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Original Article

Green Synthesis of Silver Nanoparticles using Peganum Harmala Leaf Extract

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Abstract - *Nanotechnology studies 1-100 nm nanoparticles for their unique properties, enhancing material performance across fields like medicine and chemistry. They can be synthesized through various methods. However, the biological approach is the most emerging in Preparation because this method is easier than the other methods, eco-friendly, and less time-consuming. The green synthesis was done using the aqueous solution of Peganum harmala leaf extract and AgNO3. Silver was particularly interesting for this process due to its evocative physical and chemical properties. A fixed ratio (1:5) of plant extract to metal ion was prepared, and the color change was observed, proving the formation of nanoparticles. UV-Visible F.T.I.R spectrophotometers characterized the synthesized nanoparticles.*

Keywords - *Nanotechnology, Nanoparticles, Green and Synthesis, Peganum Harmala, Silver nanoparticles.*

1. Introduction

1.1. Nanoparticles

Nanotechnology is a field involving the synthesis and development of materials at the nanoscale, typically between 1-100 nm. The term "nano" indicates one billionth (10^{-9}) units. Nanoparticles, clusters of atoms within this size range, exhibit unique properties different from bulk materials due to their high surface area to volume ratio [1]. Nanotechnology, the science of small particles, enables innovative uses at the atomic and molecular levels. Its applications are expanding rapidly, particularly in material development for medical purposes. Nanotechnology involves designing, producing, and applying materials at the nanoscale to create new materials [2,16]. Pharmaceutical nanoparticles are submicron-sized drug carriers (< 100 nm) that can be bio-degradable. These particles include nanospheres, where the drug is uniformly dispersed, and nanocapsules, where a polymeric membrane encloses the drug. Metal nanoparticles like silver and gold exhibit distinct colors due to Surface Plasmon Resonance (SPR), where free electrons oscillate in resonance with light waves, causing visible and infrared SPR bands [3, 4].

1.1.1. Types of Nanoparticles

Nanoparticles can be broadly classified into two categories: organic and inorganic nanoparticles. Organic nanoparticles include carbon nanoparticles, such as fullerenes. In contrast, inorganic nanoparticles encompass various types, including magnetic nanoparticles, noble metal nanoparticles (like gold and silver), and semiconductor nanoparticles (like titanium oxide and zinc oxide) [13]. In particular, there is significant interest in noble metal nanoparticles due to their superior material properties and functional versatility. These inorganic nanoparticles are being explored for medical imaging and disease treatment because of their unique size features and advantages over traditional chemical imaging agents and drugs. They have been widely used for cellular delivery thanks to their wide availability, rich functionality, good concordance, and capabilities for targeted drug delivery and controlled drug release[5].

1.2. Silver Nanoparticles

Silver is a soft, white, lustrous transition metal possessing high electrical and thermal conductivity. It has been known longer than the recorded history due to its medical and therapeutic benefits before the realization that microbes are agents for infections. It is used in many forms, such as coins, vessels, solutions, foils, sutures, and colloids, such as lotions, ointments, etc. It is the foremost therapeutic agent in medicine for infectious diseases and surgical infections. The benefits of silver are more than the risk factors [3].

1.3. Green Synthesis

Green Synthesis is an effective method for synthesizing silver nanoparticles using plants or microorganisms. Unlike chemical and physical methods, green synthesis is environmentally friendly and cost-effective. It can be scaled up for large-scale production. It does not require high temperature, pressure, energy, or toxic chemicals[11]. Extensive literature highlights the biological synthesis of silver nanoparticles using microorganisms like bacteria, fungi, and plants due to their antioxidant or reducing properties that reduce metal compounds into nanoparticles. However, microbe-mediated synthesis is not industrially viable due to the need for highly aseptic conditions. In contrast, plant extracts are advantageous because they are easier to handle and pose fewer biohazards[15]. T. Sriram et al. synthesized silver nanoparticles using a 1mM aqueous silver nitrate solution and leaf broth of Psidium guajava as a reductant. The reduced silver ions formed nanoparticles characterized by UV-visible spectroscopy, scanning electron microscopy (SEM), and Fourier transform infrared (FTIR) spectroscopy. UV spectroscopy showed a broad spectrum at 460 nm, SEM revealed nanoparticles with diameters ranging from 0.1µm to 0.5µm, and FTIR identified biomolecules responsible for stabilization. These nanoparticles were effective against Staphylococcus aureus and E. coli [6]. Prathna et al. used an aqueous extract of Azadirachta indica leaves to reduce silver nitrate, synthesizing nanoparticles sized 10–35 nm[7]. Colloidal silver nanoparticles were also produced using thermal treatment of silver nitrate and natural rubber latex from Hevea brasiliensis, resulting in 2–10 nm spherical nanoparticles with a face-centred cubic structure [7]. M. Singh et al. studied the aggregation behavior of silver nanoparticles prepared via green synthesis using starch as a stabilizer. NaOH's presence affected starch's protection ability, leading to different aggregation behaviors. Small-angle X-ray scattering indicated nanoparticle radii ranging from 11-17 nm [8].

1.4. Local and Medicinal Uses

The plant has various local and medicinal applications. Locally, leaf extracts are used as a tonic and blood purifier, and a decoction of the leaves is employed to treat rheumatism. The plant's smoke has antiseptic properties and is used by women postpartum to alleviate uterine inflammation and stomach pain. It also serves as a repellent for pests. The seeds, in powder form, are used to treat asthma. Medicinally, the plant exhibits insecticidal properties and functions as a brain tonic. Alkaloids hermaline and harmine from the seeds are used to treat Parkinsonism. Additionally, the seeds possess narcotic, antispasmodic, lyptonic, anodyne, amusement, emetic, and emagogue properties [10].

1.5. Applications of Silver Nanoparticles

Silver nanoparticles are valued for their unique properties due to their small size and large surface area. They are used in various fields, including biosensing, catalysis, optics, and antimicrobial applications (Figure. 1). Their applications span medical imaging, nanocomposites, filters, drug delivery, and hyperthermia[6]. Silver nanoparticles are employed as antimicrobials in healthcare, food storage, textiles, and environmental applications. They attach to bacterial membranes, disrupting functions like respiration and permeability, and cause cell death by destabilizing membranes. The effectiveness of silver nanoparticles depends on their size, shape, concentration, and charge[5]. This research aims to explore the green synthesis of silver nanoparticles using Peganum harmala leaf extract and to conduct a structural study of the synthesized nanoparticles using various instrumental techniques.

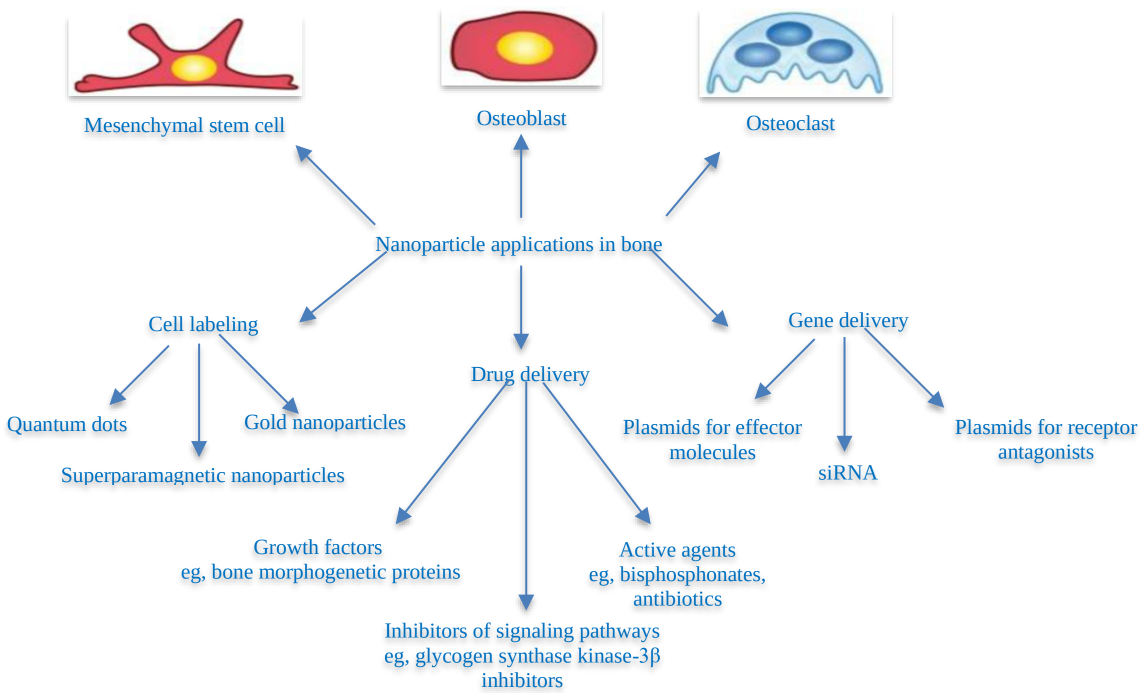

Fig. 1 Overview of Nanoparticle applications [5]

2. Materials and Methods

2.1. Materials Used

The Peganum Harmala leaves used in this study were collected from the village of Esak Chountra, Ghunde Kala, located in District Karak, Khyber Pakhtunkhwa, Pakistan, on August 21, 2021

2.2. Instrumentation

The synthesized silver nanoparticles were studied with UV-visible and F.T.I.R spectrophotometers.

2.3. Preparation of Leaf Extract

The collected samples were washed thoroughly twice/thrice with tap water to remove epiphytes and dirt particles. Then distilled water was washed to remove associated rubbish, if any.

These fresh and clean sources were shade-dried for 10 days and then powdered using a blender. About 25g of plant powder was added to 125 ml of ethanol and shacked well.

The mixture was kept for 14 days during this period, and the mixture was shacked at regular intervals. After 7 days, the mixture was filtered, and 125ml of ethanol was added to get the whole extract. The mixture was shaken at regular intervals for 7 days, filtered, and extracts were obtained[23].

2.3.1. Synthesis of Silver Nanoparticles

0.1M of aqueous solution of silver nitrate was habilitated and utilised to synthesise silver nanoparticles. 10 ml of ethanolic leaf extract of Peganum harmala was added to vigorously stirred 90 ml of aqueous solution of 0.1M silver nitrate and kept at room temperature.

Reduction occurs rapidly and is completed in 2min, as shown by the yellow color of the solution, indicating the formation of silver nanoparticles.

The mixture was then centrifuged, and the nanoparticles settled in the bottom of the centrifuge tubes. Water was then exerted out, and the nanoparticles were washed with ethanol and exerted into a china dish. Ethanol evaporated at room temperature, and the remaining nanoparticles were collected and used for further characterization [21].

2.3.2. Characterization of Silver Nanoparticles through SEM

The morphology and size of the silver nanoparticles were thoroughly examined using Scanning Electron Microscopy (SEM), explicitly utilizing the Hitachi H 7500 (Tokyo, Japan).

This analysis provided detailed insights into the shape, surface characteristics, and overall dimensions of the nanoparticles, allowing for precise characterization of their structural attributes [26].

2.3.3. General Route for Synthesis of Silver Nanoparticles using Plant Extracts

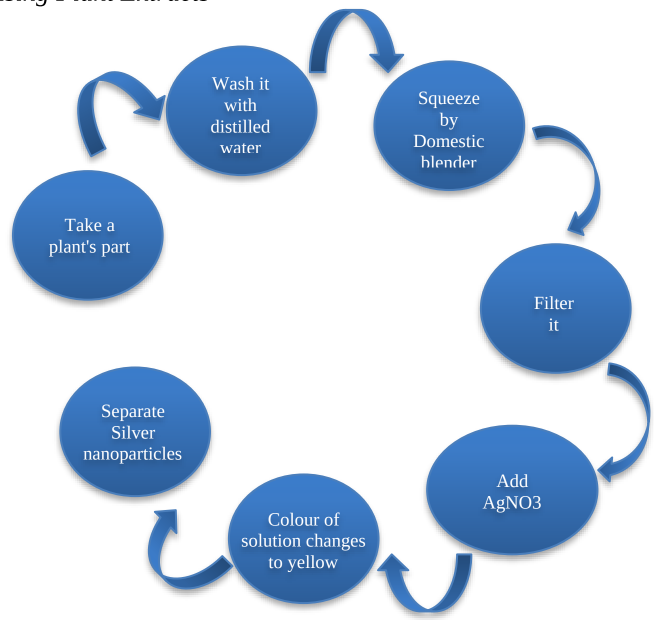

Fig. 2 Protocol for synthesis of silver nanoparticles using plant extracts

2.4. Spectroscopic Characterization Of Silver (Ag) Nanoparticles

2.4.1. UV-Visible Spectroscopy

UV-Vis spectrophotometer (Perkin-Elmer, Lambda 35, and Germany) was used to record the UV spectrum. After adding Ag NO3 to the plant extract, the spectrum was taken from 0 to 2 minutes between 350 nm to 500 nm.

2.4.2. F.T.I.R

The chemical composition of the synthesised silver nanoparticles was studied using an FTIR spectrometer (perkin-Elmer LS-55- Luminescence spectrometer). The solutions were dried at 75oC, and the powders were characterized in the range 4000–400 cm-1 using the KBr pellet method[18].

3. Result and Discussion

Plant extracts act as reducing agents for converting silver ions (Ag+) into metallic silver. Plants are sources of organic compounds that can act as ligands and attach to metal ions to stabilize them is called the Green Synthesis of metallic silver nanoparticles. In the present study, Peganum harmala leaf extract has been used as reducing potent.

3.1. UV–Vis Absorbance Study

Adding Peganum harmala leaf extract to silver nitrate (AgNO3) resulted in a color change of the solution from limpid to yellow due to the production of silver nanoparticles. The color changes arise from the excitation of Surface Plasmon vibrations (SPR) with the silver nanoparticles. The SPR of silver nanoparticles produced a peak centred near 420 nm, as shown in Figure 3.

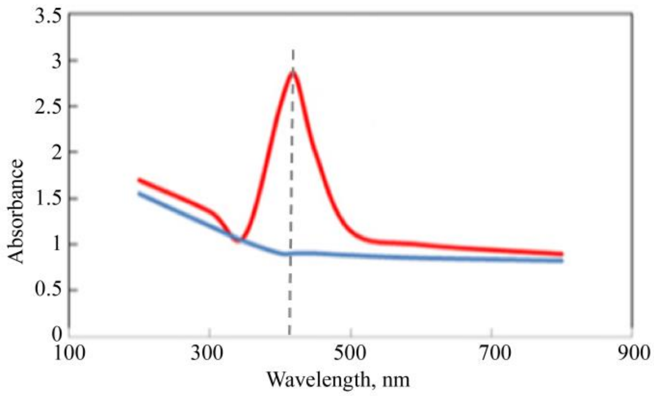

Fig. 3 UV-visible spectroscopy analysis of the silver nanoparticles

3.2. SEM Analysis

The synthesised silver nanoparticles' surface morphology and particle size were thoroughly examined using Scanning Electron Microscopy (SEM). The resulting SEM images (Fig. 4) displayed both distinct silver nanoparticles and clusters of aggregates. The individual nanoparticles were predominantly spherical, with their average size ranging from 30 to 52 nm, accompanied by observable inter-particle distances. However, some aggregation into larger particles with undefined morphologies was also apparent.

This tendency toward aggregation may be linked to secondary metabolites in the leaf extracts used during synthesis. Notably, the SEM analysis further indicated the size of some nanoparticles reaching up to 420 nm. Similar results concerning the size and morphology of silver nanoparticles have been documented in other studies employing plant extracts, such as Aloe vera (Chandran et al., 2006) [27] and Euphorbia hirta (Elumalai et al., 2010) [28], where the nanoparticles exhibited comparable dimensions and shapes produced through green synthesis methods.

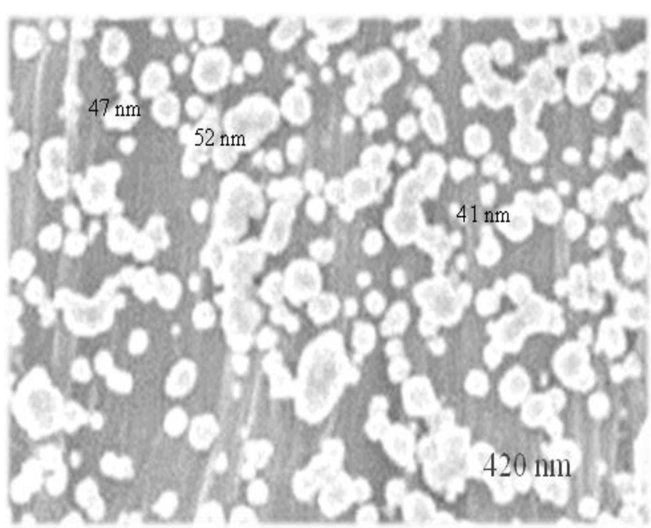

Fig. 4 SEM micrographs of the silver nanoparticles

3.3. F.T.I.R ANALYSIS

The green synthesis of silver nanoparticles using Peganum harmala leaf extract was analyzed through FTIR measurements to identify biomolecules responsible for capping and stabilizing the nanoparticles. The FTIR spectrum revealed bands between 3490-3500 cm^{-1} corresponding to O-H stretching of H-bonded alcohols and phenols, a C-H stretching band around 1500-1550 cm^{-1}, an N-H stretching band around 1450-1500 cm^{-1}, and the characteristic silver nanoparticle stretch around 500-550 cm^{-1}. These results indicate that metabolites such as terpenoids with functional groups surround the synthesized nanoparticles in Figure 5.

Similar findings have been reported in the literature; for instance, Veerasamy et al. (2011) observed comparable FTIR bands in the green synthesis of silver nanoparticles using mangosteen leaf extract, indicating the presence of biomolecules like flavonoids and terpenoids involved in nanoparticle stabilization [24]. Likewise, Ahmed et al. (2016) found that silver nanoparticles synthesized with Azadirachta indica (neem) leaf extract showed FTIR peaks for O-H and C-H stretching, suggesting the involvement of proteins and phenolic compounds in nanoparticle formation and stabilization [25]. These parallels suggest that the biomolecules present in Peganum harmala leaf extract may perform dual roles in reducing and stabilising silver nanoparticles, consistent with other studies in the field.

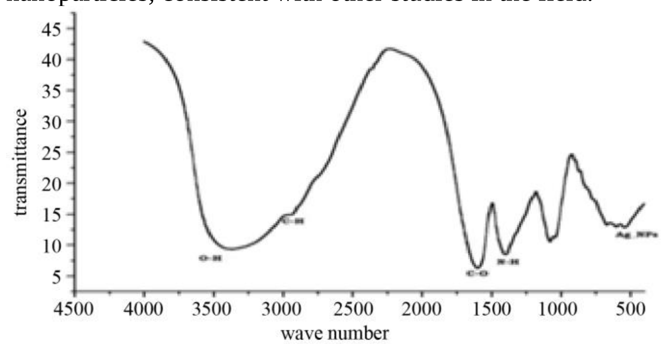

Fig. 5 F.T.I.R result of silver nanoparticles

4. Conclusion

Silver nanoparticles were successfully synthesized through a rapid and eco-friendly green synthesis method using Peganum Harmala leaf extract and silver nitrate (AgNO3). Nanoparticle formation was achieved within 2 minutes at room temperature, evidenced by a distinct color change due to surface plasmon resonance as the plant extract interacted with silver ions. A fixed 1:5 ratio of extract to metal ion was employed, and the nanoparticles were characterized using UV-visible, SEM and FTIR spectroscopy. The UV-visible analysis confirmed surface plasmon resonance, and SEM provided detailed insights into the nanoparticles' shape, surface characteristics, and overall dimensions. At the same time, FTIR spectra identified the involvement of phytochemicals in reducing and stabilizing the nanoparticles.

This study demonstrates a simple, effective, and sustainable approach to nanoparticle synthesis. However, further research is needed to identify the specific biomolecules responsible for these processes and explore the potential applications of these nanoparticles in various fields.

Author Contributions

Nasim Ullah conceived and designed the study. Aslam Khan performed most of the experiments and drafted the manuscript. Ihsan ud din helped analyze data and revise the manuscript. All authors reviewed the results and approved the final version of the manuscript.

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Conflicts of Interest

The authors declare that the research was conducted without any commercial or financial relationships that could be construed as a potential conflict of interest.

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