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Biogenic Synthesis of Nanoparticles for Sustainable Crop Production: A Review

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Abstract: Chemical fertilizers have been considered an indispensable input of modern agriculture production systems since the green revolution, but these methods have associated some environmental and ecological impacts. The main cause of environmental pollution is the loss of nutrients in gaseous form and leaching from agricultural fields. Nanotechnology offers great potential to increase the production of fertilizers with desired chemical composition and high nutrient use efficiency. Nanotechnology may provide a significant opportunity in nanoparticles to develop concentrated forms of plant nutrients with high utilization efficacy, high absorption rate, and minimum losses. Nanofertilizers are being prepared by encapsulating nutrients into nanoparticles and delivered in nano-sized emulsions. Furthermore, controlled release and targeted delivery of nanoparticles can impart the potential of sustainable and precision agriculture. Nanotechnology has evolved in a multidisciplinary field within the past few decades and played a substantial role in agriculture, industry, and pharmacology. The amalgamation of biotechnology and nanotechnology has led to the foundation of nano-biofertilizers and nanomedicine. This article highlights the types of nanoparticles, biosynthesis of nanoparticles using microbes, and uptake mechanism of nanofertilizers by plants.

Keywords: nanotechnology; nanofertilizers; metal oxides; fertilizers; nanoparticles.

1. Introduction

Chemical fertilizers have played a crucial role worldwide in maintaining adequate food supplies and increasing crop yield [1]. Several investigations have been published based on the impacts of using chemical fertilizers on the agroecosystem [2]. The long-term consumption of chemical fertilizers for land-use practices encountered environmental challenges due to the subsequent release of nutrients into the surface or groundwater and gaseous emission into the atmosphere. Many problems associated with the use of chemical fertilizers have been reported, including eutrophication, loss of biodiversity, the decline of soil fertility, soil acidification, atmospheric and groundwater pollution, and high consumption of energy in the synthesis process. Therefore, tremendous efforts have been taken over the last decade to replace chemical fertilizers with environmentally friendly nano fertilizers and biofertilizers [3,4].

The use of nanofertilizers is the most promising, environment friendly, and advanced technique for supplying nutrients and minerals to crops compared to chemical fertilizers, thus saving considerable foreign exchange in the import of fertilizers. Nanotechnology offers another intriguing application by encapsulating useful microorganisms, including bacteria or fungi, that can improve plant root health by enhancing the availability of nitrogen, phosphorous, and potassium in the root area [5].

Nanofertilizers are made up of nano-sized nitrogen molecules coated in polymer coating with biosensors that need to release the particle in soil. These are a product of nanoparticles formed with the help of nanotechnology for the improvement of nutrient efficiency. There are mainly three classes of nanoparticles that have been proposed: 1. Nanoscale fertilizers (nanoparticles that contain nutrients); 2. Nanoscale additives (traditional fertilizers with nano-sized additives); and 3. Nanoscale coatings (traditional fertilizers loaded or coated with nanoparticles). Nanoscale fertilizers have been prepared from ammonia, urea, other synthetic fertilizers, and plant wastes. A process of formulation of nano-sized N fertilizer involves the deposition of urea on calcium cyanamide [6]. The comparative analysis of potential negative and positive impacts of the conventional agriculture approach concerning nanotechnology-mediated agriculture production is depicted in Table 1. The activity of nanofertilizers further depends upon plant and soil rhizosphere growth depending upon the type, composition, and exposure concentration of nanoparticles used [7,8].

Table 1. A comparative analysis of fertilization strategies carried out in the past and a hypothesized nanotechnology-based agriculture.

Agriculture type	Potential positive impacts	Negative impacts
Conventional agriculture	-	Low productivity Stress and disease sensitive Deficiency of nutrients Poor soil biological health Microbial diversity low
Organic agriculture	Nutritive food Improves soil biological health	Low production rate according to demand Bio-fertilizers may cause pathogenic effects
Bulk-fertilizer mediated agriculture	Rate of production is high with respect to demand	Bioaccumulation of byproduct of harmful fertilizers Decreased nutritional quality Eutrophication Low microbial diversity Deplete soil biological health
Nano-fertilizer mediated Agriculture	High production rate Nutritious food quality is high Sustainable Save natural resources Maximum microbial diversity Increase soil biological health Increase nutrient mobilization Demand of fertilizers reduced	-

2. Global Status of Nano Fertilizers

Nanotechnology offers a great potential to increase fertilizer production with desired chemical composition, improve nutrient use efficiency, reduce environmental impact, and boost plant productivity. Nanofertilizers are easily absorbed by plants and can make the crops disease and drought-resistant. The bio-accessibility of nanofertilizers is determined by the morphology and size of nanoparticles [9]. A series of reactions such as oxidation, reduction, and recombination may occur to provide the appropriate amount of micronutrients to plants, rather than instantly taken up by plants. In recent times, few researchers have developed and patented a nanofertilizer known as “Nano-Leucite Fertilizer” which is eco-friendly and facilitates an enhancement in crop and food production by reducing nutrient loss. The list of a few approved nanofertilizers currently used worldwide is depicted in Table 2[10].

Table 2. List of few approved nanofertilizers used worldwide and their composition.

Nanofertilizers	Composition of nanofertilizer	Manufacturer's name
Nano Max NPK Fertilizer	Different organic acids chelated with major nutrients, organic carbon, amino acids, micronutrients/ trace elements, vitamins, and probiotic	JU Agri Sciences Pvt. Ltd., Janakpuri, New Delhi, India
Biozar Nanofertilizer	Amalgamation of organic materials, micronutrients, and macromolecules	Fanavar Nano-Pazhoohesh Markazi Company, Iran
Nano Green	Corn, grain, soybeans, potatoes, coconut and palm extracts	Nano Green Sciences, Inc, India
PPC Nano (120) ml	19.6% M protein, 0.3% Na_2O, 1.7% $(NH_4)_2SO_4$, 2.1% K_2O and 76% diluent	WAI International Development Co., Ltd., Malaysia
Nano Capsule	0.5% N, 0.7% P_2O_5, 3.9% K_2O, 2.0% Ca, 0.2% Mg, 0.8% S, 2.0% Fe, 0.004% Mn, 0.004% Zn, 0.007% Cu	The Best International Network Co., Ltd., Thailand
Nano Ultra- Fertilizer (500)g	5.5% organic matter, 10% N, 9% P_2O_5, 14% K_2O, 3% MgO	SMTET eco-technologies Co., Ltd., Taiwan
Nano Calcium (Magic Green) (1) kg	77.9% $CaCO_3$, 7.4% $MgCO_3$, 7.47% SiO_2, 0.2% K, 0.03% Na, 0.02% P, 7.4 ppm Fe, 6.3 ppm Al_2O_3, 804 ppm Sr, 278 ppm sulfate, 174 ppm Ba, 172 ppm Mn, 10 ppm Zn,	AC International Network Co., Ltd., Germany
TAG NANO (NPK, PhoS, Zinc, etc.) Fertilizers	Proteino-lacto-gluconate chelated with micronutrients, probiotics, seaweed extracts, and humic acid	Tropical Agrosystem India (P) Ltd., India

3. Synthesis of Nanoparticles by Microbes

Nanoparticles are small-sized particles of dimensions in the range of a few nanometers to 100 nanometers that exhibited unique and fascinating chemical, physical and biological properties compared to bulk counterparts due to their high surface to volume ratio. There are different types of physical, biological, chemical, and hybrid methods available to synthesize different types of nanoparticles [11]. Although physical and chemical methods for the synthesis of nanoparticles are more popular, the use of toxic chemicals limits their biomedical applications. Therefore, there is a great need to develop reliable, non-toxic, and eco-friendly methods to synthesize nanoparticles to expand their biomedical applications [12]. The chemical methods can produce nanoparticles in large quantities with a defined shape and size relatively quickly. Still, they are complicated, costly, outdated, and produce hazardous toxic wastes that cause adverse effects on the environment and human health compared to biogenic enzymatic methods. The majority of the physical and chemical methods employed to synthesize nanoparticles are very costly and contain poisonous and dangerous chemicals responsible for different biological hazards (Figure 1). The nanoparticles synthesized from the biogenic approach have a greater specific surface area, higher catalytic reactivity, and improved contact between the enzyme and metal salt due to the bacterial carrier matrix [13]. Nanoparticles are synthesized from microorganisms through enzymes which turn metal ions into element metal by grabbing target ions from their environment. The process can be classified into extracellular and intracellular synthesis based on the location of nanoparticles formation. The extracellular synthesis of nanoparticles involves the trapping of metal ions on the cell surface and reducing ions through enzymes. At the same time, the intracellular method consists of ion transportation into a microbial cell to form nanoparticles in the presence of enzymes [14]. Nanoparticles synthesized by microorganisms have been used in multiple applications, including drug carriers for targeted delivery, treatment of diseases, gene therapy, DNA analysis, biosensors, and magnetic resonance imaging (MRI). It is reported that microorganisms, including bacteria, yeast, and fungi, synthesize inorganic nanoparticles such as gold, silver, calcium, silicon, iron, and lead. These microorganisms produce intracellular and extracellular nanoparticles because of their intrinsic potential [15]. The use of microorganisms to produce nanoparticles is inexpensive, undemanding, effective, and environment-friendly approach [16].

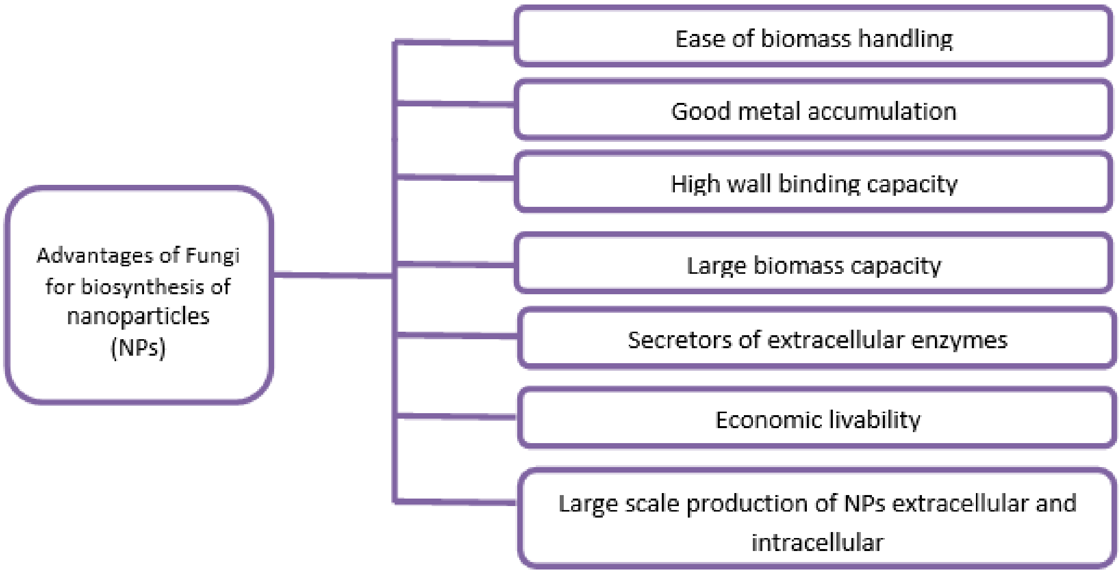

Figure 1. Some distinct advantages of fungi when used for large-scale production of nanoparticles.

3.1. Synthesis by soil fungi.

Fungi play an essential role in the biogenic synthesis of metallic nanoparticles due to their high tolerance, metal bioaccumulation capability, and easy handling. They also produce large quantities of extracellular proteins, which help in the stability of nanoparticles and enhance bioreduction, which triggers the production of biocompatible nanoparticles [17]. Compared to other microorganisms, fungal cultures provide good biomass production and do not need additional steps to extract filtrate [18]. A wide diversity is present in fungi and can be isolated, cultured, and maintained easily without using any complex instrumentation. Compared with plants, the mycelia mass of fungi is highly resistant to agitation and pressure, thus more suitable for the large-scale production of nanoparticles [19]. It is possible to synthesize nanoparticles of desired characteristics such as morphology and specific size by manipulating fungi metabolism by adjusting physicochemical culture conditions like time, pH, biomass quantity, and temperature morphology [20]. Fungi have remarkable abilities to digest extracellular food, discharging specific enzymes for hydrolyzing complicated compositions into simple molecules, which are soaked up and utilized as an energy resource. Economic livability and availability of large biomass is another advantage offered by fungi for the synthesis of metallic nanoparticles (Figure 2). In addition, several fungal species grow fast, and therefore culturing and keeping them in the laboratory are very simple [21]. Fungi can also produce metallic nanoparticles extracellularly and intracellularly via reducing enzymes [22].

In the last two decades, many fungal species such as *Aspergillus fumigates*, *Aspergillus niger*, *Colletotrichum sp.*, *Fusarium oxysporum*, *Coriolus versicolor*, *Fusarium semitectum*, *Fusarium salani*, *Penicillium brevicompactum*, *Trichoderma asperellum*,and *Volvariella volvaceae* have been explored for the synthesis of nanoparticles both extracellularly as well as intracellularly [23-25]. The shape of synthesized nanoparticles ranges from hexagonal to spherical, ranging from 5-200 nm. The extracellular synthesis of nanoparticles using fungal species has captured the exclusive attention of researchers because of the easy purification process of synthesized nanoparticles, as they do not have any cellular attachment. The common species of fungi, mostly include Ascomycetes, Basidiomycetes, and Phycomycetes, have been successfully employed for the green biosynthesis of nanoparticles. The different species of fungi belonging to different phyla used to synthesize biocompatible metal or metal oxide nanoparticles are given in Table 3.

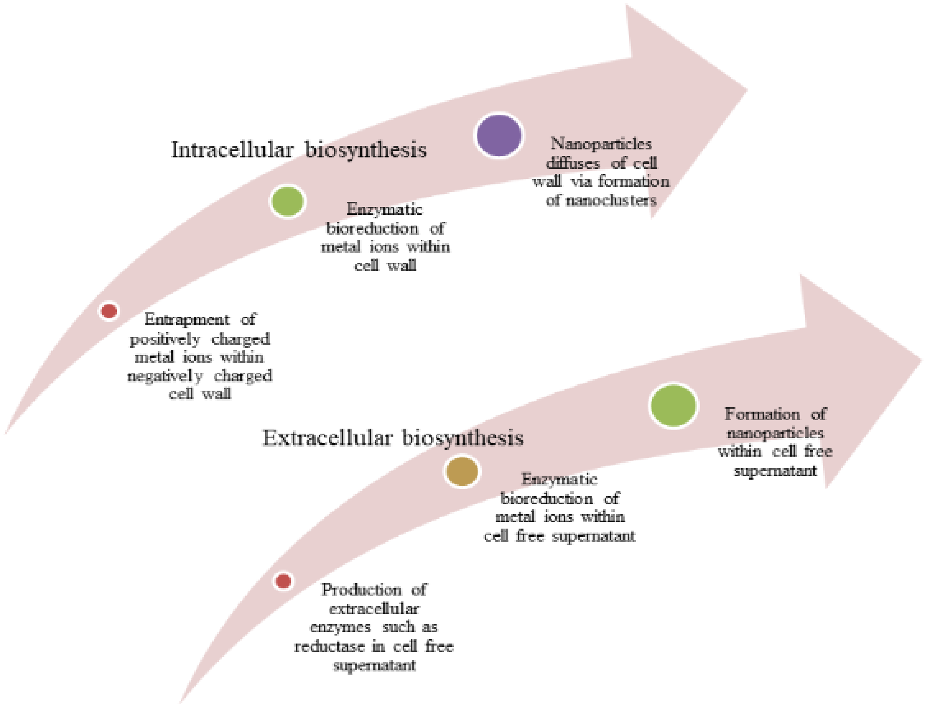

Figure 2. Schematic flow diagram for intracellular and extracellular synthesis of nanoparticles.

Table 3. List of some fungi used to synthesize metal or metal oxide nanoparticles along with their size, shape, and application.

Fungus	Nanoparticle	Size (nm)	Shape	Application	Reference
Aspergillus niger	ZnO	53-69	Spherical	Antibacterial dye degradation	[26]
Trichoderma longibrachiatum	Ag	10	Spherical	Antifungal against phytopathogenic fungi	[27]
Trichoderma harzianum	Au	32-44	Spherical	Antibacterial, dye degradation	[28]
Fusarium oxysporum	Ag	21-37	Spherical	Antimicrobial	[29]
Pleurotus ostreatus	Au	10-30	Spherical	Antimicrobial, anticancer	[30]
Phenerochaete chrysosporium	Ag	34-90	Spherical-oval	Antibacterial	[31]
Penicillium potonicum	Ag	10-15	Spherical	Antibacterial	[32]
Candida glabrata	Ag	2-15	Spherical	Antibacterial	[33]
Macrophanina phaseolina	Ag/AgCl	5-30	Spherical	Antibacterial	[34]
Cladosporium cladosporioides	Au	60	Round	Antioxidant, antibacterial	[35]

3.2. Synthesis by PGPRs.

Plant growth-promoting rhizobacteria (PGPRs) are a group of non-pathogenic organisms that occur mainly in the rhizosphere and are associated with roots of legumes. PGPRs can improve crop yield by using different mechanisms as they can fix atmospheric nitrogen into that form of nitrogen that plants can take. The nitrogen-fixing bacteria include *Rhizobium, Pseudomonas, Azospirillum, Azomonas, Bacillus, and Xanthobacter*, fix atmospheric nitrogen by symbiotically as well as non-symbiotically. The extensive and prolonged use of chemical fertilizers and pesticides have caused lethal impacts on all life forms in nature shifted the researcher's attention towards PGPRs throughout the world for improving crop productivity [36]. Moreover, the eco-friendly nature and cost-effectiveness of PGPRs make them the perfect material for application in integrated nutrient management and crop disease management. Researchers also focus on the benefits of PGPRs as biofertilizers, phytostimulant, and biocontrol agents. Microbial synthesis of nanoparticles is eco-friendly and has significant benefits against other processes since it takes place at relatively ambient temperature and pressure.

Bacterial cells have been readily used as nanofactories to synthesize different metal nanoparticles as they have a remarkable ability to reduce heavy metals. Some bacterial species have developed defense mechanisms to control stresses like the toxicity of nanomaterials. These are good options to synthesize nanoparticles due to their vast amount in the environment and ability to adjust in extreme conditions. These bacteria are fast-growing, easy to handle, and cheap to control as their incubation conditions such as temperature, time, and pH can be controlled easily [15]. Both the extracellular and intracellular approaches have been used for nanoparticles biosynthesis. The synthesized nanoparticles are widely used in several applications, mostly in the biomedical field. Recently, silver nanoparticles (AgNPs) were synthesized using *Bacillus brevis* showed remarkable antimicrobial activity against multidrug-resistant strains of *Salmonella typhi* and *Staphylococcus aureus* [31]. *Pseudomonas stutzeri* and *Bacillus sp.* also synthesized silver nanoparticles using an intracellular synthesis approach [37]. It was also reported that two different strains of *Pseudomonas aeruginosa* could synthesize gold nanoparticles of different sizes [38]. Furthermore, bimetallic nanoparticles such as Ag-Au have also been synthesized using different bacterial strains [39]. Considerable progress has been achieved in the area of PGPR biofertilizers technology throughout the world. It has been proved that PGPRs can be very effective and potential microbes for enhancing crop yield and enriching soil fertility. The different species of bacteria used to synthesize metal nanoparticles are given in Table 4.

Table 4. List of some bacterial species used to synthesize metal nanoparticles with their applications.

Bacteria	Nanoparticle	Size (nm)	Shape	Application	Reference
Actinobacter	Ag	13.2	Spherical	Antibacterial	[40]
Acinetobacter	Au	119	Spherical, triangular-polyhedral	-	[41]
Klebsiella pneumonia	Au	10-15	Spherical	Antibacterial	[42]
Sinomonas mesophila	Ag	4-50	Spherical	Antibacterial	[43]
Pseudomonas fluorescens	Au	5-50	Spherical	Antibacterial	[44]
Bacillus endophyticus	Ag	5.1	Spherical	Antimicrobial	[45]
Bacillus brevis	Ag	41-68	Spherical-oval	Antibacterial	[46]
Streptomyces griseoplanus	Ag	19.5-20.9	Spherical	Antifungal	[47]
Nocardiopsis flavascens	Ag	5-50	Spherical	Cytotoxicity	[48]
Mycobacterium sp.	Au	5-55	Spherical	Anticancer	[49]
Shewanella loihica	Cu	10–16	Spherical	Antibacterial	[50]

3.3. Mechanisms of metal nanoparticles synthesis by microorganisms.

Nanoparticles biosynthesis using microorganisms is an emerging trend in the nanotechnology field. Microorganisms, including bacteria, fungi, and viruses, act as potential biofactories to produce nanoparticles with the ability to reduce metals such as silver, gold, cadmium, etc., into their subsequent nanoparticles [51]. Microorganisms synthesize these nanoparticles either extracellularly or intracellularly using different bioreduction processes.

The extracellular process for the synthesis of metal nanoparticles is carried out by extracellular microbial enzymes [52]. Studies suggest that cofactors such as nicotinamide adenine dinucleotide phosphate (NADPH) and Nicotinamide adenine dinucleotide (NADH) dependent enzymes play a significant role as reducing agents in the synthesis process [53]. *Rhodopseudomonas capsulata* is used for the extracellular synthesis of gold nanoparticles, and the process is mediated by the secretion of NADH and NADPH-dependent enzymes. In *R. capsulata*, synthesis of gold nanoparticles is initiated via electron transfer from NADH to gold ions. It gets reduced by NADH- dependent reductase enzyme leading to the synthesis of gold nanoparticles [53]. The various mechanisms such as changes in solubility, metal complexation, extracellular precipitation, and biosorption are utilized by microbes for the synthesis of nanoparticles. Several fungi also produce extracellular enzymes such as acetyl xylan esterase, D- glucosidase, cellobiohydrolase, etc., which play a significant role in metal nanoparticles production [54]. In fungi, one mechanism involved in the extracellular synthesis of silver nanoparticles is the use of nitrate reductase secreted by fungi [55]. The nitrate reductase from *Fusarium oxysporum* was also used in an in vitro study has an oxygen-free environment, a cofactor (NADPH), and an electron carrier (4-hydroxyquinoline) for the synthesis of silver nanoparticles as it reduced silver ions. This fungus can also be considered an excellent source for the extracellular synthesis of other metal nanoparticles [56]. The enzymes from other fungal strains such as *Fusarium semitectum* and *Fusarium solani* were also utilized for the extracellular production of silver nanoparticles [57,58].

In an intracellular mechanism of synthesis of metal nanoparticles, sugar molecules play a significant role with bacterial and fungal cells. The interactions between intracellular enzymes and positively charged groups are mainly responsible for taking metal ions from the medium and subsequent reduction inside the cell [59]. When observed through a microscope, metal nanoparticles were found to be accumulated in the periplasmic space, cell membrane, and cell wall of microorganisms. This was due to the diffusion of metal ions across the membrane and reduction by enzymes resulting in the formation of metal nanoparticles. A study was adopted for the synthesis of gold nanoparticles (AuNPs) using the fungus *Verticillium* as the source of reducing enzymes. It was found that AuNPs were accumulated in the cell membrane and cell wall of fungi, indicating that Au^{3+} ions were reduced by reductase enzymes present there [60]. Another study found that *Phanerochaete chrysosporium* produced gold nanoparticles both extracellularly and intracellularly of size range 10-100 nm when incubated in ionic Au^{3+} solution. Laccase enzyme was used as an extracellular reducing agent, whereas in the intracellular process, ligninase was responsible for nanoparticle formation [61]. The shape of nanoparticles synthesized depends on the concentration of the ionic solution, incubation time, and temperature of the microorganism. Microorganisms possess the intrinsic potential for synthesis of nanoparticles by reduction mechanism via intracellular and extracellular approaches)

3.4. Nano-biofertilizers.

The indiscriminate and prolonged use of chemical fertilizers has caused lethal soil fertility degradation, pest resistivity, environmental pollution, loss of economy, and biodiversity. Hence scientists focused on safer and productive means of fertilization for agricultural practices. Nano-biotechnology helped develop novel, low-cost, and eco-friendly nano-biofertilizers with the potential properties of nanomaterials and biofertilizers. Biofertilizers are preparations containing more microorganisms that enhance soil productivity by solubilizing phosphorous, fixing atmospheric nitrogen, or stimulating plant growth by secreting growth-promoting substances [62]. Thus, nano-biofertilizers could be defined as the combination of biofertilizers with nanostructures or nanoparticles to improve the growth of plants. Some of the most important parameters in developing nano-biofertilizers include interaction between nanoparticles and microorganisms, the shelf life of biofertilizers, and their delivery. The interaction between gold particles and plant growth-promoting rhizobacteria was observed to exert positive effects [63]. But, silver nanoparticles cannot be used with biofertilizers because it causes negative effects on biological processes of microorganisms, such as alteration of the cell membrane, structure, and function [64]. The shelf life of biofertilizers is also another limiting factor in the formulations of nano-biofertilizers, which can improve the use of nanomaterials. The use of nanoformulations can enhance the stability of biofertilizers concerning heat, UV inactivation, and desiccation. For example, coatings of polymeric nanoparticles can be used to develop formulations resistant to desiccation and consequently improve the life of these products. In addition to this, nanomaterials can also be used to improve the delivery of biofertilizers to plants and soil. Hence, nano-biofertilizers can resolve some limitations of biofertilizers, but this technology still needs further research and development. Nano-biofertilizers act efficiently to enhance agricultural productivity in plant and soil systems. Nano-biofertilizers act synergistically to provide essential plant nutrients and high soil moisture retention due to nanomaterials coating and microbial components [65].

4. Stabilization and Formulations of Nanofertilizers

Nanoparticles can be defined as a system containing active components dissolved, encapsulated, or adsorbed in a matrix material used as a target delivery system having sizes ranging from 10-1000 nm. Nanoparticles increase the stability of drugs by preventing intravascular route solubilization and from degarative action of enzymes. Nanoparticles are formulated in the form of injection consisting of spherical amorphous particles for safe administration through the intravenous route. The formulations of nanoparticles are less toxic because co-solvent is not used for the solubilization of drugs. Nanoparticles have applications in plant protection, nutrition, and farm practices because of their small size, high surface-to-volume ratio, and unique optical properties [66]. A wide range of materials is used to form nanoparticles like metal oxides, ceramics, magnetic materials, lipids, polymers, and emulsions [67]. For example, chitosan nanoparticles are used in agriculture for seed treatment and as a biopesticide, which helps the plants fight against fungal infections. Different biological sources have been used for nanoparticle synthesis and are used in agriculture to improve yield [68]. Some of the nanoparticles synthesized by microorganisms are mentioned below:

4.1. Metallic nanoparticles.

Metallic nanoparticles have received much popularity because of their uniform and sharp size distribution in nanometers. Metallic nanoparticles have shown several properties, such as surface plasmon resonance and optical properties, and it has unraveled many new pathways in the field of nanotechnology. Li *et al.* [69] highlighted the recent development of the synthesis of inorganic nanoparticles include metallic nanoparticles, oxide nanoparticles, sulfide nanoparticles, and other types of nanoparticles from a microorganism. Some typical metal nanoparticles produced by microorganisms are precise in Table 5.

Table 5. Metal nanoparticles synthesized by microorganisms.

Microorganisms	Nanoparticles	Size (nm)	Shape	Location	Reference
Rhodococcus sp.	Au	5-15	Spherical	Intracellular	[70]
Shewanella oneidensis	Au	12	spherical	Extracellular	[71]
Escherichia coli	Au	20-30	Triangular, hexagon	Extracellular	[72]
Trichoderma viride	Ag	5-40	spherical	Extracellular	[74]
Bacillus licheniformis	Ag	50	Not available	Extracellular	[73]
Escherichia coli	Ag	50	Not available	Extracellular	[74]
Bacillus cereus	Ag	4-5	spherical	Intracellular	[75]
Vertcillium sp.	Ag	25	spherical	Extracellular	[76]
Fusarium oxysporum	Ag	5-50	spherical	Extracellular	[76]
Enterobacter sp	Hg	2-5	spherical	Intracellular	[77]

Microorganisms	Nanoparticles	Size (nm)	Shape	Location	Reference
Fusarium oxysporum	Au-Ag alloy	8-14	spherical	Extracellular	[76]
Desulfovibrio desulfuricans	Pd	50	spherical	Extracellular	[78]

4.2. Oxide nanoparticles.

These nanoparticles are an important type of compound nanoparticles synthesized by different microorganisms. There are two types of oxide nanoparticles: magnetic oxide nanoparticles and non-magnetic oxide nanoparticles. Magnetic oxide nanoparticles are recently developed as new materials because of their unique micro configuration and properties such as superparamagnetic and high coercive force. These nanoparticles have a broad range of applications in the biological separation and biomedicine field. The magnetic nanoparticles such as Fe_3O_4 and Fe_2O_3 have been actively investigated for targeted cancer treatment, stem cell sorting, targeted drug delivery, DNA analysis, gene therapy, and magnetic resonance imaging (MRI) [79]. The magnetic nanoparticles such as iron oxide or iron sulfides are synthesized intracellularly by magnetotactic bacteria, called bacterial magnetic nanoparticles (BacMPs). Besides magnetic oxide nanoparticles, some non-magnetic nanoparticles such as TiO_2, Sb_2O_3, SiO_2, and ZrO_2 have also been studied [80-82]. Some examples of magnetic and non-magnetic oxide nanoparticles have been listed in Table 6.

Table 6. Some oxide nanoparticles are synthesized by microorganisms.

Microorganisms	Nanoparticles	Size (nm)	Shape	Location	Reference
Rhodococcus sp.	Au	5-15	Spherical	Intracellular	[70]
Shewanella oneidensis MR-I	Fe_2O_3	30-43	pseudohexagonal	Intracellular	[83]
Yeast cells	Fe_3O_4	Not available	Wormhole like	Extracellular	[84]
Saccharomyces cerevisiae	Sb_2O_3	2-10	spherical	Intracellular	[82]
Lactobacillus sp.	$BaTiO_3$	20-80	tetragonal	Extracellular	[80]
Lactobacillus sp.	TiO_2	8-35	spherical	Extracellular	[81]
Fusarium oxysporum	TiO_2	6-13	spherical	Extracellular	[85]
Fusarium oxysporum	$BaTiO_3$	4-5	spherical	Extracellular	[86]
Fusarium oxysporum	ZrO_2	3-11	spherical	Extracellular	[87]

4.2.3. Stabilization of metallic nanoparticles.

Metallic nanoparticles combine with large surface energy to give thermodynamically favored bulk particles. In the absence of repulsive forces, metallic nanoparticles will coagulate. So, stabilization of metallic nanoparticles is mandatory for spatial confinement of the particles in a size range of nanometers. Thus, this stabilization can be attained either by electrostatic stabilization or by steric exclusion with the help of a capping agent such as surfactant, polymer, and ligands with a suitable functional group.

4.2.3.1. Electrostatic stabilization.

According to DLVO theory established by Derjaguin, Landau, Verwey, and Overbeek in 1940, the total interactions between two particles stabilized electrostatically are the combination of Van der Waals attraction electrostatic repulsion. DLVO theory is based on assumptions such as uniform surface charge density, infinite flat solid surface, and electric potential remaining unchanged (no change in concentration profiles of both counter ions and surface charge determining ions) [88]. However, despite assumptions, DLVO theory is widely accepted in the research area of colloidal science and works very well to explain the interactions between two electrically charged particles.

Electrostatic stabilisation has some drawbacks, including the fact that it is a kinetic stabilising method, applicable only to dilute systems, not applicable to electrolyte sensitive systems, and is difficult to apply to multiple phase systems (for a given condition, different solids show different properties).

4.2.3.2. Steric stabilization.

This stabilization is also known as polymeric stabilization and is widely used to stabilize colloidal dispersions. It has several advantages over electrostatic stabilization, such as a. it is not electrolyte sensitive, b. suitable to multiple phase system and c. particles are always re-dispersible due to thermodynamic method. Binding polymers achieve steric stabilization with long alkyl chains to the surface of particles [88].

4.3. Biomolecules as nanoparticles.

Various types of biomolecules such as proteins, nucleic acid, lipids, and polysaccharides have unique properties that can be utilized to synthesize nanoparticles. In recent years, significant interest has been shown in utilizing biological nanoparticles as an alternative to chemically synthesized nanoparticles. This is due to the urge for biodegradable and biocompatible nanoparticles in addition to other advantages such as non-immunogenic and eases of availability. Biological nanoparticles derived from biomolecules or organic compounds having size ranges from 10nm-1μm. They can be based on four major categories: proteins, nucleic acid, lipids, and polysaccharides. Proteins are naturally occurring materials used for the preparation of nanoparticles which attributed unique functionalities and defined primary structure to nanoparticles. These characteristics enable a variety of possibilities for surface modifications and attachment of other compounds includes therapeutics and drugs [89]. Nanoparticles based on proteins can also be processed in the form of emulsions, gels, and dried particles, offering greater stability in vivo and relatively easy to synthesize particles with controlled size [90]. Different proteins have been used to formulate nanoparticles, such as albumin, gelatin, collagen, elastin, zein, and ferritin.

Nanoparticles can also be synthesized from nucleic acid strands of DNA and RNA. The nucleic acids can be engineered to form 3-D nano-scaffolds due to the simplicity of their primary structure. Moreover, nucleic acids have a unique ability to self assemble into compact and stable structures, which helps synthesize nanoparticles with controlled size, geometry, and composition [91]. The current findings based on the development of bio-based nanoparticles have shown that the nucleic acid nanoparticles can be utilized as scaffolds and can be tagged with different types of biological and therapeutic compounds such as fluorophores, aptamers, and oligonucleotides to sustain their desired functions [92]. Nanoparticles based on lipids such as liposomes, nanoemulsions, nanostructured lipid carriers (NLC), and solid lipid nanoparticles (SLN) have been recognized among the most promising encapsulant in the field of nano-biotechnology [93]. The lipid nanoparticles showed longer shelf life and storage stability in addition to their high encapsulation efficiency. The nanoparticles based on lipids can target and entrap compounds of different solubility. Polysaccharides are naturally occurring carbohydrate polymers linked together by glycosidic bonds, which can be obtained from plants (e.g., pectin, insulin), animals (e.g., chitosan), and algae (alginates). Chitosan (a cationic polyaminosaccharide) among various polysaccharides is one of the most important polysaccharides because of its permeability enhancement properties. This polysaccharide has high-density amino groups and mucoadhesive properties, allowing effortless chemical modification and attachment with negatively charged molecules [94].

5. Nanofertilizers Uptake Mechanism by Plants

Nanofertilizers should be formulated so that they possess all desired properties such as stability, effectiveness, high solubility, time-controlled release, enhanced targeted activity with effective dosage, and less eco-toxicity with a safe, easy mode of delivery and disposal [95]. Nanoparticles have great potential for delivering nutrients to specific target sites in living systems. The loading of nutrients on the nanoparticles is mainly done by using the following steps such as a. adsorption on nanoparticles, b. attachment on nanoparticles mediated by ligands, c. encapsulation in nanoparticles and polymeric shell, d. entrapment of polymeric nanoparticles and e. synthesis of nanoparticles containing nutrients itself. The interaction and stability of chitosan nanoparticles suspensions containing N, P, and K fertilizers which could be useful in agricultural applications, was evaluated by Corradini *et al*. [96]. The mesoporous nanoparticles based on polymers also provide an efficient carrier system for agricultural compounds, which in turn improves efficiency and economic utilization. These mesoporous silica nanoparticles with a size of 150 nm have been reported for entrapment of urea [97]. The impact and efficiency of nanofertilizers on plant systems depend on how fertilizers are applied to plants.

The methods used for nano-fertilizer delivery to plants include both *in vitro* and *in vivo* methods. Under in vitro methods, two techniques, aeroponics and hydroponics, are included. In aeroponics, the roots of the plant are suspended in the air, and the nutrient solution is continuously sprayed. The gaseous environment around the roots can be controlled in this method. But this technique is not widely used because a greater amount of nutrients should be required for sustaining rapid plant growth. Hydroponics, also known as solution culture, is used for dissolved inorganic salts. In this method, plants are grown with their roots immersed in a liquid nutrient solution. While using this nutrient delivery method, the following factors should be kept in mind: maintenance of oxygen demands, volumes of nutrient solution, and pH. Due to frequent pathogen attacks and high moisture rates. Soil application and foliar application are two in vivo methods for delivering nano fertilizers to plants. Soil application is the most common method of nutrient supplement using organic and chemical fertilizers. The different factors such as soil texture, soil salinity, how long fertilizers will last in soil, and plant sensitivities to salts should need attention while choosing this method. The foliar application method is generally used for the delivery of trace elements. In this method, liquid fertilizers are directly sprayed onto leaves. The uptake of nutrients such as iron, manganese, and copper may be more efficient than the soil application method, where nutrients get adsorbed on soil particles and are less available to the root system. In this method, stomata and leaf epidermal cells are mainly involved in nutrient uptake, so the disadvantage of this method includes specific time as stomata open during morning and evening periods only, so spraying has to be done in these periods.

6. Yield and Biomass Affected by Nano Fertilizers

Micronutrients such as manganese, copper, boron, molybdenum, iron, zinc, etc., play an important role in the development and growth of the plant. Nanotechnology can be used to make the availability of micronutrients to plants. The nanoformulations of micronutrients can be sprayed on leaves or supplied to the soil for uptake by roots to enhance the soil's health. Nanofertilizers have a crucial role in plants' biochemical and physiological processes by enhancing nutrient availability, which in turn enhances metabolic activities, which promotes apical growth and photosynthetic area. It was reported by some research studies that nano NPK and a mixture of micronutrients, when applied through foliar spraying, led to increased plant height and the number of branches in black gram [98].

Similarly, Abdel-Aziz *et al*. [99] also observed an increased growth of leaves in wheat when nano NPK was applied through stomata of leaves through gas uptake. Nitrogen nanofertilizers also lead to increased leaf dry weight of peppermint by 165% over control with the application through foliar spraying. Foliar application of nTiO_2 in maize crops has been observed remarkable enhanced chlorophyll content, anthocyanins, and carotenoids, leading to increment in maize yield [100]. Nano formulations of TiO_2 also showed an improvement in spinach's growth and promoted nitrogen metabolism, protein, and chlorophyll content [101]. The application of nanofertilizers has a remarkable role in enhancing the yield of cotton production. Apart, reducing fertilizer cost and minimizing pollution hazards. In pomegranate, yield and number of fruits per tree were also increased with zinc and boron nano fertilizers. The impact of nanofertilizers on the growth and yield of different crops is depicted in Table 7 [102-105].

Table 7. Effect of nanofertilizers on yield of different crops under different climatic conditions.

Nanofertilizers	Name of crop	Increment in yield (%)
Nanofertilizer and urea	Rice	10.2
Nanofertilizer and urea	Wheat	6.5
Nano-encapsulated phosphorus	Maize	10.9
Nano-encapsulated phosphorus	Soybean	16.7
Nano-encapsulated phosphorus	Wheat	28.8
Nano chitosan-NPK fertilizers	Wheat	14.6
Nano chitosan	Tomato	20
Nano chitosan	Cucumber	9.3
Nano chitosan	Capsicum	11.5
Nano chitosan	Beet root	8.4
Nano chitosan	Pea	20
Nano iron aqueous solution	Cereals	8-17
ZnO Nanoparticles	Cucumber	6.3
ZnO Nanoparticles	Peanut	4.8
ZnO Nanoparticles	Cabbage	9.1
ZnO Nanoparticles	Cauliflower	8.3
ZnO Nanoparticles	Chickpea	14.9

7. Future Perspectives and Conclusion

Nanofertilizers have a remarkable impact in the agricultural sector for increasing productivity and resistance to abiotic stress. The potential benefits of nanofertilizers have also increased the production ability of crops under the current scenario of climatic conditions. Compared to conventional fertilizers, the advantages of nanofertilizers are reduced leaching and volatilization [106,107]. Biosynthesized nanoparticles-based fertilizers and nano biofertilizers should be explored further as a promising technology to improve yields while achieving sustainability. There have been significant developments in nanoparticles synthesized by microorganisms and the applications associated with these nanoparticles over the last decade. Thus, more research is needed for improving synthesis efficiency and controlled particle size and morphology. As the synthesis time of microorganisms produced nanoparticles is more (several hours and even a few days) than physical and chemical methods, there is a need to reduce the time of microbial synthesis of nanoparticles, which will make this route more attractive. The size and uniformity of nanoparticles are two important issues considered in the evaluation of nanoparticle synthesis. Thus, controlled particle size and uniformity must be extensively investigated, which might be achieved by varying parameters such as microorganism type, growth phase, growth medium, culture conditions, and reaction time. Several studies also showed that the nanoparticles synthesized from microorganisms might be degraded after a specific period. Therefore, the stability of nanoparticles produced by microorganisms is another important factor that requires further research and should be enhanced [108].

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Conflicts of Interest

The authors declare no conflict of interest.

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