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Plant Extract Mediated Synthesis of Transition Metal Nanoparticles: A Review

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Abstract: *Green technology is a fast evolving scientific topic that has attracted a lot of attention in recent years due to its wide range of applications. It is a multidisciplinary field that is safe, non-hazardous, and ecologically friendly, in contrast to chemical and physical approaches for nanoparticle synthesis. Because the existing biomolecules in plant extract act as both a reducing and capping agent, the produced nanoparticles are very stable. As a result, nanoparticles that have been manufactured have a wide range of potential applications in the environmental and biomedical domains. The current report contains current information on numerous green synthesis methods that rely on different plant parts for green transition metal nanoparticles synthesis.*

Keywords: *Green synthesis, Nanotechnology, Transition Metal nanoparticles, Plants extract, Biomolecules.*

I. INTRODUCTION

Nanotechnology is concerned with nanoparticles with at least one dimension of 1 to 100 nanometers. Nanotechnology has a wide range of applications, and producing functional nanomaterials for a variety of uses from biogenic resources is usually seen as a sustainable strategy [1]. Nanomaterials have automatically permeated every part of human existence, beginning with fabrics and progressing to more concerned applications such as the Agri-food, automobile, biomedical, and wastewater industries [2], with advancements of equipment to visualize and characterize them. Nanoparticles' application and exploitation provide superior features not seen in bigger size scales; therefore, nanotechnology is booming [3]. The majority of these applications have emphasized the importance of nanomaterials for increased efficiency and production. Metal nanoparticles are the fundamental building blocks of nanotechnology since they are the primary source of nanostructured devices and materials. Metal nanoparticles have been synthesized using a variety of procedures. The top-down and bottom-up strategies are the two basic methodologies used to synthesis particles. Nanomaterials can be made inadvertently, via physical or chemical means, or naturally, and their enormous demand has led to large-scale manufacturing using toxic solvents or high-energy processes [4], as shown in Fig.1. However, as public awareness of environmental and safety issues has grown, it has become necessary to adopt clean, nontoxic, and environmentally friendly methods to create metal nanoparticles. The exploitation of biological resources, such as, has risen in popularity as a method of producing transition metal nanoparticles. This biogenic synthesis is nontoxic, non-polluting, and environmentally beneficial. Biogenic synthesis is nontoxic, environmentally band cost-effective. This article also discusses numerous easy, cost-effective, environmentally friendly, and scalable tactics that have been developed using various greener approaches.

Fig. 1. Different Protocols of Synthesis of Metal nanoparticles

II. SYNTHESIS FROM PLANT EXTRACTS

Plant extracts are used to make nanoparticles, which are made from live plants. Plants have long been thought to be a more environmentally benign way of naturally producing metallic nanoparticles and using them for detoxification. For transition metal-based NP synthesis, plant components such as leaf, root, latex, seed, and stem are commonly employed [5]. Plant species that have evolved naturally and are a rich supply of phytochemicals may be useful as environmentally friendly pools for the creation of metallic nanoparticles. The production of metal nanoparticles by plant extract is depicted graphically in Figure 2. It also reduces time-consuming operations by eliminating the need for complex procedures, multiple purification steps, and the maintenance of microbial cell cultures [6]. The potential of plant extracts in the biosynthesis process is an important branch of nanoparticle biosynthesis. Important bio reductants identified in plant extracts are depicted in Figure 2. Plant extracts are bioactive polyphenols, proteins, phenolic acids, alkaloids, sugars, terpenoids, and other compounds that are primarily composed to relegate and then alleviate metallic ions [7]. The key supporting element in the diverse sizes and forms of produced nanoparticles is considered to be the discrepancy in concentration and conformation of these active biomolecules among different plants, and their consequent connection with aqueous metal ions [8]. Metal salt reduction via plant extracts is a reasonably simple ambient environment action for the synthesis of NPs. The functioning procedure is quite straightforward. The plant extract and metal salt solution are well mixed at room temperature, and the reaction begins within a few minutes. When the precursor solutions combine, biochemical salt reduction begins immediately, and nanoparticle synthesis is typically shown by a transformation in color of the reaction solution. During the synthesis process, process metal ions are changed from their monovalent or divalent oxidation states to zero-valent ones, and nucleation of the reduced metal atoms occurs. The plant extracts the nanoparticle's ability to stabilize it in the final stage of synthesis, which defines its most energetically favorable and stable form [9].

Fig. 2. Graphical representation of synthesis of metal nanoparticles using plant extract.

A. Fruit Extract

Flavonoids are a broad class of polyphenolic chemicals that can actively chelate and reduce metal ions into nanoparticles. They include bioflavonoids, flavones, chalcones, and flavanones. As a reducing agent, flavonoids include numerous functional groups capable of forming nanoparticles. With their carbonyl groups or -electrons, several flavonoids can chelate metal ions. For example, quercetin, also known as tryptophan, is a flavonoid that acts as a powerful chelating ligand. It can chelate metals in three different ways: carbonyl, hydroxyl, and catechol locations. Various metal ions, such as Fe^{+2} , Fe^{+3} , Cu^{+2} , Zn^{+2} , Al^{+3} , Cr^{+3} , Pb^{+2} , and Co^{+2} , are chelated by these groups [10,11]. To remove the hazardous azo dyes Congo red and methyl orange from water, researchers generated zero valent Cu NPs using Ripened *Duranta erecta* fruit [12] extract in 2019. In 2018, Padma et al. [13] studied the use of *Punica granatum* fruit rind extract to green synthesis Cu NPs. Kumar et al. [14] used *Terminates Chebula* fruit extract to make palladium and iron nanoparticles.

By cyclic voltammetry, polyphenolic rich T.chebula extract has a redox potential of 0.63V versus saturated calomel electrode, which aids in the reduction of iron salt to iron nanoparticles. Highly stable FeNPs were made by reducing a ferrous salt solution with T.chebula extract, which involved polyphenol complexation. The solid product was separated by centrifugation after a 5:1 ratio of fruit extract to $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ solution was reacted. According to X-ray diffraction (XRD) and transmission electron microscope (TEM) analyses, amorphous FeNPs were less than 80 nanometers in size. Salari et al [15] in the presence of *Prosopis farcta* fruit extract as a reducing agent reported the biogenesis of silver nanoparticles (AgNPs). The total phenolic components and total flavonoids in plant-AgNPs were higher than in the plant extract alone, according to the study. Nakkala et al [16] described the production of AuNPs using *Piper longum* fruit extract, along with data on their antioxidant and catalytic activity in vitro. Cu nanoparticles were synthesized in situ on reduced graphene oxide/ Fe_3O_4 using barberry fruit extract as a stabilizing and reducing agent, and were found to be useful as an active catalyst in the reaction of phenol with aryl halides to produce O-arylation of phenol [17].

B. Seed Extract

The capacity of the bio synthesized technique to design alternative, safer, more energy efficient, and less toxic ways to synthesis has received a lot of attention in recent years. The rational use of diverse chemicals in nanoparticle preparations and synthetic processes has been linked to these approaches. The green production of titanium dioxide (TiO_2) nanoparticles from titanium tetrachloride (TiCl_4) solution using *Cucurbita pepo* seeds extract was described in a prior study. Different experimental techniques were used to characterize synthesized nanoparticles [18]. The antibacterial, photocatalytic, and cytotoxic properties of AgNPs synthesized utilizing an aqueous extract of *Durio zibethinus* seed were investigated in a study. With a maximum absorbance (max) of 420 nm, surface Plasmon resonance indicated the production of AgNPs. AgNPs were found to be spherical and rod-shaped, with a size range of 20 nm to 75 nm, as revealed by SEM and TEM pictures. Antibacterial activity of AgNPs against brine shrimp was observed, as well as improved photocatalytic activity against methylene blue. In the future, synthesized AgNPs may be employed in water treatment, medicines, biomedicine, and biosensors nanotechnology. [19]. Zayed et al [20] utilizing *Pimpinella anisum* seeds extract reported green synthesis of AgNPs and AuNPs. The nanoparticles were characterized structurally and spectroscopically. When compared to AuNPs and *P. anisum* extract, biosynthesized AgNPs had better antioxidant activity.

C. Stem Extract

Valodkar et al. [21] used *Euphorbia nivulia* stem latex as a reducing and capping agent to make peptide-capped copper nanoparticles. Valodkar and colleagues investigated the biological effects on tumor cells as well as antibacterial applications. The use of medicinal plants such as *Gnidia glauca* and *Plumbago zeylanica* to effectively reduce Cu^{2+} ions to CuNPs has been reported here as a rapid, eco-friendly, and cost-effective one-pot synthesis of copper nanoparticles. The extracts' phenolic and flavonoids may be important in the synthesis and stabilization process. The nanoparticles that were shows applications in the biomedical field [22]. AgNPs were produced utilizing *Picea abies* L. stem bark extract as a reducing agent, according to Tanse et al [23]. Metal ion solution, pH, and time, all of which play a role in AgNPs formation, were evaluated. At pH = 9, TEM results revealed spherical or occasionally polygonal AgNPs with an average size of 44 nm. Antioxidant activity and antibacterial activity were observed in AgNPs against human pathogenic Gram-positive and Gram-negative bacteria.

D. Flower Extract

Karimi and Mohsenzadeh [24] investigated the phytosynthesis of copper nanoparticles using Aloe Vera flower extract. The appearance of an absorption peak at 578 nm using a spectrometer verifies the creation of Cu nanoparticles, according to the characterization data. FESEM analysis was used to investigate the form and morphology of copper nanoparticles. The presence of reductive groups on the surfaces of nanoparticles was discovered using FTIR. Copper nanoparticles (CuNPs) were synthesized by Rajesh et al [25] utilizing *Syzygium aromaticum* (clove) bud extract in a simple and environmentally acceptable green method. The X-ray diffraction (XRD) pattern of CuNPs with a face centered cubic phase reveals their high crystalline nature. The shape and size of the produced nanoparticles were studied using morphological analyses. In another investigation, Mango flower extract was used to successfully produce silver nanoparticles. The nature of AgNPs was analyzed through structural and optical investigation. AgNPs significantly limit the growth of antibacterial activity across a broad spectrum [26]. Using an aqueous extract of *Origanum vulgare* L. as a bio reductant, Shaik et al describe an ecologically friendly production of Pd nanoparticles (Pd NPs) [27]. The *Origanum vulgare* L not only functions as a bio reductant, but also as a functionalized of nanoparticles, according to an FT-IR study. Additionally, the green produced metallic Pd NPs were successfully used as catalysts for selective alcohol oxidation.

E. Root Extract

Vijaykumar et al. [28] report a simple and cost-effective eco-friendly and green synthesis of uniformly spherical and crystalline nanosilver particles in the dimensional range of 10-17 nm using AgNO₃ as a source and Asparagus racemosus root extract as a reducing and capping agent under optimized conditions.

Microbial strains were used to test the AgNPs that had been produced. In vitro antioxidant and cytotoxic activities of gold nanoparticles (Au NPs) produced from Lantana camara Linn root extract could be considered as a possible alternative for the development of anticancer drugs in the future [29].

The use of Cibotium barometz root extract in the green synthesis of AuNPs and AgNPs nanoparticles was emphasized by Wang et al [30]. AuNPs and AgNPs were formed at 548 and 412 nm, respectively, and were spherical with crystallite diameters of 6 nm and 23 nm. The study showed that AuNPs and AgNPs have potential medicinal applications as antioxidants, antibacterial agents, and drug delivery agents.

F. Leaves Extract

A number of studies has described the green synthesis of metallic nanoparticles utilizing diverse plant leaf extracts. According to Nilavukkarasi et al [31], biosynthesized silver nanoparticles from C. zeylanical leaf extract show high antibacterial activity against pathogenic microbes and have outstanding antiproliferative activities in cytotoxicity experiments. Crystalline, uniform, spherical, and monodispersed nanoparticles with an average size of 23 nm were found in biosynthesized AgNPs, and the functional groups contained in the AgNPs were validated using an FT-IR spectrum. For the synthesis of AgNPs by Azardirachta Indica (Neem) leaves extract, Nagar and Devra [32] utilized a low-cost reductant. In UV, the highest absorption peak. At 433 nm, visible spectroscopy of synthesized AgNPs was confirmed.

By using an improved oxidation technique in an aqueous media, the produced AgNPs demonstrated outstanding catalytic activity in the oxidative destruction of Acid orange 10 (AO10) and Acid orange 52 (AO52). Nagar and Devra [33] developed an innovative, easy, and environmentally friendly methodology for the manufacture of copper nanoparticles (CuNPs) and compared the catalytic activity in CuNPs/Peroxodisulphate (PDS) and CuNPs/Peroxomonosulphate (PMS) processes for the degradation of Methyl Orange (MO). The produced nanoparticles are crystalline in nature and cubical in shape, with a size of 48 nm, according to the results of the characterization.

The breakdown kinetics of Methyl Orange were accelerated by increasing the concentration of nanocatalysts, Peroxosulphate, Dye, starting pH, and high temperature. Agarwal et al [34] reported Phyto-assisted production of ZnO NPs using Cassia alata leaf extract and Zinc acetate. (0.01M). UV causes the production of ZnO NPs. The presence of a prominent peak at 320 nm was seen in visible spectra, validating the nanoparticles' production.

The existence of spherical nanoparticles with sizes ranging from 60 to 80 nm can be seen in SEM micrographs. Machado et al [35] investigated the capability of producing iron nanoparticles from a variety of tree leaves. The antioxidant potential of leaf extract was also assessed.

The findings show that dried leaves produce more antioxidant-rich extracts than non-dried leaves. The use of A. Indica leaves extract to apply green generated FeNPs has also been reported [36]. A recent study used aqueous leaf extracts of Gomphrena globosa and Gomphrena serrata to synthesize copper oxide nanoparticles. With two distinct geometries of rods and spheres, the synthesized NPs had an average particle size of 345 and 380 nm.

III. CONCLUSION

Increasing demand for green chemistry and nanotechnology has pushed for the adoption of green synthetic approaches for nanoparticle synthesis in recent decades. Plant biomolecules such as proteins/enzymes, polysaccharides, alkaloids, and alcoholic chemicals may be involved in metal nanoparticle bioreduction, production, and stability. Because of their cost-effectiveness, nontoxic method, convenient availability, and environmentally benign character, many studies have been conducted on plant extract-mediated metal nanoparticles production and applications in numerous industries. They also have a wide range of applications in catalysis, medicine, dye degradation, biotechnology, electronics, optics, and biomedical sectors, to name a few. The focus of future research will be on improving reaction conditions and developing recombinant organisms for the manufacture of transition metal nanoparticles.

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