

## Green Synthesis is Preferred over Chemical Synthesis of Nanomaterials

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### Abstract

Nanotechnology is an emerging field which includes various synthesis of nanomaterials. Nowadays, it has become an interesting topic in the field of research due to its properties like unique optical, magnetic and electrical properties, which can be applied in the field of mechanics, electronics, medicine, solar and oxide fuel batteries for energy storage, biotechnology, microbiology, environmental remediation, and material science. Varied metallic nanomaterials are being composed using copper, zinc, titanium, magnesium, silver, and gold. Nanoparticles have been seen to be produced physically and chemically, but recent advances show the major role of biological molecules in the production of metallic nanoparticles. The approaches for the nanomaterial synthesis are mainly chemical and physical approach but these approaches are very costly and can be harmful to the environment. So, to avoid these problems, plant extract from different plants are being used in the production of nanomaterials through green synthesis of nanoparticles. These biological approaches are alternative, efficient, inexpensive and environment friendly.

**Key words:** Nanoparticles size; Nanoparticles synthesis; Nanoparticles a review; Green synthesis of nanoparticles; Green synthesis of nanoparticles using plant extract; Green synthesis of bimetallic nanoparticles

### Introduction

Nanotechnology is one of the most dynamic area of research in present day material science. This field which is creating step by step is having an effect in circles of people's life and making a developing energy in the existence science, particularly biotechnology and biomedical science [1]. Nanotechnology introduces to a developing field of science that consists of formulation and implementation of materials whose components exist at nanoscale.

Nanoparticles can be described as particles ranging in size from 1-100nm. Varied metallic nanomaterials are being composed using copper, zinc, titanium, magnesium, silver, alginate and gold. Nanoparticles have been seen to be produced physically and chemically,

but recent advances show the crucial role in biological molecules in the production of metallic nanoparticles. Nanoparticles (NPs) and nanostructured materials (NSMs) represents an active field of research and in a techno-economic sector because of their alternating physical and chemical characteristics such as melting point, wettability, electrical and thermal conductivity, catalytic activity. Nanomaterials are those materials with any internal or external structures on nanoscale dimension [1]. Nanoparticles display novel properties dependent on explicit attributes, for example, shape, size and dispersion. Nanocrystalline particles have discovered colossal application in the field of high affectability bimolecular location and diagnostics, therapeutics and antimicrobials [2] catalysis and microelectronics [3].

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### Synthesis of Nanomaterials

Nowadays, nanomaterials are becoming an intriguing topic in the field of science and research due to the presence properties like unique optical, magnetic, and electrical properties. The synthesis of nanomaterials follows two approaches: -

#### Top down Approach

In this approach the big solid particles break down into small pieces by applying external force. It is done in the following ways:

- Pulse laser ablation
- Evaporation-condensation
- Ball milling.

#### Bottom up Approach

In the bottom up approach the small molecule gather and combine into big particle and matter. It is done in the following ways:

- Sol gel process
- Aerosol based process
- Atomic or molecular condensation
- Hydrothermal synthesis
- Spray drying
- Cryochemical process

The main disadvantages in these two approaches are that they undergo oxidation or reduction process and thus the nanoparticles that are formed carry a lot of toxicity. The toxicity can also be caused due to the usage of stabilising agents that are used during the process. The nanoparticles that are formed can be toxic in terms of shape, size and surface chemistry. To avoid these problems nowadays the nanomaterials are formed with the help of plant extract. The technique in which plant extract are used in the formation of nanomaterials is known as green synthesis of nanomaterials. Metallic nanoparticles produced by biological method (green synthesis) have the following uses like bio-imaging, drug transport, cancer treatment and medical diagnosis.

Anyway, there is still requirement for cost effective and eco-friendly combination nanoparticles [4]. Various approaches are accessible for the union of nanoparticles for instance, decrease in arrangement, photochemical and concoction response in disintegration of nanoparticle compounds [5], radiation based, electrochemical, microwave-based process and through green science technique [6]. The utilization of environmentally friendly materials like plant extract (leave, bud, bark, seed, stem etc..), organisms, microscopic

organisms, and catalyst for the union of nanoparticles offers various advantages of eco-friendly and similarity for pharmaceutical and other biomedical applications as they don't utilize harmful substance for the combination process [7]. Nanoparticles have for some time been perceived as having inhibitory impact on organisms present in therapeutic and modern process [8]. Use of nanoparticles to genomics, safe reaction improvement, biosensors, and clinical science, control of microorganism and recognition and focused on drug targeting [9]. Further these biosynthesis of nanoparticles were found profoundly lethal against various human pathogens.

#### Naturally Produced Nanomaterials

NPs and NSs exists in living organisms varying from microbes such as bacteria, algae and viruses to complex organisms such as plant, insects, birds, animals and humans. Modern advancements in the paraphernalia to visualize NMs help in analysing the structure of these naturally formed NMs which will eventually lead to better study of these organisms. Plants survive on the nutrients available in soil and water for their development which leads to the agglomeration of these bio-minerals in nanoform.

The plant kingdom "Plantae" consists of about 12 divisions grouped as follows:

1. Three non-vascular (they cannot circulate rainwater through their stems/leaves but must absorb it from the environment that surrounds them) phyla (bryophytes): Hepaticophyta (liverworts), Bryophyta (mosses), and Anthoceroophyta (hornworts)
2. Non vascular phyla, four of which are seedless (Pterophyta (ferns), Psilophyta (whisk ferns), Lycophyta (club mosses), and Arthropophyta (horsetails))
3. The remaining five are classified in two groups: gymnosperms (Gnetophyta, Cycadophyta, Ginkgophyta, Coniferophyta), and angiosperms (Anthophyta).

Today, botanists recognize four broad classifications within the plant kingdom that show the plants' hierarchy. These include mosses, ferns, gymnosperms, and angiosperms [10].

In this paper we will see how nanoparticles are synthesized from different groups of plant kingdom.

#### Algae

ALGAE are eukaryotic amphibian oxygenic photoautotrophs, and some of them can aggregate different substantial metals. In any

case, there are not many reports about natural union of novel metal nanoparticles utilizing green synthesis. The dried alga *Chlorella vulgaris*, a solitary celled green alga, was found to have solid restricting capacity towards tetrachloroaurate particles to shape algal-bound gold, which was in this way diminished to Au (0). Around 88% of algal-bound gold accomplished metallic state and the precious stones of gold were gathered in the internal and external pieces of cell surfaces with tetrahedral, decahedral and icosahedral structures [11]. *Spirulina platensis* a consumable blue-green alga and the dried alga was utilized for the extracellular combination of gold, silver and Au/Ag bimetallic nanoparticles [12]. Recently, Singaravelu et al. [13] and Rajasulochana et al. [14] announced the blend of extracellular metal bionanoparticles utilizing *Sargassum wightii* and *Kappaphycus alvarezii*, individually. Additionally, researchers [15] revealed the intracellular creation of gold nanoparticles utilizing *Tetraselmis chiochinesis*. Additionally, our gathering recently covered the bioreduction of Au (III)– Au (0) utilizing biomass of the dark coloured alga *Fucus vesiculosus* [16]. In this work, biosynthesis of gold nanoparticles has been researched utilizing fluid chloroaurate particles and dead green growth as a perfect innovation to extract gold. This technique shows the noteworthy favorable position of utilizing green synthesis, a boundless wellspring of crude material. The objective of this examination was to research a inexpensive and eco-friendly technique for nanoparticles development utilizing green synthesis and to decide the ideal conditions for the blend and the control of the morphology of the molecule. The accomplishment of this work was that to control the shape by methods for an organic system changing factors, for example, the kind of biomass (*Chondrus crispus* and *Spyrogira insignis*) and pH.

Nanoparticle development utilizing the red alga *C. crispus* and the green alga *S. insignis* under various trial conditions was examined in the present research. The pace of nanoparticle fabrication and in this way the size of the nanoparticles can be controlled by controlling various parameters [17]. Endeavors have likewise been made to control the shape and size of gold nanoparticles delivered extracellularly through adjusting key parameters [18, 19]. While trying to control the size and state of the metallic nanoparticles, the impact of parameters, for example, pH or time presented to metallic nanoparticles utilizing various biomasses was examined. *C. crispus* is little purplish-red ocean growth (up to 22 cm since quite a while ago) found on rough shores and in pools. Some researchers [20] have showed that algae producing polysaccharide like carrageenan can tie substantial metals. They proposed that degrees of

sulphation in carrageenans may represent their various capacities to tie substantial metals. In this work, green synthesis are proposed for the biosynthesis of gold and silver nanoparticles as an efficient, eco-accommodating and basic procedure. The gold nanoparticle size and shape could be legitimately constrained by the underlying pH estimation of the arrangement, particularly if there should be an occurrence of the red kelp *C. crispus*. The biosynthesis of gold and silver nanoparticles was additionally achieved with the green alga *S. insignis* under the ideal states of combination including the probability of metal recovery by absorption on the biomass surface. This is a primary investigation of the natural component of nanoparticle biosynthesis and a first step in controlling the size of nanoparticles.

Investigating on biogenic combination of silver and copper nanoparticles which is utilizing green growth have been unexplored; there are scarcely any practical works found on silver nanoparticles [21-25] yet on copper nanoparticles less and none utilizing green alga *Botryococcus braunii*. The present examination has demonstrated that the utilization of green alga *Botryococcus braunii* as biofactory for union of silver and copper nanoparticles and their antimicrobial exercises. To best of our insight and comprehension, there is no report on union of silver and copper nanoparticles utilizing green synthesis *Botryococcus braunii*. In this examination, we have utilized green alga *Botryococcus braunii* for biogenic agglomeration of copper and silver nanoparticles. Blended copper and silver nanoparticles were inspected for antimicrobial action against bacterial and fungal species. Moreover, UV visible spectra have been routinely utilized for portrayal of biogenically combined nanoparticles [26]. Aqueous concentrate of green alga *B. braunii* was included into aqueous arrangement of copper acetic acid derivation and silver nitrate for copper and silver nanoparticles, separately. The arrangement of copper and silver nanoparticles was characterized by colour change from light sky blue to dull dark colour and light yellow to reddish brown through visual observation means, indicating the decrease of copper and silver particles into their separate nanoparticles [26, 27]. In this decrease procedure, metal nanoparticles scatter and absorb light at a certain wavelength because of the excitations of electrons at the interface between a conveyor and a separator, the marvels called surface plasmon vibration [28]. This work exhibited an eco-friendly and helpful technique utilized for union of silver and copper nanoparticles utilizing green alga *Botryococcus braunii*. Fluid concentrate of green alga can diminish silver and copper particles into silver and

copper nanoparticles and can possibly balance out them. Biogenically incorporated nanoparticles were portrayed by different systems, for example, UV-ray spectroscopy, Fourier transform infrared spectroscopy, scanning electron microscopy, and X-ray diffraction and showed antibacterial and antifungal action. The biogenic combination of metal nanoparticles can be a promising process for production of other metal and metal oxide nanoparticles which can have natural, significant, pharmaceutical, restorative, and biotechnological applications.

Algae such as *Chlorella vulgaris* aid the formation of AgNPs [29], phytochelatin coated CdS by *Phaedactylum tricornutum* [30], and nanocomposites and nanoporous structures via coccoliths and diatoms. [31] Since very finite studies are available, the conceivable mechanisms for algae mediated nanoparticle evolution are still undefined. [32]

### Fungi

In this innovative era, which tallied on the usage of various prokaryotes such as bacteria, for the biosynthesis of nanoparticles, recently, the National Chemical Laboratory, Pune, used FUNGI, in the growth of various nanoparticles of varied chemical composition and sizes. A divergent genera of fungi are found out to be extraordinarily good at the synthesis of metal and metal sulphide nanoparticles. [33,34] Certain fungi are capable of bringing about some extracellular metabolites, which serve as an escape for its survival when exposed to some environmental stress such as predators, temperature, variations, and toxic materials (metallic ions).

For the biosynthesis of metallic NPs, derived from a fungi, its mycelium is exposed to metal salt solution. This directs the fungus to manufacture enzymes and metabolites for its existence. In this process the toxic metal ions are transformed into non-toxic metallic solid NPs through the catalytic effect of the extracellular enzymes and metabolites and enzymes of the fungus. The presence of hydrogen as enzyme in fungi such as, *Fusarium oxysporum* [35], *Trichoderma reesei* [36], *Trichoderma viridae*, was found in the cell wall suspensions [37]. Besides, extracellular enzymes, several naphthaquinones [38-40] and anthraquinones [41] with extraordinary redox properties, were found in *Fusarium oxysporum*. [42-44]. Usage of *Fusarium oxysporum* and *verticillaster* sp. in the biosynthesis of magnetite. [45] Yielding of gold nanotriangle by *Actinomyces*, a bacteria resembling fungi. [46] Intracellular synthesis of Au and Ag NPs using *Verticillaster* fungal cells. [47-49] Extracellular production of Au, Ag and bimetallic Au-Ag alloy nanoparticles

from *Fusarium oxysporum*. [50-54]. Extracellular manufacture of Ag NPs *Aspergillus fumigates*. [55]

A pathogenic yeast, which is an eco-safe reducing and capping agent, is employed for the fructification of ZnO, non-toxic, cost effective and non-hygroscopic polar inorganic crystalline material is a Lewis acid catalyst. It is utilized as a heterogenous catalyst in the synthesis of pyrazoline derivatives. Pyrazoline share exotic groups of compounds, which retain a broad spectrum of pharmacological properties such as analgesics, anti pyretic and anti androgenic activities. They also possess anti-depressant, anti-inflammatory, anti-rheumatic, anti-diabetic and anti-tumour actions.

X-ray diffraction analysis, reveal that the size of ZnO particles is about 25nm. SEM analysis reveal that the average size of the nanoparticles stands between 15nm-25nm. TEM analysis confirm that the ZnO particles are quasi-spherical and their size is equivalent to 20nm. The production of ZnO nanoparticles employing *C.albicans* as a safe, reusable, cost-efficient heterogenous catalyst, are used for the rapid and efficient synthesis of steroidal pyrazolines.

A mesophilic filamentous fungi which secretes a huge amount of cellulytic enzymes, such as, celluloses and hemicellulases, upto 100g/lit [56], which is much higher in comparison to the fungi. The range of extracellular enzymes and metabolites, it produces, are of varied type, which includes, industrial production of glucosidase, paracelsin, protein, acetyl xylemasterase, cello-biohydrolase D, cellulose, cell wall lytic enzyme, and glucose. [57] In ultra violet visible spectroscopy, there is an amplified intensity of silver solution with time, indicating the production of increased amount of Ag nanoparticles in the solution.

In fluorescent emission spectroscopy, the dissociation of silver nitrate is due to the reductase enzyme (nitrate reductase), which stands responsible for the reduction of Ag<sup>+</sup> ions and the subsequent formation of metallic silver NPs. [58]

Fourier transform infrared spectroscopy (FTIR) is a contrivance which is employed to study the existence of protein molecules in the solution, and check for the presence of C=O and N-H groups [59]. The existence of amide linkages between diverse amino acids residues, in polypeptides and proteins, give rise to well-known signatures in the infrared region of electro-magnetic spectrum. The situation of bands are close to be reported in literature for indigenously proteins. [60, 61] Measurements indicate that *Trichoderma*



reesei arise out extracellular synthesis of AgNPs with a diameter in the range of 5-50nm. This fungus is known for its efficiency in producing AgNPs and are not harmful to humans. [62]

Filamentous fungi can obtain an ample amount of metal NPs, such as, Au [63-65], Ag [66,67], iron oxide [68] and bimetallic NPs [69]. The commonly used NPs are AuNPs. The synthesis of AuNPs can be sorted into four specific categories, based on processing and the utility of fungal mycelia. In the most basic approach, washed mycelia is involved directly in the generation of NPs intracellular (in vivo) [69- 72]. The three possible in vitro methods doesn't employ this step. At first, the supernatant of the filamentous fungi which contain extracellular proteins and other secreted compounds, can be used for the production of AuNPs [73,74]. In the other approaches, the intracellular constituents of fungi are adept in yielding biologically synthesized Au nanoparticles (BioAuNPs) after the severance of cells.

Lastly, the aqueous extract in which the mycelium were kept suspended can be used for the biosynthesis of AuNPs [75-77]. These methods include the autolysis of cells followed by dissolution of membrane proteins and surface carbohydrates into the aqueous solution. But, the drawbacks still prevail these methods. Bacterial contaminations in the aqueous extract of mycelia, can lead to inaccurate outcome [78]. But, this can be overcome using antibiotics, which might influence and expedite the production of NPs. The usage of these antibiotics in the production of BioAuNPs should be shunned, because the usages of antibiotics are environmentally-unfriendly. The usage of 29 thermophilic fungal strain fermented on the two growth media (PDB and modified Czapek-Dox), was used in the manufacture of AuNPs. Similar positive results were obtained, when the three processing methods of mycelium, were grown on PDB and the usage of synthetic media i.e., modified Czapek-Doxin the growth of fungal mycelia. In PDB, components such as Glucose, amino acids, proteins, are capable of reducing Ag (III) to Ag(0). The usage of synthetic media, decreases the number of reducing agents, where glucose is used as carbon source. [79-81]

### **Bryophytes**

Biosynthesis of nanoparticles utilizing plant concentrates is the most recent most loved technique for green, eco-accommodating creation of nanoparticles as it offers one stage. As of now it is misused to a tremendous degree in light of the fact that the plants are generally dispersed, effectively accessible, safe to deal with and with a scope of metabolites [82]. Biosynthesis strategies have more

pay over other old style combination methodology because of the accessibility of progressively organic substances and eco-accommodating techniques. The rich biodiversity and simple accessibility of plant substances have been exceptionally investigated for the nanomaterials combination [83]. Silver is the one of the most popularized nano-material with 500 tons of silver nanoparticles creation every year [84] and is evaluated to increment in approaching years. Silver nanoparticles have likewise picked up importance because of their expansive range action against bacterial diseases. Plant unrefined concentrate contains novel optional metabolites, for example, phenolic corrosive, flavonoids, alkaloids and terpenoids in which these mixes are principally liable for the decrease of ionic into mass metallic nanoparticles arrangement [85]. These essential and optional metabolites are always engaged with the redox response to integrate eco-accommodating nanosized particles. Numerous past reports are exhibiting that biosynthesized nanoparticle viably controlled oxidative pressure, genotoxicity and apoptosis related changes [86].

Bryophytes are crude land plants demonstrating basic association of the thalloid plant body [87]. The bryophytes have an assortment of synthetic substances and hence can be utilized from multiple points of view. When contrasted with Angiospermic plants, Bryophytes are invaluable as the obstruction of the biochemicals could be lower because of their straightforward crude association of body. The work on bryophytes with respect to biosynthesis of nanoparticles is very small when contrasted with other plant gatherings. [88], have examined Ricciasps., Anthocerosps. What's more, Fissidens minutes for the combination of silver nanoparticles and their antibacterial movement.

Green combinations of AgNPs have been performed utilizing plant separates, microbial cell biomass or cell free development medium and biopolymers. The plants utilized for AgNPs blend extend from green growth to angiosperms; nonetheless, constrained reports are accessible for lower plants and the most reasonable decision are the angiosperm plants. The bryophytes have an assortment of synthetics and consequently can be utilized from numerous points of view. When contrasted with Angiospermic plants, Bryophytes are beneficial as the obstruction of the biochemicals could be lower because of their straightforward crude association of body.

Bryophytes demonstrate to be a novel hotspot for biosynthesis of silver nanoparticles. Because of their basic association of thallus, the extraction and amalgamation of nanoparticles is an effortless

procedure. The cloth joined nanoparticles show antibacterial movement and along these lines can be utilized on a huge scale to stay away from bacterial contaminations particularly if there should be an occurrence of consumes and skin issues. The silver nanoparticles incorporated from bryophytes appear to guarantee and successful antibacterial specialist [88] have researched Ricciasps., Anthoceros-sps. What's more, Fissidens minutes for the union of silver nanoparticles and their antibacterial action. The present survey will be useful to give new vistas to beginner researchers about future degree and to do assist examinations about utilization of the bryophytes in the biosynthesis of silver nanoparticles and their antimicrobial property. [89]

Bryophytes are crude, nonvascular land plants and show the basic association of the thalloid plant body. Among the bryophytes greeneries were the propelled gathering involved the one of a kind situation between lower cryptogams and vascular cryptogams [90]. *C. flexuosus* is an acrocorpous greenery, has a place with the request Dicranales, family Dicranaceae. It is Dioicious, fairly glossy, green to olive-green, plants in thick tufts, variable size and power, 1-10cm. High, tomentose, dichotomously spread. Leaves erect to erectopatent, flexuose, when dry  $\pm$  6mm long, lanceolate-subulate, from a more extensive base gradually narrowing down into a canaliculatesubula with incurved edges. Leaf tip edge serrate and the tip not hyaline. Costa about  $\frac{1}{2}$  the leaf base, with substereide packages on the dorsal side however the dorsal surface smooth. Alar cells darker, exceptionally swelling, rather enormous framed of huge expanded, lamina cells at base long rectangular, close to costa turning out to be about half as tight close to edge, practically rhomboidal and incrasate at edge [91].

Affirmation of biosynthesized AgNps: Present investigation is to concentrate on the green blend of silver nanoparticles utilizing *C. flexuosus* utilized with silver nitrate arrangement. Silver nanoparticle development affirmed by the light yellow shading change into ruddy dark coloured shading. Sign of shading change is the essential affirmation of nanoparticle combine. Further these incorporated silver nanoparticles were affirmed through the portrayal studies like UV-Visible spectroscopy, FTIR, FESEM, EDAX, Zeta potential, Particle size and XRD.

At present numerous methodologies have been utilized to orchestrate the silver nanoparticles in straightforward and simple strategies. It incorporates both synthetic and natural techniques. These days the nanoparticle orchestrate utilizing plants were pulled in

by numerous specialists [92]. Along these lines the greener blend procedure is (i.e union of silver nanoparticles utilizing plants) is simple and eco well disposed technique and furthermore savvy [93]. In the present investigation the greenery (Bryophyte) plant is intervened to combine the silver nanoparticles. Expansion of silver nitrate with the plant concentrate show a shading change of yellow to ruddy dark colored with a specific length of brooding time. This is the starter affirmation of silver nanoparticle. A similar outcome was acquired in the greenery plant *Fissidens minutus* [94]. Silver nitrate broke up in water transformed into silver free particles Ag<sup>+</sup> to Ag<sup>0</sup>. By adding the plant concentrate to silver nitrate, the free silver particles gets the electron moiety and it will shape into natural silver [95]. Development of rosy darker shading is because of the surface plasmon reverberation [96]. The ingestion maxima in UV-Vis is at 436nm, fundamentally the same as result were acquired in *Anthoceros* intervened AgNps where  $\lambda$  max is at 438nm [97]. FTIR examination uncovered the nearness of carbonyl mixes went about as a topping specialist to combine the AgNps. A similar outcome were accounted for in the fluid concentrate of *Amaranthus dubius* AgNps [98]. FESEM investigation demonstrated the 50 to 70nm in the CfAgNps. The outcome were understanding with *Bacillus Ag-Nps* [99]. Natural investigation demonstrated the amount of silver is trailed by C, Cl, O and Si the outcome acquired by [100] The zeta potential worth appeared for CFAgNps the negative aversion the comparative outcome were supported with *Urticadioica* incorporated AgNps [101]. Molecule size dispersion uncovered the 113nm normal size particles the comparable outcomes were gotten in the *Ficus carica* [102]. XRD example decided the normal molecule size is 51nm same outcomes were coordinated with *Argemone Mexicana* AgNps 20nm size reaches from 10 to 50nm [103].

### Pteridophytes

Aquatic macrophytes include aquatic spermatophytes (also known as flowering plants), pteridophytes (ferns) and bryophytes. Schwarz and Haves also included the charophytes (*Chara* sp. and *Nitella* sp.) as aquatic macrophytes. These aquatic macrophytes are usually classified into 4 groups:-

Group 1- emergent macrophytes

Group 2- floating leaved macrophytes

Group 3- submerged macrophytes

Group 4- free-floating macrophytes (representing plants that are non-rooted to substratum)

After extensive investigation and review of the potential of aquatic macrophytes for heavy metal removal, their abilities to hyperaccumulate heavy metals make them important for research candidates for the synthesis of metal and metal oxide nanoparticles. Metal nanoparticles especially silver ones have drawn attention of researchers because of their suitable applications in the fields of electronics, mechanics, optics, biomedical sciences, chemical industries, space industries, drug gene delivery, energy science, catalysis, optoelectronic devices, photoelectrochemical applications and non-linear optical devices.

Azolla (example; mosquito fern, duckweed fern, fairy moss, and water fern), the only genus in the family of Azollaceae, is a genus of 7 species of aquatic fern. It is a floating water fern and is common in many countries. It is used as a fertilizer in rice fields. It grows rapidly in stagnant wetlands and covers the surface of water. Azollapinnata is a free-floating aquatic fern, which grows at a fast rate, doubling its biomass in 3-5 days and fixes atmospheric nitrogen by forming a symbiotic relationship with *Anabaena azollae* (a blue-green algae). Azollapinnata has high potential for removing heavy metal ions from aqueous solutions, and thus, it is one of the best candidates for nanoparticle synthesis. Azollapinnata is suitable for wastewater treatment because of its growth at faster rate, large biomass production, relative high capability of pollutant uptake and effective purification effects due to its direct contact with contaminated water. 96% hydroalcoholic extracts of Azollapinnata successfully produced small, spherical and polydispersed silver nanoparticles with low aggregates in the early hours of the biotransformation. The conversion was quick and completed in 5 hours. Thus, this plant and extraction method seems to be very useful for industrial scale production of silver nanoparticles. [104]

The fern *Adiantum philippense* L. Is well known for its antioxidant potential and has been used in treatment of paralysis, blood diseases, epileptic fits, rabies, dysentery, elephantiasis, and wounds. It also has antimicrobial activity. Phytochemical examination of the plant detaches having a place with class *Adiantum* contains sugars, phenols, flavonoids, and terpenoids. Presence of these compounds might have a role in making *Adiantum* a potential organism for bioreduction of gold and silver salts. In the present study, *Adiantum philippense* L. extract is used for the synthesis of gold and silver nanoparticles. Researchers have developed a method for synthesis of gold and silver nanoparticles using fern *Adiantum philippense* L. at room temperature within 10 mins. The TEM and EDS analysis

results both demonstrate that nanoparticles are successfully synthesized using *Adiantum philippense* L. extract in this study. Medicinal importance of ferns makes them one of the best suitable candidates for the biosynthesis of nanoparticles and application in disease treatment. Use of such plants has a great potential in nanoscience for drug delivery and biomedical application. Exploitation of synthesized capped nanoparticles would be useful in gaining knowledge about the nature of capping agent and utilizing them for medicinal and biomedical applications. [105]

### Gymnosperm

Right from cyanobacteria to giant tree greeneries and pines are exception all because of their wide yet efficient fortunes of metabolites, fit for cooperating with one another, obeying the principles of thermodynamics. *Cycas*, which has a place with the family Cycadaceae is a typical gymnospermic plant. Alongside unsaturated fats (like palmitic, stearic, and oleic acids), they are rich in flavonoids extensively with the class of phenolic compounds. [106] The term phenolic compound grasps a wide scope of plant substances that bear in like manner a fragrant ring with at least one hydroxyl substituents. Some 10 classes of flavonoids are recognized but they are essentially hydrophilic mixes and are available in every vascular plant. *Cycas* leaves have been found to contain Amentiflavone and Hinokiflavone as trademark biflavonols. [107-111] Synthesis of metallic or metal oxide nanoparticles taking help of plant concentrates has accomplished an upsurge in the past. [112-118].

They are generally appropriate along the natural limits, are effectively accessible and safe to deal with, furnished with a wide material of metabolites, and, most importantly, they are green while undertaking any transformation. Such studies could demonstrate to have a gigantic way in the prompt future if plant tissue culture and downstream handling strategies are applied to blend metallic oxide nanoparticles on mechanical scale. In this work, *Cycas*-arranged combination of silver nanoparticles (truncated AgNPs) has been accounted for gymnosperms could likewise be taken as potentially upcoming plant examples for the combination of metal just as oxide nanoparticles. An exertion has been additionally been made to comprehend the techniques for the biosynthesis of AgNPs. Salt/metal particle alters the temperatures and increase the degrees of receptive oxygen species (ROS). Unreasonable levels of ROS lead to oxidative harm to cell particles, maturing, and cell passing. The anti-oxidative frame work is significant for the support of intracellular ROS at proper levels. [119] Mechanisms of metal detoxification by

biomolecules continues as course of time, for example, acceptance of proteins, metallo-thionein, heat-shock protein, phytochelatin, and ferritin, moving; or by activating cancer prevention agent catalysts, for example, super oxide dismutase, catalase, glutathione, and peroxidase; or through high turnover of natural acids, for example, malate, citrate, oxalate, succinate, aconitate and  $\alpha$ -keto glutarate. Different kinds of substantial metal adjustment methodologies in plants have thoroughly been studied. [120] Primarily two sorts of components may disclose the protection from the lethality of metal particles in plants. The conspicuous metal complexation procedures are the combination of phyto-chelatin and of other metal-chelating peptides.[120,121] Phytochelatin was seen as prompted by Ag, Bi, Cd, Cu, Hg, Ni, Sn, W, and Zn, though no acceptance was seen on account of Na, Mg, Al, Ca, V, Cr, Sb, Te, Mn, Fe, Co, and Cs. Glutathione functions as a precursor of phytochelatin combination. Metal-instigated phytochelatin creation diminishes cell levels of glutathione. Glutathione and its homologues, viz. Homo-glutathione and hydroxyl-methyl glutathione, are the abundant low-atomic weight thiols in plants. Glutathione was involved to assume a significant role in plants presented to metal stress. [121] Metallothionein (MT) is a family of cysteine rich, low-atomic weight (MW extending from 3500 to 14000 Da) proteins. MT have the ability to tie both physiological, (for example, zinc, copper, selenium) and xenobiotic, (for example, cadmium, mercury, silver, arsenic) metals through the thiol gathering of its cysteine deposits, which accounts to almost the 30% of its amino acid constituents. There is little data about MT genes in non-flowering plant species. In any case, genes encoding type 3MTs have been cloned from a few gymnosperms. [122] Antioxidant activity of phenolic mixes is because of their high inclination to chelate metals. Phenolics have hydroxyl and carboxyl gatherings, ready to tie especially iron and copper. They may inactivate iron particles by chelating and more over stifling the super oxide-driven Fenton reaction, which is accepted to be the most significant well spring of ROS. Tannin-rich plants, for example, tea, which are tolerant to Mn over abundance, are ensured by the immediate chelation of Mn. Plants contain two significant kinds of peroxidases, which can be isolated into two groups: peroxidases that utilizes ascorbic acid as the electron donor, and those that utilizes phenolics. Phenolics, particularly flavonoids and phenyl propanoids, are oxidized by peroxidase, and act in H<sub>2</sub>O<sub>2</sub>-searching structure. Their cancer prevention activity resides mainly in their chemical structure. There is some evidence of induction of phenolic digestion in plants as a reaction to various burdens (counting overwhelming metal stress) [123]. Reduction is cultivated because

of phytochemicals (flavonoids or other some other polyphenols) or phytochelatin/glutathione/metallothioneins present in *Cycas* leaves parenchyma. It is settled that the biflavanone, tetra hydro hinokiflavone, together with amentoflavone, has been found in the leaves of *Cycas beddomei*. [124] In *Cycas* leaf stock having admirably defined metabolite treasure, the procedure of nano-change may have come about because of redox exercises of ascorbic/dehydro-ascorbic acid and amentoflavone/hinokiflavone and involvement of ascorbate/glutathione/metallothioneins, prompting the decrease of silver particles present in the arrangement.

The decrease in response time with *Cycas* leaf has significant outcome and will empower nanoparticle biosynthesis strategies to contend with other plant-helped biosynthesis courses for the development of silver nanoparticles that areas of now are substantially quick and producible.

The progress metal nanoparticles assume a significant role in natural responses in view of their high surface to volume proportion that can drastically upgrade the collaboration among reactants and bigger number of dynamic molecules per unit region to the parent metal. Furthermore, nanocatalysis can make the items effectively removable from the response blends. There are a few techniques for the amalgamation of copper nanoparticles (CuNPs) utilizing harmful and costly synthetic mixtures, compounds in natural solvents [125,126]. The nearness of these dangerous and hazardous materials on the outside of CuNPs expands the danger issue while the utilization and transfer of harmful solvents triggers environmental issues. In any case, green synthesis of nanoparticles by various plants or gums is a natural, savvy strategy without utilization of intense synthetics.

*Ginkgo biloba* Linn is from the group of Ginkgoaceae is world's most established tree generally known as living fossils and the only surviving organism from seed plant group. It is discovered developing normally in very restricted regions in the focal Himalayan Mountain. The leaves of this species is broadly utilized as a source of natural medication for nearness of restorative phytochemicals. Additionally, the synergistic capability of CuNPs was assessed in the Huisgencyclo addition of azides also, alkynes at room temperature. The concentrate of *G. biloba* Linn leaves was got ten in fluid media which can separate the exceptionally polar Phyto-constituents of the plant like polyphenolics with conjugated double bonds (in A, B and C ring of the flavones cores) and sweet-smelling rings in their structure as significant *G. biloba* Linn constituents.



In this manner, the one focused at 235 nm (bond II) is for absorbance of ray identified with the benzoyl framework on which these spongy securities exhibit the nearness of polyphenolics. The FTIR examination was done to distinguish the conceivable bio-atoms liable for the decrease of Cu nanoparticles and topping of the bio-reduced nanoparticles. CuNPs was described utilizing the UV, FTIR, EDS and TEM. The movement of the response, arrangement and dependability of CuNPs were constrained by UV-vis spectroscopy. The blended CuNPs by this strategy are very stable and no undeniable difference in the shape, position and balance of the ingestion pinnacle is watched much following one month showing the dependability of CuNPs. Besides, the FTIR of concentrate in the wake of including  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  while development of CuNPs shows expressive contrasts in the shape also, area of sign showing the association between  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  and included locales of phytochemicals for creation of nanoparticles. The size and state of the particles were analyzed by transmission electron microscopy (TEM).

### Angiosperm

In the formation of NPs plant extract, the extract is blended with a solution of metal salt at room temperature and reaction is carried out. The Ag and Au NPs are produced in this technique [127]. The speed and amount of production of NPs count on quality and concentration of the plant extract, concentration of metal salt, pH, temperature, and contact time. [128] The *Berberis vulgaris* belonging to the species of Berberidaceae family, is the barbed shrub. It is short and native in the mountainous regions of Mediterranean in Asia and Europe. The aqueous extract of the leaf and root of *Berberis vulgaris* is used in production of AgNPs. In the conventional medicine of Iran, the fruit of *Berberis vulgaris* is known as housing and its various parts like fruit, root, leaf, flower and stem are used as anti-bacterial, anti-fever and itching treatment.

Andean blackberry (*Rubus glaucus* Benth), a dark red coloured, juicy and flavoured fruit. It is devoured in Ecuador, Peru and Colombia as fresh fruit, jam, juice, frozen pulp and to minor extent as wine [129]. It is assumed that flavonoids, ellagitannins and anthocyanins could be exercised in the green synthesis of AgNPs. Modern studies show that spherical AgNPs were prepared efficiently using Andean blackberry fruit extract as a bio-reductant and stabilizer.

Bio-production of ZnONPs by means of green synthesis technique using *Moringa oleifera* extracts as a potent chelating agent. Mechanisms of fabrication of the ZnONP through the chemical reaction of the  $\text{ZnNO}_3$  progenitor with the bioactive compounds of the

*Moringa oleifera* recommended for each of the significant family compounds like vitamins, flavonoids and phenolic acid. [130]

Green synthesis of NPs attaining attention due to its simplicity, eco-friendliness, and extensive photocatalytic activity [131-134]. The primary agent in these syntheses are believed to be polyphenols present in coffee, banana peels and other plant wastes. Biological synthesis of NPs help in advancements over other methods as it is simple and cost effective [135-137]. The extract of *Chenopodium album* leaves, *Mimosa pudica* leaves and *Aloe barbadensis* were reported in green synthesis of Ag, palladium and other NPs.

### Chemical Synthesis

Chemical synthesis is one the foremost techniques that are carried out by the usage of various precursors and diverse conditions like temperature, time, quantity of reactants, etc. The variation in these parameters lead to the differences in size, and geometries of the generated particles. Vapour transport synthesis, hydro thermal technique, precipitation method, thermal decomposition, mechanical method, chemical vapour deposition, molecular and chemical routes are some of the methods involved in chemical synthesis. [138] These methods are highly promising in fabricating excellent quality nanoparticles required for future applications.

Mechanical technique shell etching of larger grained materials to nanostructures. Solution chemical routes are of the best approaches for the formulation of nanoparticles due to the augmented homogeneity from the molecular level design of the material and cost effective quantity production. The production of particles in a solution occurs by chemical reactions forming stable nuclei with successive particle advancement. This process of precipitation is well studied. [139,140].

### Chemical, Physical and Green Approach towards Synthesis of Nanoparticles

Chemical methods have been comprehensively used to fabricate nanoparticles due to their uncomplicated nature and their potential to manufacture enormous quantity of final product. In chemical advances, the pre-eminent constituent is the metallic messenger, stabilising agents and reducing agents (both inorganic and organic). For example- Tollen's reagent, DMF, sodium borohydride, sodium citrate, elemental hydrogen, and poly (ethylene glycol) block copolymer are used.

Concoction of nanoparticles by Physical Avenue is primarily “top-down” approach which ensures the material to be reduced in size by a sundry of physical approaches like ultra-sonication, microwave (MW) radiation, electrochemical method etc.

But the physical and chemical avenues have given rise to several stresses on the environment due to their baneful metabolites. The biological molecules are less toxic and are known for their exclusive properties. So green synthesis of nanoparticles ensures the usage of eco-friendly and non-toxic reagents, for fabricating metallic nanoparticles.

Green chemistry approach is vital for forthcoming anticipation of nanoparticles. This field of nanoscience should wrap up in the blossoming of safe, eco-friendly nanoparticles and should have far reaching scope in nanotechnology. Researchers have validated that the green methods are more competent to produce nanoparticles with the edge of chances of breakdown, low cost and simplicity of characterisation. Green synthesis provides an edge over physical and chemical method as it is cost effective as well as environment friendly, easily scaled up for large scale synthesis and in this method there is no need of utilizing high pressure, temperature, energy and toxic chemical. The green way for biosynthesis of nanoparticles: different procedures for the synthesis of nano and micro length scaled inorganic materials which have contributed to the growth of relatively new and largely unexplored area of research based on the biosynthesis of nanoparticles [141]. Green synthesis of nanoparticles makes utilization of environmental friendly non-toxic and non-harmful reagent. Phytomining is the use of hyper accumulating plants to extract a metal from the biomass to return an economic profit [142]. Hyper accumulation species have a physiological technique that monitors the soil solution concentration of metals. Process of biosynthesis of nanoparticles in plants may be correlated with phyto-remediation concept in plants [143].

Extract from bio-organism may behave both as reducing and capping agent in nanoparticles synthesis. The reduction of metal ions by combination of biomolecules present in these extracts such as protein/enzymes, polysaccharide, vitamin and amino acid is eco-friendly, yet chemically complex. An extensive volume of literature report nanoparticles successfully using bioorganic compounds [144]. Biological methods are regarded as harmless, cost effective, sustainable and environmental friendly mechanisms for the synthesis of nanoparticles.

### Types of Nanomaterials

Basically NPs and NSMs can be classified into 4 material based categories.

#### Carbon Based Nanomaterials

Mostly these nanomaterials comprises of carbon and form hollow tubes, ellipsoids or spheres.

Eg: Fullerenes, carbon nanotubes, carbon nanofibres, carbon black and graphene are included under this class. [145]

#### Inorganic Based Nanomaterials

These nanomaterials comprises of metal and metal oxide NPs and NSMs. These NMs can be synthesized into metals such as Au or Ag-NPs, metal oxides such as  $\text{TiO}_2$  and ZnO NPs and semiconductors such as Si and ceramics.

#### Organic Based Nanomaterials

These consists of NMs formed chiefly from organic matter, excepting carbon based or inorganic based NMs. The usage of non-covalent interactions for the self-assembly and architecture of molecules helps to revamp the organic NMs into desired structures such as dendrimers, micelles, liposomes and polymer NPs.

#### Composite Based Nanomaterials

Composite based NMs are multiphase NPs and NSMs with one stage on the nanoscale measurements that can either couple NPs with different NPs or NPs mix with bigger or with mass kind materials (eg. Hybrid nanofibres) or more intricate structures, such as metal-organic frameworks.

#### Characterisation of Nanomaterials

In the above portion several green syntheses were made with different plant to produce silver nanoparticle. Nowadays several syntheses were done to produce gold and silver nanoparticles as they have furnished superior characteristics with useful flexibility, result in good catalytic activity and atomic behaviour. In the green synthesis of nanoparticle with different plant and to feature their antimicrobial or antifungal or antimicrobial characteristic feature a number of characterization were done and these were done in the following ways :-

1. In the green synthesis of silver nanoparticles through the plant extract of *Aloe barbadensis* and to feature their antibacterial activity number of characterization were done like UV spectroscopy, FTIR, Zeta potential

2. Again, to specify the antimicrobial function in the green synthesis of silver nanoparticle through the plant of *Moringaolefera* number of characterization were done like X-ray spectroscopy, FTIR.
3. The characterizations of nanoparticle are divided into three components namely:-
4. Spectroscopy
5. Diffraction technique
6. Microscopic technique

**Spectroscopy:** Spectroscopy is the technique of splitting light into its constituent wavelength, a same way how a prism works where light slits into a rainbow of colours.

**Diffraction technique:** The diffraction technique utilizes the wave nature of electron in studying the crystal structure of the sample in terms of chemical position and nanoscale atomic precision with high precision.

**Microscopic techniques:** Microscopy is the technique used to view objects that cannot be seen by naked eyes. The range can be anything from mm and nm.

The component has different characteristic instruments through which characterization can be done in a more suitable way.

Spectroscopy	Diffraction technique	Microscopic technique
UV-visible spectroscopy	X-ray diffraction	Scanning probe microscopy (SPM) and electron microscopy
X-ray absorption	Powder method	Scanning Tunnelling microscopy (STM), Atomic force microscopy
X-ray photoelectron spectroscopy		Near field scanning optical microscopy (NFSOM)
Nuclear magneton resonance		Transmission electron microscopy (TEM)
Infrared including fourier transform infrared spectroscopy		Scanning electron microscopy (SEM)

The characterization of nanoparticles deals with the physical and chemical properties of nanoparticles and studies the nano-toxicology and exposure assessment related to health and safety hazards. With the help of characterization we can get an idea that whether

the synthesis of nanomaterial has been done in a controlled way or not. In the field of science where the nanomaterial act as a drug delivery agent, here with the help of characterization the properties of drug can be mentioned in the form of particle size, distribution, chemical composition and kinetics of drug loading and release.

### Application of Nanomaterials

#### Silver Nanoparticles

Silver nanoparticles are nanoparticles of high chemical stability and catalytic activity. Found in various field including medical, food, health care, industrial purpose (due to physical and chemical property). The silver nanoparticle plays an important role in biomedical synthesis such as antibacterial, antifungal, anti-inflammatory, anticancer and plays an important role in diagnostic biosensor and gene therapy application (anti-cancer activity).

According to Das et al, silver NPs synthesised with the utilization of alcohol extract medicinal herbs like *Phytolaccadecandra*; *Gelsemiumsempervirens*; *Hydrastiscanadensis*; and *Thujaoccedentalis* exhibits anti-bacterial and anti-proliferative effects. [146]

The antimicrobial properties of AgNPs is relying on the amount of Ag and ration of released Ag. Ag is inactive in the form of metals and reacts with moisture in the skin and wound fluids and ionize. The ionized silver is immensely reactive and unites itself with the tissue proteins and influences structural changes in the cell wall of the bacteria and the membrane of nucleus and sooner or later leads to apoptosis. [147,148]

Several green synthesis from different plant has been done by different ways to produce silver nanoparticle

Plant and plant extract	Action
Aloe barbadensis	Antibacterial action
Moringaolefera	Antimicrobial action
Azadirachta indica	Antimicrobial action
Cycas	Antimicrobial action
Salviniaspinosa	Antibacterial action
Crocus sativus L.	Antibacterial activity

#### Gold nanoparticle

Gold nanoparticle are small gold particles with diameter 1 to 100nm. The gold nanoparticle is used in various form like as an

agent of anti-microbial, anti-fungal and anti-biotic. Gold nanoparticle can be in therapeutic drug delivery and in photodynamic therapy (light is applied to a tumor containing gold nanoparticles, the particles rapidly heat up, killing tumor cells). [149,150]

### Zinc Oxide Nanoparticles

ZnO being representative of the group II-VI semiconductor family, crystallizes in the wurzite structure. [151] The inherent ability of ZnO such as broad range of radiation, absorption, high photostability, and large electrochemical coupling coefficient, makes it appropriate for short wavelength optoelectronic and photonic devices [152,153]. Considering its hardness and rigidity, it is a chief material in the ceramic industry, whereas its low toxicity, bio-compatibility and biodegradability make it a candidate of choice for biomedicine and in ecological systems such as cosmetics [148,149]. Nevertheless, the paramount applications of ZnONPs are sensor, energy generator, optoelectronics, biomedicine, and drug delivery design [154-158].

### Carbon Nanotubes

Carbon nanotubes are allotropes of carbon and they are long, hollow structure with the walls formed by one atom thick sheet of carbon called graphene. The application of carbon nanotubes are they can be used in the cancer treatment, in electrical cables and wires, in solar cell and in fabrics. [159,160]

### Nano Rods (Quantum Dots) and Nanobots

Nano rods are the nanomaterial ranging from 1-100nm in dimension synthesized from metals or semiconducting materials. In cancer therapeutics quantum rods plays a major role. Nanobots are microscopic in size and capable of replicating using environmental resources. The applications of nanobots are they are used as detecting agents of toxic component in environment, can be used as drug delivery and in biomedical instrumentation. [161-164]

### Conclusion

Green synthesis technique provides a quicker metallic nanoparticle synthesis and they are environment-friendly, simple, prudent and reproducible methodology. In the chemical synthesis of metallic nanoparticle, the synthesized nanoparticle contains toxic by-products because they are achieved by means of oxidation, reduction or catalysis of metals with metallic nanoparticle. Hence, biological methods of nanomaterial's are much better than chemical synthesis of nanomaterials. The synthesis of nanomaterials follows two approaches- top down approach and bottom down approach. The

main disadvantage of these two approaches is that they undergo oxidation or reduction process and thus the nanoparticles that are formed carry a lot of toxicity in terms of shape, size and surface chemistry. Physical and chemical methods yield nanoparticles with well-defined shape and size, but these techniques are expensive and potentially toxic to environment. These methods require the use of very reactive and toxic reducing agents, which cause undesired detrimental impacts on the environment, plant and animal life. This has created a demand to develop clean, non-toxic, economical and environment-friendly methods to synthesize nanoparticles. These concerns have led the researchers to develop biological methods for synthesis of nanoparticles. Nanoparticle synthesis through natural means (plants) does not require any extrinsic stabilizing agents as biomolecules present within the organism stabilize it during the synthesis process so no hazardous related issue arises and are also easily available at free of cost. Various organisms act as clean, eco-friendly and sustainable precursors to produce stable and well functionalised nanoparticles. These may include bacteria, actinomycetes, fungi, yeast, etc. In this manner, it is fundamentally imperative to investigate an increasingly dependable and practical procedure for the synthesis of nanomaterials. The green technology based production processes operate under green conditions without the intervention of toxic chemicals. In conclusion, green technology processes, as described in this paper, provide a strong foundation for the production of a variety of biochemical or functionalised nanoparticles that can serve as building blocks in the improvement of new items that can be relevant in natural reclamation sectors.

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