., Rana J.S., Khatri P. and Nehra K., Comparative account of antifungal activity of green and chemically synthesized Zinc Oxide nanoparticles in combination with agricultural fungicides, *Int J Nano Dimens* **(2018)**

3. Amtout A. and Leonelli R., Optical properties of rutile near its fundamental band gap, *Phys Rev B.* **(1995)**

4. Varghese R., Jose S., H.J.P. and I.J., Comparative Studies on Bio and Chemically Synthesized Cuo Nanoparticles and Their Antibacterial Activity, *Int Res J Pharm.* **(2017)**

5. Satyanarayana T., A Review on Chemical and Physical Synthesis Methods of Nanomaterials, *Int J Res Appl Sci Eng Technol.* **(2018)**

6. Saif S., Tahir A., Asim T. and Chen Y., Plant mediated green synthesis of CuO nanoparticles: Comparison of toxicity of engineered and plant mediated CuO nanoparticles towards Daphnia magna, *Nanomaterials* **(2016)**

7. Kumar P.P.N.V., Shameem U., Kollu P., Kalyani R.L. and Pammi S.V.N., Green Synthesis of Copper Oxide Nanoparticles Using Aloe vera Leaf Extract and Its Antibacterial Activity Against Fish Bacterial Pathogens, *Bionanoscience* **(2015)**

8. Patzke G.R., Krumeich F. and Nesper R., Oxidic nanotubes and nanorods - Anisotropic modules for a future nanotechnology, *Angewandte Chemie - International Edition* **(2002)**

9. Frietsch M., Zudock F., Goschnick J. and Bruns M., CuO catalytic membrane as selectivity trimmer for metal oxide gas sensors, *Sensors Actuators, B Chem.* **(2000)**

10. Muthuvel A., Jothibas M. and Manoharan C., Synthesis of copper oxide nanoparticles by chemical and biogenic methods: photocatalytic degradation and in vitro antioxidant activity, *Nanotechnol Environ Eng.* **(2020)**

11. Babu S.G. and Karvembu R., Copper Based Nanoparticles-Catalyzed Organic Transformations, *Catal Surv from Asia* **(2013)**

12. Manyasree D., Peddi K.M. and Ravikumar R., CuO nanoparticles: Synthesis, characterization and their bactericidal efficacy, *Int J Appl Pharm.* **(2017)**

13. Nasrullah M., Gul F.Z., Hanif S., Mannan A., Naz S. and Ali J.S., Green and Chemical Syntheses of CdO NPs: A Comparative Study for Yield Attributes, Biological Characteristics and Toxicity Concerns, *ACS Omega* **(2020)**

14. Deepashree C., Komal Kumar J., Devi Prasad A. and Zarei M., FTIR spectroscopic studies on cleome gynandra - Comparative analysis of functional group before and after extraction, *Rom J Biophys*. **(2012)**

15. Khedekar S., Bedarkar P. and Prajapati P., Physicochemical characterization of Shadguna Balijarita Makaradhwaja: A preliminary study, *An Int Q J Res Ayurveda* **(2016)**

(Received 12th September 2020, accepted 18th November 2020)