Effect of Concentration, pH and Time on the Morphology of Silver Nanoparticles Synthesized by Green Method using *Phyllanthus Niruri* and *Solanum Nigrum* Leaf Extracts

M. Sundarrajan¹, A. Jeelani², V. Santhanam^{2*}, S. Durgadevi³, S. Abirami³

^{1,2,3}Department of Physics, Sri Chandrasekharendra Saraswathi Viswa Mahavidyalaya, Enathur, Kanchipuram, India; ²Department of Chemistry, Sri Chandrasekharendra Saraswathi Viswa Mahavidyalaya, Enathur, Kanchipuram, India.

ABSTRACT

Nanoparticles find many applications due to their small size and hence enhanced physical and chemical properties. Various physical, chemical and biological methods are available for nanosynthesis and they bring some contamination to the product and hence to the environment. In order to eliminate the contamination to the environment green methods are employed for nano synthesis. The green synthesis of nanoparticles are achieved by using plant products such as leaves, roots, flowers and fruits with the precursor solution. In this work, extracts from *Phyllanthus Niruri* and *Solanum Nigrum* leaves were utilized for the synthesis of silver nanoparticles (AgNps) from silver nitrate solution. Bio active molecules present in the extract act as reducing and capping agents in the green synthesis. The bioactive components of extracts and the morphology of AgNps were studied FTIR, ultraviolet-visible spectroscopy (UV-Vis), FTIR, SEM and Dynamic Light Scattering analysis (DLS).

Key Words: Green Synthesis, Silver Nanoparticles, *Phyllanthus Niruri* and *Solanum Nigrum* leaves, UV-Vis Spectroscopy, FTIR, SEM, and Dynamic Light Scattering (DLS) analysis

INTRODUCTION

Nanomaterials are special type of materials with enhanced physical and chemical properties. The enhancement in mechanical, thermal, optical and electrolytic properties of nanomaterials is solely due to their material grain size which ranges from 1-100nm. At this nano scale, the surface area of nanograins is increased to maximum extent compared to its volume and the grain surface accommodates more surface charges (1-3). Among various types of nanomaterials, metallic nanoparticles have been influencing the scientific community nearly for a century and find more applications in biomedical sciences and engineering. Silver nanoparticles (Ag-NPs) are one among them and used for various applications such as anti-bacterial agents, chemical sensors, bio medicine and water treatment (4). Silver nanoparticles have tremendous applications in nano medicine and nano sensors.

Their broad application rely in antibacterial activity of killing various micro organisms.

Nowadays various methods are employed to synthesize metal nanoparticles through physical and chemical mode. The chemical synthesis and stabilization of nanoparticles leaves toxic residues to the environment. In view of cutting down the toxic output to the environment arising from nano synthesis, green method of nanosynthesis has been popularized and implemented for the past years in the scientific communities. The green synthesis refers to synthesis of nanoparticles with the usage of parts of plants like leaves, roots, flowers, fruits and stem. The extracts acquired from the above plant parts possess natural reducing and capping agents. These bio agents are very much useful in the synthesis of silver nanoparticles from the Silver Nitrate precursor solution (5-7).

Corresponding Author:

V. Santhanam, Department of Chemistry, Sri Chandrasekharendra Saraswathi Viswa Mahavidyalaya, Enathur, Kanchipuram, India.
E-mail: rajan_sugi@yahoo.com

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In this study a new trial has been made with binary mixture of two plant product extracts instead of single one. The plant products chosen here are petals of two different flowers. The extracts obtained from

MATERIALS AND METHODS

Plant Materials

Plant parts, such as leaves, roots, fruits and stem, contain active bio ingredients and these ingredients act as reducing and capping agents in green synthesis of nano silver preparation. *Phyllanthus Niruri* and *Solanum Nigrum* leaves were taken for this study as they have various medicinal effects on human health.

Sample Collection

Phyllanthus Niruri and *Solanum Nigrum* leaves were collected from Kancheepuram situated in Kancheepuram district.

Methods

Ultraviolet-visible (UV-vis) spectroscopy analysis

The formation of silver nanoparticles was confirmed by Ultraviolet – Visible (UV-Vis) Spectroscopy using UV-Vis spectrophotometer facility at SCSVMV University, Enathur, Kancheepuram. UV-vis spectroscopy has been proved to be a very useful technique for nanoparticle study as peak positions and shapes in spectra are sensitive to particle size.

Fourier Transform Infrared (FTIR) Spectroscopy

The silver nitrate solution mixed with the extract was subjected to FTIR spectroscopy analysis using FTIR Spectrometer facility at SCSVMV University, Enathur, Kancheepuram. The FTIR absorption peaks indicated various bio-active components present in the extract.

Scanning Electron Microscope (SEM)

The formation of silver nanoparticles was initially confirmed by the change in colour of the solution from transparent to brown. The solution was subjected to SEM analysis to study the morphology of nanoparticles. SEM facility at St. Joseph's college, Trichy was utilized for this study.

Dynamic Light Scattering (DLS) and Zeta Potential analysis

DLS techniques is very much useful in detecting the silver nanoparticle size range and average particle size present in the solution, The silver nitrate solution mixed with the extract was subjected to DLS and Zeta potential analysis. Zeta potential is concerned with surface of nanomaterial and playing domination role in the stability of nanoparticles.

Preparation of leaf extract

The fresh leaves of *Phyllanthus Niruri* and *Solanum Nigrum* were washed several times with normal water and finally with distilled water. 20g of leaves (10g in each) were weighed and boiled for 1 hour in a 100 ml of distilled water and it was filtered using whattman filter paper. Then the leaf extract mixture was stored in refrigerator at 10° C for further use. This extract was used as reducing and stabilizing agent.

Preparation of silver nitrate solution

Aqueous solutions of silver nitrate were prepared with different concentrations (0.001, 0.0015, 0.002, 0.0025, 0.003M of silver nitrate) by adding the silver nitrate in 100 ml of double distilled water and it was stirred for 1 hour. Further 20 ml from each concentration was taken for the synthesis of silver nanoparticles.

Preparation of Silver nanoparticles

5 ml of leaf extract mixture was added in 20 ml of silver nitrate solution of various concentration. A change in the color of solutions from yellow to dark red and brown color indicated and confirmed the formation of silver nanoparticles.(43)

RESULTS AND DISCUSSION

UV-Vis Spectroscopic Study

To study the effect of concentration, pH and time on the morphology of synthesized silver nanoparticles, UV-Vis spectra were recorded at various conditions such as silver ion concentration (1, 1.5, 2, 2.5 and 3mM), pH (6 and 9) and time (6 and 24 hours). UV-Vis spectra recorded for all the above conditions are shown in figure1- 3.

Effect of Concentration of silver ion

UV-Vis spectra were recorded for various concentration of silver nitrate solution and shown in the figure1. From the figure it is evident that the peak intensity increases with the increase in concentration. This shows that the nano particle density increases with concentration. Further the Surface Plasmon Resonance (SPR) peak was gradually shifted towards red with respect to the concentration. The shift towards red indicates that the particle size gradually increases with concentration. The curve sharpness also increased with concentrations and this may be due to the formation spherical and cubical nanoparticles.

Effect of pH

UV-Vis spectra were recorded for various pH values of silver nitrate solution and shown in the figure 2. For lower pH values, the UV-Vis curve was smooth with a corresponding SPR peak for silver nanoparticles. When the pH value was increased, the UV-Vis curve was split up in to primary and

secondary peaks. The splitting of peaks were due to the growth of the nano particle to larger sizes and the SPR peak also shifted towards red. The same trend is observed when concentration is varied along with pH of the solution.

Effect of Time

The recorded UV-Vis spectra for samples of different retention duration after the formation are shown in figure 3. The UV-Vis spectra clearly indicates that the increase in retention time results in gradual growth of nanoparticle to larger sizes. The splitting of SPR peaks were due to the largely grown nanoparticles. The same trend is observed for all concentrations of solution.

FTIR Spectroscopic Study

FTIR analysis over the samples were carried out to identify the active biomolecules present in the plant leaves. The biomolecules act as reducing and capping agents in the green synthesis of silver nanoparticles. In FTIR spectra, peaks are observed at 3269, 1635, 516, 464 and 413cm⁻¹ as shown in figure 4. The peaks observed at 3269 cm⁻¹ corresponds to O-H stretching with strong or broad intensity of alcohol or phenol. The absorption peak at 1635 cm⁻¹ is very near to native proteins present in the leaf extract. The peak at 516cm⁻¹ is due to O-C-O in plane bending. The weak transitions at 464 cm⁻¹ may be associated with water liberations. The FTIR spectroscopy confirmed the presence of reducing and stabilizing agents present in the leaf extract mixture.

Scanning Electron Microscope

The silver nitrate (AgNO₃) solution is slowly subjected to the addition of leaf extract and which resulted in color change of the solution from transparent to brown due to the formation of silver nanoparticles. The color changes arise from the excitation of Surface Plasmon vibrations at silver nanoparticles. The solution mixture with 3mM concentration of silver nitrate was subjected SEM analysis and the images are shown in the figure 5. The SEM images show clearly the presence of nanoparticles in the nanoscale range 70 – 95 nanometer. The majority portion of nanoparticle show cubical shape. But some of the nanoparticles are in triangular and spherical shapes, but not well defined. The SEM images show approximately 30 % of particles is in nanoscale while the other exceeds in size and some of the nanoparticles are in various shapes than cubical one.

Dynamic Light Scattering and Zeta Potential Analysis

The DLS and Zeta potential analyses results are shown in figure 6-9 for 0.003mM solution after 6 hours and 24 hours. Zeta potential is a factor which determines the stability of nanoparticles. From the figure, it is evident that as retention time increases from 6 hours to 24 hours, the particle size increases. Zeta potential also reduced as retention time

increased. The calculated average particle size of silver nano particle increased from 90 nm to 94 nm with rise in retention time. This confirms the results offered by SEM images where nanoparticles with a range range 50 – 90 were detected. The Z-Average size is intensity based and higher values show the presence of large size particles in more number. Since zeta potential decides the agglomeration action in nanoparticles, agglomeration will be less if zeta potential is more and vice versa. In this study, zeta potentials are low in value and this may due to the reason of longer duration of retention.

CONCLUSIONS

From the above, it may be concluded that increase in concentration of silver nitrate in solution increased the nanoparticle density and enhances gradual growth of nanoparticles to larger sizes. This is illustrated in UV-Vis spectra through rise in absorbance and red shift of SPR peaks. The increase in pH of the solution also increases the size of nanoparticles which is shown by the splitting of SPR peak in UV-Vis spectra. In some cases the particles reaches the bulk size when pH is not maintained to a desired level. The retention time of solution also affects the size of silver nanoparticles and their stability. The increase in retention time increased the particle size and this is well illustrated in the formation of secondary peak in UV-Vis spectra.

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Figure 1: UV- Vis spectra for various concentrations of silver ion.

Figure 4: FTIR spectrum of 3mM solution with extract.

Figure 2: UV- Vis spectra for various pH values of solution with extract.

Figure 5: SEM micrograph of 3mM solution with extract.

Figure 6: Particle Size of sample with 3mM concentration after 6 hours.

Figure 3: UV- Vis spectra for various retention duration of solution with extract.

Figure 7: Particle Size of sample with 3mM concentration after 24 hours.

Figure 8: Zeta potential of sample with 3mM concentration after 24 hours.

Figure 9: Zeta potential of sample with 3mM concentration after 24 hours.