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Review

Overview on Recent Developments in the Design, Application, and Impacts of Nanofertilizers in Agriculture

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Abstract: Nutrient management is always a great concern for better crop production. The optimized use of nutrients plays a key role in sustainable crop production, which is a major global challenge as it depends mainly on synthetic fertilizers. A novel fertilizer approach is required that can boost agricultural system production while being more ecologically friendly than synthetic fertilizers. As nanotechnology has left no field untouched, including agriculture, by its scientific innovations. The use of nanofertilizers in agriculture is in the early stage of development, but they appear to have significant potential in different ways, such as increased nutrient-use efficiency, the slow release of nutrients to prevent nutrient loss, targeted delivery, improved abiotic stress tolerance, etc. This review summarizes the current knowledge on various developments in the design and formulation of nanoparticles used as nanofertilizers, their types, their mode of application, and their potential impacts on agricultural crops. The main emphasis is given on the potential benefits of nanofertilizers, and we highlight the current limitations and future challenges related to the wide-scale application before field applications. In particular, the unprecedent release of these nanomaterials into the environment may jeopardize human health and the ecosystem. As the green revolution has occurred, the production of food grains has increased at the cost of the disproportionate use of synthetic fertilizers and pesticides, which have severely damaged our ecosystem. We need to make sure that the use of these nanofertilizers reduces environmental damage, rather than increasing it. Therefore, future studies should also check the environmental risks associated with these nanofertilizers, if there are any; moreover, it should focus on green manufactured and biosynthesized nanofertilizers, as well as their safety, bioavailability, and toxicity issues, to safeguard their application for sustainable agriculture environments.

Keywords: nanofertilizers; types of nanofertilizers; design and formulation; plants; sustainable agriculture; environment

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1. Introduction

In recent agricultural applications, environmentally friendly technology has been gaining importance as a substitute for traditional pesticides and fertilizers. Nanotechnology provides a viable alternative solution to overcome the drawbacks of conventional use of fertilizers in agriculture. Therefore, the use of nanoparticles (NPs) is increasing tremendously in agriculture. This review provides a unique perspective on current advances in the design and composition of NPs as nanofertilizers, as well as their other agricultural uses. This review also describes recent investigations on NP–plant interactions, and their effects on crop plants. Figure 1 shows a graphical illustration of this review.

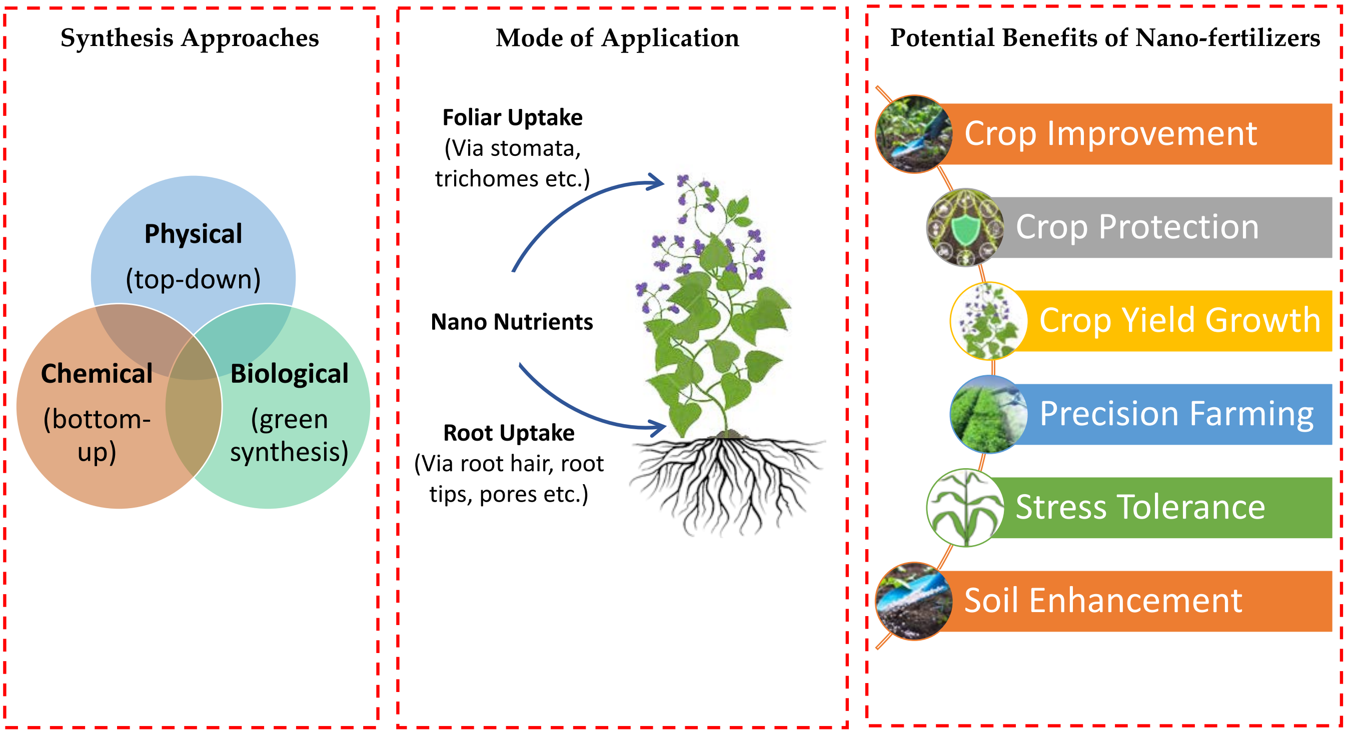

Figure 1. Graphical illustration representing the overview of the manuscript with key highlights.

Nanofertilizers are essential to reduce the use of inorganic fertilizers and reduce their antagonistic effects on the environment, as they are highly reactive, can penetrate the epidermis, and enable slow release and dispersion, thus improving nutrient-usage efficiency. They can also help to alleviate heavy-metal toxicity and abiotic stress. Contrarily, there are also reports on the toxic effects of NPs in different plants due to their deposition on the cell surfaces and in organelles, inducing oxidative stress [1]. For example, a study reported the detrimental effects of NPs, i.e., suppressing plant development, inhibiting chlorophyll synthesis, reducing photosynthetic efficiency, etc. The effects of NPs might be favorable or detrimental depending on the plant species, type of NPs employed, and concentration [2]. CuO NPs have been reported to induce cytotoxic and genotoxic effects as they penetrate cells and their different compartments [3]. Another report stated that NPs can penetrate the cell and disrupt the chloroplast and mitochondrial electron-transport system (ETS) cycle, triggering an oxidative burst due to an increase in reactive oxygen species (ROS) [4,5]. Many plant species are susceptible to oxidative stress caused by metal and metal-based NPs. ROS produce oxidative damage to chloroplast and mitochondrial DNA, which induce changes in the encoded protein, resulting in the malfunction and complete inactivation of the specified proteins [6]. The exposure of AgNPs to *Ricinus communis* seed increases ROS generation, which is implicated in the antioxidant defense system (superoxide dismutase enzyme (SOD), peroxidase (POD) activity, and phenolic acids) [7,8]. ZnO NPs have been reported to dramatically decrease ryegrass biomass, causing root-tip shrinkage and root epidermal and cortical cells to become heavily vacuolated or collapsed. Individual ZnO NPs were observed in the apoplast and protoplast of the root endodermis and stele, as well as the root surface. At a lower treatment of ZnO NPs, the translocation factor of Zn from root to shoot remained low [9]. The accumulation of CeO_2 NPs has been reported in plants without alteration, posing a risk to human health [10]. A study performed on grassland soil reported the negative effects of metal oxide NPs on soil bacterial communities [11]. These values, however, are extremely high when compared to the current real environment. However, there is a need to investigate the impacts of manufactured NPs on the rhizosphere microbiome and adopt ways to combat their potential adverse effects on agricultural soils. An interesting study was found that presented a simple, cost-effective, and practically viable wastewater treatment that utilized renewable Fe_3O_4@PW-αCFs as a supermagnetic bioadsorbent for the removal of large quantities of ENMs, including CuO, CoO, and ZnO, from various real-world wastewater samples [12]. Moreover, information about the limitations and future outlooks of using nanofertilizers as an alternative to conventional fertilizers has also been discussed.

Nanofertilizers can be composed of different NPs, i.e., carbon-based, metal oxides, and other nanoporous materials, depending on their combination and compositional properties [13]. They can be prepared via biological, chemical (bottom-up), or physical (top-down) approaches [14]. Another emerging technology that uses clean, non-hazardous, and especially environmentally friendly procedures, such as green nanotechnology or biofabrication, can also be employed to synthesize nanofertilizers, as opposed to the chemical and physical methods currently used to make nano-products [15,16]. Nanofertilizers offer a wide range of features such as the gradual and controlled release of various macro- and micro-nutrients to plants with particular concentrations, increased surface area, and appropriate size [17]. Plants respond according to the nutrients absorbed from soil that are released by these nanofertilizers. Different kinds of nanofertilizers, i.e., macronutrient nanofertilizers, micronutrient nanofertilizers, and nanomaterial-enhanced fertilizers, can be developed based on the specific nutrient supplies [18]. These nanofertilizers are attributed to improvements in solubility, in the dispersion of insoluble nutrients, in phytoavailability, and in targeted delivery to minimize nutrient losses [19]. They also work as influencers for several vitamins, proteins, coenzymes, purines, and photosynthetic pigments for plant photosynthesis and respiratory systems [20,21].

This review provides a novel overview on recent developments in the design and formulation of nanoparticles used as nanofertilizers, their types, their mode of application, and their potential impacts on agricultural crops. The main emphasis is placed on the potential benefits of nanofertilizers, and we highlight the current limitations and future challenges related to the wide-scale application of NPs before field applications. A recent study highlighted the cost and ecological effects of nanofertilizer application. In that study, the field observations based on an average of three consecutive rice-growing seasons revealed that nano-Fe^{III}-tannic acid-modified waterborne polyacrylate-coated urea outperformed the most widely used polyurethane-coated urea in terms of agronomic, environmental, and ecosystem economic performance. Nano-Fe^{III}-tannic acid-modified waterborne polyacrylate-coated urea increased yields by 8.3%, increasing farmer benefits by nearly 10% and net ecosystem economic benefits by nearly 11%, and decreased reactive nitrogen losses by nearly 24% when compared to conventional farmers' fertilizer application [22]. Moreover, another subsequent field study on wheat reported the single use of nano-Fe^{III}-tannic acid-modified waterborne polyacrylate-coated urea, with a nitrogen rates lowered by one-third having the potential to maintain a high grain yield and high net ecosystem economic benefits of wheat crop relative to those of traditional nitrogen practices; in the meantime it reduced reactive nitrogen loss by 58.8% [23].

2. Scope and Importance of Nanofertilizers

In modern agriculture, nanofertilizers are important due to their unique formulation characteristics and delivery mechanisms with optimum phytoavailability [24,25]. The small size of nanofertilizers with a high surface–mass ratio enables an increase in the absorption of nutrients via plants roots [26]. Moreover, they can also be absorbed with different dynamics relative to their bulk particles or ionic salts and have significant benefits [27–29]. These nanoscale fertilizers lower nutrient loss due to leaching, avoid chemical modifications, and help to improve nutrient-use efficiency and environmental quality [30,31].

3. Recent Developments in Designing Nanofertilizers

The major challenge in the upcoming few years would be the soil-fertility and nutrient management of crops due to the extensive use of chemical fertilizers and existing agricultural practices. The application of traditional fertilizers usually results in the significant loss of water bodies, lower crop nutrient productivity, and unfavorable environmental impacts. Thus, an environmentally friendly and innovative fertilizer method, as compared to synthetic fertilizers, is required to boost all production in our agriculture system. At this time, the usage of nanohybrid constructs such as nanofertilizers has gained a lot of interest for generating sustainable agricultural yields while also protecting the environment through smart pesticide delivery [30,32]. Engineered nanohybrid structures such as nanofertilizers have piqued the curiosity of scientists all over the world because of their useful functional assembly and controllable physicochemical features. In this regard, nanotechnology has revolutionized the design and manufacture of materials by altering their qualities and attributes to meet a variety of requirements. It is reported that the application of nanofertilizers boosted crop efficiency compared to ordinary chemical compost [33]. In addition, efforts to improve the reaction of nanofertilizers to the environment in order to detect humidity, moisture, temperature, pH, etc. have recently been undertaken [34,35]. In this context, nano-biotechnology is gaining traction as a possible alternative strategy for providing nutrients to crops in a regulated manner, with the potential to change agricultural systems. Additionally, nanofertilizers based on engineering NPs can help in the nutrition management of various crops by increasing their abiotic stress tolerance and agricultural yield [21]. Based on the latest research, this section highlights the design, interaction, and impacts of nanofertilizers with edible plants as shown in Figure 2.

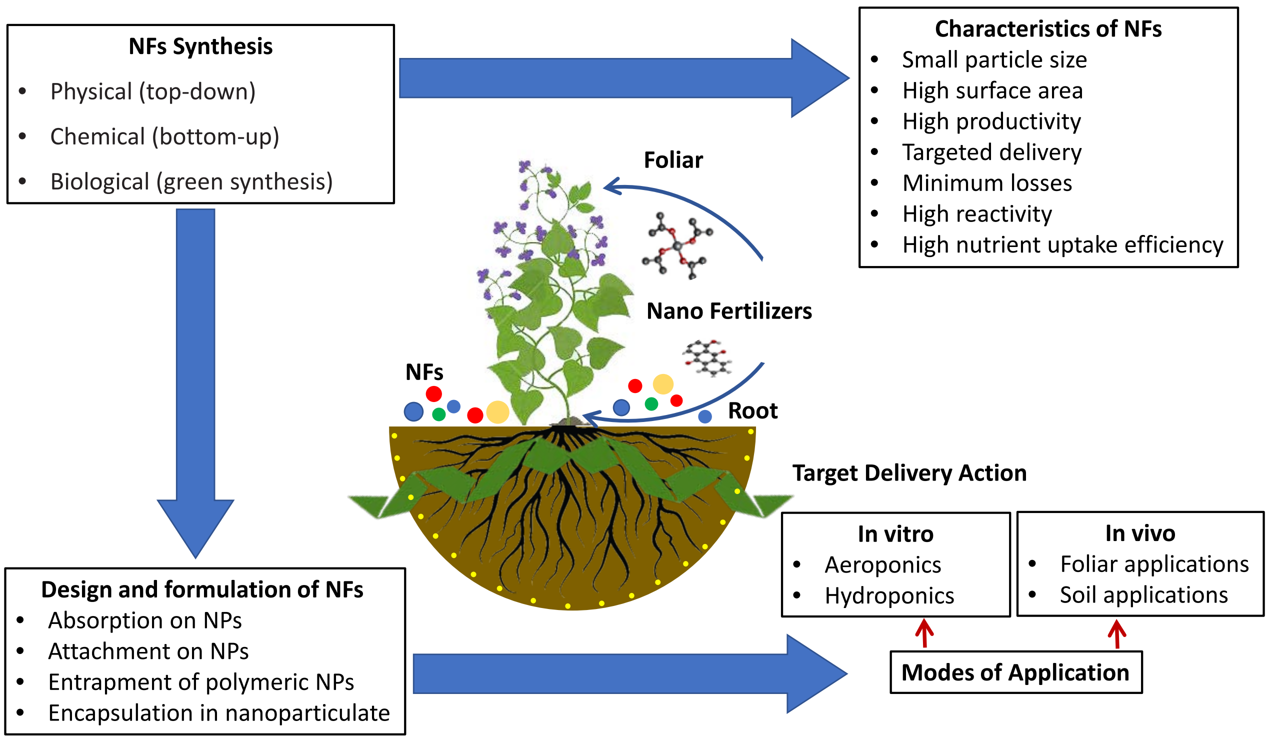

Figure 2. Overview of design and formulation of nanofertilizers based on the respective synthesis method and their characteristics.

3.1. Design and Formulation of Nanofertilizers

The usage of nutrient-rich NPs is a key component of the nanoscale fertilizer technique. Physical (top-down) and chemical (bottom-up) processes can both be used to synthesize the nanomaterials. These two approaches can be further categorized in three methods, including physical, chemical, and biological. The chemical synthesis of NPs is the focus of the bottom-up strategy, whereas the physical synthesis falls under the top-down approach and biosynthesis. Nanomaterials have been produced and employed as nanofertilizers in several studies [36–39]. Basic materials such as zeolites, copper (Cu), silver (Ag), aluminum (Al), potassium (K), carbon (C), nitrogen (N), zinc (Zn), silica (Si), magnesium (Mg), iron (Fe), sodium (Na), manganese (Mn), and calcium (Ca) can be nanostructured and used as nanofertilizers. Some other plant-based materials such as grape plant substrates [40] and banana peels [41] are used in the synthesis of nanofertilizers. Natural zeolite (which is made up of more than 50 minerals) has recently been converted into nanofertilizers. This is due to its extensive availability and low price [42]. Nanofertilizers could be customized or designed to treat a specific nutrient scarcity in plants. This is possible because atoms on the surfaces of NPs can be aligned to attain desirable properties [43]. Nanofertilizers can be prepared by following methods:

1. Absorption on NPs.
2. Attachment on NPs.
3. Entrapment of polymeric NPs.
4. Encapsulation in nanoparticulate.

Nutrient encapsulation is the most common way of synthesizing nanofertilizers with nanomaterials. Specific nutrients have been contained in nanoporous materials covered with a thin film of polymer at the nanoscale, in recent years. The encapsulation of a beneficial microbe, such as fungus or bacteria, has demonstrated the ability to increase N, P, and K availability in the root zone [44]. Conclusively, the term nanofertilizers refers to a nanomaterial that is either a plant nutrient (micro- or macronutrients) or a transporter of a plant nutrient. Additionally, nanofertilizers are the nutrients that have been encapsulated or coated with nanomaterials and can be synthesized from various synthetic materials (modified synthetic fertilizers) or green synthesis (plants extracts) through numerous mechanical, biological, and chemical methods [45].

Nanofertilizers can be categorized into three groups based on their preparation method: (1) nanoscale fertilizer, trivial in size like NPs, similar to a conventional fertilizer; (2) nanoscale additive fertilizer, an average fertilizer with additional nanomaterial; and (3) nanoscale coating fertilizer, whereby nutrients are surrounded by nanofilms or introduced into the nanoscale pores of a host material [46]. Nanocomposite structures containing encapsulated nutrients or retained in nanopores within a host material (such as clays) have been utilized to control nutrient release [47–50].

3.2. Characteristics of Nanofertilizers

Nanofertilizer synthesis based on modern formulation enhances the availability of specific nutrients, bioavailability, solubility, and the distribution of insoluble nutrients to minimize nutrient losses [19]. In one study, to boost target-specific plant absorption efficiency, nanomaterials were first produced using several engineering techniques and then encapsulated with the essential nutrients [14]. Nanofertilizers must have superior chemical stability, higher surface tension, increased absorbability, mobility, higher pH lenience, and ionizing power [51]. Due to these optimistic properties, as shown in Figure 3, nanofertilizers can possess a slow-release function, controlled and targeted delivery of various nutrients (micro and macro) to plants at a high surface area, specified concentrations, and suitable size, according to reports [17]. Nanofertilizers can (1) enhance nutrient-usage efficiency (NUE), (2) lower the chemical load to the soil, (3) lower the application frequency, and (4) minimize the negative effects of typical bulky fertilizers [52]. In other words, nanofertilizers are used to enhance the soil fertility, product quality, and bioavailability of plant nutrients [45]. These characteristics of nanofertilizers make them exceedingly suitable for their use in modern agriculture [19,51].

Nanomaterials such as nanofertilizers, owing to their extremely small size in nanometers [53], have greater absorption and retention capability when compared to bulky, synthetic chemical fertilizers. Due to greater surface area, nanofertilizers encompass more nutrients and distribute them steadily as per the requirement of crops without any harmful impacts [54]. The primary drivers of environmental devastation caused by synthetic fertilizers are lower nutrient absorption efficiency and waste of nutrients through gaseous emissions, volatilization, leaching, etc. [55,56]. However, the detrimental environmental effects are reduced by the slow and steady distribution of nutrients from nanofertilizers.

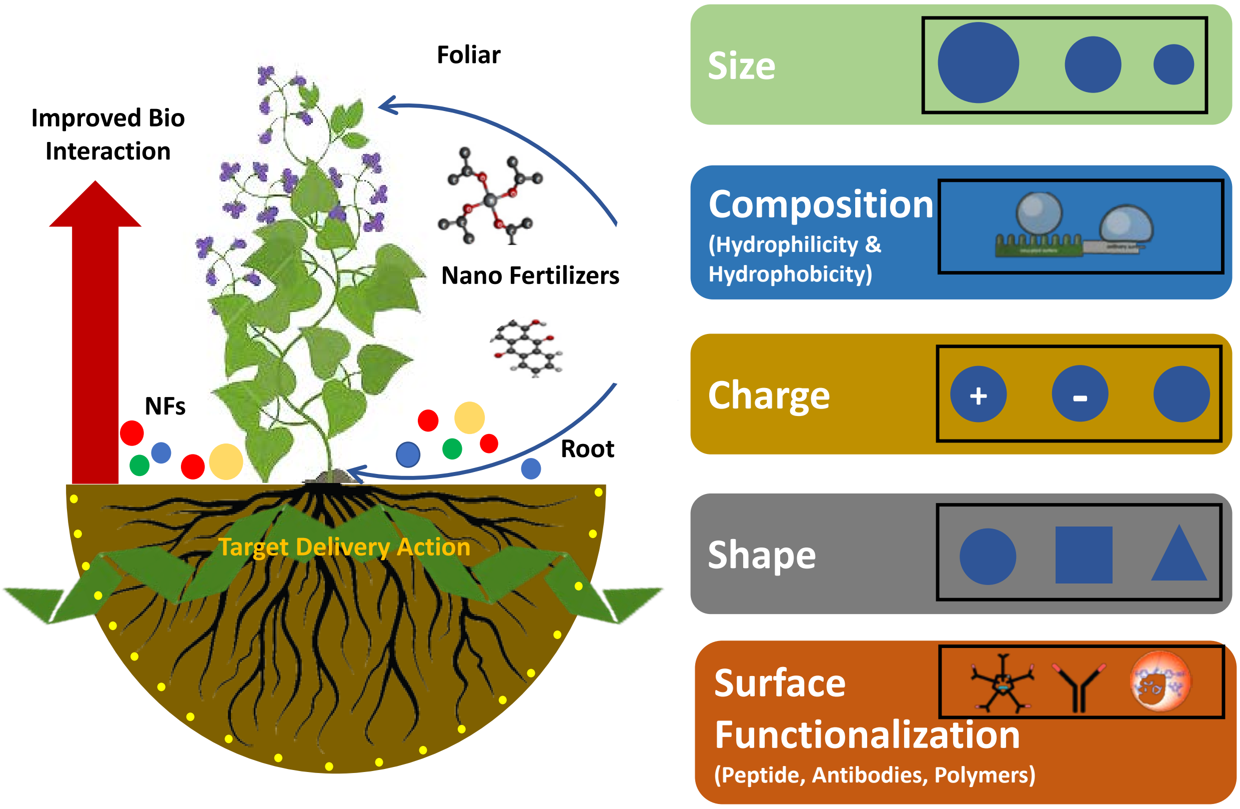

Figure 3. Illustration of nanofertilizer characteristics.

Based on the literature, plant cell walls with a pore size of 5–20 nm are used as an obstacle for self-protection. Only external agents with a smaller diameter than plant cells can get through the size exclusion limits (SELs) and generate host carriers for essential nutrients, which are normally provided in the soil or on the leaves' surface [21]. Moreover, some other NPs can also be coupled to form intracellular structures in cell walls, allowing them to enter and improve genetic features [57]. In comparison to conventional water-soluble fertilizers, nano-assisted fertilizers have demonstrated outstanding transport qualities through plant cells/tissues with regulated mobility. The roots of *Arabidopsis thaliana* plants have been reported to be penetrated by SiO_2 NPs with diameters varying between 50–200 nm [58]. Whereas TiO_2 NPs with a diameter ranging from 36–140 nm were unable to pass the root of wheat parenchyma; however, NPs with a diameter of 36 nm were able to cross the barriers in wheat to deliver to the other areas of the plant [57]. When TiO_2 NPs with a size of 30 nm were applied to maize, they did not translocate due to a larger diameter than the root cell (6.6 nm) [59]. In another study, the penetration of TiO_2 NPs into wheat plants was carried out, and it was observed that certain NPs penetrated through root cells, while others did not. The NPs were polydisperse, with the particle sizes less than 20 nm able to penetrate through roots, whereas the bigger ones agglomerated in the soil and were unable to penetrate [60]. This suggests that particle size is a crucial factor for the translocation and absorption of NFs in the plant system.

In addition to particle size, the surface charge of NFs also influences their uptake and transport in plants in a similar way [61]. The roots of *Arabidopsis thaliana* released mucilage, a sticky viscous fluid that facilitated the uptake of positively charged gold NPs (12 nm) through the roots; however, the same size (12 nm) of gold NPs with a negative charge failed to do so [62].

3.3. Controlled Release and Targeted Delivery

Nanofertilizers have the ability to foster sustainable agriculture and improve overall agricultural yield, primarily by enhancing the nutrient-use efficiency (NUE) of both the fields and greenhouse crops. When used alone or in conjunction with organic or synthetic fertilizers, nanofertilizers can release nutrients at a slow and consistent rate. They can release nutrients in 40 to 50 days, compared to 4–10 days for synthetic fertilizers. As a result, after field application, chemically synthetic urea fertilizer can quickly lose more than 70% of its nitrogen (N) content due to volatilization and leaching, leaving behind a lesser amount of 20% to be available for plants [63]. Recently, N was synthesized in the form of NFs by encapsulating urea with hydroxyapatite NPs, resulting in delayed N release to plants. Likewise, in rice (*Oryza sativa* L.) fields, the use of nanohybrid urea (a modified form of hydroxyapatite) may release N up to 12 times slower than synthetic urea, and it can improve grain production at half the pace of conventional urea. N-nanofertilizers have recently been prepared by encapsulating/coating urea with hydroxyl apatite NPs for the progressive release of N to plants [48]. Phosphorous (P)-based nanofertilizers help in the direct absorption of P by plants, resulting in lower P loss [64].

The targeted delivery and controlled release of nano-agrochemicals can effectively be achieved via surface modification. In agriculture, nanofertilizers have a major impact on seed growth and germination. They can quickly permeate to the roots and soil, enhancing nutrient release, the production of dry matter, and chlorophyll formation; this, subsequently, helps the plants to grow faster [65,66]. Agglomeration is a natural tendency of various nanomaterials which decreases their efficiency and encourages the reactive oxygen species formation [67]. To avoid agglomeration, various surfactants such as cellulose and gluconic acid; chemicals such as oleylamine and chitosan; and the polymers poly(methacrylic acid) (PMAA), poly *N*-vinyl-2pyrrolidone (PVP), poly (methyl methacrylate) (PMMA), and polyethylene glycol (PEG) are commonly used for stabilization [68,69].

3.4. Modes of Application

NFs must be applied in a way in which they can retain their vigorous properties such as efficiency, time-controlled release, solubility, targeted delivery, stability, and less toxicity. Their effectiveness and impact are primarily influenced by their mode of application for safe delivery and disposal. Various methods for the delivery of nanofertilizers to plants are listed below.

3.4.1. In Vitro Methods

Aeroponics and hydroponics are both soil-less (without soil) methods. In aeroponics, the plant's roots are suspended in the air, and the nutritional solution is continuously sprayed in the form of mist. The entire environment near the roots can easily be controlled in this way. However, this process is not widely used as it demands significant amounts of nutrients for sustainable, rapid growth [70]. On the other hand, hydroponics, also known as the "solution culture" method, involves naturally soluble inorganic salts. The roots of the plants are immersed in a nutrient-rich solution by giving special attention to the pH, oxygen availability, and volume of the solution. In some commercial applications, supporting materials (sand, gravel, etc.) are also used. The old solution is withdrawn from one end while the nutritious solution is discharged from the other. The downsides of this strategy include frequent pathogen assault and high moisture rates, which can cause soil-based plants to wilt excessively [71].

3.4.2. In Vivo Methods

In vivo methods are further categorized into foliar application and soil application.

In foliar application, micronutrients are supplied directly to the leaves by spraying liquid fertilizers. A positive point of this strategy is that it reduces the interval between fertilizer application and nutrient uptake by plants in their exponential development phase. In contrast to the method of soil application in which micronutrients such as Fe, Mn, and Cu are more soaked on the soil particles, it also improves the uptake of these mentioned micronutrients [72]. As nutrient intake involves the cells of the leaf epidermis and stomata, agronomic benefits might be observed when employed for nanofertilizer application. As stomata are involved, the time it takes for stomatal pores to open must be considered. Nitrogen, potassium, and phosphorus (NPK) with combination of NPs were studied for their foliar application. The application of Nanochitosan-NPK fertilizer on wheat produced significant results by enhancing the mobilization index, crop index, and harvest index. Nanocomposite foliar uptake in watermelon exhibited the same results [73]. Similarly, encouraging outcomes in terms of stem height, number of branches, diameter, and seed productivity were observed upon foliar application of gold NPs [74]. In addition to particle size, other aspects such as plant species, working environment (gas, light, water), and nanoparticle delivery methods should be considered for optimal foliar uptake [75].

The soil application or uptake of NFs at the root level are influenced by various parameters such as nanoparticle size, acquaintance situations, plant structure, rhizospheric activities, and crop phenology. Soil-applied nanofertilizers enter the roots through their surface and pass through a series of hurdles before reaching the plant's vascular system. The cuticle layer of roots is the initial barrier (which is similar in composition to the leaf cuticle layer). After penetrating the cuticle, NPs permeate the root epidermis. Upon reaching the root epidermis, they can either take the apoplastic or symplastic route. In the apoplastic route, nanofertilizers first penetrate cell wall pores and, subsequently, translocate into intercellular gaps [61]. The apoplastic pathway is restricted by the cell wall diameter (5–20 nm), which prevents huge NFs (>20 nm) from entering. Despite this, cell death caused by NPs may expand the pore size. However, the Casparian band, which inhibits NPs from entering the vascular cylinder directly, is a major hurdle in the apoplastic route [76], while ZnO-nanofertilizers with a size of 30 nm were found in the vascular system through a maize-cross root intersection [77]. Meanwhile, in the symplastic pathway, the plasmodesmata path is employed by NPs from one cell to another [61,78]. NPs obtain access to the aboveground portion of the plants through the central cylinder, followed by the xylem's transport stream [57].

The studies conducted by researchers for the improved growth of various crops using nanofertilizers could open new horizons in sustainable and environmentally friendly agricultural practices [79]. A few more studies performed in this context are given in Table 1, based on the characteristics of nanofertilizers along with their mode of action.

Table 1. Literature related to the design and formulation of nanofertilizers and their mode of application on plants.

Types of Nanofertilizers (NFs)	Formulation Method; Characteristics	Aim/Purpose	Mode of Application	Reference
ZnO NFs	Hydrothermal method; hexagonal in shape with crystal size of 33 nm	To investigate impact on maize (*Zea mays*) production and Zn-deficient soils	Soil and foliar	[80]
ZnO NPs	Wet chemical method; undefined spherical shape with particle size of 2.4–3.7 nm	To increase the yield of soya bean and wheat with minimum fertilizer loss	Soil and foliar	[81]
Chitosan-silicon NFs	Ionic gelation method; 360.5 ± 1.34 nm mean hydrodynamic diameter	To evaluate effect on yield, seedling growth, stored food remobilization, chlorophyll content, and antioxidative-defense status of maize (*Zea mays* L.)	Foliar	[82]
Urea-doped calcium phosphate NPs	Precipitation method; disk-shaped with particle size of 13.8 nm	To maintain the quality and yield of durum wheat (*Triticum durum* L.)	Soil	[83]
Sulphate-supplemented NPK NFs	Ionic gelation method; particle size of 450.5 nm and 145.5 nm using 1% and 0.25% chitosan solution, respectively	To examine growth as well as nutrient uptake in maize (*Zea mays* L.)	Soil	[84]
Chitosan based CNK NFs	Polymerization followed by incorporation with potassium (CNK); spherical in shape with particle size of 39–79 nm	To investigate impacts on soil conditioning and yield production of maize	Soil	[85]

Table 1. *Cont.*

Types of Nanofertilizers (NFs)	Formulation Method; Characteristics	Aim/Purpose	Mode of Application	Reference
Nano-NPK	Top-to-bottom chemical approach; uncontrolled shape with particle size of 8–9 nm	To examine the effect on quality, yield, and growth of cucumber (*Cucumis sativus* L.)	Soil	[86]
Iron, manganese, and zinc oxides NFs	Microwave-assisted hydrothermal method; average particle size of 20–60 nm	To investigate the effect on production and growth of squash *Cucurbita pepo* L	Foliar	[87]
Zn-chitosan NPs	Ionotropic gelation method; spherical in shape with particle size of 200–300 nm	Disease control to obtain high-quality maize (*Zea mays*)	Foliar	[88]
NPK NFs	Ball-milling method; particle size for N (5.56–12.3 nm), P (4.92–8.62 nm), and K (5.31–9.84 nm)	To study yield, its components, and fiber assets of cotton (*Gossypium Barbadense* L.)	Foliar and soil	[89]
Chitosan–PMAA–NPK NFs	Polymerization followed by entrapment of NPK; actual particle size of N (38.98 nm), P (87.65 nm), and K (24.07 nm)	To study dose-dependent mitosis and genotoxic effect in garden pea (*Pisum sativum* var. Master B)	Soil	[90]
Urea-Hydroxyapatite NFs	In situ coating of hydroxyapatite with urea; bead-shapes crystals with particle size of 18 nm	To evaluate rice (*Oryza sativa*) yield via slow release of nitrogen	Soil	[48]
ZnO NPs	Commercially purchased; average particle size of <35 nm	To investigate effect on grain germination and antioxidant system of maize (*Zea mays* L.) under Cd stress	Soil	[91]
Fe, Zn and NPK NFs	–	To investigate yield components and seed yield in chickpea	Foliar	[92]
Metallic oxide (ZnO, AlO, FeO, CuO, MnO, NiO) NPs	Commercially purchased; particle size of ZnO (10–30 nm), AlO (20 nm), FeO (20–40 nm), CuO (30 nm), MnO (40 nm), and NiO (10–20 nm)	To examine effect on disease progression, growth, and yield of tomatoes and eggplant	Foliar	[93]

4. Recent Literature on Nanofertilizer Applications

Both macro- and micronutrients are equally important for the healthy growth and development of plants. If one of these nutrient is missing, it can disable the seed germination process and affect the plant growth [94]. On the other hand, an excessive amount of these nutrients can also retard the plant's growth. It is difficult to obtain enough essential nutrients to meet the demands of basic cellular activity. Plants require a precise and specific nutrient supply to complete their life cycles. Mineral nutrients perform various functions in plants once absorbed by the plants [18]. These nutrients are converted into pigments, proteins, and enzymes, which are involved in signaling and cell metabolism. Both micro and macronutrients consist of N, P, K, Mn, Mg, Ca, Fe, C, O, S, Cl, H, B, Ni, Mo, Zn, and Cu, and have been known as vital nutrients for plant growth. Among them, N, P, Mg, and K are significant vital components required by the plant. They cannot be absorbed directly from the atmosphere, but they can be absorbed by plants via their roots [95]. As a result, the nanoscale dimension of nanofertilizers has emerged as a technical answer to nutrient insufficiency issues [21]. In general, nanomaterials have improved the nutritional contents of crop plants [96]. ZnO NPs with significantly better physiochemical characteristics might be used as a new fertilizer to increase food quality and agricultural productivity [97–99]. Several studies have reported the positive effects of NPs on seed germination, plant growth, and development. In several agricultural plants, such as *Triticum aestivum* [100], *Glycine max* [29], *Cucumis sativus* [101], and *Solanum lycopersicum* [102], higher seed germination and seedling development, as well as better photosynthetic efficiency, biomass, total protein, sugar, nitrogen, and micronutrients, were reported. Compared to bulk ZnO treatments, ZnO NPs (1.0 mg/L) improved shoot and root biomass with increased shoot length in *C. sativus* cultured in a gel chamber [103]. On the other hand, excess amounts of these nanomaterials can also damage the plants. For example, if ZnO NPs and their derivatives, particularly $ZnCl_2$, were present in excess in soil, plants may become poisonous [104,105], and their seed germination, growth, photosynthesis, physiological and biochemical features, yield characteristics, and nutritional quality may be affected [60,106,107]. Table 2 gives an overview of the recent studies on nanofertilizer applications.

Table 2. Overview of nanofertilizer applications on crop plants and their impacts.

Type of Nanofertilizer	Experimental Conditions	Plant	Impacts	Reference
CuO NPs	CuO NP-embedded hydrogels Exposure: 31 mg Cu/kg soil	Lettuce	CuO NP-embedded hydrogels improved P, Mn, Zn, and Mg absorption and elevated organic acid levels as compared to the sick control.	[108]
Nano-sulfur (NS)	Soil 200 mg/kg NS Period: 35 days (for seedlings), 120 days (mature plants)	Rice	Compared to untreated control plants, NS spray resulted in a 40% increase in rice seedling biomass and a 26% increase in mature plant seed production. These findings show that the effect of S fertilization on As toxicity and accumulation in rice is size-dependent.	[109]
Copper hydroxide nanowires (CNWs)	Foliar application Exposure: 32 d Concentrations: 0.36, 1.8, and 9 mg CNW/plant	Soybean (*Glycine max*)	The dose-dependent response of CNW-treated soybean plants resulted in the activation of important biological processes such as photosynthesis, energy generation, fatty acid metabolism, lignin formation, and carbohydrate metabolism.	[110]
TiO_2 NPs	Concentration: 500,750 mg kg^{-1} Medium: Soil Period: 90 days	*Oryza sativa* L.	Rice growth and nutrient availability were researched in varied soil textures. Plant growth was greatest in silty clay loam, followed by silt loam and then sandy loam. Cu (8-fold), Fe (2.3-fold), P (0.4-fold), and Zn (0.05-fold) increased in shoots treated with silty clay loam at 500 mg kg^{-1}.	[111]
Carbon dots (CD) and nitrogen (N)-doped CDs (N-CDs)	Foliar application on seedlings in hydroponics Concentration: 1, 5, 10, and 50 $mg{\cdot}L^{-1}$ Period: 7 days	Corn	When compared to the control, an application concentration of 50 mgL^{-1} or lower promoted photosynthesis and corn growth. N-CDs have the potential to improve yield and 1000-grain weight by 24.50 and 15.03 percent, respectively.	[112]
CeO_2 NPs	Medium: Soil Period: 75 days	Cabbage (*Brassica oleracea* var. capitata L).	Cabbages treated with nanofertilizers had larger circumferences (no less than 49.42 cm) than control cabbages (28.17 cm). Furthermore, when the cabbage was fertilized with NPK + CeO_2 NPs within 75 days, the average cabbage-head weight grew to three times more than the control to reach 1.88 kg/plant.	[113]
Nano-zeolite (NZ_S), Hybrid nanocomposite (HNC_{SF})	Medium: foliar and soil applied	Strawberry	Except for chlorophyll content, the NZS treatment considerably enhanced the growth metrics as compared to HNCSF and HNCF + NZs. However, HNCSF considerably (P 0.05) affected the proximate composition in terms of ash, protein, and fat, whereas HNCF + NZs increased carbohydrate and energy. All of the nanofertilizers had a variety of effects on various growth and nutritional metrics.	[114]
Copper Hydroxide Nanowires (CNW)	Concentrations: 0.36, 1.8, and 9 mg CNW/plant Period: 32 d	Soybean	CNW exposure at medium and high levels affected Co, Mn, Zn, and Fe accumulation in tissues while increasing photosynthetic activity. Proteomic and metabolomic investigations of CNW-treated soybean plant leaves indicated a dose-dependent response, resulting in the activation of fundamental biological processes such as photosynthesis, energy generation, fatty acid metabolism, lignin formation, and carbohydrate metabolism.	[110]

Table 2. *Cont.*

Type of Nanofertilizer	Experimental Conditions	Plant	Impacts	Reference
ZnO NPs	Concentrations: 0, 40, 80, 160, and 400 mg Zn/kg Medium: Soil Period: 120 d	Soybean (*Glycine max* cv. Kowsar)	All the Zn compounds (ZnO NPs, Zn^{2+}) increased seed production by up to 160 mg Zn/kg. ZnO NPs might be used as a new nanofertilizer to enrich Zn-deficient soil.	[115]
TiO_2 NPs	Concentration: 0, 50, 100, 200, and 400 mg/L Medium: Hydroponics	Coriander	Low concentrations of TiO_2 NPs improved the nutritional quality of coriander. Nano-TiO_2 can increase the nutritional content of edible tissues at an adequate concentration (50 mg/L) without being poisonous to the plant or creating a health concern to consumers.	[116]
Nanourea-Modified Hydroxyapatite NPs or Hybrid nanofertilizer (HNF)	Concentration: 50 mg Medium: Soil Period: 1, 7, and 14 days	*Abelmoschus esculentus*	Nanourea-modified hydroxyapatite NPs (HNF) were shown to be functionally useful for the delayed and sustained release of plant nutrients. The prepared HNF was administered at a rate of 50 mg/week, whereas the commercial fertilizer was applied at a rate of 5 g/week to *A. esculentus*. Because of the gradual release of HNF, the results demonstrated a considerable increase in Cu^{2+}, Fe^{2+}, and Zn^{2+} nutrient absorption in *A. esculentus*.	[50]
ZnO NPs	Concentrations: 2, 4, 8, and 16mg/L Medium: Soil	*Lycopersicum esculentum*	Growth, photosynthetic efficiency, antioxidant enzymes, and proline buildup all increased.	[102]
TiO_2 NPs	Concentration: 0, 25, 50, 150, 250, 500, and 750 mg kg^{-1} Medium: Soil Period: 90 d	*Oryza sativa*	The use of TiO_2 NPs enhanced shoot length by up to 14.5 percent. At 750 mg kg^{-1} TiO_2 NPs, the phosphorus content of rice roots, shoots, and grains rose 2.6, 2.4, and 1.3-fold, respectively.	[117]
n CeO_2	Soil microcosm *n* CeO_2 at 0, 125, 250, and 500 mg kg^{-1}	Barley (*Hordeum vulgare* L.)	In comparison to the control, nCeO_2 (250 mg kg^{-1}) increased grain Ce accumulation by up to 294 percent, which was followed by significant increases in P, K, Ca, Mg, S, Fe, Zn, Cu, and Al. Plants treated with nCeO_2 (250 mg kg^{-1}), on the other hand, did not develop grains.	[118]
TiO_2 and Fe_3O_4 NPs	Concentrations: TiO_2 and Fe_3O_4 (0, 50, 100, 150, 200, and 250 mg kg^{-1}). Medium: Soil Period: 90 d	*Lactuca sativa* (lettuce)	The impacts of TiO_2 and Fe_3O_4 NPson plant availability of naturally soil-bound inorganic phosphorus (Pi) were investigated. In response to TiO_2 NPs, a shift of up to −0.38 pH units was observed, with a substantial ($p < 0.05$) 2.9-fold increase in P absorption. Similarly, Fe_3O_4 NP treatments reduced the pH by up to −0.64 units with a substantial ($p < 0.05$) 2.8-fold increase in P absorption per plant.	[119]

Nanotechnology is a promising approach with huge potential for solving agricultural-related problems such as land degradation, nutrient insufficiency, low crop production, leaching losses, etc. [120]. According to reports, the nanostructure of nanofertilizers possesses a high surface-area-to-volume ratio, allowing plants to absorb nutrients gradually and sustainably as required [121–123]. Furthermore, nanofertilizers offer several advantages, including increased soil fertility, reduced nutrient loss, increased crop output, and reduced environmental contamination, and provide a viable habitat for microorganisms [124]. Many researchers have synthesized slow-release fertilizers by combining hydroxyapatite (HA) with urea to improve nutrient delivery to plants [50,125].

5. Other Applications of Nanotechnology in the Agricultural Sector

As an alternative to NFs, nano-based herbicides, insecticides, pesticides, and fungicides also play a role in sustainable agriculture. Nanopesticides overcome the limitations of conventional pesticides, making them highly soluble in water via encapsulation in a shell made of NPs [126]. Crop production can be improved by the efficient use of these nano-pesticides. The slow release and targeted delivery of these pesticides can be achieved using nanocarrires, referred to as "precision farming", which increases agricultural yields without damaging the water and soil [120].

It has been demonstrated that nano-enabled herbicides have a great ability to eradicate weeds and increase crop yields. Additionally, when NPs were combined with specific herbicides such as triazine, ametrine, and atrazine, the potency of these nano-enabled herbicides increased by 84 percent [127]. In a study, atrazine-loaded poly (epsilon-caprolactone) nanocapsules were applied to mustard plants (Brassica juncea) and resulted in improved herbicidal activity as compared to commercial herbicides [128]. Likewise, Si NPs were synthesized and used as nanocarriers for the controlled delivery of pesticides [129]. Additionally, nanoencapsulation lowers herbicide dosage (sustainable environment approach) without compromising efficiency. Owing to their inherent toxicity, metal oxide nanoparticles such as TiO_2, ZnO, and CuO have been extensively used for their ability to shield plants from pathogen infestations [120].

In addition to this, nanotechnology has a significant impact on food biotechnology, food packaging, food processing, food safety, food development, improved shelf lives and pathogen detection in food. The application of nanotechnology has also facilitated gene sequencing, and increased the identification and application of plant trait means and altered plants' capacity to adapt to environmental stresses and diseases [130]. Some other applications of nanotechnology in the agricultural sector are illustrated in Figure 4.

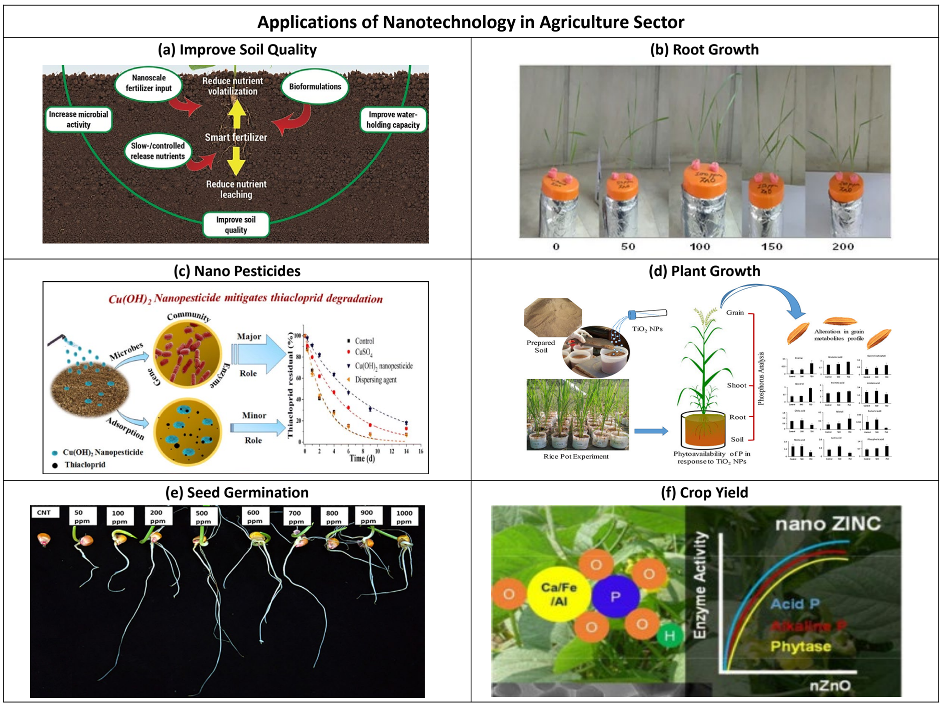

Figure 4. Application of nanotechnology in agriculture sector for (**a**) improved soil quality, Reprinted from reference (adapted with permission from Ref. [131], 2018, *Adv. Agron.*), with permission from Elsevier, (**b**) root growth (adapted with permission from Ref. [132], 2021, *Maize. Plants*), (**c**) nanopesticides (adapted with permission from Ref. [133], 2019, *Environ. Int.*), (**d**) plant growth (adapted with permission from Ref. [117], 2017, *J. Agric. Food Chem.*), (**e**) seed germination (adapted with permission from Ref. [134], 2020, *Arab. J. Chem.*), and (**f**) crop yield (adapted with permission from Ref. [135], 2016, *J. Agric. Food Chem.*).

6. Limitations Regarding the Use of Nanofertilizers

Innovative development in agriculture is a crucial prospect to limit expanded global food demand. The two most important factors for establishing a proper crop-yield framework are climate-change mitigation and sustainable agricultural escalation. However, the situation during the last few decades demonstrates that excessive nanofertilizer application has a negative impact on the environment, as well as on living systems. Even though the use of nanofertilizers is beneficial to the conventional agriculture system, some researchers are concerned about their negative impacts. Due to their reactive nature, NPs can interact with various environmental components, which results in their transformation through the alteration of their physicochemical properties. These transformed NFs may cause toxicity upon their reaction with soil components. On the other hand, the accumulation of these NFs may lead to the production of reactive oxygen species, growth inhibition, and, ultimately, cell death. However, the accumulation of NFs in food might be lethal to humans. In a study, an absorption and translocation analysis of CeO_2 NPs was conducted in cucumber plants whereby 15% of Ce^{4+} was reduced to Ce^{3+} and the transformed products were ultimately transported to phloem. These transported species might be harmful to human health and their safety concerns must be evaluated [136].

The excessive use of NFs in agricultural practices can result in irreversible and unwanted environmental concerns. Concerns about workers' safety during their production and field application have been highlighted by the reactivity and unpredictability of nanomaterials. Therefore, it is crucial to evaluate the risks and identify the negative effects of these NFs, including their life cycle analysis [137]. Moreover, we need to ensure the use of these nanofertilizers at an optimum level only, to avoid their excessive or extra release in the environment. On a global scale, the green revolution increased food grain production at the cost of the disproportionate use of artificial/synthetic pesticides and fertilizers, both of which have gravely harmed our ecosystem. We need to make sure that we are not repeating the same mistakes, so future studies should also check the environmental risks associated with these nanofertilizers, if there are any. Moreover, to boost up crop yield in sustainable agriculture, green synthesized or bio-synthesized nanofertilizers or nano-biofertilizers should be investigated [138]. In this context, the vigilant and research-based application of nanofertilizers must be examined in detail prior to the distribution or marketing of nanofertilizers commercially. Future research should focus on the toxicity, bioavailability, and safety of various NPs or NFs before their application in agricultural production.

7. Conclusions and Future Perspectives

From the perspective of sustainable agriculture, nanotechnology has the capability to produce novel and innovative nano-based fertilizers, to maintain agricultural security while considering the environmental challenges. NFs have advantages over conventional fertilizers due to their higher surface-to-volume ratio and controlled release of nutrients. For instance, NFs release nutrients up to 12 times slower as compared to synthetic fertilizers, and they can boost crop yields and quality features dramatically. Similarly, the use of nanofertilizers might be helpful in decreasing the dosage of fertilizers by delivering active ingredients more efficiently; increasing NUE values and nutrient uptake; and reducing the loss of fertilizers via runoff, leaching, volatilization, and energy consumption during crop production. For example, synthetic fertilizers or nanofertilizers take 4–10 days to actively release nutrients, which is accomplished in 40–50 days using conventional fertilizers. Consequently, synthetic fertilizers, specifically N-urea, after application in the field, can lose more than 50% of its nutrients rapidly through volatilization and leaching. Additionally, nano-sensors and seed coverings with nanofertilizers might reduce agricultural production costs and environmental problems. The advantages of NFs have exposed innovative vistas towards efficient and sustainable agriculture; however, the behavior of various nanomaterials varies differently for different plant species, and accurate information on the combined features (allowable limit, eco-toxicity, efficiency) of distinct nanomaterials is vague. In this context, a viable basic platform for nanofertilizers in the upcoming smart agriculture system, extensive research on improved synthesis techniques, and a variety of remediation and inhabiting databases are potentially required for sustainable agricultural practices.

The vigilant and research-based application of nanofertilizers must be examined in detail prior to the distribution or marketing of nanofertilizers commercially. Future research should focus on the toxicity, bioavailability, and safety of various NPs or nanofertilizers before their application in agricultural production. Moreover, we need to ensure the use of these nanofertilizers at an optimum level only, to avoid their excessive or extra release in the environment. On a global scale, the green revolution increased food grain production at the cost of the disproportionate use of artificial/synthetic pesticides and fertilizers, both of which have gravely harmed our ecosystem. We need to make sure that we are not repeating the same mistakes, so future studies should also check the environmental risks associated with these nanofertilizers, if there are any.

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