Original Research Paper
Volume-8 | Issue-11 | November-2018 | PRINT ISSN No 2249-555X
Chemistry

ECO-FRIENDLY SYNTHESIS OF SILVER NANOPARTICLES BY GREEN ROUTE, REACTION STUDY AND CHARACTERIZATION

Hema S. Koli	Department of Chemistry , Abeda Inamdar College Camp , Pune Affiliated to Savitribai Phule Pune University
Vaidehi Pathania	Department of Chemistry , Nowrosjee Wadia College, Pune
B.B. Bahule*	Department of Chemistry , Nowrosjee Wadia College, Pune *Corresponding Author
R.P. Yadav	Department of Chemistry , Nowrosjee Wadia College, Pune

ABSTRACT Silver nanoparticles can be synthesized by using biological, chemical, physical methods and also by employing of different kinds of reducing agents. However the physical and chemical methods employed are expensive and the reagents used are harmful. The present method deals with biological green synthesis of silver nanoparticles which are then studied for their reaction time and characterization. The silver nitrate solution is reduced using concentrate of *kinnow* variety of hybrid mandarin citrus plant fruit readily available in markets of Maharashtra, India. The natural fruit extract is added to the solution of Silver Nitrate which yields silver nanoparticles. The silver nanoparticles (AgNPs) are characterized by UV Spectrometer and Scanning Electron Microscope (SEM) technique. This work proves the efficacy of biomaterials for the synthesis of nanoparticles obeying the rules of green chemistry.

KEYWORDS : Silver Nanoparticles, Green synthesis, Kinnow fruit, SEM

INTRODUCTION

Nanoparticles are building blocks of practical nanotechnology and are chemically and physically manipulated for specific applications. They are prepared and used at a very small scale. Nanoparticles are developed to exhibit novel characteristics as compared to the same material without nano scale features such as chemical reactivity, increased strength and conductivity. These tiny liltle chunks of materials are so small that they can move around and do things in ways that we don't fully understand. For example really tiny particles could potentially be absorbed through skin. In the environment nanoparticles might be absorbed into insects or fish that are at the bottom of the food chain for larger animals, including human beings [1].

Two key factors ,which are important in deciding the properties of nanomaterials are quantum effects and structures . The tiny structures mean they have a greater relative surface area than other materials and this can alter or improve properties such as strength and electrical characteristics or reactivity. The quantum effect can affect the electrical, magnetic or optical performance of nanoparticles [2].

Nanoparticles have been known to impart some extra properties to day to day products. Silver nanoparticles have antimicrobial activity that can be utilized for medical aspects such as wound dressing, sterilizing, chemotherapy, antibiotics and even household applications [3].

AgNPs play an important role in nano science, nano medicine, organic synthesis as a green catalyst. Although several noble metals have been used for various purposes AgNPs have been used in cancer diagnosis and therapy.In order to fulfill the requirements of AgNPs, various methods have been adopted for synthesis. Generally conventional physical and chemical methods seem to be very expensive and hazardous. Interestingly biologically prepared AgNPs show high yield, solubility and high stability [4].

Among several methods for AgNPs synthesis biological method seems to be simple rapid non-toxic dependable reproducible and green that can produce well defined size and morphology. Silver nanoparticles have also been demonstrated to exhibit antimicrobial properties both against bacteria and viruses with close attachment of the nanoparticles themselves with the microbial cells [5].

In vitro study of the AgNPs-based dressing, Acticoat Flex 3 applied to a 3D fibroblast cell culture and to a real partial thickness burn patient showed that AgNPs greatly reduce mitochondrial activity and cellular staining techniques [6] revealed nuclear integrity with no signs of cell death.

The reduction of 4-nitrophenol (4-NP) to 4-aminophenol (4-AP) efficiently carried out in the presence of Breyniarhamnoides-AgNPs and NaBH4 and found to be depend upon the nanoparticle size or the stem extract concentrations [7].

Conductive Applications: Silver nanoparticles are used in conductive inks and integrated into composites to enhance thermal and electrical conductivity [8].

Optical Applications: Silver nanoparticles are used to efficiently harvest light and for enhanced optical spectroscopies including metal-enhanced fluorescence (MEF) and surface-enhanced Raman scattering (SERS) [9,10].

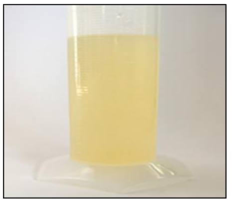
SYNTHESIS OF SILVER NANOPARTICLES

Preparation of solution of silver nitrate

Aqueous solution of 10,000 ppm of $AgNO_3$ is prepared by dissolving 1 g of silver nitrate in 100 ml distilled water. Simillarally 1000 ppm of $AgNO_3$ is prepared by dissolving 1 g of silver nitrate in 100 ml distilled water.

Preparation of extracts of kinnow

Fresh kinnow mandarin hybrid fruits were purchased from local fruit market. The juice was squeezed, sieved and stored as an extract for the synthesis of silver nanoparticles.



Mixing of the above two solutions

Solution 1 : 9 ml of 10,000 ppm $AgNO_3$ is taken in a 50 ml beaker. 1ml of kinnow extract is added to the beaker.

Solution 2 : 9 ml of 1000ppm $AgNO_3$ is taken in a 50 ml beaker. 1ml of kinnow extract is added to the beaker.

Solution 3 : 9 ml of 1000ppm $AgNO_3$ is taken in a 50 ml beaker.

1ml of kinnow extract (5 ml diluted to 50 ml with distilled water) is added to the beaker.

Reaction Study and Observations

Colour Change : After 15 minutes of mixing the solutions in the ratio 9:1

(Aqueous AgNO3: kinnow extract)

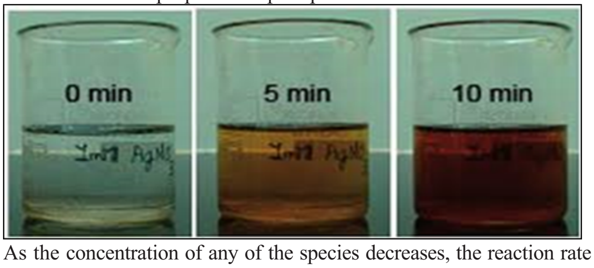
Solution 1 : Dark purple-black precipitation is observed.
Solution 2 : Brownish colored precipitation is observed.
Solution 3 : Light yellow colored precipitation is observed.

After 1 hour of mixing the solutions in the ratio 9:1 (Aqueous AgNO3: kinnow extract)

Solution 1 : Dark purple-black precipitation is observed.
Solution 2 : Dark purple-black precipitation is observed
Solution 3 : Yellow colored precipitation is observed.

After 1 day of mixing the solutions in the ratio 9:1 (Aqueous AgNO3: kinnow extract)

Solution 1 : Dark purple-black precipitation is observed.
Solution 2 : Dark purple-black precipitation is observed
Solution 3 : Dark purple-black precipitation is observed.



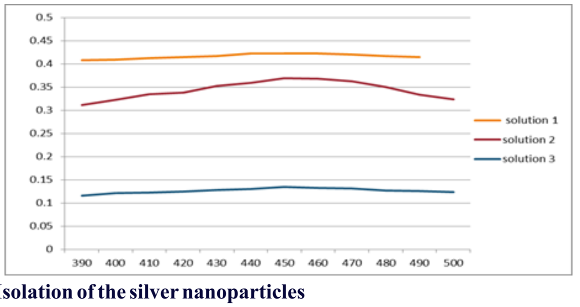
As the concentration of any of the species decreases, the reaction rate also decreases. Concentration of Solution 1 is maximum and thus it reached the state of equilibrium earliest compared to other two solutions.

In solution 2 concentration (1000ppm) is lower than that of concentration of solution1 (10,000ppm), thus it showed a slow reaction and have taken 30min to show characteristic colour of silver nanoparticles.

In solution 3 concentration of AgNO3 was same as that of solution 2 but the concentration of kinnow extract is lowered. As in previous solutions we have used non diluted extracts, but in this solution we have diluted kinnow extract. (5ml diluted to 50ml with distilled water). It showed the characteristic colour of AgNPs after a period of approximately 24 hours.

Comparative UV-Visible spectra :
It is observed that all the three solutions shows value of maximum wavelength at 450 nm but the absorbance values for solution 1 is highest followed by solution 2 and solution 3 has the least absorbance values measured after 30 minutes.

It shows that the particle size formed in each solution is same as the maximum wavelength is similar in all three cases. But the absorption value trend is goes on decreasing with decrease in concentration. It means that the formation of silver nanoparticle is directly proportional to the concentration.



Isolation of the silver nanoparticles
The solution containing the signatory colour of AgNPs were then transferred on to a Petri dish by pouring and left in the oven for drying at 24hr 250°C. Decomposition of organic matter and evaporation of moisture and impurities results in completely dried black shiny AgNPs .

CHARACTERIZATION

Determination test for presence of Silver Metal:
The presence of silver and its quantitative analysis is done by titration method. Ag0 is converted to Ag+1 and then is estimated by KSCN Process.

Disintegration of sample:

a. Weigh accurately 0.034g of isolated sample of AgNPs.
b. Add 5 ml HNO3 to it and disintegrate the sample by heating. Cover it with inverted funnel.
c. Heat till complete sample get dissolved in acid. If required add more acid to the solution slowly.
d. Add little water and again heat it.
e. Cool the sample and dilute it up to the mark in a volumetric flask of 100 ml.

$$2Ag^0 + 2HNO_3 \longrightarrow 2AgNO_3 + H_2$$

Preparation of ferric indicator:
A saturated solution of ferric ammonium sulphate is made in distilled water. To it 2-3 drops of 6N acetic acid is added.

This indicator is kept in ice cold condition.

Titration with KSCN

a. Take 10 ml of disintegrated sample in a conical flask.
b. To it add freshly prepared cold ferric indicator.
c. Titrate this solution with potassium thiocyanate (KSCN)
d. The end point is observed as colour change from brown to bluish-green colour.

Relation to be used
1 ml 1N KSCN = 0.10788g Ag

Observation table

	I	II	III	C.B.R.
Initial	0.0ml	0.0ml	0.0ml	
Final	2.2ml	2.3ml	2.2ml	2.2ml
Difference	2.2ml	2.3ml	2.2ml	

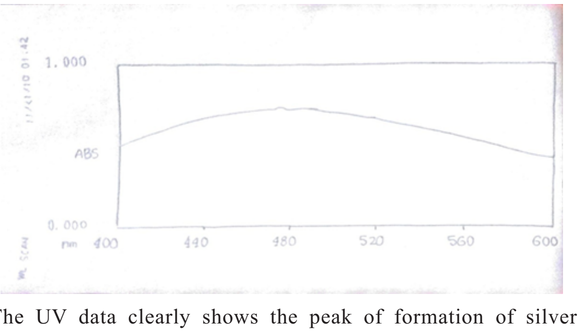
Calculation
0.034g sample =0.0237g Ag
100g sample = 69.7% of silver

The instrument was the run on its operated voltage and the graph was dictated with peak at 473nmwavelength and 0.71 absorbance. Change in colour was visually observed in the silver nitrate solution added to the biological extracts.

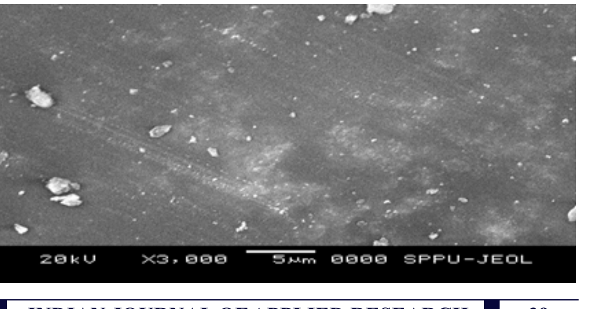
This bioreduction was UV analysed to check out the stability of silver nanoparticles and also give the confirmation of formation of silver nanoparticles

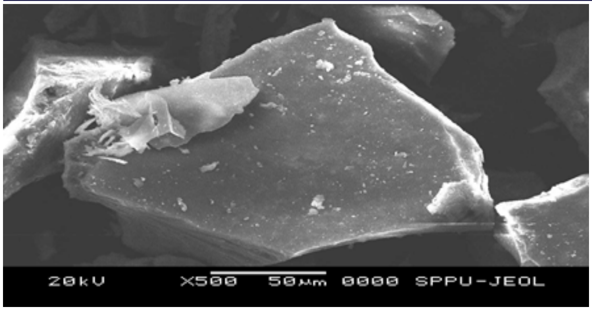
Spectroscopic analysis is commonly carried out in solution or liquid forms.

Organic compounds especially with a high degree of conjugation also absorb light in the UV or visible region of the electromagnetic spectrum.



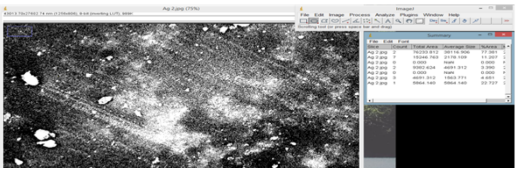
The UV data clearly shows the peak of formation of silver nanoparticles at 478nm wavelength and the absorbtion given by the instrument is 0.71. This was the second method of characterization that confirmed the silver nanoparticle formation as the typical peak for UV spectroscopy should range between 400-600 nm.





This SEM image provided further insight into the morphology and size of the produced nanoparticles. It is evident from the figure that the biosynthesized silver nanoparticles are in different size and shapes and mostly observed as individual particles as well as a few aggregates.

SEM-mediated characterization of biosynthesized nanomaterials has been performed by several investigators. Particle size analysis revealed that the silver nanoparticles are in the size range of 20-70nm with average size being 40nm.



The final average size was determined by using IMAGEJ software that clearly showed the analyzed particles with its average size in nm^2, square root of the nanoparticle size was taken to be considered as the actual nm size

Results and Discussion

Plants contain a complex network of antioxidant metabolites and enzymes that work together to prevent oxidative damage to cellular components. Kinnow mandarin hybrid fruit contains a number of essential nutrients, including vitamin C, manganese, and fibres. It also contains beneficial plant phytochemicals carotenoids, isohesperridin, terpeniol, naringin, limonin, flavonoids, hesperidin, and limonene which have antioxidant and anti-cancer activities. These anti-oxidative compounds delay or inhibit the oxidation of molecules by inhibiting the initiation or propagation of oxidative chain reaction. The anti-oxidative activity of phenolic compounds is mainly due to their redox property, which plays an important role in absorbing and neutralizing free radicals, quenching singlet and triplet oxygen or decomposing peroxides. Several reports have conclusively shown close relationship between total phenolic contents and anti-oxidative capacity. The antioxidant activity is the result of a combination of different compounds having synergistic and antagonistic effect due to phenolic nucleus forms a resonance stabilized phenoxy radical which accounts for potent antioxidant property . UV absorption by Ferulic acid catalyzes the formation of stable phenoxy radical. By virtue of effectively scavenging deleterious radicals and suppressing radiation-induced oxidative reactions, Ferulic acid may serve as an important antioxidant. This radical is highly resonance stabilized since the unpaired oxygen although present, may be delocalised across the whole molecule.

CONCLUSION

The rapid synthesis of stable silver nanoparticles of average size 40 nm using kinnow juice is demonstrated. Achievement of such rapid time scales for synthesis of silver nanoparticles makes it more efficient as a biosynthetic pathway.

Probably the biomolecules responsible for the reduction and stabilisation of AgNPs are phenols apart from the various enzymes and phytochemicals which are present in the versatile fruit. The phenolics in kinnow exhibit excellent antioxidant activity and these phenols can react with a free radical to form the phenoxy radicals. Therefore, the use of natural anti-oxidants for the synthesis of AgNPs seems to be a good alternative which can be due to its benign composition.

ACKNOWLEDGEMENTS

The authors are thankful to the Principal, Abeda Inamdar College Pune for providing the infrastructural facility for research work.The help from the Head, Department of Chemistry , Abeda Inamdar College is duly acknowledged.

REFERENCES

1. Christopher P.Shaw, David G.Fernig and Raphael Levy.,(2011), Journal of Material Chemistry.,21,12181-12187.
2. Oleksander L.Stroyuk, A.I.Kryukov, S.Ya.Kuchmil and V.D.Pokhodenko.,(2005), Theoretical and Experimental Chemistry., 41,(2),67-91.
3. O.V.Salata.,(2004),Journal of Nanobiotechnology.,2,1-6.
4. Praphulla Rao, Chandraprsad M.S, Jahnavi Rao, Aishwarya P and Shrinidhi Shetty.,(2014), International journal of Multidisciplinary and Current Research.,2, 165-169.
5. Sovan Lal Pal, Utpal Jana, P.K.Manna,G.P.Mohanta and R.Madhavan.,(2011), Applied Pharmaceutical Science., 1,(6),228-234.
6. Wan Rui Ma, Li Jing, Alexandra Valladares, Suresh L Mehta, Zhi Zhong Wang, P.Andy Li, Zhong J.Bang.,(2015), International Journal of Biological Sciences.,11,8,860-867.
7. Narayen Pradhan and Tarashankar Pal,(2002),Collides and surfaces A – Physiochemical and Engineering Aspects., 196,(2,3),247-257.
8. Keunju Park and Jongkook Lee,(2008), Collides and surfaces A – Physiochemical and Engineering Aspects., (313-314),351-354.
9. David D.Evanoff Jr. and George Chumanov.,(2005), ChemphysChem.,6,1221-1231.
10. Byung-hee Choi, Hyun-Ho Lee, Sunmi Jin, Sangki Chun and Sang-Ho Kim.,Nanotechnology,(2007),18,7.