Green synthesis and characterization of copper nanoparticles using different plant sources

Abstract

This research aimed at exploring eco-friendly green synthesis of CuNPs using different plant species used for research purpose were *Nyctanthes arbor-tristris* (Night jasmine), *Gardenia jasminoides* (Cape jasmine), *Tabernaemontana divartica* (Crape jasmine), *Cascabela thevetia* (Yellow oleander), *Clerodendrum inerme* (Glory bower), *Hibiscus rosa-sinensis* (China rose) and *Allamanda cathartica* (Allamanda) for synthesizing CuNPs. Out of seven ornamental plant species CuNPs were synthesized from three species *viz*. Night jasmine, Yellow oleander, Allamanda which were confirmed through UV-VIS spectrophotometer in wavelength 250-450 nm. The SPR peak was recorded at 301.00 nm, 300.50 nm and 300.00 nm for Allamanda, Yellow oleander and Night jasmine respectively that confirmed the formation of CuNPs. FTIR analysis of CuNPs showed different functional groups such as O−H, N−H, S−H, O=C=O, C≡C, C=O, N−O, C−H, M−O for Allamanda, O−H, N≡N, N−H, C−Cl for Yellow oleander and O−H, C−N, −C≡C−, =C−H, N−O for Night jasmine. DLS study revealed the average size of CuNPs as 125 nm, 120 nm and 100 nm for Allamanda, Yellow oleander and Night jasmine respectively. Zeta potential recorded for Allamanda, Yellow oleander and Night jasmine were -13.7 mV, -10.03 mV and -12.6 mV respectively. TEM micrograph clearly indicated that all the green synthesized CuNPs were spherical in morphology and the average size were 14.05 nm, 16.96 nm and 11.58 nm for Allamanda, Yellow oleander and Night Jasmine respectively.

Keywords: Copper nanoparticles, Green synthesis, Ornamental plants, TEM

Introduction:

Nanotechnology is the science that largely deals with synthesis and application of nanosize particles (1-100 nm or 1.0×10^{-9}m) of any material. When a material is reduced to nanosize, it acts differently and expresses some new properties completely lacking in its macroscale form. The recent development and implementation of nanotechnology have led to a new era called nano-revolution. It unfolds the role of plants in green synthesis of nanoparticles for synthesizing stable nanoparticles. Nanoparticles can be synthesized using various approaches including chemical, physical and biological methods. Physical and chemical methods used for production of nanoparticles though lead to monodisperse nanoparticles, but they are less stable and various toxic chemicals are used. Therefore, development of clean, non-toxic, biocompatible and eco-friendly method of synthesis of nanoaprticles has to be developed. Thus, there is an increasing demand for "green nanotechnology" (Singhal *et al*., 2011).

Among the various biological methods of nanoparticles synthesis microbe mediated synthesis is not of industrial feasibility due to the requirement of highly aseptic conditions and their maintenance. Green synthesis nanoparticle using plant extracts offers an alternative approach to resolve these problems. It was a simple, environment friendly, and economical green synthesis procedure. The extract of plants was very cheap and stable against harsh environmental conditions (Amaliyah et al., 2020; Hasheminya and Dehghannya, 2020; Khatami et al., 2020). Therefore, the use of plant extracts for synthesis of nanoparticles is potentially advantageous over microorganisms due to the ease of improvement, less biohazard and doesn't require any maintenance (Kalimuthu *et al*., 2010). According to Amin *et al*. (2012) functional groups such as phenolics and alkaloids present in plant extract are responsible for capping and stabilizing of nanoparticles. The stability of nanoparticles can be attributed to the formation of stable bonding between metallic nanoparticles and phytochemicals present in leaf extract (Kancha *et al*., 2010). Among the various nanoparticles, metal nanoparticles assume special importance because of their easier and cheaper mode of synthesis and promising in applications. Copper nanoparticles (CuNPs) have recently attracted special attention because of their low cost and novel, optical, mechanical, catalytic, electrical and thermal conduction properties, which are different from that of their bulk metals (Lee *et al*., 2009). In view of the ever increasing demand for copper nanoparticles, the present work has been planned to synthesize and characterize copper nanoparticle.

Materials and methods:

Based on certain criterion seven ornamental plants were selected for biosynthesis of CuNPs *viz. Nyctanthes arbor-tristris* (Night jasmine), *Gardenia jasminoides* (Cape jasmine), *Tabernaemontana divartica* (Crape jasmine), *Cascabela thevetia* (Yellow oleander), *Clerodendrum inerme* (Glory bower), *Hibiscus rosa-sinensis* (China rose) and *Allamanda cathartica* (Allamanda). The plant extract was used as reducing as well as capping agent.

i. Preparation of plant extract:

Leaves were cleaned thoroughly using sterile distilled water and cut into small pieces of 5-6mm sizes. Then 10 g of chopped leaves were transferred to 150ml of sterile distilled water and then ground with the help of mechanical mixer grinder (Bajaj Glory 500W) and microwaved at 320 MHz for 4 minutes. Solution was then removed from the microwave and cooled to ambient temperature (24±1°C). After the preparation of extract, it was filtered through Whatman filter paper no. 1 and again centrifuged at 10,000 rpm for 15 minutes for further purification of the sample. The supernatant was collected and stored at 4°C for future use.

ii.Synthesis of CuNPs using plant extracts:

For synthesis of CuNPs, 1ml of $CuSO_4.5H_2O$ solution was added drop by drop to the 100 ml of plant extract in an Erlenmeyer flask which was kept in the magnetic stirrer for 15 minutes. The whole mixture was then kept at rotary shaker (REICO, Horizontal shaker) and maintained dark condition by wrapping the flask with aluminium foil. After 4-5 days the colour of the solution starts to change from light brown to dark coffee brown. The change in colour indicated the formation of CuNPs.

ii. Characterization of green synthesized CuNPs:

Characterization of CuNPs was done by different equipments like UV-VIS spectrophotometer, Fourier Transform Infrared (FTIR) spectrometer, Dynamic Light Scattering, Zeta Potential and Transmission Electron Microscopy.

Result

Out of seven plants tested, three plant species were successfully utilized for synthesizing nanoparticles. Biological reduction of Cu^{2+} into CuNPs during exposure of $CuSO_4.5H_2O$ to extract of three ornamental plants *viz*. Night jasmine, Allamanda and Yellow oleander which was confirmed by the colour change from light brown to dark brown colour (Table 1) as explained by Krithiga *et al*. (2013). The colour changes occur in the solution after the completion of the reaction which was due to the surface plasmon resonance phenomenon (Jha *et al*., 2009). Lee *et al*. (2013) reported biologically synthesized CuNPs ranged in size from 40-100 nm using plant extract of *Magnolia kobus* leaf as reducing agent. Gopinath *et al.* (2014) studied the synthesis of CuNPs from *Nerium oleander* leaf aqueous extract where the *Nerium oleander* acts as a reducing agent. *Cassia fistula* flower extract are also used for synthesising CuNPs (Valli and Suganya, 2015). The result obtained in this investigation is interesting because it can serve as a foundation in terms of identification of potential plants for synthesizing CuNPs.

The sharp bands of CuNPs in UV-VIS spectroscopy were observed at 301 nm in case of Allamanda whereas the bands for Night jasmine and Yellow oleander were observed at 300.5 nm and 300 nm respectively [Fig 1(a-c) and Table 2] which is in agreement with the earlier report of Gopinath *et al*. (2014) who reported that Surface Plasmon Resonance (SPR) band for CuNPs occurs at 250-450 nm.

Fourier Transform Infra-Red (FTIR) measurements were carried out to identify the biomolecules for capping and efficient stabilization of the CuNPs synthesized using plant extracts. Allamanda mediated CuNPs displayed strong peaks at 3590.00 cm^{-1} and 3394.00 cm^{-1} resulted from stretching of O−H bonds of alcohol and carboxylic acid. Night jasmine mediated CuNPs showed strong peak at 3686.95 cm^{-1}, 3530.48 cm^{-1} and 3373.91 cm^{-1} resulted from O−H band of alcohol whereas Yellow oleander mediated CuNPs exhibited strong absorption peaks at 3537.45 cm^{-1} and 2326.15 cm^{-1} result from stretching of O−H and N≡N respectively Fig. 2(a-c) and Table 3. Similar findings were reported by Jayandran *et al*. (2015) where they found O−H band in the range of 3500-3200 cm^{-1} which was assigned to phenolic group using lemon extract and curcumin from turmeric. Kulkarni and Kulkarni, (2013) also reported O−H stretching at band 3373.00 cm^{-1} in green synthesized CuNPs using *Ocimum sanctum* leaf extract.

In this experiment, zeta potential was determined and recorded the charge of green synthesized CuNPs as −10.03mV, −13.7mV and −12.6mV for Yellow oleander, Allamanda and Night jasmine respectively [Fig. 4(a-c) and Table 5]. Negative zeta potential value observed in this study indicated that the green synthesized nanoparticles were relatively stable on their dispersion. Saif *et al*. (2016) reported that zeta potential in plant mediated CuO nanoparticles shifted from −9.27 ±1.10 to 16.25±0.36 after 72 hrs. Cuevas *et al*. (2015) also found that zeta potential value of -2mV when copper and copper oxide nanoparticles were biosynthesize using *Stereum hirsutum*.

Discussion

The particle size distribution of synthesized CuNPs through DLS for different plant extracts of Allamanda, Yellow oleander and Night jasmine are shown in Fig. 3(a-c). From the figure it was observed that the particles obtained are polydispersed in mixture with an average size of 125 nm, 120nm and 100nm for Allamanda, Yellow oleander and Night jasmine mediated CuNPs respectively (Table 4). This is in confirmation with the Kathad and Gajera, (2014) where they found *Artabotrys odoratissimus* mediated CuNPs showed average particle size of 135nm. The DLS study revealed that the CuNPs synthesized by Night jasmine falls under 1-100nm range while CuNPs synthesized by other two plants extract unable to maintain their size under 100nm. This may be due to the fact that they tend to agglomerate fast than the night jasmine mediated CuNPs. Size and shape of nanoparticles are influenced by many factors such as method use for synthesis, pH of the solution, precursor concentration, reductant concentration, time of incubation, temperature as well as method of preparation (Jain and Mehata, 2017).

A spectral analysis was followed by Transmission Electron Microscopic (TEM) analysis to determine the structure and morphology of CuNPs. It showed that the particles were polydispersed and the sizes of nanoparticles were 14.05 nm, 16.95 nm, and 11.58 nm for Allamanda, Yellow oleander and Night jasmine mediated CuNPs respectively (Plate 1). The majority of morphology was spherical in shape. Similar findings were reported by Hariprasad *et al.* (2016) and Subhankari and Nayak, (2013) where they found that the average size of green synthesized CuNP was 50 nm. Das *et al.* (2011) reported TEM image of gold nanoparticle synthesized using Night jasmine and revealed that synthesized nanoparticles were spherical in shape with an average diameter of 19.8 ± 5.0 nm. Karunakaran *et al.* (2016) studied TEM analysis of AgNPs synthesized using Allamanda shows nanoparticles are spherical in shape with size of 39nm.

Conclusion

Green synthesis of copper nanoparticles by using plants is safe, non-toxic, eco-friendly, which can be manufactured at large scale. In this study CuNPs was successfully synthesized by biological method using plant extracts *viz.* Night jasmine, Yellow oleander, Allamanda by modifying the shaking time of extracts and putting it in dark condition for 72-96 hrs. Synthesized nanoparticle can be further used for study on antimicrobial property and their toxicity level to the environment.

Table 1 Plants used for synthesis of CuNPs

Sl. No.	Plant sample	Parts used	Nanoparticle formed	Plant parts that formed nanoparticles
1	Night jasmine	Leaf, seed, flower	Yes	Leaf
2	Cape jasmine	Leaf, flower	No	-
3	Crape jasmine	Leaf, flower	No	-
4	Yellow oleander	Leaf, flower, seed	Yes	Leaf
5	Glory bower	Leaf, flower	No	-
6	China rose	Leaf, flower	No	-
7	Allamanda	Leaf, flower	Yes	Leaf

Table 2 UV-VIS spectrum analysis of plant mediated CuNPs

Plant Extract	Cu precursor	SPR peak (nm)
Allamanda	$CuSO_4.5H_2O$	301.00
Yellow oleander	$CuSO_4.5H_2O$	300.50
Night jasmine	$CuSO_4.5H_2O$	300.00

Table 3 FTIR analysis of plant mediated CuNPs

Plant extracts	Cu precursor	Wave number (cm^{-1})	Functional groups
Allamanda	$CuSO_4.5H_2O$	3595.00, 3394.00	O−H
		3173.92	N−H
		2812.00	C−H
		2634.00	S−H
		2318.00	O=C=O

		2154.00	C≡C
		1805.00	C=O
		1519.00	N=O
		1394.00	C−H
		879.00	M−O
Yellow oleander	$CuSO_4.5H_2O$	3537.45	O−H
		2326.15	N≡N
		1527.62	N−H
		640.00	C−Cl
Night jasmine	$CuSO_4.5H_2O$	3686.95, 3530.48, 3373.91	O−H
		3254.17	C−N
		2156.52	−C≡C−
		1650.86	=C−H
		1521.73	N−O

Table 4 DLS analysis of plant mediated CuNPs

Plant extracts	Copper precursor	Average particle size (nm)
Allamanda	$CuSO_4.5H_2O$	125
Yellow oleander	$CuSO_4.5H_2O$	120
Night jasmine	$CuSO_4.5H_2O$	100

Table 5 Zeta potential analysis of plant mediated CuNPs

Plant extracts	Copper precursor	Charge of Nanoparticles
Allamanda	$CuSO_4.5H_2O$	-13.7 mV
Yellow oleander	$CuSO_4.5H_2O$	-10.03 mV
Night jasmine	$CuSO_4.5H_2O$	-12.6 mV

Table 6 TEM analysis of plant mediated CuNPs

Plant extracts	Copper precursor	Shape	Average particle size diameter (nm)
Allamanda	$CuSO_4.5H_2O$	Spherical	14.05
Yellow oleander	$CuSO_4.5H_2O$	Spherical	16.95
Night jasmine	$CuSO_4.5H_2O$	Spherical	11.58

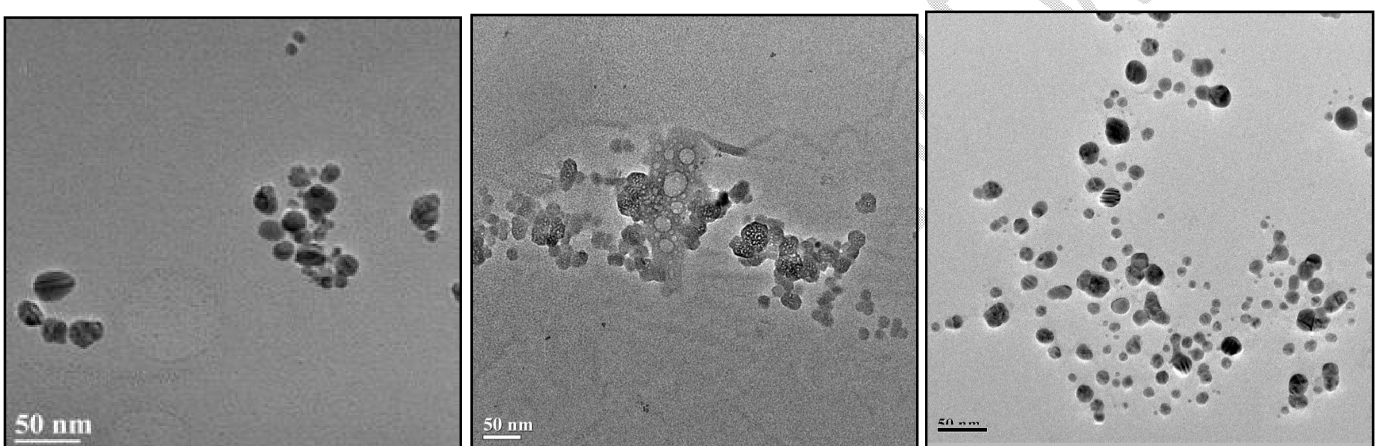

Plate 1: TEM image of copper nanoparticle synthesized from plant extracts using a) Allamanda, b) Yellow oleander and c) Night jasmine

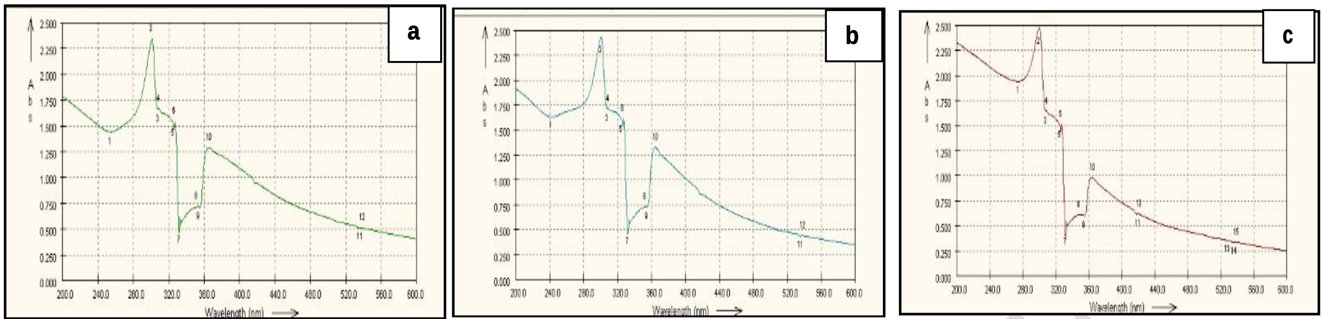

Fig. 1 UV-VIS spectrum of copper nanoparticle synthesized from plant extracts using (a) Allamanda, (b) Yellow oleander and (c) Night jasmine

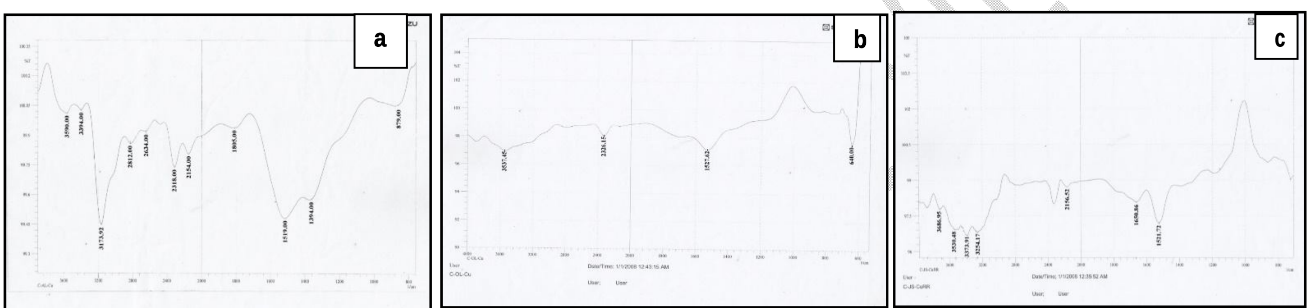

Fig. 2 Fourier Transform-Infra Red spectrum of copper nanoparticle synthesized from plant extracts using (a) Allamanda, (b) Yellow oleander and (c) Night jasmine

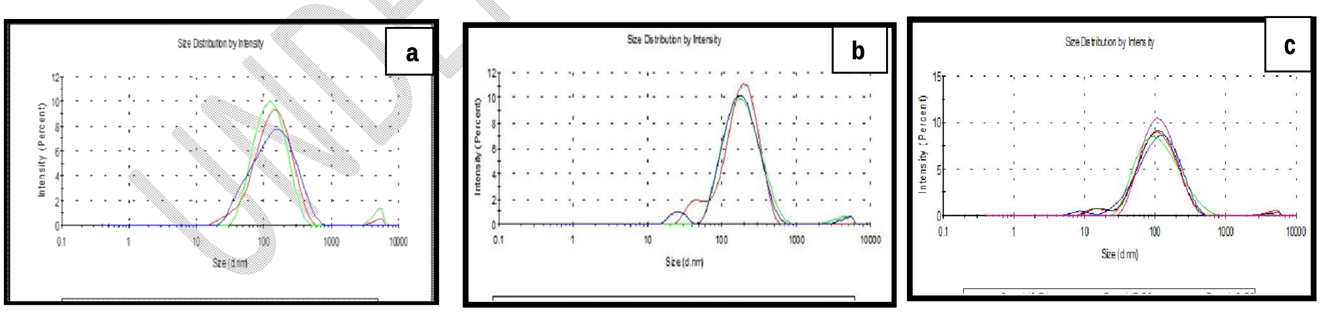

Fig. 3 Dynamic Light Scattering pattern of copper nanoparticle synthesized from plant extracts using (a) Allamanda, (b) Yellow oleander and (c) Night jasmine

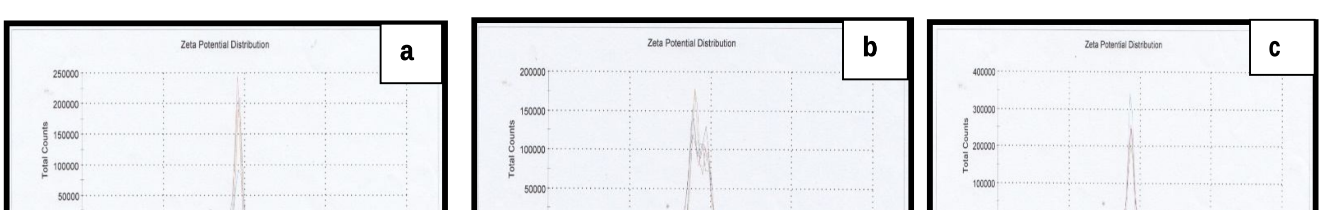

Fig. 4 Zeta potential analysis of copper nanoparticle synthesized from plant extracts using (a) Yellow oleander, (b) Allamanda and (c) Night jasmine

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