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Green synthesized metallic nanoparticles and their applications: A review

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ABSTRACT

Metallic nanoparticles (MNPs) were synthesized using different methods. Physical and chemical methods were the most common for the synthesis of MNPs. Most recently, biosynthesis of MNPs has been promoted as the best option which is an eco-friendly, inexpensive and energy-effective method. There are several ways to confirm the formation and characterization of MNPs such as UV light, FTIR, XRD, DLS, ICPs, TEM, SEM, and zeta potential. The mechanism of synthesis involves extracellular and intracellular routes. The extracted NPs can be applied in a variety of applications, including medical, Environmental, industrial, and agricultural applications.

Keywords: *Metallic Nanoparticles, Green synthesis, antimicrobial activity, characterization of metallic nano particle.*

1. Introduction

In the past few years, nanomaterials have gained significant attention. For instance, metallic nanoparticles are considered a potential technology for several applications in different areas, due to their uniformity, high stability, biological activity, Magnetic properties, catalytic activity, and good electrical conductivity (Duan et al. 2018; Xu et al. 2023). Nanoparticles can be classified into zero, first, second, and third dimensions (Khan and Hossain, 2022). Each dimension expresses a significant form of nanomaterials, the zero dimension is what we can call a nanoparticle in the range between 1-100nm, also it includes quantum dots which are in the range from 1-10nm for instance (Harish et al. 2018).

The method of synthesis of nanoparticles can be described with two basic techniques, top-down and bottom-up (Arole and Munde, 2014). The Top-down expresses the synthesis of nanoscale materials by cutting the bulk materials into smaller parts till we get the nanoparticle, on the other hand, the bottom-up technique renders the particles by adding atoms together to attain the correct nanoparticles.

Green synthesis of metallic nanoparticles (MNPs) is considered a bottom-up technique, in which atoms get reduced in a biological process and start gathering to form a nanoparticle and then hinder the process preventing the overgrowth of these particles (Arole and Munde, 2014). The capping agent is the name of that compound that can hinder this process (Pedroso-Santana and Fleitas-Salazar, 2023). Plants and microorganisms are regarded as machines for green methods of the synthesis of MNPs, as they produce large amounts of secondary metabolites such as (flavonoids, alkaloids, terpenoids, polyphenolics, enzymes, proteins, sugars, and vitamins), sometimes primary metabolites which can reduce the precursor into a zero-valent metal form in the nanoscale (Ahmad et al. 2019). Moreover, the synthesis of NPs using green methods is considered eco-friendly, cost-effective, and easily available, in which no heat or energy is required for the sustainability of this process (Shamaila et al. 2016).

Simply the process of synthesis includes three major steps in terms of mechanism, first is the reduction of metal ions in the form of precursor into the zero valent state, second, is he Nucleation which includes the gathering of atoms, finally, capping agents start to surround the nuclei and may bond withF them to guarantee the fixed size of nanoparticles (Sabir et al. 2022).

The NP can be metal alone, metal oxide, or a composite (Falcaro et al. 2016). Metals such as Ag, Au, Se, and Zn are the most used in applications, on the other hand, oxides such as ZnO have several applications as well. Magnetic Nanoparticles (MNPs) have found diverse applications across various domains, demonstrating their versatility and efficacy. Within the environmental sector, MNPs have exhibited utility in pivotal areas such as water treatment (Goutam et al., 2020; Idris and Roy, 2023). In medicine, MNPs have demonstrated significant potential in multifaceted applications, including drug delivery systems, wound healing modalities (Balaure et al., 2019; Ullah and Lim, 2022). In the industrial, encompasses applications in paints, cosmetics, automobiles, semiconductors, packaging materials, and catalytic processes (Madkour, 2018).

In the agricultural domain, MNPs have been instrumental in the development of innovative solutions, notably contributing to the formulation of advanced fertilizers and biochar. (V. Kumar et al. 2023). Furthermore, Micronutrients such as molybdenum (Mo), copper (Cu), iron (Fe), nickel (Ni), manganese (Mn), and Zinc (Zn) can used as nanofertilizers (Dikshit et al., 2021).

2. Methods of synthesis

There are two ways to synthesize nanoparticles: top-down and bottom-up. The top-down method uses a variety of physical procedures, such as evaporation-condensation, laser ablation, or other techniques, to shatter bulk materials into small particles, as shown in Fig.1. As opposed to this, the bottom-up approach grows NPs by first assembling atoms into nuclei. Bottom-up approaches refer to the biological and chemical techniques utilized in NP synthesis. Several chemical, physical, and biological methods have been applied to create nanomaterials with certain sizes and forms (Grzelczak et al. 2008).

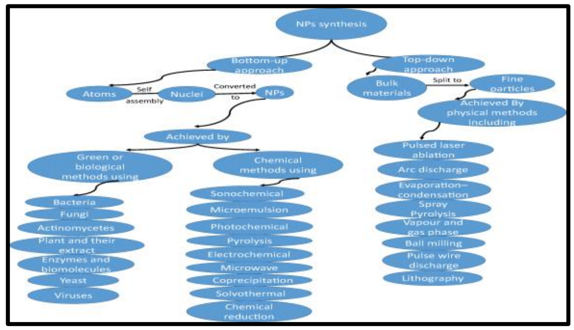

Figure 1: Synthesis of metallic nanoparticles using different methods. (Salem and Fouda, 2011).

2.1 Physical and Chemical Techniques for NP Synthesis:

Researchers have developed diverse chemical and physical methods to synthesize nanoparticles (NPs) in various shapes and sizes for plenty of applications (Salem and Fouda, 2011). Techniques like photolithography and electrochemical synthesis offer precise control over NP morphology (Amani et al. 2019). but often at the expense of sustainability and safety. The primary limitations of traditional methods include a high cost, toxicity Hazardous chemicals that pose environmental and health risks, energy inefficiency as the processes require significant energy consumption, Complexity due to stringent control over reaction parameters (pressure, pH, temperature) adds difficulties, Waste generation as harmful byproducts(Shamaila et al. 2016).

These shortcomings highlight the urgent need for eco-friendly alternatives. Biological and green synthesis approaches emerge as promising solutions, utilizing naturally derived and non-toxic materials and processes. By minimizing environmental impact and health risks, green methods pave the way for sustainable NPs production (Álvarez-Chimal and Arenas-Alatorre 2023). Therefore, Embracing such eco-friendly approaches will unlock the full potential of NPs while ensuring a safer and cleaner future.

2.2 Green synthesis of NPs

Traditional MNPs synthesis methods, while offering precise control over morphology, often suffer from drawbacks such as high cost, toxicity, and environmental concerns. In response, green or biological synthesis has emerged as a promising alternative ((Álvarez-Chimal and Arenas-Alatorre 2023). By utilizing naturally derived materials and mild reaction conditions, this approach minimizes these limitations and promotes sustainability (Malhotra and Alghuthaymi 2022).

Biomass filtrates obtained from diverse biological sources, including bacteria, fungi, actinomycetes, and plant extracts, have been successfully employed for green synthesis. Diverse metal NPs, ranging from silver and gold to copper and magnesium, have been produced using this approach (Gade et al. 2014). Moreover, a plethora of reports demonstrate the biofabrication of nanoparticles like silver, gold alloys, tellurium, platinum, and quantum dots utilizing various microorganisms (Fouda et al., 2018; Mohamed et al., 2019; Narayanan and Sakthivel, 2010; Saad et al., 2018). Recent advancements have expanded the range of organisms employed for green synthesis.

Green synthesis operates through a bottom-up approach, where biomolecules like enzymes, proteins, and sugars present in the biomass filtrate facilitate the oxidation/reduction of metal ions into nanoparticles (Prabhu and Poulose, 2012). However, a comprehensive understanding of the precise mechanisms employed by different microorganisms remains elusive. Each microbial species likely utilizes multiple pathways to interact with metal ions, and the resulting size, shape, and morphology of the nanoparticles are further influenced by biochemical processing, environmental factors like temperature and pH, and the specific microorganism employed (Makarov et al., 2014).Despite its advantages, several challenges impede the widespread adoption of green synthesis such as optimizing the synthesis process for precise control over nanoparticle size and shape, as these features directly impact their biological activities. Moreover, Deciphering the specific roles of individual biomass components requires detailed chemical analysis, posing another analytical challenge, in addition, Scaling up green NP production to commercially viable levels requires further research and development (Lu and Ozcan n.d.). Finally, Elucidating the precise mechanisms of bio fabrication is crucial for optimizing and advancing technology (Noor Javed et al. n.d.).

Furthermore, bridging the gap between basic science, chemical engineering, and industrial production is essential for the successful transition of green nanomaterials to commercial applications. Overall, while challenges remain, green synthesis exhibits great potential for sustainable and eco-friendly NP production. Continued research and development efforts hold the key to overcoming these hurdles and unlocking the full potential of this exciting field (Noor Javed et al. n.d.).

2.3 Bacterial-mediated NPs

Green synthesis of nanoparticles (NPs) using bacteria has emerged as a promising alternative to traditional methods, offering advantages in terms of cost, environmental impact, and ease of production. Among various biological agents, bacteria stand out due to their: Favourable growth conditions, requiring minimal resource investment, and being readily manipulated for process optimization. Facile purification, simplifying downstream processing, and minimizing contamination. High yield, Enabling efficient NP production through rapid bacterial growth. These attributes have earned bacteria the title of "factories of nanomaterials" and made them the preferred platform for bio-fabrication (Tsekhmistrenko et al. 2020).

Bacteria display versatility in NP synthesis, demonstrated by the successful production of silver nanoparticles (Ag-NPs) with controllable size ranges by diverse species like *Bacillus thuringiensis*, *Bacillus licheniformis*, and *Klebsiella pneumonia.* Moreover, their ability to synthesize NPs both intracellularly and extracellularly offers several advantages. Scalability, Easy adaptation to large-scale production for commercial applications. Flexibility, tailoring bacterial strains and growth conditions to achieve desired NP properties. Cost-effectiveness, Simplified purification, and waste management due to intrinsic bioremediation capabilities (Sriram, Kalishwaralal, and Gurunathan 2012).

2.4 Algal-mediated NPs synthesis

Marine microorganisms, particularly algae, have emerged as dual protagonists in environmental remediation and nanomaterial synthesis. Their remarkable abilities extend beyond heavy metal uptake to the biosynthesis of metallic NPs. As an illustrative example, Chlorella vulgaris, a green alga, has been successfully employed to produce Au-NPs through the reduction of tetrachloroaurate ions (Luangpipat et al., 2011). Similarly, *Fucus vesiculosus*, a brown alga, demonstrates the promising potential for the bio reduction and biosorption of Au (III) ions. This eco-friendly approach holds significant promise as a sustainable alternative for gold recovery from microelectronic scrap leachates and dilute hydrometallurgical solutions. Furthermore, diatoms, another crucial group of algae, offer valuable resources for the fabrication of siliceous materials (Kroger et al., 1999).

2.5 Synthesis of NPs by fungi and yeast

Fungi have become prominent players in the field of green nanomaterials synthesis, lauded for their efficient biofabrication capabilities. Their extensive repertoire of metabolic products, encompassing proteins and enzymes, empowers them to produce diverse nanoparticles (NPs) with remarkable efficiency (Fouda et al. 2018). This, coupled with their ease of cultivation and manipulation in laboratory settings, positions them as valuable additions to the arsenal of microorganisms employed in nanosynthesis (Spagnoletti et al. 2019). Several factors contribute to the widespread adoption of fungi for NP synthesis. Firstly, fungi readily secrete enzymes and proteins, enabling large-scale enzyme production and enhancing NP creation (Chan and Don, 2012). Secondly, fungal biomass is cost-effective and environmentally friendly, aligning with the principles of green nanotechnology. As a third advantage, Scalability and ease of processing that fungal mycelia offer a large surface area, ideal for scaling up production and simplifying downstream processing, also it can be involved in a continuous system that will be suitable for commercial production. Finally, Metal tolerance and bioaccumulation found in Certain fungal species exhibit remarkable tolerance and bioaccumulation capabilities for metals, making them effective candidates for bioremediation and metal recovery (Sastry et al. 2003).

Beyond these advantages, fungi also exhibit notable versatility in NP fabrication: Diverse NP structures: Fungi can generate NPs in various morphologies, including meso- and nanostructures, through enzymatic reduction (intracellular or extracellular) and biomimetic mineralization (Durán et al. 2005). A broad spectrum of NPs: A plethora of fungal species can produce metal NPs like gold and silver, with examples such as *Phanerochaete chrysosporium*, *Pleurotus sajorcaju*, and *Coriolus versicolor* (El Domany et al. 2018; Elamawi, Al-Harbi, and Hendi 2018). Expanding NP repertoire: Research continues to unveil the potential of fungi for synthesizing other NPs, including zinc oxide, iron oxide, and metal sulfides (Mohamed et al., 2019).

This potent bio-fabrication prowess paves the way for a new scientific domain: myco-nanotechnology. This promising field, at the intersection of mycology and nanotechnology, harnesses the vast fungal diversity to develop novel nanomaterials with diverse applications, particularly in the field of medicine (Mandal et al., 2006; Mohmed et al., 2017).

3. Characterization

Metallic nanoparticles can be characterized using several techniques, such as UV, TEM, SEM, XRD, DLS, Zeta potential. Which they can be classified into two major types, structural characterization and compositional characterization as shown in Fig. 2.

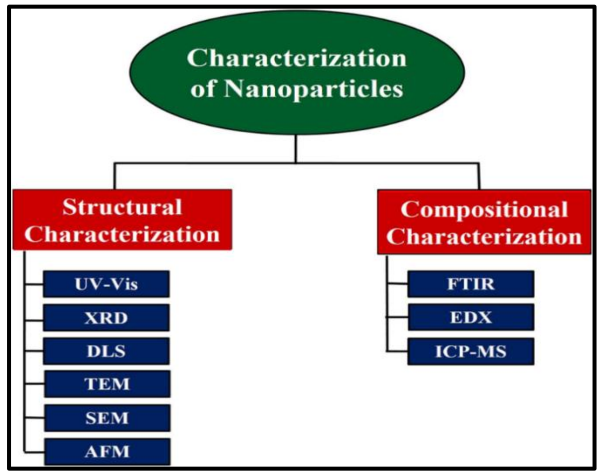

Figure 2: Characterization of metallic nanoparticles (Ghosh et al. 2021).

3.1 Fourier transform infrared spectroscopy (FT-IR):

Imagine a molecular fingerprint scanner. FT-IR analyzes the light absorbed by nanoparticles, revealing the unique signatures of stabilizing agents, through its functional groups (Shukla and Iravani, 2017).

3.2 UV-Vis spectrophotometry

This technique acts as a prism, dissecting the colors of light absorbed or scattered by nanoparticles. By analyzing the light spectrum, scientists gain insights into their size, formation, stability, and interactions with their watery surroundings (M. Kumar et al., 2023).

3.3 Scanning electron microscope (SEM)

Instead of light, SEM utilizes a focused beam of electrons to create high-definition portraits of nanoparticles. This allows researchers to visualize their shape, size, texture, and distribution, providing a detailed picture of their morphology (Kumar et al., 2018).

3.4 X-ray diffraction (XRD)

XRD acts as an X-ray detective, firing beams of X-rays at the nanoparticles and analyzing the resulting diffraction patterns. This technique reveals the atomic arrangement within the material, allowing for the determination of crystal structure, calculation of nanoparticle size, and confirmation of their presence (M. Kumar et al., 2023).

3.5 Intracranial pressure (ICP) spectrometry

ICP spectrometry, like a metal detective, measures the concentration of metals present in solutions before and after their interaction with nanoparticles. This technique reveals the amount of metal released during these interactions, providing insights into their potential environmental and health implications (Naghdi et al., 2018).

3.6 Atomic force microscopy (AFM)

Imagine a nanoscale tactile sensor. AFM gently scans the surface of nanoparticles, measuring their shape, size, and surface area with exquisite precision. This technique provides valuable insights into the physical properties of these tiny entities (Sathishkumar et al., 2018).

3.7 Transmission electron microscope (TEM)

TEM acts like a magnifying glass for the atomic world. By bombarding nanoparticles with a high-energy electron beam, TEM generates detailed images that reveal their internal structure, size, and intricate crystal lattice arrangement (Pérez-Beltrán et al., 2021).

3.8 Annular dark-field imaging (HAADF)

This specialized TEM technique sheds light on the interactions between nanoparticles and bacteria. By analyzing the intensity variations in the dark-field image, researchers can visualize the size distribution of nanoparticles interacting with different bacterial types, providing crucial information about their potential biological effects (Pérez-Beltrán et al., 2021).

3.9 Zeta potential:

Zeta potential quantifies the electrostatic potential difference between the charged surface of a nanoparticle and the bulk surrounding liquid. This critical parameter serves as a potent indicator of colloidal stability and aggregation behavior of NPs. A high absolute zeta potential, be it positive or negative, translates to greater electrostatic repulsion between particles, effectively preventing aggregation and promoting long-term colloidal stability. Zeta potential measurements are intricately linked to various factors, including surface charge**,** ionic strength of the suspending medium, and its pH. Consequently, manipulating these parameters allows for fine-tuning of NP stability and behavior for tailored applications (Bagherpour et al., 2018).

3.10 Dynamic light scattering (DLS)

Used to measure the particle size of dispersing colloidal samples, to study the stability of formulations, and to detect the presence of aggregation or agglomeration (Bagherpour et al., 2018; Ijaz et al., 2020).

4. The mechanism of synthesis, and natural compounds responsible for the reduction process

The synthesis of MNPs by microbes primarily relies on reduction reactions**.** Cellular peptides and polysaccharides facilitate enzymatic oxidation, reduction, sorption, and chelation of metal ions, driving MNP formation via both intracellular and extracellular pathways as indicated in Fig. 3 (Bahrulolum et al., 2021).

The respiration processes of microbes may contribute to the synthesis of diverse metal oxides (Kim et al. 2018). The movement of electrons from reduced organic compounds to oxidized inorganic compounds can be enhanced by microbial dissimilatory anaerobic respiration, which is associated with crystallization and nanoparticle formation. There is strong evidence that Shewanella can oxidize organic acids as electron donors and make reductions for inorganic metals as electron acceptors. (Harris et al. 2018; Heidelberg et al. 2002). Microorganisms such as bacteria have developed mechanisms for detoxifying the immediate environment by converting toxic metal species into nanoparticles (Deplanche and Macaskie, 2008; Murray et al., 2017). Also, biomolecules secreted by bacteria were used as capping as well as stabilizing agents of nanoparticle synthesis. The nanoparticle synthesis by the microbial process is indicated in Figure 3. Usually, nanoparticles are formed by trapping metal ions on the surface of or inside microbial cells, then enzymes reduce the trapped metal ions to nanoparticles.

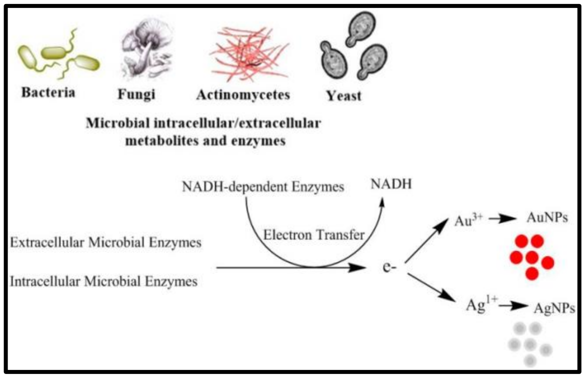

Figure 3: The mechanism of synthesis of metallic nanoparticles using microorganisms (Ovais et al. 2018).

5- Applications

The flexible properties of metallic nanoparticles (MNPs) have ignited a revolution in diverse fields, offering promising solutions for a range of challenges. Their unique optical, electronic, and catalytic capabilities translate into a multitude of applications spanning environmental remediation, healthcare breakthroughs, industrial innovations, and agricultural advancements as shown in Fig. 4 (Goutam et al., 2020; Idris and Roy, 2023).

5.1 Environmental applications:

5.1.1 Water Purification

MNPs exhibit exceptional adsorption and catalytic properties, enabling efficient removal of pollutants like heavy metals, organic dyes, and pesticides from water bodies (Salem and Fouda, 2011). Silver and gold NPs, for instance, possess potent antimicrobial activity, contributing to water disinfection (Goutam et al., 2020; Idris and Roy, 2023).

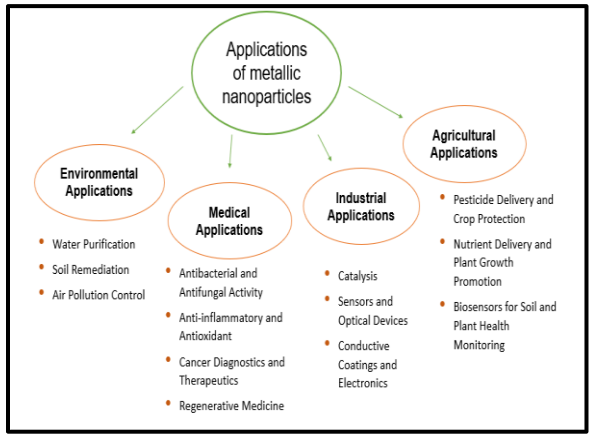

Figure 4: Different applications of metallic nanoparticles.

5.1.2 Soil Remediation

MNPs can immobilize and degrade harmful contaminants in soil, including heavy metals, persistent organic pollutants, and radioactive materials. Iron and titanium dioxide NPs effectively catalyze the breakdown of these pollutants, restoring soil health (Alazaiza et al., 2021; Javed et al., 2020).

5.1.3 Air Pollution Control

MNPs with high surface area and catalytic activity can capture and oxidize harmful airborne pollutants like NOx and SOx, promoting cleaner air and mitigating the adverse effects of air pollution. Gold and copper NPs show promise in catalytic converters for reducing vehicular emissions (Gopinath et al., 2021).

5.2 Medical applications:

5.2.1 Antibacterial and Antifungal Activity

MNPs like silver and copper exhibit intrinsic antimicrobial properties, effectively inhibiting the growth of bacteria and fungi. These potential holds promise for combating antibiotic-resistant pathogens and developing topical antimicrobial coatings for medical devices (Noor et al., 2020).

5.2.2 Anti-inflammatory and Antioxidant Functions

Gold and cerium NPs exhibit potent anti-inflammatory and antioxidant properties, offering therapeutic potential for inflammatory diseases like arthritis and neurodegenerative disorders (Wang et al. 2020). Their ability to scavenge free radicals and mitigate oxidative stress makes them promising candidates for drug development (Vijayan et al., 2019).

5.2.3 Cancer Diagnostics and Therapeutics

MNPs possess unique optical and targeting properties, enabling their use in cancer imaging and targeted drug delivery. Gold and iron oxide NPs offer high contrast for tumor visualization in imaging techniques like MRI and CT scans (Ali et al. 2021). Additionally, MNPs can be conjugated with anticancer drugs for site-specific delivery, maximizing therapeutic efficacy while minimizing side effects (Yu et al., 2010).

5.2.4 Regenerative Medicine

MNPs are being explored in bone and tissue regeneration due to their ability to stimulate cell growth and differentiation. Calcium phosphate NPs, for example, can mimic the mineral composition of bone and promote bone regeneration. Similarly, gold and silver NPs can be used to engineer scaffolds for tissue regeneration, offering potential for wound healing and organ repair (Balaure et al., 2019; Ullah and Lim, 2022).

5.3. Industrial applications:

5.3.1 Catalysis

MNPs exhibit superior catalytic activity compared to bulk materials, making them ideal for diverse industrial processes. Platinum and palladium NPs find extensive use in catalytic converters, while gold and silver NPs catalyze various chemical reactions in the chemical and pharmaceutical industries (Honarmand et al., 2019; Naik et al., 2021).

5.3.2 Sensors and Optical Devices

MNPs exhibit unique optical and electronic properties, enabling their use in highly sensitive sensors for detecting environmental pollutants, biological agents, and even cancer biomarkers. Additionally, their tunable surface plasmon resonance properties make them valuable components in optical devices like solar cells and light-emitting diodes (Ally and Gumbi, 2023).

5.3.3 Conductive Coatings and Electronics

MNPs can be used to develop conductive coatings for electronic devices, offering improved conductivity and corrosion resistance. Silver and gold NPs, for instance, can be used in electrodes and circuits for miniaturized electronics and flexible electronics applications (Lalegül-Ülker and Elçin, 2021).

5.4 Agricultural applications:

5.4.1 Pesticide Delivery and Crop Protection

MNPs offer a controlled and targeted approach to pesticide delivery, reducing environmental impact and optimizing pesticide efficacy. Polymers coated with MNPs can release pesticides slowly and directly onto plant tissues, minimizing off-target effects and enhancing pest control (Farooq et al., 2022).

5.4.2 Nutrient Delivery and Plant Growth Promotion

MNPs can be used to deliver essential nutrients like iron and copper directly to plant roots, improving nutrient uptake and enhancing plant growth (Zhou et al. 2020). Additionally, MNPs are being explored for their potential to stimulate plant defence mechanisms and improve stress tolerance.

5.4.3 Biosensors for Soil and Plant Health Monitoring

MNPs can be functionalized to act as biosensors for detecting plant diseases, nutrient deficiencies, and soil contamination. This real-time monitoring capability allows for early intervention and improved agricultural management practices (Idris and Roy, 2023).

6. Conclusion

In conclusion, the benefit of synthesized MNPs using green methods such as bacteria, fungi, and Algae can be ascribed to the fact that it is low in cost, eco-friendly, and safer for human use. Moreover, MNPs have introduced themselves as an effective application in many challenging topics. From environmental cleanup to medical breakthroughs and industrial advancements to agricultural innovations, MNPs offer unparalleled solutions for a multitude of challenges, paving the way for a sustainable and prosperous future.

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