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Green Synthesis of Silver Nanoparticles Using Ziziphus Oenoplia (L) Root and Bark Extract: Spectral Characterization

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The synthesis of nanoparticles gained a significant demand with the development of environmentally friendly methods of generation. Nanoparticles play an important role in medicine, electronics, and catalysis. The green synthesis method employing plant extracts is increasingly replacing chemical synthesis because of its ecologically and toxicologically safer impact. The purpose of this work was to study the green synthesis of AgNPs using a Ziziphus oenoplia (L) Mill root and bark extract as a reducing and stabilising agent. The obtained nanoparticles were subjected to UV–vis, FTIR spectroscopy followed by XRD and EDX with SEM analysis. The UV-Vis spectroscopy results revealed a peak value between 400-500nm, FTIR spectroscopy different functional group formation of AgNPs, and XRD examination have a crystalline nature with an average size of 18.33nm. The results of SEM images shows that nanoparticles were most irregular and spherical in shape. Energy dispersive x-ray spectroscopy (EDX) of silver nanoparticles quantified 62.3 percentage of Ag. The results showed that Ziziphus oenoplia mill extract allowed the production of stable AgNPs with potential use in bio-medical and catalytic fields.

Keywords: Green Synthesis, Nanoparticle Synthesis, Silver Nanoparticles, Spectroscopic Characterization, Ziziphus oenoplia Extract.

1. Introduction

Nanoparticles play a significant role in pharmaceutical, biomedical, and biotechnological industries. The field of nanotechnology is rapidly expanding, impacting various aspects of human life and sparking interest across biological sciences, agriculture, biomedical research, the food industry, textiles, environmental ecosystems, and more (Zhang et al., 2020). Due to their small size, large surface area to volume ratio, and wide range of optical, chemical, magnetic, and mechanical properties, nanoparticles show promise as antibiotics, antioxidants, and anti-cancer agents (Tanase et al., 2019). Metal nanoparticles, including zinc, silver, copper, gold, platinum, magnesium, and titanium, have garnered significant attention in biological applications due to their multifunctional diagnostic capabilities (Behboodi et al., 2019). The plant-mediated synthesis of nanoparticles is increasingly valued for its low toxicity, efficiency, eco-friendliness, and short processing time (Gengan et al., 2013). Green-synthesized nanoparticles hold promise across a wide range of applications, driven by their biocompatibility, adjustable physicochemical properties, and sustainable origins (Kumar et al., 2020; Adeyemi et al., 2022). Plants offer a rich source of bioactive compounds that can help reduce, stabilise, and cap metabolites, facilitating the conversion of metal ions into nanoparticles. This approach enables the synthesis of nanoparticles with specific characteristics, such as flaviolin, polysaccharides, alkaloid amines, proteins, terpenoids, polyphenols, tannins, and aldehydes (Rajan et al., 2015). While the green synthesis of AgNPs using plant leaves has been well-studied, there remains a limited exploration of green synthesis involving wild and native plant species with biomedical applications (Waghchaure et al., 2023; Chandrasekharan et al., 2022; Shreyash et al., 2021; Jabeen et al., 2021). Ziziphus oenoplia Mill, a thorny straggling shrub belongs to Rhamnaceae family, is commonly known as Makai in Hindi and jackal jujube or wild jujube in English. This plant is native to the hotter regions of India and is traditionally used in Thai folk medicine for its anti-infectious, antidiabetic, and antidiuretic properties. Keeping in view the present study was performed by using a plant Ziziphus oenoplia The overall results revealed that investigation included spectral characterization of the compounds assessed using UV-Vis spectrometry, Fourier-transform infrared spectroscopy, X-ray diffraction, scanning electron microscopy, and energy-dispersive X-ray spectroscopy. The purpose of the research was to gain a detailed insight into the properties of the synthesised AgNPs and their possible applications.

2. Materials and Methods:

2.1 Plant collection

Ziziphus oenoplia root and bark were harvested from their natural habitat. The plant materials were immediately placed in sterilized zip lock bags and transported to the laboratory. The root and bark of the Ziziphus Oenoplia were gathered from Kothagudem, Bhadradri Kothagudem district in Telangana state and it was identified authentication its taxonomical position with the help of a taxonomist from the Department of Botany Osmania university with Voucher No: OUAS. -177. To prepare Cleanse the collected roots and bark to eliminate any dirt, soil, and extraneous material. Proceed to dry the plant material and grind it with a blender to produce a powder for extract preparation. after all soxhlet extraction method are used for crude extraction using ethanol solvent. the solvent containing the extract is siphoned once the process has finished the ethanol should be evaporated using a rotary evaporator and the extracted powder is stored for further use.

2.2 Extract preparation of silver nanoparticles:

Prepare the silver nanoparticles extract by combining 5 grams of dried powdered root and bark from Ziziphus oenoplia with 100 ml of distilled water in a conical flask, to obtain the fusion boiled at 70ºc for a 5-minute boiling process. Post boiling, double-filter the extract and store it at a temperature of 4°C for future use.

2.3 Green synthesis of silver nanoparticles(AgNPs)

To synthesise silver nanoparticles, we mixed a 5mM AgNO3 powder in 100 mL of deionised water to create the aqueous silver nitrate (AgNO3) solution at a fixed ratio. Subsequently, we combined 200µl of Z. oenoplia Mill root and bark extract with 100 ml of double-distilled water, and the solution was added and continuously stirred for 1 hour at 70°C. Afterwards, the mixture was cooled to room temperature, filtered through Whatman No.1 filter paper, and centrifuged for 2 minutes at 10000 rpm in Eppendorf tubes. Post-centrifugation, the supernatant was removed, and the pellet containing silver nanoparticles was reconstituted in deionised water. This centrifugation process was repeated three times. At the end of each centrifugation cycle, the supernatant was discarded, and the resultant nanoparticle-containing pellets were dried and stored in a sealed container.

2.4. Characterization of silver nanoparticles

2.4.1 UV-visible spectroscopic analysis: The reaction compound was subjected to verification for the reduction of silver ions and the synthesis of AgNPs using ultraviolet-visible spectroscopy. UV-visible spectroscopy (Shimadzu, Japan) was utilised to analyse the peaks of Z.o AgNPs within the wavelength range of 200-900 nm, showing a prominent absorbance peak on a UV-Vis spectrometer.

2.4.2 FTIR (Fourier transform infrared) analysis:

The FTIR spectroscopy method is based on the interaction between a sample and infrared radiation, determining the absorption/transmission frequencies and their strengths. It was utilised to qualitatively confirm the surface groups of the nanoparticles, and a spectrum was obtained using an FTIR spectrophotometer (Spectrum 65, PerkinElmer, WA, USA).

2.4.3. XRD analysis:

The XRD analysis was utilised to examine the crystalline characteristics of the nanoparticles. The average grain size of the silver nanoparticles, synthesised in an eco-friendly manner, the analysis was carried out using an Ultima IV-Rigaku diffractometer equipped with cukα radiation at 45 Kv and 30 mA, in Tokyo, Japan. was determined using the Full Width at Half Maximum formula and the Debye-Scherrer equation:

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

Where:

- D: average crystallite size (nm)
- K: Scherrer constant (K ranges from 0.68 to 2.08; K = 0.98 for spherical crystallites with irregular symmetry)
- λ: X-ray wavelength (for standard XRD, Cu Kα average = 1.54178 Å)

- β: Full width at half maximum (FWHM) of the XRD peak

The broadening of the observed XRD peak may be attributed to the crystallite size (Scherrer's formula).

2.4.3 Scanning Electron Microscopy (SEM) Analysis

The dimensions and morphology of the Z.o-AgNPs were analysed using Scanning electron microscopy (SEM), specifically the Carl Zeiss Microscopy GmbH, EVO18 model from Jena, Germany. To prepare the samples the z.o-AgNPs were dispersed in 100% ethanol through ultrasonication. The solution was then deposited onto a glass slide and left to air dry, allowing the solvents to evaporate completely. Subsequently, a thin layer of gold, approximately 3 nm in thickness, was sputtered onto the sample using a vacuum sputter coater.

2.4.4 Energy-Dispersive X-ray (EDX) Analysis

The elemental composition analysis of the biosynthesised silver nanoparticles was carried out through energy-dispersive X-ray (EDX) detection, following calibration, as outlined by Zahran et al. This EDX analysis system (Quantax 200 with X Flash® 6130) study aimed to investigate the elemental composition of the bio-synthesized nanoparticles using the dried nanoparticle powder.

3. Results and Discussion

The green synthesis of silver nanoparticles (AgNPs) utilising Z.oenoplia (L) Mill extract was notably characterised by the colour transition of the reaction from brown to colloidal brown, affirming the formation of AgNPs.

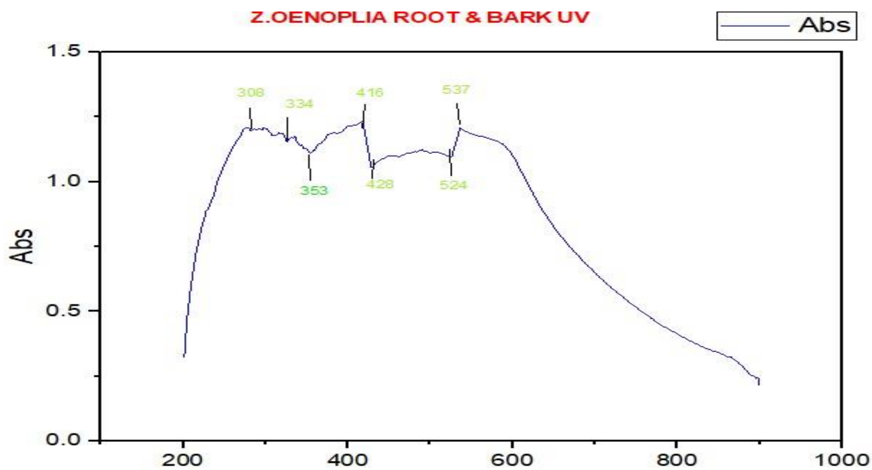

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Fig.1: UV-Vis spectrum of the synthesised Ag nanoparticles.

The peak at 418nm corresponds to the AgNPs range due to Surface Plasmon resonance (SPR) vibration excitation in the particles. The position of the SPR band in UV-Vis spectra is influenced by particle size, shape, interaction with the medium, and the extent of charge transfer between the medium and the particles. Analysis of the UV-Vis spectra revealed a broad peak at around 416 nm, indicating the green synthesis of AgNPs. These findings are consistent with the results of Roy et al. (2015) and align with observations in the literature including Oliveria et al. 2019.

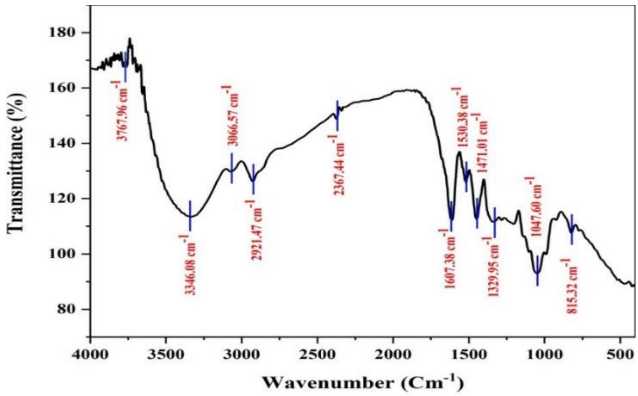

Fig.2: Fourier Transform Infrared (FT-IR) analysis of green synthetic silver nanoparticles.

Fourier transform infrared spectrum revealed the presence of distinct functional groups in above Fig.2. The FT-IR spectrum displayed peaks at 1047 cm^{-1}, 1329 cm^{-1}, 1607 cm^{-1}, 3346 cm^{-1}, and 3767 cm^{-1}, indicating specific functional groups such as primary alcohol (C-O stretching strong), alcohol (O-H medium), α,β-unsaturated ketone (C=C stretching strong), aliphatic primary amine (N-H stretching medium), and alcohol (OH stretching medium sharp) respectively (Gowmathi et al., 2017; Jain and Mehta, 2017; Singh et al., 2018).

The X-ray diffraction analysis of Fig. 3 the synthesised silver nanoparticles displayed peaks at 20.49º, 26.24º, 27.52º, 36.47º, 39.14º, 42.08º, 45.34º, 49.76º, 54.59º, 59.66º, 61.61º, and 67.89º, corresponding to planes 9.02, 66.56, 19.36, 2.70, 6.12, 9.16, 3.18, 5.02, 4.99, 6.54, 3.16, and 10.61 respectively, confirming the presence of silver nanoparticles. The average nanoparticle size was determined to be 18.33 nm (Table 1). Similar X-ray diffraction patterns were observed in silver nanoparticles synthesised using other plant extracts (Ajitha et al., 2015; Jain and Mehta, 2017; Oliveira et al., 2019).

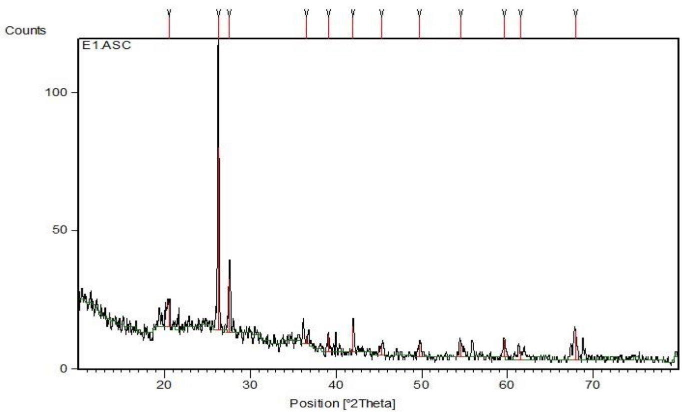

Fig.3 : X-ray diffraction patterns of fabricated silver nanoparticles annotated with Bragg peak positions.

Table.1 calculating the average size of silver nanoparticles

Pos. [°2Th.]	Height [cts]	FWHM [°2Th.]	d-spacing [Å]	Rel. Int. [%]
20.4970	9.02	0.4723	4.33311	13.55
26.2497	66.56	0.4723	3.39510	100.00
27.5223	19.36	0.4723	3.24093	29.08
36.4748	2.70	0.9446	2.46341	4.06
39.1424	6.12	0.3936	2.30145	9.20
42.0800	9.16	0.4723	2.14734	13.76
45.3467	3.18	0.9446	1.99996	4.77
49.7645	5.02	0.4723	1.83227	7.54
54.5908	4.99	0.4723	1.68115	7.50
59.6644	6.54	0.4723	1.54974	9.83
61.6127	3.16	0.9446	1.50533	4.75
67.8985	10.61	0.5760	1.37933	15.94

Average size=18.33nm

The SEM images fig. 4a, 4b of the silver nanoparticles produced using ziziphus oenoplia mill root and bark extract display predominantly spherical and irregularly shaped nanoparticles of various sizes. Within the images, clusters of AgNP are visible, likely formed due to NP aggregation during sample preparation, leading to size variations. Remarkably, the nanoparticles appear to be stabilized by a capping agent as they do not directly interact, even when aggregated. These findings align with a study conducted by Sigamoney et al., 2016.

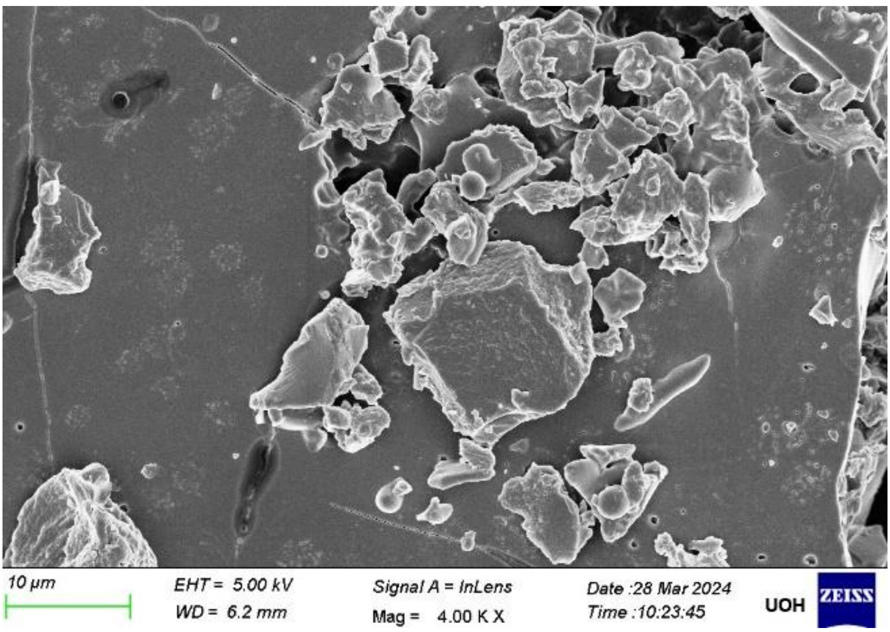

Fig.4a Shows silver Nano particles of SEM.

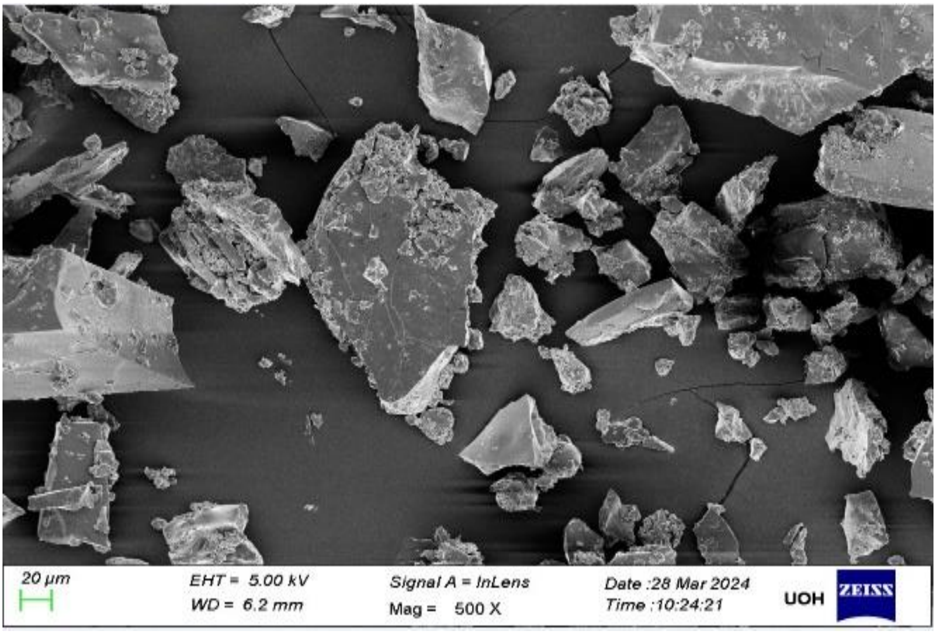

Fig. 4b SEM representation of the AgNPs showing irregular spherical shape.

The energy-dispersive X-ray analysis (EDX) of the nanoparticles is depicted in Figure 5a,5b,5c. The composition of the powdered samples was determined using a scanning electron microscope (SEM) equipped with an EDX detector. The EDX analysis identified a prominent signal in the silver region at around 2-3 keV, indicative of surface plasmon resonance. The investigation uncovered specific contaminants, such as chlorine, potassium, and trace amounts of magnesium and silicon in the spectra. These elements were crucial for stabilizing and reducing biosynthesized silver nanoparticles (AgNPs) and were linked to the organic compounds found in the root and bark extract of Z. oenoplia AgNPs. (Jagtap and Bapat, 2013)

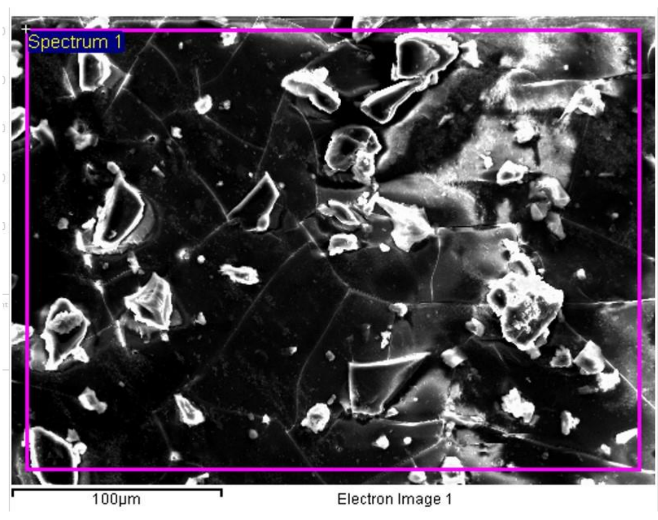

Fig.5a EDX pattern of silver nanoparticles.

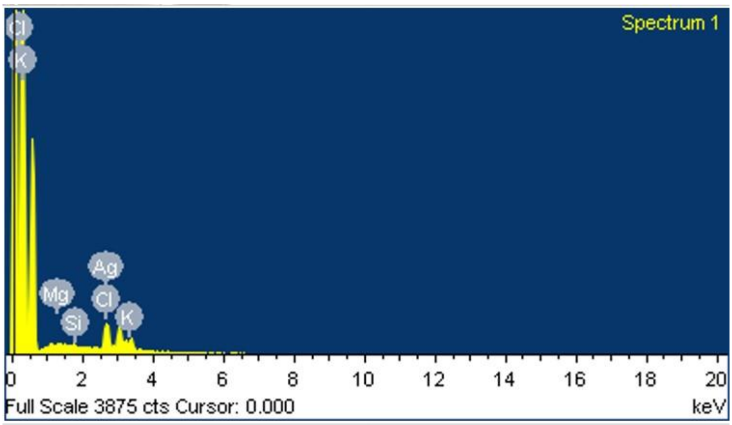

Fig.5b: EDX pattern of silver nanoparticles.

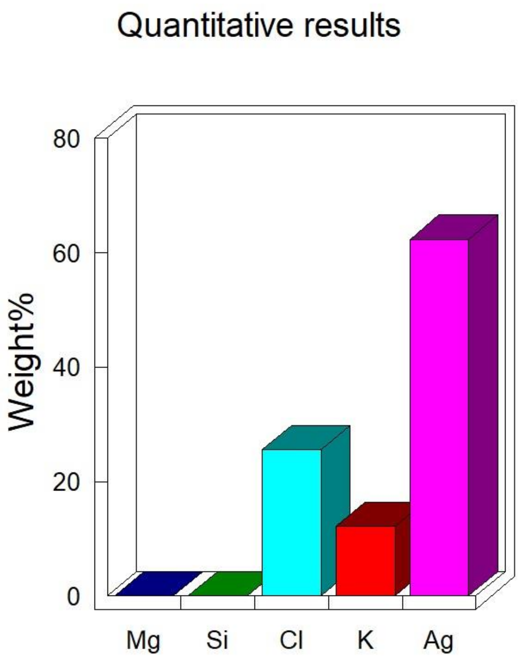

Fig.5c EDX pattern of silver nanoparticles.

In this context, the efficient green synthesis of silver nanoparticles using Ziziphus oenoplia root and bark extract was confirmed, which was possible due to the reducing and stabilizing properties of phytochemicals existing in the plant. To sum up, the green synthesis of AgNPs using extracts of Ziziphus oenoplia root and bark was successfully presented and analyzed including all-spectroscopic identification of their formation, stability, and biological activity. These results confirmed the perspectives of the field research of green nanotechnology and the potential of the development of novel efficient multifunctional nanomaterials for biomedical applications.

4. Conclusion

In conclusion, we were able to successfully synthesize AgNPs utilizing Z. oenoplia root and bark extracts for the first time through a green synthesis route. The primary objective of this method is to utilize the natural reducing and capping characteristics of the phytochemicals present in the plant extracts, providing a more environmentally friendly and sustainable alternative to the conventional chemical synthesis pathway. Through visual observation and Uv-Spectrophotometry, the colour change and major SPR peak obtained at approximately 416 nm confirmed the synthesis of AgNPs. Upon completing the FTIR test, the -OH, -C=O and -C=C- functional groups found in the plant extracts are linked to flavonoids, terpenoids, and polyphenolics, which are responsible for reducing and capping the AgNPs. Further structural characterizations of the nanoparticles, such as SEM and XRD, indicated the identical spherical shape, uniform size distribution, and crystalline nature. Moreover, the biologically synthesized AgNPs. The AgNPs also showed prominent antioxidant behaviour, which is the product of a collaborative effort between the Ag core and the bioactive phytochemicals released from the Z. oenoplia plant extracts. By achieving the final goal, the green synthesis approach produces a less environmentally damaging and financially damaging pattern while retaining the nanoparticle's biological activities. Ultimately, this study may bring about substantial progress toward sustainable nanotechnology and novel strategies in manufacturing multidisciplinary nanomaterials with extensive medicinal results.

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