



Biosynthesis of Silver Nanoparticles (Tea Leaves') Reducing Method and their Optical Properties

Rajesh Kumar Meena and Neelu Chouhan*

Department of Pure and Applied Chemistry, University of Kota, Kota- 324005 Rajasthan, India
niloochauhan@hotmail.com

Available online at: www.isca.in, www.isca.me

Received 15th September 2016, revised 2nd October 2016, accepted 25th October 2016

Abstract

In this study, we report the synthesis of silver nanoparticles (AgNPs) by using a simple green synthesis method. 30 nm sized AgNPs prepared by using tea extract and Ag salt at normal room temperature. The AgNPs synthesized via this one-pot greener approach, can be used as a promising material in different fields such as cosmetics, foods, medicine and pollutant degradation, etc. This environment benign did not use of any extra capping or reducing agent or template. As synthesized nanoparticles were evidenced by advance analysis techniques such as: UV-Vis spectroscopy, transmission electron microscopy (TEM), powder X-ray diffraction (PXRD) and fourier transform infrared (FTIR) spectroscopy, etc. X-ray analysis exhibits that the pure silver nanoparticles were grown in a single phase (face-centered cubic structure). Particle size was confirmed by the TEM images of the well dispersed sample. This method can also be facilitated for other metals such as gold (Au), copper (Cu), palladium (Pd) and platinum (Pt).

Keywords: Tea leaves, Capping agent, Bioreduction, AgNPs.

Introduction

Nanosciences is an emerging field of research nowadays because of its wide range application in the field of electronics¹⁻³ fuel cells, batteries, agriculture, food industry, and medical sciences⁴. Noble metal nanoparticles *e.g.*, Au, Ag, Pd and Pt are prepared through different techniques and their characterizations expose interesting properties make them greatly significant for research. The nanoparticles synthesized through chemical method cannot be considered as an environment benign because of their hazardous effect on human health, but in recent times the fabrication of NPs by green synthesis method has pulled the interest amongst researchers because of its ecofriendly character. The synthesis of noble metal NPs using greener routes is a major agenda of nowadays scientific research⁵. Silver nanoparticles are also extensively studied owing to their unique properties such as excellent electrical and thermal conductivity and non-linear optical behaviour and catalytic activity, chemical stability antifungal and antimicrobial effects⁶. Indeed many reports are there on the synthesis of metal NPs using a variety of methods like microorganisms⁷ and plant extracts.

Greener synthetic approaches for the synthesis of metal NPs have attracted considerable interest. It reduces the utilization and generation of hazardous chemicals that can be produced by different type of physical and chemical method, which are not good for living being and environment⁸. Moreover, the green production of NPs has a numeral benefits over pure chemical methods because it is a comparatively cost effective, healthy and easy to handle method. Therefore, green synthetic methodology has attracted enormous attention of researcher's to

synthesize a range of metal NPs⁹ due to their fascinating, and outstanding properties with respect to their bulk counterparts^{10,11}. Among the various practicing green methods, biogenesis is a promising method for the synthesis of metal NPs, in which the extract of different part of the plant has been used for reduction of metal ions¹²⁻¹⁴. Every part of the plants such as leaf, stem, flower, bark, leaves' and skin of the fruits can be employed for the production of metal nano particles. The excess of reports have been documented recently stating the wide range of nanoparticles production using plant extracts such as Ag,¹⁵ Au,¹⁶ Fe,¹⁷ Pd,¹⁸ ZnO/Au and ZnO/Ag,¹⁹ quantum dots CdS,²⁰ etc. Here, we have synthesized the silver nanoparticles via biogenesis by utilising tea leaves'.

Here, we have introduced the convenient and simple route to synthesize the silver nanoparticles using biogenesis. The applications of AgNPs include in the numerous areas such as electronic, optical, catalytic, chemical, photo-electrochemical, magnetic, antibacterial, and biological labelling. It also has been proved an efficient antimicrobial, antifungal, antioxidant agent in medical field. Due to their non-toxic action towards animal cells and highly toxic activity towards bacteria including microorganisms like *Pseudomonas Aeruginosa*, *E-coli*, *Staphylococcus Aureus* etc. Ag NPs are referred to be the protected and effective bactericidal metal²¹⁻²³.

Within this report we mainly focus on the Tea aqueous leaves' extract as they are the most significant and valuable piece of this plant. The tea extract contains few important phyto-chemicals *i.e.* nicotinic acid, proteins, lipids, ploy-phenols, saponins and alkaloids²⁴. These were used to synthesize AgNPs via a

convenient and highly reproducible method. The most important benefit of this process is, necessity of any external capping and reducing agent can also be eliminated, synthesis can occur at room temperature and aqueous medium synthesis.

Materials and Methods

Required materials: Clean tea leaves were collected from tea garden of Agriculture University Kota. Silver nitrate (AgNO_3) was purchased from Merck, Germany. All of the chemicals used in the study are of analytical grade and used without any purification. Deionised water was used throughout in the experiment to prepare all the solutions.

Preparation of Dried Biomass: 2gm of tea leaves were collected and transferred to a beaker containing 25 ml of deionised water. The combination was thoroughly agitated for the complete night via a magnetic stirrer. The extract was then filtered to achieve the deep pink coloured solution. The liquor was centrifuged and filtered one more time to remove impurities. This extract was further filtered and stored at 4°C until the use for current study.

Synthesis of nanoparticles: For green synthesis of silver nanoparticles, 2.0ml aqueous tea leaves' extract was taken for the reaction. Freshly prepared 25 mL of 10^{-3} M silver nitrate solution was mixed drop by drop into the plant extract. The reaction mixture filtered was incubated in dark and at ambient temperature till the colour of the solution transformed from colourless to light green. Afterwards the AgNPs were dried at 90°C .

Characterization of nanoparticles: The synthesised nanoparticles were carefully characterized by means of advance analytical techniques. The absorption spectra were recorded using UV-Vis spectroscopy (Schimadzu UV- 1600 model 2010) over a range of wavelength i.e. 200-800 nm, where water is used as a reference. The surface morphology of the AgNPs was examined using a JEOL-2010F TEM operating with electron beam of energy of 200 kV. FTIR (UV 3000+ Lab India, 2011) was examined to achieve broad spectrum of nanoparticles over a narrow series. This process gives us information regarding phytochemicals that have enclosed the particles through synthesis method. The XRD investigations were performed using Rigaku (Ultima IV) diffractometer with Cu-K α radiation at 25°C to determine the phase purity and the crystal structure of the NPs.

Results and Discussion

Synthesis and characterization of silver nanoparticles: Aqueous tea leaves' extract act as a reducing agent as well as capping agent during the silver nanoparticle production. Which reduces silver ions to nano silver hence, the colour will be change from light pink to green, as shown in Figure-1. The appearance of the aqueous silver nanoparticles was light green

in colour due to excitation of surface plasmon vibration in silver nanoparticles.²⁵ UV-Vis spectroscopy could be used to examine size and shape controlled by nanoparticles in aqueous suspensions. The peak attributed to the surface plasmon resonance is observed at 460 nm. The broad UV-Vis- absorption spectrum of the sample was obtained between the wavelength range in 200nm-800nm. Figures-2 and 3, shows the corresponding UV-Vis spectrum recorded for pure Tea extract and mixture of Tea with AgNO_3 after 24 hours aging that gives rise to the two absorption bands: first around 280 nm ($\pi-\pi^*$ transition) and second the characteristic first excitonic UV peak between 340-580nm (d-d transition) with a well defined peak at 460 nm, as shown in figure Figure-2 and 3. The first excitonic UV peak the nanoparticles was experimentally obtained due to the surface plasmon resonance (SPR) exhibited by silver nanoparticles. Which will caused when AgNP solution exposed to electromagnetic radiation and resulted oscillation gives a typical peak value.²⁶

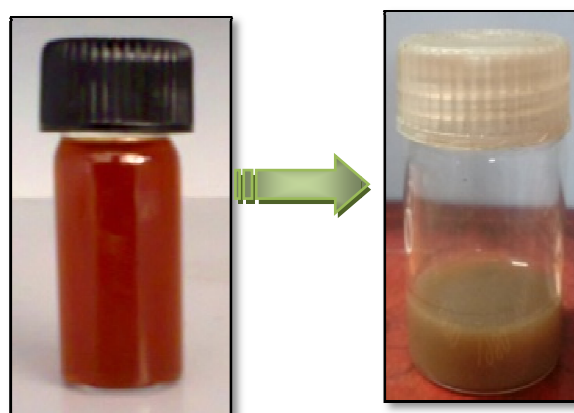


Figure-1
(a) Aqueous Tea leaves' extract (b) AgNPs after 24h incubation

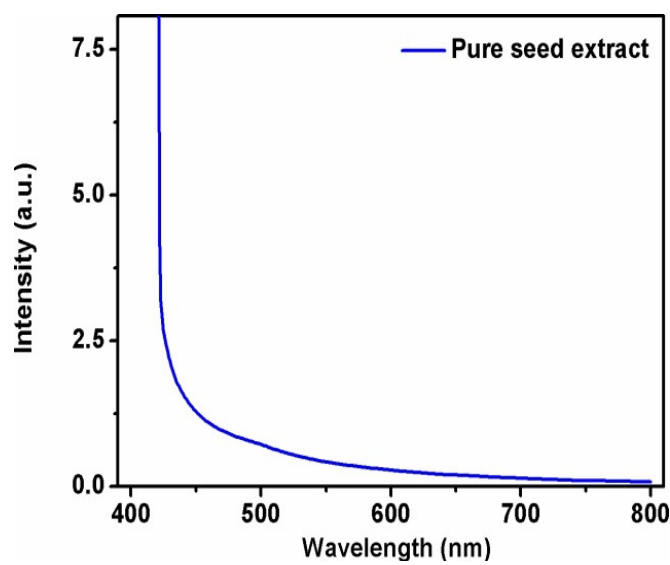


Figure-2
Uv-Vis spectra of pure Tea leaves extract

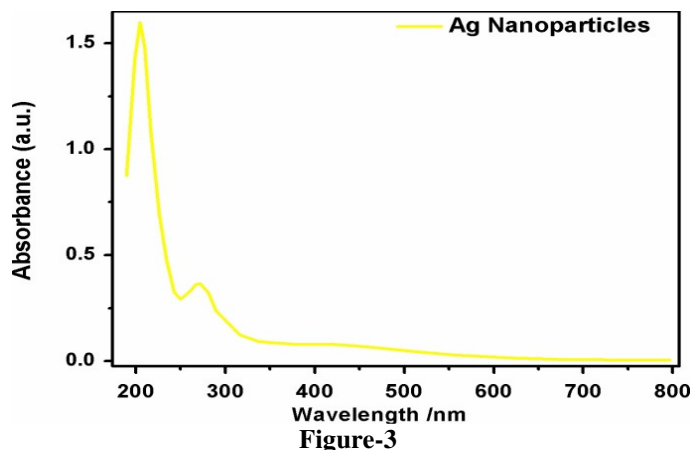


Figure-3
Silver nanoparticles produced by extract of Tea leaves

TEM image of the NPs corresponds to the topography of the AgNPs (Figure-4), which exhibits the particle size in between 20-50 nm and recommended the presence of approximately spherical silver nanoparticles in the solution. The Transmission Electron Micrograph image indicates the dispersity and morphology of the silver nanoparticles. These particles are rounded in shape and distributed in smaller and bigger size zones. These silver nanoparticles may be due to the capping of phytochemicals such as polyphenols or due to the formation of the cluster.

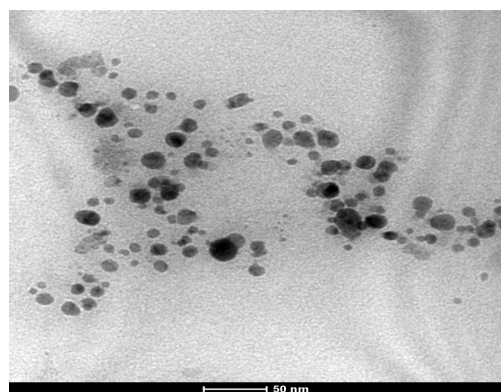
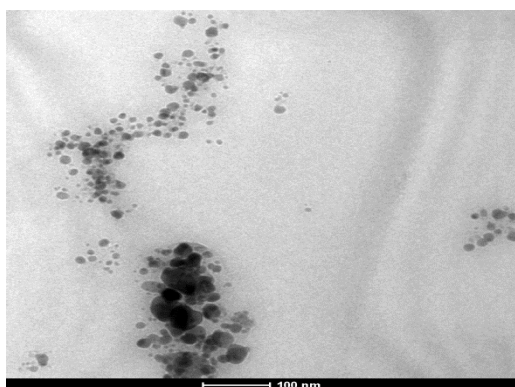


Figure-4

TEM images of AgNPs produced by Tea leaves' extract

The XRD patterns of the powdered silver nanoparticles taken using $\text{CuK}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$) gives major peaks at 38.09° , 44.12° and 64.37° that can be indexed to the (111), (200) and (220) planes of a cubic crystal system ($a = 4.0686 \text{ \AA}$) and corresponding well with the standard JCPDS file No.04-0783 of pure silver metal. Broadness in patterns reflected the small particle size of the AgNPs and spin plasmonic resonance phenomena (Figure-5).

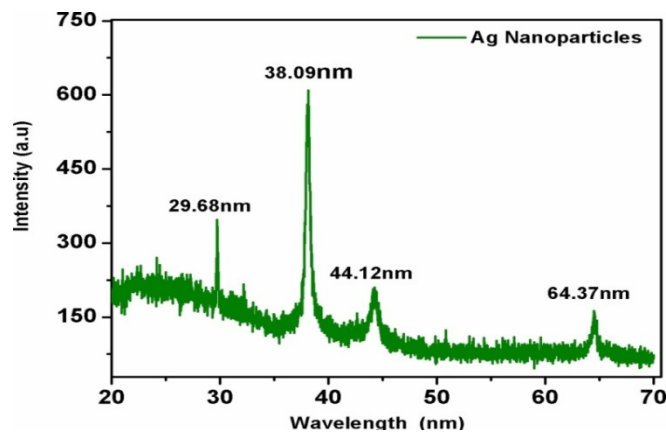


Figure-5

XRD plot of synthesized AgNPs via extract of tea leaves'

The Debye-Scherrer formula ($D_p = K\lambda / \beta \cos\theta$ with $K = 0.89$, $\lambda =$ wavelength of the radiation, $\beta =$ full width at half maximum, $\theta =$ incident angle of radiation beam, $D_p =$ particle size) was also used for calculation of the particle size i.e. $\sim 20\text{-}50 \text{ nm}$. FTIR investigation also gives a series of peaks for the AgNPs sample belong to the sequence of the phytochemicals present in the sample that acts as a reducing agent (Figure-6). FTIR investigations on the biosynthesized AgNPs was passed out in the range of $4000\text{-}500 \text{ cm}^{-1}$ wave number to make out the most likely interactions between the Ag ions and phytochemicals present in tea leaves' extract that used to stabilize the AgNPs. Figure-6 definite the existence of plant peptides visible due to the bending formed by amide bonds. AgNPs exhibits prominent peaks at 3379.76 , 1696.45 and 1648.73 cm^{-1} , representing the contribution of N-H stretching vibrations, N-H bending vibrations and C=O stretching vibrations that refers to the Tea-AgNPs aggregates. The C-N and C-O-C stretching vibration suggested the existence of a lot of phytochemicals on the surface of the NPs.

Green production method of AgNPs is an additional way to chemical and physical synthesis methods and it is used to reduce metal ion of silver to nano silver. Green Synthesis of the silver nanoparticles has been earlier reported using plant's leaves' extracts as well as different kind of plant body parts. The phytochemicals present in the leaves' extract, which are responsible for reducing the silver salts and producing stable silver nanoparticles without using any capping agent²⁷. Furthermore, the antimicrobial, antifungal and antioxidant activities of the nanoparticles are also improved by the existence of the phytochemicals.

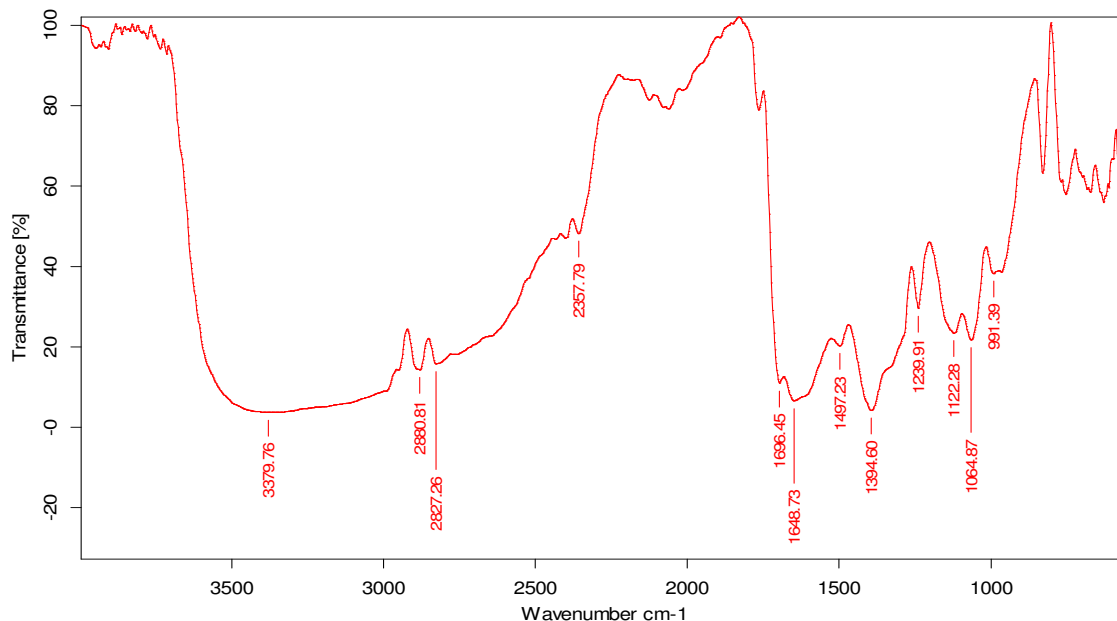


Figure-6
FTIR spectra of AgNPs synthesized by plant tea leaves' extract

Conclusion

In this current study we have planned and an ecofriendly synthesis of AgNPs using tea leaves' extracts via biological method, in which tea leaves' extract act as a reducing agent. In green synthesis method, tea leaves' extract are responsible for reduction of silver metal to nano size. The synthesized silver nanoparticles were subjected to advance analysis technique such as a TEM, XRD, Uv-Vis spectroscopy and FTIR in order to characterize them.

The formation of nanoparticles as well as size was also confirmed by UV-Vis spectroscopy; while crystalline properties of the nanoparticles and average particle size is investigated by XRD analysis and the TEM image show visibly the formation of nanoparticles. To the best of our information this is the unique information of the explanation that lead the path to produce the tea mediated AgNPs. These research works are further extended to investigate the synthesis and optical properties of AgNPs formed by the other plant leaves' extracts.

Acknowledgment

The authors are sincerely thankful to the Department of Science and Technology and their sub wing Science and Engineering Research Board of the, India (SB/S1/PC-31/2012) for their financial support. The instrumental supports for TEM measurements from MRC, MNIT Jaipur, are acknowledged. RKM also thanks Pragati Fageria from Department of Chemistry, University of Rajasthan, Jaipur for assistance with powder XRD measurements.

References

1. Alqudami A. and Annapoorni S. (2007). Fluorescence from metallic silver and iron nanoparticles prepared by exploding wire technique. *Plasmonics.*, 2(1), 5-13.
2. Korbekandi H. and Iravani S. (2012). Silver Nanoparticles. *Nanotechnology and Nanomaterials.*, 3, 5-16.
3. Brigger I., Dubernet C. and Couvreur P. (2002). Nanoparticles in cancer therapy and diagnosis. *Adv Drug Deliv Rev.*, 64, 24-36.
4. Basarkar A. and Singh J. Poly. (2009). Poly (lactide-co-glycolide)-polymethacrylate nanoparticles for intramuscular delivery of plasmid encoding interleukin-10 to prevent autoimmune diabetes in mice. *Pharm Res.*, 26, 72-81.
5. Roy K., Mao H.Q., Huang S.K. and Leong K.W. (1991). Oral gene delivery with chitosan-DNA nanoparticles generates immunologic protection in a murine model of peanut allergy. *Nat. Med.*, 5, 387-391.
6. Wilson D.S., Dalmasso G., Wang L., Sitaraman S.V., Merlin D. and Murthy N. (2010). Orally delivered thioketal nanoparticles loaded with TNF- α -siRNA target inflammation and inhibit gene expression in the intestines. *Nat. Mater.*, 9, 923-928.
7. Mano Priya M., Karunai Selvia B. and John Paul J.A. (2011). Green Synthesis of Silver Nanoparticles from the Leaf Extracts of Euphorbia Hirta and Nerium Indicum. *Digest .J. Nanomat. Biostruct.*, 6(2), 869-877.

8. Li S., Shen Y., Xie A., Yu X., Qui L., Zhang L. and Zhang Q. (2007). Green synthesis of silver nanoparticles using *Capsicum annuum* L. extract. *Green Chem.*, 9, 852.
9. Christopher L., Kitchens, Douglas E., Hirt, Scott M., Husson, Alexey A. and Vertegel (2010). Synthesis, Stabilization, and Characterization of Metal Nanoparticles. The Graduate School of Clemson University.
10. Salam H.A., Rajiv P., Kamaraj M., Jagadeeswaran P., Gunalan S. and Sivaraj R. (2012). Plants: Green Route for Nanoparticle Synthesis. *Inter.Res.J.Bio. Sci.*, 1(5), 85-90.
11. Geoprincy G., Vidhyasrr B.N., Poonguzhali U., Gandhi N. and Renganathan S. (2013). A review on green synthesis of silver nano particles. *Asian.J.Pharma.Clini.res.*, 6(1), 8-12.
12. Akl M. Awwad and Nida M. (2012). Green Synthesis of Silver Nanoparticles by Mulberry Leaves Extract. *Nanoscience and Nanotechnology*, 2(4), 125-128.
13. Umesh B.J. and Vishwas A.B. (2013). Green synthesis of silver nanoparticles using *Artocarpus heterophyllus* Lam. Leaves' extract and its antibacterial activity. *Industrial Crops and Products*, 46, 132-137.
14. Nethra Devi C., Sivakumar P. and Renganathan S. (2012). Green synthesis of silver nanoparticles using *Datura metel* flower extract and evaluation of their antimicrobial activity. *Inter.J. Nanomat.Biostruct*, 2(2), 16-21.
15. Song J.Y. and Kim B.S. (2009). Rapid biological synthesis of silver nanoparticles using plant leaf extracts. *Bioprocess Biosyst Eng.*, 32, 79-84.
16. Huang J., Li Q., Sun D., Lu Y., Su Y., Yang X., Wang H., Wang Y., Shao W., He N., Hong J. and Chen C. (2007). Biosynthesis of silver and gold nanoparticles by using novel sun-dried *Cinnamomum camphora* leaves. *Nanotechnol.*, 18, 105-104.
17. Pattanayak M. and Nayak P.L. (2013). Green Synthesis and Characterization of Zero Valent Iron Nanoparticles from the Leaf Extract of *Azadirachta indica* (*Neem*). *World Journal of Nano Science & Technology*, 2(1), 6-9.
18. Nadagouda M.N. and Varma R.S. (2008). Green synthesis of silver and palladium nanoparticles at room temperature using coffee and tea extract. *Green Chem.*, 10, 859-862.
19. Fageria P., Gangopadhyay S. and Pande S. (2014). Synthesis of ZnO/Au and ZnO/Ag nanoparticles and their photocatalytic application using UV and visible light. *RSC Adv.*, 4, 24962-24972.
20. Ahmad A., Mukherjee P., Mandal D., Senapati S., Khan M.I., Kumar R. and Sastry M. (2002). Enzyme Mediated Extracellular Synthesis of CdS Nanoparticles by the Fungus, *Fusarium oxysporum*. *J.Am. Chem. Soc.*, 124, 12108-12109.
21. Kalimuthu K., Babu RS., Venkataraman D., Bilal M. and Gurunathan S. (2008). Biosynthesis of silver nanocrystals by *Bacillus licheniformis*. *Colloids Surf B.*, 65(1), 150-153.
22. Wijnhoven S.W.P., Peijnenburg W.J.G.M., Herberts C.A., Hagens W.I., Oomen A.G. and Heugens E.H.W et al. (2009). Nano-silver: a review of available data and knowledge gaps in human and environmental risk assessment. *Nano Toxicology*, 3, 109-138.
23. Klueh U., Wagner V., Kelly S., Johnson A. and Bryers JD. (2000). Efficacy of silver-coated fabric to prevent bacterial colonization and subsequent device-based biofilm formation. *J. Biomed. Mater. Res.*, 53(6), 621-631.
24. Jani R., Udipi S.A. and Ghugre P.S. (2009). Mineral content of complementary foods. *Indian J Pediatr*, 76, 37-44.
25. Mulvaney P. (1996). Surface plasmon spectroscopy of nanosized metal particles. *Langmuir*, 12, 788-800.
26. Abu Bakar N.H.H, Ismail J. and Abu Bakar M. (2007). Synthesis and Characterization of Silver Nanoparticles in Natural Rubber. *Mater. Chem. Phys.*, 104, 276-283.
27. Meena R.K. and Chouhan N. (2015). Biosynthesis of Silver Nanoparticles from Plant (Fenugreek Leaves') Reducing Method and their Optical Properties. *Research Journal of Recent Sciences*, 4(IVC-2015), 1-5.