Chapter 5
Environmentally Benign Synthesis of Metal Nanoparticles for Fertilizer Applications in Agriculture

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1 Introduction

The global population has been growing steadily over the past few centuries. According to the Food and Agriculture Organization of the United Nations (FAO, 2009), the global population will grow by 2.3 billion, between 2009 and 2050, and to feed a world population of 9.1 billion people in 2050, food production will have to increase by 70%. However, the productivity of crops has been decreasing due to biotic and abiotic stresses, climate change, and lack of water. As a result, agricultural development is being severely affected worldwide (Vijayakumar et al., 2022). As such, world agriculture is beset with a wide range of challenges, such as stagnating crop yields, low nutrient utilization efficiency, declining soil organic matter, deficiencies of several nutrients, shrinking arable lands, less water availability, shortage of labor, etc. (Raliya et al., 2017). Moreover, with a declining rural labor force and increasing food and fiber needs, agriculture is facing multiple challenges in the twenty-first century, which include producing more food and fibers to feed a growing population, producing more feedstocks for a growing bioenergy market, contributing to the overall development of many agriculture-dependent developing countries, adopting more sustainable and efficient production methods, and adapting to climate change (FAO, 2009). To resolve these issues, farming communities have been using chemical fertilizers and pesticides and genetically modified or disease-resistant crop varieties for the past five decades (Chhipa, 2017).

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Although the use of chemical fertilizers and pesticides significantly enhance food production, food quality and soil fertility are negatively impacted. Moreover, the application of fertilizers and pesticides is not efficient from the standpoint of economy. Most of the applied agrochemicals are lost via different processes such as leaching, mineralization, and bioconversion (Bollag et al., 1992). From an estimate, 40–70% nitrogen (N), 80–90% phosphorus (P), and 50–90% potassium (K) fertilizers were found to be either lost or fixed in soils, leading to economic losses (El-Saadony et al., 2021). Additionally, the overuse of pesticides and artificial fertilizers has disrupted many ecosystems and created several health risks. Therefore, a different solution is required for precision farming and improving the existing circumstance. Nanotechnology is a key strategy for resolving this problem.

After biotechnology, nanotechnology is the fifth breakthrough technology of the century. It has demonstrated a broad range of applications in many fields, including agriculture, medicine, biology, physics, chemistry, electronics, energy, materials science, and environmental science (Chhipa, 2017). The Greek term “nano” signifies “one billionth of something.” One nanometer is defined as one billionth of a meter. The science of nanotechnology focuses on creating and modifying materials with sizes between one and one hundred nanometers (1–100 nm) (Vijayakumar et al., 2022). With a focus on protecting soil and promoting environmental sustainability, nanotechnology is quickly becoming the essential enabling technology that helps boost agricultural output. The major drivers for motivating the scientific community to concentrate on advancing the expansion of nano-agrotechnology are challenging climatic conditions and increased global food security (Sangeetha et al., 2017). The improvement in nanotechnology has gained momentum through the innovation of nanoparticles (NPs). Surface area, pore size, particle shape, and reactivity are some of the distinct physical and chemical characteristics that define nanoparticles (NPs). Because of their widespread use in the agricultural sector, NPs are also known as “magic bullets.” Nanoparticles can be employed as nanofertilizers, nanopesticides, and nanoherbicides, which can help crops grow more productively, reduce the overuse of chemical fertilizers, and improve their ability to withstand biotic stress. They control plant growth and boost metabolic activity. Depending on the type and concentration employed, NPs may have a beneficial or detrimental impact on the growth and yield of different plant species (Goswami & Mathur, 2019).

Site-directed delivery and controlled delivery of functional components are two features of nano-enabled agrochemicals that increase their efficiency and capacity for managing pests and illnesses. As a result, they present a fresh method of lowering the toxicity of agrochemicals to human health by minimizing their long-term consequences and reducing environmental pollution by lowering their volatilization, leaching, and drainage. Such nano-enabled agrochemicals improve crop nutrient uptake, solubility, and stability and also provide a workable alternative for managing pests and diseases (Rodrigues et al., 2017; Duhan et al., 2017; Aranaz et al., 2010; Sarkar et al., 2022).

2 Synthesis of Metal Nanoparticles

For the creation and stabilization of metallic nanoparticles, a variety of physical and chemical techniques, including electrochemical changes, chemical reduction, and photochemical reduction, are frequently used. The choice of metallic nanoparticle preparation technique is crucial because processes used in nanoparticle synthesis, such as the kinetics of metal ions' interactions with reducing agents, the process by which stabilizing agents adhere to metal nanoparticles, and various experimental techniques, have a significant impact on the stability, physicochemical properties, and morphology (structure and size) of the nanoparticles (Jamkhande et al., 2019). Metal nanoparticles can be produced using a variety of techniques. However, their synthesis can be roughly categorized into two approaches: (i) the top-down approach and (ii) the bottom-up approach.

2.1 Top-Down and Bottom-Up Approaches

2.1.1 Top-Down Approach

In the top-down method, bulk materials are split to create nanostructured materials. Top-down techniques include electro-explosion, mechanical milling, laser ablation, etching, and sputtering (Baig et al., 2021). The major drawbacks of the top-down method include elevated levels of contaminants in the finished product and poor control over the size and surface structure of the resultant NPs (Zulfiqar et al., 2019; Ndaba et al., 2022). Inadequacies in the surface structure indicate a significant disadvantage of the top-down method. Due to their high aspect ratio, these surface structure restrictions can have a considerable negative impact on the physical characteristics and surface chemistry of metallic NPs (Saratale et al., 2018a, b).

2.1.2 Bottom-Up Approach

The bottom-up method entails creating NPs from much smaller units like atoms and molecules. This method involves common chemical processes along with biological processes. Since the procedure provides for better control of particle size and reduces the quantity of contaminants in the finished product, NPs manufactured utilizing the bottom-up method are more homogeneous (Ndaba et al., 2022).

The fundamental distinction between the two approaches is the raw material used to prepare the nanoparticles. While atoms or molecules are the starting material in bottom-up approaches, top-down methods start with bulk material and use various physical, chemical, and mechanical processes to reduce the particle size to nanoparticles (Jamkhande et al., 2019). These two methodologies primarily rely on diverse physical, chemical, and biological techniques. Most of the physical

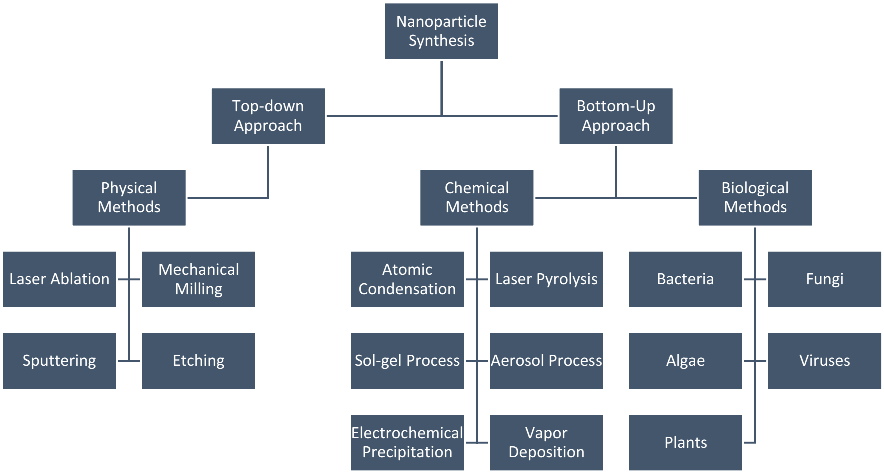

Fig. 5.1 There are two main methods for synthesizing nanoparticles: top-down and bottom-up. (1) Top-down strategy: Using mechanical or chemical methods, the top-down strategy breaks down large materials into smaller nanoparticles. Starting with a huge piece of material, this method often includes shrinking it down to the desired nanoparticle size range using physical or chemical procedures. Top-down techniques include milling, lithography, and etching as examples. (2) Bottom-up strategy: In the bottom-up strategy, individual atoms or molecules are put together to create nanoparticles. In this method, the required nanoparticle structure is built up from individual atoms or molecules using chemical or physical processes. Chemical vapor deposition, sol–gel synthesis, and coprecipitation are a few examples of bottom-up techniques

approaches, along with some chemical ways, are included in the top-down strategy; meanwhile, the bottom-up approach primarily concentrates on chemical and biological processes to synthesize metal nanoparticles. Figure 5.1 depicts the top-down and bottom-up approaches.

2.2 Physical, Chemical, and Biological Methods

2.2.1 Physical Methods

Top-down is a physical procedure dependent on material milling. This method's drawbacks include a lack of control over nanoparticle size and a higher level of contaminants. Mechanical milling, laser ablation, sputtering, and other typical physical processes are utilized to create metal nanoparticles.

Mechanical Milling

A feasible method for creating materials at the nanoscale from bulk materials is mechanical milling. It is a useful technique for creating mixtures of various phases and is useful in the creation of nanocomposites (Baig et al., 2021). It involves the structural decomposition of coarser particles into smaller ones. In this technique, a container is filled with bulk powder and numerous large balls. With the aid of a high-speed spinning ball, high mechanical energy is imparted to bulk powder material. Various high-energy mills can be used for particle size reduction. According to Rajput (2015), these high-energy mills include:

- Attrition ball mill
- Planetary ball mill
- Vibrating ball mill
- Low-energy tumbling mill
- High-energy ball mill

In each of these methods, large, freely moving, high-energy balls can either fall freely and strike the powder or can roll down the surface of the chamber housing the bulk powder material in a succession of parallel layers. It is a commonly used technique for mechanical alloying to create amorphous alloys for a variety of uses, including metal–metal, transition metal–metalloid, and metal–carbon systems.

Laser Ablation

The laser irradiation employed in the laser ablation method causes the particle size to be reduced to the nanoscale. After being covered by a thin layer, the solid target material is exposed to pulsed laser irradiation. The most used lasers are copper vapor lasers, titanium-doped sapphire lasers, Nd: YAG (neodymium-doped yttrium aluminum garnet) lasers at 106 m output, and their harmonics. When a material is exposed to laser energy, it breaks down into tiny pieces called nanoparticles (Jamkhande et al., 2019). This method is used to produce aluminum oxide (Al_2O_3) metal nanoparticles and other metalloid nanoparticles.

Sputtering

Ion sputtering is a technique that involves vaporizing a material by sputtering with a stream of ions from an inert gas. It involves bombarding solid surfaces with high-energy particles, such as plasma or gas, to create nanomaterials. Sputtering is believed to be a useful technique for creating thin nanomaterial films (Baig et al., 2021). It can be carried out in a variety of ways, including using radio-frequency diodes, magnetrons, and direct current (DC) diodes. Recently, employing magnetron sputtering of metal targets, this technique has been used to create nanoparticles from a variety of metals.

2.2.2 Chemical Methods

Sol–Gel Process

Compared to regular molecules or nanoparticles, colloidal particles are significantly bigger. However, colloids become bulky when mixed with a liquid, whereas nanoscale molecules always appear transparent. It involves the development of networks through the production of colloidal suspension (sol) and gelatin to create a network in a continuous liquid phase (gel). Metal alkoxide and alkoxysilane ions serve as the precursor to the synthesis of these colloids. Tetramethoxysilane (TMOS) and tetraethoxysilane (TEOS), which create silica gels, are the most often utilized. Alkoxides cannot be mixed with water. They are silica, aluminum, titanium, zirconium, and many more organometallic precursors. Alcohol is utilized as a mutual solvent. An initial homogeneous solution of one or more chosen alkoxides is used in the sol–gel procedure. These serve as organic precursors to materials like zirconia, titania, alumina, silica, and more. The catalyst controls pH and initiates the reaction. Four phases are involved in sol–gel formation: 1. hydrolysis, 2. condensation, 3. growth of particles, and 4. agglomeration of particles (Rajput, 2015).

Electrochemical Precipitation

This strategy uses an arrested precipitation mechanism to manage size. The fundamental strategy is to create and study the nanomaterial in situ, or in the same liquid media, to prevent physical changes and the accumulation of microscopic crystallites. Double-layer repulsion of crystallites utilizing nonaqueous solvents at lower temperatures for synthesis was used to control thermal coagulation and Oswald ripening. The synthesis involved constituent materials reacting with one another in an appropriate solvent. Prior to the precipitation reaction, the dopant is incorporated into the parent solution. A surfactant is employed to keep the produced particles apart. The resulting nanocrystals are centrifuged apart, cleaned, and vacuum dried. The dried material is then subjected to ultraviolet (UV) curing to see whether the surfactant capping coating on the nanocluster's surface could polymerize and provide real quantum confinement (Rajput, 2015).

Vapor Deposition

A solid is deposited on a heated surface through a chemical reaction from the vapor or gas phase in a process known as chemical vapor deposition (CVD). In thermal CVD, a high temperature of more than 900 °C activates the process. An exhaust system, a deposition chamber, and a gas supply system make up a typical apparatus. Plasma at temperatures between 300 and 700 °C initiates the reaction in plasma CVD. Pyrolysis takes place in laser CVD when a heat-absorbing substrate is heated by a laser's thermal energy. Ultraviolet radiation that has enough photon energy to break the chemical bond in the reactant molecules is used to trigger the chemical reaction in photo-laser CVD. This method involves photon activation of the reaction, and deposition takes place at room temperature. Nanocomposite powders can be synthesized using CVD (Rajput, 2015).

2.2.3 Biological Methods

The biological method involves various biological entities such as microbes (bacteria, algae, fungi, viruses), plants, organic wastes, etc.

3 Why Environmentally Benign Synthesis of Metal Nanoparticles (NPs) Is Necessary

Although physical and chemical processes have been employed for decades to produce nanoparticles, there are still many issues with them. The basic drawbacks of physical procedures are (i) excessive production cost, (ii) consumption of large amounts of energy, and (iii) low manufacturing yield (Shedbalkar et al., 2014).

According to Gahlawat and Choudhury (2019), chemical methods result in more uniform NPs in terms of size and shape, and the reduction step does not require as much energy. Therefore, the most preferred method of NP synthesis throughout the past decade has been chemical synthesis. However, chemical techniques of NP synthesis entail the use of toxic chemicals that are associated with cytotoxicity, carcinogenicity, and genotoxicity, contributing to the notion that such processes are environmentally hazardous.

In contrast, NPs produced by biological means are regarded as clean, safe, economical, and nontoxic when compared to conventional ways; as such, they are suggested as potential environmentally friendly substitutes for chemical and physical processes. Plants and microbes have the ability to gather and absorb metallic ions from their surroundings, making them suitable candidates for the synthesis of nanomaterials. Although a wide variety of biological entities are utilized in the production of NPs, plants, algae, fungi, yeast, bacteria, actinomycetes, and viruses are the most frequently used bioorganisms (Saratale et al., 2018a).

3.1 Green Synthesis of Metal Nanoparticles

The biological synthesis of metal NPs has advanced significantly and is currently being developed as an alternative environmentally friendly procedure. The environmentally benign biological synthesis of NPs is commonly referred to as "green synthesis" or "green chemistry" processes. Using entire cells, metabolites, or extracts from plants and microbes as environmentally friendly raw materials, the green synthesis of nanoparticles creates metallic nanoparticles. It has advantages over chemical and physical processes in that it is secure, straightforward, cost-effective, reasonably reproducible, and it frequently produces more stable materials (Adelere & Lateef, 2016).

Plants and plant parts have been extensively used recently in the synthesis of numerous nanoparticles due to the rich biodiversity of plants and their potential secondary metabolites. Alkaloids, flavonoids, saponins, steroids, tannins, and other beneficial natural chemicals are prevalent in plant extracts. These items can be made from a variety of plant parts, including leaves, stems, roots, shoots, flowers, barks, and seeds. In the bioreduction technique used to create metallic nanoparticles, they serve as reducing and stabilizing agents. Many greener nanoparticles, including cobalt, copper, silver, gold, palladium, platinum, zinc oxide, and magnetite, have been successfully synthesized using plants (Adelere & Lateef, 2016).

A wide range of materials, including plants and plant products, algae, fungi, yeasts, bacteria, and viruses, can be used in the biological production of NPs. Precursors of noble metal salts are combined with biomaterials to begin the production of NPs. Proteins, alkaloids, flavonoids, reducing sugars, polyphenols, and other substances are present in biomaterials and act as reducing and capping agents for the synthesis of NPs from their metal salt predecessors. The color shift of the colloidal solution can be used to visually check the reduction of the metal salt precursor to its subsequent NPs. In the recent past, several research documented the synthesis of Ag, Au, Cu, Pt, Cd, Pt, Pd, Ru, Rh, etc. utilizing different biological agents (Dikshit et al., 2021). Figure 5.2 describes the general steps in the biosynthesis of metal nanoparticles both using microorganisms and plant elements.

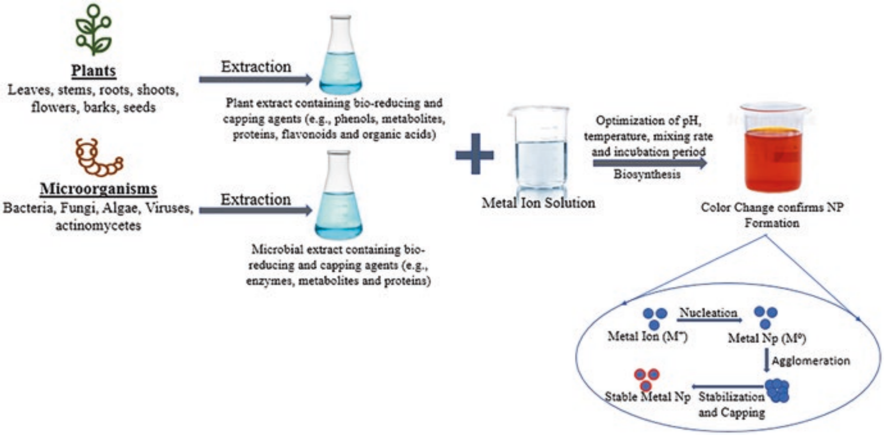

Fig. 5.2 A schematic representation of metallic nanoparticle biosynthesis. (Modified from Kumari et al. (2020), Ndaba et al. (2022), and Dikshit et al. (2021))

3.2 Microbial Synthesis of Metal NPs

Various microorganisms are involved in the production of metal nanoparticles because of their properties. Among the microorganisms, bacteria, fungi, algae, and viruses are the most common. Bacteria and viruses can survive in various adverse environments, and, owing to their ease of culture and less production costs, they can be broadly used to produce MtNPs.

3.2.1 Bacteria-Mediated Synthesis of Nanoparticles

Diverse groups of bacteria were used to synthesize various metal nanoparticles. As they can grow faster and can adapt to different adverse environments, bacteria are used nowadays for production, although the mechanism is not yet fully understood.

A *Bacillus subtilis* EWP-46 cell-free extract was used for the reduction of nitrate in silver NP (AgNP) production. Several variables, including hydrogen ion concentration, temperature, silver ion (Ag^+ ion), and time, influenced the formation of AgNPs. More AgNPs were found to be produced when the conditions were held constant at pH 10.0, 60 °C, 1.0 mM Ag^+ ion, and 720 min. AgNPs were tested against Gram-positive (*Staphylococcus aureus*) and Gram-negative (*Pseudomonas fluorescens*) bacteria to determine their primary inhibitory focus and least bactericidal convergence (Velmurugan et al., 2014).

In another study, *Bacillus licheniformis* cell-free extract (BLCFE)-coated silver nanoparticles were produced by the organism with an average particle size of 18–63 nm, and the synthesized nanoparticles resulted in disintegrated biofilm production of *Vibrio parahaemolyticus* (Shanthi et al., 2016).

Ghorbani (2017) used *Salmonella typhimurium* for the fast production of AgNPs. Table 5.1 summarizes some of the past research studies that were conducted involving the green synthesis of metallic nanoparticles using bacteria.

3.2.2 Fungi-Mediated Synthesis of Metal Nanoparticles

For the biological synthesis of metal nanoparticles, several fungal families have been investigated, including *Alternaria*, *Amylomyces*, *Aspergillus*, *Bipolaris*, *Candida*, *Cladosporium*, *Colletotrichum*, *Coriolus*, *Cylindrocladium*, *Fusarium*, *Ganoderma*, *Helminthosporium*, *Humicola*, *Lecanicillium*, *Mucor*, *Neurospora*, *Penicillium*, *Pestalotiopsis*, and *Phanerochaete*. The *Aspergillus* and *Fusarium* fungus families have been the most thoroughly studied for the nanosynthesis of the following metals and their metal oxides: Au, Ag, Ti, Zn, Ce, Fe, Mg, P, and Pt (Chhipa, 2019).

Trichoderma reesei, among the *Trichoderma* species, is used for the mycosynthesis of AgNPs. The ability of this fungi to detoxify microclimates makes them eligible for the biosynthesis of nanoparticles. These AgNPs have antimicrobial or

Table 5.1 Metallic nanoparticles synthesized using bacteria and the size and morphology of the synthesized nanoparticles

Bacteria	Metallic nanoparticles	Size (nm)	Morphology	Cellular location	References
Bacillus subtilis	Ag	3–20	Spherical	ND	Alsamhary (2020)
Bacillus licheniformis	Ag	40	ND	ND	Kalishwaralal et al. (2008)
Pseudomonas stutzeri	Ag	200	Triangular	ND	Klaus et al. (1999)
Actinobacteria	Ag	13.2	Spherical	ND	Wypij et al. (2017)
Ochrobactrum anthropi	Ag	38–85	Spherical	ND	Thomas et al. (2014)
Pantoea ananatis	Ag	8.06–91.31	Spherical	ND	Monowar et al. (2018)
Corynebacterium sp. SH09	Ag	10–15	ND	Intracellular	Narayanan and Sakthivel (2010)
Escherichia coli	Ag	50	Irregular	ND	Gurunathan et al. (2009)
Morganella sp.	Ag	20 ± 5	Spherical	Extracellular	Parikh et al. (2008)
Bacillus cereus	Ag	4–5	Spherical	Intracellular	Babu and Gunasekaran (2009)
Bacillus licheniformis	Ag	50	Irregular	Intracellular	Kalimuthu et al. (2008)
Corynebacterium glutamicum	Ag	5–50	Irregular	Extracellular	Sneha et al. (2010)
Lactobacillus sp.	Ti	40–60	Spherical	Extracellular	Prasad et al. (2007)
Desulfobacteraceae	ZnS	2–5	Spherical	Intracellular	Labrenz et al. (2000)
Desulfobacteraceae	ZnS	2–5	Biofilm	ND	Labrenz et al. (2000)
Aquaspirillum magnetotacticum	Fe_3O_4	40–50	Octahedral prism	Intracellular	Mann et al. (1984)
Magnetospirillum magnetotacticum	Fe_3O_4	47.1	Cuboctahedron	Intracellular	Philip (2009)
Magnetospirillum magnetotacticum (MS-1)	Fe_3O_4	~ 50	Cuboctahedron	Intracellular	Lee et al. (2004)
Shewanella oneidensis	Fe_3O_4	40–50	Rectangular, rhombic, hexagonal	ND	Suresh et al. (2011)
Lactobacillus acidophilus	Se	2–15	Spherical	ND	Alam et al. (2020)
Lysinibacillus sp. ZYM-1	Se	100–200	Cubic	ND	Che et al. (2017)

Modified from Dikshit et al. (2021) and Saratale et al. (2018a, b)
ND not defined

antibacterial abilities, which work against Gram-positive and Gram-negative microorganisms like bacteria (Vahabi & Dorcheh, 2014).

The fungal strains of *Aspergillus flavus* SP-3, *Trichoderma gamsii* SP-4, *Talaromyces flavus* SP-5, and *Aspergillus oryzae* SP-6 were treated with silver nitrate to produce AgNPs in an experiment by Anand et al. (2015). The synthesized nanoparticles had an average size of 20–60 nm and had antimicrobial properties against both Gram-positive and Gram-negative bacteria.

An *Aspergillus terreus* filtrate was used for AgNP production in an experiment conducted by Li et al. (2011). The synthesized particle size ranged from 1 to 20 nm. NADH was present in the fungal filtrate, and it acted as a secondary metabolite to convert metal precursors to metal nanoparticles.

Pestalotiopsis longiseta was used for the extracellular production of AgNPs. The particle size ranged from 123 to 195 nm (Vardhana & Kathiravan, 2015). Table 5.2 summarizes the names of the fungi that were used to produce MtNPs.

3.2.3 Algae-Mediated Synthesis of Nanoparticles

Spirogyra varians is utilized for the production of AgNPs and is considered the most feasible method. The produced nanoparticles can be effectively used as an antibacterial agent (Salari et al., 2016). Table 5.3 summarizes the algae used for MtNP production.

3.3 Plant-Mediated Synthesis of Nanoparticles

Anogeissus latifolia, a protein-rich edible gum is used to produce AgNPs. The gum extracts are used to convert metal precursors to metal nanoparticles. The synthesized particles are size controlled and easy to handle. The gum encapsulates AgNPs and increases their efficiency as the reaction time increases and it gets more time to get involved in various biological and antimicrobial activities (Kora et al., 2012) (Table 5.4). Table 5.4 summarizes the use of some plant extracts for the synthesis of various MtNPs.

4 Characterization of Metal Nanoparticles

The exploration of nanoparticles' uses, absorption, and toxicology depends heavily on their characterization. Nanoparticles are characterized using a variety of techniques depending on the matrix, analyte, concentration, complexity, and intrinsic qualities (Singh et al., 2021). The characterization of metal nanoparticles can be divided into two parts: (i) structural characterization and (ii) morphological

Table 5.2 Metallic nanoparticles synthesized using fungi and the size and morphology of the synthesized nanoparticles

Fungi	Metallic nanoparticles	Size	Morphology	Cellular location	References
Fusarium oxysporum	Ag	5–50	ND	Extracellular	Senapati et al. (2004)
Fusarium solani USM 3799	Ag	16.23	Spherical	Extracellular	Ingle et al. (2009)
Coriolus versicolor	Ag	25–75	Spherical	Extracellular	Sanghi and Verma (2009)
Aspergillus niger	Ag	20	Spherical	Extracellular	Gade et al. (2008)
Phoma glomerata	Ag	60–80	Spherical	Extracellular	Birla et al. (2009)
Penicillium brevicompactum	Ag	58.35 ± 17.88	ND	Extracellular	Shaligram et al. (2009)
Cladosporium cladosporioides	Ag	10–100	Spherical	Extracellular	Balaji et al. (2009)
Penicillium fellutanum	Ag	5–25	Spherical	Extracellular	Kathiresan et al. (2009)
Aspergillus fumigatus	Ag	5–25	Spherical	Extra cellular	Bhainsa and D'souza (2006).
Fusarium oxysporum	Ag	5–15	Variable	ND	Mohammadian (2007)
Fusarium semitectum	Ag	10–60	Spherical	ND	Basavaraja et al. (2008)
Verticillium sp.	Ag	5–50	Spherical	ND	Senapati et al. (2004)
Yeast strain MKY3	Ag	2–5	Hexagonal	Extracellular	Kowshik et al. (2002a)
Yeast strain MKY3	Ag	9–25	Irregular	ND	Kowshik et al. (2002a)
Fusarium oxysporum	Si	5–15	Quasi-spherical	Extracellular	Bansal et al. (2005)
Fusarium oxysporum	Ti	6–13	Spherical	Extracellular	Bansal et al. (2005)
Fusarium oxysporum	Zr	3–11	Quasi-spherical	Extracellular	Bansal et al. (2004)
Fusarium oxysporum	TiO_2	6–13	Spherical	ND	Bansal et al. (2005)
Fusarium oxysporum	ZrO_2	3–11	Spherical	ND	Bansal et al. (2004)
Schizosaccharomyces pombe	CdS	1–1.5	Wurtzite-hexagonal	Intracellular	Kowshik et al. (2002b)
Yeast	CdS	3.6	Spherical	ND	Prasad and Jha (2010)
Torulopsis sp.	PbS	2–5	Spherical	Intracellular	Kowshik et al. (2002b)
Yeast	Fe_3O_4	<100	Wormhole-like	ND	Zhou et al. (2009)
Saccharomyces cerevisiae	$^{Sb}2^{O}3$	2–10	Spherical	ND	Jha et al. (2009)

Modified from Saratale et al. (2018a, b)

Table 5.3 Metallic nanoparticle synthesized using algae and the size and morphology of the synthesized nanoparticles

Algal species	NPs	Size of NPs (nm)	Morphology	References
Cystophora moniliformis	Ag	50–100	Spherical	Prasad et al. (2013)
Caulerpa racemosa	Ag	05–25	Spherical, triangular	Kathiraven et al. (2015)
Chaetomorpha linum	Ag	03–44	Clusters	Nuraje et al. (2014)
Scenedesmus sp.	Ag	15–20	Spherical, crystalline	Jena et al. (2014)
Gracilaria corticata	Ag	18–46	Nanospheres	Kumar et al. (2012)
Leptolyngbya valderianum	Ag	02–20	Spherical, intracellular	Roychoudhury and Pal (2014)
Pithophora oedogonia	Ag	25–44	Cubical, hexagonal	Sinha et al. (2015)
Porphyra vietnamensis	Ag	13 ± 03	Spherical	Venkatpurwar and Pokharkar (2011)
Sargassum tenerrimum	Ag	20	Spherical	Kumar et al. (2012)
Sargassum wightii	Ag	08–27	ND	Saratale et al. (2017)
Spirogyra varians	Ag	35	Quasi-spheres	Salari et al. (2016)
Ulva lactuca	Ag	–	Spherical	Murugan et al. (2015)
Sargassum muticum	Ag	43–79	Spherical	Madhiyazhagan et al. (2015)
Gelidium amansii	Ag	27–54	Spherical	Pugazhendhi et al. (2018)
Laminaria japonica	Ag	31	Spherical to oval	Kim et al. (2018)
Chlorococcum sp. MM11	Fe	20–50	Spherical	Vigneshwaran et al. (2006)
Sargassum bovinum	Pd	05–10	Octahedral	Momeni and Nabipour (2015)

Modified from Saratale et al. (2018a, b)

characterization. Researchers mostly employ Fourier transform infrared (FTIR) spectroscopy, X-ray diffraction (XRD), and X-ray fluorescence (XRF) techniques for the structural characterization of nanomaterials. Scanning electron microscopy (SEM), transmission electron microscopy (TEM), and energy-dispersive X-ray spectroscopy (EDS) techniques can all be used to analyze the morphology of nanomaterials (Samaddar et al., 2018).

4.1 Structural Characterization

FTIR spectroscopy is used to characterize the vibrational modes of the precursors and synthesized nanoparticles. The presence of impurities in the final product can also be determined using an FTIR spectrogram. If the product's spectrogram shows

Table 5.4 Metallic nanoparticles synthesized using plant extracts and the size of the synthesized nanoparticles

NPs	Plants	Parts	Extractants	Precursors	Size (nm)
AuNPs	*Butea monosperma*	Leaf	Water	$HAuCl_4$	10–100
	Pelargonium graveolens	Leaf	Water	$HAuCl_4$	20–40
	Salix alba	Leaf	Water	$HAuCl_4·3H_2O$	50–80
	Guazuma ulmifolia L.	Bark	Water	$HAuCl_4·3H_2O$	20–25
	Nerium oleander	Bark	Methanol	$HAuCl_4$	20–40
	Rubia cordifolia	Fruit	Ethanol	$HAuCl_4$	5–20
	Litsea cubeba	Fruit	Water	$HAuCl_4·3H_2O$	8–18
	Piper longum	Fruit	Water	$HAuCl_4$	20–200
	Hibiscus sabdariffa	Flower	Water	$HAuCl_4·3H_2O$	15–45
	Coleus forskohlii	Root	Water	$HAuCl_4$	5–18
	Stachys lavandulifolia	Overground part	Overground part	$HAuCl_4$	34–80
AgNPs	*Lotus garcinii*	Leaf	Water	$AgNO_3$	7–20
	Morinda citrifolia	Leaf	Methanol	$AgNO_3$	10–100
	Prunus mume	Fruit	Water	$AgNO_3$	~30
	Eugenia stipitata McVaugh	Fruit	Water	$AgNO_3$	15–45
	Aconitum toxicum Reichenb.	Root	96% ethanol	$AgNO_3$	53–67
	Catharanthus roseus	Bark	Water	$AgNO_3$	1–26
CuNPs	*Ocimum sanctum*	Leaf	Water	$CuSO_4·5H_2O$	50–70
	Hibiscus rosa-sinensis	Flower	Water	$Cu(CH_3COO)_2·H_2O$	0.115–1.1 μm
PtNPs	*Costus speciosus*	Leaf	95% ethanol	Platinum 2,4-pentanedionate	10–50

Modified from Bao et al. (2021)

peaks at a different level than the precursor's, then this indicates that there might be some impurities present in the final product. The features of MtNPs, including chemical concentration, surface chemistry, surface functional groups, and atomic organization and transmission, are measured using Fourier transform infrared (FTIR) spectroscopy.

The crystalline structure of synthetic nano-samples is investigated using X-ray diffraction (XRD).

The content of different particles contained in the produced nanomaterials is identified using X-ray fluorescence (XRF) analysis. According to an experiment by Li et al. (2016), produced α-Fe_2O_3 contained various impurities such as 0.898% SiO_2, 0.486% TiO_2, and 0.112% MgO.

4.2 Morphological Characterization

Scanning electron microscopy (SEM) is used to morphologically characterize metal nanoparticles. Since the application of metallic nanoparticles is largely dependent on the particle size and shape of the NPs, SEM is used to characterize the internal dispersion of the NPs.

Energy-dispersive X-ray spectroscopic analysis is performed alongside SEM imaging to investigate the distribution pattern of other metal species on synthesized NPs (Samaddar et al., 2018). In an experiment by Fang et al. (2011), the EDS analysis showed that the amount of nickel (Ni) and Zn on zero-valent FeNPs was too low to be detected. Energy-dispersive X-ray spectroscopy (EDS) is typically used to analyze the elemental composition of MtNPs.

Transmission electron microscopic images are used to determine the particle size or pore size of NPs. Since the synthesis of nanoparticles is size-dependent, a change in temperature can cause alterations in NP size. Therefore, TEM images are used to identify any size change during the synthesis process (Samaddar et al., 2018). The position, size, and shape of MtNPs can be seen using transmission electron microscopy (TEM), scanning electron microscopy (SEM), and atomic force microscopy (AFM).

UV–visible (UV-vis) spectroscopy is another method that is used for structural characterization. MtNPs are typically tested for stability and synthesis using UV–visible spectroscopy.

The size of the NPs at an extremely low level can be estimated using a dynamic light scattering (DLS)/zeta potential size analyzer. Zeta potential describes the surface condition of a nanoparticle and predicts its stability over time (Singh et al., 2021). The size and surface charge of MtNPs is mostly assessed using the dynamic light scattering (DLS) method.

5 Use of Metallic Nanoparticles in Sustainable Agriculture

The primary issue with excessive and prolonged use of chemical fertilizers in agriculture is the decline in soil fertility, which ultimately has an impact on the output of agricultural goods. According to the literature, weeds cause 13% damage, plant infections cause 13% loss, and insect pests cause 14% loss globally. The loss value of crops has been calculated to be USD 2000 billion annually. As a result, it is crucial to increase crops that are resistant to pests and droughts to enhance crop productivity (Rai & Ingle, 2012; Saratale et al., 2018a). Nanomaterials can be applied to soil systems as both nanofertilizers and nanopesticides. The term “nanofertilizers” refers to nanomaterials that are either nutrients themselves or act as carriers or additions for the nutrients (by, for example, combining with minerals) (macro- or micronutrients). Nutrients can also be enclosed within nanoparticles to create these types of fertilizers (Saleem & Zaidi, 2020).

Nanomaterials that can provide one or more nutrients to plants to promote their development and production are known as nanofertilizers. One of the possible methods for boosting plant growth and productivity to meet the world's rising food demand is the use of nanoparticle fertilizers. The distribution of chemicals to the desired places is made possible by the nanofertilizers' extremely high sorption capacity, surface area, and regulated chemical release kinetics (Snehal & Lohani, 2018). With higher nutrient use efficiency, nanofertilizers can boost crop output and quality while lowering production costs, resulting in sustainable agriculture. Nanofertilizers are organic fertilizers or smart fertilizers that provide plants tiny but potent doses of nutrients. Encapsulating nanofertilizers can increase nutrient uptake, which eventually lowers nutrient loss, promotes healthy plant development, and enhances crop quality. By preventing nutrients from interacting with soil, water, air, and microbes, nanoformulations minimize the risk of environmental degradation by providing progressive and controlled release of nutrients to the target regions. The usage of MtNP-based nanofertilizers was found to have a great potential to boost crop productivity (Bahrulolum et al., 2021). The effects of metal nanoparticles as nanofertilizers can be discussed in two pathways. The produced nanoparticles can be applied directly on soil or can be used through foliar application.

MtNPs, which include silver, gold, cadmium, copper, zinc, iron, and selenium (Se), have a variety of uses in agriculture, including promoting plant development, having antibacterial and antifungal effects, and acting as nanofertilizers and nanobiosensors (Bahrulolum et al., 2021). Zn and Fe, two nanonutrients produced by biosynthesis, help plants cope with stress and avoid cell damage. Different microbially produced nanonutrients, such as those containing boron, iron, sulfur, molybdenum, magnesium, nitrogen, phosphorus, and potassium, improved grain yield by 12%–54% and dry matter yield by 18%–34% in crops of cauliflower, capsicum, castor, cluster beans, chickpeas, maize, mung beans, pearl millet, rice, tomatoes, and wheat, depending on the nutrient ratios (Chhipa, 2019).

Acid phosphatase, alkaline phosphatase, aryl sulfatase, cellulase, dehydrogenase, esterase, hemicellulase, lignase, and nitrate reductase had an increase in rhizosphere activity between 18% and 283%. Nutrient usage efficiency was also enhanced by 3- to 20-fold by nanofertilizers. Smart nanonutrients' large surface area and targeted delivery could drastically reduce the amount of nanofertilizers used at the field level from kilograms to milligrams, thus reducing fertilizer leaching and eutrophication (Chhipa, 2019).

NPs' actual functionality is determined by how they interact with the substrate on which they have been used. The uptake and distribution of NPs in crops directly affect their actual influence and impact (Singh et al., 2021).

5.1 *Silver Nanoparticles (AgNPs)*

Silver ions make up a significant portion of these nanoparticles (10–20 nm in size). Inside living systems, these particles are highly active and effective. Various harmful microorganisms have been fought off using silver nanoparticles. Silver nanoparticles, for instance, have been used to treat spot blotch disease. They are also used to break seed dormancy, boost seed vigor index, and raise seedling fresh weight, among other things. Silver nanoparticles are simple to synthesize and safe for the environment. Research on the ability of plants to withstand stress brought on by silver nanoparticles is still ongoing (Singh et al., 2021).

5.2 Zinc Oxide Nanoparticles (ZnO NPs)

Due to the lower availability of zinc and its restricted amount in calcium carbonate-enriched soils due to their alkaline pH, both soils and plants commonly suffer from zinc deficiency. Zinc sulfate fertilizers are used as an alternative to lessen this. Despite this, plants still experience zinc deficiency. Due to their tiny size and wide surface area, zinc oxide nanoparticles are the ideal solution to treat zinc deficiency since they are quickly absorbed by plants. The 100-nm size of zinc oxide nanoparticles makes them particularly effective. In order to synthesize zinc oxide nanoparticles, zinc sulfate heptahydrate is typically dissolved in water. Concomitantly, a bioactive extract is obtained from desirable living organisms such as plants and animals. Water or ethanol are used to prepare the extract. The two prepared solutions are then combined at the proper pH to produce the desired zinc oxide nanoparticles. These nanoparticles may offer a low-cost, environmentally safe, and long-lasting solution to a few plant-related issues, including pathogenic invasions and zinc shortages (Singh et al., 2021).

5.3 Titanium Dioxide Nanoparticles (TiO_2 NPs)

Titanium dioxide nanoparticles (TiO_2 NPs), which range in size from 5 to 30 nm, are widely produced and applied owing to their photocatalytic properties. Therefore, they are utilized in pigment formation. These nanoparticles help plants grow and photosynthesize more. Broad beans (a common leguminous crop) had their soil salinity reduced by titanium dioxide nanoparticles ($nTiO_2$) (Abdel Latef et al., 2018). Additionally, it is applied via roots or foliar spray at extremely low concentrations to promote plant growth, enzymatic activity, photosynthesis of chlorophyll content that promotes nutrient uptake, and stress tolerance and to increase crop yield and quality (Singh et al., 2021).

5.4 Iron Oxide Nanoparticles (Fe_2O_3 NPs)

Due to their ability to substitute conventionally ineffective Fe fertilizers, iron oxide nanoparticles (Fe_2O_3 NPs) are vital oxide nanomaterials that are extensively used in agriculture. They typically range in size from 10 to 20 nm and exhibit a unique sort of magnetism. They can take on a variety of forms, including rods, spheres, cubes, self-oriented flowers, etc. Fe is naturally abundant mostly in the form of Fe^{3+}, whereas plants and other living things can only take up Fe^{2+} (Singh et al., 2021). Fe mediates a few physiological responses in plants, including leghemoglobin generation in nodules, chlorophyll synthesis, redox reaction, respiration, etc. However, Fe must be applied in optimum amounts, as both deficiency and excess are harmful to plants. Fe deficiency is a common problem in various crops. According to Sánchez-Alcalá et al., *Arachis hypogaea* (peanut) is extremely susceptible to Fe deficiency. As demonstrated by the peanut, soybean, and wheat crops, studies have shown that iron oxide nanoparticles have a good impact on plant development and productivity (Sánchez-Alcalá et al., 2014).

5.5 Copper Nanoparticles (CuNPs)

Due to characteristics such as their extremely small size and high surface area to volume ratio as compared to materials formed from bigger particles, CuNPs perform better than bulk copper particles. CuNPs have several uses in agriculture due to their antifungal and antibacterial actions against Gram-positive and Gram-negative bacteria as well as harmful fungi. CuNPs show antifungal efficacy against plant pathogenic fungi such *Phytophthora infestans*, *Fusarium oxysporum*, *Fusarium culmorum*, and *Fusarium graminearum*. At doses under 100 ppm, they have also been shown to behave as germination promoters and growth stimulants in several plants. CuNPs have been synthesized thus far using a variety of chemical, physical, and green synthesis techniques in diverse quantities, configurations, and morphologies (Bahrulolum et al., 2021).

5.6 Selenium Nanoparticles (SeNPs)

Most living things require selenium, which is present in soil, water, seeds, animals, and food. Se fertilizers must be added to the soil to enhance the Se content in plant nutrients, and Se levels in food must be balanced, as SeNPs boost the plant's capacity to suppress infections and activate antifungal characteristics. Se-balanced food processing is a quick procedure that aids in resolving the Se imbalance problem in agriculture. It is crucial to ensure the optimum amount of selenium in the soil, and fertilizers made of pure selenium compounds are employed to achieve this. However, Se fertilizers only last for one or a few harvests in rich topsoil, and, over a short time, inorganic Se compounds are washed away by rain into the infertile horizons beneath the soil. Organic Se compounds are not actively leached, but they are readily broken down after application. SeNPs have the benefit of not slowly leaching from the soil and not dissolving in water or aqueous solutions, making them excellent nanofertilizers (Bahrulolum et al., 2021).

6 Other Uses

In addition to agriculture, nanoparticles are employed in plasmonics, optoelectronics, surface-enhanced Raman scattering (SERS), biological sensors, catalysts, sorbents, energy production, and DNA sequencing. The easy growth of fungi and their abundant production of reducing and stabilizing agents make mycosynthesis of nanomaterials an efficient method in industrial manufacturing. At the laboratory scale, new cutting-edge nanotechnology offers a superior answer to sustainable agriculture. Nanoparticle applications are still in their infancy, including those such as nanofertilizers, nanopesticides, nanofungicides, nanoherbicides, nanosensors for pathogen detection, and nanomaterials for pesticide sorption. In addition to this, nanoparticles utilized in the food packaging sector are also widely accepted. Many packaged food products have longer shelf lives owing to nanocoating and wrapping in wrappers that include nanomaterials (nanofilms) (Chhipa, 2019).

6.1 Nanopesticides

The widespread use of chemical pesticides is a major global concern since they can cause serious problems like biomagnification. Many organophosphate insecticides build up in the animal adipose tissue and affect the food chain. The creation and application of nanoparticles with an organic origin and pesticidal characteristics is a practical remedy for this issue (Singh et al., 2021).

With regard to fungi that cause fungal plant diseases, silver nanomaterials have shown antifungal activity against *Alternaria alternata*, *Botrytis cinerea*, *Bipolaris sorokiniana*, *Magnaporthe grisea*, *Sclerotium*, *Sclerotium cepivorum*, *Candida tropicalis*, *Candida parapsilosis*, *C. albicans*, *Colletotrichum gloeosporioides*, and *Raffaelea* sp. Similar to this, ZnO exhibits antifungal action against *Penicillium expansum*, *B. cinerea*, and *A. niger.* The cell wall is damaged by nanopesticide's interaction with fungus hyphae, which prevents conidial germination and fungal growth (Chhipa, 2019).

In recent studies, a *Taraxacum officinale* leaf extract has been used to produce AgNPs, which exhibited significant antibacterial action against two significant phytopathogens, *Xanthomonas axonopodis* and *Pseudomonas syringae*. A tetracycline-containing nanoformulation demonstrated increased antibacterial activity against phytopathogens. Additionally, it was discovered in this study that synthetic AgNPs had a stronger antibacterial impact than those sold in stores. In order to manage phytopathogens, these AgNPs may be used as a less expensive substitute for commercial pesticides (Saratale et al., 2018a).

Cu-based nanoparticles (Cu/Cu_2O NPs, Cu_2O NPs, and CuO NPs) have been identified as promising agro-fungicides and have been shown to be effective against a variety of phytopathogens, including *Fusarium* sp., *Phoma destructiva*, *Cochliobolus lunatus*, *A. alternata*, *F. oxysporum*, *Penicillium italicum*, *Penicillium*

Digitatum, and *Rhizoctonia solani*). Giannousi et al. (2013) reported the use of Cu_2O NPs as agro-fungicides to control the important plant pathogen *Phytophthora infestans*. It is interesting to note that CuNPs cause oxidative stress, which can function differently depending on the species of fungus.

6.2 Nanosensors

In addition to the use of nanopesticides and nanofertilizers, nanosensors were created to identify plant diseases, plant hormones, soil moisture, and residual pesticides. Nanosensors are useful in providing real-time information on field conditions and soil health. Chemical sensors based on carbon nanomaterials were created to detect pesticide residues in plants. Additionally, *Xanthomonas axonopodis*, the causative agent of the bacterial spot illness, was targeted for detection using nanoprobes. To find the pathogen, they combined anti-rabbit secondary antibodies with silica nanoparticles (Chhipa, 2019).

7 Conclusions

Considering the growing population demand for food and the critical environmental issues, precision farming is an obvious solution. The application of metal nanoparticles is essential for achieving precision farming. Typical production processes of metal nanoparticles are fraught with a number of problems, including the use of hazardous solvents, the generation of toxic by-products products and the consumption of high energy. As a result, environmentally friendly production routes, such as "green synthesis," are being adopted more and more for metal nanoparticles. The green synthesis process has a variety of environmental benefits, including its efficiency, cost-effectiveness, and eco-friendliness. The green synthesis process is likely to play an enormous role in achieving sustainable agriculture. Metal nanoparticles produced via green synthesis are not only eco-friendly but are also capable of being delivered to specific sites over a long period of time. As a result, these nanoparticles are good candidates for slow-release fertilizers. Metal nanoparticles offer advantageous qualities that can be used to improve plant growth through both soil and foliar applications. High germination rates, high growth rates, etc. are only a few of the plant growth indices that are improved by the usage of metal nanoparticles. In addition to their use as fertilizers, metal nanoparticles can also be used as nanosensors, soil and water amendment tools, and other applications that can be crucial for achieving increased and sustainable agricultural output.

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