A Simple and Green Method for the Synthesis of Silver Nanoparticles Using Ricinus Communis Leaf Extract

Uthirappan Mani[1], Sujatha Dhanasingh[1], Rajeswari Arunachalam[1], Edwin Paul[2], Ponnusamy Shanmugam[3], Chellan Rose*[1], Asit Baran Mandal[4]

[1]Department of Biotechnology, CSIR- Central Leather Research Institute, Adyar, Chennai- 600020, India
[2]Centralized Sophisticated Instruments Laboratory, CSIR- Central Leather Research Institute, Adyar, Chennai- 600020, India
[3]Organic Chemistry Division, CSIR- Central Leather Research Institute, Adyar, Chennai- 600020, India
[4]Chemical Laboratory, CSIR- Central Leather Research Institute, Adyar, Chennai- 600020, India
*chellanrose@yahoo.co.uk

***Abstract*- A simple and green approach for the synthesis of nanocrystals of silver (Ag) using *Ricinus communis* leaf extract at room temperature is described. Treatment of aqueous silver ions with aqueous leaf extract got Ag^+ ions reduced and resulted in the formation of silver nanoparticles (NPs). The silver NPs were characterized by UV-Vis spectroscopy, X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), thermo gravimetric analysis (TGA), differential scanning calorimetry (DSC), Fourier-transform infra red spectroscopy (FTIR) and high-resolution transmission electron microscopy (HRTEM). The nanoparticles obtained are in the size range of 20-30 nm and crystallized in the form of face centered cubic (*fcc*) symmetry. This green chemical method has several advantages such as cost-effectiveness, compatibility for biomedical and pharmaceutical applications as well as for large scale commercial production.**

Keywords- Metals; Electron Microscopy; X-Ray Diffraction; Optical Properties

I. INTRODUCTION

Noble metal nanoparticles such as gold, silver, copper and platinum have received increasing interest because of its potential applications in science and technology particularly in catalysis, catalysts for the growth of nanowires, nanomedicines and nanoelectronics [1-7]. Their unique catalytic and optical properties can be tailored by controlling the size, shape, and elemental composition as well as the internal and surface structure of the nanoparticles [8]. Utilization of nontoxic chemicals, environmentally benign solvents and renewable materials are some of the key issues that merit important consideration in a green synthesis strategy. Use of biological materials such as micro-organisms [9-12], plant extracts [13-18] or plant biomass [19] as reducing agents could be an alternative to chemical and physical methods for the production of nanoparticles in an eco-friendly manner. Often, the nanoparticles produced by biological methods outweigh due to their specific characteristics for a desired application. Accordingly, the present study focused to synthesize silver NPs using leaf extract of *Ricinus communis*, as a reductant.

Ricinus communis L. (Euphorbiaceae) is a soft wooden small tree, wide spread throughout tropical and warm temperature regions of the Globe. It possesses dose-dependent hepatoprotective, choleretic and anti-cholestatic activities [20]. These leaves contain bioactive constituents such as tannins, phlobatannins, flavonoids, terpenoids, and cardiac glycosides [21].

II. EXPERIMENTAL

A. Preparation of Leaf Extracts

Ricinus communis leaves were collected from the garden of this Institute and washed several times with de-ionized water before it is extracted. A 20 g of this leaves after removing water by using filter paper were finely cut and stirred with 100 ml de-ionized water at 80°C for 2 min, and filtered to get the extract. The filtrate is used as reducing agent and stabilizer.

B. Synthesis of Silver Nps Using Leaf Extracts

For the silver NPs synthesis, 5 ml of *R. communis* leaf extract was added to 45 ml of 1 mM aqueous $AgNO_3$ solution in a 250 ml Erlenmeyer flask. The flask was then incubated in the dark (to minimize the photo oxidation of silver nitrate), at room temperature. A control setup was also maintained without leaf extract. The silver NPs solution thus obtained was purified by repeated centrifugation at 10,000 rpm for 15 min followed by re-dispersion of the pellet in deionized water. Then, the silver NPs were freeze dried using VirTis freeze mobile 6ES freeze drier.

C. Characterization Studies

The biosynthesis of silver NPs was monitored periodically and the absorption maxima were scanned by UV-Vis spectra, at the wavelength of 200-1100 nm in Hitachi U-1800 spectrophotometer at a resolution of 1 nm.

The X-ray diffraction measurements were carried out on a Rigaku Miniflex X-ray diffractometer at a scanning rate of 20 min^{-1} with an operating voltage of 30 kV and a current of 15 mA with Cu Kα radiation (1.5405 Å) monochromatic filter in the range 10-80°.

A Hitachi S-3400 N SEM equipped with an EDS elemental microanalysis system was used to study the characteristic of the NPs and its topology.

The morphology and size of the nanoparticles were investigated using the higher solution images obtained with a JEOL3010 transmission electron microscope.

Infra red (IR) spectrum was obtained using the KBr pellet technique on an ABB MB3000 spectrophotometer where it was scanned between 4000 and 500 cm^{-1} at a resolution of 4 cm^{-1} in transmittance mode.

Thermo gravimetric analyzer (TGA, Q50) was used to investigate the weight loss of the surface capped silver NPs. The thermal behavior of silver NPs was determined by using standard differential scanning calorimeter (DSC, TA Instruments, model Q200).

III. RESULTS AND DISCUSSION

A. Uv-Vis Absorbance Spectroscopy

An extract of *R. communis* leaf was used in this work for the extracellular synthesis of silver nanoparticles. After addition of the extract to 1mM $AgNO_3$, the solution turns golden yellow within a minute, indicating the initial formation of silver NPs. This color change arises because of the excitation of surface plasmon resonance (SPR) with the silver NPs. Fig. 1 shows the UV-Vis spectra of aqueous silver nitrate–Ricinus leaf extract reaction mixture recorded between 300 and 1100 nm at different time intervals. It was observed from the data that the silver surface plasmon resonance band occurs at 450 nm and steadily increases in intensity as a function of time of reaction without any shift in the wavelength. After 3 h of incubation, no change in intensity of color at 450 nm was observed, indicating the complete reduction of silver ions. (Fig.1 inset).

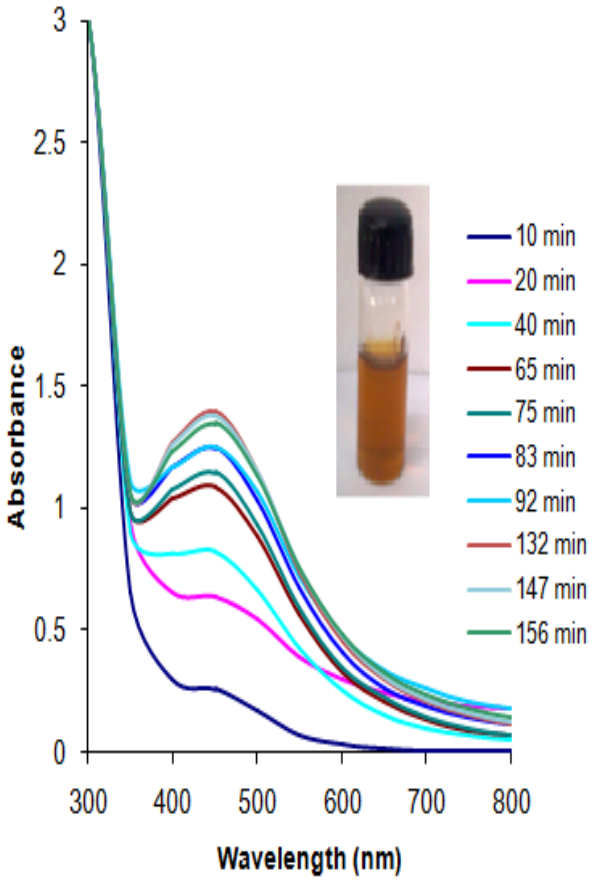

Fig. 1 UV- Vis spectra of nanoparticles measured at the time of reaction of *Ricinus communis* leaf extract with aqueous solution of 1mM $AgNO_3$; the inset is synthesized Ag nanoparticles showing brownish red color after 3 h of incubation

B. Xrd and Eds Analysis

The crystalline nature of silver NPs was confirmed from the X-ray diffraction analysis. Fig. 2a shows the XRD patterns of silver NPs synthesized from leaf extracts of *R. communis.* A number of Bragg reflections with 2θ values of 38.03°, 46.18°, 63.43° and 77.18° correspond to the (111), (200), (220) and (311) set of lattice planes which may be indexed as the band for face centered cubic (*fcc*) structures of silver. The unassigned peaks could be due to the crystallization of bioorganic phase that occurs on the surface of the silver NPs [19]. Metallic silver nanocrystals generally show typical optical observation peak approximately at 3 keV due to surface plasmon resonance. EDS profile in Fig. 2b shows strong silver signal along with weak oxygen and carbon peak, which may have originated from the biomolecules that are bound to the surface of the silver NPs [15].

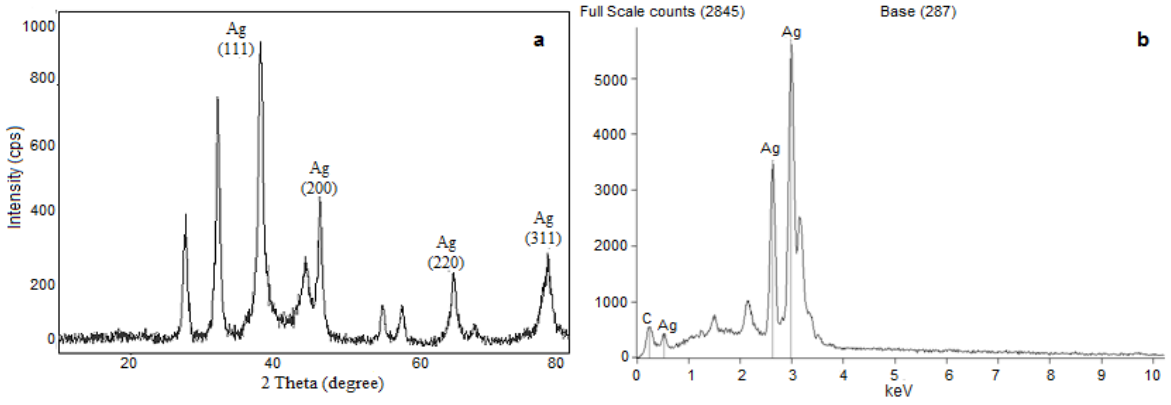

Fig. 2 (a) XRD spectrum of silver nanoparticles synthesized by *Ricinus communis* leaf extract;

(b) EDS profile of silver nanoparticles

C. Electron Microscopic Studies

SEM analysis was carried out to understand the topology of silver NPs, which showed the biosynthesis of monodisperse spherical silver NPs (Fig. 3). TEM images at different resolutions (Fig. 4a-e), show silver nanoparticles which are quiet monodisperse in the size range of 20-30 nm. These nanoparticles appear to have assembled into very open, quasi-linear superstructures rather than a dense closely packed assembly. The data also reveal that nanoparticles are not in physical contact but are evenly separated. Fig. 4f shows the selected area electron diffraction (SAED) pattern of the silver NPs. The ring-like diffraction pattern indicates that the particles are crystalline. The diffraction rings could be indexed on the basis of the *fcc* structure of silver. Four rings arise due to reflections from (111), (200), (220) and (311) lattice planes of *fcc* silver, respectively. This is evident by sharp Braggs reflection observed in the XRD spectrum.

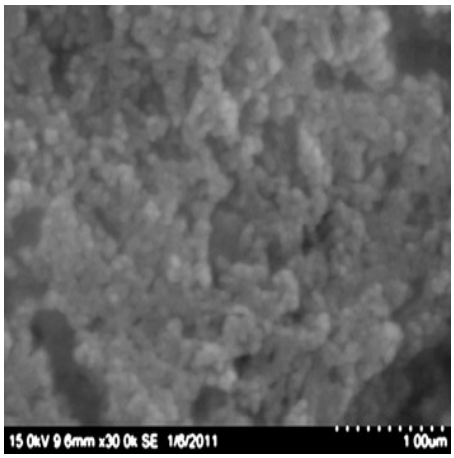

Fig. 3 (a) SEM micrograph of silver nanoparticles formed after reaction of leaf extract with 1mM $AgNO_3$ for 3 h

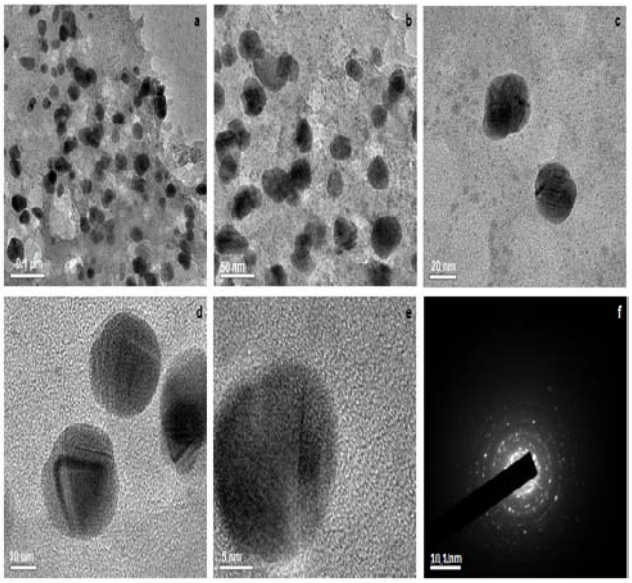

Fig. 4 (a-e) TEM images of silver nanoparticles at different resolution (f) SAED pattern

D. Ftir Analysis

FTIR measurements were carried out to identify the possible biomolecules responsible for capping and efficient stabilization of the silver NPs synthesized by plant leaf extract (Fig. 5). The silver nanoparticles showed peaks at 1037 cm^{-1} (ether linkages), 1334 cm^{-1} (-O-H bending), 1213 cm^{-1} (ether linkages), 1505 cm^{-1} (=NH) and 1632 cm^{-1} (amide I) suggest the presence of flavonoids and terpenoids adsorbed on the surface of silver NPs [22]. This bioorganic phase was also observed in XRD data as unassigned peaks which confirm that these molecules of the leaf extract are responsible for the reduction of Ag^{+} to Ag°.

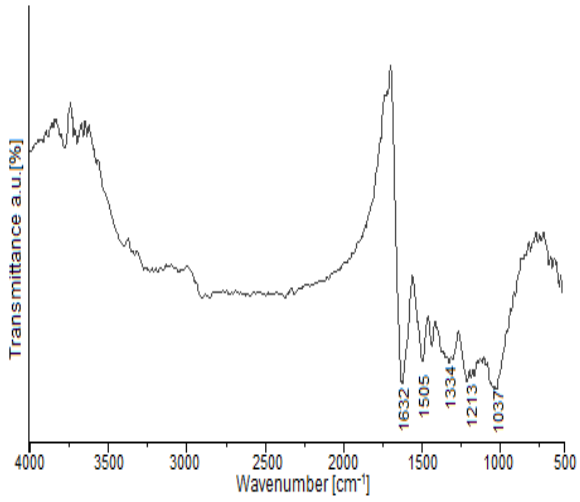

Fig. 5 FTIR spectrum of Ag nanoparticles synthesized by reduction of Ag^+ ions by *R.communis* leaf extract

E. Thermal Studies

The thermal stability of NPs was studied using TGA which showed the NPs began to degrade at around 220°C. Also, there is a steady weight loss until 800°C. The total weight loss up to 800°C for silver NPs (Fig. 6a) is about 28.51%. The observed behavior is most likely as a consequence of the surface desorption of bio-organic compounds present in nano particle powder. Thus, plant leaf extract-stabilized silver NPs are expected to be made up of molecules responsible for the reduction of metal ion and stabilizing the particles in the solution [23]. According to the DSC curve seen in Fig. 6b, the silver NPs showed an endothermic peak at 69°C. The denaturation enthalpy of these nanoparticles is closer to a single stage decomposition of the compound, as obtained from TGA curve. The earliest weight loss for silver NPs occurred at 75°C. Therefore, the decomposition temperature by thermo gravimetric study and the denaturation temperature by DSC curve for these nanoparticles are in good agreement. This result suggests that the phytochemicals are responsible for the reduction of Ag^+ to Ag° (nanoparticle) could be a thermally low stable compound, which gets extracted in water.

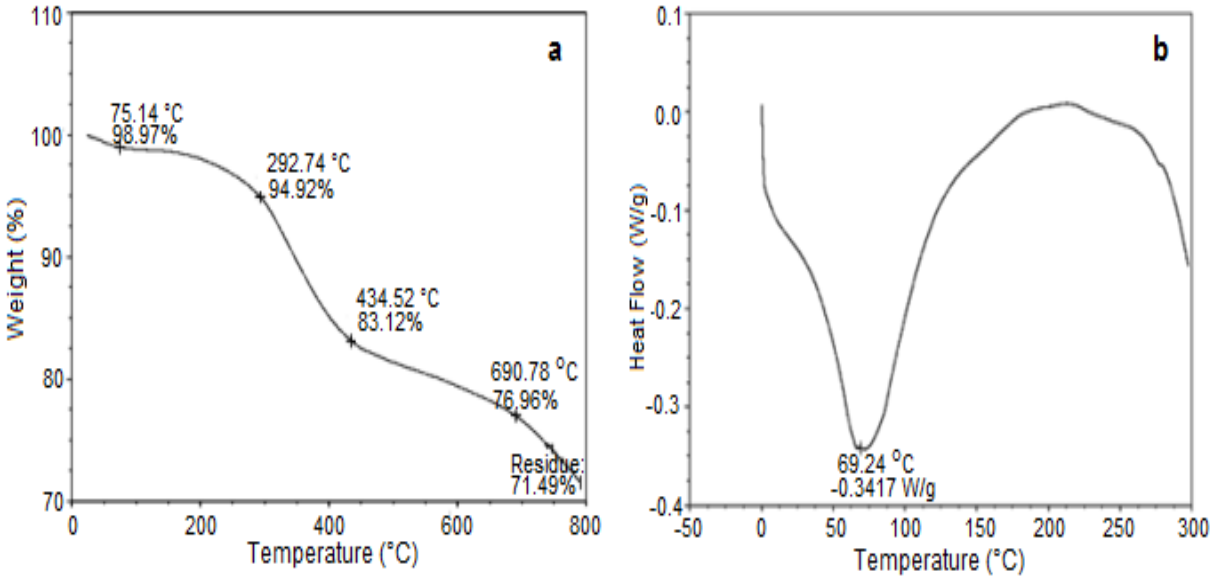

Fig. 6 (a) TG and (b) DSC curves of silver nanoparticles synthesized by reacting $AgNO_3$ with Ricinus leaf extract

IV. CONCLUSIONS

In summary, for the first time, we have synthesized Ag nanoparticles using *R.communis* aqueous leaf extract. Specifically, we describe an environment friendly one-step method to synthesize Ag nanoparticle, by reduction of corresponding metal solutions using *R.communis* extract without usage of any special capping agents at room temperature. This green approach may find various medicinal as well as technological applications. The method is general and may extend to other noble metals such as Au, Pd and Pt.

REFERENCES

[1] R. Narayanan, M.A. El-Sayed, Nano Lett. 4 (2004)1343-1348.

[2] B. Wu, A. Heidelberg, John J. Boland, J. Nat. Mater. 4 (2005) 525-529.
[3] P. V. Asharani, Ng. Xinyi, M.P. Hande, S. Valiyaveettil, Nanomedicine. 5 (2010) 51-64.
[4] Prashant V. Kamat, J. Phys. Chem. B. 106 (2002) 7729-7744.
[5] X. Wang, Y. Li, Chem. Commun. (2007) 2901-2910.
[6] L. Neeta, R. Ramakrishnan, B. Li, S. Subramanian, R.S. Barhate, Y. Liu, R. Seeram, Biotechnol. Bioeng, 97 (2007) 1357–1365.
[7] Subramanian Sundarrajan, Arun Richard Chandrasekaran and Seeram Ramakrishna, J. Am. Ceram. Soc. 93 (2010) 3955-3975.
[8] D. Ferrer, A. Torres-Castro, X. Gao, S. Sepulveda-Guzman, U. Ortiz-Mendez, M. Jose- Yacamán, Nano Lett. 7 (2007) 1701-1705.
[9] R. Varshney, A.N. Mishra, S. Bhadauria, M.S. Gaur, Dig. J. Nanomater Bios. 4 (2009) 349-355.
[10] A.R. Shahverdi, S. Minaeian, H.R. Shahverdi, H. Jamalifar, A.A. Nohi, Process Biochem. 42 (2007) 919-923.
[11] M. Gajbhiye, J. Kesharwani, A. Ingle, A. Gade, M. Rai, Nanomed. Nanotechnol. 5 (2009) 382-386.
[12] K. Kalishwaralal, V. Deepak, S. Ramkumarpandian, H. Nellaiah, G. Sangiliyandi, Materials Letters. 62 (2008) 4411-4413.
[13] S. Li, Y.Shen, A. Xie, X. Yu, L. Qiu, L. Zhang, Q. Zhang, Green Chem. 9 (2007) 852-858.
[14] R. Sathyavathi, M. Bala Murali Krishna, D. Narayana Rao, J. Nanosci Nanotechno. 11 (2011) 2031-2035.
[15] J.Y. Song, B.S. Kim, Bioprocess Biosyst. Eng. 32 (2009) 79-84.
[16] S. Shiv Shankar, Akhilesh Rai, Absar Ahmad, Murali Sastry, J. Colloid Interface Sci. 275 (2004) 496-502.
[17] Alfredo R. Vilchis-Nestor, Victor Sanchez-Mendieta, Marco A. Camacho-Lopez, Rosa M. Gomez-Espinosa, Miguel A. Camacho-Lopez, Jesus A. Arenas-Alatorre, Materials Letters. 62 (2008) 3103-3105.
[18] K. Badri Narayanan, N. Sakthivel, Materials Letters. 62 (2008) 4588-4590.
[19] R.W. Raut, N.S. Kolekar, J.R. Lakkakula, V.D. Mendhulkar, S.B. Kashid, Nano-Micro Lett. 2 (2010) 106-113.
[20] P.K.S. Visen, B. Shukla, G.K. Patnaik, S.C. Tripathi, D.K. Kulshreshtha, R.C. Srimal, B.N. Dhawan, Drug Develop. Res. 1992; 26: 183-193.
[21] O.I. Oyewole, A.A. Owoseni, E.O. Faboro, J. Med. Plant Res. 4 (2010) 2004-2008.
[22] J.Y. Song, E.Y. Kwon, B.S. Kim, Bioproc. Biosyst. Eng. 33 (2010) 159-164.
[23] J. Kasthuri, K. Kathiravan, N. Rajendiran, J. Nanopart Res. 11 (2009) 1075-1085.