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Rapid and large-scale green synthesis of silver nanoparticles using *Ailanthus altissima* leaves extract

Akl M. Awwad[a*], Nida M. Salem[b], Qusay M. Ibrahim[a]

[a]*Department of Bionanotechnology, Royal Scientific Society, P.O. Box 1438, Tel: +9626 5344701, Fax: +9626 5344806, Amman, Jordan*

[b]*Department of Plant Protection, Faculty of Agriculture, the University of Jordan, Amman, Jordan*

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- **<u>Novelty and Highlights:</u>**

1 –Green synthesis of AgNPs using *Ailanthus altissima* leaf extract

2 – Facile approach and essentially suitable for scale-up

3 –Biomolecules of the leaves extract play as reducing and capping agent.

- **<u>Graphical Abstract:</u>**

Large scale and green method for synthesis silver nanoparticles using aqueous leaf extract of *Ailanthus altissima*.

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Article/ A. M. Awwad et. al.

Rapid and large-scale green synthesis of silver nanoparticles using *Ailanthus altissima* leaves extract

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Abstract: Large-scale and green method for synthesis silver nanoparticles using aqueous leaf extract of *Ailanthus altissima*. X-ray diffraction (XRD) and transmission electron microscopy (TEM) investigations indicate that synthesized silver nanoparticles are spherical in shape with an average diameter size of 20 nm. Ultraviolet-visible spectroscopy (UV-vis) and energy-dispersive X-ray spectroscopy (EDS) indicate the formation of silver nanoparticles with surface Plasmon resonance (SPR) peak at 430 nm. Fourier transform infrared spectroscopy (FT-IR) spectra show the different functional groups of biomolecules of leaves participated in reduction silver ions and capping of silver nanoparticles. The particle size could be controlled by changing the quantity of leaf extract and silver ion concentration.

Key words: *Silver, Nanoparticles, Green synthesis, Ailanthus altissima.*

Introduction

Silver nanoparticles originate tremendous applications in antimicrobials, catalysis, sensors, and creams. Many approaches were developed for the synthesis of silver nanoparticles such as electrochemical, chemical reduction, and thermal decomposition [1-4]. These procedures have many difficulties because the use hazardous materials, high energy consumption and uneconomical purification. The use of biological approaches for synthesis of silver nanoparticles has been suggested as valuable unconventional to physical and chemical methods. The synthesis of silver nanoparticles using different leaves extract of plants has been recently reported. Leaves extract of plants such as *Skimmia laureola* [5], *Grewia flaviscences* [6], *Eucalyptus* [7], *Prunus yedoensis* [8], *Dalbergia spinose* [9], *Caesalpinia coriaria* [10], *Cynodon dactylon* [11], *Ixora coccinea* [12], *Abutilon indicum* [13], *Tephrosia purpurea* [14], *Stevia rebaudiana* [15], *Ficus benghalensis* [16], *Arbutus unedo* [17], *Cissus quadrangularis* [18], *Ocimum tenuiflorum* [19], *Ceratonia siliqua* [20], *Mulberry* [21], *Coleus romaticus* [22] are used widely to produce silver nanoparticles. This work reports a simple, cost-effective approach for the synthesis of silver nanoparticles at ambient temperature with the possibility of scale-up the production of silver nanoparticles using *Ailanthus altissima* leaves extract.

The leaves of *Ailanthus altissima* tree are large, odd- or even-pinnately compound, and arranged alternately on the stem. The tree is medium-sized tree with heights between 17 and 27 meters and a diameter at breast height of about 1 meter.

Experimental

Materials silver nitrate ($AgNO_3$) was obtained from Aldrich Chemicals. Fresh leaves of *Ailanthus altissima* have been collected from different places in Jordan.

Preparation of Ailanthus altissima leaves extract The freshly *Ailanthus altissima* leaves were several times cleaned by washing using distilled water to clear the dust particles and then dried in sun to eliminate the moisture. The extract of *Ailanthus altissima* leaves was prepared by mixing of the fine cut leaves (10 g) in 400 mL of sterile distilled water. The mixture was then boiled for 10 minutes until the color of the aqueous solution changes from watery to redish-brown color. Then the extract was cooled to room temperature and filtered with Whatman No. 1 filter paper to remove the heavy biomaterials. The extract was stored at room temperature in order to be used for further experiments.

Qualitative phytochemical analysis qualitative phytochemical analysis [23, 24] of the aqueous extract of *Ailanthus altissima* leaves confirmed the presence of bioactive constituents which act as reducing, capping agent in the synthesis of silver nanoparticles.

Synthesis of silver nanoparticles (AgNPS) In one pot reaction, aqueous extract of *Ailanthus altissima* leaves was added drop by drop to 100 mL of 1mM aqueous $AgNO_3$ solution under stirring at room temperature. As soon as, *Ailanthus altissima* leaves extract was mixed in aqueous solution of silver ion complex, it starts to change color from whitish to yellowish brown and black within 1 minute due to excitation of surface plasmon resonance which indicates the formation of silver nanoparticles. Different $AgNO_3$ concentrations of 0.5, 0.8, 1, 2, 4, 6, 8, 10, 15, 20, 30, 40 and 50mM were used. The color of the solutions changed rapidly from faint yellow to stronger reddish brown color and then to black color depending on the starting $AgNO_3$ concentration. The formation of AgNPs was monitored by visual inspection and UV–vis Spectrophotometer. The silver nanoparticles obtained by were centrifuged at 10,000 rpm for 5 min and subsequently dispersed in sterile distilled water to get rid of any uncoordinated biological materials.

Characterization techniques UV-vis absorption spectra were measured using Shimadzu UV-1601 spectrophotometer. Crystalline metallic silver nanoparticles were examined by X-ray diffractometer (Shimadzu XRD-6000) equipped with Cu Kα radiation source using Ni as filter and at a setting of 30 kV/30 mA. FTIR Spectra was obtained with IR-Prestige-21 Shimaduz FTIR spectrophotometer. The size and morphology of AgNPs were examined by transmission electron microscopy SEM-JEOL 1010 operated at an accelerating voltage of 100 kV.

Results and discussion

UV-vis spectroscopy study the mixture of *Ailanthus altissima* leaves extract and silver nitrate solution was subjected to UV-vis spectra, based on the color change and the absorbance of the reaction medium was noted. **Fig. 1** showed surface Plasmon resonance (SPR) bands of the colloidal silver nanoparticles were centered at around 430 nm. In the present study, the absorption spectra of silver nanoparticles synthesized using *Ailanthus altissima* leaves extract reveals the conversion of silver ions to silver nanoparticles with almost 100% bioreduction of metal ions as evidenced by qualitative testing of supernatant after the purification of silver nanoparticles. The difference in the rate of bioreduction observed may be assign to the differences in the activities of the aminoacids and flavonoids present in *Ailanthus altissima* leaves extract. The entire reaction mixture is turned to black color, and exhibit an absorbance peak around 430 nm characteristic of AgNPs nanoparticle.

X-ray diffraction analysis The XRD pattern, **Fig. 2** indicates four distinct diffraction peaks at 2θ values of 38.43°, 44.53°, 64.67° and 77.49° indexed as (111), (200), (220) and (311) lattice planes of face centred cubic (fcc) structure of metallic silver and is consistence with JCPDS data No. 87-0720. The broadening and strong signals of pattern evinces that the products are nanosized and well crystallized respectively.

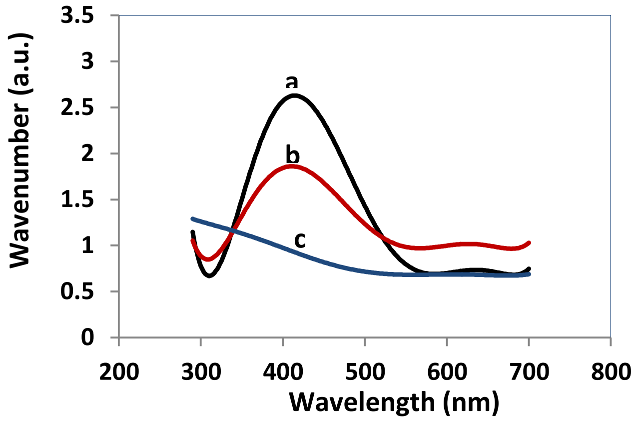

Fig. 1. UV-vis absorption spectra of silver nanoparticles as a function of time for reaction of 1mM aqueous solution: a = 1 min, b = 0.5 min, and c = *Ailanthus altissima* leaves extract.

One can calculate the values of average crystallite size (D) from XRD spectrum using Debye-Scherrer equation [16]:

$$D = K\lambda/\beta cos\theta$$

where K denotes the Scherrer's constant, λ is the X-ray wavelength, β the full-width at half-maximum of diffraction line in radian and θ is half diffraction angle. The size of the silver nanocrystallites was calculated 12 nm. The assigned peaks at 2θ = 27.52°, 31.94°, and 45.84° denoted by (*) are thought to be related to crystalline and amorphous organic phase

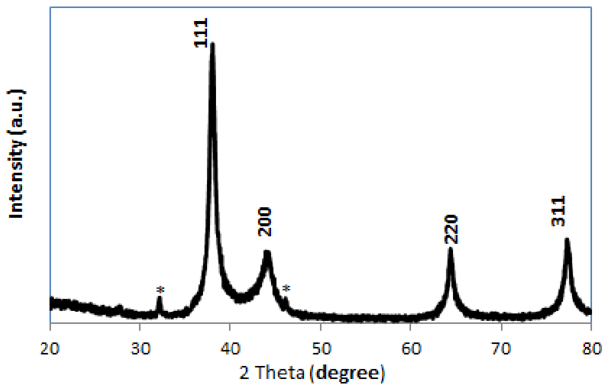

Fig. 2. XRD spectrum of biosynthesized silver nanoparticles.

Fourier transform infrared (FT-IR) analysis Fourier transform infrared spectroscopy is used to identify and get an approximate identification of the possible biomolecules in plant extract are responsible for reducing, capping and stabilization of the AgNPs with the *Ailanthus altissima leaves* extract. The FT-IR spectrum obtained for *Ailanthus altissima* leaves extract, **Fig. 3** displays a number of absorption peaks, reflecting its complex nature due to biomolecules. Strong peak at 3444 cm^{-1} can be attributed hydrogen bonded O-H groups of alcohols and phenols and also to the presence of amines N-H of amide. The bands at 2920 cm^{-1} and 2854 cm^{-1} are assigned to $–CH_2$ and C-H stretching mode in alkanes. The strong peak at 1735 cm^{-1} in *Ailanthus altissima* leaves extract could be attributed to C=C stretching vibrations about C=O amide conjugated C=O of the proteins that are responsible for reducing, capping and stabilizing of AgNPs. The bands at 1616 cm^{-1} can be allocated to the stretching vibration of C-OH bond from proteins (amide I) of the leaves extract, whereas the band at 1543 cm^{-1} is characteristic of amide II. The peak at 1450 cm^{-1} is characteristic to the C-N stretching of aliphatic amines. Peaks in the region 1327 cm^{-1}, 1215 cm^{-1} and 1041 cm^{-1} may be attributed to the presence of the stretching vibrations of carboxylic acids and amino groups.

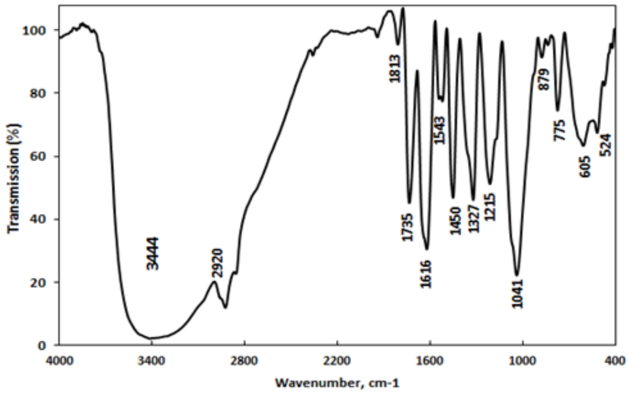

Fig. 3. FT-IR spectrum of *Ailanthus altissima* leaves extract.

FT-IR analysis of was carried out for biosynthesized silver nanoparticles by using *Ailanthus altissima* leaves extract to identify the possible biomolecules responsible for the reduction, capping, and stabilization of nanoparticles. FT-IR spectrum of AgNPs is illustrated in **Fig. 4**. Small shifts in band position with *Ailanthus altissima* leaves extract and AgNPs suggest that the nature of coordination of capping agents on different AgNPs surface.

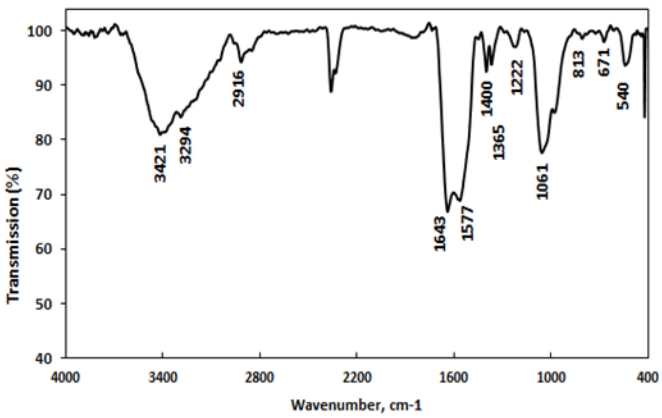

Fig. 4. FT-IR spectrum of synthesized AgNPs.

Transmission electron microscopy (TEM) images

Morphology and particles size of biosynthesized silver nanoparticles were determined by TEM image, **Fig. 5**. The silver nanoparticles synthesized by this green method were spherical in shape and with average range 20 nm. AgNPs were monodisperse with some particles of different size.

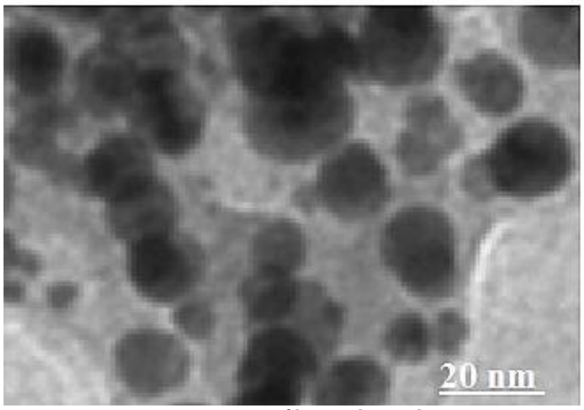

Fig. 5. TEM images of biosynthesized AgNPs

Energy dispersive X-ray spectroscopy (EDS) analysis **Fig. 6** shows the strong signal in the silver region and confirmed the formation of silver nanoparticles and suggesting the presence of silver (Ag) as a predominant element with an optical absorption peak at 3 keV due to the SPR effect.

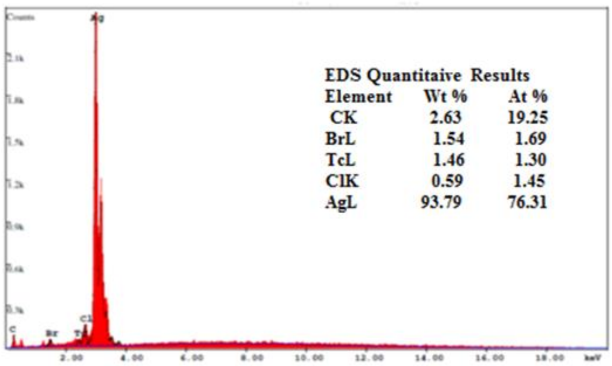

Fig. 6. Energy dispersive X-ray spectrum (EDS) of silver nanoparticles.

Conclusions

In the present study, we reported for the first time green synthesis of silver nanoparticles using aqueous leaves extract of *Ailanthus altissima* at room temperature within 1 minute. Facile and green method using *Ailanthus altissima* leaves extract for synthesis AgNPs is most suitable for scale-up, thus this method will be an alternative to whole physical and/or chemical methods. The physical property of synthesized AgNPs was characterized using UV-visible spectroscopy, XRD, TEM, EDS, and FT-IR techniques. The crystalline nature of biosynthesized AgNPs is evident from XRD diffraction peaks. The average crystallite size of nanoparticles deduced from XRD results is found to be 5-20 nm. Morphological studies showed the formation of spherical nanoparticles.

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