Omnipotent Plant Sources Assisted Green Synthesis of Silver Nanoparticles: A Promising Chemical Sensing Tool

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Abstract: This article aims to analyze the various sensor applications of silver nanoparticles synthesized from green materials, particularly plant-based sources. The current shape in the field of nanotechnology is the synthesis of metal nanoparticles via environmentally friendly and more reliable green materials. The green route synthesis is found to be a promising method because of its congenial properties. It is economical, affable, and reproducible. Heavy metals have been dispersed widely in the environment, and they are well known for their virulent effects. Numerous methods are available to sense and detect those metals. The headway in the domain of nanotechnology is to synthesize AgNPs from green plants and to steer clear of the hazardous effects of metals. Efficacious synthetic routes via plant-mediated synthesized AgNPs open up easy and efficient sensing of hazardous metals in the environment. AgNPs have attracted many researchers because they have good biocompatibility and other outstanding properties. Remarkable electronic, catalytic, and optical properties have enabled AgNPs to be used as sensors in medical, biological, and chemical fields. This review highlights the application of PAGS-AgNPs as a chemical sensor for detecting heavy metals and organic compounds in the environment.

Keywords: Green synthesis; silver nanoparticles; plant extracts; sensor; plant material-assisted green synthesis; applications.

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1. INTRODUCTION

Nanomaterials have gained significant attention and are in high demand nowadays since they possess innate properties that deviate from the bulk. Particle dimensions ranging from 100 nm to less than 100 nm are categorised as nanoparticles. As the size of NPs decreases, a pronounced change in properties arises that makes them suitable materials that can be used in a wide variety of fields. Quantum effects and surface behaviour come into play in the above size range (1-3). A well-tunability of properties can be achieved by means of quantum effects. A researcher can fine-tune the material to bring about a drastic change in its optical and electrical properties, melting point, boiling point, fluorescence, and many others, as shown in Figure 1 (4-6). The surface-to-volume ratio also plays a crucial role in catalytic studies and sensing properties. Controlling the agglomeration of nanoparticles is crucial to maintaining the properties mentioned above. A significant lead of nanomaterials over bulk materials in various fields like biomedical, drug delivery, bioimaging, tissue engineering, DNA nanotechnology, environmental remediation, agriculture, and catalytic fields is due to their significant surface modification along with their tunable physical properties (7). Several researchers have reported different metal-based nanoparticles for several biomedical applications, environmental remediation, and catalytic functions. Attributable to their remarkable characteristics and utility, MNPs like silver, gold, and copper were mainly focused on (8-9).

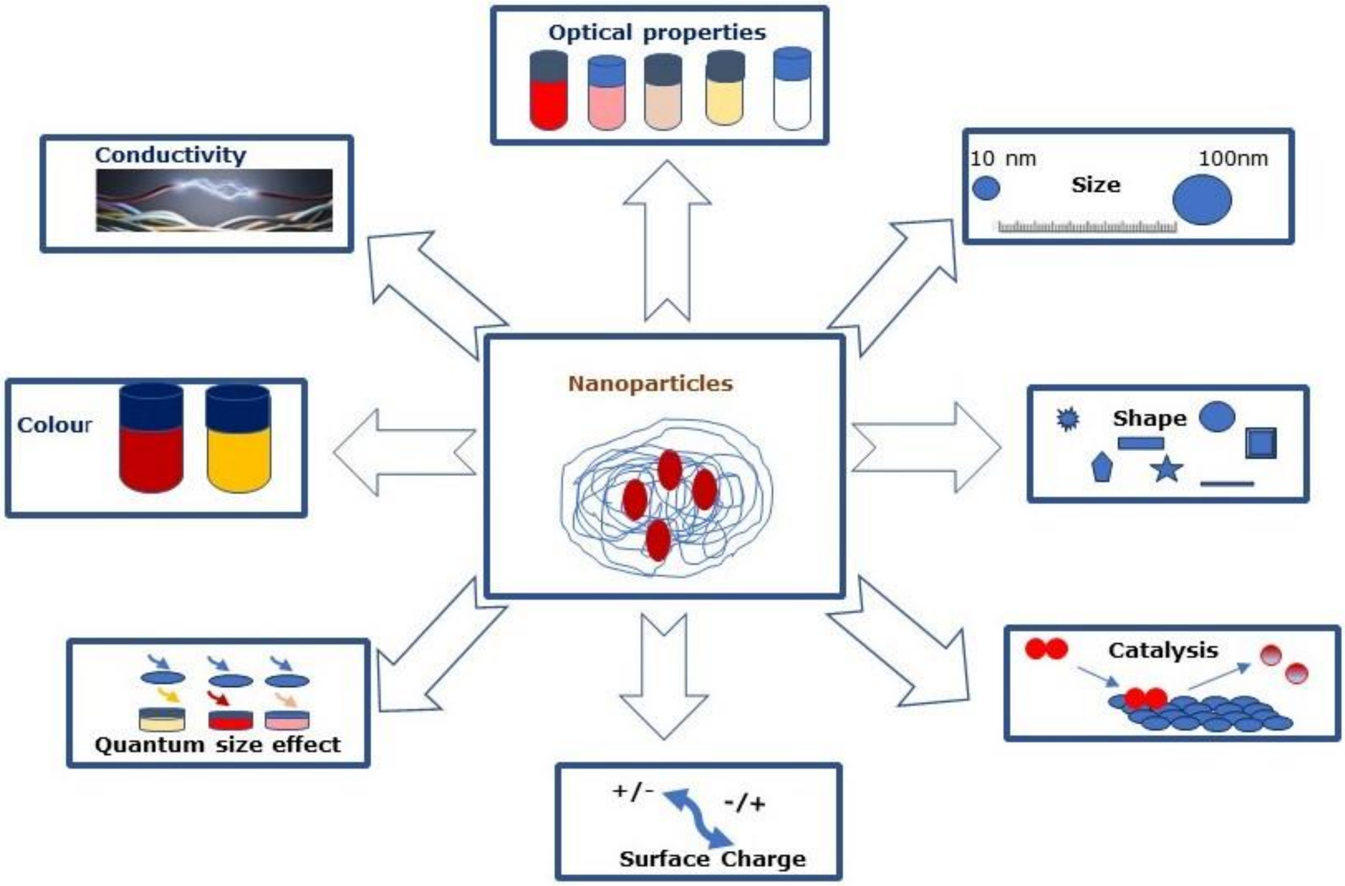

Figure 1: Properties of metal nanoparticles (NPs).

The main pathways for synthesizing nanoparticles traditionally adhered to by researchers are the bottom-up method and top–down method, i.e., building nanoparticles from molecular components by the self-assembly method and constructing nanoparticles from larger entities, respectively, as shown in Figure 2. The above-mentioned methods provide large-scale production and a well-controlled size and shape. But the negative impact of these methods is related to environmental issues and economic concerns. Furthermore, conventional methods require hazardous chemicals and solvents that cannot be used in the medical and clinical fields. To resolve this problem, researchers nowadays prefer to use green route synthesis over conventional methods. The blooming of green protocols for the synthesis of nanoparticles rebuffs the use of hazardous chemicals and solvents and the production of by-products (10-12).

The greener route is the safest and non-hazardous route for the synthesis of MNPs. It has many strategic and prospective advantages over other methods due to its eco-friendly nature and inexpensiveness. Moreover, the greener route of synthesis does not incorporate any hazardous chemicals, high temperature, or pressure. In addition, the framework and stabilization were achieved by the slow crystallization of MNPs (13). Many researchers have reported that plants seem to be the best contenders compared to microorganisms for the synthesis of MNPs on a larger scale. Various plant parts, such as fruits, stems, roots, flowers, gums, seeds, and leaves, contain numerous biomolecules that can act as reducing and stabilizing agents for the synthesis of nanoparticles at a faster rate compared to the use of microorganisms. It can also be used to produce nanoparticles of different sizes and shapes (14-15).

A miscellany of metabolites found in plants, including carbohydrates, polypeptides, terpenoids, flavonoids, enzymes, alkaloids, phenolic compounds, and vitamins, possess many vital functionalities. These functionalities serve as ligands, anchoring the organic moiety onto the NPs (16). The various plant sources used to synthesize MNPs are shown in Figure 3. The plant materials are rich in phytochemical constituents like flavonoids and polyphenols. These chemicals are natural antioxidants and can serve as reducing agents. The functional molecules within plant materials react with metal ions, initiating the nucleation step of nanoparticle formation and further assisting in the reduction of metal ions to their zero-valent state, facilitating the formation of metal NPs. The various functional, natural polymeric moieties present in the plant materials, such as polypeptide and polysaccharide units, adhere to the surface of the AgNPs as a capping agent, thus preventing the agglomeration of the nanoparticles and aiding in the stabilization of silver nanoparticles.

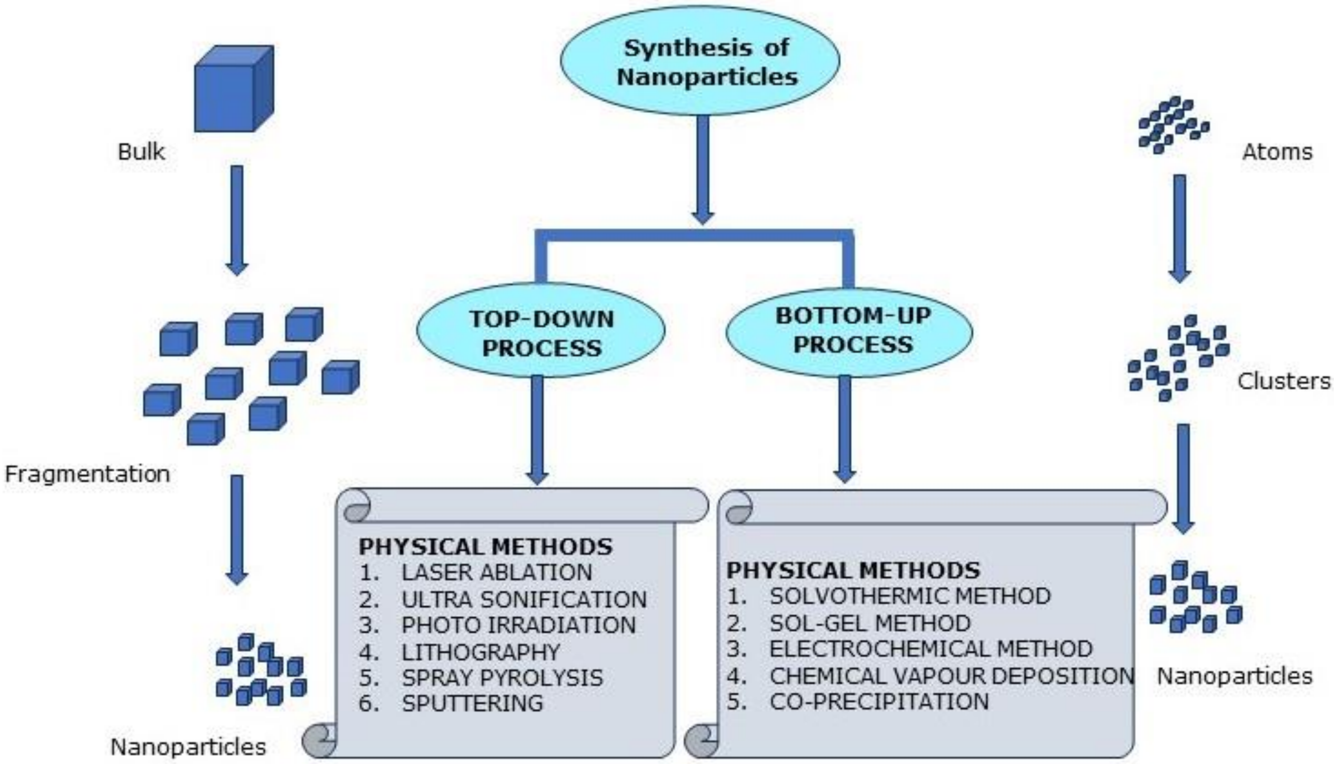

Figure 2: General methods of nanoparticle synthesis.

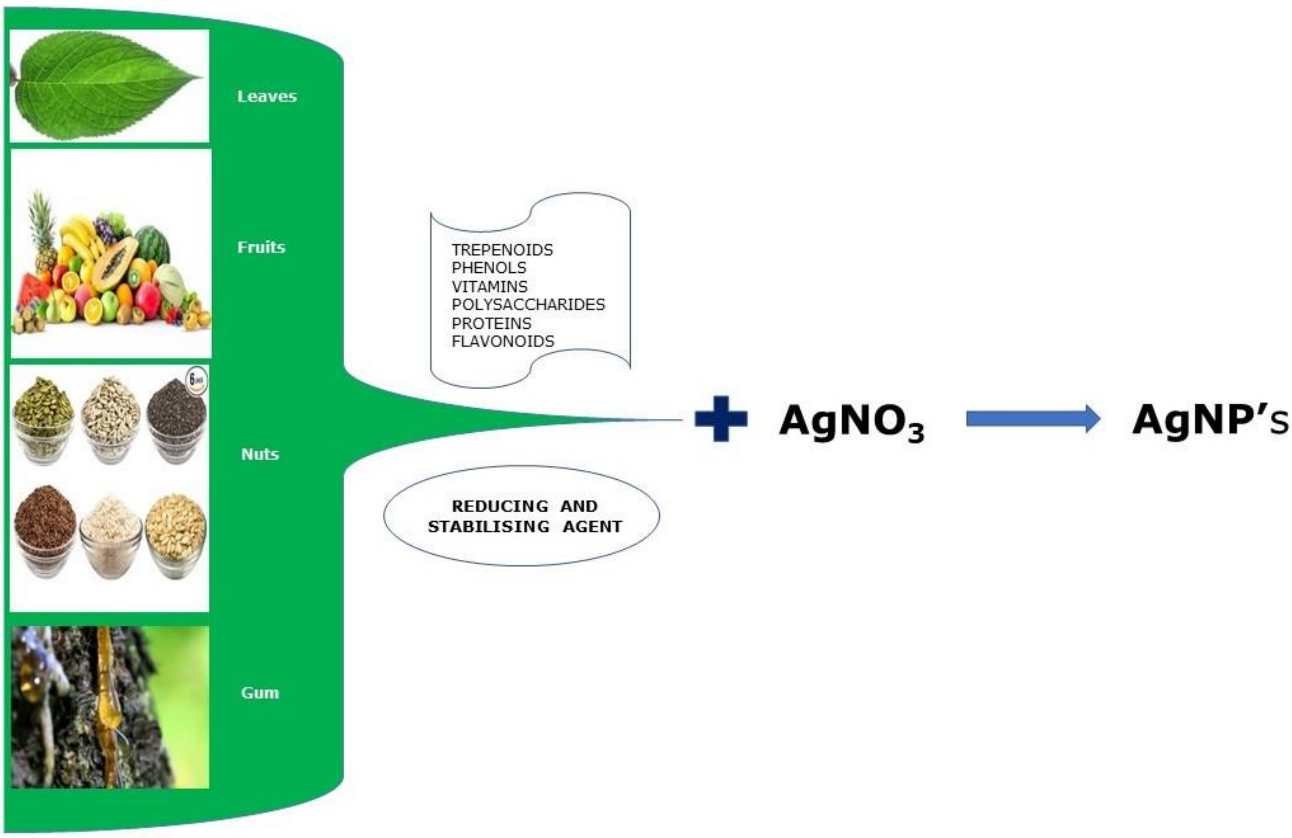

Figure 3: Various plant sources for silver nanoparticle synthesis.

This article discusses the literature based on the sensing applications of AgNPs. In particular, the plant material-assisted green synthesized AgNPs are focused. These PAGS-AgNPs serve as efficient, tiny functional materials and are used as a sensing tool. In this review, the greener route for the synthesis of AgNPs is briefly elaborated. The greener route is inclined towards the Sustainable Development Goals (SDG) because it is performed in ambient conditions and products are environment-friendly (SDG-3), cost-effective and safe (SDG-7), and fast and easy to scale up (SDG-9).

PAGS-AgNPs offer many features to serve as an excellent probing tool for sensing applications. We aimed to spotlight a few literature findings under this category. The prominent characteristics of the NPs are the surface plasmon resonance (SPR) and their absorption peak in the UV-Visible spectra. Changes in this SPR behaviour of the PAGS-AgNPs were analyzed by the researchers for the sensing of the probe. All AgNPs have a unique colour, and variation of this colour upon addition of a selective metal-ion/chemical was employed for its detection purpose. Researchers also monitored the alteration in the electrochemical characteristics of the PAGS-AgNPs by adding H_2O_2, phenol, and nitrobenzene and utilizing them for sensing applications. In the literature, PAGS-AgNPs show significant fluorescence. The FRET process in the presence of metal ions was resorted to for sensing purposes.

2. EXPERIMENTAL SECTION

2.1. Characterisation of Green Synthesised Nanoparticles

The characterization of green synthesized MNPs can be carried out using numerous techniques, as shown in Figure 4 (17-18). This article tries to enlighten us about the application of green synthesized AgNPs as sensors in various fields.

2.2. Greener Strategy for AgNPs Synthesis

MNPs have potential roles in the biomedical field, environmental remediation, food packaging, electronic components, catalytic agents, and semiconductors (19-21). Among the various MNPs available, AgNPs are found to be a fascinating nanomaterial for environmental systems and biomedical applications. It plays a crucial role in the diagnosis and treatment of viral diseases. AgNPs act as biosensors for sensing metal ions, pesticides, and fungicides in the environment. It also plays a key role in the degradation of harmful synthetic organic dyes, which are very hazardous to humans and the environment. Moreover, MNPs have been used in antiparasitic, antiviral, antifungicidal, anti-diabetic, and anticancer therapies. For wound repair and bone healing, AgNPs show bactericidal effects (22-29). Plant-based sources for AgNPs synthesis dominate the literature in the greener approach. Recent reviews based on the green synthesis of AgNPs are listed in Table 1. The various plant-based methodologies were discussed in the references therein.

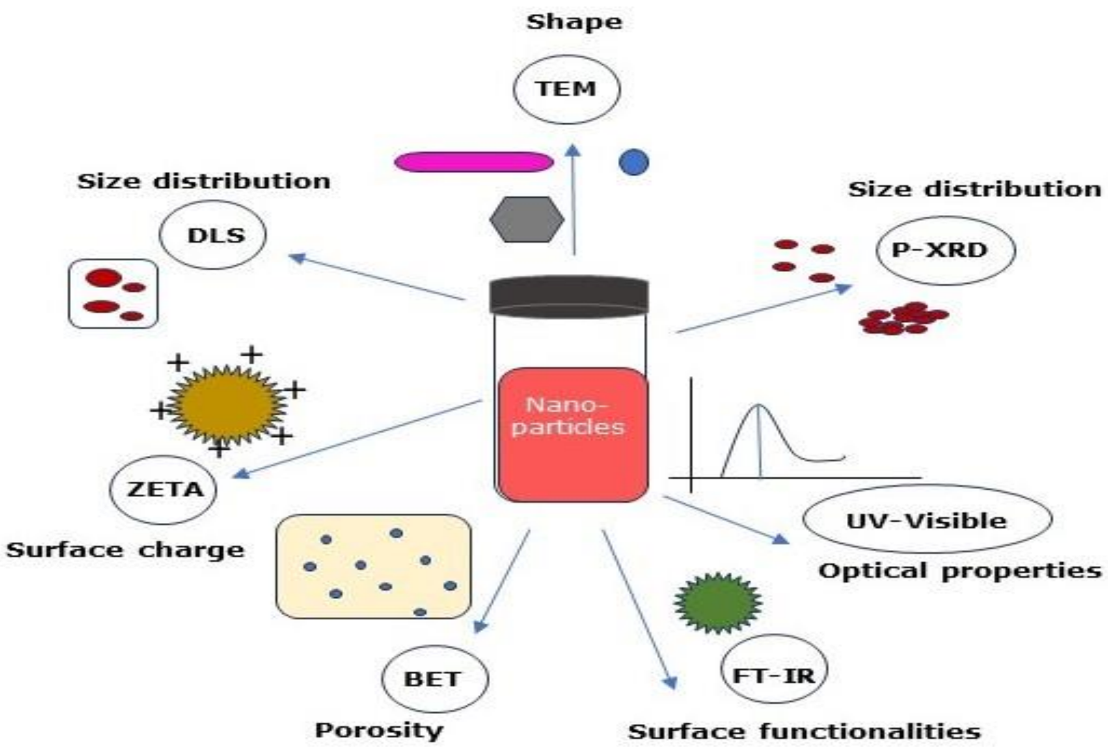

Figure 4: General characterisation techniques of metal nanoparticles (MNPs).

Table 1: Literature reviews based on the green synthesis of AgNPs.

Green synthesis methodology	Remarks	References cited therein Plant-based synthesis (total synthesis-based)	Ref.
Discussed biological approaches	Bio-medical applications Nano bio-sensors Agricultural engineering Applications in clothing and fabrics	90 (134)	30
Various biological approaches (both from plant extract and microorganisms)	Bioactivities	38 (60)	31
Major focus based on plant sources Discussed Extract preparation Steps involved Mechanism Factors	Characterization techniques Biological applications	>40	32
Discussed biological approaches	Bioactivities	78 (120)	33
Exclusively based on fruit and vegetable sources	Factors affecting synthesis	33	34

This review assessed recent advancements in the environmentally friendly synthesis of silver nanoparticles (AgNPs) and their potential applications in sensing. PAGS is reviewed exclusively due to their precise control over NPs size, shape, and composition. AgNPs are produced from various plant parts, such as leaves, roots, gums, flowers, seeds, stems, and fruits. Research has shown that biomolecules, including alkaloids, phenolic compounds, terpenoids, enzymes, co-enzymes, proteins, polysaccharides, lipids, etc., are present in the plant extract. These molecules act as both reducing and capping agents for the synthesis of AgNPs. In literature reports, the general procedure for synthesizing AgNPs is mixing silver nitrate solution with reducing agents extracted from plants. Plant extracts are obtained using the below-mentioned standard procedure Flow chart-1.

Earlier literature reports confirm the AgNPs formation by the colour change of the reaction medium to brownish or brown-orange colour (30-34). In 2022, Deepa and co-researchers reported that the presence of phenolic acid and flavonoids in the vegetable peels of pea (*Pisum sativum*) and bottle gourd (*Lagenaria siceraria*) constitutes potential functional groups contributing to the stability of nanoparticle synthesis (35). Lakshmanan et al. (2017) reported that rich concentrations of both enzyme and non-enzyme-based antioxidant molecules, including ascorbic acid, glutathione-S-transferase, superoxide dismutase, peroxidase, and polyphenol oxidase, were present in the *C. viscosa* fruit extract. Reduced glutathione, flavonoids, and a-tocopherol are present in *C. viscosa* fruit extract, which acts as a capping and reducing agents in the synthesis of silver nanoparticles (36). The study by Samrot and coworkers shows that *Azadirachta indica* gum contains complex polysaccharides that act as capping and reducing agents in the synthesis of silver nanoparticles (37). Anthocyanin-containing purple heart-shaped ornamental plant was utilized by M. Saquib Hasnain et al. in 2019. It is anticipated to help with the reduction of silver ions during the anthocyanin-mediated synthesis of silver nanoparticles (38). Manik et al. (2020) revealed that bio compounds such as flavonoids, alkaloids, and polyphenols present in the leaves of *Artocarpus heterophylus* and *Azadirachta indica* act as reducing and stabilizing agents for AgNPs synthesis (39). Sandhanasamy Devanesan et al. (2021) synthesized spherical AgNPs from Abelmoschus esculentus (L.) freshly picked flowers (40). Biomolecules such as polyphenolic compounds, catechins, flavanol, and tannins are responsible for the reduction and stability of AgNPs.

2.2.1. Stepwise procedure for plant-material assisted green synthesis (PAGS) of silver nanoparticles (AgNPs).

The step-by-step procedure used by several researchers to create AgNPs utilizing plant extracts is illustrated in Flow Chart 1.

Literature methods available in the extraction of plant material (Figure 5).

Fresh plant parts were chosen. (Step 1) 

↓

Dust and dirt are removed by washing with tap water. (Step 2) 

↓

Twice washed with deionized water to remove future impurities. (Step 3)

↓

Chosen plant parts were finely chopped and dried in shade for a few days. (Step 4) 

↓

Dried plant parts were made into fine powder using a blender or domestic grinder and stored airtight for further use. (Step 5) 

↓

The powders were dissolved in distilled water or sometimes using organic solvents. (As mentioned below in Fig.4) (Step 6) 

↓

The extract is concentrated by evaporating the solvents (Step 7)

↓

Silver Nitrate ($AgNO_3$) is stirred along with plant extract. The reaction mixture is then left alone until the colourless $AgNO_3$ transforms into a reddish-brown hue (Step 8)

↓

AgNPs formation was characterisied by several analytical studies. (Step 9)

↓

AgNPs are stored in tightly sealed vials at lower temperatures and used for further studies. (Step10)

Flow chart 1: Procedural sequence of PAGS-AgNPs synthesis.

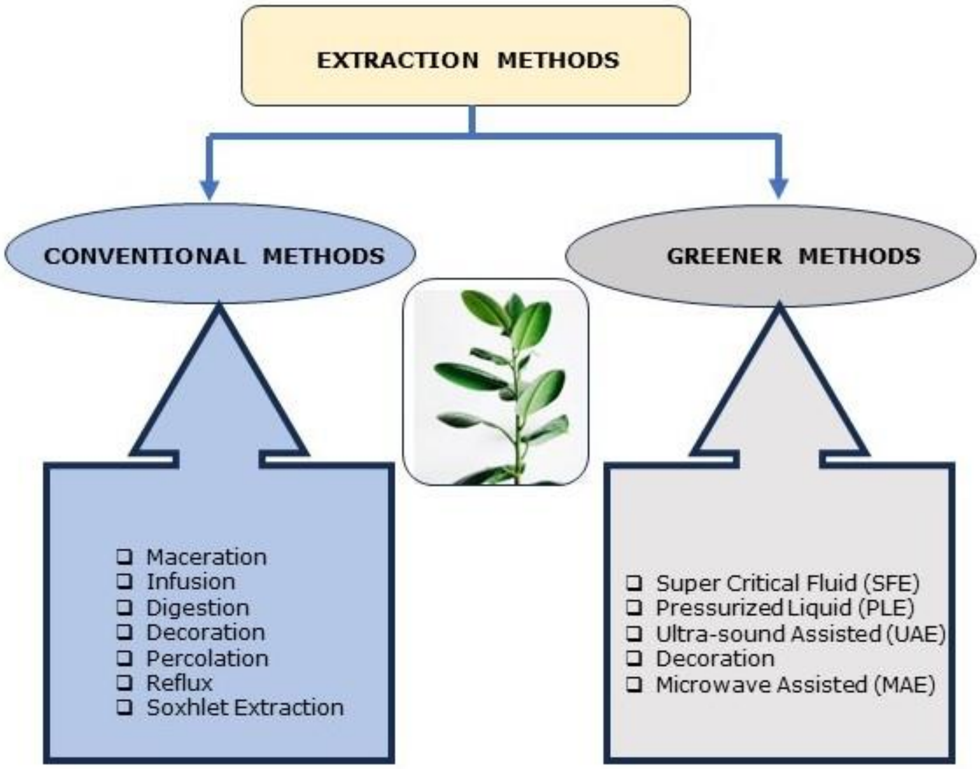

Figure 5: General plant extraction techniques.

2.3. Mechanism of Synthesis of AgNPs from Plant Sources.

Several researchers have reported a disparate variety of plant sources for synthesizing AgNPs. The phytochemical constituents act as reducing agents and stabilize the nanoparticles from agglomeration. Most literature studies show that no additional reducing agents are required (41).

The following steps are involved in the synthesis of AgNPs as shown in Figure 6.

a) Organic moieties present in the plant material add electrons to the Ag^{+}.

b) Reduction of Ag^{+} to Ag^{0} followed by nucleation, occurs.

c) The agglomerating agent present in plants stabilizes the formed nanoparticles.

The agglomeration of nanoparticles occurs due to the attraction and adhesion of particles using weak vanderwals forces. It is reported in the literature that small nanosized particles agglomerate faster compared to larger-sized nanoparticles. The phytochemical constituents in plant extract not only act as a reducing agent but also help to control the agglomeration by sticking to the nanoparticle surface.

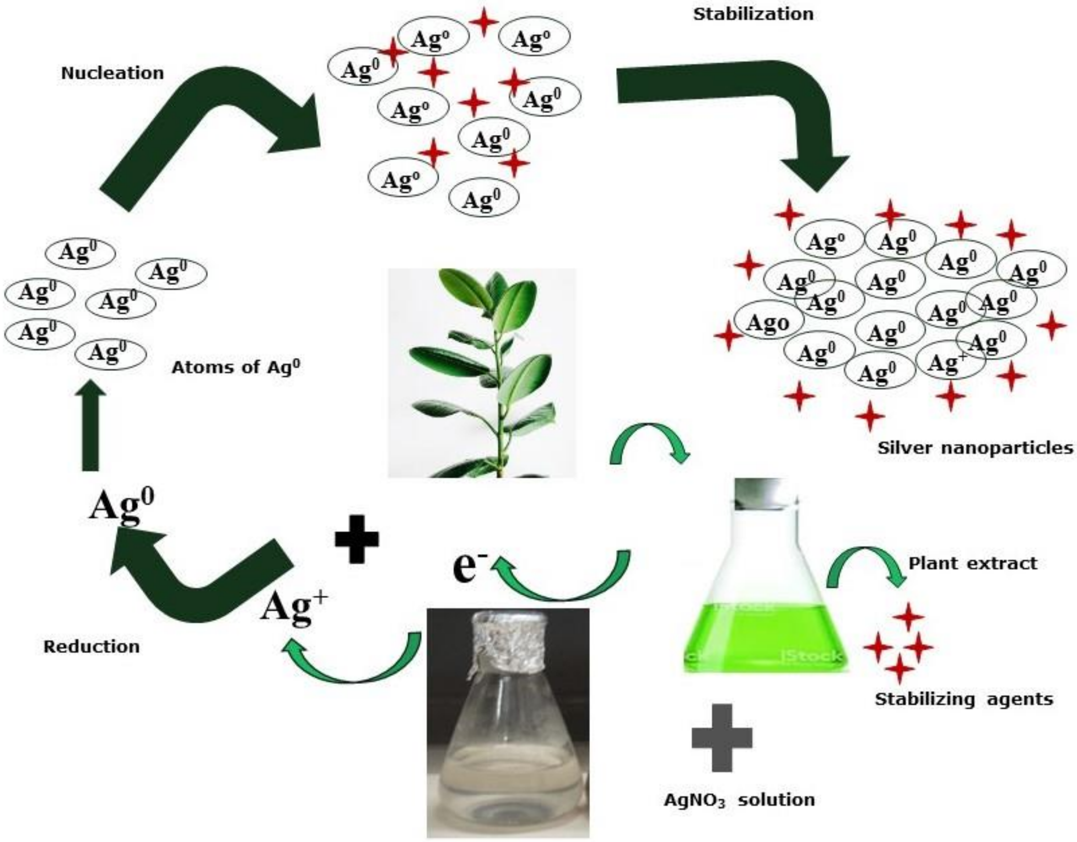

Figure 6. General mechanism for the formation of PAGS-AgNPs.

3. RESULTS AND DISCUSSION

3.1. Applications of PAGS-AgNPs

Researchers were attracted by the astounding properties of AgNPs compared to their bulk analogs and included them in numerous applications. Due to their excellent biocompatibility, size, and shape, AgNPs find their applications in the fields of solar cells, bio-sensing, image sensing, catalysis, nano-device fabrication, optical detectors, drug delivery, and so on (42-43). There have been several reviews in the past on the applications of AgNPs in various fields. A few of them are highlighted here. The author presents a bird's-eye view of the therapeutic application of green synthesized AgNPs (44). Kareem et al. (2020) shed light on the photocatalytic applications of AgNPs in a recent review (45). The review report by Mousavi et al. (2018) reveals that PAGS- AgNPs are more preferred for antimicrobial, antibacterial, and anticancer activity (46). The synthesis and application of various PAGS-AgNPs are reviewed by Jaffri and Shahzad Ahmad (47). The adaptability of PAGS-AgNPs in various medical fields was highlighted by Ill-Min Chung et al. in their review (48). A comprehensive review by Moradi et al., exclusively addressing AgNPs synthesized from medicinal plant materials and correlating plant materials and their correlation of plant biological constituents with various applications, is well presented in the literature (49). Fahimirad et al. discussed the superiority of the green synthesis method compared to physio-chemical methods and also considered it a better candidate for medical applications (50). PAGS-AgNPs applications in cancer diagnosis and treatment were exclusively reviewed by Rath et al*.* (51).

3.2. Application of PAGS-AgNPs as Sensors.

Faraday & Philos, in 1857, were the first to recognize the fact that colloidal suspension has strong light absorption and scattering, resulting in intense colors. The optical excitation of the surface plasmon resonance (SPR) originates from the absorbed light. It excites the electrons in the conduction band of the nanoparticle. This absorption attains large molar extinction coefficients and relevant scattering as the particles reach a size larger than a few hundred atoms/molecules (nanometers). This optical scattering property is utilized in biosystems for imaging detection methods and is also applied as a diagnostic tool in various biological systems, such as cancer cells. The plasmon resonance response sensitivity can be enhanced by varying the geometries with the purpose of finding the best nanoparticle configuration. The same is exemplified in many theoretical and experimental studies of metal nanoparticles.

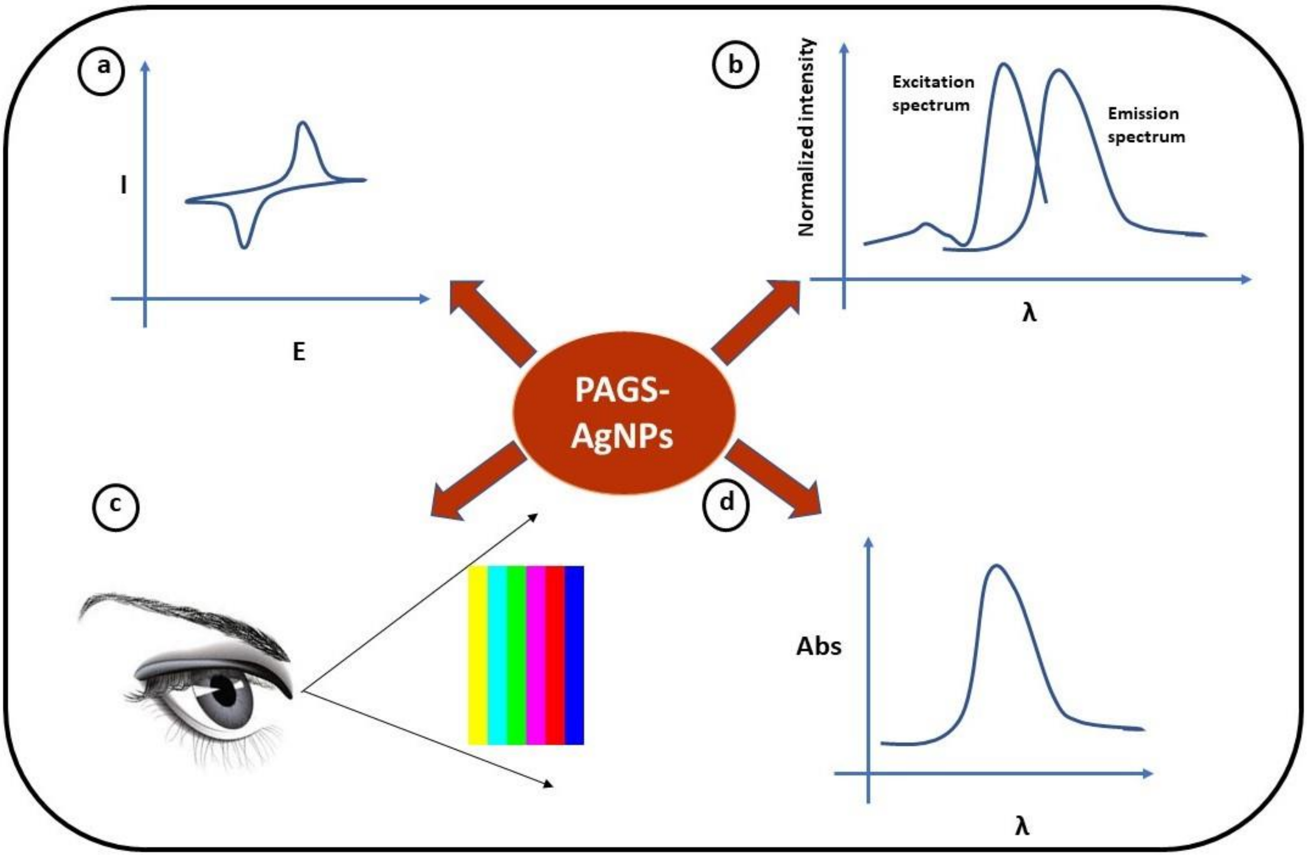

Figure 7: Scheme representing sensing methods by PAGS-AgNPs.
a) Electrochemical techniques **b)** Fluorometry **c)** Naked eye detection **d)** UV-Visible spectrometry.

The sensing application of silver nanoparticles (AgNPs) was well documented in the form of several reviews. Various modifications of electrodes for electrochemical sensing of chemicals are discussed in detail in the recent review (52). A review in 2021 highlighted AgNP-modifier-based electrochemical sensors as systematic tools for detecting various organic pollutants in water (53). The utility of AgNPs as an electrochemical biosensor is also highlighted in the review (54). Pomal et al. exclusively reviewed the sensing of mercury ions by colorimetric and fluorometric methods by PAGS-AgNPs (55). Jouybana and Rahimpour extensively reviewed the spectro-chemical sensing of pharmaceutical compounds by the LSPR of AgNPs (56). The chemical contaminants in the food are sensed by various NPs, including AgNPs, as presented in the review of 2019 (57). The focus of the current review is only on four sensing platforms for the detection of specific chemicals, which are schematically represented in Figure 7.

3.3. PAGS-AgNPs Sensor for H_2O_2 Detection.

The literature recently reported the naked-eye detection of H_2O_2 using a sucrose solution in an alkaline medium (58). Even though the synthesized AgNPs were not from a plant-mediated route, the method adopted shows a close resemblance to a plant-mediated route. Since sucrose is a plant derivative and does not violate the greener route, the utility of the AgNPs can be extended for plant-mediated routes with minor modifications. The authors analyzed the colour change based on the red, blue, and green color intensity variations. Since the AgNPs are yellow, their complementary blue color was monitored. The authors were able to show a significant change in the blue color intensity at 1 x 10^{-3} M concentration of H_2O_2, which is the detection limit in most of the literature reports. The simplified scheme for analyte detection by the colorimetric method is represented in Figure 9.

Researchers cast the cellulose fibers with AgNPs for H_2O_2 detection (59). It is an attempt to extend the plant-mediated AgNPs towards the paper-based technical application end to detect hydrogen peroxide. Literature shows that green silver nanoparticles synthesized using *Mangifera indica* leaf extracts were characterized by UV–Visible spectroscopy and TEM. These PAGS-AgNPs are drop-casted on the cellulose substrate and applied for sensing H_2O_2. The change in colour of the substrate from yellow to white upon increasing the concentration from µM to mM confirms its presence.

Researchers also successfully fabricated the optical fiber using plant-mediated AgNPs for sensing purposes (60). They also demonstrated the effect of the concentration of the anchoring agent locust bean gum (LGB) on the synthesized AgNPs absorbance, showing a decrease in the absorbance of AgNPs by increasing the concentration of LGB. They concluded that the above effect may be due to the strong capping of the anchoring agent and, consequently, the deep burying of the NPs beneath the anchoring agent, thus reducing the absorbance. The fabricated optical fiber shows effective sensing properties for H_2O_2 detection. The power output was significantly lowered by the mM concentration of H_2O_2 solution. The added H_2O_2 decreases the concentration of AgNPs, which is a consequence of oxidation and, in-turn, a decrease in the back scattering of light from AgNPs. These results open up plant-mediated AgNPs applications in the field of optical fiber-based sensing. The concentrations of H_2O_2 were measured as the output voltage of the optical fiber immersed in the AgNPs and H_2O_2 mixture. The observed results were the consequence of the degradation of AgNPs by the addition of H_2O_2 to the solution. As the NP concentration diminished, an alteration of the colour and refractive index of the medium was observed. The decrease in backscattering light intensity from AgNPs acts as a mirror, and as a result, power output also decreases. This phenomenon was utilized for the sensing purpose of H_2O_2. The utility of the environmentally friendly renewable source, ambient conditions, and its sensing features further widen the scope of green nanoparticle synthesis.

Researchers showed that the AgNPs synthesized using *Atalantia monophylla* leaf extracts show H_2O_2 sensing characteristics besides their antimicrobial activity against pathogenic microorganisms (61). The authors characterized the AgNPs by various spectroscopic techniques like Ultraviolet–Visible spectroscopy, photo-luminescence spectroscopy, SEM with EDAX, and TEM. The anchoring of the plant extract constituents was analyzed by FTIR studies, confirming the functional group on silver nanoparticles. They have also highlighted that the antimicrobial activity of AgNPs was found to be superior to that of the standard antibiotics.

Researchers also prepared stable AgNPs by using azadirachtin as an anchoring and reducing agent (62). The authors modified the glassy carbron electrode (GCE) with PAGS-AgNPs and used it for the sensing purpose of H_2O_2. The modified GCE sensitivity was retained for H_2O_2 detection for 100 days, even after exposure to air. The AgNPs attached to the GC were more stable than the unmodified NPs and the sensitivity was not diminished. The sensitivity was measured for tap water using the AgNPs-modified GC. The results showed an increase in the recovery percentage as the concentration increased. The simplified scheme for the detection of analytes by the electrochemical method is represented in Figure 8.

Researchers observed the change in optical characteristics of the colloidal AgNPs at a wavelength of 425 nm (63). The SPR decreases with an increase in hydrogen peroxide concentration. The observed phenomenon was due to the formation of Ag_2O with the addition of H_2O_2 at the expense of AgNPs. The change of colour to yellow from brownish red was observed by the addition of 30 mM H_2O_2 solution. Even the colour change was evident to the naked eye, which was further confirmed by the UV-Visible spectrometer measurements. The summary of the PAGS-AgNPs as H_2O_2 sensors is tabulated in Table 2.

3.4. PAGS-AgNPs Sensor for NH_3 Detection

In 2021, researchers reported the detection of H_2O_2 and NH_3 in water from the tannery outlet near University, Khon Kean, Thailand, using the plant-mediated AgNPs synthesized (63). The reports revealed that 2 mL of the environmental water contained 50 mM of hydrogen peroxide and 30 ppm of ammonia, respectively. The result was a significant step towards plant-mediated AgNPs for sensing hydrogen peroxide and ammonia in water resources.

In 2019, a research group used a leaf extract of *C. cneorum* in an aqueous medium to synthesize stable AgNPs (64). They drop-cast the filter paper with PAGS-AgNPs and used it for sensing purposes after drying. The changes in the surface plasmon resonance (SPR) peak of the PAGS-AgNPs were used for the detection of ammonia through the UV–Visible spectrophotometer. The authors varied the concentration of ammonia from 5 – 300 ppm, and the SPR spectra showed an increase in intensity as concentration increased, accompanied by a blue shift of the peak. The blue shift is due to the accumulation of positive charge by the formation of the coordination complex $[Ag(NH_3)_2]^+$ and also to the change in the dielectric constant of the solution.

Rapid sensing of ammonia in an aqueous medium up to a detection limit of 1 ppm at ambient conditions was published by researchers (65). AgNPs synthesized using an aqueous solution of polysaccharide from *Cyamopsis tetragonaloba*, commonly known as guar gum (GG), act as a reducing and capping agent. The uniformity of the particle size was well characterized by the available techniques. The ammonia in an aqueous medium was detected using the surface plasmon resonance (SPR) of the AgNPs. This optical method of sensing ammonia in an aqueous medium at lower limits can prove vital in the field of biomedical applications in the future. Since the sensing parameter can be useful in the clinical and medical diagnostics of ammonia detection in biological fluids like sweat, plasma, cerebrospinal fluid, and saliva, it can serve as a better sensor for biological samples. A report on optical sensing of ammonia by the PAGS-AgNPs, synthesized using chemically modified guargum (carboxymethyl guar gum), is available (66).

Very recently, researchers reported plant-mediated AgNPs for sensor studies based on the SPR properties of the nanoparticles. The synthesized AgNPs that exhibit good sensing features with quick response and relaxation are claimed to be a simple and affordable material for industrial production (67). Researchers were successful in producing monodisperse AgNPs from durian fruit shells as anchoring agents. This material, if developed, can be a future candidate in the field of sensors for the diagnostics of biological samples.

Table 2. Literature Summary of PAGS-AgNPs as H_2O_2 sensors.

Plant material	Significance / relevant property	Detection limit	Technique used	Ref
Sucrose solution	Naked eye / (RGB) color values	1 x 10^{-3} M	Colorimetric detection	58
Leaves of *Mangifera indica*	Paper based technique	Significant only above mM	Colorimetric detection	59
LBG extracted from the seeds of *Ceratonia siliqua*	Fiber based sensor	0.1 mM	Photo detector / Out voltage measured in the fiber	60
Atalantia monophylla leaf extracts	Antimicrobial activity is also studied	40 mM	UV spectroscopy (Fluorescence also measured for AgNP alone)	61
Neem kernel extract	GC electrode	1 mM	Amperometry	62
Sugarcane leaves extract	Water resource from tannery tested / SPR	30 mM	UV-Visible spectrophotometer	63

The research group used AgNPs synthesized from the aqueous fruit extract of *T. Chebul* (68). These PAGS-AgNPs showed excellent optical sensing features for ammonia detection, exhibiting linear changes in the SPR with the concentration of NH_3 in the medium. The authors highlighted the change in intensity of the peak along with the blue shift caused by the significant change in the NH_3 concentration of the medium. The authors confirmed the reduction in the size of the AgNPs from 30 nm to 50 nm in the control experiment with the addition of NH_3, using the TEM images. The reduction in the size of NPs was stated to be due to the formation of soluble diamine complexes with phenolate ions present in the fruit extract. The role of the phenolate ion is to speed up the nucleation step prior to the size reduction.

Researchers reported the viability of large-scale production of plant-mediated AgNPs using the fresh aqueous extract of *D. erecta* fruits. They used the synthesized AgNPs for colorimetric sensing of Cr^{6+} and NH_3 (69). The sensing characteristics of the AgNPs were attributed to the constituent organic moieties, such as the bulky hydroxyl groups found in polyphenols and flavonoids from the plant extracts. The SPR-based sensing showed a detection limit of 0.5 ppm and a fast response time for AgNPs. It can pave the way for sensors in the field of medical diagnostics to have lower detection limits in the future. The summary of the PAGS-AgNPs as NH_3 sensors is tabulated in Table 3.

Table 3: Literature summary of PAGS-AgNPs as NH_3 sensors.

Plant material	Detection limit (ppm)	Significance / property	Technique used	Ref
Sugarcane leaves extract	5	Water resource from tannery tested / SPR	UV-Visible spectrophotometry	63
Leaf extract *C. cneorum*	5	Sensing strip / novel cellulose filter paper-based AgNPs	Colorimetry	64
Polysaccharide GG	1	Applicable for biological fluids / SPR	UV-Visible spectrophotometry	65
Durian fruit shell extract	500	Applicable for biological fluids / SPR	UV-Visible spectrophotometry	67
Fruit extract of *T. chebula*	100	Size reduction / SPR	UV-Visible spectrophotometry	68
D. erecta fruit extract	0.5	Detection of Cr^{6+} also	Colorimetry	69

3.5. PAGS-AgNPsSensor for Phenol Detection

Very recently, researchers reported the synthesis of AgNPs using five different leaf sources, such as basil, geranium, eucalyptus, melia, and ruta by a greener route (70). Among them, AgNPs using Melia azedarach (AgNPs-M) were found to show exciting electrochemical properties, that the research group has captured toward selective sensitivity for phenol. The AgNPs-M-modified GCE electrode was used for phenol sensing. This group has fabricated the novel GCE by drop-casting the AgNPs-M onto the surface of glassy carbon transducers and using them as modified nanosensors. The AgNPs-M modified GCE showed good selectivity for sensing phenol, bisphenol A, and catechol. Particularly, the sensitivity of phenol was significant and excellent since its limit of detection is about 0.42 µM. The authors also showed reproducibility and sensitivity with the RSD values. The applicability of AgNPs-M modified GCE as a phenol sensor was also successfully tested for tap and mineral water. The test was conducted with a water sample and a phosphate buffer solution with 5–8 µM phenol added to the buffer solution. The employed modified GCE produced excellent results with a recovery percentage >100. This work has enough potential to be adopted as a sustainable large-scale production of the AgNPs-M modified GCE nanosensor since the material production is simple, cost-effective, enormously available, and environmentally friendly. The authors showed adequate results for proving the potential of the novel material as a nanosensor and with minor surface engineering, it can prove to be a future candidate for phenol sensing in water quality monitoring. The simplified scheme for the detection of analyte by electrochemical method is represented in Figure 8.

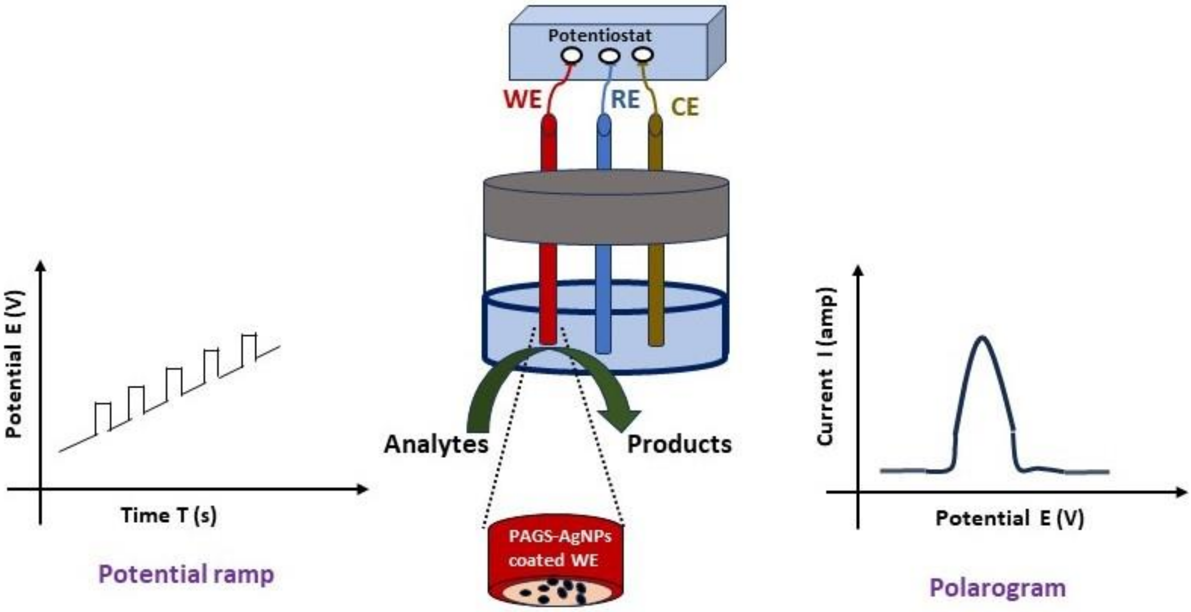

Figure 8: Scheme representing electrochemical sensing method by PAGS-AgNPs.

3.6. PAGS-AgNPs Sensor for Nitrobenzene Detection

Nitrobenzene (NB) was used as a reagent in many organic industries. The surface water gets contaminated with the NB by the release of untreated effluent from the organic industries. The World Health Organization (WHO) prescribed the limit for the concentration of nitrobenzene as 2 mg/L in water bodies, and beyond this limit, it becomes hazardous to the environment. Hence, the continuous assessment of the NB level in the environmental water becomes inevitable. Also, economically viable detection methods are the focus of the current research. In that connection, researchers reported the synthesis of silver nanoparticles (AgNPs) by microwave using a Eucalyptus extract from the bark of the tree as a reducing and stabilizing agent. These AgNPs coated on the GCE were used for the electrochemical sensing of nitrobenzene (71). Hemicellulose, present in the bark of the Eucalyptus tree, acts as a reducing agent for synthesis. The AgNPs synthesized using hemicellulose were used to modify GCE and were further utilized for sensing NB in water. The authors exhibited many advantages of AgNPs/GCE electrodes, such as good sensitivity in the range of 5–40 μM, a minimal LOD of 0.027 μM and specific detection of NB in the presence of other interfering species widely ranging from organic nature (aniline, toluene, phenol), inorganic compounds (urea) and many inorganic salts (ammonium nitrate, ammonium chloride, calcium chloride, sodium sulfate, potassium chloride, and sodium chloride). The authors also showed good recovery results for NB, which argues for the emulation of the method as the front-runner for practical applicability studies.

3.7. PAGS-AgNPs Sensor for Metal Ion Detection

Many of the heavy metals are known to be environmental contaminants. Monitoring their limits has become essential in the modern world. Their detection, particularly in water, becomes a matter of prime importance because of the ever-increasing health hazards related to them. Many research groups focus on that aspect and produce commandable results, but the search for better sensing material is still not over. Plant-mediated AgNPs are a promising candidate in this field because of their low-cost production. Plant material-assisted synthesis of AgNPs has thrown up a brand-new, environmentally-friendly pathway for metal sensing probes. *Artemisia vulgaris* mediated silver nanoparticles (AgNPs) are employed as colorimetric analyzers for mercury, a hazardous metal in an aqueous solution (72). In an aqueous solution, the Artemisia-modified reddish-brown AgNPs solution was selectively decolourized by the addition of Hg^{2+}. The color change was evident with the unaided eyes, whereas the remaining metal solution did not undergo any discernible colour change. This plant-mediated nanoparticle can serve as a probe for the sensing activity toward Hg^{2+}. It also shows an excellent catalytic-reducing property in a short time of 8 min by converting 4-nitrophenol to aminophenol. This plant mediated AgNPs is environment friendly because of its dual behaviour of Hg sensing and reduction of 4-nitrophenol. When fine-tuned, it could serve as a future material for several industrial applications.

Researchers have reported the use of an extract from *Diospyros discolor Willd* (Bisbul) leaves for synthesizing silver nanoparticles (73). Several research groups have utilized silver nanoparticles (AgNPs) as a material for sensing various heavy metals. Reports suggest that the AgNPs obtained from plant sources can be developed into materials for the detection of heavy metals in the environment. The color change of the plant-mediated AgNPs up to the addition of metal ions is utilized for detection by the colorimetric method. In the report, the presence of various metal ions, namely Mg^{2+}, Mn^{2+}, Pb^{2+}, Zn^{2+}, Co^{2+}, and Fe^{2+} was analyzed by AgNPs obtained from a biosynthetic approach using bisbul leaves, commonly known as antler orchid and it selectively detected the presence of Fe^{2+}. The report showed a solution discoloration ranging from brownish to greenish, a distinct colour change when the synthesized AgNPs were added to Fe^{2+} ion solution in concentrations ranging from 0.1 – 1000 mg/L . AgNPs agglomerate with the addition of excess Fe^{2+}. This detection method can be enhanced and refined to find Fe^{2+} metal ions in the surrounding environment. These biosynthetic AgNPs were assessed using analytical methods such as particle size analysis (PSA).

Recently, researchers used *Sapindus mukorossi* extract (SME) to produce AgNPs and applied them for effective sensing of Fe^{2+} and Fe^{3+} ions in solution (74). The detailed analysis includes various metal ion interferences in the sensing of Fe^{2+} and Fe^{3+} ions. They examined the interference by adding 1000 µM concentrations of Li^{+}, Na^{+}, Ca^{2+}, K^{+}, Mg^{2+}, Cr^{3+}, Ba^{2+}, Mn^{2+}, Ni^{2+}, Co^{2+}, Cd^{2+}, Cu^{2+}, Pb^{2+} and Zn^{2+} to 100 µM concentrated Fe^{2+} and Fe^{3+} solutions. Real-time analysis using river water and bottled water spiked with Fe^{2+} and Fe^{3+} ions was also performed. Interestingly, the presence of Fe^{2+} ions drove the AgNPs solution's SPR band intensity to rise. In contrast, the presence of Fe^{3+} ions caused it to drop, with no noteworthy changes seen for other metal ions. While the AgNPs absorption peak remained unaltered when additional metal ions were added, the addition of Fe^{2+} and Fe^{3+} ions alone caused a shift in colour to black and white, respectively, indicating the selectivity nature of SME@AgNPs towards colorimetric detection.

The reduction of any Ag^{+} in the medium by Fe^{2+} ions as well as Fe^{2+}/Fe^{3+} hydroxides to elemental silver and the Ligand to Metal Charge-Transfer process plays a major role in the red shift that occurred as the concentration of Fe^{2+} ions rises. The literature showed the AgNP could be used to sense eight metal ions in water by colour change; the sensitivity is also confirmed by the UV-visible spectrometry (75). Even though the synthetic route was not plant-mediated, it is worthwhile to mention these green-synthesized AgNPs here to gauge the future prospects of PAGS AgNPs.

Hg^{2+} and Pb^{2+} are the most hazardous contaminants in water. Their complete ignorance of usage is not possible since both of these metals play a major role in many of the industrial processes. Probing their presence and analyzing their quantity in water bodies has become highly unavoidable. Researchers have shown their potential for the detection of these two metals with low detection limits. Various literatures have highlighted the capacity of plant-mediated AgNPs as a colorimetric probe for detecting heavy metals. In that regard, AgNPs synthesized utilizing the extract from the environmentally beneficial root Bistorta amplexicaulis serve as a dual Hg^{2+}/Pb^{2+} colorimetric sensor (76). Changes in absorption spectrum of plant-mediated AgNPs were analyzed for the detection of common heavy metal cations. This report proved that the colorimetric sensor based on AgNPs could be applied for detecting Hg^{2+} and Pb^{2+} with detection limits in 0.1 mM range. The Pb^{2+} ions decrease the absorbance of AgNPs significantly, and a hypsochromic shift in the SPR band of AgNPs and the Hg^{2+} ions, causing the naked eye's detection of it by the colour change to bright yellow from dark brown, confirms its role as a colorimetric sensor. The simplified scheme for analyte detection by the colorimetric method is represented in Figure 9.

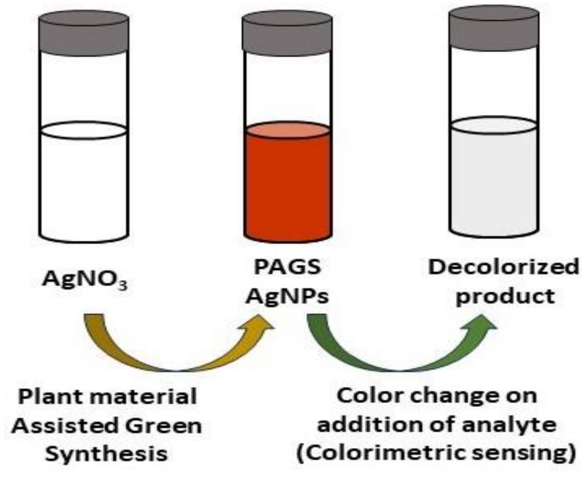

Figure 9: Scheme representing colorimetric sensing method by PAGS-AgNPs.

A gum acacia-mediated, simple, and environmentally friendly technique for generating silver nanoparticles was reported in the literature (77). The synthesized AgNPs demonstrated good sensitivity towards Hg(II) and S^{2-}. The reported plant-mediated AgNPs exhibit a fluorescence band around 500-600 nm when excited at 300 nm. The fluorescence intensity was enhanced by the addition of nano-molar concentrations of

Hg(II), which showed a downward trend by the addition of micromolar concentrations of S^{2-} ions and malachite green dye. The authors demonstrated the fluoroscence variation of the AgNPs with variations in Hg(II), S^{2-} and the dye. The results highlight the material utilized for the future development of an Ag@Hg nanoalloy. The literature reports of PAGS-AgNPs as phenol, nitrobenzene, and metal ion sensors are summarized in Table 4.

4. CONCLUSION

The remarkable features of nanoparticles have made them important in various industries. Technologies utilizing the nanoparticles have considerable potential because they can transform unstable, poorly soluble, and poorly absorbed physiologically active compounds into viable deliverable chemicals. Compared to conventional biosensors, the performance of nano-biochemical sensors is good in terms of sensitivity, selectivity, linearity, stability, response time, and repeatability. The current review offers a brief and informative overview of greener synthetic routes for the generation of AgNPs. The plant material-assisted AgNPs synthetic route is an extensive area and a complex phenomenon. This route often displays diverse behaviors, selectivity, and sensitivity. This complexity can be used as an advantage to extrapolate the research to newer limits. In the literature, many researchers used the plant material without purification for the synthesis of PAGS-AgNPs, which contains various phytochemical constituents like flavonoids, terpenoids, alkaloids, polysaccharides, polyphenols etc. The activity of a particular phytochemical residue may support or reinforce other constituents, potentially providing advantages in sensing applications and opening up opportunities for further investigations and inventions.

Plant material-assisted AgNPs were functionalized by the functionalities present in the plant materials. These functional nanoparticles offer various advantages due to their versatile characteristics:

a) In sensing applications, the functionality present on the surface of NPs plays a prominent role in determining the selectivity and specificity of the analyte detected.
b) Nanoparticles with functional moieties can easily be adsorbed on the substrate for application as a sensing probe, like electrodes, fibers, paper, etc.
c) Researchers have the advantage of experimenting with the controllables towards the size of the NPs, and as a consequence, the current LOD limits can be lowered further by varying the concentration of the plant material in the synthetic step.

The review takes the opportunity to combine various viewpoints and terminologies used in PAGS-AgNPs-based sensors towards H_2O_2, ammonia, phenol, nitrobenzene, and metal ion sensing. The literature reports cited here highlight the advantages of the respective materials, which leads to potential directions for additional advances to be investigated for future research and developments to be explored, emphasizing the challenges for PAGS-AgNPs-based flexible sensors. This review presents four sensing platforms explored by PAGS-AgNPs as sensors. UV-visible spectroscopy, calorimetry, electrochemical, and fluorescence are the four prominently used techniques by researchers in the literature. Among them, electrochemical sensing seems to be more versatile in terms of the diversity of the chemical nature of the analyte. Naked eye detection (including colorimetry and UVV spectrometry) is the simplest one, covering a wider range of publications, and its simplicity might attract many applications in the future. The fluorescence PAGS-AgNPs sensors have limited publications, but the cost-effective synthetic route has an edge over current fluorescent probes in biochemical sensors.

Table 4. Literature Summary of PAGS-AgNPs as Phenol, Nitrobenzene and Metal ion sensors.

Plant material	Detection limit	Significance / property / analyte	Technique	Ref.
leaf extracts of *Melia*	0.42 μM	Drop cast modified GCE **Phenol**	Differential pulse voltammetry (DPV)	70
Eucalyptus bark extract	0.027 μM	Drop cast modified GCE **Nitrobenzene**	Differential pulse voltammetry (DPV)	71
Artemisia vulgaris leaf extract	20–600 μL (Hg^{2+})	Catalytic activity studied	UV-Visible spectrophotometry	72
Extract of *Diospyros discolor Willd*. (Bisbul) leaves	0.1 mg /L (Fe^{2+})	Visual detection without any aid	Colorimetric detection	73
Sapindus mukorossi pericarp extract	1 μM - 5 μM (Fe^{2+}, Fe^{3+})	Visual detection without any aid	Colorimetric detection	74
Sodium citrate	1×10^{-5} M	Eight metal ions detection	UV-Visible spectrophotometry	75
Roots extract of *Bistorta amplexicaulis*	0.8 μM (Hg^{2+}) and 0.2 μM (Pb^{2+})	Dual sensor for Hg^{2+} and Pb^{2+}	Colorimetric detection	76
Gum acacia (*Acacia senegal*)	2.1 nmol L^{-1} (Hg^{2+}) 1.3 μmol L^{-1} (S^{2-}) 1.6 μM L^{-1} (Malachite green)	Dual sensor for Hg^{2+} and S^{2-}	Fluorescence spectroscopy	77

5. CONFLICT OF INTEREST

The authors have no conflicts of interest.

6. ABBREVIATIONS

MNPs – metal nanoparticles,
NPs – nanoparticles
PAGS – plant-assisted green synthesis
AgNPs – silver nanoparticles
SPR – surface plasmon resonance
GCE – glassy carbon electrode

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