agrochemicals

Review

Nanofertilizers: The Next Generation of Agrochemicals for Long-Term Impact on Sustainability in Farming Systems

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Abstract: The microflora of the soil is adversely affected by chemical fertilizers. Excessive use of chemical fertilizers has increased crop yield dramatically at the cost of soil vigor. The pH of the soil is temporarily changed by chemical fertilizers, which kill the beneficial soil microflora and can cause absorption stress on crop plants. This leads to higher dosages during the application, causing groundwater leaching and environmental toxicity. Nanofertilizers (NFs) reduce the quantity of fertilizer needed in agriculture, enhance nutrient uptake efficiency, and decrease fertilizer loss due to runoff and leaching. Moreover, NFs can be used for soil or foliar applications and have shown promising results in a variety of plant species. The main constituents of nanomaterials are micro- and macronutrient precursors and their properties at the nanoscale. Innovative approaches to their application as a growth promoter for crops, their modes of application, and the mechanism of absorption in plant tissues are reviewed in this article. In addition, the review analyzes potential shortcomings and future considerations for the commercial agricultural application of NFs.

Keywords: nano-fertilizer; sustainable agriculture; eco-friendly; agro-economics

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1. Introduction

Plant nutrients or fertilizers are materials that are responsible for plant growth and development with elements or nutrients. Due to the excessive use of fertilizers, the fertility of the soil has been decreased by destroying the beneficial microbes, and, therefore, there is a dire need for alternative and eco-friendly nanofertilizers (NFs) that are the most vital application of nanotechnology in the agricultural sector [1]. Nutrient carriers or transporters using substrates with nano dimensions of 1–100 nm are being developed. NFs can be manufactured from conventional fertilizers, bulk fertilizer materials, or extracted from other plants by encapsulating/coating them with nanomaterials (NMs). In addition to having a large surface area, nanoparticles can hold plenty of nutrients while slowly and steadily releasing them. The crop is then able to absorb nutrients according to its needs without any adverse effects that are found with traditional fertilizers [2]. Various metabolic reactions in the plant are facilitated by the extra surface area, such as enhanced photosynthesis, resulting in increased productivity. Since NFs deliver nutrients directly to the plants, ecotoxicity is reduced, and loss of nutrients to the soil or groundwater is prevented [3]. There is a range of particle sizes between 1 and 100 nanometers for NFs. The application sites, such as soil or leaves surface, promote more penetration of nanoparticles into the plant. The nanoparticles are more likely to diffuse into the crop from the surface if they are smaller than the pore size of the leaves and roots [4], making them more effective at uptake and use. Photosynthesis, nutrient absorption efficacy, photosynthate accumulation, nutrient translocation, and pest and pathogen resistance are significantly improved by NFs. In addition to increasing productivity, this also improves soil quality, leading to enhanced crop yields.

The use of NFs is an eco-friendly and more effective alternative to chemical fertilizers. As a result of their physio-chemical properties, NFs are promising agrochemicals. In this review, we examine the role of NFs in agriculture, their mode of application, and their prospects [5]. Owing to the smaller size (1–100 nm) and larger surface area, nano-enabled products, such as nano-insecticides, nano-pesticides, and nano-fertilizers, NPs perform an important role in sustainable agriculture [6]. Recent research has suggested that nanoparticles could be used to control plant pests, such as insects, fungi, and weeds [7,8]. It has been suggested that NFs could supply nutrients to plants more effectively and therefore improve crop productivity significantly [9].

By meeting the nutritional requirements of plants without affecting agricultural yields, NFs have the potential to completely transform current food production systems. The increased surface area to volume ratio and better mobility of these sub-microscopic particles aid in boosting plant nutrient absorption and agricultural productivity. As a result, NFs can be viewed as a "smart system of nutrients" that, by increasing food grain yield, can aid in reducing hunger and poverty. By 2030, these cutting-edge nanofertilizers may be crucial to attaining the sustainable development goals of ending world hunger and ensuring food security and improving global agricultural practices' overall sustainability. Thus, the current review focuses on the timely need for NFs for sustainable agricultural practices. Here, the role performed by metal oxide nanoparticles (NPs), nanocomposites, and conjugated nanoparticles are discussed. Moreover, their use in fertilizing crops for growth enhancement, stress tolerance, and commercial production are also examined.

2. Chemical Fertilizers and Their Drawbacks

Traditionally, fertilizers deliver nutrients in chemical forms that plants cannot readily absorb. Moreover, most of the macronutrients added by these chemical fertilizers are very poorly soluble in soil, leading to very low consumption. As a result, there is a need for repetitive application of these chemical fertilizers. Increasing food demand requires farmers to use more chemical fertilizers, which in turn affects soil and environmental health. As a result of the excessive use of chemical fertilizers, the soil structure and mineral cycles are irreversibly damaged. In addition, excessive and disproportionate fertilizer application harms soil microflora, plants, and ultimately, food chains throughout ecosystems, leading to inherited mutations in future generations. Agricultural nitrogen (N) and phosphorus (P) fertilizers have been identified as the major anthropogenic factor leading to worldwide eutrophication problems [4]. A farmer's profit margin is reduced when he uses chemical fertilizers. In addition, the prolonged use of conventional fertilizers has led to severe environmental repercussions worldwide, such as groundwater contamination, water eutrophication, chemical burning, soil degradation, and air pollution [10,11]. As a result of high release rates of nutrients, conventional fertilizers negatively affect the nutrient use efficiency (NUE) of crops and/or by converting nutrients that are not bioavailable to crops [12,13].

3. Advantages of Nanofertilizers over the Traditional Chemical Fertilizers

Farmers and gardeners now have access to nanofertilizers, a relatively new type of fertilizer. They are a desirable alternative for individuals wishing to improve the health and production of their plant and soil fertility because they have numerous advantages over conventional chemical fertilizers.

The improved effectiveness of nanofertilizers in delivering nutrients directly into plant cells is its most significant benefit. By doing this, plants get all the nutrients they need without any excess ending up in the soil or running off into nearby waterbodies, such as lakes and streams, which could damage the environment due to nutrient pollution from too much nitrogen or phosphorus in these bodies of water. Additionally, adopting goods based on nanotechnology results in lower costs for farmers and less overall environmental impact for important applications because they are more effective at delivering vital nutrients than conventional fertilizer products.

Micronutrients, such as zinc or iron, which may not be easily accessible by conventional methods, can dramatically affect crop yields if low levels exist in soils. It is a sort of specialized plant nutrition requirement that can be targeted using nanofertilizer technology. Researchers can now create slow-release formulations thanks to nanoparticles, which reduce the risk of leaching while still providing plants with the necessary nutrition during critical growth stages, such as flowering and fruiting when higher levels of some minerals are needed to support reproductive processes and help crops grown in these conditions produce to their highest potential.

Furthermore, it can be used in conjunction with nanobiofertilizers (NBFs) to improve crop plant stress tolerance. Although it has the potential to launch a new crop management strategy, its limitations should be carefully examined before implementation [5].

In fact, nanotechnology offers several distinct advantages over conventional approaches to agricultural production, including improved nutrient availability. Greater efficiencies in application rates targeted delivery of specific micronutrients need slower releases, reduce leaching losses, and enhance yield potentials (Table 1). All of these explain why it is becoming an increasingly popular choice among growers today.

Table 1. Differential Features of Nanofertilizers and Traditional Fertilizers [14].

Properties	Nanofertilizers	Traditional Fertilizers
Solubility and Dispersion of the mineral nutrients.	Nano-sized advantages the mineral nutrient by improving solubility, dispersion, and can achieve enhanced bioavailability.	Due to large-sized particles, it can show limited solubility and dispersion hence leading to poor bioavailability to the plants.
Deprivation rate of Nutrients in Fertilizer.	Nano-sized enables the retention in the soil particle for a prolonged period.	Significantly leached, rain-off, and drifts can occur in the methods.
Superintend releasing Mode.	Release rate and pattern of nutrients can be precisely controlled by encapsulating the nanofertilizers in the polymer matrix, supporting sustainable practices.	Direct exposure to fertilizers might be toxic in excess dosage and can also damage the ecosystem associated with the crop field.
Nutrient Uptake Efficiency.	Nanostructured Fertilizer can save the excess use and increases the efficiency in uptake ratio during controlled cultivation.	Large-sized Chemical Composite is difficult to uptake by plants hence reducing efficiency and resource utilization.
Prolongation of effective nutrient release.	Nanostructured formulation can extend the nutrient supply to the plant for a prolonged time by controlled released efficiency.	Readily available at the time of delivery or foliar leading to the loss of rest nutrients into the soil, forming insoluble salts.

4. Need for the Development of Nanofertilizers

Due to the surge in population in the past few decades, agriculture productivity has increased to meet the needs of billions of people, especially in developing countries. Soil nutrient deficiencies cause great economic losses for farmers and significant decreases in nutritional quality and quantity of grain for humans and livestock [15]. In order to increase crop production, techniques, such as hydroponics, can be used. However, these techniques are very expensive. Thus, there is a need for affordable and sustainable technology to provide nutritional supplements and improve crop production by reducing resource consumption and fertilizer usage. The traditional method of fertilizer usage involves the use of much more fertilizer than is necessary, whereas the nanotechnological approach emphasizes the use of less quantity of fertilizer. With the advancement of nanotechnology, nanoparticles of physiologically vital metals can now be mass-produced, which can be used to enhance fertilizer formulations for enhanced uptake in plant cells and nutrient conservation. In addition, NFs can reduce nutrient losses through leaching, thus improving nutrient use efficiency and addressing environmental concerns generated due to the heavy use of fertilizer [16]. Nanostructured fertilizers can improve nutrient use efficiency through targeted delivery and slow or controlled release mechanisms. In response to environmental triggers and biological demands, they could precisely release their active ingredients. In addition, NFs have demonstrated enhanced crop productivity by increasing the rates of photosynthesis, seed germination, seedling growth, carbohydrate and protein synthesis, and nitrogen metabolism [15].

5. Types of Nanofertilizers

There are different types of NFs based on the type of nutrient and carrier, such as macronutrient-based, micronutrient-based, carbon-based, and polymer-based (shown in Figure 1 below).

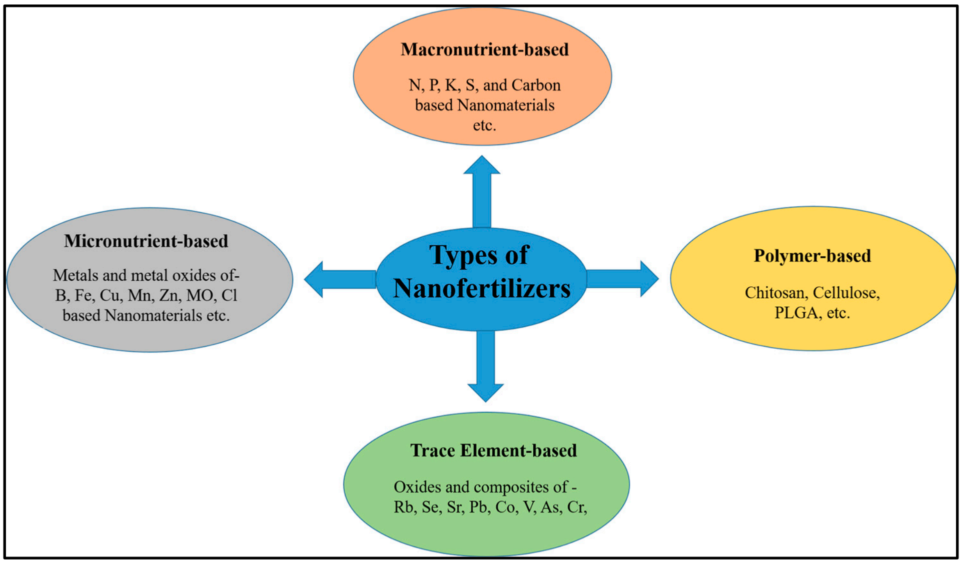

Figure 1. Represents the various types of NFs used in agriculture.

5.1. Macronutrient-Based Nanofertilizers

Macronutrients (e.g., nitrogen (N), phosphorus (P), potassium (K), magnesium (Mg), sulfur (S), and calcium (Ca)) have been combined with nanomaterials for the purpose of delivering an accurate amount of nutrients to the crops and minimizing their bulk requirements, with the extra benefit of decreasing purchasing and transportation costs. The major macronutrients are nitrogen (N), phosphorus (P), and potassium (K). Nitrogen is essential for plant development since it performs a fundamental role in energy metabolism and protein synthesis. Nitrogen is absorbed by the plant in the form of nitrate. Nutrients contain nitrogen, which is an essential nutrient for energy metabolism and protein synthesis. Plants cannot use N in its atmospheric form even though it makes up about 78% of the atmosphere. Nitrate (NO_3^-) and ammonium (NH_4^+) are specific chemical forms of N that plants can absorb. Due to its low affinity for soil particle surfaces, negatively charged nitrate is not readily absorbed by the soil, so it is deficient there. Combining nitrogen with hydroxyapatite and zeolite increases nitrogen absorption in soil and slows nitrogen release [2]. As with N, P is essential for transporting and storing energy, photosynthesis execution, root growth, flowering, and the production of organic compounds [17]. Potassium is crucial to photosynthesis, photon translocation, protein synthesis, ionic balance, regulating plant stomata and water use, activating plant enzymes, and many other processes. It is known to activate at least sixty enzymes involved in plant growth [2]. Among sulfur (S), calcium (Ca), and magnesium (Mg), Ca-based NFs' performs a crucial role in stabilizing cell walls, retaining minerals in the soil, transporting minerals, neutralizing toxic substances, and forming seeds; magnesium is essential for plant growth because it is present at the core of chlorophyll molecules and activates enzymes. In addition to aiding in chlorophyll formation, sulfur enhances the efficiency of nitrogen and the defenses of plants. In addition, it is necessary to produce a few amino acids [17,18].

5.2. Micronutrient-Based Nanofertilizers

Plants require micronutrients in much smaller amounts than macronutrients for growth. B, Fe, Cu, Mn, Zn, Mo, and Cl elements are found in micronutrients [19]. The electron transfer system, chlorophyll biosynthesis, and certain enzyme functions require iron, particularly heme proteins. Different metabolic enzymes use zinc for their catalytic activities and processes, such as cell division, tryptophan synthesis, photosynthesis, protein synthesis, and maintaining membrane structure and potential. Zn deficiency is common worldwide due to the low bioavailability of Zn in plant-based diets [16]. Nitrate reductase in plants is dependent on molybdenum. Mo is also an important element in nitrogenase, which is essential for nitrogen fixation of legume crops. In addition to mitochondrial respiration, cellular transport, antioxidative activity, protein trafficking, and hormone signaling, copper performs an important role in several physiological processes. Cell cycle regulation, nucleic acid synthesis, cell elongation, and membrane function are all regulated by Boron [15].

5.3. Polymer-Based Nanofertilizers

Nanoparticles can be carried by polymers, such as chitosan, alginate, albumin, and others. Polymers, such as those mentioned above, are being extensively investigated for their application in the delivery of NPs to plants. A cationic biopolymer, chitosan is inexpensive and used to enhance plant growth, seed germination, nutrient uptake, photosynthetic rate, and crop yield. Moreover, antimicrobial properties of chitosan have been demonstrated in various studies [20,21]. Zn-chitosan NPs can promote the growth of wheat plants when applied in foliar mode [22]. Cu-Chitosan NPs have potential growth promotion in corn and tomato plants [23,24].

5.4. Zeolite-Based Nanofertilizers

Minerals, such as zeolite, are naturally occurring. By releasing nutrients gradually to the crop plant, zeolite-based NFs increase the crops' accessibility to nutrients throughout their growth cycle. This prevents nutrient loss due to denitrification, volatilization, leaching, and nitrogen fixation in the soil. Due to their large surface area and ability to modulate the release of nitrogen, nanozeolites and their combinations have been widely employed for designing NFs [25]. Zeolite-based composite fertilizers are known for increasing nutrient use efficiency in lettuce plants [26]. Furthermore, zeolite-based nitrogen fertilizers have been reported to have growth-promoting activity in maize yield and quality of alfisols and inceptisols [27]. In this context, zeolites have been recently studied for their characteristic property of carriers of nanofertilizers [28].

5.5. Carbon-Based Nanofertilizers

Carbon is a key component for the existence of life on Earth. A carbon nanotube (CNT) is an engineered carbon nanomaterial that has exceptional physicochemical properties and stability. Growing plants in nutrient media with CNTs increased seed germination and shoot length. CNTs (carbon nanotubes) can penetrate the tomato seed coat promoting the water uptake inside the seeds and affecting their growth rates and germination [29]. The growth rate of tobacco cells was enhanced by treatment with CNTs [30]. Similarly, callus, embryogenesis and embryo germination, root elongation, and rooting stages were studied in date palms. The results indicated that the treatment with CNTs affected the culture of the cells irrespective of the growth stage. The number of roots and rate of embryo germination was enhanced [31].

5.6. Trace Elements Based Nanofertilizers

Minerals or trace metals are present in very small amounts in living tissues. Some of them are essential nutritionally, while others are not. The total number of trace elements is fourteen, for example. Iron (Fe), copper (Cu), zinc (Zn), strontium (Sr), molybdenum (Mo), manganese (Mn), rubidium (Rb), selenium (Se), lead (Pb), cobalt (Co), vanadium (V), arsenic (As), chromium (Cr), and cadmium (Cd) [32,33]. NPs synthesized from trace elements are safer because of their ease of fabrication and have various applications, including human feed and medicine [34,35] and poultry feed supplements [36,37].

6. Nano-Biofertilizers for Sustainable Agriculture

Natural ecosystems and human life are adversely affected by the overreliance on chemical fertilizers. A novel alternative to these chemical fertilizers is biofertilizers, which have emerged as a renewable, supplementary, and eco-friendly source of plant nutrients. Biofertilizers are mainly composed of formulations based on microorganisms, which can be applied to the surface, soil, or seeds to improve growth characteristics by supplying essential nutrients to the plant [38]. These include various groups, such as nitrogen fixing, phosphorous solubilizing and mobilizing, plant growth-promoting rhizobacteria (PGPRs), and mycorrhizal biofertilizers. Due to their poor shelf-life, crop specificity, instability in the field due to soil and environmental constraints, limited availability of beneficial microflora, susceptibility to harsh environments, and high dose requirements, their use is limited [7,8]. In this context, nanomaterial-based fertilizers have been developed and explored to overcome these drawbacks. By virtue of their unique size-dependent and optical properties, high surface area to volume ratio, and controlled release of micronutrients, NBFs are an attractive alternative to chemical fertilizers. By coating organic fertilizer (biofertilizer) with nanomaterials, NBFs are produced by reducing organic fertilizer (biofertilizer) to the nanoscale (1–100 nm). Growth-promoting bacteria or micronutrients are coated on polymer by a process called nanoencapsulation. To increase nutrient absorption efficiency and minimize application losses, chitosan and zeolite are primarily used. As a result of NBFs, native microflora is enhanced, and enzyme activity and crop resistance to disease are improved. In their rhizospheres, NBFs increased plant stress tolerance several times with almost 30% nutrient immobilization. Furthermore, NBFs are less toxic, highly stable, cost-effective, and eco-friendly. They minimize nutrient loss due to soil leaching, gasification, erosion, etc. However, despite these advantages, NBFs suffer from some disadvantages, including a lack of technical expertise, labor-intensive production methods, and a need to evaluate the risks prior to commercial and large-scale use [39,40]. Table 2 states the major differences between bionanofertilizers and nanobiofertilizers.

Table 2. The basic difference between Bionanofertilizers and nanobiofertilizers.

Characteristic	Bionanofertilizers	Nanobiofertilizers
Synthesis of NPs	Biological method	Biological, chemical, or Physical
Structure	Biologically synthesized NPs as fertilizer	Nano-encapsulated Organic Molecules as fertilizer
Encapsulation	Biomolecules from biological materials	Nanomaterial
Core	Micro/macronutrient element	Inorganic and organic
Example	MgO [41], ZnO [42],	Phosphorous-hydroxyapatite NPs [9] and Zn-Chitosan NPs [22]

Some of the major applications and modes of action for the popularly used nanomaterials are given in Table 3 below:

Table 3. Applications of various nanoparticles in agriculture.

Sr. No.	Type of Nanoparticle Used	Mode of Application	Crop Used	References
1	N (urea-coated hydroxyapatite)	Soil application	Rice	[41]
2	P (coated hydroxyapatite)	Foliar spray	Soybean	[42]
3	K	Foliar spray	Basil	[43]
4	Ca	Foliar spray	Basil	[43]
5	Mg (MgO)	Foliar spray	Cluster bean	[44]
6	Zn (ZnO)	Foliar spray	Pearl Millet	[45]
7	Zn (Zn-chitosan)	Foliar spray	Wheat	[22]
8	Fe (Fe_2O_3)	Foliar spray	Wheat, watermelon, corn, tomato, peanut	[45–48]
9	Fe (Fe_2O_3)	Seed treatment	Rice	[49]
10	Cu (Cu−chitosan)	Seed treatment	Tomato	[23]
11	Cu (Cu−chitosan)	Foliar spray	Corn	[24]
12	S	Seed treatment	Sunflower	[50]
13	Mn	Seed treatment	Mung bean	[51]
14	Ti (nanoanatase TiO_2)	Soil application	Spinach	[52]
15	Ni	Seed treatment	Wheat	[53]
16	B	Foliar spray	Mung bean	[54]
17	Mo	Foliar spray	Chickpea	[55]
18	Zn and Mg-doped hydroxyapatite modified with urea	Foliar spray, soil applicant	Wheat	[56]
19	Urea–hydroxyapatite nanohybrid	Soil applicant	Tea plant (*Camellia sinensis* (L.) Kuntze)	[6]
20	Phosphorous-Containing HydroxyapatiteNanoparticles (nHAP)	Foliar spray	Pomegranate (*Punica granatum* L.)	[9]
21	Integrated Nanofertilizers(N, P, K, Mg, S, Si, Ca, Fe, Cu, Zn, Co, and Ag)	Foliar spray and soil applicant	*Polyscias fruticosa* and *Asparagus officinalis*	[57]

7. Nanofertilizers for Improving Biotic and Abiotic Stress Tolerance

As a novel and eco-friendly stress-tolerance component in crop plants, NFs are being studied. Crops are always subject to varying environmental stresses, which have always been a major threat to any crop plant and its desired yield. Stresses can be both biotic and abiotic. Various stressors tend to promote the formation of reactive oxygen species (ROS) and the deposition of toxic ions causing damage to biochemical pathways and actively growing tissues. The use of NPs can be an efficient and promising approach for combating different biotic and abiotic stresses [58–60].

Abiotic stresses are mainly caused by environmental factors, such as temperature (extreme cold or heat), soil composition (salt concentration and nutrient availability), pH, drought, flooding, soil moisture content, humidity, etc. [59,61]. NPs in the form of nanofertilizers are employed and studied for their dual action in plant growth promotion and mitigating abiotic stress [62]. Stress tolerance in plants has been reported to improve with a wide range of NFs. This includes CeO_2 NPs and nanofertilizers (N, P, K, Zn, Fe) [63]; nanoboron, nanosilica, and nanozinc [64]; nano-urea-amorphous calcium phosphate (NU-ACP) [65]; nano-liposome-containing Fe^{2+} [66]; nanochelated fertilizer (N, P, K, Fe, Zn, Mn) [67], etc. These NFs have been shown to enhance the uptake of nutrients, improve growth and photosynthetic performance under drought, increase biomass, increase cell membrane stability under salinity stress, etc. [68].

Biotic stresses in plants include infections due to bacteria, fungi, nematodes, insects, viruses, etc. The most common pathogens in crops are bacteria and fungi. They cause various diseases in crop plants and hamper productivity [59]. Numerous Gram-positive and Gram-negative bacterial pathogens are reported to be inhibited by the application of NPs [69,70]. Various zinc nanoparticles and composites have been explored against *Xanthomonas axonopodis* pv. Phaseoli, *X. citri*, *X. oryzae* pv. *Oryzae* (strain GZ 0003), etc. [71]. Fungal pathogens belonging to genera, such as *Fusarium*, *Pythium*, *Aspergillus*, *Colletotrichum*, etc., are effectively controlled by Cu, CuO, ZnO, Ag, Au, MgO, TiO, and nanoparticles [72]. *Ralstonia solanacearum*, a soil-borne causative agent of bacterial wilt in tomatoes, can be efficiently managed through CuO, ZnO, and FeO NPs [73]. Various antiviral nanomaterials are also competent against plant viruses, such as Turnip Mosaic virus (TuMV) in tobacco [74], barley yellow mosaic virus (BaYMV), potato virus Y (PVY), and tomato mosaic virus (ToMV), and many more can be controlled using various nanoparticles [75]. Thus, the stress due to various biotic stress components can be mitigated using nanomaterials in an eco-friendly and sustainable way [76].

8. Large-Scale Production and Commercialization of Nanofertilizers

A great deal of attention has been paid to the development of processes for producing NMs on a commercial and large-scale in the past decade. Many of the nano-derived products are already available. Nevertheless, large-scale industrial production of NFs has not yet been achieved. Nanofertilizers need to be well-characterized and well-identified before they can be applied to agriculture. Prior to commercialization, thorough studies and science-based evidence are necessary. Large-scale production of NFs is currently lacking due to reports indicating their toxicity at higher concentrations, a lack of soil- or field-based research focusing on crop nutrients, the type of nanomaterial used as fertilizer, an effective and efficient method of application, and most importantly, the lack of economically efficient production technology. A detailed field study and research findings are needed to motivate industries to produce NFs [77].

Currently, there are no diseases that have been reported to be directly linked to nanoparticles and their functionalized products. Commercial production, however, should be preceded by establishing ethical guidelines and safety measures before they are used in agriculture and in humans. NPs can cross the membrane barrier due to their size, allowing them to enter the human body in a multimodal manner. These issues need to be addressed urgently. However, using NFs in agriculture has been reported to have beneficial, growth-promoting effects at very low concentrations. Considering various research studies, it is evident that NFs do not cause any significant toxic effect on the environment at such low concentrations [78–81].

At the laboratory scale, NFs are produced by using various biological and precursor materials, such as bacteria, fungi, and plants (demonstrated in Figures 2 and 3 below) [4]. In view of the beneficial properties shown by nanofertilizers, more attention has been given to the initiation of development and commercial production. The idea of NFs being commercialized is still in its early stages, and it will take time and effort to become popular. There are very few NFs that are produced on a large scale. Further increase in production scale will require a thorough investigation of technology and scientific research. This must be followed by setting up pilot plants prior to full-scale production. Simultaneously, a well-versed quality check facility and the low-cost production of the final product must be the key factors taken into consideration. By overcoming all the above-mentioned problems, the target of large-scale production can be achieved.

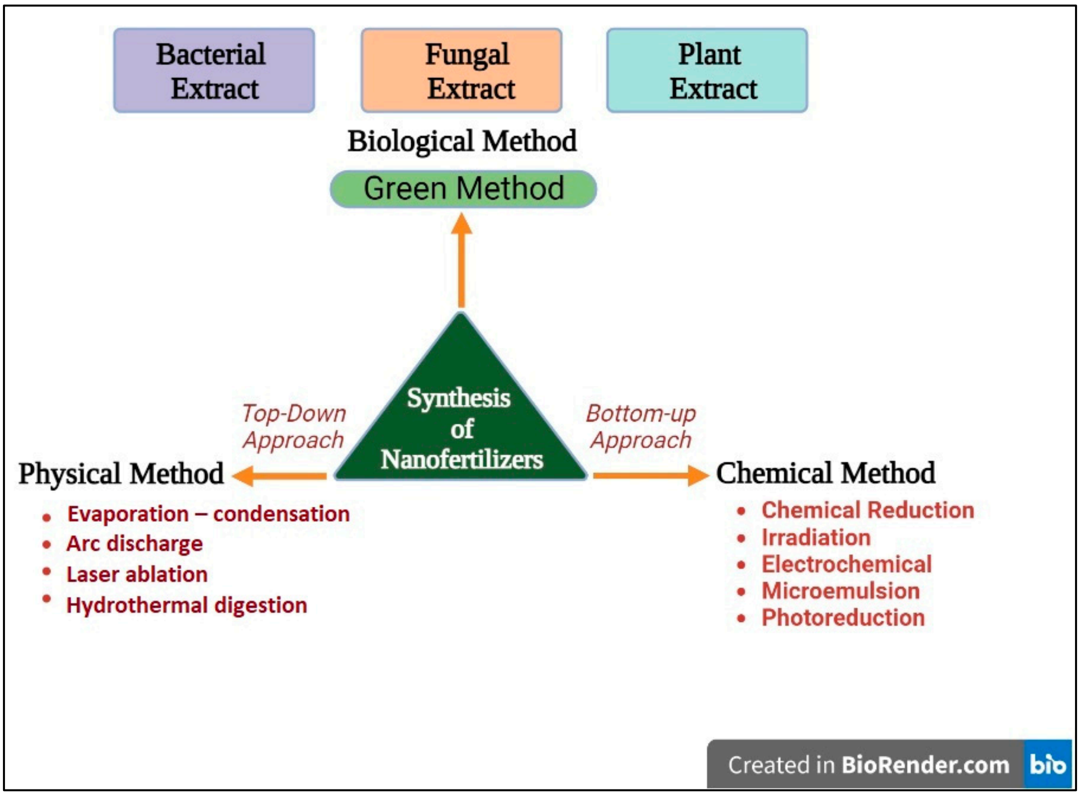

Figure 2. Various methods of nanofertilizers synthesis (Created with BioRender online free version).

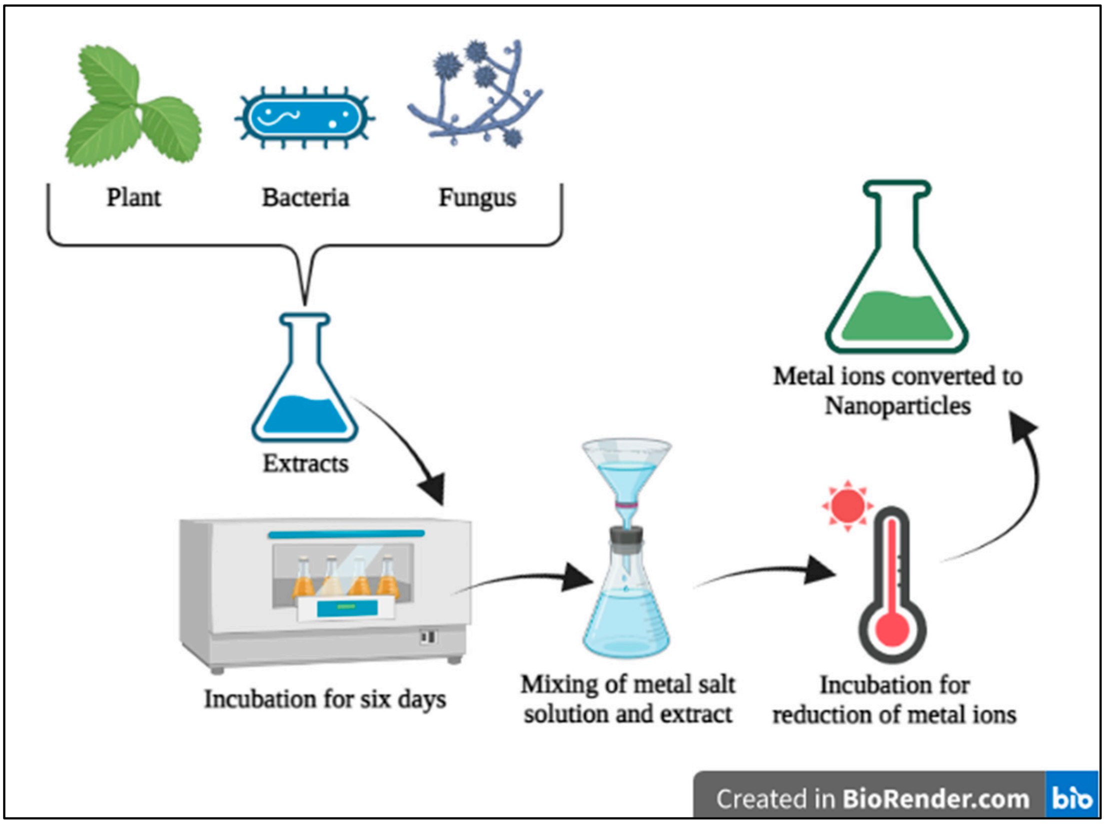

Figure 3. Schematic for biological synthesis of nanofertilizers (adapted from [38]) (Created with BioRender online free version).

9. Modes of Nanofertilizers Application

There are different ways of applying NFs, including soil application, seed treatment, foliar spray, dusting, fogging, emulsion, etc. A few methods are described below. In Table 1, different nanoparticles are shown with their host plant, their mode of application, and their mode of action.

9.1. Soil Application

Soil application is the most common method of providing a nutrient supplement to plants. It is critical to consider various factors, such as how long the fertilizer will stay in the soil, soil texture, soil salinity, plant sensitivity to salts, salt content, and pH of the modification, when applying this method of fertilizer. When fertilizers are mixed in the soil, the exposure and localized concentration of the particles become much higher as compared to foliar spray [16]. Negative soil particles affect the adsorption of mineral nutrients. The anion exchange capacity of most agricultural soils is less than the cation exchange capacity. Nitrate, among the anion, remains mobile in soil solution and is susceptible to leaching by water passing through the soil [82].

9.2. Seed Treatment

Seed treatment or soil application of fertilizer is based on nutrient deficiencies in the soil, whereas foliar application is based on plant symptoms of nutrient deficiency [83]. Iron oxide (Fe_3O_4) NPs are known for their root elongation and growth promotion activity in the case of rice plants. However, above higher concentrations, they cause phytotoxicity [49]. Seedling growth promotion is seen in maize when treated with copper-chitosan (Cu-Cht) NPs [23]. Similarly, manganese NPs are reported to exhibit induction and enhanced nitrogen metabolism in non-nodulated plants [51]. Nano-TiO_2 promotes the growth of naturally aged seeds of spinach [52]. Nickle NPs show a prominent effect on the morphophysiological features of wheat [53]. The literature indicates that the various types of NPs thus can be used as potent seed priming and germination promotion agents.

9.3. Foliar Spray

In this method of application, liquid fertilizers are directly applied. Foliar fertilization provides speedy utilization of nutrients, and it takes less time to replenish the observed deficiencies than soil application. Comparative investigations of nanoparticle delivery to plants by spraying on the leaves versus soil amendment show that foliar application has substantial advantages for nanoscale nutrient uptake. For some of the immobilized nutrients in the soil, such as iron, manganese, and copper, the foliar application is more effective and economical compared to soil application. The limitations of this method are specific times (morning and evening) of spraying, as the stomata are open during these time periods. Additionally, there is the possibility of plant damage if the correct concentration of fertilizers is not applied [83].

9.4. Aeroponics Treatment

Aeroponics is an effective technique for the soilless cultivation of horticultural crop plants, in which nutrients are made available through the mist of oxygen in the growth chamber [84]. Here, nutrient materials are continuously made available to plants as foliar sprays or in the form of dust on the roots [85]. The gaseous exchange in plants occurs through the stomatal openings. Nanofertilizers can be much more beneficial compared to chemical fertilizers and can be used instead of micronutrients. These NFs increase nutrient efficiency by 2–20%. As the rate of nanosized nutrient uptake depends upon their size and shape. It is easier for smaller particles to penetrate the cuticle and for larger particles to pass through non-cuticle parts, such as hydathodes, stomata, and stigma. Thus, NFs can be designed to be the desired size and shape for use in aeroponics treatment based on the requirements and expected effect on the plant body [86]. The technique of using nanofertilizers for aeroponic treatments could be an efficient way of optimizing nutrient utilization with minimal losses.

9.5. Hydroponics Treatment

Hydroponics technology utilizes micronutrients in a soil-less manner, where water is the main supply medium. NFs can be made available to hydroponic systems in the form of stable colloids of nano-encapsulated plant nutrients. Micro- and macro-nutrients and other agrochemicals can be encapsulated in nanoparticles and used for the treatment of hydroponic systems [87]. The development of thorough and comprehensive knowledge must be the primary goal for the application of NFs in aeroponics and hydroponics based on detailed research. Nanotechnology-based approaches are, therefore, proving to be an effective methodology for nutrient utilization and negligible resource loss [80,82,87–89].

10. Mechanism of Uptake of NFs by Plants

The uptake, translocation, and aggregation of nanoparticles are subject to plant species, age, growth environment, and the physicochemical properties, functionalization, stability, and mode of delivery of nanoparticles. The pathways for the uptake and transportation of NFs are illustrated in Figure 4.

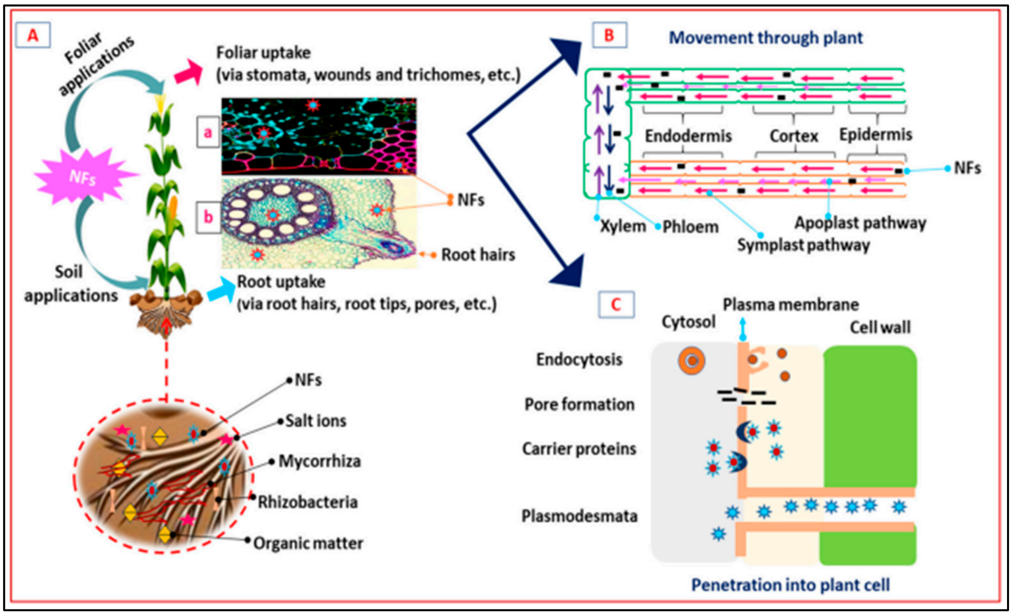

Figure 4. The uptake of nanofertilizers (NFs) via various channels and their translocation paths across multiple plant sections are depicted schematically. (**A**) NF traits affect absorption and translocation in plants: (a) T.S. of maize leaf and (b) T.S. of maize roots. (**B**) NFs may use apoplastic or simplistic pathways for moving up and down. (**C**) Various strategies were proposed for the internal distribution of NFs inside the cells through endocytosis and pore formation mediated by carrier proteins via plasmodesmata (Adapted with permission from Reference [56], published by Nanomaterials, MDPI, 2022).

NFs enter plant tissue either through roots or through upper parts. The size, shape, and interaction behavior of nanoparticles with cell walls are also crucial factors in the absorption of NFs in plants. The size exclusion limit of the cell wall (5–20 nm) acts as a barrier that limits the entry of larger particles into plant cells [90]. As a result of surface-functionalized nanoparticles, the pore size is enlarged, or a new cell wall pore is induced, improving nanoparticle uptake. The schematic translocation of the nanofertilizers in the cellular mechanisms of the plant systems is illustrated in Figure 5 below.

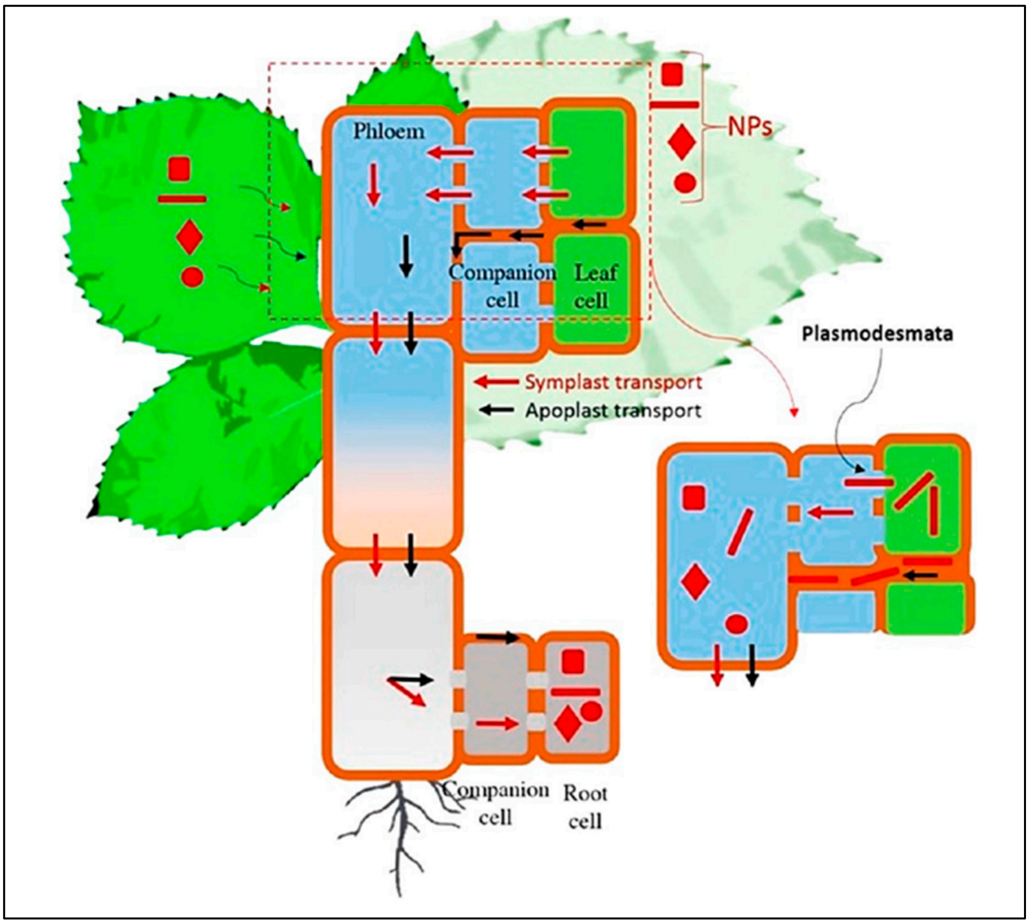

Figure 5. Mechanistic understanding of nanoparticle transport within plant cells. The representation describes how nanoparticles transport through apoplast and symplast pathways in plant cells, along with the pressure gradient or mass flow of the photosynthetic product. The inset represents the favorable transport of the nanostructure (rod shape) more through the apoplast pathway than the symplast pathway. NPs stand for nanoparticles. The color gradient in the phloem represents the mass concentration of photosynthesized nanoparticles. (Adapted with permission from Reference [16], published by Frontiers, 2016).

Other possible routes for the uptake of nanoparticles into plant cells include binding to carrier proteins through aquaporin, ion channels, and complex formation with membrane transporters, root exudates, or endocytosis [91,92]. Nanocarriers protect encapsulated nutrients from soil filtration and retain them in the soil around the roots. Encapsulated components may enter the soil network through hydrogen bonds, molecular forces, surface tension, or viscous forces, thus extending their spatial scale [93]. For foliar applications, NPs may penetrate through stomata or the base of the trichome in leaves or cuticles [91]. After entering the cell through stomatal openings, nanoparticles can be transported apoplastically or symplastically through the vascular system. The NPs may be transported via plasmodesmata from one cell to the other.

NPs are well known for their regulatory effect on plant growth. However, above certain concentrations, the negative impact starts to appear. The fate of nanoparticles and their eco-toxicity is an attribute of their unique physio-chemical properties. Among all the nanoparticles, almost all types of nanoparticles cause either phytotoxicity or genotoxicity depending upon their structure and functionalization. Phytotoxicity is directly related to the NPs availability to the plants and soil surrounding them. Thus, the unnecessary release of the NPs into the environment will surely lead to their increased interaction with the flora and fauna present in the ecosystem. This may trigger oxidative stress and will interfere with plant growth regulation and may lead to genotoxicity. To ameliorate these toxicities due to NPs, it is required to design globally accepted detection and characterization techniques. It is necessary to define the permissible limit of NPs considering every aspect of the application mode. Further research and appropriate funds are needed to understand the NPs' mechanism of interaction with environmental components and epigenetic factors. A thorough understanding of manufacturing techniques, detection and characterization, methods of application, dosage optimization, monitoring their release into the ecosystem, and risk assessment is required [94].

11. Current Status of Nanofertilizers in Crop Production

In recent agricultural practices, nanofertilizers are readily available in marketplaces, but specifically, agricultural fertilizers are still not designed by the leading fertilizer companies [95]. Studies of the nanofertilizers uptake from the soil, their bioavailability, and possible toxicity of several metal oxides NPs, such as Al_2O_3, TiO_2, CeO_2, FeO, and ZnO. NPs were supported intensively in the present decade for agricultural productivity [77]. Some of the leading producers of nanofertilizers are listed below (Table 4).

Table 4. Some commercial products of nanofertilizers [53,95–97].

Commercial Product	Content	Company
Nano-GroTM	Plant growth regulator and immunity enhancer	Agro Nanotechnology Corp., Miami, FL, USA
Nano Green	Extracts of corn, grain, soybeans, potatoes, coconut, and palm	Nano Green Sciences, Inc., Delhi, India
Nano-Ag Answer®	Microorganisms, sea kelp, and mineral electrolyte	Urth Agriculture, Monterey, CA, USA
Biozar Nano-Fertilizer	Combination of organic materials, micronutrients, and macromolecules	Fanavar Nano-Pazhoohesh Markazi Company, Tehran, Iran
Nano Max NPK Fertilizer	Multiple organic acids chelated with major nutrients, amino acids, organic carbon, organic micronutrients/trace elements, vitamins, and probiotics	JU Agri Sciences Pvt. Ltd., Janakpuri, New Delhi, India
Master Nano Chitosan Organic Fertilizer	Water soluble liquid chitosan, organic acid, salicylic acids, and phenolic compounds	Pannaraj Intertrade, Bangkok, Thailand
TAG NANO (NPK, PhoS, Zinc, Cal, etc.) fertilizers	Proteino-lacto-gluconate chelated with micronutrients, vitamins, probiotics, seaweed extracts, and humic acid	Tropical Agrosystem India (P) Ltd., Karnal, India
Nualgi Foliar Spray	Combining 12 essential nutrients loaded in nano-silica (henceforth NF-A)	Nualgi America, Inc., San Marcos, CA, USA [97]
NovaLand-Nano	Nano macro- and micro-elements for plant growth (henceforth NF-B)	Land Green & Technology Co., Ltd., Taiwan [97]
Titanium dioxide [TiO_2]—universal pigment [20 nm]	Titanium dioxide 99%	Land Green & Technology Co., Ltd., Taiwan
Silicon dioxide [SiO_2]—universal stabilizer agent [20–60 nm]	Silicon dioxide 99%	Land Green & Technology Co., Ltd., Taiwan
Manganese dioxide [MnO_2]—universal purifier [1–50 nm]	Manganese dioxide 99.9%	Land Green & Technology Co., Ltd., Taiwan
Selenium colloid [Se]—universal antioxidant [1–20 nm]	Selenium colloid 99.9%	Land Green & Technology Co., Ltd., Taiwan
Nano Urea (Liquid)	Nitrogen supplement for crops	Indian Farmers Fertilizer Cooperative Ltd., New Delhi, India
Poly olefin resin-coated urea	N supplement for plants	Japan
Neem Coated Urea	N supplement for plants	Aditya Birla Nuvo Ltd., Veraval, India
nano-organic compound fertilizer	Plant Growth promoters in vegetables, crops, and flowers	Lazuriton Nano Biotechnology Co., Ltd., Taiwan

Table 4. *Cont.*

Commercial Product	Content	Company
Hibong biological fulvic acid	Nano fertilizer, humic acid. Chitosan oligosacchairides $\geq$ 30 g/L, N $\geq$ 46 g/L, $P_2O_5 \geq$ 21 g/L, K2O $\geq$ 62 g/L, organic matter: 130 g/L	Qingdao Hibong Fertilizer Co., Ltd., Qingdao, China
Seaweed nano organic carbon fertilizer	NPK: 2–3–3, seaweed extract $\geq$ 5%, organic matter: 35%, humic acid $\geq$ 5%, amino acid $\geq$ 5%	Qingdao Hibong Fertilizer Co., Ltd., Qingdao, China
Supplementary powder (Nano capsule)	N, 0.5%; K_2O, 3.9%; Ca, 2.0%; Mg, 0.2%; S, 0.75%; P_2O_5, 0.7%; Fe, 0.03%; Cu, 0.007%; Zn, 0.004%; Mn, 0.004%;	The Best International Network Co., Ltd., Bangkok, Thailand
TAG nano (NPK, Zinc, PhoS, Cal, etc.) fertilizers	Proteino-lacto-gluconate chelated with micronutrients, vitamins, probiotics, seaweed extracts, and humic acid	Tropical Agrosystem India (P) Ltd., New Delhi, India
P, K	Fertilizer with a high content of P (30%) and K (20%)	Fosvit K30; Kimitec Group, Spain
B	Used as micronutrient	Nano Bor 20%; Alert Biotech, Nashik, India
Zn	Growth enhancer	Nano Zinc Chelate Fertilizer; AFME Trading Group, UK
Fe, Ca	Plant growth regulator and accelerator	Nano Iron and Calcium, Potassium Chelate Fertilizer; AFME Trading Group, UK
Nano micronutrient (EcoStar) (500) g	Zn, 6%; B, 2%; Cu, 1%; Fe, 6%+; EDTA Mo, 0.05%; Mn, 5%+; and AMINOS, 5%	Shan Maw Myae Trading Co., Ltd., Yangon, India
Nano ultra-fertilizer (500) g	Organic matter, 5.5%; nitrogen, 10%; P_2O_5, 9%; K_2O, 14%; P_2O_5, 8%; K_2O, 14%; and MgO, 3%	SMTET Eco-technologies Co., Ltd., Taiwan
Nano calcium (magic green) (1) kg	$CaCO_3$, 77.9%; $MgCO_3$, 7.4%; SiO_2, 7.47%; K, 0.2%; Na, 0.03%; P., 0.02%; Fe-7.4 ppm; Al_2O_3, 6.3 ppm; Sr, 804 ppm; sulfate, 278 ppm; Ba, 174 ppm; Mn, 172 ppm; and Zn, 10 ppm	AC International Network Co., Ltd., Germany
PPC nano (120) mL	M protein, 19.6%; Na_2O, 0.3%; K_2O, 2.1%; (NH4)2SO4, 1.7%; and diluent, 76%	WAI International Development Co., Ltd., Sungai Buloh, Malaysia
Plant nutrition powder (green nano)	N, 0.5%; P_2O_5, 0.7%; K_2O, 3.9%; Ca, 2.0%; Mg, 0.2%; S, 0.8%; Fe, 1.0%; Mn, 49 ppm; Cu, 17 ppm; and Zn, 12 ppm	Green Organic World Co., Ltd., Surin, Thailand

In the present century, smart agriculture is a way to achieve priority of short- and long-term development in the countenance of climate change and serves as a link to others [98]. It seeks to support countries and other functional aspects in securing the necessary agricultural functions [99].

Recently, studies have focused on understanding the effect of nanofertilizers on plants based on the growing conditions in the farming system. Nanofertilizer encourages to development of plant growth parameters, such as the height of plants, number of leaves per plant, leaf area, the difference in fresh and dry matter content, chlorophyll content, roots, and rate of photosynthesis. This results in keen consideration of an increase in the yield due to a higher translocation rate of photosynthesis to various parts of the plant as compared to chemical fertilizers. Some specialists are focusing on improving the nutrient efficiency of plants depending on nanotechnology (nanofertilizers) [100–102]. The studies related to growth parameters need firm acceptability of the nanofertilizers followed by thorough field experiments. Thus, assisting the researchers and policymakers in the recommendation of the application of specific dosages in the actual fields on a bulk level without causing a significant hazardous effect on the environment would be required.

12. Fabrication of Safe Nanofertilizers

There is an urgent need for designing and fabricating NFs with the desired catalytic activity. This is due to various factors, such as decreasing crop yield, loss in organic content of the soil, increased multi-nutrient deficiency, and adverse climate. NMs or NPs for nanofertilizers can be synthesized by different approaches, top-down, bottom-up, or using biological approaches [5,103]. NPs can bind cargo molecules and control their release, for example, micronutrients making them an efficient system for target-specific delivery of loaded nutritional molecules [104,105]. Thus, the release of fertilizers over a longer period minimizes nutrient loss while considering environmental safety [106,107].

Several physical and chemical methods have been reported for the synthesis of NFs. The inert gas condensation method [108,109], aerosol synthesis method [110], high energy ball mill [111,112], bottom-up and top-down approaches [113,114], mechanical attrition, mechanical alloying [115], etc., are examples of physical methods. Methods for chemical synthesis of NPs include chemical vapor deposition [116], chemical precipitation [117], a sol-gel technique [118], electrodeposition [119], photochemical synthesis [120], etc. Unfortunately, these methods have some major disadvantages, such as source and precursor incompatibility, evaporation rate, flow rate, gas composition, impurities, costly production, high-temperature requirements, etc. [121]. To overcome these drawbacks, the methods of NPs and NMs fabrication must be designed in such a way that they are safe for operating personnel. In addition, they must cause no harm to humans or the environment. For this, biosafety measures must be followed when manufacturing NPs [122,123].

In order to prevent any harm to the ecosystem and humans due to chemical or physical methods, an alternative biological method of nanofertilizer synthesis is used [124]. Biological methods of NFs synthesis have received increasing attention to cope with the growing need and demands to develop reliable, environmentally safe, and non-toxic methods [125]. Biosynthesized NPs have a higher surface-to-volume ratio, higher catalytic reactivity, and better contact between biomolecules and metal salts. Several biomolecules and organic compounds are involved in the stabilization of nanoparticles, including proteins, enzymes, sugars, and various phytochemical compounds, such as terpenoids, phenolics, etc. [14,122,124,126]. The biosafety of NFs is an integral part of precision agriculture for a sustainable future [127]. Despite their wide applications, the impacts of NPs on humans and the environment are unknown. There is a need not only to understand their adverse effects but also to develop guidelines for their agricultural applications [128]. Biocatalytic activity and secured applications of NPs are attributed to their size and structure, the precursor used, the method of synthesis, the biomaterial used for stabilization, etc. As a result, it becomes imperative to determine the active concentration, optimum size, and shape to evaluate the toxicity effects of NPs [76,122,129].

13. Challenges in Nanofertilizers Application

In agriculture, nanomaterials can be applied as nanofertilizers and as carriers of fungicides/pesticides. NFs are used as growth promoters, soil fertilizers, and to improve the quality and quantity of agricultural produce [130]. NFs are one of the key components of nano-based precision and sustainable farming and field applications [38,131]. Less efficient utilization of chemical fertilizers leads to the accumulation of chemicals in water bodies, causing eutrophication. In order to overcome this, nano-based products are becoming increasingly popular for field applications in agriculture. For field application of NFs, it is deemed necessary to thoroughly evaluate their optimum activity and concentration for the most effective results considering high yields and low losses [96]. To reduce the likelihood of harm to other biotic factors in the ecosystem, residual amounts of NFs should be quantified during in planta studies [132].

Meanwhile, safety measures should be designed and implemented at the same time. This is in order to define the type, size, and shape of nanoparticles that can be used for crop production. Along with solubility, stability, surface reactivity, and charges, these factors perform a major role in agricultural production. The reactivity of NFs in plants is still non-specific and irrespective of the plant species under investigation possibly because there are no defined protocols for their field applications. Inevitably, the mechanism of NFs and other nano-based agrochemicals and their absorption in plants is still not well understood [96,133]. Research groups, sponsoring organizations, policymakers, and leaders of the private and public sectors working in related fields must heed the call to familiarize themselves with specific guidelines for the use of NFs that maintain farmers at the center of the status quo [134].

14. Prospects and Future Directions

Extensive research is required to understand the characteristics of nanofertilizers, the mechanism of action of nanofertilizers concerning the mode of application and type of NFs and their impact on the plant. When the concentration of NFs exceeds a certain limit, it can negatively affect plants, such as stunting their growth and yield. Hence, optimization of the dose quantity of different NFs for different plants is very critical. A systematic and in-depth analysis concerning the possible health impacts, clearance, and safe disposal of NMs can lead to enhancements in the designing of additional applications of nanofertilizers [135].

Thus, it is strongly recommended that future research should be focused on defining the dosage for field application of nanofertilizers on a commercial level. The technological development should primarily focus on the farmer-centric recommendations of nanofertilizers. Furthermore, it is expected that the development and validation of nanofertilizers will contrast the production of chemical fertilizers, promoting the nanofertilizer industry. This will help policymakers to decide the dosage and time for nanofertilizer application.

The delivery of nanofertilizers as next-generation fertilizers for agricultural applications faces difficulties even though they are both economically and environmentally sustainable. Along with scaling up the procedure for large-scale distribution, it is necessary to guarantee the availability of raw materials for the synthesis of NFs on an industrial scale. Once these issues are resolved, it will be simple to produce commercially viable NFs using the appropriate processes, which will pave the way for a day when even a minimal amount of use of these fertilizers will result in the desired higher agricultural yield [136,137].

To ensure ongoing development and technological commercialization, an integrated analysis of these smart fertilizers based on nanotechnology can also be carried out. If slow release nanofertilizers can be advanced to have a remarkable impact on the environment, energy, and economy, it will be a major success. Additionally, to make nanofertilizers an economically feasible endeavor, research and technological interventions that concentrate on the optimization of manufacturing processes and the search for affordable non-polluting or biodegradable continuous matrix materials are advised.

To enable efficient restoration, approaches that can sensitively and selectively detect and monitor environmental contaminants in various biological matrices are required. Additionally, it is critical that governments and businesses support research teams that are testing the safety of nanomaterials using various animal models. This research will serve as the foundation for more effective regulations, which are still insufficient or nonexistent in certain nations [136,137].

15. Conclusions

The world population is increasing, and so is the need to produce more food. Nutrient deficiency is a major cause of low crop productivity and significant economic losses in the agriculture sector. Even though chemical fertilizer applications can boost crop productivity, it is not a viable option in the long run. A vital effort of current agricultural research is to find an alternative to chemical fertilizers, which would enable a more environmentally friendly approach to agriculture.

In recent years, nanotechnology has emerged as a significant component of the agriculture industry. Smart fertilizers based on nanotechnology have been created to enhance agricultural yields and improve soil health. Furthermore, an integrated study of these nano-based smart fertilizers can be undertaken to assure ongoing technological improvements and commercialization. This analysis should concentrate on optimizing fabrication techniques and identifying non-toxic or biodegradable, low-cost continuous matrix materials to make nanofertilizers economically viable businesses.

The potential implications of this research are enormous, particularly in terms of improving environmental sustainability and energy efficiency in farming methods around the world. Slow release nanofertilizer solutions, for example, might cut water usage by up to 20% while increasing nutrient uptake by up to 40%. Furthermore, when improved production techniques are applied on a large scale in various nations across the world, there will be less need for chemical-based fertilizer applications, resulting in decreased carbon emissions related to agricultural activities.

It is expected that nanofertilizers will change the way we think about sustainable farming practices around the world, leading to more efficient use of resources, such as water and land, while lowering reliance on hazardous chemicals that can harm our ecosystem over time. Slow release nanofertilizers may really have a phenomenal impact not only on our environment but also on energy consumption levels and economic growth in many locations throughout the world, with sustained support from both public institutions and private corporations, universities, farmer groups, and so on.

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