Chapter

Sustainable Utilization of Renewable Plant – Based Material for the Green Synthesis of Metal Nanoparticles

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Abstract

Despite the fact that biotechnology and nanotechnology have been developed for ages to assist vastly different domains including medical, industry, human health, and welfare, they have achieved impressive strides recently. The creation of metallic nanoparticles (NPs) quickly, sustainably, and without toxicity is crucial for the field of nanobiotechnology. An emerging field is the synthesis of metallic NPs (AgNPs, AuNPs, PtNPs, PdNPs, SeNPs, CuNPs, MgONPs etc.) using biological systems, particularly plants. Plant tissues, extracts, extrude, and other plant parts have all been widely employed to make metallic nanoparticles. If plant-based NPs are created extracellularly and their size, shape, and dispersion are managed, the benefit of using them can be exponentially ramped up. In order to produce nanoparticles on a large scale industrially, it is suggested that "green" synthesis of nanoparticles be a feasible prospect. This is because it is extremely very cost-effective. Plant-based NPs have identified a niche to demonstrate their application in every area of research, including agriculture, health, and the solution to the world's energy dilemma. In this light, the current chapter makes an effort to emphasis the environmentally friendly methods of "green" nanomaterial synthesis, characterization, and applications across different industries.

Keywords: nanoparticles, sustainability, metallic nanoparticles, green nanomaterial, green synthesis, environmental friendly

1. Introduction

There are numerous scientific and technological applications for the rapidly increasing, multidisciplinary subject of nanotechnology. To develop new techniques for managing and producing nanoparticles (NPs), this field integrates key ideas from a number of fields, including chemistry, engineering, physics, and biology [1–7]. Conglomerates of atoms fuse together in a controlled way to generate metallic nanoparticles, which range in size from 1 to 100 nm. They display a variety of qualities that depend on their size and shape and notably distinguish them from bulk materials. They can be synthesized through chemical or physical processes, resulting in a variety of nanoparticle shapes and properties. The massive amount of nanoparticles produced by wet synthesis techniques including electrochemical, sonochemical, and polyol reduction has shown them to be cost-effective, but because they require the use of hazardous chemicals and solvents, they cannot be applied in medical and clinic contexts [6–8]. During the last several decades, metal nanoparticles having distinct physicochemical properties have received significant attention in the development of new technology because of having a massive surface area by volume ratio, easy synthesis approach, and extensive potential applications. Scientists are currently working on green synthesis techniques to swap out harmful components for non-toxic, biocompatible, and environmentally friendly compounds. The scientific community has taken a great interest in the fabrication of metallic nanoparticles employing plant systems (live plants, plant extracts, and phytochemicals). Plants and their products can be used as a tremendous source of renewable and sustainable materials for nanoparticle synthesis [8, 9] because they can easily transform light energy into chemical energy [8–10] and because they can ingest, collect, use, and recycle diverse mineral species. Normal temperature and atmospheric pressure are required by plant-based methods using aqueous extract to make very stable nanoparticles, resulting in a quick and affordable bulk production [8]. There is little information on the intracellular synthesis of metallic nanoparticles because doing so involves laborious and expensive processing steps. The typical characteristics used to characterize this type of nanoparticle include size, shape, and general composition [5–8]. Since noble metals like gold, silver, platinum, and palladium have ions with large positive electrochemical potential and formed nanoparticles that are relatively inert, stable, and smaller than those formed by other metals; they have been the focus of metallic nanoparticle synthesis using plant systems [8, 11]. Plant-based NP green synthesis is now regarded as a gold standard. Among these green biological techniques owing to its ease of use and the diversity of plants. The idea of "Green Chemistry" for "Sustainable Development" has been extensively researched during the past 10 years [12]. A sustainable development is one that balances the requirements of the present with the ability of future generations to meet those needs [13]. Sustainable growth is crucial for many chemistry-based industries since it raises issues such pollution and the indiscriminate use of natural resources [14]. The three most crucial prerequisites for the green synthesis of NPs are the choice of a green or ecologically friendly solvent (the most frequently used being water, ethanol, and their mixes), a suitable non-toxic reducing agent, and a safe chemical for stabilization. For this green synthesis, fungi, algae, bacteria, and plants have all been employed. However, it has been frequently used to synthesize various NPs from plant components, including like leaves, fruits, roots, stems, and seeds [15]. On the contrary, NPs with specific size, shape, and content can be made using plant extracts. Additionally, a variety of phytochemicals included in their extract may serve as organic stabilizing and/or reducing agents for the formation of NPs [12]. It is widely acknowledged that plant-derived NPs have a lower risk of having negative side effects on people than chemically produced NPs do. Additionally, they have a high biological potential and can be used in a variety of fields, including agriculture, food science and technology, bioengineering, cosmetics or nanomedicine, and human health protection [3–5, 8]. This chapter overviews the green synthesis and characterization of metal nanoparticlesand the applications of such nanoparticles in treatment of antimicrobial, anticancer, reduce metal toxicity, dye degradation, and wastewater treatment and not for other biological, chemical, and physical methods.

2. Plants as nanoassemblers of metallic nanoparticles

It is generally known that plants can withstand hazardous soil minerals and organic chemicals and are well equipped to fight against environmental threats. Plants have a wide range of defense mechanisms to combat devastating chemical assaults. Using reducing enzymes and proteins that sequester toxic metals, they can change the redox states of hazardous metals and convert them into non-toxic ones. The ultimate outcome of these metal ions is their transformation into a neutral oxidation state, after which each atom is formed into nanoscalesized particles. The metal resistance of eukaryotes is due to the intracellular compartmentation of harmful ions in complexes and within intracellular organelles [16]. In eukaryotes, three principal compounds are involved in the sequestration of metal ions [15]:

I. Glutathione (GSH)

II. Phytochelatinsand

III. Cysteine-richmetallothioneins [16].

3. Synthesis of metal nanoparticles (MNPs)

For the synthesis of noble metal and metal oxides Nanoparticles of a particular shape and scale, a number of physical, chemical, and biological approaches are used [17]. These methods can be studied by two way approach, which can be applied to any nanoscale science study, one is the top-bottom and the other one is the bottom-top approach. Each of these methods has precise definitions and specifications **(Figure 1)** [18, 19].

3.1 Top-bottom approach

The desired bulk of materials are broken down into nanosized particles using this method. Mechanical milling or alloying and sputtering are some examples of this top-bottom method for particle size reduction. Because a material's surface structure plays a vital role in surface chemistry and material's physical characterization, so, this approach may create surface imperfections in the product, resulting in severe prohibitions [18, 20].

3.2 Bottom-top approach

The synthesis process in the bottom-top approach, begins with the formation of nuclei by the self-assembly of atoms/molecules followed by the synthesis of nanosized particles. This method includes co-precipitation, micro-emulsion method, pyrolysis, sol-gel, atomic condensation, plant and microorganism based synthesis. This approach of nanoparticles synthesis is primarily based on two methods; the chemical method and the biological method [21–26].

3.2.1 Chemical method

Chemical reduction, electrochemical reduction, photochemical reduction, and heat evaporation are various chemical methods employed for the synthesis of metal and

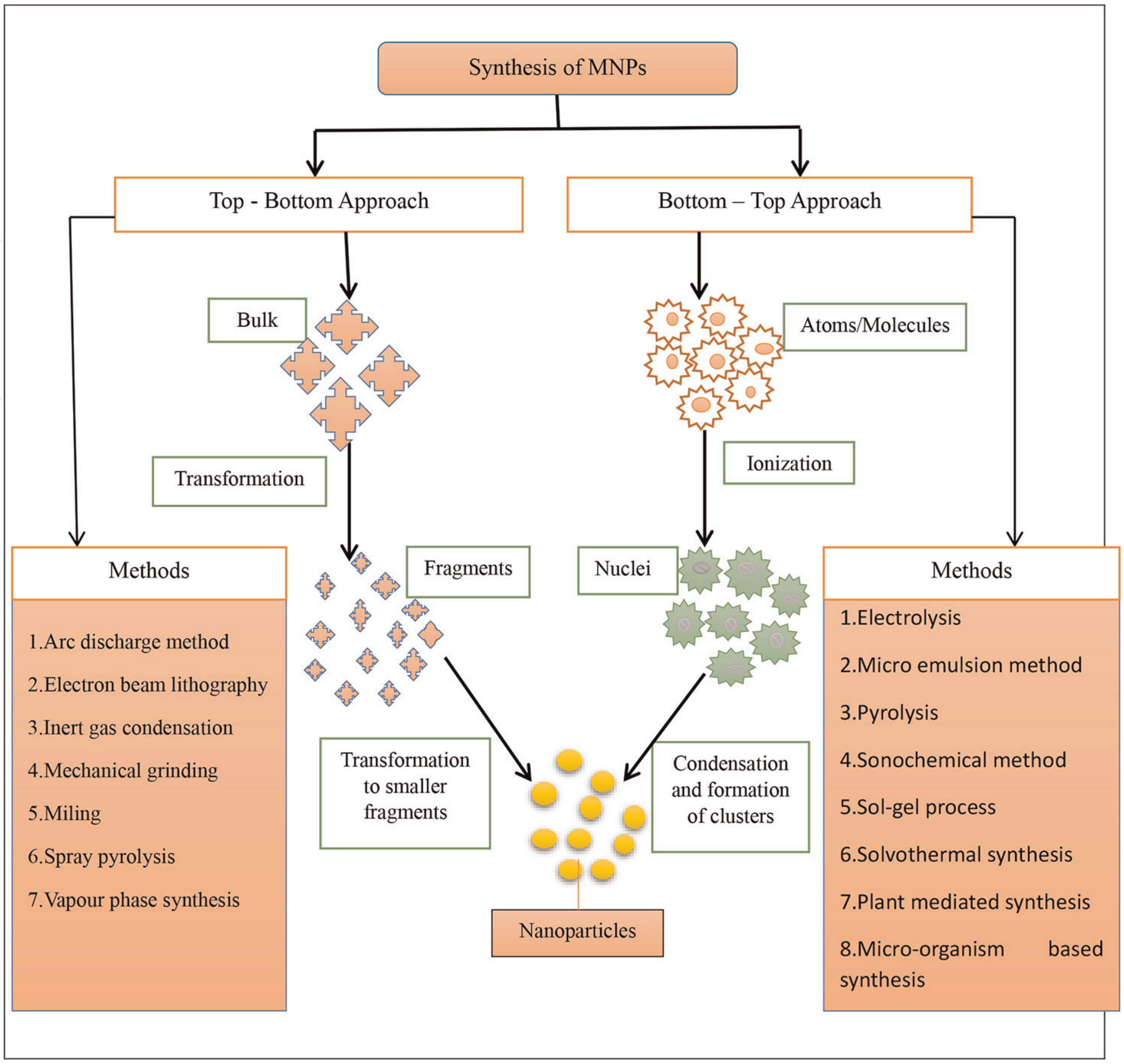

Figure 1.
A various physical, chemical, and biological approaches for the synthesis of noble metal and metal oxides nanoparticles.

metal oxides nanoparticles because of their quick reaction time and capability to produce monodispersed MNPs [27–32].

3.2.2 Biological method

However, all these aforementioned methods are capable of successfully forming the different types of metal nanoparticles (MNPs). Moreover, these methods have few disadvantages too, such as the high capital investment, high energy demands, and their non-eco-friendly nature too. Since, they contribute greatly to environmental pollution because of the uses of hazardous chemicals and reducing agents, which are responsible for multiple biological threats [33]. Therefore, an alternative way to avoid the aforementioned disadvantages is to move towards the biological method. In this method, different parts of plants (root, shoot, leaves, gums, flowers, barks, stem), microorganisms (bacteria, fungi, virus, yeast), enzymes, industrial and agricultural waste are used for the synthesis of MNPs. This method allows synthesis under non-toxic aqueous solvents such as water [34–37]. The use of an environmentally safe approach provides significant advantages such as low capital investment, low energy requirements, eco-friendly nature, potential to avoid the use of harsh substances and can be easily scaled up for large-scale synthesis as well [38]. So, green methods provide advancement over numerous chemical and physical approaches [37].

3.2.2.1 Plant-mediated method

Recently, among the numerous green approaches, plant-mediated nanoparticle synthesis has become increasingly popular due to their expeditious reaction rates, environmentally safe nature, and the rich diversity of plants compared to microorganisms [20, 39–41]. It replaces the complex procedure of nanoparticle synthesis and is regarded to be beneficial due to the easy accessibility of various phytochemical constituents. Plant extracts are said to have antioxidant and reducing characteristics, which are amenable for the reduction of metal salts to their respective NPs [42]. The present article explains the plant-mediated synthesis of metal and metal oxide nanoparticles.

4. Preparation of plant extract for green synthesis of metal nanoparticles (MNPs)

In a single-step green synthesis approach, for the reduction and stabilization of various metal and metal oxide nanoparticles, a wide variety of plants can be used. A green approach for the fabrication of metal and metal oxide nanoparticles using plant extracts has been adopted by many scientists in order to uncover their multitudinous applications. A great potential of plants, is the accumulation of a larger extent of heavy metals in their miscellaneous parts. Plant-extract based biosynthesis approaches have gained a lot of importance because of being a systematic, worthwhile, simple, feasible and eminent method of NPs synthesis. Gold and silver NPs are the first nanoparticles to be studied in a plant-mediated approach of nanoparticles synthesis [15]. A wide variety of plants including *Catharanthus roseus, argemone Mexicana, Ficus benghalensis, Pongamia pinnata, Phoenix dactylifera, Polyscias Scutellaria, Dillenia indica, Gnidia glauca, Garcinia mangostana, Zingiber officinale, Tilia, Ziziphus spina-christi, Magnolia champaca,Syzygium alternifolium, Eclipta prostrate, Xanthan gum, Cinnamomum camphora, Mimosa pudica, Glycosmis mauritiana, Acacia nilotica, Barni and Ajwa, Ocimum sanctum,* and *Taraxacum laevigatum* are used for the fabrication of metal and metal oxide nanoparticles, which are presented in this chapter. Plant materials selection, plant materials drying temperature, most appropriate solvent, and different temperatures for extraction of various plant materials are the different steps involved in the preparation of plant extract.

4.1 Plant materials selection

For the synthesis of plant extract, divergent parts of the plant such as shoot, stem, root, leave, flower, gum, bark, peel, seed, etc. are generally used [8]. These plant parts may either be utilized as fresh or in dried form. Because of the variations in water content between different tissues of plants, dry form is more desirable than that of the fresh form [43]. The dried plant is typically crushed into fine powder, while the fresh plant is grated into small units. Because of the enlarged surface area, this stage of size reduction allows an improvement in the rate of extraction. By using various polar or non-polar solvents (such as water, ethanol, acetone, benzene, ethyl acetate, methanol, etc.) plant materials extraction process is possible [44].

4.2 Plant materials drying temperature

Various reports suggested the different temperatures for drying the plant materials (leaf, root, bark, flower, gum, fruit, shoot, rhizome, etc.). Different parts of the plant can be dried either directly under the sun or in the shade. Both of these approaches are economical, but a few days are required to dry the sample completely [45, 46]. Some reports suggested the sample could be dried in the oven, thus reducing the time needed for the drying procedure to several hours [47]. However, some studies have demonstrated that drying by cooling is the best method that simultaneously retains the reduced material as biomolecules are temperature-sensitive [48]. When drying temperature ranges from 50 to 1000°C, some researchers examined variations in phenolic content in citrus peel extract. The research showed a proportional relationship between the phenolic content and drying temperature [49]. In addition, it was also reported that attempts to dry samples at higher temperatures could alter the molecular structure.

4.3 Solvents for plant extraction

The fundamental component of any synthesis process is the solvent system, whether it is a green approach or not [15]. Extraction apparently happens when a solvent is diffused through plant tissues and solubilizes compounds having similar polarities. Generally, water, methanol, ethanol, ethyl acetate, benzene, acetic acid, and acetone are used as a solvent. Therefore, during the extraction process, types of solvent greatly influence the volume of the extracted reducing agents. The procedure for the extraction of plant materials can simply be carried out by dissolving the plant material in water with constant stirring [44, 50, 51]. For any kind of synthesis process, an ideal and the most appropriate solvent is water. According to Sheldon, “no solvent is the best solvent, but water is the ideal one if a solvent is desirable”. The most commonly and easily accessible solvent found on earth is water [15]. Experiments that use water as a solvent are much safer for health and environment, than using chemical solvents [52]. A factor that is responsible for the partial oxidation of green synthesized metal and metal oxide nanoparticles is the oxygen present in a water molecule, due to which, their chemical reactivity is enhanced and they also have a great impact on the development of metal and metal oxide nanoparticles [15]. In this study, we have presented only those reports in which water is used as a solvent in the synthesis of plant extracts.

4.4 Plant-extraction temperature

Various studies show that the extraction temperature of plant material generally lies between 30 and 120°C. The concentration of the antioxidant increases with increasing temperature. The amount of antioxidants will be degraded, if the temperature is very high [53]. The influence of heat on the quality of plant extracts is substantial. In order to achieve optimum yield, the plant should be processed at an optimum temperature.

4.5 Characterization of plant extract

The extract obtained is analyzed using the Liquid Chromatography-Mass Spectrometry (LC-MS) technique. Mass spectrometry coupled with liquid chromatography separation has established a technique employed for both targeted and non-target analysis of complex biological samples [54]. The mixture of multiple components is separated by liquid chromatography, and the structural identity to the individualcomponents having high molecular specificity and sensitivity to the identification is provided by the mass spectrometry. Plant extract primarily consists of flavonoids, catechins, phenolic acid derivatives, mostly chlorogenic acid, protocatechuic acid, caffeic acid, and small amounts of aldehydes. For the reduction of metal ions and the effective stabilization of synthesized nanoparticles, substances responsible are the rich source of phenolic acid and flavonoids present in plant extract, as suggested by a report [55]. The various chemical groups like alkaloids, proteins, alkyl halides, 18α-Glycyrrhetinic acid, and ruspolinone in plant extract act either as reducing or stabilizing agents for nanoparticles' synthesis as suggested by another report of LC-MS analysis [56]. The LC-MS analysis of one another report suggested the presence of phenolic compounds, reducing sugar like O-glucose, and eleutherosides A and E [57]. Several studies of LC-MS analysis revealed the presence of numerous bioactive compounds like carbohydrates, proteins, alkaloids, tannins, saponins, flavonoids, terpenoids, glycosides, and phenols. The plant extract is found to exhibit significant antioxidant and antimicrobial properties [58].

5. Synthesis of metal/metal oxides nanoparticles from plant extract

Fabrication of metal and metal oxide nanoparticles involves the addition of an aqueous solution of metal salt in an appropriate volume of an aqueous plant extract containing various phytochemicals. These phytochemicals perform as a reducing or capping agent that reduces the metal ion from Mn^+ to M^0. Appropriate heating agents are used to heat the extracts. This setup is incubated in the dark for certain hours. A control setup is maintained. The alteration in color of the solution reveals the formation of metal and metal oxide nanoparticles. Then this solution is centrifuged at the required rpm and then it is filtered. The formed precipitate is washed with suitable solvents to remove impurities. Carbohydrates, amino acids, proteins, tannins, flavonoids, saponins, steroids, alkaloids, terpenoids, poly-phenol compounds, and glycosides are some important phytochemicals present in plant-extract, and are responsible for the bio-reduction of nanoparticles. Different plants have varying levels of phytochemicals. Plant extracts perform the reduction of metal salt into metal nanoparticles in a short period of time as compared to microorganisms which demand a longer incubation time. An excellent, economical and safe source for the synthesis of both metals as well as metal oxide nanoparticles is the use of plant extract in the biosynthesis process [15]. The rate of NPs reduction and stabilization is increased by the biomolecules present in plant extracts and they act as both reducing as well as capping agents [59]. Hence, MNPs synthesized by any other method are comparatively less stable than MNPs synthesized by the plant-mediated method [60]. The stability of MNPs is due to the development of a strong bonding interaction between metal salts and phytochemicals present in the plant extract [61].

5.1 Mechanism for the synthesis of metal/metal oxide nanoparticles

The possible chemical mechanism for the fabrication of MNPs using plant extract is shown below in **Figure 2**. The exact fundamental mechanism for MNPs synthesis, by using plant extract is still not fully understood. In general, three different phases

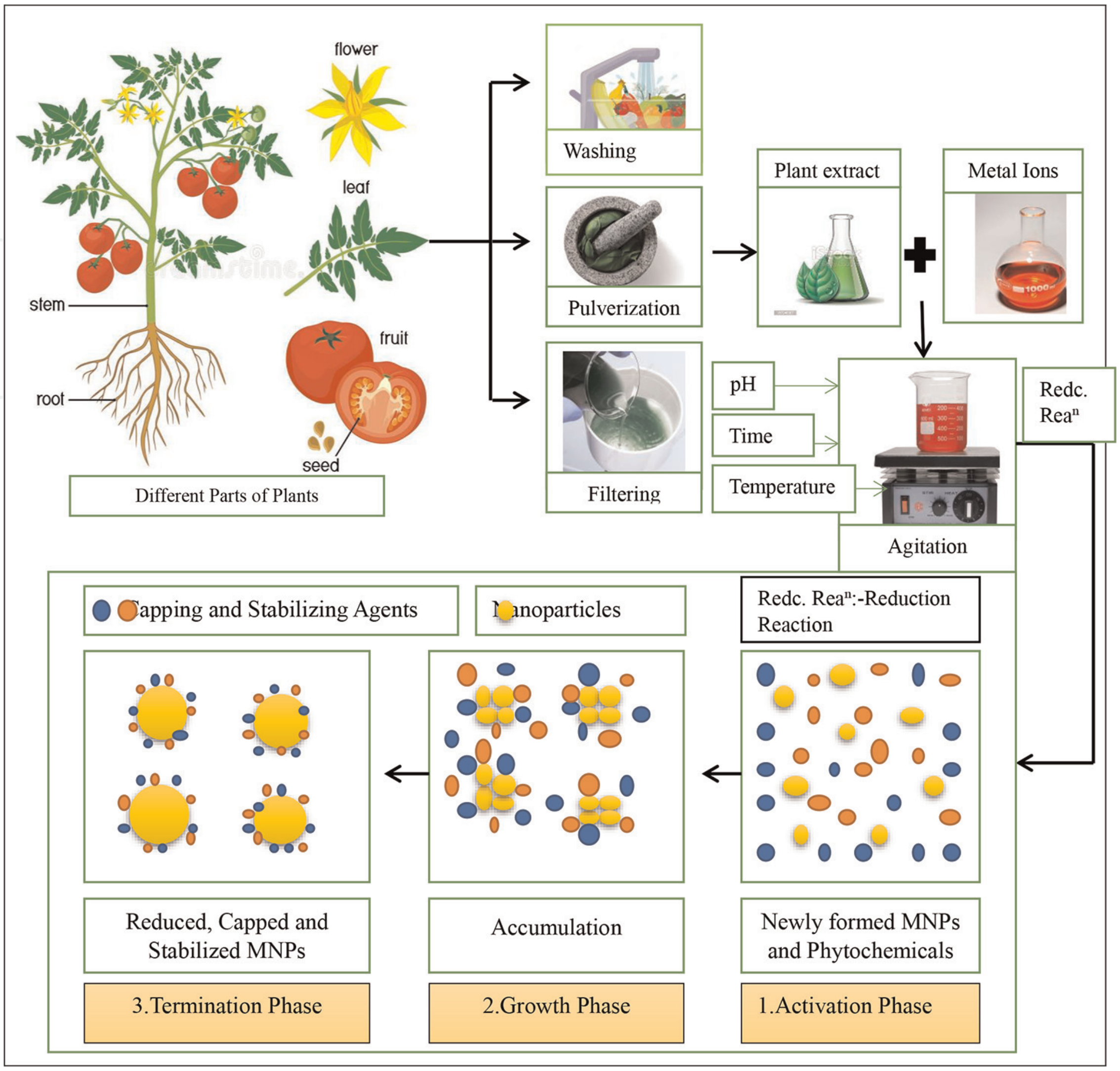

Figure 2.
Mechanism for the synthesis of metal/metal oxide nanoparticles.

are involved in the fabrication of metal and metal oxides nanoparticles from plant extracts. These three phases are;

1. The first one is the activation phase (reduction of metal salts using plant extract and nucleation procedure of the reduced metal ions),

2. The second one is the growth phase (a spontaneous combination of larger particles with smaller ones) via an approach called Ostwald ripening,

3. The third one is the termination phase (i.e., explaining the final structure of MNPs) [15].

6. Factors influencing the green synthesis of various metallic nanoparticles

Different parameters, including pH, temperature, reaction time, and reactant concentration, can be adjusted for the green synthesis of nanoparticle morphological characterization. The influence of environmental conditions on the synthesis of nanoparticles has been widely acknowledged by these parameters, and these aspects may play a crucial role in the optimisation of metallic nanoparticle synthesis [62].

6.1 Temperature

Around the world, several degrees of study reports are being conducted to understand how temperature affects nanoparticles. The most significant element affecting the dimension, morphology, and level of synthesis of the nanoparticles is temperature. Temperature can be used to customize the size of the synthesis of nanoparticles and the different types of forms (triangle, octahedral platelets, spherical, and rod). The development of nucleation centres is strengthened when temperature rises due to the reaction response rate [63]. The reaction time is a significant factor that has the greatest impact on the shape, size, and yield of synthesized nanoparticles during the green synthesis of nanoparticles [64, 65].

6.2 pH

The structure of nanoparticles is significantly influenced by the pH of the reaction. Namely, temperature and pH both affect how nucleation centres occur. Increases in pH automatically result in more nucleation centres, which is crucial to accelerating the production of metal nanoparticles. It has been acknowledged that pH plays a key role in determining the size and structural shape of the nanoparticles [66]. A key role in the production of nanoparticles is played by the medium pH reaction [67].

6.3 Reaction time

Along with temperature and pH, the reaction time has the greatest influence on how nanoparticles behave structurally. Reaction time is important for the production and magnetic characteristics of magnetic nanoparticles, according to *Karade et al.* [68, 69].

7. Characterization and properties of metal nanoparticles

7.1 Characterization of metal nanoparticles

The nanoparticle characterization can be classified according to the physical and chemical instrumentation analysis including UV–Vis spectroscopy, Fourier transforms infrared spectroscopy (FT-IR), Transmission Electron Microscopy (TEM), scanning electron microscope (SEM), X-ray diffraction (XRD) [70, 71].

7.1.1 FTIR

In FT-IR analysis, the sample is exposed to infrared red rays, some of which are absorbed by it, and the remainder of which pass through. The spectrum shows wavelength-dependent absorption or transmission, which characterizes the sample materials [72]. A good, affordable, straightforward, and non-invasive method to identify the role of biomolecules in the reduction of nanoparticles (silver nitrate to silver) is FTIR analysis [73].

7.1.2 UV: Visible spectrophotometry

The size range of 2–100 nm is used in the analysis of nanoparticles using UV-Visible absorption spectroscopy, and the nanoparticle size level varies from different metals. The wavelengths used to analyze the nanoparticles identified by UV-Vis absorption spectroscopy typically ranges from 300 to 800 nm. Strong absorption occurs when metallic nanoparticles are synthesized in specific salt conditions, producing a point spectrum in the audible range [74]. Previous research findings shown that the absorption of wavelengths 200–800 was suitable for classifying nanoparticles with a size range of 2–100 nm [75].

7.1.3 Scanning electron microscope (SEM)

SEM can be used to characterize nanoparticle's distribution, morphology, size, and form of synthesized nanoparticles are all determined by this instrumentation examination [70, 71]. The SEM study measured how a morphological structure changed both before and after treatment. According to earlier research, observable changes in cell shape and the presence of nanoparticle perforations in the cell wall are utilized as indications of the antibacterial activity of nanoparticles [76, 77].

7.1.4 X-ray diffraction (XRD)

XRD is able to analyze the atomic structures of materials. The qualitative and quantitative levels of materials can be determined with the use of this technology. Crystalline nanoparticle size and structure were identified and verified by XRD analysis [70, 71]. To analyze the particle dimension of nanoparticles from XRD data, the Debye–Scherrer formula was applied by ruling the width of the Bragg refection law. The equation is as follows:

$$(\mathrm{D} = \mathrm{K}\lambda/\beta\ \cos\ \theta)$$

Where, d is the particle size (nm), K is the constant called as Scherrer constant, λ is the wavelength of X-ray, β is the full width half maximum, and θ is the angle of diffraction (half of Bragg's angle) that corresponds to the lattice plane [78].

7.1.5 Transmission electron microscopy (TEM)

Transmission electron microscopy (TEM) categorized and confirmed the crystal structure and particle size of material at the nanoscale level [70, 71]. TEM studies of various data revealed that most of the green synthesized metal/metal oxide nanoparticles are spherical in shape, and having a size range between 2 and 50 nm [8].

Table 1 summarizes the important examples of plant-mediated synthesized metal and metal oxide nanoparticles along with various phytochemicals which are responsible for their reduction. In addition, some important features of MNPs, such as their shape and size are also mentioned in the **Table 1**.

7.2 Properties of metal nanoparticles

Researchers are much more interested in nanoparticles (NPs) because they differ from their bulk counterparts in several ways. At the nanoscale, material properties

S. No.	Plants	Part used	MNPs	Size (nm)	Shape	λ_{max} (cm)	Bond present	Reference
1.	*H. trichophylla*	Flower	Ag	20–50	Spherical	448	O–H, C–N, C–C, N–O, C–N, C–Br	[79]
2.	*E. scaber*	Leaf	Ag	37.86	Spherical	420	O–H, C=O, C=C	[80]
3.	*T. ofcinale*	Leaf	Co	50–100	Spherical	464	–OH, C–H, –C=O–, C–N, C–O	[81]
4.	*T. collinus*	Whole plant	Ag	7–18	Spherical	400	–OH, –NH, C–O, –NH2, C–C	[82]
5.	*G. tournefortii*	Leaf	Au	40–45	Spherical	528	C=C, C=O, –C–O, –C–O–C	[83]
6.	*C. pumilio*	Aerial	Ag	6–8	Spherical	446	O–H, –CH, C=O, C–O–C, C=O	[84]
7.	*A. hispidum*	Leaf	CuO	5–25	Spherical	390	C–H, C=C, O–H, C–O, Cu–O	[85]
8.	*A. vulgaris*	Leaf	Au	12	Spherical, triangular, hexagonal	560	O–H, C–H, N–H, C–N, C–O	[86]
9.	*A. conyzoides*	Leaf	Ag	14–48	Spherical	443	N–H, C–H, C=O, C–OH	[87]
10.	*A. hispidum*	Leaf	Ag	25–45	Quasi-spherical	417	-OH, C–H, C=O, C–O	[88]
11.	*A. turcomanica*	Leaf	Ag	20–60	Spherical	430	O–H, C–H, C=O, C–O–C	[89]
12.	*D. anomala*	Root	Ag	8.7	Round, rod-like, hexagonal, uneven shapes	424	-OH, –NH, C=C, C–O–C,=C–H, C=O, N–H	[90]
13.	*T. ofcinale*	Leaf	Ag	5–30	Spherical	546	C=C, C=O, C–OH, –NH2, –OH	[91]
14.	*S. indicus*	Leaf	Au	25	Spherical	531	OH, C–H, –C=O, –C–O–C, C–H, N–H, C–Cl	[92]
15.	*Z. elegans*	Whole plant	Au	< 25	Spherical	530	O–H, C–H	[93]
16.	*D. tombolens*	Aerial	MnO	38	Spherical	240	O–H, C=C, C=O	[94]
17.	*X. strumerium*	Leaf	Ag	20–50	Spherical	450	O–H, C=C, C–F, C–N, –C–O	[95]
18.	*E. purpurea*	Whole plant	TiO_2	120	Spherical	280	C–O, C–H, C=C, O–H	[96]
19.	*A. annua*	Stem bark	ZnO	20	Spherical	330	C–O, N–H, C=C, C=O	[97]
20.	*T. procumbens*	Leaf	Ag	54.34	Oval, spherical	425	C–H, C=C=C, C=O, N–O, S=O	[98]
21.	*P. leubnitziae*	Whole plant	Ag	100	Spherical	400	C–H, O–H, C=C, C-N,=CH	[99]

S. No.	Plants	Part used	MNPs	Size (nm)	Shape	λ_{max} (cm)	Bond present	Reference
22.	*O. vulgare*	Leaf	Pd	2–20	Spherical	320	O–H, C=O, C–O, C–H	[100]
23.	*T. procumbens*	Leaf	CuO	16	Rod, spherical	236	N–H, C–H, C=O	[101]
24.	*S. costus*	Root	MgO	30–34	Spherical	250	OH, C–H, C=O, Mg–O	[102]
25.	*C. paradisi*	Peel	Ag	14.84	Spherical	405	O–H, –NH2, C=O, C=C	[103]

Table 1.
Important examples of plant-mediated synthesized metal and metal oxide nanoparticles along with various bonds present, their shape, size and wavelength (λ_{max}).

differ significantly. Materials' properties can change as a result of the size-induced metal-insulator transition (also known as the quantum size effect). In the nanorange, a material's surface atom content rises as size decreases. This causes the surface-to-volume ratio to rise sharply, which has an impact on the material's surface-related properties. The following are a few notable characteristics and advantageous properties of NPs in general:

- High surface-to-volume ratios produce far more active sites per unit area than their bulk equivalents.
- Higher zeta potential precludes nanocluster aggregation in solution.
- Separation and recyclability make them more cost-effective and reduce the chance that the catalyst may become contaminated with the final product [6].

8. Applications of plant-derived NPs

Nanoparticles are currently in great commercial demand due to their diverse applications in industries, electronics, the environment, energy, and, most notably, biological disciplines. NPs, such as the well-known Ag and Au NPs, have been extensively researched in this field and are of great interest for biological applications. In general, plant-derived green NPs are less likely to cause severe side effects in humans when compared to chemically synthesized NPs, and have a wide range of applications, including but not limited to:

- Nanomedicine and human health protection (antimicrobial, antiparasitic, antiproliferative, pro-apoptotic, pro- or anti-oxidative depending on the context, anti-inflammatory activities, etc.) [2, 104–107].
- Agriculture (target-specific delivery of biomolecules, improved nutrient uptake, detection and management of plant diseases, precision farming with controlled release of agrochemicals, etc.) [108, 109].

- Food science and technology (processing, storage, and packaging methods); bioengineering (biocatalysts, photocatalysts, biosensors, etc.) [3].

- Cosmetics (sunscreen, anti-aging, hair growth, bioactive chemical delivery, nano-emulsion, etc.); and food science and technology (processing, storage, and packaging methods) [5].

8.1 Wastewater treatment

Recently, wastewater treatment has gained significant interest, as clean water is vital to life-sustaining processes. Nowadays, industrial plants produce an increased volume of wastewater, which often causes major environmental problems. Wastewater released during various industrial processes contains various forms of organic pollutants such as organic dyes, phenols, pesticides, herbicides, fertilizers, hydrocarbons, detergents, and oils. They are extremely poisonous and difficult to deteriorate. It is therefore important to establish an efficient and economical technique, to minimize the concentration of organic contaminants prior to the discharge of wastewater into the aquatic environment. Among the diverse physical, chemical, and biological approaches, which are used to manage emissions, a significant role is played by plant-mediated metal nanoparticles in the removal and deterioration of organic pollutants due to their specific scale, strong catalytic activity, and physicochemical properties [110].

8.2 Cosmetics

The food and cosmetic sectors employ metal nanoparticles as a preservative. For many industrial uses, primarily in cosmetics, pharmaceutical coating materials, and food preservatives, new dimensions of metallic nanoparticles are utilized. Gold, silver, and platinum nanoparticles of various sizes are widely used in commercial items like shampoo, soap, detergent, and shoes. The majority of the chemical components are synthetic, and they have negative impacts on people. The green metallic nanoparticles are a substitute for preservatives in the food and healthcare industries as a result [5, 111, 112].

8.3 Nanoparticles in food industry

Nano-Ag is employed in many mechanical devices because silver metal is a highly heat-conducting substance. It is primarily utilized in heat-sensitive equipment as PCR lids and UV spectrophotometers. Nanosilver is used as coated materials to make the instrumentation parts. With minimal influence to the samples, it is extremely stable at high temperatures. Due to the numerous open scale operations used in the food industry, including in the production, processing, and shipping of raw materials, the food products suffer from high levels of microbial contamination. Therefore, a cost-effective biosensor must be created to assess the products' quality. Metallic nanoparticles have been developed as biosensors, and they are economically favorable and effective in detecting pathogens and keeping track of contaminants at various stages [8, 113].

8.4 Biohydrogen production

There are several reports on the application of nanomaterials in the biohydrogen manufacturing industries [114, 115]. Biohydrogen processing is a very complex process that is influenced by various factors, including the nature of the substrates, metal ions, working state, etc. [116–119]. Apart from various experimental designs, microorganisms have vital importance in the biohydrogen production process. It has been predicted that nanoparticles will support microorganisms under anaerobic conditions because the transfer of electrons is more efficient for acceptors [120]. Kinetics of bioprocesses can be boosted by the use of certain nanoparticles as they improve the capacity of microorganisms as biocatalysts by enhancing their ability to respond quickly to electron donors [121]. One study stated that biohydrogen fermentation is significantly boosted by the addition of goldnanoparticles (AuNPs) (5 nm). In the presence of the gold and silver nanoparticles, the conversion rate of the substrate to biohydrogen through fermentation can also be improved [115, 122].

8.5 Drug and medicine

Over the past 10 years, medications made with nanotechnology have received a lot of interest. The special characteristics of NPs, such as their small size and propensity to pass through delicate blood arteries, junctions, and barriers, have made this field one of the most extensively examined and investigated [123]. In terms of increasing medication bioavailability, solubility, toxicity protection, pharmacological activities, distribution, and protection against chemical and physical deterioration as well as increased stability of pharmaceuticals inside the body, they have several benefits [124]. Nanomedicines have demonstrated a greater ability to bind with biomolecules and a decrease in tissue oxidative stress and inflammation. Over the years, thousands of unique nanomedicines have been developed; they have a variety of uses in treating various ailments. Few have been licensed for therapeutic use, and many more are undergoing clinical studies. The use of nanomaterials as pharmaceuticals and medicine entails the development of nanotechnologies for medical applications, including highly advanced medical intervention at the molecular level to cure diseases. It serves as a research platform for the development of therapeutic nanomaterials or nanomedicines. The advancement of nanomedicines has opened up new opportunities in medical sciences, particularly in drug delivery techniques. Their structural properties give them a great modality for particular site targeting and rapid penetration inside the cell/diseased site [125]. Various types of NPs were found based on therapeutic necessity, depending on their application and origin. Top performers include liposomal, polymeric protein, metal-based, and FeONPs.

8.6 Synthesis of heterocyclic compounds

Recent examples of various metal nanoparticles which are used in synthesis of heterocyclic compounds like acridine, coumarins, quinoxaline, naphthoxazinones, pyran, pyrazole, and 1,2,3-triazoles are presented here. Because of having a wide variety of pharmacological applications, the synthesis of heterocyclic compounds constitutes the most significant portion of organic reactions. Various approaches like utilization of catalyst, ultrasound irradiation and microwave irradiation methods have been adopted for the synthesis of heterocyclic compounds. Even though these approaches have their own advantages, they also have certain disadvantages like expensive instruments, inaccessible materials, non-recyclable and non-selectivity, and so on. To overcome these aforementioned disadvantages, metal nanoparticles play a significant role in the organic synthesis of heterocyclic compounds by catalyzing these reactions [126–132]. The utilization of various metal and metal oxide nanoparticles in different fields along with responsible phytochemicals which are responsible for their reduction is presented below in **Table 2**.

S. No.	Plants	Part used	MNPs	Phytochemicals responsible	Applications	Reference
1.	*Vitex negundo*	Leaf	Ag	Alkaloids, glycosides, favonoids, phenolic compounds, reducing sugars, resin, tannins	Broad spectrum antibacterial response.	[133]
2.	*Carica papaya*	Leaf	Ag	Alkaloids, saponin, tannin, favonoids, anthraquinone (free and bound), phlobatannin, cardiac glycosides, terpenoids, and proanthocyanidin	Antiviral activity	[134]
3.	*Andrographis paniculata*	Leaf	Ag	Diterpenoids, favonoids, and polyphenols	Antiviral activity	[135]
4.	*Piper nigrum*	Leaf	Ag	Palmitic, hexadecenoic, stearic, linoleic, oleic, higher saturated acids, arachidic, and behenic acids	Anticancer activity	[136]
5.	*Ficus benghalensis*	Leaf	Ag	Flavonoids, phenols, terpenoids, and terpenes	Antimicrobial response	[137]
6.	*Syzygium cumini*	Seed	Ag	Gallic acid, P-coumaric acid, quercet in, 3,4-dihyroxybenzoic acid	Antifungal activity	[138]
7.	*Artemisia vulgaris*	Leaf	Ag	Sabinene, B-thujone, chrysanthenone, camphor, borneol, and germacrene D	Antibacterial, antifertility, antimalarial, antitumor.	[139]
8.	*Andrographis echioides*	Leaf	Ag	Two new 2′-oxygenated favonoids and two new phenyl glycosides	Antibacterial activity	[140]
9.	*Alcea rosea*	Flower	Ag	Ferulic acid, cafeic acid, tricin, luteolin-3′,4′-dimethyl ether	Antibacterial activity	[141]
10.	*Centella asiatica*	Leaf	Ag	Isoprenoids and phenylpropanoid derivatives	Antimicrobial activity	[142]
11.	*Anethum graveolens*	Leaf	Ag	Anethine, phellandrene, and d-limonene, and its leaves are rich in tannins, steroids, terpenoids, and favonoids	Antiparasitic activity	[143]
12.	*Punica granatum*	Fruit	Au	Phenolic acids, hydrolysable tannins, and favonoids	Antibacterial activity	[144]
13.	*Syzygium aromaticum*	Bud	Au	Sesquiterpenes, monoterpenes, hydrocarbon, and phenolic compounds	Anticancer activity	[145]

S. No.	Plants	Part used	MNPs	Phytochemicals responsible	Applications	Reference
14.	*Lantana camara*	Leaf	Au	Flavonoids, carbohydrates, proteins, alkaloids, glycosides, saponins, steroids, triterpenes, and tannin	Antibacterial activity and dye degradation.	[146]
15.	*Psoralea corylifolia*	Leaf	Fe	Apocarotenoids, chalcone, dipeptide, elliptosides, essential oils, fatty acids, favonoids, histamine, imidazolyl carboxylic acid, prosapogenins, steroids, triterpene saponins, and triterpenoids	Antitumor activity	[147]
16.	*Sageretia thea*	Leaf	Fe	Alkaloids, favonoids, steroids, terpenoids	Antibacterial activity	[148]
17.	*Theobroma cacao*	Seed	Se	Procyanidins, theobromine, (−)-epicatechin, catechins, and cafeine	Antibacterial activity	[149]
18.	*Pelargonium zonale*	Leaf	Se	Linalool, citronellol and geraniol, and their esters, menthone, nerol, isomenthone, rose oxides, terpineol, pinene, and myrcene	Antibacterial and antifungal activity.	[150]
19.	*Allium sativum*	Bud	Se	Alkaloid, saponins, favonoids, glycoside, anthraquinones, tannin, and terpenoids	Antioxidant activity	[151]
20.	*Limnophila rugosa*	Leaf	Au	Phenolics, favonoids, terpenoids, and amino acids	Catalytic activity in the reduction of different nitrophenols.	[152]
21.	*Syzygium jambos (L.) Alston*	Leaf	Fe	Flavonoids, ellagitannins, phloroglucinols, and phenolic acids	Removal of chromium metal from environment.	[153]
22.	*Cupressus sempervirens*	Leaf	Fe	Cosmosiin, cafeic acid, and P-coumaric acid cupressufavone, amentofavone, rutin, quercitrin, quercet in, myricitrin	Wastewater treatment	[154]
23.	*Camellia sinensis*	Leaf	Fe	Epigallocatechin gallate (EGCG), epicatechin 3-gallate (EGC), epigallocatechin (ECG), epicatechin (EC) and catechin	Reduction of bromophenol blue indicator.	[155]
24.	*Eucalyptus globules*	Leaf	Fe	Saponins, tannins, phenols, and glycosides	Wastewater treatment	[156]
25.	*Camellia sinensis*	Leaf	Fe	Alkaloids, favonoids, steroids, terpenoids, carotenoids, benzoic acid, ascorbic acid, tocopherols, folic acid, and tannins	Dye degradiation	[157]

S. No.	Plants	Part used	MNPs	Phytochemicals responsible	Applications	Reference
26.	*Duranta erectai*	Fruit	Cu	Flavonoids, phenols, saponins, sterols, tannins, alkaloids	Water treatment process	[158]
27.	*Ziziphus mauritiana*	Fruit	ZnO	Flavonoids, phenols, saponins, sterols, tannins, alkaloids	Degradation of Methylene blue and Eriochrome black-T dyes.	[159]
28.	*Dalbergia coromandeliana*	Root	Au	Alkaloid, saponins, favonoids, glycoside, anthraquinones, tannin, and terpenoids	Degradation of Methyl orange and Congo red dyes.	[160]
29.	*Dahlia pinnata*	Leaf	Ag	Flavonoids, phenols, saponins, sterols, tannins, alkaloids	Detection of Hg^{+2} metal ions.	[161]
30.	*Phoenix dactylifera*	Leaf	Au	Phenolics, favonoids, terpenoids, and amino acids	Reduction of 4-nitrophenol	[162]

Table 2.
Utilization of various metal nanoparticles in different fields along with responsible phytochemicals.

9. Toxicity of metal nanoparticles

Because of their unique physicochemical features, nanoparticles have a wide range of applications in industries such as electronics, agriculture, chemicals, pharmaceuticals, and food [163]. Metal oxide NPs such as Silicon oxide (SiO_2), titanium dioxide (TiO_2), zinc oxide (ZnO), aluminum hydroxide [$Al(OH)_3$], cerium oxide (CeO), copper oxide (CuO), silver (Ag), nanoclays, carbon nanotubes, nanocellulose, and others are the most often employed NPs by diverse industries [164, 165]. However, the large release of NPs into the environment (air, water, and soil) by various sectors is producing nanowaste, which is hazardous to living beings and threatens ecosystem equilibrium. Size, nature, reactivity, mobility, stability, surface chemistry, aggregation, and storage time are all factors that influence NP toxicity. NPs have a negative impact on human's health and animal. The use of NPs has increased the risk of a variety of diseases in humans, including diabetes, cancer, bronchial asthma, allergies, inflammation, and so on [8]. The toxicity of several NPs such as Au, TiO_2, and others has also been found to impair the animal reproductive system [166, 167]. NPs enter the animal body by ingestion and inhalation and are absorbed by cells via the processes of phagocytosis and endocytosis, where they generate reactive oxygen species (ROS), resulting in lipid peroxidation, mitochondrial damage, and other effects. Many NPs such as Ag, Cu, ZnO, Ni, and others have also lowered the enzymatic activity of many bacteria. Furthermore, excessive NP production has an impact on the ecosystem's food chain [168].

9.1 Impact of nanoparticle toxicity on plants

Plants are fundamentally important because they undergo photosynthesis and emit oxygen into the environment. Because all plant parts (roots, shoots, and leaves) are in direct touch with environmental matrices (air, water, and soil), plants may be more affected by NPs contamination than other living beings. NPs in the atmosphere can enter the plant body through stomatal holes on leaves [169], whereas those in soil and water can be preferentially uptaken by plant roots [170]. Plant growth and development have been hampered by NPs, which are harmful to them. The generation of ROS, which results in lipid peroxidation and ultimately damages DNA, reduces photosynthetic pigments, increases plant biomass, decreases in soluble protein content, etc., is the main cause of plant toxicity [171]. Plants do, however, have a defense mechanism against oxidative stress in the form of enzyme- and non-enzyme-based antioxidants, which may become ineffective at increasing oxygen concentrations [172].

9.2 Toxicity of nanoparticle-based drugs

A two-edged sword exists in the commercial use of NPs as medicines for the treatment of diseases. The potential mechanism of nanomaterials' interactions with biological systems and their effects are yet unknown, despite the fact that numerous research are being conducted across the globe to examine the harmful effects of exposure to NMs. NPs can quickly overcome membrane barriers and go through the bloodstream, according to research. At the molecular and cellular levels, this can then have a negative impact on tissues and organs [173]. The ability of NPs to pass through the blood-brain barrier (BBB) and enter the brain has been proven [174]. The interaction of a nanoparticle with the biological environment and the ensuing hazardous effects are determined by its small size, high surface area to mass ratio (SA/MR), and surface properties. Because of their special makeup, NMs can damage cells by passing through cell and tissue membranes and cellular compartments with ease. Additionally, active chemical interactions with biological macromolecules are still possible due to the huge SA/MR of NPs. The same chemical's adsorption characteristics, surface reactivity, and potential toxicity are all further enhanced by an increase in surface area [173]. From their point of entrance, the respiratory tract, to secondary organs, NPs have a propensity to overcome cell barriers, enter the cells by a variety of pathways, and begin interacting with subcellular structures. NPs are ideally suited for therapeutic and diagnostic usage due to their characteristics. NPs are moved neuronally through perineural translocations as well as retrograde and anterograde movement in axons and dendrites. However, the possible negative effects (such as oxidative stress) are mostly felt by the target organs, such as the central nervous system (CNS) [174]. The effectiveness and duration of the drug's circulation inside the systemic circulation are increased and the size of NPs plays a significant role in renal clearance and preventing immune activation [123].

10. Major challenges and future perspective

In recent years, research on NPs and their prospective applications has advanced by leaps and bounds. Numerous researches have described the green synthesis of metallic NPs using various biological sources such as plants, bacteria, fungi, and yeast. However, significant hurdles remain, limiting its large-scale manufacture and subsequent uses. Some of the significant issues encountered during the synthesis are listed below:

- In order to manage the size and form of the NPs, detailed optimisation studies on reactants (plant extract, microbe inoculum, fermentation medium composition, etc.) and process parameters (temperature, pH, rotational speed, etc.) are necessary.

- Research should also concentrate on improving various physicochemical properties of NPs for specific applications.

- Each metabolite found in plant extracts as well as the cellular elements of microorganisms should have its role in the synthesis of NPs thoroughly examined.

- Commercial scale-up of NP production utilizing green synthesis techniques needs to be given top priority.

- Various reaction parameters need to be optimized in order to increase NPs yield and stability with shorter reaction times.

By overcoming these obstacles, it might be possible to produce NPs on a large scale more cheaply and efficiently using green synthesis techniques than with traditional techniques. Another crucial area that needs to be researched is the extraction and purification of NPs from the reaction mixture. For the NPs to be used more widely in a variety of disciplines, a thorough toxicological analysis of their effects on both plants and animals is required. In addition to wild type strains, genetically altered microorganisms with the capacity to create more enzymes, proteins, and biomolecules could improve the biosynthesis as well as the stabilization of NPs. In addition, improving the ability of genetically modified microbes to tolerate metal build up could offer a cutting-edge strategy for producing and utilizing metal nanoparticles (NPs) through the green synthesis process.

11. Conclusions

The current review focuses on the green extraction and utilization of metal NPs obtained from plants and microorganisms. In comparison to other conventional procedures such as physical and chemical methods, green synthesis methods give a clean, non-toxic, and environmentally friendly approach to the synthesis of metal NPs. Plant materials such as leaf extract, fruit extract, seed, fruit, bark, and so on, as well as microorganisms such as bacteria, fungus, actinomycetes, and so on, have shown potential for the production of various metal and metal oxide NPs (e.g., Au, Ag, Pt, Pd, Ni, Se, Cu, CuO, and TiO_2). The size and form of NPs, as well as the pace of reaction, are greatly influenced by experimental parameters such as reaction time, reactant concentration, pH, temperature, aeration, salt content, and so on. The shape, size, and morphology of biosynthesized NPs have been determined using several characterization techniques such as UV-VIS spectroscopy, FTIR, XRD, SEM, TEM, EDX, and AFM. However, various aspects, including bioavailability, adverse responses, cellular interactions, bio dispersion, and biodegradation, must be considered in translational research. The accumulation of these NPs in the environment and their reception by biological systems can have disastrous repercussions, as evidenced by NPs causing DNA and membrane damage, protein misfolding, and mitochondrial damage in a number of studies. Although multiple studies have shown the biological synthesis of metal NPs, further research is required to broaden their uses and ensure their commercialization success.

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