Journal of Chemical and Pharmaceutical Research, 2014, 6(6):1089-1093



Research Article

ISSN : 0975-7384 CODEN(USA) : JCPRC5

Competence of different methods in the biosynthesis of silver nanoparticles

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ABSTRACT

Nanosilver has become one of the widely used nanomaterial in consumer products. The formation of nanoparticles depends on several factors like the concentration of silver ions, time and method of synthesis. In the present work nanosilver particles were synthesized using four different edible plants by three different methods employing heat and sound waves. Rapid reduction of silver ions to nanosilver was noticed in all methods, sonication method being quicker comparatively. The synthesized silver nanoparticles were characterized by UV-visible spectroscopy, XRD, Debye-Scherrer's equation and SEM analysis. In sonication method, nanoparticles of size less than 50 nm were obtained. The SEM analysis revealed that the nanoparticles were well dispersed without agglomeration. The successful utilization of sonic waves in the formation of silver nanoparticles is quite apparent from the results.

Key words: Nanosilver, SEM, XRD, UV-visible spectroscopy.

INTRODUCTION

Many advancements and new applications with improvised technologies have generated from the science of Nanotechnology [1]. The word "nano" has more implications in all fields of research due to its physicochemical characteristics such as high surface area to volume ratio and also smaller size particles with high potential. Synthesis of nanoparticles of different shapes, size and chemical composition forms the basic research in the field of Nanochemistry as difference in size and shape tends to change the entire property of the particle. Metal nanoparticles like gold, silver find diverse applications in many fields [2-3]. These applications also depend on the size, morphology and nature of the nanoparticles used.

Biological synthesis of advanced nanomaterials of gold and silver using the natural products (fruits, honey, leaves, plants) and bio-organisms (fungi, bacteria and proteins) have received more attention by the researchers. This paves a pathway to the development of environmentally benign technologies in the synthesis of nanoparticles [4]. Due to the diverse applications of silver nanoparticles in fields like microbiology, catalysis, electrical conductivity, magnetic and optical polarizability, DNA sequencing and surface-enhanced Raman scattering (SERS), many techniques were put forward for the synthesis of nanosilver particles. Various chemical reduction, photoreduction, microwave irradiation and physical methods were adopted for the preparation of silver nanoparticles. In recent times, synthesis of eco-friendly metal nanoparticles has become a great challenge [5-7]. Taking into consideration the aforesaid significance of the nanoparticles synthesis and factors involved, the present work is focused on biogenic synthetic methods employing different synthetic conditions.

Amaranth remains to be vital in the area of scientific research for both human nutritional needs and foraging applications. *Amaranthus dubius* and *Amaranthus polygonoides* belongs to the family Amaranthaceae. These plants are good sources of protein and also rich source of amino acids. *Alternanthera sessilis* is a weed and a source of secondary metabolites like flavonols, triterpenoids, steroids and tannins; β -sitosterol, stigmasterol, campesterol,

lupeol. *Portulaca oleracea* also contains vitamins, minerals (especially potassium), fatty acids, especially omega-3 acids, glutathione, glutamic acid and aspartic acid [8].

Properties of biological molecules present in the aforesaid plants, its inexpensiveness and easy availability makes them a choicest biogenic source for nanoparticle synthesis. There are various methods available for the synthesis of nanoparticles and the optimization of the method is a challenge to chemists. Hence this paper is focused on finding the competency of different methods in the synthesis of silver nanoparticles. Four different plant extracts were taken up for the biosynthesis of silver nanoparticles using silver nitrate as the nanosilver source. Four different methods of synthesis were employed viz. room temperature, higher temperature $(75^{\circ}C)$ and sonication.

EXPERIMENTAL SECTION

i. Materials

Four plants namely *Amaranthus dubius, Amaranthus polygonoides, Alternanthera sessilis* and *Portulaca oleracea* were collected from retail shop in Coimbatore. Silver nitrate was purchased from Himedia chemicals, India.

ii. Methods

a) Preparation of plant extracts

The plant samples (20g) were washed, cut into small pieces and boiled with double distilled water (100 ml) for 10 min, filtered and refrigerated.

b)Synthesis of silver nanoparticles

Different concentrations (6ml, 7ml, 8ml, 9ml and 10ml) of silver nitrate solution (3mM) were treated with the aqueous extracts (1ml) under various conditions viz. room temperature (RT), higher temperature (75°C) (HT) and sonication (SN). The formation of nanosilver was visually monitored periodically.

c) Characterization of biogenically synthesized silver nanoparticles

The synthesized silver nanoparticles using *Amaranthus dubius, Amaranthus polygonoides, Alternanthera sessilis* and *Portulaca oleracea* were characterized by UV-Visible spectroscopy (Double beam spectrophotometer – 2202 - SYSTRONICS), X-ray diffraction study (Lab X XRD-6000 - SHIMADZU), Fourier transform Infrared spectroscopy (BRUKER FTIR Tensor-27) and Scanning electron Microscopy (TESCAN with Vega TC software) analysis.

RESULTS AND DISCUSSION

The formation of silver nanoparticles using the aqueous extract of *Amaranthus dubius, Amaranthus polygonoides, Alternanthera sessilis* and *Portulaca oleracea* was evidenced by the visual colour change (yellow to reddish brown). The time of formation of nanosilver (fig.1) varied depending on the nature of the phytoconstituents present in the plant extracts, various conditions of biosynthesis and different methods. The UV-Visible spectrum of the nanosilver synthesized using *A. dubius, A. polygonoides, A. sessilis* and *P. oleracea* shows the absorption bands at 420nm, 420nm, 425nm and 421nm respectively (fig. 2). It was observed that as the concentration of silver nitrate increases the intensity of the absorption bands also increased revealing the production of more nanoparticles.

The sonication method was found to facilitate the synthesis of nanoparticles in *Portulaca oleracea* and *Alternanthera sessilis* compared to that of other methods. This may be due to the unusual physical and chemical effects produced by the liberated radicals in terms of reaction pathways and mechanisms. Moreover, ultrasonic waves will provide highly-intensive mixing and thus accelerating the chemical dynamics and rates of the reactions. The properties such as size, shape and agglomeration would also be controlled by sonication method [9-10].

Rapid reduction of nanosilver synthesis *using A. dubius* and *A. polygonoides* was achieved at higher temperature (75°C) due to the utilization of silver ions in the formation of nuclei whereas the secondary reduction was stopped on the surface preformed nuclei. The higher rate of reduction of silver ions and narrow peaks in UV indicating nanoparticles with smaller size were obtained at higher temperature. The studies reveal high temperatures to be more favorable for the formation of silver nanoparticles [11-12].

The XRD pattern showed two sharp peaks at 38° and 32° which may be indexed to (111) and (101) planes of silver with face centered cubic lattice (JCPDS no. 04-0783) for *A.dubius* and *A. polygonoides* respectively (fig.3 A&B). The XRD pattern of silver nanoparticles synthesized using *A. sessilis* and *P. oleracea* shows only one peak at 2θ = 32° corresponding to the diffraction plane (101) of silver with fcc lattice (fig.3 C&D). The crystallite size of the four different synthesized silver nanoparticles was calculated by Debye – Scherrer's equation is given in table 1.



Fig. 1 Time of formation of AgNP's using the aqueous extract of four different plants



Fig. 2 UV-Visible spectrum of the nanosilver synthesized using A. dubius, A. polygonoides, A. sessilis and P. oleracea

S. No	Plants mediated AgNP's	2θ (degrees)	$\mathbf{D} = \mathbf{k} \lambda / \beta. \operatorname{Cos}\theta (\mathbf{nm})$
1.	A.dubius - AgNP's	38, 32	12.9
2.	A. polygonoides - AgNP's	38, 32	16.03
3.	A. sessilis - AgNP's	32	32.81
4.	P. oleracea - AgNP's	32	32.24

The crystallite size of the silver nanoparticles synthesized using *A.dubius* was smaller in size (12.9nm) compared to that of *A. polygonoides*, *A. sessilis* and *P. oleracea mediated* AgNP's. The nanoparticles which are smaller in size are anticipated to exhibit better antibacterial properties.

The SEM micrograph of the synthesized AgNP's using *A.dubius* and *A. polygonoides* revealed spherical shape particles with agglomeration (fig 4a & b). Particle size of less than 50 nm was obtained for *A. sessilis* and *P. oleracea* mediated nanoparticles without agglomeration (figure 4c & d). The presence of various phytoconstituents in the plant samples taken for study might be responsible for the variation in the size of the nanosilver along with other parameters like different methods of formation adopted in the study, concentration variation etc.

The FTIR spectral data of the synthesized silver nanoparticles is given in the table 2. The IR frequencies of the synthesized nanosilver using *A. dubius*, *A. polygonoides*, *A. sessilis* and *P. oleracea* reveal the presence of -NH or -OH, C=O, C-H, CC and CN triple bond functional groups that are responsible for the reduction of silver ions. These groups find source in the plant extracts which have been used as capping agents.



Fig. 3 XRD patterns of synthesized nanosilver using A.dubius (A), A. polygonoides (B), A. sessilis (C) and P. oleracea (D)



Fig. 4 SEM mircographs of synthesized nanosilver using A.dubius (A), A. polygonoides (B), sessilis (C) and P. oleracea (D)

S.No	Plants mediated AgNP's	IR frequencies	Functional groups
1.	A.dubius- AgNP's	3285 cm^{-1}	-NH or -OH
		1634 cm^{-1}	C=O
		$2471 \text{ cm}^{-1}, 2411 \text{ cm}^{-1}, 2115 \text{ cm}^{-1}, 2172 \text{ cm}^{-1}$	C-H, CC triple bond
			CN triple bond
2.	A. polygonoides- AgNP's	$1595 \text{ cm}^{-1}, 1484 \text{ cm}^{-1}$	-C-C- in aromatic ring.
		$1667 \text{ cm}^{-1} 2422 \text{ cm}^{-1}$,	C=N
		2507 cm^{-1}	CN triple bond
3.	P. oleracea- AgNP's	3277 cm^{-1} , 1635 cm ⁻¹	–NH or –OH, C=O
		2119 cm^{-1}	CN triple bond
4.	A. sessilis- AgNP's	3253 cm^{-1} , 1634 cm $^{-1}$	–NH or –OH
		$2190 \text{ cm}^{-1}, 2040 \text{ cm}^{-1}$	CC or CN

Table 2 IR Frequencies of the synthesized silver nanoparticles

CONCLUSION

Biosynthesis of silver nanoparticles using *A.dubius, A. polygonoides, A. sessilis* and *P. oleracea* was achieved by implementing the green chemistry principles. Higher temperature method and sonication method prove to facilitate the synthesis of silver nanoparticles. The phytoconstituents in plants were found to play a foremost role in control over the size, shape and aggregation of nanosilver. The particle size of nanosilver was found to less than 50 nm as confirmed by XRD and SEM analysis. The FTIR spectra revealed that all the four plant extracts taken up for study can act as effective reducing and capping agents being responsible for the stabilization of the synthesized nanosilver particles.

Acknowledgement

The authors sincerely thank the authorities of Avinashilingam Institute for Home Science and Higher Education for Women, Coimbatore, Tamil Nadu, for providing research facilities, Karunya University for recording XRD and Periyar Maniammai University for recording SEM.

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