



Review

Nano-Biofertilizers Synthesis and Applications in Agroecosystems

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Abstract: Green chemistry and nanobiotechnology have great potential for generating new and significant products that are favorable to the environment, industry, and consumers. The nanoforms of metals and nanocomposites are more effective and efficient agents than their bulkier counterparts because of their distinctive physical, chemical, and optical properties. Green technology is a rapidly growing scientific field that has recently received attention due to its many applications. Different nanoparticle dimensions, sizes, and bioactivities will develop as a consequence of changes in the biomaterials employed for synthesis. The existing understanding of several green synthesis methods, that depend on different plant components and microorganisms for the production of nanoparticles, is summarized in the current review. Employing these materials minimizes synthesis costs while minimizing the use of hazardous chemicals and promoting “biosynthesis.” To produce metal nanoparticles efficiently, bio-reduction is influenced by the abundance of essential enzymes, proteins, and biomolecules. Rapid biosynthetic regeneration makes this characteristic sufficient for their employment in a range of situations. In this review, we explore the biosynthesis of nanomaterials and their potential in sustainable agriculture. Biosynthesized nanofertilizers, or bionanofertilizers, are a revolutionary new class of fertilizer that has been developed with the help of nanotechnology. These fertilizers offer many advantages over traditional fertilization methods and can be used to increase crop yields while reducing the environmental impact of fertilizers. Bionanofertilizer are an inexpensive way to increase plant growth and production, and to improve the use of nutrients by plants and the health of the soil. According to our survey, nanotechnology presents a wide range of prospects by offering a cutting-edge and environmentally friendly alternative in the agricultural sector.

Keywords: green nanotechnology; nanomaterials; biosynthesis; nanofertilizers

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1. Introduction

Electronics, energy, health, transportation, space technology, and the biological sciences are just a few of the industries that have benefited greatly from the development of nanotechnology, an emerging field of research [1]. Nanotechnology has the potential to solve several problems in forestry, ecology, and agriculture. Nanoparticles (NPs) are universally recognized as having at least two dimensions and a size between 1 and 100 nm [2,3]. Since the physicochemical manufacturing of these nanoparticles necessitates a significant number of dangerous chemicals and harsh circumstances, green techniques make use of biological sources. The ‘green’ concept and ecological themes have recently been linked to nanotechnology [4]. Green nanotechnology refers to the application of nanotechnology to enhance the environmental sustainability of processes, and to lower costs and potential environmental risks from produced negative externalities. [5–7].

Green nanotechnology can assist in resolving environmental issues by such means as the use of fewer nonrenewable resources, the production of smaller amounts of greenhouse gases, the reduction of the consumption of fossil fuels, and the reduction of shipping weights or vehicle weights, which reduces pollution from fuel combustion [8–10].

The use of nanofertilizers, which unlike traditional fertilizers can progressively feed plants in a regulated manner, is now one of the most significant applications of nanotechnology in agriculture. In addition to being easily absorbed, nanofertilizers also have a slow release and are only required in small amounts, which minimizes the usage of fertilizers and their negative effects on the environment [11]. The use of nanotechnology in agriculture comprises the regulated delivery of specific compounds, particularly fertilizer and insecticides; however, the effectiveness of uptake and use as well as the impact of nanoparticles on plant metabolism differ depending on the species. Plants were examined to determine how they would react to metallic nanofertilizers such as Cu, Mn, Zn, and Fe as well as to chemical nanoparticles including Al, Ce, La, and Ti [12]. Metal nanoparticles (MNPs) are widely used as nanopesticides, nanofungicides, nanobiosensors, and nanofertilizers to increase agricultural production. These nanotechnology-based products can increase agricultural quality and productivity, reduce chemical contamination, and even protect crops from environmental challenges [13,14]. These days, the benefit of a targeted, gradual release of nutrients that control plant growth originates from nano-based solutions [15]. This increases the fertilizer's efficiency, prolonging the period that nutrients are available effectively, and lowering leaching and ecotoxicity as a result [16]. Fertilizers are either sprayed into the leaves of plants or injected into the soil, depending on how well the plant will absorb them. The majority of fertilizers that are used to provide plants with additional nutrients are inorganic, and comprise a significant percentage of fertilizer.

A fertilizer is a material, whether organic or synthetic, that provides the chemical components required to increase plant growth and production and enhance natural fertility by compensating for micronutrient deficiencies. Nanofertilizers can be encapsulated to increase nutrient absorption, which reduces nutrient loss, encourages healthy plant development, and improves crop quality [17,18]. The efficiency of conventional fertilizers is naturally limited due to the insufficient availability, in the soil, of several elements that plants require. Underutilization of the crop at the desired endpoint and inefficient delivery to the target can both contribute to this [19]. As a potential cure, the use of nanofertilizers has been suggested [18]. These fertilizers boost crop output while improving plant performance, availability, and the use of macro- and micronutrients. Nanofertilizers are thought of as intelligent delivery systems because of their huge interfacial area, sorption capacity, and controlled-release dynamics to specific sites [20]. Using different formulations, three different types of nanofertilizer may be identified: (a) Nanoscale fertilizer, which is regular fertilizer that often presents as nanoparticles due to its decrease in size. (a), (b) nanoscale coating fertilizer in which nutrients are intercalated into the nanoscale pores of a host material, and (c) nanoscale additive fertilizer in which nanoparticles are coated with fertilizer [21,22]. It is anticipated that the size of the worldwide nanofertilizer market will rise at a compound annual growth rate (CAGR) of 14.8% from 2022 to 2030 (Figure 1). In 2021, the market was forecast to be worth 2705.5 million US dollars. This rise can be ascribed to the rising demand for agricultural products with high yields, which is a direct result of the growing global population (<https://www.grandviewresearch.com/industry-analysis/nano-fertilizer-market-report> accessed on 12 December 2022).

The employment of green nanotechnology for the production of metal nanoparticles, their application as nanofertilizers in agriculture, their effects as growth promoters and nutritional supplements, and their environmental impact assessment are all covered in the current paper.

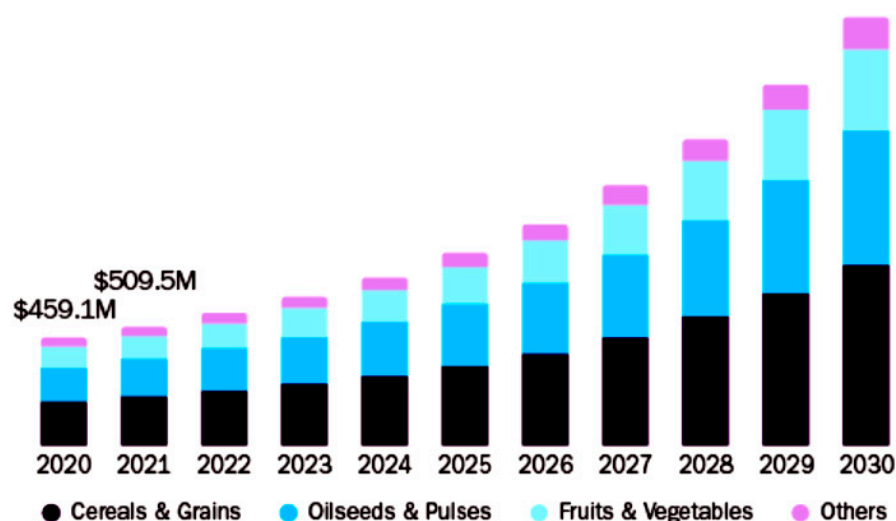


Figure 1. A prediction of the global market for major crops using nanofertilizers for the years 2022–2030. (Source: <https://www.grandviewresearch.com/industry-analysis/nano-fertilizer-market-report> accessed on 12 December 2022).

2. Biogenic Synthesis of Nanomaterials as Nanofertilizers

Nanotechnology is critically dependent on the usage of biosynthetic or “green” technologies, which are inexpensive, environmentally friendly, and produce minimal contamination [23,24]. By encouraging biological molecules to proceed through precisely controlled hierarchical assemblages, it is possible to produce metal NPs in an environmentally benign manner. [25,26]. The biosynthesis of nanoparticles is a bottom-up strategy that is both efficient and enables the rapid creation of significant quantities of NPs. Nanoparticles manufactured using biological or green technology have many advantages over conventionally produced ones, including better stability and perfect size. Numerous biological organisms, such as algae, fungi, bacteria, and various plants with leaves, fruits, roots, flowers, and seeds, are accountable for biosynthesis [27]. These organisms are considered to be potential mediators of NP synthesis because of their unique ability to absorb and concentrate metallic ions from their environment [28].

2.1. Microbe-Mediated Synthesis

Microorganisms as nanofactories represent enormous promise as energy-efficient, low-cost, and non-toxic technologies that can produce MNPs more quickly than physicochemical processes [14]. The nanomaterials are obtained from the microbes via two different methods including intracellular and extracellular. Intracellular biosynthesis involves unique transport systems in microorganisms in which the cell wall plays an important role due to its negative charge—positively charged metal ions are deposited in negatively charged cell walls through electrostatic interactions. After transport into the cells of the microorganism, ions are reduced using metabolic reactions mediated by enzymes such as nitrate reductase to form MNPs [29]. While in the extracellular mechanism, the metal ions are converted to their respective NPs via the nitrate-reductase synthesis method [30].

Extracellular synthesis is one of the different green MNP production processes, and it is particularly interesting since it avoids the requirement for expensive and time-consuming subsequent processing steps to recover intracellular nanoparticles [13,31]. Microorganisms hold a unique place among the numerous biological sources for the synthesis of MNPs because of their rapid growth rate, ease of cultivation, and ability to develop under circumstances of ambient temperature, pH, and pressure. This is known as “green synthesis,” which is mediated by microorganisms. [32]. It has been proven that a variety of microorganisms, including bacteria, fungi, yeasts, and microalgae, can create MNPs either intracellularly or extracellularly (Table 1).

A wide range of microorganisms can be used as potential biofactories to create several MNPs that contain metals such as silver, gold, copper, zinc, titanium, palladium, and nickel in an environmentally benign and affordable manner. This allows MNPs with a specific form, size, composition, and particle mono-dispersity to be generated [33,34]. In general, microorganisms occurring in metal-rich habitats are very resistant to these metals due to the uptake and chelation of the metals by intracellular and extracellular proteins. As a result, this technique, which imitates the natural bio-mineralization process, may be advantageous for the synthesis of MNPs [35,36].

Microorganisms contain a variety of different components, including proteins, enzymes, and other biological substances, which are all crucial to the reduction of MNPs. Since bacteria have a remarkable capacity to reduce heavy metals, they have been widely exploited as nano factories to produce various metal nanoparticles. To resist pressures such as the toxicity of nanomaterials, several bacterial species have evolved defense mechanisms [37,38]. These bacteria are suitable options for nanoparticle synthesis due to their abundance in the environment and adaptability to harsh circumstances [39]. França Betten-court et al. [40] used 12 bacterium supernatants containing auxin complex (indole-3-acetic, IAA) to synthesize iron and manganese mono- and bimetallic nanoparticles (NPs) and evaluated them as plant nanofertilizers. The generated NPs confirmed their suitability as micronutrient fertilizers for agricultural growth. The use of bimetallic NPs in particular exhibited positive benefits on maize seedling growth by enhancing seed germination, root growth, and fresh and dry weights.

Nanoparticles can be produced by microalgae either intracellularly or extracellularly. Developing the required microalgae, allowing them to interact with the precursor solution, and separating and purifying them are all steps in intracellular synthesis [41].

It has been discovered that the fungal system is a flexible biological system that can generate metal nanoparticles both intracellularly and extracellularly. Numerous fungi have been studied for the production of different metal nanoparticles of varied shapes and sizes due to their broad dispersion in nature and the fact that they are preferred to other biological systems [42]. *Ganoderma lucidum* extract was used by Sedefoglu et al. [43] to physiologically generate ZnO nanoparticles. *Lepidium sativum*, or garden cress, has been the subject of research into the properties of nanofertilizers. It was discovered that the pure wurtzite phase with p63 mc space group characterizes the structural features of ZnO NPs. The effect of nanofertilizers on garden cress, *Lepidium sativum*, was investigated. ZnO nanoparticles were produced at 250 ppm using a 25 mL extract concentration, and the contents of the radicle, plumule lengths, fresh weights, and dry weights of *L. sativum* increased at rates of 45%, 41%, 16%, and 33%, respectively. This study was the first to report the use of green-generated ZnO with *G. lucidum* extracts as a nanonutrient.

Table 1. Green synthesis of nanofertilizers using different microbes.

S.N.	Bio-Extract	Nanoparticles	Characterization Results	Applications	Ref
1	Twelve bacteria supernatants containing auxin complex (indole-3-acetic, IAA)	Iron and manganese mono- and bimetallic nanoparticles	λ_{\max} : 250–300 nm. Spherical shape with size 26.65 nm of FeOx NPs, MnOx NPs at around 22.32 nm, and MnOx/FeOx NPs at around 23.42 nm	Plant growth, especially in germination, root growth, and fresh weight in maize plantlets. Used as micronutrient nanofertilizer.	[40]
2	<i>Ganoderma lucidum</i> extract	Zinc Oxide nanoparticle	Three hexagonal shapes (discs, rods, and pyramids)	Nanofertilizers properties on <i>Lepidium sativum</i>	[43]
3	Calcium phosphate (CaP) biological hard tissues	CaP nanoparticles	Round-shaped with a size of 10–25 nm	Multinutrient nanofertilizers	[44]
4	Using microalgal algal extract	Iron-oxide nanoparticles	Spherical biofabricated Fe ₃ O ₄ -NPs particle size was 76.5 nm	Plant growth stimulant	[45]
5	Using <i>Lactobacillus casei</i> Subsp. <i>Casei</i>	Copper-oxide nanoparticles	Spherical in shape with 30 nm to 75 nm size range	Plant micronutrient	[46]
6	<i>Acidophilus</i> , <i>Lactobacillus casei</i> , and <i>Bifidobacterium</i> sp.	Se nanoparticles	Nanoparticle size ranged from 100–500 nm	Plant disease enhancer and nanofertilizer	[47]
7	Microalgae	Silver nanoparticles	Nanoparticle size ranged from 13 to 31 nm	Act as nanofertilizer, have antioxidative properties	[48]

2.2. Plant-Mediated Synthesis

In comparison to microbes, plants are easily available natural sources that produce greater quantities of bimolecular reducing agents. Extracts from a wide range of plant materials, such as stalks, leaflets, roots, blooms, and fruits, have been used to synthesize metallic NPs [13] (Table 2). To prepare plant extract, plant matter is cleansed, dried, boiled, and then filtered. The plant filtrate is then combined with a metallic salt solution and further incubated to produce metallic nanoparticles [49]. Terpenoids, flavones, quinones, ketones, and aldehydes are some of the phytochemicals found in plant extracts that act as electron donors to change metal ions into nanoparticles (NPs) in aqueous solutions (Figure 2).

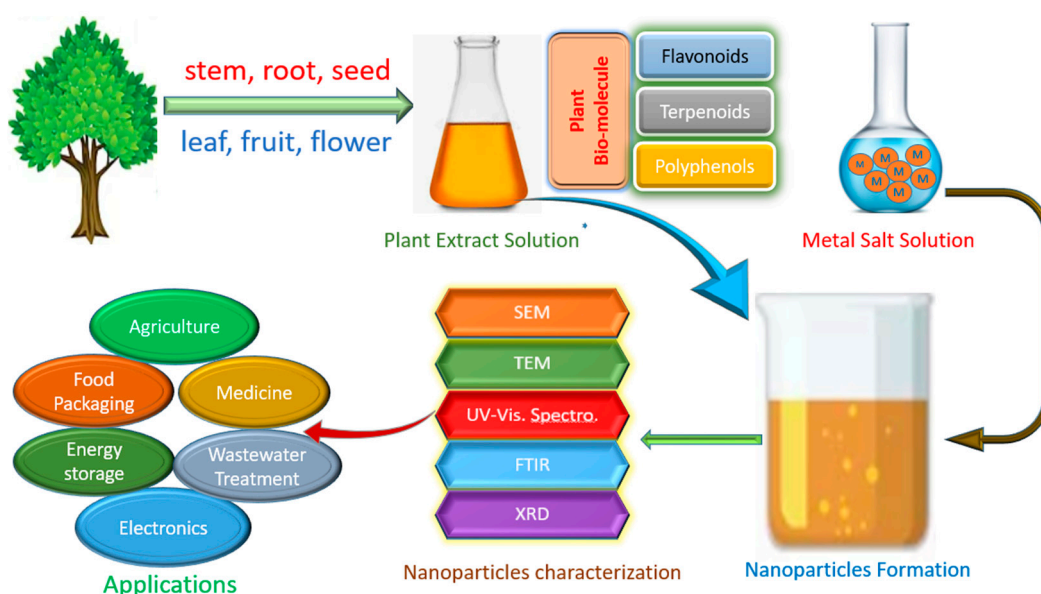


Figure 2. Plant-mediated synthesis of nanoparticles from various plant extracts.

Plant extracts contain several reducing agents that also serve as capping agents to stabilize metallic NPs when they are produced [50,51].

Elham Rostamizadeh et al. [52] recently created Fe_2O_3 nanoparticles utilizing the fruit extract of *C. mas*. Compared to equivalent quantities of bulk counterparts, the growth of barley seedlings was improved by synthetic Fe_2O_3 nanoparticles. The nano-form stimulated root biomass by an average of 42%, compared to the bulk counterparts' average of 18%. Lower concentrations of Fe_2O_3 nanoparticles boosted the transfer of iron from the root to the shoot, according to research by Rui et al. [53]. Additionally, it was noticed that the adsorption of Fe_2O_3 nanoparticles to soil particles could decrease nutrient loss and improve the fertilizer's cost-effectiveness. Ahmed Shebl et al. have developed a successful green chemistry approach for the hydrothermal synthesis of Zn, Mn, and Fe nano oxides [54]. Throughout two seasons in 2017 and 2018, they examined the impact of foliar treatments of micronutrient-oxide nanoparticles of zinc, iron, and manganese as well as combinations of these oxides on the development, performance, and quality of squash plants. The observed results demonstrated that spraying the plants with manganese-oxide nanoparticles produced the best fruit and vegetative development characteristics, yield, and photosynthetic pigment content.

Manpreet Singh et al. [55] reported the green synthesis of zinc-oxide nanoparticles (ZnO NPs) with spherical morphology and an average size of 50 nm, using an aqueous extract of *Azadirachta indica* leaves. The peak of UV-visible absorbance was found near 363 nm. Mung bean seeds were used to test the synthetic nanoparticles' ability to stimulate seed germination. In comparison to untreated seeds, a significant improvement in seed germination was seen after the plant was treated with ZnO nanoparticles. Overall, com-

pared to untreated seeds, seedlings treated with green ZnO NPs displayed longer roots and shoots by 237 and 168%, respectively.

The extract from the leaves of the *Calotropis* plant was used in the green production of zinc-oxide nanoparticles. The maximum UV-Vis absorption maxima were spherical, with a peak near 350 nm. When ZnO nanoparticles were applied topically to nursery-stage tree seedlings of the neem (*Azadirachta indica*), karanj (*Pongamia pinnata*), and milkwood-pine (*Alstonia scholaris*), growth was noticeably accelerated. *Alstonia scholaris*, one of the three treated seedlings, developed to its maximum height [56]. Varada V. Ukidave and Lalit T. Ingale did work using *Coriandrum sativum* leaf extract to green synthesize zinc-oxide nanoparticles [57]. The effects of zinc-oxide nanoparticles as fertilizer on the Bengal gram, Turkish gram, and green gram plants were studied in vitro. For an evaluation of the growth-stimulating effects of zinc-oxide nanoparticles, various media's protein and chlorophyll contents, seed germination rates, root and shoot lengths, fresh weights, and dried weights were assessed. The green manufacturing of 100 nm-sized zinc-oxide nanoparticles was verified using the transmission microscopy technique. Plants successfully germinated in MS media and MS media Plus nanoparticles with a 100% success rate. Following MS media, MS media only with nanoparticles, and MS medium without zinc in the current investigation, it was shown that MS medium + nanoparticles had the maximum root length, shoot length, and weight. It has been demonstrated that zinc-oxide nanoparticles promote plant growth, aid in seed germination, and increase plant protein and chlorophyll levels. In media treated with zinc-oxide nanoparticles, green gram and Turkish gram showed significantly improved growth and development when compared to Bengal gram. According to the findings of the protein examination, the protein content in green gram (1.26 mg/mL), Turkish gram (1.19 mg/mL), and Bengal gram (1.23 mg/mL) plants were higher after 7 days than that in the roots and shoots. In prior applications, the plant had seedlings with a chlorophyll content of 12.6 mg/L, according to the results of the application of MS media + ZnO nanoparticles. On the other side, a zinc deficiency inhibits plant development and the production of chlorophyll and proteins. This research provides credence to the idea that zinc-oxide nanoparticles derived from *Coriandrum sativum* leaves can be produced sustainably and function as biofertilizers.

In a green synthesis of TiO₂ nanoparticles for crop-farming yield enhancement, *Citrus medica* L. fruit peel extract was used as a reduction and capping media, according to Prakashraj et al. [58]. This revealed their crystalline structure and spherical form with 20–30 nm dimensions. Synthesized TiO₂ nanoparticles were found to be effective at improving *Capsicum annum* seed germination and other growth traits. As a result, the agro-food industry can use TiO₂ nanoparticles generated from fruit peel extract of *C. medica* L as a catalyst and nutrition. Jaspreet et al. [59] created green ZnO NPs by extracting the leaves of *Aloe barbadensis* Mill. The average particle size of green ZnO NPs was 35 nm, a far smaller value than that produced using traditional chemical techniques (e.g., 48 nm). The optimal ZnO NP concentrations for wheat (*Triticum aestivum* L.) seedling emergence and germination were then investigated at various NP levels. Compared to the control seeds, the seeds treated with green ZnO NPs grew better. Additionally, the root and shoot length of the wheat-seed samples that had been exposed to moderate amounts of green ZnO NPs (e.g., 62 mg/L) were significantly increased ($p = 0.005$) when compared with other concentrations or those created chemically (by 50% and 105%, respectively). This has led to the identification of the potential for green ZnO NPs as a nano-based nutrition source for agricultural applications.

The development of the nanofertilizer nanoparticles ZnO MnO-NPs and FeO ZnO-NPs and evaluation of their effectiveness in promoting the growth of *Andean lupin* (*Lupinus mutabilis* sweet) and cabbage (*Brassica oleracea* var. *capitata*) crops was carried out by Murgueitio-Herrera et al. [60] using *Andean blueberry* extract. Both plants contained zinc, which has advantageous properties for plant growth. Foliar NP sprays were applied at the phenological stage of the vegetative growth of the *Andean lupin* or cabbage plants growing in greenhouses. The sizes of the NPs, which are 9.5 nm for ZnO, 7.8 nm for

FeO, and 10.5 nm for MnO, make it easier for plant stomata to bind to them. In *An-dean lupin*, treatment with 270 ppm of iron and zinc increased height by 6%, root size by 19%, chlorophyll-content index by 3.5%, and leaf area by 300%; however, treatment with 540 ppm of iron and zinc did not appear to increase any of the variables. At a concentration of 270 ppm, the ZnO MnO-NPs in cabbage exhibited increases of 10.3% in root size, 55.1% in dry biomass, 7.1% in chlorophyll content, and 25.6% in leaf area. Cabbage plants treated at a dose of 540 ppm produced increases in root size of 1.3% and chlorophyll content of 1.8%, when compared to the control, which was sprayed with distilled water. Consequently, the spraying of nanofertilizers at 270 ppm produced a significant improvement in the development of both plants.

One of the essential elements needed to support plant development and metabolism is zinc. Ahmed, et al. [61] reported on the green production of zinc nanoparticles (Zn NPs) using clove buds (plant material) and examined how the Zn NPs affected the growth and yield of *Pisum sativum* L. In comparison to the control and plants treated with zinc sulfate, the greatest growth and yield were obtained at 400 and 600 ppm. In conclusion, green-produced zinc nanoparticles can improve the productivity and growth of crop pea plants. Reshma et al. [62] examined the effects of zinc nanoparticles (Zn NPs) produced biologically using moringa-leaf extract on amaranth seed germination, growth characteristics, and zinc content. Plant metabolites such as amino acids, alkaloids, flavonoids, sugars, and fatty acids are abundant in moringa leaves. The maximum plant height and fresh weight were obtained with a foliar treatment of 10 ppm biosynthesized zinc NPs. Zinc NPs at a concentration of 10 ppm resulted in better nutrient recovery and improved yield and productivity relative to the nutrient input, according to the nutrient-use efficiency indices, even though increasing the concentration of zinc applied via the foliar route led to higher zinc content in the plant biomass.

Mathew et al. [63] used *Cuminum cyminum* seed extract for the synthesis of Titanium dioxide nanoparticles (TiO₂ NPs) for seed germination and germination indices of mung bean to promote sustainable and biocompatible nano agriculture (*Vigna radiata*) and analyze plant growth parameters such as root length, shoot length, germination percentage, the germination rate. The results indicated significantly enhanced values of germination indices. Six potential TiO₂ NP concentrations (25, 50, 100, 150, 200, and 250 g mL⁻¹) were examined alongside the absolute control. The mung bean seeds' ability to germinate and thrive was affected by the TiO₂ NPs absorption.

Table 2. Green synthesis of nanofertilizers using different plant extracts.

S.N.	Bio-Extract	Nanoparticles	Characterization Results	Applications	Ref
1	Pomegranate peel (PPE) and coffee ground (CE) extracts	Phosphorous-containing hydroxyapatite nanoparticles (nHAP)	Average diameters were 167.5 nm, 153 nm (nHAPs CE), and 229.6 nm, 120.6 nm (nHAPs PPE), respectively	Investigating improvements in <i>Punica granatum</i> L., metabolites, photosynthetic activity, carbohydrate levels, and biocompatibility.	[64]
2	Using Bamboo using rice husk using sugar beet bagasse	Silicon nanoparticles	-	Soil application, foliar application	[3]
3	Fruit extracts of <i>Cornelian cherry</i>	Iron-oxide nanoparticles	Spherical shape with size 20 to 40 nm	Stimulation in both root and shoot biomass	[52]
4	Leaf extract of <i>Aloe barbadensis</i> Mill	Zinc-oxide nanoparticles	Spherical shape with a size of 35 nm	Nutrient source for plant growth	[59]
5	Flower extract of <i>Elaeagnus Angustifolia</i>	Zinc-oxide nanoparticles	λ_{max} : 330–340 nm, irregular to nearly spherical shape	Germination and metabolic activities of the plant	[65]
6	<i>Berberis pachyacantha</i> leaf extract (BPL)	Nickel-oxide nanoparticles	Rhombohedral structure with a size of 22.53 nm	Seed germination	[66]
7	<i>Coriandrum sativum</i> leaves extract	Zinc-oxide nanoparticles	Rod-shaped and polycrystalline with a size of 100 nm	Growing effects of fertilizer on green grain, Turkish gram, and Bengal gram plants	[57]
8	Clove buds (plant material)	Zinc nanoparticles	-	Growth and yield of <i>Pisum sativum</i> L.	[61]

Table 2. Cont.

S.N.	Bio-Extract	Nanoparticles	Characterization Results	Applications	Ref
9	Leaves of <i>Zataria multiflora</i> Boiss	Zinc nanostructure	-	Foliar application on pomace extract of <i>Punica granatum</i>	[67]
10	<i>Citrus medica</i> peel extract	Zinc oxide nanoparticles	λ_{\max} : 375 nm, the average crystallite size of 20–30 nm	ZnO nanofertilizer improves the growth and yield of <i>Abelmoschus esculentus</i>	[68]
11	Leaf extract of <i>Parthenium hysterophorus</i>	Zinc oxide nanoparticles	Spherical with a size of 10 nm	Germination of seeds and vegetative growth of <i>Sesamum indicum</i> h	[69]
12	The seed extract of black seeds (<i>Nigella sativa</i> L.)	Zinc-oxide nanoparticles	Spherical shape with a size of 24 nm	Nano-supplement to improve the production of <i>B. oleracea</i> var. <i>Italica</i>	[70]
13	Vegetable peel extract	Zinc-oxide nanoparticles	-	Boost the value of cluster bean (<i>Cyamopsis tetragonoloba</i>) seeds as well as the higher yield of cluster bean pods	[71]
14	<i>Cassia occidentalis</i> L. flower extract	Iron-oxide nanoparticles	Irregular surfaces with size 20–50 nm	Enhance germination and overall seedling growth	[72]
15	Leaf extract of <i>Cassia fistula</i>	Copper-oxide nanoparticles)	λ_{\max} : 320 nm, spherical-shaped with size 12–38 nm	Root and foliar application	[73]
16	<i>Panicum sumatrense</i> grains aqueous extract	Copper-oxide nanoparticles	λ_{\max} : 305 nm, crystallite with size 25 nm	Enhance plant growth	[74]
17	Microalgal algal extract	Iron-oxide nanoparticles	Spherical shape with size 76.5 nm	Plant growth stimulant	[75]
18	Leaf extracts of <i>Moringa oleifera</i> L	Bimetallic Ag/ZnO nanomaterials	λ_{\max} : 366 to 379 nm, spherical shape with sizes from 46 nm to 66 nm	Nitrogen-based fertilizers on biochemical and yield attributes of two wheat varieties	[76]
19	Peel extract of <i>Citrus reticulata</i> .	Zinc-oxide nanoparticles	Spherical shape with 23–90 nm size Hexagonal structure with 8.89 to 8.62 nm size	Boosting seed germination of <i>Brassica nigra</i> seeds	[77]
20	Seeds of <i>Juniperus procera</i>	Ag-containing nanoparticles	λ_{\max} : 400 and 262 nm, spherical with average size 100 nm	Seed germination	[78]

3. Agro-Applications of Green Synthesized Nanoparticles

The green revolution, which fulfilled the increasing population's food needs, increased crop yields per unit of land, but it has also seen an increase in the usage of artificial fertilizers in agriculture [79]. The world's food security is protected by the widespread use of these inorganic chemical-based fertilizers, but environmental and human health are seriously endangered [80]. Continuous use of chemical fertilizers results in massive mineral waste, the annual addition of large amounts of synthetic nutrients to the soil that is not taken by plants, the production of greenhouse gases, the eutrophication of aquatic ecosystems, and the salinization of soil [81]. Agricultural techniques must be modified, and perhaps even revolutionized, to successfully counteract the negative pressure from a changing climate, a growing population, and the loss of arable land. A major worldwide challenge is achieving and maintaining global food security [18]. In the future, agriculture could be supported nanotechnology in the following fields: security requirements for food production and distribution systems; intelligent systems for detecting and treating plant diseases; development of new instruments for cellular and biological research; and recycling of agricultural waste. As a result, the development of targeted, controlled-release fertilizers is necessary to boost crop productivity.

By improving the effectiveness of agricultural inputs to enable site-targeted regulated distribution of nutrients and ensure the least usage of agri-inputs, nanoparticles increase crop productivity [82]. The efficacy of various NPs has been assessed in terms of plant growth and production, disease suppression, and nutritional enhancement [83]. The uptake of nanoparticles by leaves is significantly influenced by the delivery channels for the nanomaterials. By reducing the need for biocides, making plants more robust and able to withstand abiotic challenges, and by enhancing metabolite production to enhance taste and shelf life, nanofertilizers can help improve human health and nutrition (Figure 3). In

addition to having a rapid absorption rate, nanofertilizers also have a slow-release rate and are only needed in small quantities, which can reduce fertilizer consumption and environmental damage [84]. It is important to understand that maximizing profits for a targeted agribusiness feature depends on selecting the proper concentration of NPs [85].

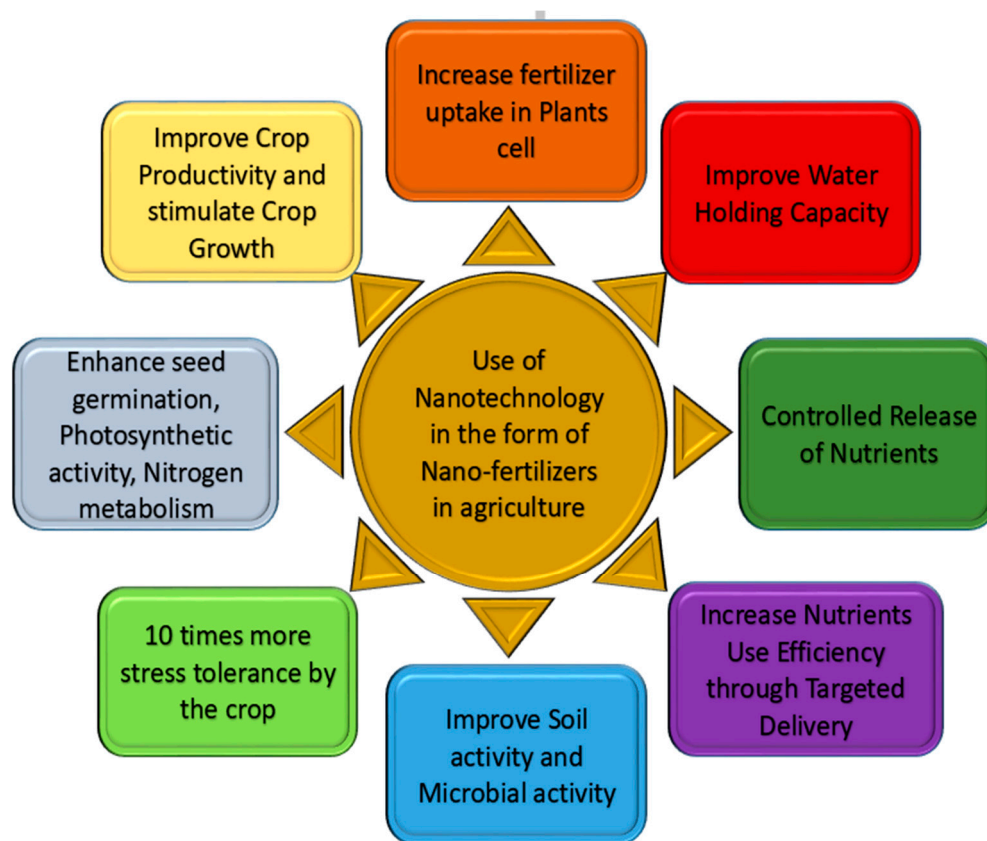


Figure 3. Different applications of nanobiofertilizers in the field of agriculture.

3.1. Silver NPs as Nanofertilizers

It was generally recognized that silver prevents disease-causing bacteria from surviving. Highly effective at killing germs, silver is also completely safe for use on people and is used in the treatment of an incredible range of bacterial, viral, and fungal diseases. Numerous nanoparticles have already been found to directly influence microorganisms through their anti-microbial characteristics. Since green silver nanoparticles (Ag NPs) have a larger surface area accessible for contact, they would have a greater bactericidal effect [86].

However, it's also plausible that Ag NPs do not just interact with membrane surfaces; they can also enter the bacteria itself [87]. The antibacterial, antifungal, and agricultural applications of green-produced AgNPs make them promising active substances [88]. Plant growth and development are positively impacted by Ag NPs [89]. According to recent research, silver nanoparticles collect in the *Escherichia coli* cell wall and damage it, increasing cell permeability and ultimately cell death [90]. Application of green-produced silver nanoparticles caused a progressive decrease in nutrient usage, raised chlorophyll content significantly, increased leaf area, and improved yield while also dramatically increasing N, P, and K use efficiency [91]. When compared to regular fertilizers, application of a control-release fertilizer coated with nanomaterials boosted the production of Chinese cabbage and greatly increased nutrient usage efficiency [92]. The status of nitrogen, phosphorus, and potassium in tomato fruit is significantly impacted by the addition of Ag NPs in plant media when compared to the control. The highest values were achieved at 20 ppm nanosilver [93].

3.2. Chitosan Nanoparticles

It was evident from the analysis of the effects of chitosan nanofertilization on *in vitro* seed germination that chitosan actively participates in biochemical and molecular processes in plant cells. These processes result in the production of several biomolecules that support plant development and defense against a variety of biotic and abiotic stressors. To better comprehend the plant's biochemical reaction to chitosan nanofertilization, Sharma et al. [94] applied a chitosan nanofertilizer for seed treatment and as a foliar spray and greatly boosted plant-growth metrics in maize plants including water, bulk chitosan, sulfuric acid, and copper sulfate. These findings demonstrated that a nanofertilizer at concentrations ranging from 0.01% to 0.16% has a stimulatory effect on all measures of plant development, including plant height, root length, root number, and stem diameter. All of the growth metrics reached their maximum values when the nanofertilizer concentration increased from 0.01 to 0.16. Maximum values for all the growth parameters were recorded at 0.16% concentration (Figure 4).



Figure 4. Chitosan bionanofertilizer impact on plant development (Reprinted from Sharma et al. [94]).

Chitosan nanocomposite films were investigated by Hartoyo et al. [95] as favorable growth media for rice seedlings produced in tropical peatland. Chitosan was reinforced with lignocellulose nanofibers, activated carbon nanoparticles, and non-activated carbon nanoparticles to create chitosan nanocomposites (LCNFs). In a germination test, chitosan nanocomposites produced, in the Dendang paddy variety, the best growth patterns, whilst in a greenhouse test, the nanocomposites produced, in the Indragiri paddy variety, the best growth patterns. On fungi and mycorrhiza, all chitosan nanocomposites showed a synergistic biofertilizing effect. Chitosan nanocomposites can speed up peatland restoration in tropical locations and be utilized as a growth regulator for peatland paddy varieties.

The tripolyphosphate and chitosan solution underwent ionic gelation to produce chitosan nanoparticles. Coffee seedlings were treated with the nanofertilizer in a greenhouse environment. The findings demonstrated that the nanofertilizer improved nutrient uptake, photosynthesis, and coffee-plant development. The amount of nitrogen, phosphorus, and potassium in the leaves of treated plots increased by 17.04%, 16.31%, and 67.50%, respectively, compared to the control, while the amount of total chlorophyll rose by 30.68% and the net rate of photosynthesis increased by 71.7% after the application of the nanofertilizer. Application of nanofertilizer also increased plant height, leaf area, and leaf number of coffee seedlings. Enhancing the use efficiency of fertilizers for coffee plants may be achieved by using nanofertilizers [96].

3.3. Copper NPs as Nanofertilizers

Macronutrients and micronutrients are important mineral components in the agricultural system for the proper development of vegetative and reproductive tissues in plants. Plants need to have a higher concentration of the macronutrients calcium, magnesium, potassium, nitrogen, sulfur, and phosphorus. As opposed to macronutrients, which are needed in higher amounts, micronutrients such as copper, nickel, iron, molybdenum, manganese, boron, zinc, and chlorine are needed in lower amounts [76]. As a micronutrient, Cu is crucial for the production of chlorophyll and other plant pigments, as well as for the metabolism of proteins and carbohydrates [97]. The straightforward and environmentally safe *Azadirachta indica* leaf broth is used to generate copper nanoparticles (Cu NPs). In addition to reducing the metal ions, the biomolecules in the leaf broth help to stabilize the metal nanoparticles. This green synthesis method is simple, affordable, and free of toxic and dangerous substances [98]. Different Cu NPs concentrations improved productivity, quality, bioactive chemical content, protein content, plant height, root length, weight, and seedling germination [99]. Cu NPs had an impact on maize crops; the results showed improved growth in normal conditions and decreased curling and wilting of leaves in water-shortage areas. Additionally, maize plants under stress were observed to have enhanced pigments, seed quantity, yield, and water retention [100]. When Cu NPs were added to the soil, the copper ions (Cu^{2+}) were leached off. The ions are transported from the root system to other plant parts through the stem. Because copper is a major component of the plastocyanin pigment of chlorophyll, it participates in a variety of metabolic activities in plant cells, including photosynthesis [101]. Cu NPs showed antibacterial action against hazardous microorganisms such as *Vibrio cholerae*, *Bacillus subtilis*, *Pseudomonas aeruginosa*, and *Staphylococcus aureus* [102]. Respiratory oxygen species are a result of aerobic metabolism and an activated form of atmospheric oxygen. If ROS levels rise in cells, this results in oxidative damage to proteins, RNA, and DNA molecules as well as membranes (lipid peroxidation), and it can even cause the cell to die due to oxidative stress [103]. When applied to *E. coli*, copper nanoparticles cause a significant amount of reactive oxygen species (ROS) to be released, which in turn causes DNA degeneration, lipid oxidation, and finally, tissue damage [104].

3.4. Iron Nanoparticles as Nanofertilizers

Several metabolic functions, including respiration, photosynthesis, and chlorophyll production, depend on iron (Fe), as an important element [105]. The employment of plant extracts along with bacteria, fungi, algae, yeast, and other microorganisms as well as enzymes during the process known as “green synthesis” of NPs is crucial since it lowers the danger of additional contamination. When utilized as a reducing and capping agent, *Azadirachta indica* leaf extract can yield exceptionally stable Fe NPs [106]. Because of their magnetic properties and nanoscale size, iron nanoparticles (Fe NPs) are handled as special nanofertilizers. Various plant species can develop more quickly and be more resilient to stress when given an optimal amount of iron nanoparticles [107]. Iron-oxide nanoparticles’ effectiveness as nanofertilizers can replace chemical Fe fertilizers, which have multiple inadequacies [52]. Investigations have shown that providing peanut (*Arachis hypogaea*) plants with Fe_2O_3 NPs as nanofertilizer enhances the plants’ root and stem length, biomass, height, and antioxidant enzyme and phytohormone contents [53]. Iron nanoparticles have many benefits when used as a reactive material in permeable reactive barriers, including an increase in the rate of reductive degradation reaction, a reduction in the reductant dosage, control over the risk of release of toxic intermediates, and the production of a nontoxic end-product [108]. By changing the arrangement of the leaves, raising the number of chloroplasts and grana, controlling the formation of vascular bundles, and increasing the number of chloroplasts, various concentrations of Fe NPs stimulated plant growth at the cellular level [109].

3.5. Zinc Nanoparticles as Nanofertilizers

For plants to function normally, nutrients are essential, particularly as they grow and develop. In the absence of essential nutrients, plants cannot complete their life cycles and carry out their physiological tasks, which slows plant development and reduces agricultural yield [110]. The most typical micronutrient deficiency limiting agricultural productivity globally is zinc insufficiency. The development and use of fertilizers in nanoforms is one of the most practical ways to significantly raise global agricultural yields. ZnO NPs, or zinc-oxide nanoparticles, are regarded as safe substances for use with living things. Due to their antibacterial action, previous research has demonstrated the potential of ZnO NPs in promoting seed germination and plant growth as well as in the prevention of plant disease and in the protection of plants [111]. In the green synthesis of ZnO NPs, compounds present in the plant extract react with a zinc salt to reduce or form complexes with the metal [112]. In addition to having an impact on plant development and growth, biologically produced ZnO nanoparticles also made soil enzymes including phytase, acid phosphatase, and alkaline phosphatase more active [113]. There has been extensive research on the impact of ZnO NPs on agricultural plants and, in addition to having an impact on plant development and growth, biologically produced ZnO nanoparticles have been shown to make soil enzymes including phytase, acid phosphatase, and alkaline phosphatase more active [114].

4. Conclusions

In the drive for more ecologically friendly processes, green chemistry is a cutting-edge and emerging resource. Due to its advantages over conventional physicochemical approaches, using green extracts for the synthesis of metal NPs has recently attracted more attention. This review focuses on the diverse microorganisms and plant components' ability to create metal nanoparticles. Functional groups play a dual role as reducing and capping agents in the biologically active compounds that are released by microbes and plants. MNPs produced through green synthesis have prospective uses in agribusiness, particularly as nanofertilizers, and their performance has been proven in research. Green chemistry has been used to successfully create iron, manganese, silver, zinc, and manganese nanoparticles, which have then been used as foliar nanofertilizers for crop growth. Nanoparticles laden with organic fertilizers have promise as "nutrient boosters," allowing for the delayed and continuous release of nutrients to plants, guaranteeing appropriate nutrition throughout growth. The primary benefit of using bionanofertilizer is their ability to reduce the amount of chemical fertilizer required for crops by providing targeted delivery systems that deliver nutrients directly into plant cells, where they can be absorbed more efficiently than through traditional methods such as broadcast applications, seed dressing, or foliar sprays. This reduces energy costs associated with production since less fuel is needed for transport between fields, storage facilities, etc., resulting in lower carbon emissions overall—making it a much more environmentally friendly option compared to other forms of fertilizer application. Additionally, because these synthetic nanoparticles are smaller than conventional particles, they require less water, which helps conserve resources even further during times when water availability may be limited due to drought conditions or other factors affecting local weather patterns. Finally, one major advantage offered by biosynthesized nanofertilizers lies in their ability to improve nutrient-use efficiency, meaning not only do you get higher yields but also better-quality produce since fewer nutrients are lost in transit from field-to-table, thanks again, largely, in part, to their size, which allows them access into areas that larger molecules cannot reach, thus increasing their absorption rate significantly when applied correctly. All this makes them an ideal choice for farmers looking to increase productivity without compromising on quality while, at the same time, also helping protect the environment from potential damage caused by excessive amounts of chemicals being released into the atmosphere each year via agricultural practices worldwide. Better knowledge of the mechanisms involved in metal-nanoparticle creation and managing

the morphology, size, and dispersion should be the main goals of future research. New opportunities could soon be accompanied by novel approaches to problems.

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