STUDY OF ANTIOXIDANT PROPERTIES OF SILVER NANOPARTICLES SYNTHESIZED BY PALMYRA PULP AND SPROUT EXTRACTS IN THE PRESENCE OF SOLAR IRRADIATION

Samudrika Aththanayake [1,2], Gobika Thiripuranathar[2*], Sagarika Ekanayake[1]

[1]Department of Biochemistry, Faculty of Medicine, University of Sri Jayewardenepra, Gangodavila, Nugegoda.

[2]College of Chemical Sciences, Institute of Chemistry Ceylon, Rajagiriya 10107, Sri Lanka.

**tgobika@ichemc.edu.lk, TP: +94772123062*

The process of green nanoparticle (NP) synthesis is a biologically feasible process due to the presence of a diverse array of bioactive compounds. The aim of this research was to synthesize silver nanoparticles (Ag NPs) utilizing palmyra fruit pulp and sprout extracts under solar irradiation and compare their antioxidant properties. Ag NPs were synthesized with aqueous extracts of palmyra fruit pulp and sprouts with $AgNO_3$ solution as the ion precursor. Qualitative phytochemical analysis was conducted to identify the phytochemicals present in the plant extracts. UV-Vis, FTIR, SEM, TEM, and XRD were used to characterize the synthesized Ag NPs. To evaluate the antioxidant activity of NPs, DPPH, ABTS, and FRAP assays were conducted. The phytochemical screening of plant extracts revealed the presence of primary and secondary metabolites. Both extract-mediated synthesized Ag NPs had surface plasmon resonance peaks in the range of 430-440 nm. FTIR results confirmed that functional groups of bioactive compounds are present on the surface of phytogenic Ag NPs. SEM revealed spherical particles in both extracts whereas TEM revealed that the sizes of pulp and sprout-mediated NPs were 17 ± 2 nm and 13 ± 3 nm, respectively. The XRD spectra confirmed that pulp and sprout-mediated Ag NPs were pure crystalline. The DPPH radical scavenging capacity for the pulp and sprout-mediated Ag NPs showed IC_{50} values of 22 ± 2 ppm and 21 ± 1 ppm, respectively and ABTS radical scavenging assay indicated that IC_{50} values as 91 ± 1 ppm and 60 ± 2 ppm, respectively. Similarly, phytogenic Ag NPs displayed higher FRAP scavenging power than the respective extracts. Sprout-mediated Ag NPs have a higher antioxidant potential than pulp-mediated Ag NPs due to their smaller size. Hence, biosynthesized pulp NPs could be utilized as a sustainable source for various industrial applications.

Keywords: Aqueous extract, Antioxidant activity, Palmyra fruit pulp, Sprout, Silver nanoparticles

STUDY OF ANTIOXIDANT PROPERTIES OF SILVER NANOPARTICLES SYNTHESIZED BY PALMYRA PULP AND SPROUT EXTRACTS IN THE PRESENCE OF SOLAR IRRADIATION

Samudrika Aththanayake [1,2], Gobika Thiripuranathar[2*], Sagarika Ekanayake[1]

[1]Department of Biochemistry, Faculty of Medicine, University of Sri Jayewardenepra, Gangodavila, Nugegoda.

[2]College of Chemical Sciences, Institute of Chemistry Ceylon, Rajagiriya 10107, Sri Lanka.

**tgobika@ichemc.edu.lk, TP: +94772123062*

INTRODUCTION

Palmyra tree has a wide range of uses, including food, beverage, fiber, medicine, and timber. Various parts of the Palmyra plant have been reported to contain biological and pharmacological activities [1]. Green nanotechnology is a sustainable approach for synthesizing many metals, metal oxide nanoparticles (NPs), and their nanocomposites (NCs) with diverse applications in various fields. The plant-mediated synthesis of silver nanoparticles (Ag NPs) is a green and self-sustaining process with low chemical usage that overcomes the drawbacks of traditional physicochemical synthesis [2]. Ag NPs synthesis is the most commercialized research area due to its immense properties, such as antioxidant, antimicrobial, anti-inflammatory, anti-cancer, photocatalytic, optoelectronic, and so on. As a result, Ag NPs have been used in several industries, including cosmetics, medicine, environmental remediation, agriculture, food, and textile [3],[4],[5]. Due to the rich bioactive component profile of both parts of palmyra pulp and sprout, they facilitate the synthesis of NPs. The fresh pulp is rich in vitamins A and C, essential amino acids such as lysine, phenylalanine, and glutamate and is a rich source of bioactive compounds such as carotenoids, flavonoids, saponins, and phenolic compounds [4]. Palmyra sprouts are rich in calories, a good source of vitamin E, and contain flavonoids and phenolic acids, which have antioxidant properties [3]. Hence, the focus of this research was to synthesize Ag NPs using bioactive compounds from the palmyra pulp and sprout aqueous extracts which are commonly consumed in Sri Lanka, by applying low-cost and environmentally friendly techniques. Furthermore, we aimed to assess the antioxidant activity of the synthesized NPs and compare their efficiency with the respective plant extracts.

METHODOLOGY

Preparation of plant extract- The ripped palmyra fruits were collected from the trees near the Kilinochchi area, and the palmyra sprouts were collected from the local market from Dehiwala. The mature fruit pulp was squeezed using muslin cloth without fibre. The obtained pulp was freeze-dried to get the dry weight of the pulp. The dried pulp sample (10 g) was dissolved in 200 mL of distilled water, and the mixture was continuously stirred under 70 °C for 30 minutes to get the pulp extract. The sprouts were washed thoroughly and then rinsed with distilled water. The sprouts were cut into thin slices and oven-dried at 45 °C for three days. The dried sprout sample was powdered using an electrical grinder. The same procedure was followed to prepare the sprout extract. The aqueous extracts were filtered through the Whatman No.1 filter paper [2].

Phytochemical screening- Aqueous extracts of palmyra pulp and sprout were screened for the presence of different classes of phytochemicals using standard procedures [6].

Optimization of Ag NPs synthesis- Synthesis of Ag NPs was carried out by mixing aqueous pulp and sprout extracts with different concentrations of $AgNO_3$ solution (0.01 M, 0.05 M, 0.1 M) in different ratios (aqueous extract: $AgNO_3$) such as 1:1, 1:3, and 2:5. The effect of irradiation methods was assessed by varying different irradiation sources such as solar, microwave, and ultraviolet. To determine the effect of the time period on NP synthesis, reactions were performed at different time intervals (0.5–24 h) [2].

Synthesis of Ag NPs using palmyra pulp and sprout extracts-Using aqueous pulp and sprout extracts, Ag NPs were synthesized under optimized conditions. Accordingly, 5 mL of pulp and sprout extracts were separately added to 15 mL of 0.05 M of $AgNO_3$ solution. Then the mixture was subjected to solar irradiation. The resultant mixture was incubated for 24 hours at room temperature. The synthesized Ag NP solution was then centrifuged at 5000 rpm for 20 minutes. The centrifuged crude was washed with distilled water and dried at 70 °C in an oven [3].

Characterization of phytogenic Ag NPs-The surface plasmon resonance (SPR) peak of Ag NPs was determined using a wavelength range of 300-700 nm. The functional groups of phytochemicals present in the extracts used in the bioreduction were determined using a Fourier transform infrared (FTIR) spectrometer in the range of 500 – 4000 cm^{-1}. Morphological analysis was carried out using Scanning electron microscopy (SEM) and Transmission electron microscopy (TEM) analysis was used to determine the particle size. X-ray diffraction (XRD) was used for the structural analysis.

Antioxidant potential of phytogenic Ag NPs- 2,2-Diphenyl-1-picrylhydrazyl (DPPH), 2,2′-azinobis-(3-ethylbenzthiazolin-6-sulfonic acid) (ABTS), and Ferric reducing antioxidant power (FRAP) assays were used with standard procedures to determine the antioxidant potential of biogenic Ag NPs compared to respective plant extract and metal ion precursor [7], [8].

RESULTS AND DISCUSSION

Phytochemical screening of palmyra pulp and sprout extracts- Preliminary screening of phytochemicals showed the presence of carbohydrates, proteins, fatty acids, saponins, phenols, tannins, flavonoids, and alkaloids in the palmyra pulp and sprout extracts.

UV-Vis spectra analysis- The synthesis of Ag NPs was confirmed by the appearance of an SPR peak between 430 to 440 nm as shown in Figure 1.

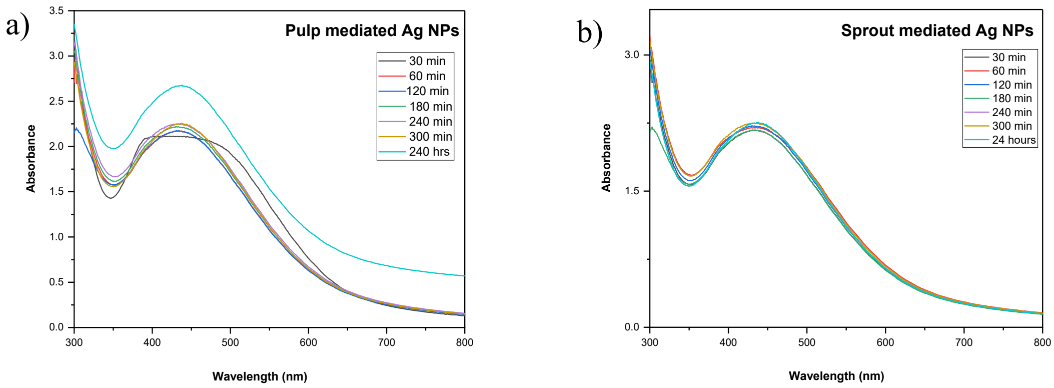


Figure 1: UV–Visible spectra obtained for the synthesis of Ag NPs under optimized conditions using a) palmyra pulp and b) palmyra sprout

FTIR analysis- The bands obtained from the biomass of plant materials were used as references, where the functional group was involved in the reducing, capping and stabilization process of Ag NPs synthesis (Figure 2).

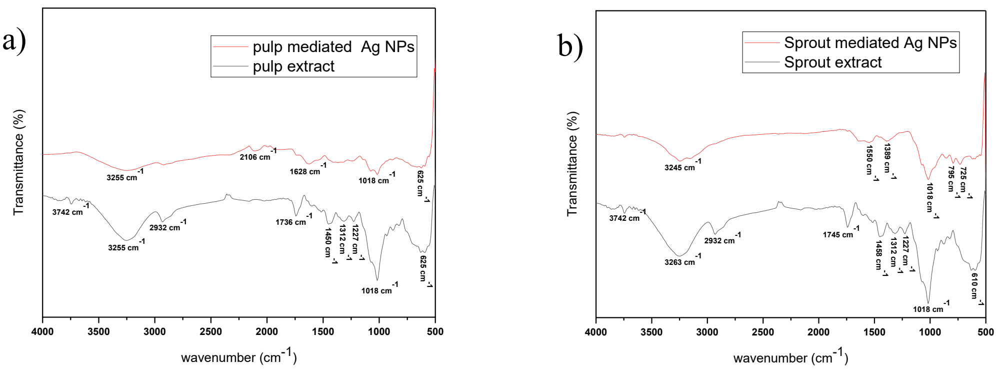


Figure 2: Functional groups present in a) palmyra pulp and pulp mediated Ag NPs b) palmyra sprout and sprout mediated Ag NPs.

The FTIR spectra of the palmyra pulp and sprout extracts revealed the presence of various functional groups (Table 1) responsible for metal ion reduction.

Table 1: FTIR peaks of NPs synthesized using palmyra pulp and sprout extracts

Frequency range (cm^{-1})	Functional group

3200 – 3300	Amines and amides (N-H stretching) Alcohol and phenols (O-H stretching)
2100 - 2330	Alkene (C≡C stretching)
1500 - 1640	Diketones (C = O stretching)
1234 - 1385	Alkyl Ketone and (–C-H (CH_3) bending symmetric stretching)
1026 - 1084	Ester group (C-O stretching)
590 - 770	Halogen compounds

The FTIR spectra provide information on functional groups or biomolecules on the surface of the biosynthesized NPs. The obtained functional groups on biosynthesized NPs (hydroxyl, protein, and carboxyl) verified the presence of biomolecules of plant materials, which were involved in the biosynthesis process.

SEM analysis- The SEM images of palmyra pulp and sprout-mediated synthesized Ag NPs under solar irradiation indicated that the Ag NPs are spherical as well as nearly spherical and were monodispersed with agglomeration (Figure 3).

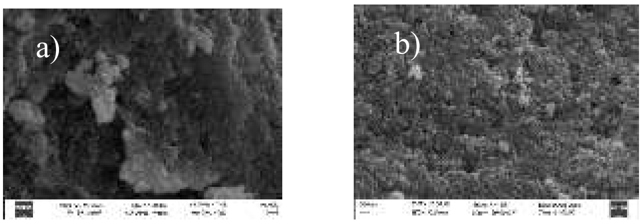


Figure 3: SEM images of (a) pulp mediated AgNPs, (b) sprout mediated Ag NPs

TEM analysis- The TEM analysis indicated that the average particle sizes of pulp and sprout-mediated Ag NPs were 17 ± 2 nm and 13 ± 3 nm, respectively. According to TEM pulp and sprout mediated AgNPs were approximately spherical shaped (Figure 4).

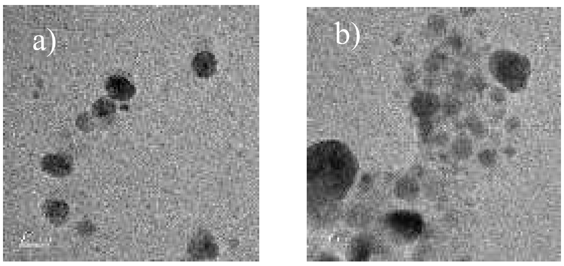


Figure 4: TEM images of a) pulp mediated AgNPs b) sprout mediated Ag NPs

XRD analysis- The characteristic peaks in the pulp and sprout mediated Ag NP sample were 31.95°, 37.8°, 45.95°, 67.2°, and 76.5°, which corresponds to the (101), (111), (200), (220), and (311) planes of Ag, respectively. According to available literature (JCPDS, File No. 4-0783) [5], all of the peaks in the XRD pattern can be easily indexed to a face-centered cubic structure of Ag. The presence of extra peaks near 26.65°, 27.5°, 54.5°, and

57.2° in both plant-mediated Ag NP samples were due to the presence of bio-organic phase on the surface of particles (Figure 5). The crystallite sizes of Ag NP synthesized from pulp and sprout were 18.5 nm and 14.5 nm, respectively.

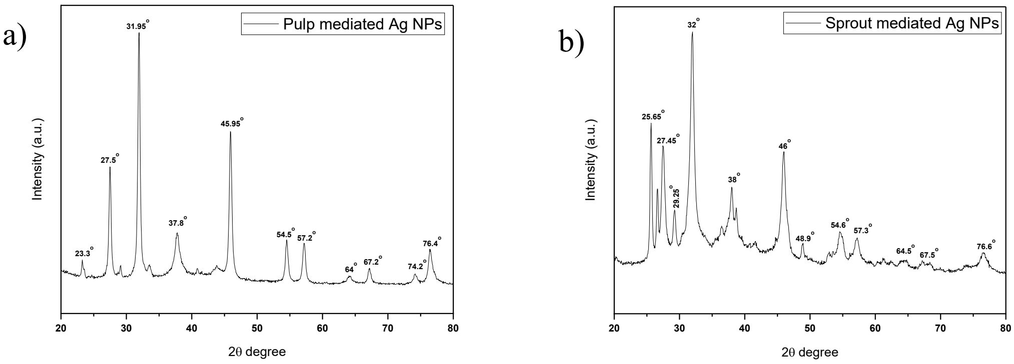
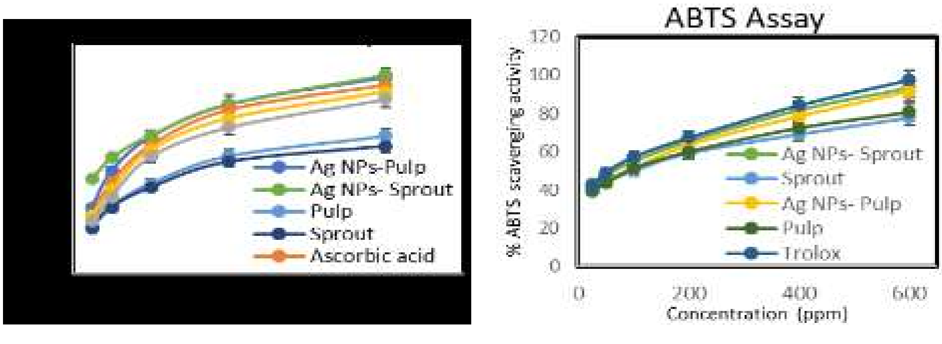


Figure 5: XRD patterns for a) pulp mediated Ag NPs and b) sprout mediated Ag NPs

Antioxidant activity- The Figures 6 provides data on free radical scavenging activities of Ag NPs and plant extracts comparing to the standards. The results revealed that pulp and sprout mediated Ag NPs scavenged DPPH and $ABTS^{\bullet+}$ free radicals in a concentration dependent manner. The IC_{50} values of DPPH and $ABTS^{\bullet+}$ radical scavenging assay for sprout mediated Ag NPs were estimated to be 21 ± 1 ppm and 60 ± 2 ppm, respectively and pulp mediated Ag NPs were 22 ± 2 ppm and 91 ± 1 ppm, respectively. Therefore, the palmyra sprout mediated Ag NPs had greater potential to scavenge $ABTS^{\bullet+}$ and DPPH free radicals than pulp-mediated Ag NPs. Further, it is evident that the antioxidant activity depends on the particle size as the sprout mediated synthesized NPs have lower particle sizes than the pulp mediated. The ability of palmyra pulp and sprout mediated Ag NPs to reduce Fe^{3+} ferric cyanide complex to Fe^{2+} ferrous cyanide increased with the increased concentrations. Maximum absorbance for FRAP was 0.55 at 500 ppm. Compared to ascorbic acid in the FRAP assay, the phytogenic NPs exhibited the highest antioxidant power.



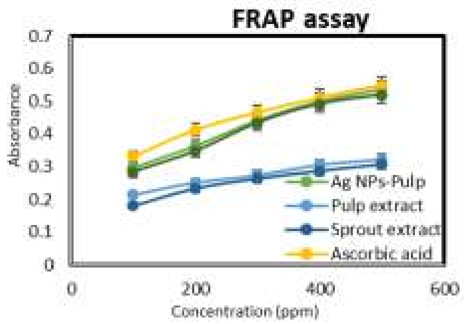


Figure 6: DPPH, ABTS$^{\bullet+}$ free radical scavenging activity, and FRAP assay of Ag NPs and plant materials.

CONCLUSIONS/RECOMMENDATIONS

Ag NPs have been effectively biosynthesized using palmyra pulp and sprout. Synthesized NPs were optimized by varying the parameters and preliminarily confirmed SPR peaks ranging from 430-440 nm. FTIR analysis revealed that phytochemicals present in plant extracts acted as reducing and capping agents. The SEM and TEM analysis revealed that palmyra sprout-mediated synthesized Ag NPs had smaller average particle sizes below 20 nm with spherical shapes. The XRD confirmed the formation of pure Ag NPs with distinctive peaks indexed to a face-centred cubic structure of Ag with crystalline sizes for pulp and sprout-mediated NPs. Both TEM and XRD analysis indicated that sprout-mediated Ag NPs have smaller particle size. The pulp and sprout-mediated Ag NPs displayed higher DPPH, ABTS$^{\bullet+}$ radical scavenging capacities and FRAP inhibition power than the respective plant extract, indicating that the sprout extracts contain excellent reducing and capping agents for the biogenic synthesis of smaller-size Ag NPs. The Ag NPs produced through synthesis display notable antioxidant capabilities, and this tendency becomes more pronounced as the NPs decrease in size. This discovery highlights the effectiveness of green synthesis in generating NPs that possess valuable functional attributes, including enhanced antioxidant activity.

REFERENCES

[1] Thevamirtha, C., Monichan, S. and Selvakumar, P.M., (2021). Carbon-based Materials from Borassus flabellifer and their Applications. *J. Environ. Nanotechnol*, *10*(4), pp.08-12.

[2] Perera, K.M.K.G., Kuruppu, K.A.S.S., Chamara, A.M.R. and Thiripuranathar, G., (2020). Characterization of spherical Ag nanoparticles synthesized from the agricultural wastes of Garcinia mangostana and Nephelium lappaceum and their applications as a photo catalyzer and fluorescence quencher. *SN Applied Sciences*, *2*(12), p.1974.

[3] Mahardika, D.P., Yusrita, E., Surya, A. and Juariah, S., (2021). Phytogenic silver nanoparticle (AgNP) from Ananas comosus (L) Merr. peel extract to inhibiting the pathogen resistance. In *Journal of Physics: Conference Series* (Vol. 1811, No. 1, p. 012124). IOP Publishing.

[4] Sumi, M.B., Devadiga, A., Shetty K, V. and MB, S., (2017). Solar photocatalytically active, engineered silver nanoparticle synthesis using aqueous extract of mesocarp of Cocos nucifera (Red Spicata Dwarf). *Journal of Experimental Nanoscience*, *12*(1), pp.14-32.

[5] Bedlovičová, Z., Strapáč, I., Baláž, M. and Salayová, A., (2020). A brief overview on antioxidant activity determination of silver nanoparticles. *Molecules*, *25*(14), p.3191.

[5] Smieja, J.M. and Babcock, K.E., (2017). The intersection of green chemistry and Steelcase's path to circular economy. *Green Chemistry Letters and Reviews*, *10*(4), pp.331-335.

[7] Junaid, R. and Patil, M., (2020). Qualitative test for preliminary phytochemical screening. *International Journal of Chemical Studies*, *8*(2), pp.603-608.

[8] Leaves, L. and Leaves, L., (2014). Antioxidant activity by DPPH radical scavenging method of ageratum conyzoides. *American Journal of Ethnomedicine*, *1*(4), pp.244-249.