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RESEARCH ARTICLE

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# SYNTHESIS AND CHARACTERIZATION OF SILVER NANOPARTICLES FROM *VENTILAGO DENTICULATA* WILLD

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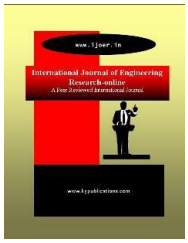

**ABSTRACT**

The present investigation reports the synthesis and characterization of AgNPs using the n-hexane leaf extract of *Ventilago denticulata* Willd by chemical reduction method. Green synthesized nanoparticles have been characterized by UV-Vis spectroscopy, SEM-EDX, TEM, XRD and FTIR. The formation of the silver nanoparticles was monitored using UV-Vis absorption spectroscopy. The UV-Vis spectroscopy revealed the formation of silver nanopartícles by exhibing the typical surface plasmon absorption maxima at 432-435 nm from the UV–Vis spectrum. TEM micrograph confirms the formation of spherical nanoparticles without any agglomeration and particle size range was found to be 35 nm. FTIR results revealed that different functional groups of leaf extract might be responsible for the reduction of $Ag^+$ into AgNPs. The X-ray diffraction studies indicated that the resulting AgNPs were highly crystalline with face-centered cubic geometry. Scanning electron microscopy (SEM) analysis revealed the formation of AgNPs and the surface morphology has been determined. The energy-dispersive spectroscopy (EDX) of the nanoparticles dispersion confirmed the presence of elemental silver signal no peaks of other impurity were detected. This environmentally friendly green synthesis is an eco-friendly approach to conventional chemical synthesis and can potentially be used in various areas such as food, cosmetics, and medical applications and hope the recent technology can provide next generation of anti-microbial agents.



## 1.0 Introduction

The synthesis of nanocrystals is in the limelight in modern nanotechnology. Biosynthesis of nanoparticles by plant extracts is currently under exploitation [1]. In present situation, silver nanoparticles (AgNPs) are in great use in the medicinal, pharmaceutical, agricultural industry and in water purification. These nanoparticles can be synthesized either chemically or biologically [4]. But the chemical process for synthesis of silver nanoparticles is more elaborate and leaves behind toxic effect that adversely affects the ecosystem. On the other hand, biological synthesis of silver nanoparticles is less time consuming, less costly, and more

ecofriendly; therefore, in recent time, scientists are looking forward to the possible biological methods for the synthesis of silver nanoparticles [2-3].

*Ventilago* is a genus of plants in the family Rhamnaceae (Figure 1). It includes about 35 species found in the tropics southern India. *Ventilago denticulata Willd* is a Climbing shrub, stems sometimes twining. Leaves alternate, pinnately veined. *V. denticulata Willd* commonly called the Red Creeper is an extensively branched, woody climber with hanging branches. The stem and root bark of this plant is a source of a red dye 'ventilagin', which is used for coloring cotton, wool and tasar. Stem bark when powdered and mixed with sesame oil, can be externally applied to treat skin diseases and sprains. Root bark is used for atonic dyspepsia, mild fever and debility. Sap is used for the treatment of deafness. The ethanolic extract of plant also shows antiinflammatory activity [5]. The plant is rich in many pharmaceutical active ingredients. The stem bark contains friedelin and several anthraquinones. The root contains anthraquinones, ventinones A and B. Major constituents of the root bark are emodin, its glucoside and corresponding analogues, ventiloquinones. The fruit, leaves and stem give lupeol, beta-sitosterol and its glucoside [6]. The ethanolic extract from Rhang Dang leaves exhibited a strong antioxidant activity and prevented hemolysis.

***Botanical Classifications***
*Tracheophyta*
*Magnoliopsida*
*Rosales*
*Rhamnaceae*
*Ventilago*
*Ventilago denticulate*

Figure 1: *Ventilago denticulata Willd*

In the present study, the green synthesis of silver nanoparticles from the *Ventilago denticulata* Willd leaf extract has been carried out and characterized by UV-Vis spectra, SEM, EDX, XRD, TEM, and FTIR analysis.

**2. Materials and Method**

All chemicals and reagents had analytical grade. Silver nitrate, n-hexane with high purity purchased from Sd Fine/Merck India Chemicals, India.

**2.1 Apparatus and Instruments:** The conventional Soxhlet extraction apparatus was used, which consists of a condenser, a Soxhlet chamber, and an extraction flask. The extractor thimble was permeable one with 44 mm internal diameter and 200 mm external length. The rotary evaporator was used for evaporation of solvent of extracted material.

**2.2 Sampling and extraction**

***Plant Material*:** Fresh roots of *Ventilago denticulata* Willd leaves in bulk collected in the month of August 2012 from Nallamala Forest area, Andhra Pradesh. Fresh leaves collected in bulk, cut in to small pieces washed and dried in sunlight for one month completely to eliminate surface moisture. Then leaf powder packed into envelops and kept in oven at 55$^{o}$C temperature for further dryness. Dried material was grinded separately in a mortar obtained fine powder and sieved; which was then kept in plastic bags for further use.

***Preparation of plant extract:*** A bout 150 g of leaf powder dipped into a beaker containing 200 ml acetone to remove chlorophyll and stirred at 2000x speed on magnetic stirrer. After that the leaf powder was filtered

using Whatmann filter paper and filtrate was collected and dried in an air over for half an hour at 50°C. The dry leaf powder material passed through sieve (100μ). The coarse powdered drug (100 grams) was extracted in Soxhlet apparatus for 48 h with n-hexane as a solvent (2L), the extract obtained was concentrated under reduced pressure in rotatory evaporator below 60°C temperature to get semisolid sticky light green residue (15 gm). Then the filtered extract was stored in refrigerator at 4°C for further use in synthesis of silver nanoparticles.

**2.3 Synthesis of AgNPs (SNPs):** The synthesis of silver nanoparticles was done by mixing *Ventilago denticulata* Willd leaves extract and 1 mM of aqueous silver nitrate solution ($AgNO_3$) in the ratio 1:20 added to plant extract ethanolic solution and heated at 80 ± 2°C until the colour of the solution was changed from colour less to thick brown (Figure 2). Resulted solutions were settled for 24 hours in dark to avoid any further photochemical reactions, after that the solution was centrifuged at 5000 rpm for 10 minutes with magnetic shaker. The supernatant was discarded and the pellet was air dried in the incubator.

The bioreduction of $Ag^+$ ions was monitored by periodic sampling by the UV spectrophotometer. The AgNPs in the freeze-drying bottle were suspended in ultrahigh purity water for all characterization methods and antibacterial assays. During biosynthesis of silver nanoparticles when stem extract was added to 100 ml of 1 mM $AgNO_3$ salt, the ionization took place as follows:

$$AgNO_3(aq) \leftrightarrow Ag^+(aq) + NO_3^-(aq)$$

$$e^- + Ag^+ \rightarrow Ag^o$$

It is assumed that the silver ions enter inside the plant cell via the $H^+$ATPase protein embedded in the thylakoid membrane by an electro genic pump. Synthesis of silver nanoparticles is a photochemical reduction reaction.

**2.4 Characterization techniques**

- UV–visible spectroscopy: The formation of dark brown color during the synthesis was confirmed as the formation of AgNPs. The reduction of the pure AgNPs was recorded under UV–visible spectroscopy using ELico model UV–visible spectrophotometer between 300 nm and 700 nm. The UV–visible spectra of the plant leaf extract and silver nitrate solution were also recorded.
- FTIR analysis was done using Perkin Elmer Spectrum, and was used to identify the chemical constituents in the region of 400-4000 $cm^{-1}$ of the Ag-NPs
- XRD measurement: XRD measurements of Ag-NPs were cast into glass slides were done by Phillips PW 1830 instrument. The operating voltage of 40 kV and current of 30 mA with Cu kα radiation of 0.1541 nm wavelength, in the 2θ range 10- 80º, step size 0.02/θ.
- The morphology of the Ag-NPs was analyzed using an SEM. The powdered Ag-NPs were uniformly spread and sputter coated with platinum in an ion coater for 120 seconds, then observed by SEM JEOL-JSM 6360 MODEL, JAPAN). The size distribution of the nanoparticle was obtained by counting 150 particles from an enlarged SEM image. Elemental analysis of the powdered Ag-NPs was conducted using an EDX detector (EDS, EDAX Inc., Mahwah, NJ, USA) attached to the SEM machine.
- TEM analysis of Ag-NPs: Sample for TEM analysis was prepared, as mentioned in IR sample preparations. The sample was first sonicated (Vibronics VS 80) for 5 minutes. Ag-NPs were loaded on carbon coated copper grids, and solvent was allowed to evaporate under Infra light for 30 minutes. TEM measurements were performed on Phillips model CM 20 instrument, operated at an accelerating voltage at 200 kV.

**3. Results and discussion**

In this study, the silver nanoparticles were synthesized and studied using the extract of the leaves of *Ventilago denticulata* Willd.

**3.1 UV-VIS Spectra analysis**

The reduction of pure $Ag^+$ ions was monitored by measuring the UV-Vis spectrum of the reaction medium at 24 h after diluting a small aliquot of the sample into distilled water.

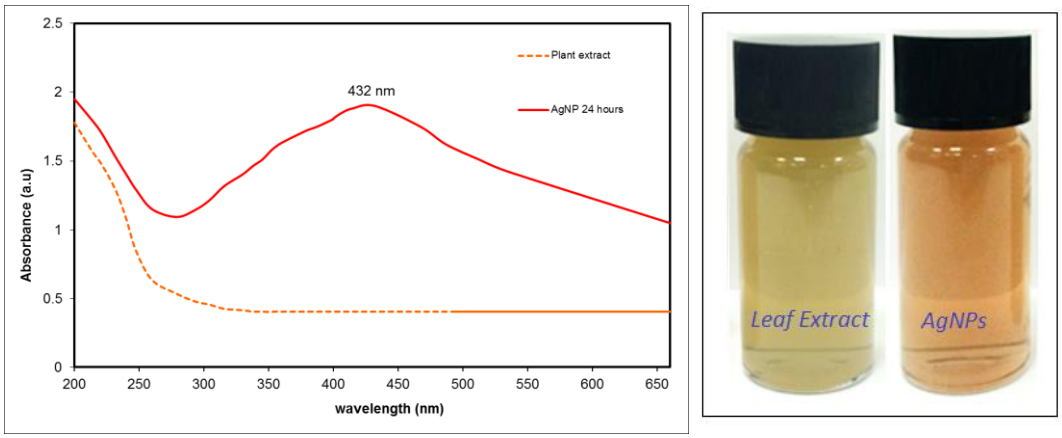


Figure 2: Silver nanoparticles before and after bio reduction ($Ag^+$ to $Ag^o$) –UV Visible absorption spectra of SNPs after bio reduction (Right side: colour change during reduction process

Figure 2 shows a set of digital images of the suspensions and the UV-Vis absorption spectra of Ag NPs. The formation of the Silver nanoparticles through the reduction of the aqueous metal ions can easily be followed by UV-Vis spectroscopy. During the process of the Ag NPs reduction, it is well-known that Ag NPs exhibit a watery-reddish color in the reaction mixture, which arises due to the excitation of surface plasmon vibrations in the metal NPs [7]. As the Silver nitration solution was mixed in the aqueous solution of the leaf extract, it started to change the color from green watery to reddish brown due to reduction of silver ion; which indicated formation of AgNPs.

AgNPs with complex structures usually exhibit more than one peak [8], whereas spherical particles show only one size-dependent SPR peak [9]. As shown in Figure 2 (left), the spectrum of Ag NPs in aqueous solution displays one band at 432nm that might indicate the information of spherical AgNPs and this band (432 nm) could be attributed to the out-of plane dipole resonance peak [10]. In each nanorod-aggregate, the conduction electrons near each nanorod surface become delocalized and are shared amongst neighboring nanorods, which shifts the surface plasmon resonance to lower energies, moves the absorption peak to longer wavelengths and broadens the absorption spectrum.

**3.2 FT IR analysis**

In order to investigate the potential formation of bonds in the present system, the FT-IR spectra were recorded (Figure 3). Perkin-Elmer spectrometer FTIR Spectrum in the range 4000-400 $cm^{-1}$ at a resolution of 4 $cm^{-1}$ was used for the analysis. The sample was mixed with KBr crystals. Thin sample disc was prepared by pressing with the disc preparing machine and placed in Fourier Transform Infrared [FTIR] for the analysis of the nanoparticles.

The FTIR spectrum of the leaf extract of *Ventilago denticulata* Willd. is shown by Figure 3. The absorption bands at 3309, 3312 $cm^{-1}$ are associated with NH (amide) and OH (alcohol) stretching. The peak at 2948 cm−1 is associated with anti-symmetric of $CH_2$, respectively. The peak for the carbonyl group was found at 1716$cm^{-1}$. The FTIR spectrum of silver nanoparticles is also shown in Figure 3. The peak for -NH/-OH stretching was obtained at 3312 $cm^{-1}$. The peak at 2952 $cm^{-1}$ is associated with $CH_2$ stretching. The peak for the carbonyl group was obtained at 1692 $cm^{-1}$. The carbonyl groups proved the presence of terpenoids that are adsorbed on the surface of metal nano-sized particles by interaction through $\pi$-electrons in the carbonyl groups in the absence of sufficient concentration of chelating agents. It was also confirmed that the carbonyl group from the protein and amino acid had stronger ability to bind with metal nanoparticles or act as capping and stabilizing agents. Peaks around the values ~1384 $cm^{-1}$ (C–O stretch), ~1085 $cm^{-1}$ (C–O) which correspond to various oxygen containing functional groups, and majority of these peaks are also present in the IR spectrum of AgNPs with some minimal shifts.

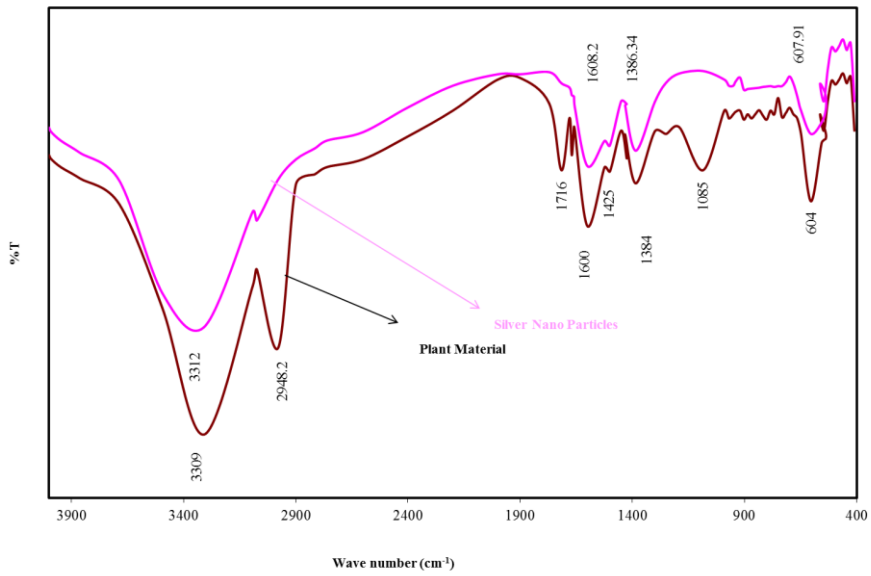


Figure 3: Comparison of the IR spectra of pure *Ventilago denticulata* Willd leaf extracts Ag NPs

**3.3 XRD Studies**: The structure of prepared ball-like silver nanoparticles has been studied by X-ray diffraction (XRD) analysis. A typical XRD pattern of the particles was shown in Figure 4. The sharp peaks in XRD pattern prove the high crystallinity of Ag nanorod aggregates. The four diffraction peaks observed 22.17°, 38.28°, 44.45°, 65.24° and 79.49° are corresponding to (111), (200), (220), (311) and (222) Bragg's reflections of the face-centered cubic structure of Ag, respectively (JCPDS ICDD 04–0783) [11]. There is no peak of other impurities being found from the pattern, which indicates pure Ag crystals were obtained under the present method. The unassigned diffraction peaks could be due to the crystallization of bio-organic phase that occurred on the surface of the biosynthesized Ag-NPs. The size of the synthesized Ag-NPs was calculated from X-ray line broadening using the Debye-Scherrer formula given as $D = 0.9\lambda/\beta \cos\theta$, where D was the average size of crystalline (Å), λ was the X-ray wavelength used (Å) in measurement, β the angular line width at half maximum intensity and θ the Braggs angle (degrees) and observed as 32 nm. Hence, the synthesized Ag was in nano size only. Other minor peaks are due to noise only.

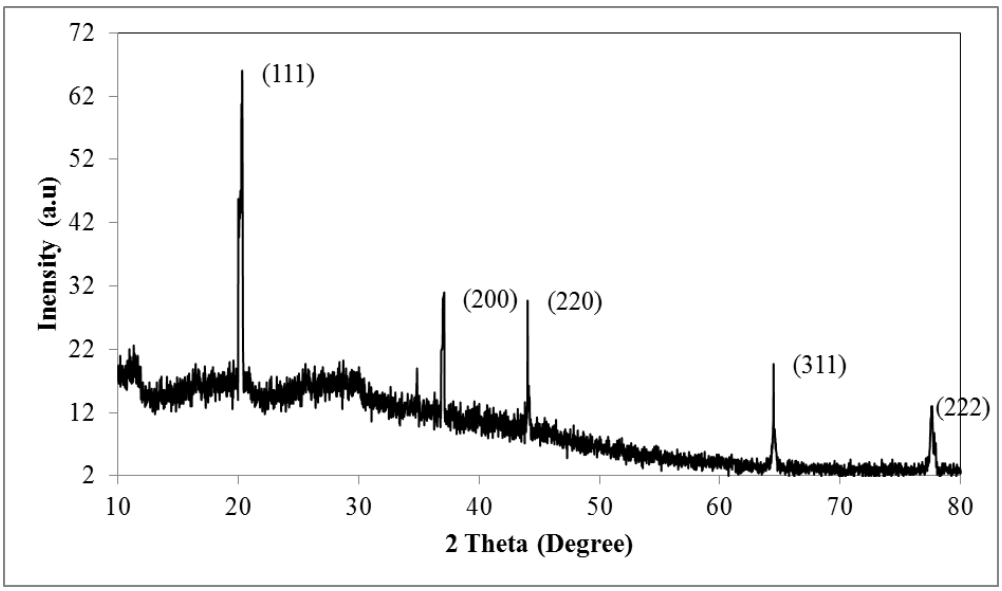


Figure 4: Representative XRD profile of AgNPs.

**3.4: SEM-EDX Studies:** The morphology and size of silver nanoparticles was revealed by scanning electron microscopic (SEM) analysis. SEM images showed that Ag-NPs have been formed and $Ag^+$ ions have been completely consumed. The SEM image showed relatively polydispersed shape nanoparticle formed with diameter range 35-40 nm. Similar phenomenon was reported by Chandran et al [13]

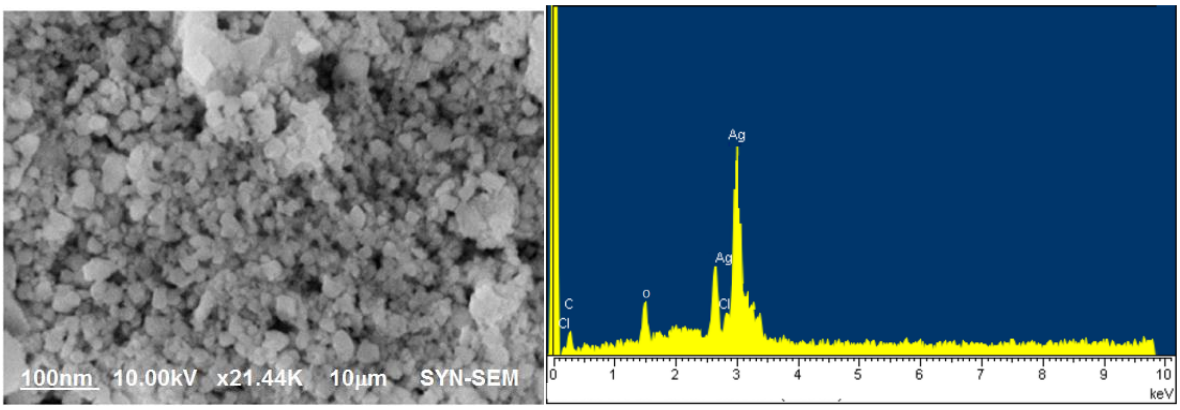


Figure 5: SEM analysis and EDX spectrum of synthesized silver nanoparticles

The elemental composition of the green synthesized sample was also determined by energy-dispersive X-ray spectroscopy (EDX), which reveals the clear elemental composition profile of the AgNPs as shown in Figure 5. The intense signal at 3 keV strongly suggests that Ag was the major element, which has an optical absorption in this range due to the surface plasmon resonance (SPR) [12]

**3.5. TEM and Particle distribution studies:** The morphology and size distribution of the synthesized AgNPs were determined by TEM analysis. The TEM image in Figure 6 shows that the particles were polydispersed and mostly spherical. The particle size from histograms for the AgNPs suggests that the particles ranged in size from 35 nm to 40 nm with an average diameter of 33.2 nm. The size distribution curve [(Figure 6 (right)] shows that the particles are in the range 15–60 nm with average particle diameter of ± 5 nm.

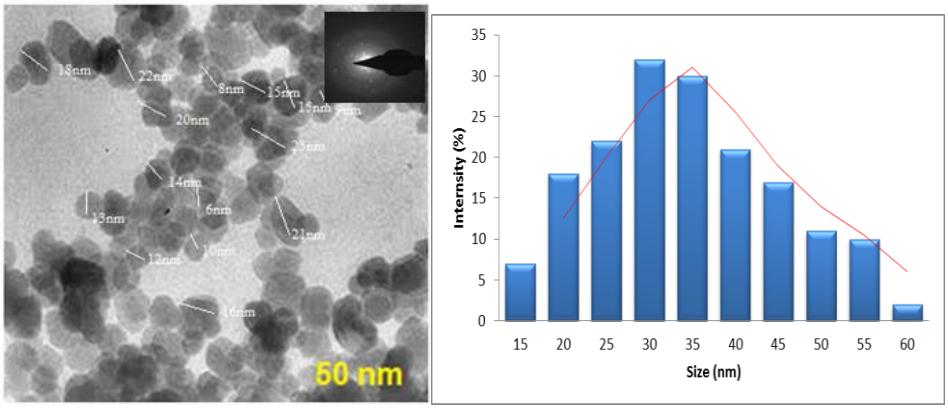


Figure 6: TEM image of synthesized silver nanoparticles (left), particle size distribution (middle) and inset picture is SAED pattern (right side*) Ventilago denticulata* Willd leaf extract

Figure 6 (inset) shows selected area electron diffraction pattern (SAED) of the silver nanoparticles. The silver particles are crystalline, as can be seen from the selected area diffraction pattern recorded from one of the nanoparticles in the aggregate. SAED spots that corresponded to the different crystallographic planes of face-centered cubic (fcc) structure of elemental silver.

**Conclusion**

In conclusion, there has been an exponentially increasing interest in biological synthesis of AgNPs. In this study, AgNPs were synthesized by an ecofriendly and convenient method using agents *Ventilago denticulate* leaf n- hexane extract at ambient temperature. *Ventilago denticulata* leaf n- hexane extract has been used as a reducing agent for the synthesis of silver nitrate into silver nanoparticles. Green synthesized

silver nanoparticles are confirmed by color change which was monitored quantitatively by UV-Vis spectroscopy at 432 nm. Further characterization with SEM and TEM analysis shows the spherical, polydisperse AgNPs of particle size ranging from 15 to 60 nm with an average size of 35 nm. FTIR showed the structure, the respective bands of the synthesized nanoparticles, and the stretch of bonds.

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