ENVIROMENT FRIENDLY (GREEN) METHOD FOR THE SYNTHESIS OF ZINC NANOPARTICLES BY USING CONOCARPUS ERECTUS LEAVES EXTRACT

Kashif Ahmed*, Hafiz Abdul Rehman, Azeem Arif Aziz, Shumaila Meraj and Niaz Ahmed

Department of Chemistry, N.E.D. University of Engineering & Technology, Karachi, Pakistan.

ABSTRACT

In the present work total reducing strength or phenolic compounds in leaves extracts of *Conocarpus erectus* and *Nerium indicum* were determined and then zinc nanoparticles were synthesized by using only methanol extract of *Conocarpus erectus* leaves as reducing agent because of its higher values of total phenolic compounds ($296 \pm 9 \mu g/g$) in comparison to *Nerium indicum* ($185 \pm 6 \mu g/g$). Characterization of the green synthesized Zn NPs was performed by SEM (Scanning Electron Microscope) and XRD (X-Ray Diffractometer) techniques. The size of Zn nanoparticles was estimated in the range of 10-70 nm. The usage of plant extract for the preparation of Zn nanoparticles makes the process cost effective, non-toxic and green method.

Keywords: Green Synthesis, Conocarpus erectus, Nerium indicum, Zn NPs

INTRODUCTION

Nanoparticles are those particulate materials which have at least one dimension of less than 100 nm (Vidya *et al.*, 2013). Almost in all human related areas, exploration and advancement in this particular field of Nanotechnology is rising fast all over the world. Because of unique characteristic features like magnetic, electrical, catalytic, and optical properties, metal nanoparticles are of great importance (Singhal *et al.*, 2011). There exist various methods for the synthesis of zinc nanoparticles like micelle, sol-gel process, hydrothermal method, chemical precipitation, and CVD (chemical vapour deposition) which may produce some toxic chemical substances adsorbed on the metal surface that may have opposing effects in health uses (Hudlikar *et al.*, 2012). In recent years, Biological (or green) approach using plants or plant extracts and microorganisms for the syntheses of metal nano particles has been advised as substitutes to hazardous (chemical) methods (Alagumuthu and Kirubha, 2012).

Phenolic compounds like tannins, flavonoids and phenolic acids are considered to be involved in redox activities so they are key performer to the reducing or antioxidant activity of medicinal plants, fruits or vegetables. The phenolic compounds because of their redox activities behave as hydrogen donators, reducing agents, singlet oxygen quenchers and also metal chelating agent (Rice-Evans *et al.*, 2004). In plant extracts there are numerous types of phenolic compounds. They are highly reactive compounds and get involved in redox reactions. The presence of total phenolic substances within the plant extract could be liable for metal ions reduction and creation of the respective metal's nanoparticles (Nasrollahzadeh and Sajadi, 2015).

Conocarpus erectus is a species of family Combretaceae. It is an evergreen tree and grows on coastal areas of hot regions of the world (Bailey, 1976). Nerium indicum is also an evergreen shrub or small tree of family Apocynaceae. It also grows everywhere in tropical regions (Vinayagam and Sudha, 2011). Though extract of both compounds have been reported rich in phenolic compounds but Conocarpus leaf extract was reported to have a large variety of these compounds.

The aim of present work was to synthesize zinc nanoparticles by using leaf extracts of plant (*Conocarpus erectus* or *Nerium indicum*) having higher values of total phenolic compounds because to the best of our knowledge through literature it was the first time to use plant leaf extract (*Conocarpus erectus* or *Nerium indicum*) for the green synthesis of zinc nanoparticles.

MATERIALS AND METHODS

All chemicals which were utilized throughout the experimental work were of laboratory grade from Merck (Germany) and Sigma-Aldrich (USA). Equipment were Analytical balance (Sartorius Germany), Scanning Electron Microscope (Hitachi S4160), X-Ray Diffractometer (Karaltay, DX-2700 MIN), Hot plate/ magnetic stirrer (MS-H-Pro+) vacuum filtration assembly (Thomas 4595D45), Thermostat/incubator (Seimens), Spectrophotometer (Tomos), grinder (West point)

KASHIF AHMED ET AL.

Preparation of extract of samples

Samples (*Conocarpus erectus* and *Nerium indicum*) were obtained from the Main Campus of NED University Karachi and they were dried in shade for one week and then they were grinded. 100 g of shade-dried leaves were grinded to form powder then it was added to 500 mL methanol, ethanol and distillated/deionized water in 1L flask and mixed vigorously. The preparation of plant extract was performed by using hot plate/magnetic stirrer at 50° C for 1 h. The acquired plant extract was filtered by vacuum filtration assembly.

Determination of total reducing strength or total phenolic compounds

Total reducing strength or total phenolic compounds in all plant extracts were determined as described by singleton *et al.* (1999) with the help of spectrophotometer. Briefly 0.5 mL of extract added with 10 % Folin-Ciocalteu's reagent (2.5 mL in equal volume of 7.5 % NaHCO₃). Blank was prepared by adding methanol (0.5 mL), 10 % Folin-Ciocalteu's reagent (It was dissolved in water and 7.5 % NaHCO₃ in equal volumes of 2.5 mL). The reaction mixtures were incubated at a temperature of 45° C for 45 minutes in an incubator/thermostat. The absorbance of solution was noted at 765 nm wavelength using spectrophotometer. Standard solution of Gallic acid was used as standard.

Green synthesis of zinc nanoparticles

The zinc nanoparticles were prepared in a 250 mL conical flask in which 50 mL cent molar solution of zinc sulphate was mixed with 10 mL of the plant extract (100 g of dried leaves powder was added to 500 mL methanol, ethanol and deionized/distillated water in 1L flask) along with vigorous shaking on a hot plate till the appearance of yellowish colour.

Characterization

The external appearance and size of produced Zn NPs were characterized by using SEM (Scanning Electron Microscope) and X-Ray Diffractometer (XRD).

RESULTS AND DISCUSSIONS

Total phenolic compounds

Leaves extracts (water, ethanol and methanol) of *Conocarpus erectus* and *Nerium indicum* were investigated for total phenolic compounds and results are presented in table 1. It can be seen that the total phenolic compounds were found higher in methanol extracts (*Conocarpus erectus*, $296 \pm 9 \mu g/g$; *Nerium indicum*, $185 \pm 6 \mu g/g$) lower in water extract (*Conocarpus erectus*, $59 \pm 8 \mu g/g$; *Nerium indicum*, $27 \pm 2 \mu g/g$). As methanol leaf extract of *Conocarpus erectus* contained higher values of phenolics so in the present study it was used for the green synthesis of Zn NPs.

El-Sayed S. Abdel-Hameed *et al.* (2012) have reported that the total phenolic compounds were higher in ethyl acetate fraction of fruits and flowers (303.45 and 301.15 mg/g GAE, respectively) whereas they were lower (186.21 and 181.61 mg/g GAE) in leaves and stem. On the contrary, our results shows that the methanol extracts of leaves contain higher values which might be due to environmental effect and choice of solvent (Ahmed *et al.*, 2015). Vinayagam and Sudha (2011) have reported that the total reducing strength (total phenolic compounds) was found to be higher in *Nerium indicum* flower extract (449 mg/100g), as compared to leaves 227mg/100g. Our selection of leaves extract as raw material for the green preparation of zinc nanoparticles is only due to the abundance and availability of leaves throughout the year.

Table 1. Total phenolic compounds in leaves extract of *Conocarpus erectus* and *Nerium indicum*.

Plant	Total Phenolic Compounds (μg/g)		
	Water	Ethanol	Methanol
Conocarpus erectus	59 ± 8	158 ± 5	296 ± 9
Nerium indicum	27 ± 2	149 ± 5	185 ± 6

Green synthesis of Zinc nanoparticles

In the present work our main focus was on the synthesis of Zn NPs using reducing properties of total phenolic compounds inside the plant leaves according to the scheme/mechanism (Fig. 1). Of course, the effect of other phytochemicals inside the plant is also possible (Nasrollahzadeh and Sajadi, 2015).

Fig. 1. Scheme / Mechanism for the formation of Zn NPs by phenolic compounds.

The SEM analysis is helpful in determining the structure of the Nanoparticles (or reaction products) that were fashioned. The SEM image (Fig. 2) disclosed a number of discrete zinc nanoparticles as well as larger groups. The SEM image of Zn NPs also revealed that quite spherical shaped nanoparticles were fashioned with the diameter range 10-70 nm whereas grouped particles were fashioned above the range 100 nm. Similar types of images for zinc nanoparticles were also reported by Rataboul *et al.* (2002) and Vidya *et al.* (2013).

The powdered sample was used for XRD Analysis in order to confirm the presence of Zn NPs. Relative intensities and Peak positions for green synthesized Zn NPs (Fig. 3) were matched to values from JCPDS (Joint Committee on Powder Diffraction Standards) card for Zn (JCPDS PDF #00-004-0831). The careful observations of peaks in the graph revealed that they are fairly agreed with the literature report (JCPDS PDF #00-004-0831).

CONCLUSION

It was concluded that methanol extract of *Conocarpus erectus* leaves contained higher value of total phenolic compounds (296 \pm 9 μ g/g) than *Nerium indicum* (185 \pm 6 μ g/g). It is also concluded that extract of *Conocarpus erectus* leaves can be utilized as a good reductant for the non-toxic or green synthesis of metal (Zn) nanoparticles.

344 KASHIF AHMED *ET AL.*,

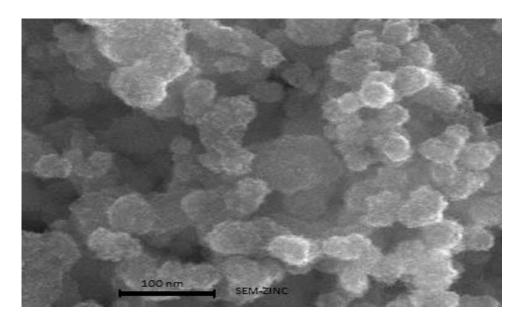


Fig. 2. Scanning Electron Microscope Image of Green synthesized Zn NPs by Conocarpus erectus.

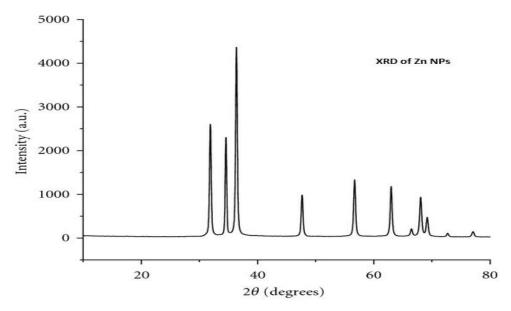


Fig. 3. XRD of Green synthesized Zn NPs by leaf extract of Conocarpus erectus.

REFERENCES

Ahmed K., S. Munawar, T. Mahmood and I. Mahmood (2015). Biochemical Analysis of Some Species of Seaweeds from Karachi Coastal Area. *FUUAST J. Biol.*, 5(1): 43-45.

Alagumuthu G. and R. Kirubha (2012). Green synthesis of silver nanoparticles using *Cissus quadrangularis* plant extract and their antibacterial activity University. *International Journal of Nanomaterials and Biostructures*, 2(3): 30-33

Bailey, L.H. (1976). *Hortus Third: A Concise Dictionary of Plants Cultivated in the United States and Canada*. New York, MacMillan Collier MacMillan, p.306.

- El-Sayed S. Abdel-Hameed, A. S. Bazaid, M. M. Shohayeb, M. M. Sayed and E. A. El-Wakil (2012). Phytochemical Studies and Evaluation of Antioxidant, Anticancer and Antimicrobial Properties of Conocarpus erectus L. Growing in Taif, Saudi Arabia. *European Journal of Medicinal Plants* 2(2): 93-112.
- Hudlikar M., S. Joglekar, M. Dhaygude and K. Kodam (2012) Latex-mediated synthesis of ZnS nanoparticles. *Journal of Nanoparticle Research*. 14: 865-869.
- Nasrollahzadeh M. and S. M. Sajadi (2015). Green synthesis of copper nanoparticles using Ginkgo biloba L. leaf extract and their catalytic activity for the Huisgen [3 + 2] cycloaddition of azides and alkynes at room temperature. *J. Colloid Interface Sci.*, 457: 141-147
- Rataboul F., C. Nayral, M. J. Casanove, A. Maisonnat, B. Chaudret (2002). Synthesis and characterization of monodisperse zinc and zinc oxide nanoparticles from the organometallic precursor [Zn (C 6 H 11) 2]. *J. organometallic Chem.*, 1(643): 307-312.
- Rice-Evans, C. (2004). Flavonoids and Isoflavones: absorption, metabolism and bioactivity. *Free Rad. Biol.*, 36: 827-828.
- Singhal G., R. Bhavesh, K. Kasariya, A. R. Sharma and R. P. Singh (2011). Biosynthesis of silver nanoparticles using *Ocimum sanctum* (Tulsi) leaf extract and screening its antimicrobial activity. *Journal of Nanoparticle Research*, 13: 2981–2988.
- Singleton, V.L., R. Orthofer, R. M. Lamuela-raventos (1999). Analysis of total phenols and other oxidation substrates and antioxidants by means of Folin-Ciocalteu reagent. *Methods Enzymol*. 299: 152-178.
- Vidya, C., S. Hirematha, M. N. Chandraprabhab, M. A. L. Antonyraja, I. V. Gopala, A. Jaina and K. Bansal (2013). Green synthesis of ZnO nanoparticles by *Calotropis gigantea*. Proc. of Nat. Conf. on Women in Sci. & Eng. (NCWSE 2013), SDMCET Dharwad. *Int. J. C. Eng. Technol.*, 118-123.
- Vinayagam A. and P. N. Sudha (2011) Antioxidant activity of methanolic extracts of leaves and flowers of *Nerium indicum IJPSR*, 2(6): 1548-1553.

(Accepted for publication May 2016)