

Review Article

Synthesis of Phyto Based Metal Nanoparticles: A Green Approach

Abstract

In recent years, changing material properties is gaining a significant research interest. Besides, applying the fundamentals of basic science to different applications is also more encouraged and on-demand. In this view, material science has become a common interest in various fields, starting from chemistry, physics, biology, and engineering. The common platform for all these sectors is nanoscience and nanotechnology. The main motto is changing material properties while converting it from bulk to its nano size level. The changes in properties like optical, mechanical, and others make the synthesized nanomaterials for implementation in various applications for humankind. Besides the success of this idea, the toxicity of the materials used during the synthesis becomes a question to researchers, as it hinders the sustainable development concept. If not total, a certain decrement in the toxic material utilization gives a pavement towards green technology. In this view, various researchers adopted plant materials as sources for synthesizing the nanomaterial in this decade. The present review highlights the utilization of coinage metal (Ag, Au, and Cu) salt to synthesize nanoparticles by using plant sources like leaf, bark and their characterization study along with their applications.

Key words: Nano particles, Green chemistry, Coinage metals, Plant extracts, Nano technology

1. INTRODUCTION

The application of facts for human benefit is referred to as technology. Nanotechnology is described as the study and management of matter at scales of a few hundred nanometers (nm), where unusual phenomena allow for novel applications to be developed. Nanotechnology is distinctive as it will enable us to examine and modify objects on a nanoscale. The name "nano" originated from Greek which means "dwarf." A nanometer is a SI unit of length equal to 10^{-9} or one billionth of a meter. Materials can change their entire properties from physical to biological when transformed to nano range from their bulk. These materials have an impact on all the fields of science and technology. Nanotechnology is a broad term that encompasses a wide range of subjects, from fundamental materials research to personal care applications¹. Nanotechnology is a technological-scientific platform that allows chemistry, physics, biology, biotechnology, information technology, and engineering to move to the molecular level. One can recognize the 21st century as the nanotechnology era, a rising and active area². Figure 1 shows various methods through which one can synthesize the nanoparticles. It also highlights the importance of plant-based nanoparticles along with different sources.

The applications of nanotechnology can be precious and can significantly influence society. Various industrial sectors have already enclosed nanotechnology, including food technology and energy technology, to medical products. Besides having unknown health risks, nanomaterials may also offer new prospects to reduce pollution. The standard human defense mechanisms associated with these nanoparticles may not be able to reply satisfactorily.

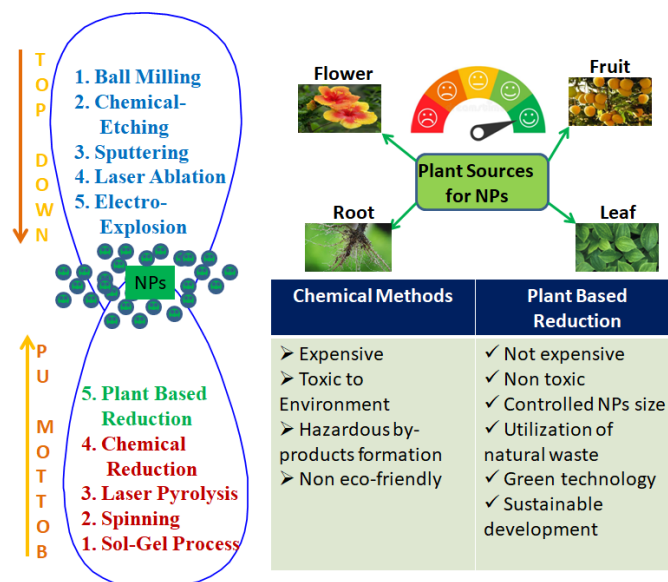


Figure 1: Synthetic routes, plant sources and merits of plant based nanoparticles (NPs)

Green nanotechnology (GN) is the application of nanotechnology to improve the ecological sustainability of processes that have a negative impact on the environment by following twelve green chemistry principles *viz.* Prevention, Designing safer chemicals, Atom economy, Inherently safer chemistry for accident prevention, Reduce derivatives, Less hazardous chemical synthesis, Safer solvents, and auxiliaries, Catalysis, Design for energy efficiency, use of renewable feed stocks, Design for degradation, and Real-time analysis for pollution prevention³. Significantly, current technology encourages the usage of nanomaterial-based products and replaces old products with more environmentally friendly alternatives throughout the product lifecycle.

Specifically, there are two critical aspects of GN. One is finding a solution to environmental challenges, and the second one is the production of environmentally safer NPs. The GN mainly aspires to invent environmentally-sustainable manufacturing processes to manage rising problems like water contamination and other areas of environmental concern.

GN advocates the use of non-toxic components in nano-products and less energy and renewable inputs whenever possible⁴. Nanotechnology-based solutions can clean hazardous waste sites, desalinate water, treat pollutants and even sense and monitor pollution better than traditional products⁵. They are also helpful for autos and other modes of transportation that conserve fuel and minimize pollution because of their lightweight nature^{6, 7}. Because of their adjustable size, shape, and surface features, nanoparticles (NPs) have gotten a lot of interest. The synthesis of NPs revealed that they could have a variety of forms, including rod-shaped, irregular, decahedral, icosahedral, and hexagonal⁸. Hence, GN is a sustainable approach to nanotechnology that aims to make all presently available processes more environmentally friendly.

2. Nanoparticles (NPs) Synthesis from Plant Extracts

The tremendous growth in nanotechnology research shows the opportunity of green chemistry to manufacture plant (Phyto) based nanomaterials. Even though microorganism-based materials have environmental sustainability, they have difficulty maintaining culture and cost-effectiveness⁹. Hence plant mediated NPs synthesis has several advantages. Plant-mediated NPs (also known as Green synthesis) has recently got a lot of attention because of their wide range of applications and Physico-chemical characteristics. Green synthesis offers the advantage of being environmentally friendly as well as often results in stable materials. Chemical reduction, sol-gel, and other methods for NPs synthesis are available. Unfortunately, these technologies involve hazardous chemicals, demand a lot of energy, and produce toxic waste. Plants are known as chemical factories of nature and produce different compounds with little maintenance. Proteins, flavonoids, polyphenols, terpenoids, and other phyto-compounds found in plant extracts operate as reducing and capping agents. The compounds present in the plant extract play an essential role in lowering precursor salt to get desired NPs. Plant extracts can make NPs, which is a feasible and straightforward alternative to chemical methods. Gold (Au), Silver (Ag), Platinum (Pt), Copper (Cu), Nickel (Ni), and Titanium oxide (TiO₂) have all been synthesized by using different natural resources and extensively investigated¹⁰.

Several studies reported that the plant materials such as stem, root, fruit, seed, peel, leaves, and flower are used to develop metallic NPs¹¹. The extraction procedure is typically carried out at room temperature, with water or organic solvents being utilized depending on the type of phytochemicals required. Different factors like plant extract, metal precursor, reaction duration, and even extract and precursor concentrations are the influencing parameters during the NPs synthesis. UV-Vis spectrometer (UV-Vis), Scanning electron microscopy (SEM), Atomic force microscopy (AFM), Transmission electron microscopy (TEM), X-ray diffractometer (XRD), Photoluminescence analysis (PL), and other instrument techniques are used to characterize the obtained NPs. In this review, the discussion is restricted to synthesis and applications of group-11 coinage metal NPs viz. Silver NPs, Gold NPs, Copper NPs, synthesized by a green approach, *i.e.*, by using plant sources like leaves and fruits, etc.

2.1 Silver Nanoparticles (AgNPs) from Plant Extracts

Synthesis of AgNPs is of most attention on humankind because of their vast range of applications such as antimicrobial agents, antioxidants, sensing, surgical masks manufacture, and even data storage. Traditionally, Silver (Ag) and AgNPs were in medical fields in the form of topical ointments to prevent infection against burn and wound¹². Plant-based green synthesis can create AgNPs quickly faster than the usual chemical method. It is shown that Geranium leaf extract is reduced to aqueous silver ion solution to highly stable and crystalline AgNPs. Analytical analysis by TEM showed that these particles are arranged in quasilinear superstructures in the range of 16-40 nm. This study proved that the *Candida albicans* and *Candidatropicalis* are all susceptible to silver's antifungal properties¹³. Alfalfa sprouts were one of the first plants used to make metallic NPs¹⁴. It showed that, depending on the nature of the plant extract, the creation of metal NPs could be accomplished efficiently in a metal salt solution. The concentration of the extract, metal salt, temperature, pH, and contact time is the primary influencing parameters after selecting the plant extract.

The synthesis of AgNPs was carried out using ethanol extracts from *Cardiospermumhalicacabum L.* leaves, *Impatiens balsamina L.* leaves, and *Lantana camara L.* fruit, to evaluate the antibacterial activity¹⁵. The aqueous extract of fresh leaves of *L. camara*, and *I. balsamina* are used to synthesize AgNPs. *Syzygiumcumini* fruit extract was used to synthesize the AgNPs of approximately 93 nm, which has a better radical scavenger than its extract alone. *Centellaasiatica* is an Asian-based plant having medicinal value. Various researches have been used to synthesize different NPs by using this plant. N. Bharadvaja and his co-workers used this plant leaf extract to synthesize AgNPs by taking silver nitrate as a precursor and synthesizing copper NPs to degrade dyes. They have also observed a high quantity of NPs generation during the synthesis, indicating a change in intensity of the solution color upon changing the silver nitrate concentrations from 1mM to 4mM. The synthesized NPs has been studied by their UV-Vis spectra showed a characteristic peak for silver in the range of 330-550 nm. SEM analysis revealed that these AgNPs were spherical with 30-50 nm in size¹⁶. Singh *et al.* used the first time *Argemonemaxicana* leaf extract to synthesize highly stable and crystalline AgNPs in a size range of 15-30 nm in place of the traditional chemical approach¹⁷. The authors also examined that the formed NPs were in polydispersed nature by which observed on UV-Vis spectra. The absorption spectra location also supported the AgNPs formation. XRD reveals that these NPs were in the 10-50 nm range, having hexagonal and cubic shapes. At a 30 ppm concentration of these particles, they were toxic against pathogenic bacteria and fungi.

Bonde S. had synthesized the AgNPs by using *Foeniculumvulgare* extract and 1mM silver nitrate solution¹⁸. The nanoparticle tracking and analysis (NTA) study demonstrated that these polydispersed NPs ranged between 18 and 83 nm in size. It was observed by the disc diffusion method, and also these AgNPs had antibacterial action on *Staphylococcus aureus* and *Escherichia coli*. The author also observed that, after combining these NPs with commercial antibiotics, the antibacterial action was significant against two human pathogenic bacteria. Interestingly, these AgNPs with Vancomycin, an antibiotic, combination showed high activity against *E. coli*, whereas after AgNPs combination with Gentamicine showed better activity for *S. Aureus*. *Solanumtorvum* leaf extract was used to synthesize 14 nm-sized spherical AgNPs by Govindarajuet *al.*¹⁹. The present synthesis of AgNPs were formed in 60 min by the silver ions reduction. A color change of the solution confirmed the formations of these NPs and their UV-vis absorption spectra initially. Interestingly, the surface plasmon absorbance did not change even after a long time indicates the stability of the formed AgNPs. XRD peaks at 111, 200, and 220 show that the formed NPs are in face-centered cubic nature and have an average size of 14 nm. Their TEM results also confirm this size. TEM image showed the formed NPs were spherical in structure. Finally, these leaf extract-mediated AgNPs showed high antimicrobial activity against bacterial and fungal pathogens. Using the agar well diffusion method, the subjected pathogens: *Pseudomonas Aspergillusflavus*, *aeruginosa*, *Staphylococcus aureus*, and *Aspergillusniger* species were observed for antimicrobial activity. The authors concluded that the binding of the formed AgNPs to the bacteria depends on their size, which means smaller NPs have better bactericidal effects than larger ones.

In 2014, V. K. Thirumalairajet *al.* synthesized AgNPs using seaweed *Sargassumwrightii* extract and a 2 mM silver nitrate solution to study antibacterial activity²⁰. The formed NPs were analyzed by SEM analysis and observed that the average size was found to be 48.78 nm. The authors studied the antibacterial activity of different pathogenic organisms *viz.* *B. cereus*, *B. anthracis*, *S. aureus*, and *V. alginolyticus*. The solvent extract of the seaweed alone showed other activity on these organisms. Specifically, the acetone extract exhibited the

highest activity against *S. aureus*, whereas petroleum ether extract showed improved antibacterial activity on *B. cereus* and *B. anthracis*. The synthesized 32 and 43 nm-sized AgNPs showed good antibacterial activity on the selected microorganisms at 130 micrograms dose.

Resistance of mosquitoes towards insecticides has also been a challenge to humankind. By keeping the effect of dengue and its mortality rate in India and Africa along with the WHO report, C. D. Patilet *al.* studied the activity of AgNPs against the larvae of *Aedes aegypti* and *Anopheles stephensi*²¹. In this study, AgNPs were prepared using *Plumeria rubra* plant latex as a natural resource for the synthesis of AgNPs. These NPs were highly toxic to the mentioned larvae in comparison to their latex extract alone. This is the first study on the said target. It was observed that the crude latex extract showed less toxicity than AgNPs for both mosquito species. Specifically, *A. stephensi* larvae were more prone than *A. aegypti* to the NPs. Particle size analysis in this study reveals that the average size of the NPs was 105 nm, and these NPs were negatively charged as per their Zeta potential result, and 80 % of particles are under 70 nm in size. According to Ahmed *et al.*, the green synthesized AgNPs showed the best antibacterial activities against both gram-negative and gram-positive microorganisms. In this study, AgNPs were synthesized in fifteen minutes without any hazardous chemical, *i.e.*, using *Azadirachta indica* aqueous leaf extract²². Traditionally this plant is used as a home remedy for different infections in India. The DLS analysis indicates the formed NPs were in 34 nm size. TEM analysis revealed that the formed NPs were spherical to some irregular in shape. Also, the particle size is a good agreement with the DLR histogram as 34 nm. The PL spectra of these AgNPs were exhibited two intense high emissions (280 and 600 nm) at a specific excitation wavelength, *i.e.*, 300 nm.

Annet *al.* synthesized AgNPs using different concentrations of dissimilar fruit waste peel (*Citrus limon*, *Citrus sinensis*, and *Citrus limetta*) extract along with 4 mM silver ion solution in 30 min and studied their antimicrobial, antioxidant, and cytotoxic activities²³. It was observed that out of selected peel extracts, *Citrus limon* took more time to form required nanoparticles. It is also spotted that *C. limon* has lesser antibacterial activity than *C. sinensis* and *C. limetta* towards *E. coli* and *S. aureus*²⁴. At the same time, Lakshmanan *et al.* synthesized AgNPs by using *Cleome viscosa L.* extract to assess anticancer activity successfully. It is well known that AgNPs cross the blood-brain barrier and cause several neurological changes due to their dissemination into the surroundings. Hence Aisha Khatoon *et al.* elected acetylcholinesterase, one of the neurological enzymes, to study the neurotoxic potential by synthesizing AgNPs from natural resources²⁵. The authors have used a well-known plant extract, *Mentha Piperita*, to synthesize AgNPs. SEM and TEM analysis showed that the formed NPs were spherical with a size of 35 nm. First time *Tectonagrandis* seeds have been used to synthesize AgNPs using 1 mM silver nitrate solution for antimicrobial action study²⁶. TEM analysis showed the synthesized AgNPs had a dimension in the range of 10-30 nm, and EDS revealed the silver particles were in pure form. SEM images showed the formed NPs were spherical with a size below 100 nm.

Syngonium podophyllum extract mediated AgNPs were synthesized and studied their anticandidal activity by M. Yasiret *al.*²⁷. In this study, the AgNPs were synthesized by changing different parameters at 80°C. Advanced AFM study revealed the particles were in the size of 40 nm in a spherical shape. S. Arokiyarajet *al.* studied cytotoxic effects besides the antibacterial effect utilizing *Chrysanthemum indicum L* mediated AgNPs. TEM analysis revealed their size as 37.71-71.99 nm in a spherical shape. These NPs significantly affected different bacteria, namely *Pseudomonas aeruginosa*, *Klebsiella pneumonia*, and *Escherichia*

coli. Besides this, these particles showed no toxicity on 3T3 mouse embryo fibroblast cells²⁸. The recent examination reveals the high-level antimicrobial activity of AgNPs, which were synthesized by using *Lysilomaacapulcensis* by Diana Gariboet *al.*²⁹

2.2 Gold Nanoparticles (AuNPs) from Plant Extracts

Another important type of nanoparticle for a range of applications is AuNPs. These particles have unique electrical and magnetic properties, making them attractive to researchers for various applications. By the continuous effort by global researchers, there are many areas where the AuNPs have applicability, *viz.* cancer therapy, biological sensing therapy, tissue imaging, DNA labelling, and even drug delivery.

K. Chandranet *al.* chose two medicinally essential plants, namely *Cucurbitapepo* and *Malvacrispa*, to synthesize the AuNPs for their potent antibacterial agent against food spoilage pathogens³⁰. By changing the parameters of the reaction medium, the authors were able to control the size and shape of the NPs successfully. The FT-IR analysis revealed that the bio molecules present in the extract were responsible for converting the salt solution into NPs. It is also observed that the conductivity of the medium increases during in antibacterial activity study. This was a clear indication that the synthesized NPs damaged the cell membrane of the pathogens. The absorption band at 540 nm of these NPs has also confirmed the conversion of H₂AuCl₄ to Au NPs. The only difference is that *Cucurbitapepo* extract took 150 min to synthesize the required NPs, whereas *Malvacrispa* extract took 120 min only.

Breast cancer is one of the major causes of women's death in the current century. The reports also alarming the situation continues and searching for a better drug that can inhibit the cancer cell's growth. Research reveals that the plant-based synthesis of NPs looks like better promising candidates than the traditional chemical method. C. Krishnarajetal. selected *Acalyphaindica* as a source to synthesize the AuNPs along with AgNPs³¹. Their study mainly concentrated on the cytotoxic effect of AuNPs against human breast cancer cells, MDA-MB-231. The authors synthesized AuNPs using 1 mM H₂AuCl₄ solution at 37° C for 30 min. The formation is confirmed initially by a colour change of the solution to a violent pinkish colour, and showed absorption spectra at 540 nm. These NPs characterization by microscopy reveals that these were less than 30 nm in size with spherical. In addition, XRD reveals that the formed NPs were crystalline. A recent study on Grape-based AuNPs synthesis and their application towards HBL-100, a human Brest cancer cell, encourages the idea of using natural materials for the NPs synthesis. By keeping in mind the toxic effect of traditional reducing agents, waste management (as the grape waste is rich in polyphenols), and even various biomedical applications, K. Krishnaswamyet *al.* synthesized AuNPs using grape waste (seed, skin, and stalk)³². Interestingly there was no such a high agglomeration of the NPs in water during synthesis. TEM images revealed that the synthesized NPs were in size range of 20-25 nm with quasi-spherical in shape. B. Sadeghiet *al.* used *Stevia rebaudiana* plant's leaf extract for synthesizing AuNPs is having a positive effect on human health as anti-hypertensive and so on³³. After the successful synthesis of the NPs, it was observed that these NPs have spherical shapes in the range of 5-20 nm. Its XRD output showed that the formed AuNPs were in a face-centered cubic structure with 17 nm in size.

Alijabaliet *al.* synthesized monodisperseAuNPs by using leaf extract of *Ziziphuszizyphus* and 1 mM gold chloride solution for their antibacterial and antifungal study at ambient temperature³⁴. UV-vis spectra of these NPs showed in the range of 525-540 nm, confirming the AuNPs generation by this method. TEM analysis revealed that the maximum percentage

of the formed NPs were majorly spherical with monodispersity. This monodispersity was also observed in their dynamic light scattering analysis. Finally, the authors have observed that the synthesized AuNPs had biological activity at a particular concentration of the NPs only. It is well known that AuNPs by electron relay effect can act as redox catalysts in the degradation of dyes. In keeping this in view, Bogireddy *et al.* used an extract of *Sterculiaacuminata* fruit to synthesize spherical AuNPs after examining the active compounds present in the extract by high-pressure liquid chromatography (HPLC) analysis³⁵. It is observed that the formed 18.79 nm size NPs has superior catalytic action on different organic dyes, namely 4-nitrophenol, methylene blue, and methyl orange. For the first time, the authors also studied the catalytic activity on direct blue 24 (DB24). In another study, Y. Yulizaret *et al.* used *Polysciasscutellaria* leaf extract to study the catalytic activity on methylene blue dye by synthesizing AuNPs³⁶. The generation of these highly stable NPs took two hours under UV radiation source as the active compounds were in less percentage in the extract. Initially, the change in solution colour is pink and the absorption spectra confirm this method's successful generation of AuNPs. It was observed that these NPs were in a face-centered cubic structure. The morphology study by TEM and particle size analysis revealed that the AuNPs were in spheres shape with a 5–20 nm diameter. The Cytotoxicity of AuNPs has been studied, besides their cellular uptake and catalysis activity, using *Mimosa tenuiflora* bark extract for the first time by E. Rodríguez-León *et al.*³⁷. The colloids (AuMt) formed by the AuNPs and extract were found to be in the range of 20–200 nm. The minor AuMt's catalytic degradation has shown methylene blue comes to 50 % in 190 seconds. Also, a moderate cytotoxic effect was observed on human umbilical vein endothelial cells. The authors have used Confocal laser scanning microscopy to study the cellular internalization of AuMt on targeted cells.

Omar S. El Mitwalliet *et al.* used *cinnamon* bark extract to prepare eco-friendly AuNPs to study eosin Y dye³⁸. The surface plasmon resonance was observed at 535 nm for the synthesized spherical AuNPs. TEM showed that the formed AuNPs were spherical with a particle size distribution of 35 nm. But after adding eosin, it is reduced to 5 nm level, whereas on the addition of albumin bovine protein, it was increased to 26 nm. A fluorescence quenching study has been done using a fluorometer to understand the dye degradation, which interns useful for biosensing applications. Different volumes of AuNPs were added to the eosin dye solution and observed a decrease in the fluorescence intensity. Besides, it is observed that a red shift upon the increase of AuNPs in fluorescence spectra. This has indicated that the dye is adsorbed onto the synthesized NPs and showing the possibility of its real application. AuNPs were studied mainly for their anti-cancer activity like human lung cancer, uterus cancer, lung epithelial cancer, etc. Shuiqin Li *et al.* recently synthesized 36.4 nm sizes with face-centered cubic structured AuNPs quickly by using *MenthaLongifolia* leaf extract and studied their anti-human breast carcinoma properties³⁹. In this study, the authors have taken various breast cancer cells *viz.* breast adenocarcinoma (MCF7), breast carcinoma (Hs 578VSt), breast infiltrating ductal cell carcinoma (Hs 319.T), and breast infiltrating lobular carcinoma (UACC-3133). The superior activity by using the current AuNPs was observed on UACC-3133 cells. One of the best parts of this study is recovering and recycling the catalyst multiple times, which matches the green chemistry principles mentioned earlier.

2.3 Copper Nanoparticle (CuNPs) Synthesis from Plant Extracts

Copper nanoparticles (CuNPs) are very attractive due to their various properties like high thermal conductivity, antibacterial and antifungal activity, optical and catalytic properties, and even water treatment ability as compared to their bulk. As copper is an effective agent with low toxicity, it can be important in the biomedical field for various ailment. Hence phyto

based synthesis of these NPs has emergent importance compare to traditional methods. Various authors have been used different natural sources for synthesizing CuNPs. Some sources are: *Euphorbia esula*, *Punicagranatum*, *Ocimum sanctum*, *Ginkgo biloba*, *Calotropisprocera*, *Lawsoniainermis*, *Citrus medicalinn*, *Camellia sinensis*, *Daturainnoxia*, *Syzygiumaromaticum*, *Sesamumindicum*, *Citrus limon*, *Turmeric curcumin*, *Gloriosasuperba L.*, and *Ficuscarica*, *Aegleng*. These natural plant sources have been used to produce copper salts (precursors) such as copper sulfate, copper chloride, cupric acetate, and copper nitrate. Combining different concentrations of these salts with various concentrations of plant extracts and changing the reaction parameters leads to the generation of highly stable CuNPs. The availability and cost of copper are better than metals (Ag and Au).

Patel et al. synthesized CuNPs using Indian's holiest plants, *Ocimum sanctum* leaf extract, to check their efficacy against human pathogenic bacterium through bio-reduction⁴⁰. The formation of the NPs are confirmed by their optical properties like the colour change from bluish-green to yellow and their absorption spectra (586 nm). Particle size analysis reported that the formed CuNPs were in the range of 55-350 nm. SEM has shown the NPs were spherical, with sizes ranging from 8-140 nm. These CuNPs showed antibacterial activity against gram-positive and gram-negative species with an improvement compared to leaf extract alone. This is due to the large surface area of the synthesized NPs, which intern inhibits the cell growth. It is well known that the spice plants had the antiviral property. Rajesh et al. successfully synthesized CuNPs by using extract of *Syzygiumaromaticum* bud through an eco-friendly method for antibacterial activity against pathogens (*Bacillus spp.* and *Penicillium spp.*)⁴¹. During the generation of CuNPs, a color change of the solution was observed, from blue to pale green, which indicates the formation of desired NPs. XRD characterization revealed that the crystals had an fcc structure, which was also confirmed by their selected area electron diffraction pattern. The Debye-Scherrer calculations showed that the size of these particles was 12 nm approximately. The SEM images of these homogeneous NPs have disclosed the shape as spherical with 20 nm particle size. TEM also revealed that these NPs were segregated without any agglomeration. The obtained Zeta potential value (-1.3 mV) suggests that the generated NPs had high stability due to particle's repulsive nature. The antibacterial study on the generated CuNPs clarifies that the *Bacillus spp.* is a more effective bacterial action besides exhibiting prominent fungicide activity against *Penicillium spp.*

One of the high water pollutant dyes having cationic nature in the textile industry is crystal violet which causes damage to mammalian cells. Due to its cationic nature can enter and accumulate in the cytoplasm quickly and causes high risk. Hence Khaniet al. selected *Ziziphus* fruit extract as a bio-reductant to synthesize CuNPs⁴². These NPs were used to remove crystal violet (Triphenylmethane dye) from an aqueous solution. It is observed that the CuNPs were adsorbed 95% of the dye in a short time. It has been tested even in tested by taking industrial wastewater. These CuNPs were tester by agar well diffusion for their biological activity. Specifically, the methanolic extract-based CuNPs have higher antibacterial activity against *Escherichia coli* and *Staphylococcus aureus* than aqueous extract.

In 2018, N. Nagar et al. synthesized highly stable CuNPs having a cubic structure successfully by using a broth of *Azadirachtaindicaleaves*⁴³. The generated NPs were challenging for a long time in colloidal conditions at 4°C, and XRD identified that the synthesized NPs were in face-centered cubic (fcc) structure with an average particle size of 48 nm. TEM analysis revealed that these particles were in a cubical structure. The high stability of the CuNPs was supported by their zeta potential value (-17.5 mV). The results also confirm that plant-based NPs synthesis is faster than the micro-organisms method. *Ageratum houstonianumis* was used to synthesize CuNPs by S. K. Chandrakeret al.⁴⁴. The

synthesized NPs had antibacterial activity on *Escherichia coli* (Gram-negative bacterium) besides showing photocatalytic degradation of synthetic dyes viz. Methylene blue, Methyl orange, Rhodamine-B, and Congo red. During the formation of these NPs using copper chloride and plant extract, there is a light greenish color development in the solution that confirms the generation of CuNPs and later by the position of the UV-vis absorption spectra. It took 24 h time to complete the entire conversion of copper ion to its neutral state. XRD analyzed the generated NPs were cubic in nature. SEM analysis revealed that the CuNPs are in different shapes like cubic, hexagonal, and rectangular, and the majority of these NPs were in agglomerated form. The same has been observed even in TEM also. TEM specified that the NPs had an average particle size of 80 nm. It is also proved that these NPs had a semi-conducting nature by evaluating their bandgap (4.5 eV) using a UV-vis spectrometer. Surprisingly, these NPs had high dye degradation activity towards Congo red solution only in daylight, which indicates a change in solution color from red to colorless. It took almost two hours for this change. These NPs also showed their antibacterial activity against gram-negative bacteria, *E. coli*.

H. C. Anand Murthy *et al.* prepared CuNPs by using *Hagenia abyssinica* (Brace) JF. Gmel medicinal plant to study antibacterial property of the infectious diseases caused pathogens viz. *E. coli*, *Pseudomonas aeruginosa*, *Staphylococcus aureus*, and *Bacillus subtilis*⁴⁵. The electron microscopes (SEM and TEM) reveal the possible shapes, including spherical, triangular, hexagonal, and cylindrical shapes with an average particle size of 34.76 nm. Also, researchers have been used leaf extract from *Jatropha curcas* as biomaterial to synthesize CuNPs. The synthesized NPs are with the average particle sizes of 10 nm, and showed photocatalytic activity on methylene blue dye⁴⁶. A 10-20 nm-sized CuNPs were synthesized from *Cissus vitifolia* by S. Wu *et al.* and also tested its antioxidant and antibacterial activity against urinary tract infection pathogens and observed their stranger action⁴⁷.

2.4 A Comparative study of Nanoparticles synthesized by Green approach

Besides understanding the effect of various nanoparticles in the synthesis, attempts have also been made comparatively. Mukundan *et al.* made silver (AgNPs) and gold (AuNPs) nanoparticles by with *Bauhinia tomentosa* Linn extract, aqueous silver salt (AgNO_3) solution, and gold salt ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$) solution under normal atmospheric conditions⁴⁸. During the process, colour change of the solution indicates the reduction of the ions (Ag^+) and gold (Au^{3+}) to their neutral state i.e., Ag^0 and Au^0 , respectively. The lyophilized powder was initially studied using UV-visible spectrophotometer and FTIR. These nanoparticles were spherical with polydispersity. Also, the typical particle size of the AgNPs and AuNPs was found to be 18.45 and 27.8 nm, respectively. Further in vitro anticancer efficacy has been studied on three cells, namely A-549, HEP-2 and MCF-7 cells. Further various attempts have been made to make a comparative study of nanoparticles. In the line, Nasrullah *et al.* synthesized cadmium oxide nanoparticles (CdO-NPs) using a traditional chemical and plant-based approach⁴⁹. In this, cadmium nitrate was reduced with sodium hydroxide in a chemical process, while in the biological approach, the precursor ions were reduced by extracts of *Artemisia scoparia* and *Cannabis sativa*. The analytical results significantly affect nanoparticle properties based on selecting a route to make them. Still, there is a gap in understanding the nanoparticles comparatively to apply for real-time application.

2.5 Importance of green synthesis

Green synthesis processes of nanomaterials are a rapidly expanding field. Due to their environmental friendliness, biocompatibility, and sensitivities, biogenic nanoparticles have broader applications in biomedical science and environmental remediation⁵⁰. These nanoparticles have a promising role in the health sector because of antimicrobial drug's resistance to new microbial species. This antimicrobial activity generally depends upon the material employed to synthesize the nanoparticles and the size of the nanoparticles⁵¹. Due to the non-toxic character of AuNPs, they are best suited for the progress of new antibacterial agents. It is also well known that the green approached nanoparticles have an improved antimicrobial activity compared to chemically synthesized analogous. The Phyto (plant) employed to synthesize nanoparticles have medicinal properties⁵².

4-Nitrophenol and its analogous are used to fabricate herbicides. But they can notably harm the water ecosystem as familiar organic pollutants⁵³. Hence it becomes an important one for ecological concerns. As a result, the decline of these pollutants is essential. The simple and most effective way to reduce 4-nitrophenol is to introduce catalysts such as AuNPs and AgNPs. Metal nanoparticles exhibit worthy catalytic potential because of their high surface adsorption capacity and high surface area to volume ratio. Organic dyes are another group of organic pollutants used in diverse applications, including paper mills, plastic, leather, and textile⁵⁴. After the fabrication process in the textile region, nearly 15% of dyes are discharged in an unused form and become a significant source of water pollution. They generate unwanted turbidity in the water, which will diminish sunlight access. This situation leads to the resistance of photochemical synthesis, which hampers the growth of aquatic life. Besides, heavy metals are well-known for various pollutions starting from air to water⁵⁵. Hence for health and environmental sustainability, nanoparticles are becoming an essential role in reducing the pollutant for mankind. Metal oxide semiconductor nanoparticles have been applied preferentially for the photocatalytic activity of dyes. In particular, plant-based nanoparticle synthesis is likely to be involved in environmental pollution control soon.

CONCLUSION

In the 21st century, the synthesis of nanomaterials has been becoming an encouraging area. This is because of its protrude behaviour to various areas, from all basic science to engineering fields. It has broad applications including sensing the pollutants, changing the properties of existing materials, and biological activity. Even though nonmaterials were revolutionary, they have drawbacks concerning the basic materials used for synthesizing the same. Hence utilization of naturally available plant materials for synthesizing the nonmaterial had shown a pavement for adopting green chemistry principles. In the present review, the authors mainly discussed the synthesis methodology adopted by various renowned researchers and their characterization results of various nanomaterials, namely Silver, Gold, and Copper nanomaterials, using Phyto-based materials as reducing agents. The methodologies from this study provided safe and stable nanomaterials besides having the advantages of cost-effectiveness and eco-friendly nature. These points are very much crucial in the mass-scale production of various nanomaterials. But still, research needs to be done to overcome some of the technical issues by which one can make the route to convent small

scale to the bulk level of these nanomaterials. Hence, this study provides knowledge to understand the biochemical mechanism during nanomaterials synthesis by using plant-based material to make the green synthesis more economical.

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