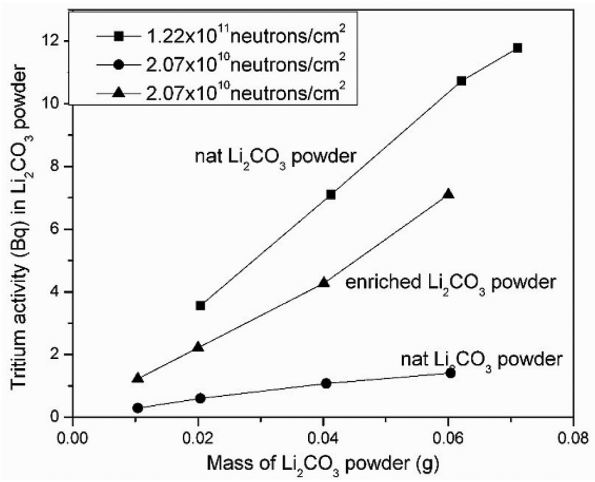

Figure 5. Calibration curve for tritium activity at two different neutron fluences.

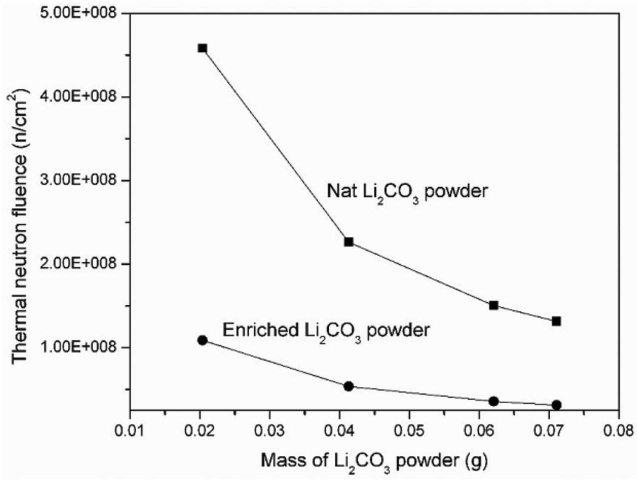

Figure 6. Minimum detectable neutron fluence with mass of Li_2CO_3 powder (g).

lower limit of thermal flux is about 1.1 E6 n/cm^2/sec.

Thermal neutron measurements using Li_2CO_3 powder offer advantages such as low flux measurements, large cross-section and do not need immediate counting. The disadvantage is that the sample cannot be reused as in conventional standard gold foil methods. The minimum thermal fluence that can be measured using liquid scintillation is 1.31 E8 n/cm^2 and 3.12 E7 n/cm^2 for 70 mg of natural and enriched Li_2CO_3 powder respectively.

1. Dierckx, R., *Nucl. Instrum. Methods*, 1973, **107**, 397–398.
2. Sato, S., Ochiai, K., Hori, J., Verzilov, Y., Klix, A., Wada, M., Terada, Y., Yamauchi, M., Morimoto, Y. and Nishitani, T., *Nucl. Fusion*, 2003, **43**, 7–15.
3. Batistoni, P. *et al.*, *Fusion Eng. Des.*, 2005, **75**, 911–915.
4. Verzilov, Y., Maekawa, F. and Oyana, Y., *J. Nucl. Sci. Technol.*, 1996, **33**, 390–395.

ACKNOWLEDGEMENTS. We thank Dr D. N. Sharma, former Director Health, Safety and Environment Group, BARC, Mumbai for constant encouragement during the work. Thanks are due to Dr C. V. Srinivasa Rao, Dr Tejan Kumar Basu and Dr Shrichand Jakhar of the Institute for Plasma Research, Gujarat, for encouragement.

Received 18 February 2015; accepted 23 April 2015

R. V. KOLEKAR[1]
S. P. D. BHADE[1,]*
RAJIV KUMAR[2]
PRIYANKA REDDY[1]
RAJVIR SINGH[1]
K. S. PRADEEPKUMAR[1]

[1]*Radiation Safety Systems Division, and*
[2]*Reactor Physics and Design Division, Bhabha Atomic Research Centre, Mumbai 400 085, India*
**For correspondence.*
e-mail: sonali@barc.gov.in

Biosynthesis of copper nanoparticles using aqueous extract of *Eucalyptus* sp. plant leaves

Nanobiotechnology is an enabling technology that deals with nanometer-sized materials in diverse fields of science such as biotechnology, nanotechnology, physics, chemistry and materials science. In addition to many physical and chemical methods which have been developed for preparing metallic nanoparticles, nanobiotechnology also serves as a significant technique in the progress of clean, non-toxic and environment friendly procedures for synthesis and assembly of metallic nanoparticles[1]. The biosynthesis of nanoparticles has attracted attention of many researchers owing to their physical and chemical processes being expensive and drastic reaction conditions. As a result, search for new inexpensive routes for synthesis of nanoparticles, scientists used microorganisms and plant extracts. Nature has devised diverse processes for synthesis of nano- and micro-length scaled inorganic materials which have contributed to the enhancement of fairly innovative and largely new area of research based on biosynthesis of nanomaterials[2]. Among the metal nanoparticles, copper nanoparticles are potentially attractive, which may be due to their good optical, electrical and thermal properties, superior strength, use as sensors, catalysts, and its bactericidal effect as antimicrobial and antifungal agents. Copper is highly toxic to microorganisms such as bacteria (*E. coli*, *Staphylococcus aureus*, *Pseudomonas aeruginosa*) and non-toxic to animal cells, due to which it is considered an effective bactericidal metal. It is also considered safe for human beings for applications such as food package and in water treatment[3,4]. Copper nanoparticles are attractive to many researchers due to its lower cost compared to noble metals such as Ag, Au and Pt.

Hence, they are potentially applied in the fields of catalysis, cooling fluids and conductive links. Due to plasmon surface resonance, Cu nanoparticles exhibit enhanced nonlinear optical properties, which allow wide applications in optical devices and nonlinear optical materials, such as optical switches or photochromic glasses[5].

Copper nanoparticles have been successfully synthesized by γ-radiolysis[6], laser irradiation[7], thermal decomposition[8], thiol-induced reduction in supercritical water[9], reduction in microemulsions[10], reverse micelles[11], vapour deposition[12], sonoelectrochemical[13], flame spray[14] and chemical reduction[15]. However, these methods suffer from drawbacks such as unsafe reaction condition, use of expensive chemicals and instruments and longer reaction time. To overcome these problems some green methods for synthesis of copper nanoparticles are reported using plant leaf extracts such as *Capparis zeylanica* Linn[4], tamarind, lemon juice[16], *Ocimum sanctum* as capping agents[17], *Magnolia kobus* leaf extract[18], *Syzygium aromaticum* (cloves) aqueous extract[19], *Aegle marmelos*[20] and *Nerium oleander*[21]. Hence there is scope to develop new methods for the synthesis of Cu nanoparticles. In this study, copper nanoparticles are synthesized using the leaf extract of *Eucalyptus* sp.

All chemicals and reagents used in this experiment are of analytical grade (Loba Chemicals). *Eucalyptus* sp. leaves were collected from Rajgurunagar village in Pune, Maharashtra. The leaves were thoroughly washed and dried in shade. To prepare the plant broth solution, 20 g dried leaves of *Eucalyptus* sp. leaves were cut into small pieces and washed with distilled water. This was taken in a 250 ml beaker with 100 ml of distilled water and boiled for 20 min at 80°C. The extract was filtered through Whatman filter no. 1, stored at 5°C and used within a week. The colour of the extract was brown.

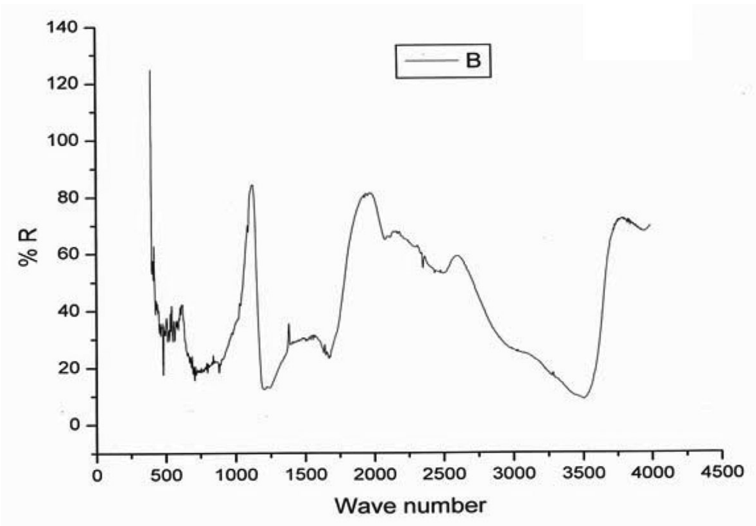

Figure 1. FTIR spectra of copper nanoparticles synthesized using *Eucalyptus* sp. leaf extract.

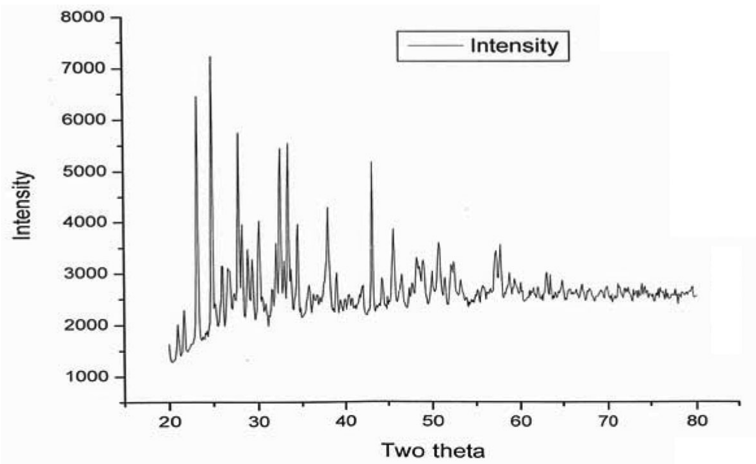

Figure 2. XRD of copper nanoparticles using *Eucalyptus* sp. leaf extract.

Ten ml of *Eucalyptus* sp. leaf extract was added to 100 ml of 1 mM aqueous copper sulphate solution in a 250 ml Erlenmeyer flask. The colour of the solution changes from blue to pale yellow when the solution of *Eucalyptus* sp. leaf extract and copper sulphate solution was stirred for homogeneous mixing. The flask was kept at room temperature overnight and the Cu nanoparticles separated out which settled at the bottom of this solution. The Cu nanoparticle thus obtained was purified by repeated centrifugation method at 12,000 rpm for 15 min followed by redispersion of the pellet in deionized water. Later the Cu nanoparticles were dried in an oven at 80°C.

The synthesized Cu nanoparticles were characterized by pH of solution, UV-visible, FTIR and XRD. pH of copper sulphate solution changed from 2.16 to 2.83 when added with *Eucalyptus* sp. leaf extract. The pH of coriander leaf extract was 6.96. From this it was confirmed that the capping between Cu and *Eucalyptus* sp. leaf extract has taken place.

The reduction of copper sulphate to pure Cu nanoparticle was monitored by using ultraviolet visible spectrophotometer. UV-Vis spectral analysis was done using a double beam spectrophotometer 2203 Systronics in the range 400–700. The absorption spectrum of pale yellow nanoparticle solution prepared with the proposed method showed a plasmon absorption band with a maximum of 572 nm.

FTIR spectra of biosynthesized copper nanoparticles were recorded to identify the capping and efficient stabilization of metal nanoparticles by biomolecules present in *Eucalyptus* sp. leaf extract. The FTIR spectrum of synthesized Cu nanoparticles using *Eucalyptus* sp. leaf extract is shown in Figure 1. The band at 3500 cm^{-1} corresponds to O–H stretching of alcohols and phenols. The band at 1594 cm^{-1} corresponds to N–H band of primary amines. The peak at 1454 cm^{-1} corresponds to C–N stretching of aromatic amino group. The band at 1689 cm^{-1} corresponds to carbonyl group of flavonoids,

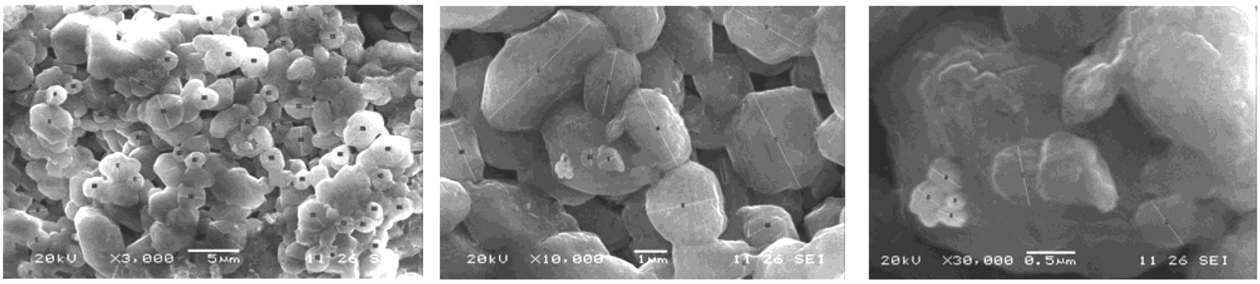

Figure 3. SEM image of copper nanoparticles.

phenolic acids, etc. The band at 1238 cm^{-1} corresponds to C–O linkages of phenol, acid and flavonoids. The band at 500 cm^{-1} corresponds to copper. Therefore, the synthesized copper nanoparticles were surrounded by proteins and metabolites such as phenolic acid, carboxylic acid and flavonoids. From the analysis of FTIR studies it was confirmed that phenolic compounds have stronger ability to bind metal indicating that phenols could possibly form metal nanoparticles to prevent agglomeration and thereby stabilize the medium. This suggests that biological molecules could possibly perform dual functions of formation and stabilization of Cu nanoparticles in aqueous medium.

XRD pattern of synthesized Cu nanoparticles using *Eucalyptus* sp. leaf extract is shown in Figure 2. The sample demonstrated a high crystallinity level with diffraction angles of 23.18, 24.87, 27.86, 32.53, 33.42, 34.52, 38.02, 42.97 and 45.55 which correspond to the characteristic of face-centred cubic of copper lines indexed at (210), (111), (210) and (220). The diffraction angle observed at 23.18° is related to the *Eucalyptus* sp. leaf extract. The average size of copper nanoparticles was found to be 38.62 nm. The size of the nanoparticles was determined using Debye–Scherrer equation, which may indicate a high surface area and surface area-to-volume ratio of nanocrystals. The equation is given below

$$D = k\lambda/\beta \cos\theta,$$

where D is the grain size, K the Scherrer's constant (0.9 to 1.0 for spherical particle), β the width at half maxima of peaks in XRD, θ the corresponding angle for peaks and λ is the X-ray wavelength.

The size of copper nanoparticle is found to be in the 27.65–48.19 nm range.

The morphology of the *Eucalyptus* sp. leaf extract prepared copper nanoparticles was determined using scanning electron microscope (SEM) (Figure 3). The typical SEM image reveals that the product mainly consists of particle-like Cu-nano crowded together with biomolecules of *Eucalyptus* sp. leaf extract. However, further observations with higher magnification reveal that these crowded Cu nanoparticles are groups of smaller nanoparticles which exhibit good uniformity.

We have reported green synthesis of Cu nanoparticles using *Eucalyptus* sp. leaf extract. The *Eucalyptus* sp. leaf extract was found efficient for synthesis of copper nanoparticles. This method has merits over other reported methods such as easy availability of starting materials, inexpensive process, ease of conduction at any college level laboratory, simple reaction conditions, avoidance of use of expensive, hazardous and toxic reagents and pollution free.

1. Salata, O. V., *J. Nanobiotechnol.*, 2004, **2**, 3.
2. Mohanpuria, P., Rana, K. N. and Yadav, S. K., *J. Nanoparticle Res.*, 2008, **10**, 507–517.
3. Subhankari, I. and Nayak, P., *World J. Nanosci. Technol.*, 2013, **2**, 14–17.
4. Saranyaadevi, K., Subha, V., Ravindran, R. E. and Renganathan, S., *Int. J. Chem. Tech. Res.*, 2014, **6**, 4533–4541.
5. Soomro, R., Sherazi, S., Sirajuddin, M., N., Shah, M., Kalwar, N., Hallam, K. and Shah, A., *Adv. Mat. Lett.*, 2014, **5**, 191–198.
6. Joshi, S. S., Patil, S. F., Iyer, V. and Mahumuni, S. *Nanostructured Mat.*, 1998, **10**, 1135–1114.
7. Yeh, M. S., Yang, Y. S., Lee, Y. P., Lee, H. F., Yeh, Y. H. and Yeh, C. S., *J. Phys. Chem. B*, 1999, **103**, 6851–6857.
8. Kim, Y. H., Lee, D. K., Jo, B. G., Jeong, J. H. and Kang, Y. S., *Colloids Surf. A*, 2006, **284–285**, 364–368; Hambrock, J., Becker, R., Birkner, A., Weiß, J. and Fischer, R., *Chem. Commun.*, 2002, **1**, 68–69.
9. Ziegler, K. J., Doty, R. C., Johnston, K. P. and Korgel, B. A., *J. Am. Chem. Soc.*, 2001, **123**, 7797–7803.
10. Haram, S. K., Mahadeshwar, A. R. and Dixit, S. G., *J. Phys. Chem.*, 1996, **100**, 5868–5873.
11. Lisiecki, I., Bjorling, M., Motte, L., Ninham, B. and Pileni, M., *Langmuir*, 1995, **11**, 2385–2392.
12. Ponce, A. A. and Klabunde, K. J., *J. Mol. Cataly.*, 2005, **A225**, 1–6.
13. Haas, I., Shanmugam, S. and Gedanken, A., *J. Phys. Chem. B*, 2006, **110**, 16947–16952.
14. Athanassiou, E. K., Grass, R. N. and Stark, W. J., *Nanotechnology*, 2006, **17**, 1668–1673.
15. Chen, L., Zhang, D., Chen, J., Zhou, H. and Wan, H., *Mat. Sci. Eng.*, 2006, **A415**, 156–161; Ang, T. P., Wee, T. S. A. and Chin, W. S., *J. Phys. Chem.*, 2004, **B108**, 11001–11010.
16. Sastry, A. B. S., Karthik, A. R., Linga, P. R. and Murthy, B. S., *Environ. Chem. Lett.*, 2013, **11**, 183–187.
17. Kulkarni, V. D. and Kulkarni, P. S., *Int. J. Chem. Stud.*, 2013, **1**, 1–4.
18. Lee, H. J., Song, J. Y. and Kim, B. S., *J. Chem. Technol. Biotechnol.*, 2013, **88**, 1971–1977.
19. Subhankari, I. and Nayak, P. L., *World J. Nanosci. Technol.*, 2013, **2**, 10–13.
20. Kulkarni, V. and Kulkarni, P., *Nanosci. Nanotechnol. – An Indian J.*, 2014, **8**, 401–404.
21. Gopinath, M., Subbaiya, R., Selvam, M. M. and Suresh, D., *Int. J. Curr. Microbiol. Appl. Sci.*, 2014, **3**, 814–818.

Received 18 February 2015; accepted 1 April 2015

VASUDEO KULKARNI[1]
SAMPAT SURYAWANSHI[2]
PRAMOD KULKARNI[2,*]

[1]*Department of Physics, and*
[2]*Department of Chemistry,*
Hutatma Rajguru Mahavidyalaya,
Rajgurunagar,
Pune 410 505, India
**For correspondence.*
e-mail: pramodskulkarni3@gmail.com