Nanotechnology in the Life Sciences

Kamel A. Abd-Elsalam
Mousa A. Alghuthaymi *Editors*

Nanofertilizers for Sustainable Agroecosystems

Recent Advances and Future Trends

Springer

Nanotechnology in the Life Sciences

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Nano and biotechnology are two of the 21st century's most promising technologies. Nanotechnology is demarcated as the design, development, and application of materials and devices whose least functional make up is on a nanometer scale (1 to 100 nm). Meanwhile, biotechnology deals with metabolic and other physiological developments of biological subjects including microorganisms. These microbial processes have opened up new opportunities to explore novel applications, for example, the biosynthesis of metal nanomaterials, with the implication that these two technologies (i.e., thus nanobiotechnology) can play a vital role in developing and executing many valuable tools in the study of life. Nanotechnology is very diverse, ranging from extensions of conventional device physics to completely new approaches based upon molecular self-assembly, from developing new materials with dimensions on the nanoscale, to investigating whether we can directly control matters on/in the atomic scale level. This idea entails its application to diverse fields of science such as plant biology, organic chemistry, agriculture, the food industry, and more.

Nanobiotechnology offers a wide range of uses in medicine, agriculture, and the environment. Many diseases that do not have cures today may be cured by nanotechnology in the future. Use of nanotechnology in medical therapeutics needs adequate evaluation of its risk and safety factors. Scientists who are against the use of nanotechnology also agree that advancement in nanotechnology should continue because this field promises great benefits, but testing should be carried out to ensure its safety in people. It is possible that nanomedicine in the future will play a crucial role in the treatment of human and plant diseases, and also in the enhancement of normal human physiology and plant systems, respectively. If everything proceeds as expected, nanobiotechnology will, one day, become an inevitable part of our everyday life and will help save many lives.

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Preface

Large-scale chemical fertilizer application causes irreparable damage to soil structure, mineral cycles, soil microbial flora, plants, and other food chains across ecosystems, culminating in heritable mutations in future generations of consumers. However, the use of agrochemicals has also raised concerns about their impact on the environment and human health. These concerns have led to the development of new technologies, such as nano-agrochemicals, which aim to address these issues. Nanotechnology is the next revolutionary technology in agriculture which can provide sustainable tools to conventional farming practice in the form of nanofertilizer. Nano-agrochemicals are a new generation of agrochemicals that incorporate nanotechnology to improve their efficiency and reduce their negative impact on the environment. They are designed to deliver agrochemicals to plants more efficiently and precisely, reducing the amount of chemicals needed and minimizing their exposure to the environment. Reduction of chemical fertilizers and pesticide would be beneficial in improving the soil health and maintain soil geobiological cycle, which improves the food and nutrition quality of crop production. A better way forward for the nanofertilizer industry is to focus on macro elements (N, P, K), as switching to nanofertilizers might result in large environmental benefits by replacing the majority of these nutrients.

This book, *Nanofertilizers for Sustainable Agroecosystems: Recent Advances and Future Trends*, is the first volume of the original book series approved by Springer Publishing Ltd. Nanofertilizers are nanomaterials responsible for providing one or more types of nutrients to the growing plants and support their growth and improve production. Nanofertilizers can achieve better efficiency due to a several-fold increase in surface-to-volume ratio of nano-forms of nutrients, and due to their suitability for foliar application where environmental losses are further minimized. Furthermore, the biosynthesis of nanomaterials using bacteria, algae, yeast, fungus, actinomycetes, and plants has opened a new avenue of research to produce inorganic nanoparticles as ecologically friendly fertilizers. Nanostructured fertilizers can improve nutrient use efficiency through strategies such as targeted distribution and progressive or controlled release. They could precisely release their active molecules in response to environmental cues and biological demands. Recent research suggests that nanofertilizers can increase agricultural productivity by speeding up seed germination, seedling growth, photosynthetic activity, nitrogen metabolism, and carbohydrate and protein synthesis. The potential agricultural benefits of nanofertilizers, their modes of action, and the fate of nanomaterials in soil are all discussed in this book. Finally, nanofertilizer formulation and delivery, applications, uptake, translocation, and fate in plants, as well as their impact on plant physiology and metabolism will be discussed. It has been suggested that nutrient nanoformulation is a valuable method that has the potential to alter the agriculture sector and provide solutions to current and future concerns concerning sustainable and climate-sensitive crops.

Furthermore, formulation methods, handling, and application technologies can also be devised for the better utilization of NPs in the agriculture sector. Moreover, compared to commercially available fertilizers, chemical and biogenic nanostructured selected metals can provide a cheap and reliable alternative for mineral nutrients, and such studies may expand the frontiers for nanoparticle-based technologies in plant promotions. We wish to thank the Springer officials, particularly senior editor Eric Stannard and Kenneth Teng for their generous support and efforts in accomplishing this volume. We are highly delighted and thankful to all our contributing authors for their vigorous support and outstanding cooperation to write altruistically these authoritative and valuable chapters. We also want to thank all the reviewers for spending their precious time during the review of chapters. We would also like to thank our family members and colleagues for their continuous support and assistance. With a bouquet of information on the different aspects of plant promotions from nanomaterials, the editors hope that this book is a valuable resource for the students of different divisions and the researchers and academicians, working in the field of Agronomy, Crops Science, nanotechnology, plant sciences, agrochemical industry, and the scholars interested in strengthening their knowledge in nanobiotechnology.

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About the Editors

Kamel A. Abd-Elsalam, Ph.D. is currently a Research Professor at the Plant Pathology Research Institute, Agricultural Research Center, Giza, Egypt. Dr. Kamel's research interests include developing, improving, and deploying plant biosecurity diagnostic tools, understanding and exploiting fungal pathogen genomes, and developing eco-friendly hybrid nanomaterials for controlling toxicogenic fungi, plant diseases, and agroecosystems applications. He has published 23 books related to nanobiotechnology applications in agriculture and plant protection, which were published by the world's major publishing houses (Springer, Taylor & Francis, and Elsevier). Since 2019, he has served as the Editor-in-Chief of the Elsevier book series Nanobiotechnology for Plant Protection; he also serves as the Series Editor of the Elsevier book series Applications of Genome Modified Plants and Microbes in Food and Agriculture. He has also participated as an active member of the Elsevier Advisory Panel, giving feedback and suggestions for improvement of Elsevier's products and services since 2020. He has published more than 214 scientific research papers in international and regional specialized scientific journals with a high impact factor, and has an h-index of 39, i-10 index of 108 with 5911+ citations. Also, he served as a Guest Editor for the *Journal of Fungi, Plants, and Microorganisms*, and as a Reviewer and Editor for *Frontiers in Genomic Assay Technology* and refereed for several reputed journals. He was ranked in Top 2% most influential scientist in the world in nanobiotechnology for 2020 and 2021 by Stanford University. In 2014, he was awarded the Federation of Arab Scientific Study Councils

Prize for excellent scientific research in biotechnology (fungal genomics) (first ranking). Dr. Kamel earned his Ph.D. in Molecular Plant Pathology from Christian Alberchts University of Kiel (Germany) and Suez Canal University (Egypt), and in 2008, he was awarded a post-doctoral fellowship from the same institution. Dr. Kamel was a visiting associate professor at Mae Fah Luang University in Thailand, the Institute of Microbiology at TUM in Germany, the Laboratory of Phytopathology at Wageningen University in the Netherlands, and the Plant Protection Department at Sassari University in Italy and Moscow University in Russia.

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Chapter 1
Maximizing Crop Yield with Macro and Micro Nano Enhanced Fertilizers

M. Reshma Anjum, J. Maheswari, K. Anusha, B. Sravya, G. Narasimha, and Kamel A. Abd-Elsalam

1 Introduction

The term "nanomaterials (NMs)" refers to materials having diameters ranging from 1 to 100 nm. Nanomaterials are special because of their small size and large surface area, which can have optical, physical, and biological effects. They are used in a variety of fields, including health, medicine, electronics, and agriculture, due to their special qualities (Rawtani et al., 2018; Seku et al., 2021). The process of engineering materials at the atomic level or at the molecular level is known as nanotechnology.

At present, conventional fertilizers, which are used in agriculture to increase crop yield, are widely being utilized across the world. The extensive use of commercial fertilizers, on the other hand, decreases the efficiency with which soil nutrients are utilized (Preetha & Balakrishnan, 2017). Excessive fertilizer use can cause heavy metals to enter the soil, plant system, and food chain, thus posing severe health concerns (Mahmoud et al., 2017). Nitrate contamination and eutrophication are caused by commercial fertilizer pollution in both subsurface and surface water systems. Toxic chemicals produced by fertilizer runoff eventually end up in aquatic bodies such as oceans, rivers, and ponds, causing considerable ecological damage.

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The use of traditional fertilizers generates large amounts of trash, which can cause a variety of health problems and have a detrimental effect on the economy (Khan et al., 2021). Discovering innovative and sophisticated methods is encouraged in order to overcome the excessive use of fertilizers without compromising yield. Nanotechnology, namely, the use of nanofertilizers (NFs), is one of the viable answers. Due to high surface area to volume ratio of nanoparticles (NPs), they are smaller in size and more reactive than are bulk materials and are believed to have the potential to transform agricultural systems (Singh, 2012). In agriculture, nanoparticles aim to reduce the number of pesticides distributed, reduce nutrient losses in fertilization, and enhance output through insect and nutrient control. NPs have several potential advantages, including improved food quality and safety, reduced agricultural inputs, and soil enrichment of absorbing nanoscale nutrients, among others (Prasad et al., 2017).

Nanotechnology, in fact, has the potential to enhance the whole existing agricultural and food sector by inventing new tools for plant disease treatment (Sharon et al., 2010), pathogen detection (Zuo et al., 2013), and enhancing plant nutrient absorption (Subramanian et al., 2015). Furthermore, nanotechnology has attracted increased interest in the agricultural area, particularly in the development of novel nanofertilizers to improve the efficiency and bioavailability of these new fertilizers while reducing their loss to the environment (Salama et al., 2019). A nanofertilizer is a nano-sized fertilizer with nanoparticles and nutrient encapsulation that may systematically release micro- and macronutrients to particular plant locations. By absorption or adsorption in a matrix, the nanostructured components in nanofertilizers are frequently integrated with a carrier complex. Chitosan (CS), polyacrylic acid, clay, and zeolite have all been described as nanofertilizer carriers (Cairo et al., 2017). Nanomaterials interact with fertilizers due to their high reactivity, resulting in enhanced and effective nutrient uptake for plants (Prasad et al., 2017). When nanofertilizers are used correctly, they may feed plants slowly, thus increasing nitrogen use efficiency (NUE), preventing leaching, minimizing volatilization, and lowering the overall environmental hazards (Solanki et al., 2015). Because of their high specific surface area, small size, and increased reactivity, nanofertilizers promote nutrient bioavailability. Nutrients may be encapsulated using nanomaterials by three distinct methods (Iqbal, 2019): (1) nanomaterials are encapsulated within them, (2) nanomaterials are applied as a layer, and (3) nanoemulsions are used to deliver the product.

Nanofertilizers perform a critical function in improving the yield of a wide range of crops. The nutrient usage efficiency of conventional fertilizers hardly reaches 30–35%, 18–20%, and 35–40% for N, P, and K, respectively, which has been stable for decades. Nanofertilizers are known to deliver nutrients slowly and gradually over a period of more than 30 days, which may help improve nutrient usage efficiency while avoiding side effects (Subramanian et al., 2015). Because of their ability to increase yield, reduce pollution, improve soil fertility, deliver slowly over a long period of time, significantly reduce nutrient loss, and provide a favorable environment for microorganisms, nanofertilizers have gained more attention from soil scientists and environmentalists (Vitosh et al., 1994). Nanofertilizers might be used as a powder or a liquid with a particle size of fewer than 100 nm (Jampílek & Kráľová, 2015). Then, nanofertilizer efficacy is determined by three variables: internal factors, extrinsic factors, and administration method. The method of nanoformulation preparation, the particle size of the nanoformulation, and surface coating are all intrinsic variables. However, extrinsic factors such as soil depth, soil pH, soil texture, temperature, organic matter, and microbial activity may also affect the potential use of nanofertilizers (El-Ramady et al., 2018a, b). Moreover, the route of administration/mode of application through plant roots or leaves (foliar) also plays a significant role in the absorption, behavior, and bioavailability of nanofertilizers. Depending on the nutritional requirements of plants, nanofertilizers are classified into three categories: macro-nanofertilizers, micro-nanofertilizers, and nanoparticulate fertilizers (Chhipa & Joshi, 2016). The following are some of the common characteristics of nanofertilizers: (1) they supply the necessary nutrients for promoting plant development through foliar and soil applications, (2) they are eco-friendly and low-cost sources of plant nutrients, (3) they have high fertilization efficiency, (4) they complement mineral fertilizers, and (5) they safeguard the environment from pollution threats. Accordingly, these nanofertilizers enable us to eliminate drinking water pollution and eutrophication and, as such, may be viewed as emerging alternatives to synthetic fertilizers (Guru et al., 2015). This chapter's purpose is to provide a detailed review of the various ways in which nano-enhanced fertilizers might increase crop production in agricultural settings. The reader will walk away with a solid comprehension of the many types of syntheses, characterization, and nanofertilizers. Additionally, a discussion of the possible benefits of utilizing nano-enhanced fertilizers in agricultural settings is included.

2 Synthesis of Nanofertilizers

Nanofertilizers are developed to increase the use of nutrient efficiencies by taking advantage of the distinctive properties of nanoparticles. Nanofertilizers are synthesized by stimulating nutrients individually or in mixtures against adsorbents with nano-dimensions. NFs are obtained through different methods such as the top-down method, bottom-up method, and biological synthesis, as shown in Fig. 1.1.

The top-down method involves physical methods for the production process, initiated by breaking down larger elements to yield small nanometric-scale materials (i.e., nanoparticles) using machine-driven abrasion. Examples of the top-down method include ball/pearl milling, high-pressure homogenization, microfluidization, nanocochleates, enantiomorphs, and controlled flow activation technology (Prasad Yadav et al., 2012). The methods based on this notion have some drawbacks, for instance, larger amounts of impurities and low control of particle size and uniformity. The bottom-up method starts with one molecule and moves by associating other molecules in the solution to form NPs by using chemical reactions. Examples of the bottom-up method involve hydrosol methods, precipitation methods, and spray freezing into liquid or supercritical fluid technology and

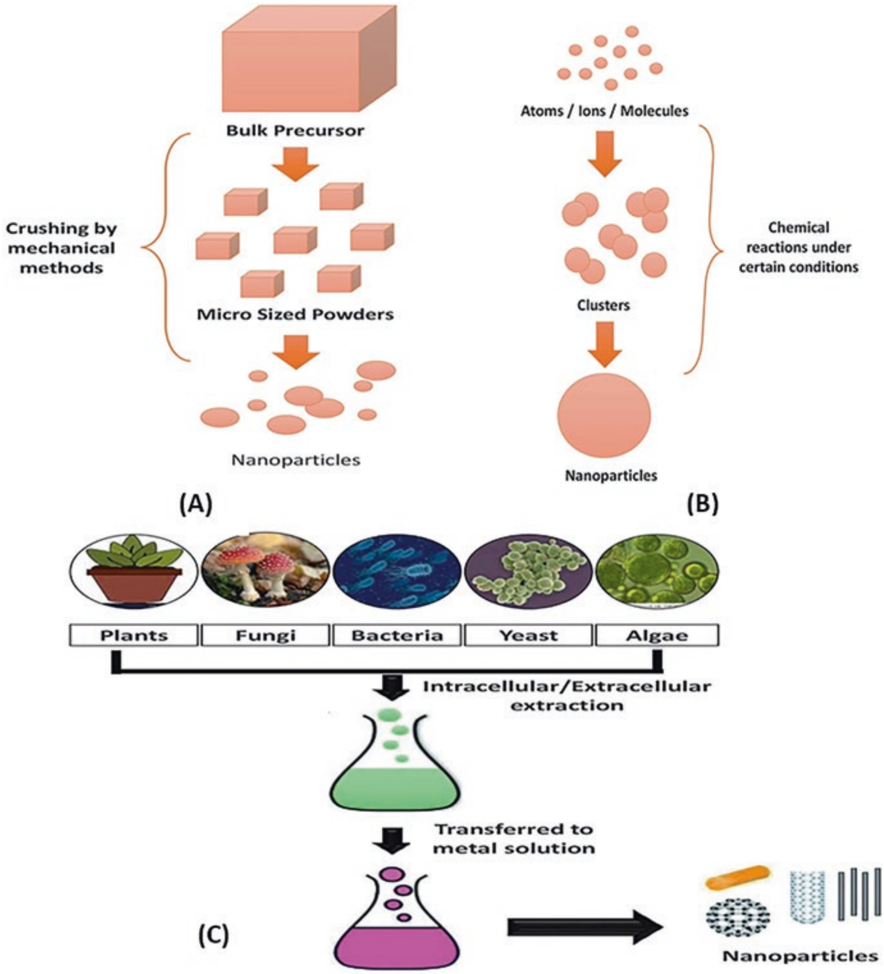

Fig. 1.1 (**a**) The top-down method; (**b**) bottom-up method; (**c**) biological method

self-assembly. Based on different varieties of nanomaterials, methods such as solvent diffusion, ionic gelation, complex coacervation, polyelectrolyte complex formation, solvent evaporation, coprecipitation, solid lipid NPs, self-assembly, and nanostructured lipid carrier suspensions are used (Abdel-Aziz & Rizwan, 2019). The bottom-up method is a chemically controlled synthetic process; as a result, it permits superior control of the nanostructure's size and reduction of scum (Singh & Rattanpal, 2014). Besides the top-down and bottom-up methods, there are many natural sources for the biological synthesis of NFs such as plants, bacteria, yeasts, and fungi. The major advantage of NFs synthesized through biological methods is the low cytotoxicity of the end product. Therefore, it is observed that there are many possibilities for the manufacturing of NFs and various advantages such as improved yield, a decrease in energy costs, and synthesis of materials with greater efficacy.

The incorporation of these physiognomies is likely to result in the production of agrochemicals that exhibit greater performance and supportable applications.

Metal oxides such as silver oxide (AgO), zinc oxide (ZnO), and magnesium oxide (MgO) are mostly used for the development of inorganic nanostructures. Organic compounds, carbon (C), polymers, and other compounds are mainly used as nanomaterials (da Silva Jr. et al., 2020). NFs can be synthesized based on the encapsulation technique. Encapsulation of fertilizers inside a nanoparticle is one of the novel amenities that can be performed in three ways: (a) by coating using a thin polymer film, (b) by encapsulating the nutrient within nanoporous materials, and (c) by delivering as particles or suspensions of nanoscale dimensions (Rai et al., 2012).

3 Characterization of Nanofertilizers

The shape, surface area, and surface chemistry of the produced nanofertilizers are all determined throughout the characterization process. Figure 1.2 shows the various characterization methods of nanoparticles, namely, X-ray diffraction (XRD), Fourier transform infrared (FTIR) spectroscopy, transmission electron microscopy (TEM), scanning electron microscopy (SEM), and zeta potential (Shebl et al., 2019).

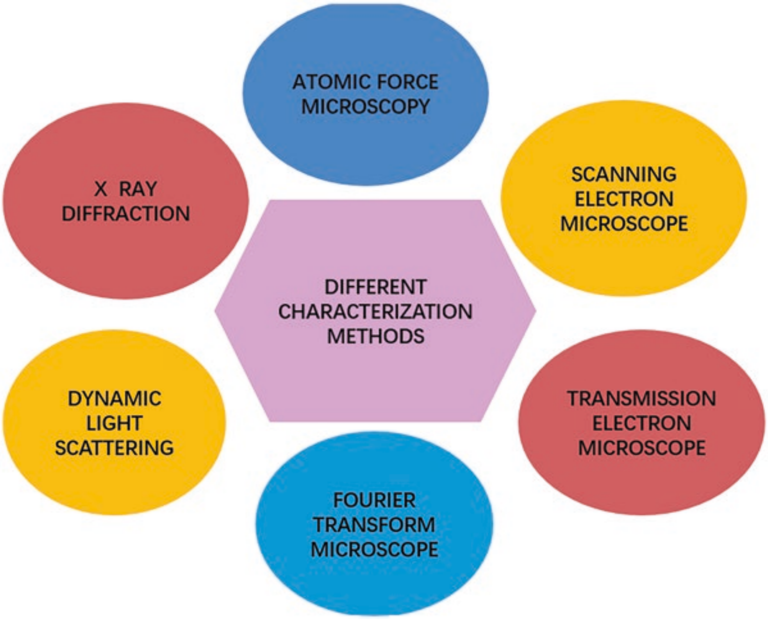

Fig. 1.2 Characterization methods of nanoparticles

3.1 X-Ray Crystallography

By penetrating X-rays deeply into the material, XRD is a widely utilized analytical method for observing the structural behavior and creation of synthetic nanocomposites. The diffraction pattern that results verifies the creation of crystalline nanoparticles. The Debye–Scherer equation is used to quantify particle size from XRD data by calculating the width of the Bragg reflection law according to the equation:

$$d = K\lambda / \beta \cos\theta,$$

where d is the particle size (in nanometers), K is the Scherrer constant, λ is the wavelength of the X-ray, β is the full width at half maximum, and θ is the diffraction angle that corresponds to the lattice plane (Prathna et al., 2011).

3.2 Fourier Transform Infrared Spectroscopy

In the wavelength range of 500–4000 cm^{-1}, Fourier transform infrared (FTIR) spectroscopy may be used to investigate the surface chemistry of synthesized nanocomposites with a resolution of 1 cm^{-1} (Rajeshkumar & Bharath, 2017). Infrared rays travel through the sample in FTIR spectroscopy; some are absorbed by the sample, whereas the rest pass through. The spectra that arise show the absorption and transmission properties of the sample material. To assess the function of biological molecules, FTIR spectroscopy is a cost-effective, suitable, easy, and noninvasive method (Rohman & Che Man, 2010).

3.3 Scanning Electron Microscopy

A scanning electron microscope is used to examine the topography and morphology of nanocomposites and to compute the size of different nanoparticles at the micro- and nanoscales. A high-energy electron beam is directed at the sample's surface using the microscope, and the backscattered electrons generate the sample's distinctive characteristics (Hudlikar et al., 2012).

3.4 Transmission Electron Microscopy

Transmission electron microscopy (TEM) is a highly helpful method for characterizing nanocomposites because it offers information on nanoparticle size and shape. Transmission electron microscopic pictures have a 1000-fold greater resolution than do SEM images and provide more precise information on the size, shape, and crystallography of nanoparticles (Almatroudi, 2020).

3.5 Zeta Potential

With particular operating parameters such as pH, temperature, and wavelength, the zeta potential is utilized to measure the particle size distribution of produced nanofertilizers (Patra & Baek, 2014).

3.6 Other Methods

A conductivity meter is used to measure physical characteristics such as pH and total dissolved solids (TDSs). To better understand the weight loss and reaction type of the produced nanocomposite fertilizer, thermo gravimetry/differential thermal analysis, (TG/DTA) studies are performed.

4 Types of Nanofertilizers

Nanoparticulate transporters assist in increasing agricultural output by modifying the role of fertilizers. Different kinds of NPs can be used as fertilizers or fertilizer delivery vehicles. Nanofertilizers are classified into three categories based on the type of nutrition they contain: macronutrient-based, micronutrient-based, and nanobiofertilizer-based. Figure 1.3 shows the types of nanomaterials used for plants and their role in plant growth and development.

4.1 Macronutrient-Based Nanofertilizers

An adequate amount of macro- and micronutrients, such as carbon, oxygen, hydrogen, nitrogen, phosphorus, potassium, calcium, sulfur, and magnesium, is required for plant nutrition. The first three are structural components that are taken from the environment, whereas the latter six are soil-derived. Macronutrients are classified into two categories: primary/main and secondary. Although the main macronutrients (N, P, K) are ingested in greater quantities, secondary macronutrients (Ca, Mg, and S), which comprise calcium, magnesium, and sulfur, are also essential for plant development.

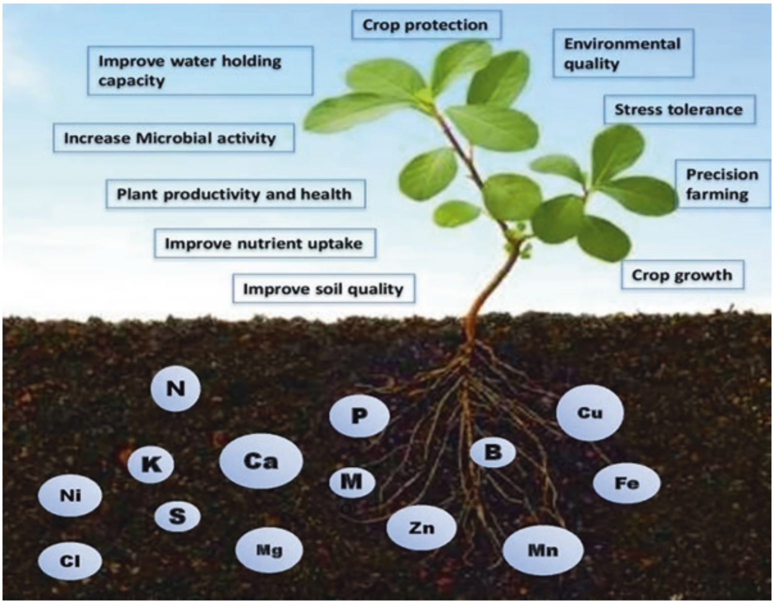

Fig. 1.3 Macro- and micro-nanominerals are available to plants, which results in various beneficial effects in the overall plant growth and development

4.1.1 Nitrogen Nanofertilizers

Nitrogen is the most important mineral ingredient for plants, and it is found in a variety of amino acids, proteins, DNA (deoxyribonucleic acid), ATP (adenine triphosphate), chlorophylls, and cell structure units. N is required for the majority of metabolic activities and regulatory pathways in plants (Preetha & Balakrishnan, 2017). Organic nitrogen molecules, ammonium (NH_4^+) ions, and nitrate (NO_3^-) ions are the three types of nitrogen accessible to plants. The majority of nitrogen is not entirely accessible to plants. This is because negatively charged nitrate has a lower affinity toward soil particle surfaces than does positively charged nitrate and, so, does not get readily absorbed by the soil. Because excess nitrogen is lost through denitrification, volatilization, and leaching during and shortly after field application, the widespread use of traditional nitrogenous fertilizers, such as urea, has generated many environmental problems. In comparison to the optimum ratio of 4:2:1, the present NPK ratio is 8.2:3.2:1, resulting in groundwater contamination and eutrophication in aquatic systems. As a result, there is a requirement for delivery systems that can release fertilizers at a slow pace in order to produce a sustained release of nitrogen during the crop season.

Various research studies have shown that nitrogen-based fertilizers, as opposed to conventional mineral urea, have a greater potential to improve output while reducing the drawbacks of conventional fertilizers. Nanocarriers like zeolites, chitosan, or clay can sync up with plant needs and deliver fertilizers at a steady rate, leading to better plant absorption and justifiable use of nitrogen. Nanozeolites and their mixes are widely used in the design of nanofertilizers due to features such as high surface area and the ability to synchronize nitrogen release (Preetha & Balakrishnan, 2017). According to certain reports, zeolites have the ability to reduce ammonia volatilization by sequestering ammonium N at exchange sites. Ammonia volatilization was observed to have reduced by 50% when 6.25% zeolite was added to the mix. Another benefit is that zeolite-bound ammonium is a suitable slow-release nitrogen source for plants. The plant growth substance, unlike conventionally used fertilizers, substantially minimizes nutrient loss to groundwater and the environment (Lefcourt & Meisinger, 2001). To regulate the retention and release of NH_4^+, zeolites can be used as fertilizer additions to decrease N-urea losses. The addition of a zeolite to a nitrogen source has been shown in the literature to increase nitrogen usage efficiency (McGilloway et al., 2003). In comparison to conventional urea, some researchers created intercalated nitrogen nanofertilizer (zeo-urea) formulations and showed a consistent improvement in maize crop growth, yield, quality, and nutrient absorption (Manikandan & Subramanian, 2016). The use of N NFs on starflower (*Borago officinalis* L.) led to a substantial increase in plant growth and, as a result, increased essential oil yields (Mahmoodi, 2017). Similarly, urea-modified zeolites were found to improve soybean (*Glycine max* L.) seed production when compared to synthetic fertilizers (Liu & Lal, 2014). *Brassica napus* L. was effectively grown using an N NF made by depositing urea onto a nanofilm (DeRosa et al., 2010). Similarly, both nano-N and chelated nano-N were beneficial in boosting yield and lowering nitrate leaching in a potato crop (*Solanum tuberosum* L.) (Zareabyaneh & Bayatvarkeshi, 2015).

Another study (Rajonee et al., 2016) found that a zeolite-based nitrogen nanofertilizer not only increased N accumulation in plants but also improved pH, moisture, and N accessibility in the soil after treatment compared to a traditional fertilizer. Finally, NFs are highly suggested since they can produce a delayed release of nitrogen, minimize volatilization and leaching rates, increase nutrient absorption, and boost crop growth and production.

4.1.2 Phosphorus Nanofertilizers

Phosphorus (P) is the second most important nutrient for optimum plant growth after nitrogen (N), as it is a structural component of phosphoproteins, phospholipids, sugar phosphates, coenzymes, nucleic acids, and metabolic substrates in plants, and it plays an important role in processes like photosynthesis, respiration, and DNA biosynthesis (Soliman et al., 2016). Phosphorus is required for the development of reproductive structures in crops at an early stage. Root stimulation, enhanced stalk and stem strength, improved flower formation and seed production, more uniform and earlier crop maturity, greater legume N-fixing ability, and improved crop quality and resistance to plant diseases are some of the particular growth characteristics linked to phosphorus (Preetha & Balakrishnan, 2017). Several factors can restrict the availability of P to plants, even if the amount of P in soils is considerably higher than what is required for plant development (Sohrt et al., 2017). Its immobilization with clay particles in the soil, for example, or its complexes with iron (Fe), aluminum hydroxides, and calcium in the soil limit its availability (Bindraban et al., 2020). Plants only absorb 10–20% of the given P fertilizers.

The increased usage of N fertilizers has exacerbated the problem by altering P microbial biomass and its ratios to N and C microbial biomass (Fan et al., 2017). To address these issues, a group of researchers developed and tested a nanotechnology-based method for phosphorus fertilizers. They showed that NFs can gradually deliver P for up to 40–50 days after application, whereas conventional phosphorus synthetic fertilizers deliver all nutrients within 8–10 days. As a result, it has been suggested that using NFs or slow-release materials like zeolites could increase the NUE of P for a variety of field crops (Bansiwal et al., 2006). In addition to contributing to a high NUE, a biosafety nanofertilizer, a source of P, was shown to considerably enhance fresh and dry biomass, increase fruit production, and improve quality by several times (Patra et al., 2013). Nanohydroxyapatite-based fertilizer increased the growth rate and seed production of soybean plants by 32.6% and 20.4%, respectively, as compared to the conventional P fertilizer (Liu & Lal, 2014). On *Adansonia digitata*, the use of hydroxyapatite NPs as a fertilizer carrier was investigated, and it was shown that hydroxyapatite NPs resulted in improved plant growth metrics, chemical contents, and anticancer activity of leaves when compared to various sources of P nanofertilizers (Soliman et al., 2016). The phosphorous usage efficiency of surface-modified zeolites has also been found to be higher than the traditional system's 20% (Preetha & Balakrishnan, 2017). In conclusion, P applied in the form of NFs might be a good alternative, especially in smart agriculture, since it has a long-term slow-release substance, which can decrease P leaching into groundwater and improve crop production and quality.

4.1.3 Potassium Nanofertilizers

Potassium (K) is the third most essential macronutrient after nitrogen and phosphorus. Even though potassium is not found in any plant structures or compounds, it plays a vital regulatory role in plants. It is required for virtually all of a plant's physiochemical activities, including its growth and reproduction (Preetha & Balakrishnan, 2017). Photosynthesis, photosynthetic translocation, protein synthesis, blooming stimulation, cell tissue strengthening, management of ionic equilibrium, regulation of plant stomata and water consumption, activation of more than 60 plant enzymes, and many other activities all require potassium (Preetha & Balakrishnan, 2017). Potassium-deficient plants are more susceptible to droughts, excess water, and extreme heat and cold (Taha et al., 2020). Pests, illnesses, and nematode assaults are also less resistant to them. Because of its major impacts on quality variables such as size, shape, color, taste, shelf life, fiber quality, and other quality measures, potassium is also known as a quality nutrient (Preetha & Balakrishnan, 2017). However, a K fertilizer's maximum usage efficiency is generally between 30% and 50% (Battaglia et al., 2018), implying that up to 50–70% of an applied K fertilizer might be wasted, resulting in significant economic losses and negative impacts on soil health and water quality (Czymmek et al., 2020). Several researchers have created and synthesized potassium nanofertilizers, concluding that they work better than traditional fertilizers. Some natural zeolites have high levels of exchangeable K^+, which can help plants develop faster in a potting medium. Data on the delayed-release impact of K from K-zeolites are available in Hershey et al. (1980). Because of their ion exchangeability with the chosen nutrient cations, zeolites can become an ideal plant development medium for delivering additional essential nutrient cations and anions to plant roots (Zhou & Huang, 2007). With a rise in equilibrium K concentration, the potassium sorbed on zeolites increases (Rezaei & Movahedi Naeini, 2009). A nano-potassium fertilizer formulation with a delayed K release rate was investigated and produced by certain researchers. The authors concluded that using a nano-potassium fertilizer might minimize K losses in the soil while also ensuring a longer-term supply of K to crops (Kubavat et al., 2020). In hot pepper (*Capsicum annum* L.), K-loaded zeolites enhanced the yield, harvest index, K concentration, and chlorophyll content (Jun-Xi Li et al., 2010). Due to enhanced nitrogen absorption, the assessed nano-K fertilizer for foliar application on *Cucurbita pepo* produced more leaves, higher product quality, disease and insect resistance, and drought tolerance (Fatemehsafavi, 2016). Lithovit, a nanofertilizer, has been shown to boost plant growth and production by increasing natural photosynthesis by providing carbon dioxide (CO_2) at the right concentration (Attia et al., 2016). It has been discovered that plants treated with nanofertilizers have greater K content than plants treated with conventional fertilizers (Rajonee et al., 2017). The root elongation rate was decreased in a dose-dependent manner when chitosan and methacrylic acid NPs were employed to encapsulate N, P, and K for assessment on garden peas. Despite the fact that lower doses resulted in the overexpression of several key proteins, all concentrations had genotoxic effects (Khalifa & Hasaneen, 2018). In comparison to other treatments, potassium nanofertilizer application at 150 + 150 ppm resulted in a substantial increase in nutritional content in peanut plant shoots and seeds (Afify et al., 2019). As a result, by decreasing K losses in the soil, K NFs can maintain soil health and enhance water quality.

4.1.4 Calcium Nanofertilizers

Calcium is important for mineral retention and movement in the soil as well as for neutralizing harmful chemicals, cell wall stability, and seed development. Although foliar calcium treatment has the ability to raise calcium concentration in fruits, it still has limited effectiveness in some cases, which can be attributed to calcium absorption limitations such as epidermal features, fruit penetration, cuticle structure and presence, and poor phloem Ca translocation rates (Wojcik, 2001; Danner et al., 2015). The impact of spraying calcium nanofertilizer and calcium chloride on the quantitative and qualitative parameters of preharvest apple fruits was demonstrated and the result showed that both fruit quality and quantity were considerably enhanced by nanocalcium treatment, with a maximum concentration of 2%

(Ranjbar et al., 2019). The impact of foliar application of nano-$CaCO_3$ on lisianthus development and blooming has also been studied. Spraying nanofertilizer at a concentration of 500 mg/L resulted in flowering 15 days earlier than for control plants, with a 56.3% increase in the number of flowers (Seydmohammadi et al., 2019).

4.1.5 Magnesium Nanofertilizers

Magnesium is essential for plant development because it makes up the core of the chlorophyll molecule, making it essential for photosynthesis. Mg is commonly lost from soil due to mobilization, leaching, and incorrect fertilizer application. The presence of other cations such as NH_4, Ca, and K affects magnesium absorption. The combination of magnesium and iron nanoparticulate solutions for foliar treatment in black-eyed peas improved virtually all of the studied characteristics (Delfani et al., 2014). Magnesium hydroxide NPs have also been investigated for their efficiency in seed germination and plant growth enhancement in vitro and in vivo on *Zea mays*. At a concentration of 500 ppm, the particles were shown to have 100% seed germination and enhanced growth (Shinde et al., 2020).

4.1.6 Sulfur Nanofertilizers

Sulfur is a secondary macronutrient that aids in the synthesis of chlorophyll, enhances nitrogen efficiency, and aids in plant defenses. The most frequent sources of S are sulfate (SO_4^{2-}) and elemental sulfur (S_8). Sulfate salts are easily taken up by plants, but the low S content does not fulfill the crop's desire for a significant sulfur feed. Furthermore, difficulties with SO_4^{2-} leaking result in considerable losses and environmental concerns. Elemental sulfur (S_8) has considerably greater S concentrations, but plants can only absorb it after biological oxidation by soil microbes, which are greatly controlled by fertilizer particle size (Valle et al., 2019). As a result, particle size reduction may have a substantial impact on the oxidation rate. As a result, developing sulfur nanofertilizers may be a viable option. The impact of sulfur nanofertilizers on the development and nutrition of *Ocimum basilicum* in response to salt stress was investigated and shown to have no significant influence on the characteristics studied (Alipour, 2016). Green synthesis of sulfur NPs was accomplished using *Ocimum basilicum* leaf extract, which was applied to *Helianthus annuus* seeds at various doses (12.5, 25, 50, 100, and 200 M) and irrigated with 100 mM $MnSO_4$ for pot study. Sulfur NPs were shown to reduce Mn absorption, improve S metabolism, increase seedling water content, and abolish physiological drought, indicating that sulfur nanofertilizers might mitigate the negative effects of Mn stress (Ragab & Saad-Allah, 2020).

4.2 Micronutrient Nanofertilizers

Many micronutrients, including silica, zinc, copper, and iron, have been synthesized at the nanoscale and used in plant growth management. Micronutrients are essential minerals that are needed in smaller amounts than N, P, and K and yet are critical for plant metabolic activities. Boron (B), copper (Cu), iron (Fe), manganese (Mn), molybdenum (Mo), zinc (Zn), chloride (Cl), and nickel (Ni) are a few examples of micronutrients. Despite the fact that micronutrients are only required in trace amounts, they are critical for healthy plant growth, profitable crop production, and increasing plant tolerance to a variety of stresses, including high pH, low organic matter, salt stress, prolonged drought, high bicarbonate content in irrigation water, and imbalanced NPK fertilizer application. Low crop quality and yield, imperfect plant morphology (such as fewer small xylem vessels), pervasive infection of numerous diseases and pests, low stimulation of phytosiderophores, and lower fertilizer use efficiency are some of the negative impacts of micronutrient deficiency-induced stress in plants. The production of micronutrients by nanoscale structures may improve their absorption and bioavailability, aid in the proper distribution of such micronutrients, and reduce micronutrient adsorption and attachment to soil colloids.

4.2.1 Iron Nanofertilizers

Iron (Fe) is a necessary nutrient for chlorophyll synthesis, DNA synthesis, chloroplast structure, respiration, and other metabolic pathways. Although plants require a tiny amount of Fe for growth, its deficiency or excess has a negative impact on the physiological and metabolic functions of plants, thus lowering output (Palmqvist et al., 2017). Because iron makes up about 5% of the earth's crust, soil contains plenty of it. However, due to the presence of insoluble ferric complexes at neutral pH values, a significant proportion of iron is unavailable to plants.

The use of highly persistent and slow-release nanoformulations to make iron available to plants is a promising strategy. In a wide pH range, iron chelate nanofertilizers are highly stable and provide a delayed release of iron. Another advantage of iron-based nanofertilizers is that they are free of ethylene-based chemicals, which cause plants to age into senescence prematurely (Armin et al., 2014). When compared to the controls, foliar application of iron nanoparticles (500 mg/L) to black-eyed peas significantly increased the number of pods per plant by 47%, the weight of 1000 seeds by 7%, the Fe content in leaves by 34%, and the chlorophyll content by 10%. Fe NFs have been shown in many studies to promote the germination and growth of various crops when compared with controls and/or synthetic Fe sources (Srivastava et al., 2014). In field trials, FeNP-treated peanut (*Arachis hypogaea* L.) plants grew healthier roots than did nontreated plants (Rui et al., 2016). In comparison to the controls (ferrous sulfate; $FeSO_4$), FeNP administration (2–6 nm) resulted in longer radical elongation during germination and higher fresh biomass in green gram (*Vigna radiate* L.) (Raju et al., 2016). Fe NFs (Fe_2O_3) in various doses (0, 5, 10, 20, 30, and 40 mM) have been employed on rose periwinkle (*Catharanthus roseus*). It was discovered that Fe NFs improved various growth parameters as well as chlorophyll and protein content when compared to plants that did not receive Fe NFs. In another study, iron oxide NPs (Fe_2O_3 NPs) were applied to plants at various concentrations for 70 days, resulting in considerable increases in growth metrics, photosynthetic pigments, and total protein content, with the largest quantity at a concentration of 30 μM (Askary et al., 2016). The use of γ-Fe_2O_3 NPs (20–100 mg/L) raised the Cl concentration in watermelon and *Zea mays* (Hu et al., 2018). In soybean plants, lower concentrations (0–0.75 g/L) of ferrous oxide NPs were found to increase Cl content and lipid and protein levels, whereas higher doses (0.75–1.0 g/L) reduced these parameters (Sheykhbaglou et al., 2018). A study of the effects of nanoscale zero-valent iron (nZVI) on a terrestrial crop, *Medicago sativa* (Alfalfa), found that 20-day-old seedlings had higher chlorophyll content, although carbohydrate and lignin content fell marginally (Kim et al., 2019). Cornelian cherry fruit extract was used to make Fe_2O_3 NPs, which resulted in statistically significant root and shoot biomass stimulation (Rostamizadeh et al., 2020). To summarize, Fe NFs can be an excellent alternative supply, especially in soils with Fe deficit.

4.2.2 Copper Nanofertilizers

Copper is required for a variety of physiological processes, including mitochondrial respiration, cellular transportation, and cofactors of antioxidant enzymes such as superoxide dismutase and ascorbate oxidase, as well as for protein trafficking and plant hormone signaling. Copper fertilizers are mostly used in crop protection formulations since copper is essential for plant health and nourishment. Copper deficiency causes a variety of problems, including necrosis, stunted development, reduced seed, grain, and fruit output, and, eventually, low crop yield (Priyanka et al., 2019). Due to their large surface area, high solubility, and reactivity, soil application of copper NPs in the form of fertilizers provides a likely route of exposure to plants The use of a CuONP nanofertilizer in the field enhanced the germination and root development of soybeans and chickpeas (*Cicer arietinum* L.) in recent experiments (Adhikari et al., 2012). Similarly, the germination rates of 65%, 80%, and 80% for soybean seeds treated with Cu, Co, and Fe nanocrystalline powders (40–60 nm), respectively, were greater than the 55% germination rate in a control sample (zero NF) (Ngo et al., 2014). Furthermore, after the application of CuNPs at a dosage of 5 mg/L, flavonoid content, sulfur assimilation, and the production of proline and glutathione in *Arabidopsis thaliana* improved (Nair & Chung, 2014). Copper NPs (CuNPs) biosynthesized (using *Citrus medica* L. fruit) at dosages of up to 20 g/mL enhanced the mitotic index in *Allium* extract, actively dividing cells (Nagaonkar et al., 2015). CuNP treatment, on the other hand, inhibited the development of water lettuce (*Pistia stratiotes* L.) (Olkhovych et al., 2016) and reduced the hardness of cucumber fruits (Hong et al., 2016). CuNPs were used to improve stress tolerance in wheat, as evidenced by the increased levels of proteins involved in starch breakdown and glycolysis, superoxide dismutase activity, sugar content, and Cu content in CuNP-treated seeds (Yasmeen et al., 2017). When pigeon pea (*Cajanus cajan* L.) seedlings were treated with biogenic CuNPs of 20 nm size, there was a significant increase in root length, height, and fresh and dry weights (Shende et al., 2017). The yield, nutraceutical characteristics, total antioxidant capacity, and lycopene content of CuNPs encapsulated in chitosan/polyvinyl alcohol (CS/PVA) hydrogels were all enhanced (Hernández et al., 2017). CuNP treatment of tomato plants has been shown to increase the firmness of the fruits while also increasing vitamin C, lycopene content, antioxidant capacity, and superoxide dismutase and catalase activity (López-Vargas et al., 2018). Cu-chitosan NPs sprayed on the leaves of finger millet plants, either alone or in conjunction with seed coating, increased yield and growth profiles as well as defense enzymes, thus leading to the prevention of blast disease (Sathiyabama & Manikandan, 2018). In conclusion, Cu NFs can considerably and favorably improve biochemical and yield characteristics, although the rate of administration must be carefully monitored.

4.2.3 Zinc Nanofertilizers

Zinc plays an important role in plant growth because it is a structural component and cofactor for numerous proteins and enzymes, for instance, isomerases, dehydrogenases, aldolases, RNA and DNA polymerases, and transphosphorylases. It is also involved in the biosynthesis of carbohydrates, maintenance of membrane structure and potential, protein metabolism, and regulation of cell division and defends plants against environmental stress and pathogens (Schmidt & Szakal, 2007; Broadley et al., 2007). The major limitation of conventional fertilizers is that most of the additional Zn is fixed in the soil, but zinc-based NFs show great potential (Wang et al., 2016). Zinc oxide (ZnO) is a form of zinc NFs, which are often used in contemporary agriculture as they are cost-effective and more efficient than synthetic fertilizers. They increase the growth, yield, and quality of crops. Foliar spray, seed priming (Sharifi, 2016), and soil mixing are the methods used for the application of Zn NFs to plants. High doses of Zn can negatively affect the development of plant growth by making certain metabolic changes in plants. The gradual release of Zn is due to the limited solubility of minerals and the sequestration effect of exchange, which releases trace nutrients to zeolite exchange sites where they are more readily available for plant absorption. Zeolite in the soil helps release trace elements and their uptake by plants. The existence of zeolites in unbiased soil enhances the release of certain cationic micronutrients. Germination in ryegrass was improved due to the entry of ZnO NPs into the root tissue (Lin & Xing, 2008). Using pumpkin plants as model crops, an elegant experiment was carried out to visualize the carbon-coated nanotubes in plant cells. Based on the study, the nanotubes serve as a supervisory tool to improve the nutrient transport system for plants (González-Melendi et al., 2007). ZnO NPs rich in zinc increases the level of indole-3-acetic acid (IAA) in roots, which, consecutively, increases the growth rate of plants (Pandey et al., 2010). In pearl millets, crop yield was enhanced by ZnNPs synthesized by biological methods and are used as NFs. A high concentration (1000 mg/kg) of ZnO NPs applied to the soil inhibits plant growth, but, at a low concentration (≤100 mg/kg), Zn uptake is enhanced by the cucumber plant (Tarafdar et al., 2014). Lisianthus showed improved chlorophyll content in leaf and petal anthocyanin besides an increased number of flowers, lateral branches, and leaves by foliar application of ZnNPs. ZnO NPs improved the sprouting of tomato (*Lycopersicon esculentum*) and cabbage (*Brassica botrytis*) (Broos et al., 2007) and sugar and protein content as well as antioxidant activities (Singh et al., 2013). Likewise, ZnNP application can increase leaf area, shoot growth, protein content, dry weight, and final yield in pearl millet, sunflower, maize, rice, potato, and sugarcane (Moghaddasi et al., 2017). Studies have demonstrated that the use of nanofertilizers in a number of crops, including cereals, vegetables, and fruits, can boost the rates of seed germination, root growth, plant height, biomass output, and yield. In addition, the use of nanofertilizers can lessen the amount of fertilizers required, which, in turn, can lessen the negative effects that agriculture has on the environment. The use of nanofertilizers can also boost the crop's nutrient content, resulting in food that is healthier and more nutritious (Zhang et al., 2022). It has been demonstrated that increasing the amount of zinc oxide nanoparticles used as a fertilizer can enhance the amount of zinc found in wheat grains, which is critical for maintaining human health. In conclusion, NFs have been used to improve plant growth and seed germination due to their ability to transfer across seed teguments, where they can increase oxygen and water uptake as well as improve tolerance against stresses that affect initial plant growth. This has been done in order to take advantage of the fact that NFs have the potential to improve plant growth and seed germination (Fig. 1.4).

4.2.4 Manganese Nanofertilizers

Manganese (Mn) is a crucial micronutrient that is involved in several biochemical processes such as biosynthesis of fatty acids, proteins and ATP, N metabolism, and photosynthesis. Irrespective of this, Mn can be noxious to various plants depending on the chemical nature of the acidic soil. Mn supports plants in dealing with various kinds of stresses. In comparison with commercially available MnSO4, MnNPs have been confirmed to be a better source of Mn. Research has proven that there was a significant increase in the yield and growth of maize, wheat, soybean, common beans, and sugarcane on the application of Mn (Fageria, 2001). On treatment with MnNPs, the yield of eggplant (*Solanum melongena* L.) enhanced by 22% (Elmer & White, 2016) and there was a considerable increase in the root length of lettuce (*Lactuca sativa* L.) with respect to Mn ions as compared to controls (Liu et al., 2016). However, MnNPs do not show any effect on the root length of white mustard (*Sinapis alba*) (Landa et al., 2016), watermelon (*Citrullus lanatus*) yield, and seed germination of lettuce (Liu et al., 2016). The MnNPs at the physiological level increase the activity of the electron transport chain by binding with the chlorophyll-binding protein (CP43) of photosystem II. Accordingly, plants fertilized with Mn nanoparticles exhibit a positive shift in their photosynthesis and nitrogen

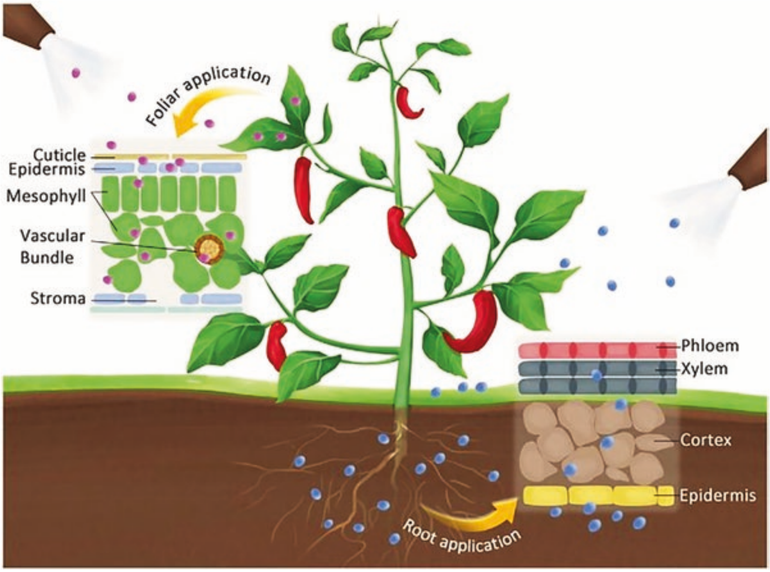

Fig. 1.4 The usage of nanofertilizers has been shown to promote the development of plants and germination of seeds. Nanofertilizers are a type of fertilizer that contains nanoparticles that have the potential to improve the availability of nutrients to plants and their ability to absorb those nutrients. Because of the high surface area to volume ratio of these nanoparticles, they are able to interact with plant roots and soil in a more productive manner, which ultimately results in increased nutrient uptake and utilization by plants. (Reprinted from Zhang et al., (2022). Under Creative Commons Attribution (CC BY) license (Wiley-VCH GmbH))

assimilation rates compared with their counterparts without Mn NPs. (Pradhan et al., 2013). MnNPs, as a nano-priming agent, help improve salinity stress in *Capsicum annuum*, which significantly improves root growth in salt-stressed and non-salt seedlings (Ye et al., 2020).

4.2.5 Boron Nanofertilizers

Boron (B) is an essential micronutrient required in lesser amounts by plants and plays a significant role in the formation of the cell wall, elongation of pollen grains and tubes, and transfer of photosynthetic products to the active areas of growth. It is also crucial for bark formation, transfer of certain hormones that affect stem and root growth, pollen germination, and flowering. For effective nitrogen fixation and nodule formation in legumes, an adequate amount of B is required. B deficit can be reduced by the use of conventional fertilizers, but the application of fertilizers frequently disrupts soil fertility and therefore results in environmental pollution. Nanotechnology has been considered as an alternate technique and is effectively used for the acquisition of B. Studies have proven that there is a significant increase in plant growth and yield by the usage of B NFs or NPs. B and its NPs sprayed at different concentrations exhibit greater results on increasing seed yield, the number of pods, and plant height at a concentration of 90 mg/L as compared with controls (B) (Ibrahim & Al Farttoosi, 2019). B NFs applied to an alfalfa (*Medicago sativa*) crop grown on calcareous soil reaped a maximum yield with appropriate forage quality (Taherian et al., 2019). Olive trees on treatment with nano-boron and nano-zinc at different concentrations produced a maximum quantity of fruits with high oil content (Genaidy et al., 2020). In conclusion, the application of B NFs can increase both crop yield and quality.

4.2.6 Molybdenum Nanofertilizers

Molybdenum (Mo) is essential in extremely minute quantities. The insufficiency of Mo is occasional; however, its insufficiency is usually found in *Euphorbia pulcherrima* (Thomas et al., 2017). Mo is a crucial component for the enzymes that change nitrate into nitrite and then ammonia before using it in the plant to synthesise amino acids. Besides, Mo is an essential constituent in the nitrogenase enzyme in nitrogen-fixing bacteria, which are crucial for leguminous plant crops. Likewise, Mo is used in plants for the conversion of organic forms from inorganic phosphorus. Efforts are made to study the properties of molybdenum NPs (MoNPs) as a fertilizer, due to the appealing aid of nanofertilizers. Application of MoNP solution, intact or in a mixture with microbes as a source of Mo, to chickpeas results in increased crop yield, disease resistance, and performance of legumes besides other crops (Taran et al., 2014). MoNPs synthesized using fungus such as *Aspergillus tubingensis* TFR29 at a standardized dose of 4 ppm show significant enhancement in root length, root space, root width, number of tips, beneficial enzymes, grain yield, and microbial activities in the rhizosphere (Thomas et al., 2017).

4.2.7 Silicon (Si) Nanofertilizers

Although silicon (Si) is not necessary for the completion of the plant biorhythm, it does offer some advantages to some plants in both normal and stressful situations. Because of this, it is divided into essential and optional micronutrients for plants. However, mono-silicic acid is the solitary form by which plants take up soil Si. Si plays an extensive role in improving resistance in plants against salinity, heat and water stresses, and heavy metal toxicity (Rastogi et al., 2019). The overall plant productivity can be improved by the application of silicon dioxide (SiO_2) along with organic fertilizers (Janmohammadi et al., 2016). In addition, the mesoporous structure of SiNPs makes them suitable nanocarriers for several molecules that are useful in agricultural systems. For instance, nanozeolites and nanosensors, which encompass the structure of SiNPs are effectively used in agriculture for improving the water-holding capacity of soil and monitoring soil dampness, respectively (Rastogi et al., 2019). Seedling vigor index (SVI) increased by up to 3.7-fold as compared with SiO_2 when seeds were primed with diverse concentrations (0.04–0.125 w/v) of a CS-Si nanofertilizer (Kumaraswamy et al., 2021). For emerging new varieties, which are resistant to several biotic and abiotic factors, SiNP-arbitrated targeting of biomolecules would be beneficial. These nanoparticles can offer eco-friendly and sustainable alternatives to numerous chemical fertilizers without damaging the environment. Si-NPs may therefore offer effective remedies for a variety of agricultural issues, including drought, pathogenicity, weeds, and crop production.

4.2.8 Nickel Nanofertilizers

Even though nickel (Ni) has been recognized as a trace mineral, its acceptance is highly significant for diverse enzymatic actions to maintain the cellular redox condition and some further activities responsible for physical, biochemical, and growth responses (Yusuf et al., 2010). NiNPs of 5 nm do not show any effect on the growth of wheat seedlings at low concentrations (0.01 and 0.1 mg/L), even though a slight upsurge was observed in the content of Chla and Chlb after subsequent application of NiNPs at 0.01 mg/L concentration (Zotikova et al., 2018).

4.3 Biofertilizer-Based Nanofertilizers (Nanobiofertilizers)

The term "nanobiofertilizer" refers to the purposeful coexistence of a biocompatible nanomaterial and a biological source-driven fertilizer, both of which have great efficacy. These features are designed to allow for slow and steady nutrient release over the course of a crop's life cycle, resulting in improved nutrient utilization as well as increased crop output and productivity (Duhan et al., 2017). Probably, investigations over the last decade have revealed a progressive change in attention from chemical fertilizers to nano- and biofertilizers (Dhir, 2017). The use of nutrients in combination with biofertilizers at the nanoscale has been proposed as a cost-effective strategy for promoting proper nutrient control in smart agriculture (Kalia & Kaur, 2019). Biologically helpful microorganisms such as blue-green algae, mycorrhizae, bacteria such as *Rhizobium*, *Azospirillum*, and *Acetobacter*, and phosphate-solubilizing bacteria such as the *Pseudomonas* and *Bacillus* species make up a biofertilizer. These beneficial characteristics, although revolutionary and renewable, do not come without a price. Some of the technology's limitations include vulnerability to nanoscale texture retention, poor on-field stability, varying activities under changing environmental conditions (pH sensitivity, temperature, and radiation exposure), a scarcity of useful bacterial strains, susceptibility to decomposition, and a disproportionately high dose necessity for a large area.

The nanoscale composition of a biofertilizer solves these problems by providing structural protection to biofertilizer nutrients and plant development factors, promoting microorganisms by nanoencapsulation-mediated nanoscale polymer coating

(Golbashy et al., 2016). In addition to boosting the benefits of biofertilizers, combining NFs with NMs and bioinoculants helps assure planned and targeted nutrient delivery to crops. According to research, NPs can influence the plant microbiome by improving nutrient availability or indirectly boosting the actions of plant growth-promoting *Rhizobacteria*. As a result, various NF application modalities are advised, such as applying NFs and biofertilizers independently or as nano-augmented biofertilizers (Gouda et al., 2018). The impacts of NMs are dose-dependent, meaning that larger concentrations have a negative impact on both flora and fauna. As a result, if they limit the growth of vegetation, their uses would be troublesome. As a result, appropriate and safer ways can improve the merits of using NPs at lower dosages that are less harmful to the environment. The nanoencapsulation method could be utilized as an effective alternative to extend the structural protection of a biofertilizer that has been delivered, improve its chemical shelf life, and disperse it in fertilizer formulations, enabling a sustained delivery. Aside from increasing nutrient release properties, the method also improves field performance and significantly lowers costs.

The nanobiofertilizer technique has several significant advantages, including enhanced inorganic nutrient use, greater crop product quality, and improved disease resistance. Through the nanoencapsulation phenomena, nanomaterials such as chitosan, zeolites, and polymers facilitate significant improvements in the uptake of organic nutrients, producing a continuous abundant quantity of nutrition for plants (Qureshi et al., 2018). A biofertilizer's extensive surface coating of NPs increases the dispersion of constituent nutrients. The constant release of biofertilizers from bound nanocarriers also provides long-term availability of the applied nutrients throughout the plant's life cycle (El-Ramady et al., 2018a, b). The organic content of nanobiofertilizers benefits in a synergistic way by enhancing soil nutritional quality through numerous processes. Despite providing necessary hormonal activities, some of these probable methods comprise atmospheric nitrogen fixation, siderophore creation, and phosphate solubilization through the activities of P-solubilizing bacterial and fungal strains (Mala et al., 2017).

By shortening the time it takes for wheat plants to reach physiological maturity, nanobiofertilizers improve spike length, spike quantity, grain production, and weight (Mardalipour et al., 2014). Treating *Brassica oleracea* plants using CS-urea NPs (1000 mg/L) and plant mycorrhiza reduced chemical nitrogen fertilizer input by 33.3%; this is similar to applying an entire dose of urea (Shams, 2019). The creation and execution of these compositions are hampered by a lack of basic knowledge about the interactions between NPs and plants. NFs have been shown to boost the harvest growth of plants and their components by lengthening the growing period (Mardalipour et al., 2014). In numerous investigations, the overall better response of nanobiofertilizer administration in agricultural plants has been documented, in terms of improved qualitative and quantitative crop growth metrics.

5 Nanotechnological Applications in Plant Promotions

The world's current task is to increase agricultural yields. There are several reasons why the yield will be insufficient when the world population hits nine billion people by 2050, as predicted. As a result, more acreage is required. It is anticipated that farming practices will lead to the depletion of the primary land. Other reasons might include shrinking land area, owing to urbanization, reduced nutrient availability in soil, falling soil organic materials, declining water resources and agricultural output, and the usage of synthetic fertilizers. Farmers' usage of synthetic fertilizers is hazardous to both individuals and the environment since large portions of these fertilizers remain in the soil. As a result, eco-friendly fertilizers must be used to replace conventional fertilizers. Nanoscience and technology play a significant role in resolving these issues. Many nanoparticles that have a wide range of uses in agriculture have been found. As a result, synthetic fertilizers are being phased out in favor of nanofertilizers, which are nontoxic to humans and the environment while simultaneously assisting in plant growth and development.

The discipline of nanotechnology has recently emerged as a potentially fruitful area for the development of novel approaches to bolstering the growth and health of plants. The creation of nanofertilizers is one way that nanotechnology is being put to use in the field of plant nutrition (Jiang et al., 2021). These are fertilizers that contain nanoparticles, which have the potential to boost the uptake and utilization of nutrients by plants, which, in turn, leads to increased plant growth and productivity. In addition, the use of nanofertilizers can lessen the amount of fertilizer that is required, which, in turn, can lessen the negative effects that agriculture has on the environment. It is anticipated that traditional fertilizers will be replaced by nanofertilizers by a factor of 50% in order to increase soil fertility. The creation of nanosensors that are able to monitor the state of a plant's health in real time as well as the conditions of its environment is another application of nanotechnology. As a result of their ability to detect shifts in humidity, temperature, light, and nutrient levels, nanosensors contribute significantly to the field of precision agriculture by giving farmers the ability to maximize crop development and output. The development of nanopesticides, which are pesticides that incorporate nanoparticles and may target specific pests without harming beneficial insects or the environment, is another use of nanotechnology that can be employed in the pest control industry. Nanopesticides can also minimize the amount of pesticide that is required, which, in turn, can lower the negative influence that agriculture has on the environment (Singh et al., 2013; Bhagavanth Reddy et al., 2022). In addition, nanotechnology can be utilized to construct nanocarriers, which are able to transfer nutrients, insecticides, and other bioactive compounds directly to plant cells. This enhances the effectiveness of these substances while simultaneously lowering the environmental impact they have (Fig. 1.5).

Nanomaterials as nanofertilizers have provided agriculture with a plethora of new opportunities. Nanofertilizers are the greatest choice for replacing macro- and micronutrients (Shukla et al., 2019). To increase soil fertility, nanofertilizers are

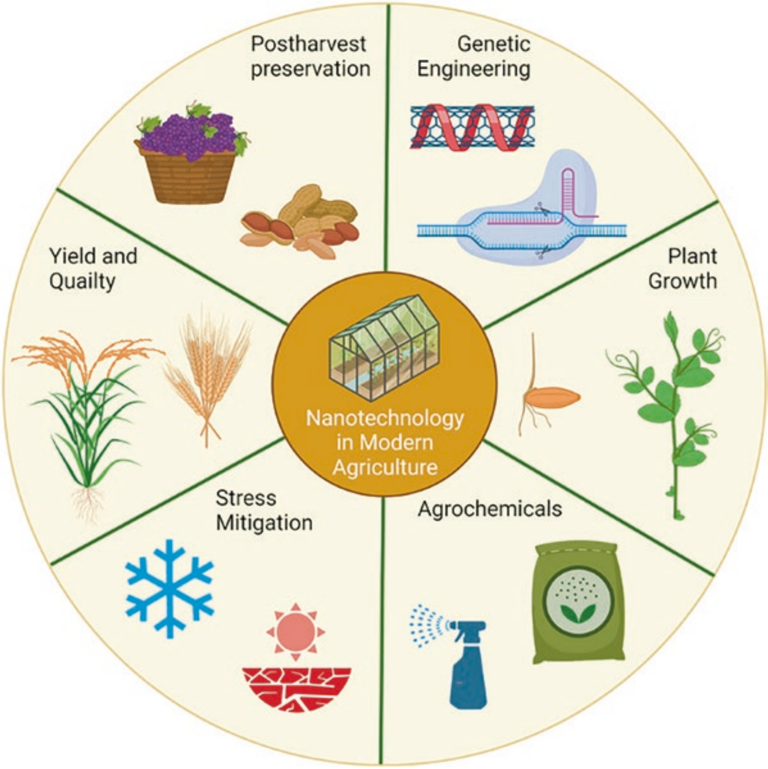

Fig. 1.5 The discipline of nanotechnology has recently emerged as a potentially fruitful area for the development of novel approaches to bolstering the growth and health of plants. The application of nanotechnology in plant promotion is a viable technique for generating environmentally friendly and sustainable solutions to boost plant growth and production while simultaneously lowering the negative impact that agriculture has on the surrounding environment. (Reprinted from Jiang et al. (2021). Under Creative Commons Attribution (CC BY) license (Springer *Nature*))

created by encapsulating plant nutrients into nanomaterials. Nanofertilizers come in a variety of shapes and sizes. They are (1) micronutrient nanoformulations, (2) macronutrient nanoformulations, and (3) nutrient-loaded nanomaterials (Kah et al., 2018). Control or delayed-release fertilizers, magnetic fertilizers, or nanocomposite fertilizers are all examples of integrated nanodevices that aid in the synthesis of micro- and macronutrients with desirable characteristics (Panpatte et al., 2016). Slow-release nanofertilizers have recently been utilized to reduce environmental contamination and the consumption of traditional fertilizers (Guo et al., 2005). Nanotechnological applications include agricultural chemical delivery systems, sensing systems to monitor environmental stress and crop status, and improving plant resistance to environmental issues and diseases. Some of the macro/micronutrient nanofertilizer applications are depicted in Table 1.1.

Table 1.1 A list of micro- and macronutrient nanoparticle types and their role as nanobiofertilizers

S. no.	Macro/micronutrient	Type	Role of NPs	References
1.	Nitrogen	Nanoparticle nanoformulation	Absorb soil nitrogen	Khan and Rizvi (2017)
2.	Phosphorous	Nanofertilizer	Improve water quality; lower eutrophication	
3.	Titanium	Nanoparticle	Increase light intensity absorption and photo-induced energy transfer	Sekhon (2014)
4.	Zinc	Nanoparticle	Enhance zinc availability to plant leaves	Khan and Rizvi (2017)
5.	Phosphorous	Nanofertilizer	Increase soybean seed quality yield	Sindhu et al. (2020)
6.	Intercalated nitrogen	Nanofertilizer	Yield, growth, quality, and nutrient absorption	
7.	Potassium	Nanoparticle	Increase leaf surface area, yield, and chlorophyll	Ardalani et al. (2014)
8.	Calcium	Nanofertilizer	Boost apple crop yields	Sindhu et al. (2020)
9.	Magnesium	Nanofertilizer	Improve seed germination	Sindhu et al. (2020)
10.	Sulfur	Nanoparticle	Sulfur metabolism, water content, manganese absorption	Ragab and Saad-Allah (2020)
11.	Iron	Nanoparticle	Seed weight, iron, and chlorophyll content	Sindhu et al. (2020)
12.	Zinc oxide	Nanoparticle	Increase leaf chlorophyll and petal anthocyanin content	Seydmohammadi et al. (2019)
13.	Copper	Nanoparticle	Enhance root length, height, and fresh and dry weights	Shende et al. (2017)
14.	Manganese	Nanoparticle	Extend root length	Sindhu et al. (2020)
15.	Boron	Nanoparticle	Boost plant height, pod quantity, seed production	
16.	Molybdenum	Nanoparticle	Increase yield, plant performance, and disease resistance	
17.	Engineered molybdenum	Nanoparticle	Enhance root area, root tip, root length, root diameter	

Nanobiofertilizers aid in the overall optimization of photosynthesis, nutrient absorption and translocation, and product and quality improvement (Sindhu et al., 2020). Nanopesticides, on the other hand, can effectively regulate delivery and make the medication effective even at low concentrations. According to research, nanopesticides are efficient in controlling bacteria, fungi, and insects. Many nanopesticides have been shown to have an effect on disease-causing insects. Because of their long-lasting release in soil, nanopesticides are more efficient in killing insects than are traditional pesticides, which wash away after rains (Khan & Rizvi, 2017). Nanoherbicide formulations are designed to eliminate herbicides' harmful features. They extend the shelf life of chemicals while also being plant-specific. They have their own means of preventing it from deteriorating as a result of environmental influences (Paramo et al., 2020).

The use of nanoparticles in the development of new products such as nanosensors play an important role in agriculture (Shang et al., 2019). For successful agricultural and environmental systems, nanosensors are utilized to monitor crop development, soil conditions, nutrient shortage, water scarcity, toxicity, plant diseases, plant health, product quality, and overall safety. Combining them with nanosensors results in nanobiosensors. These sensors are precise, quick, and sensitive. They contain a biological component that is linked to an active energy converter molecule. When there is an environmental shift, this aids in the detection of changes in the surrounding molecules (Ghasemnezhad et al., 2019). Bionic plants are those that have nanomaterials implanted into their cells and chloroplasts, allowing them to sense changes in both the environment and within the plant. These will play a bigger part in hybrid bionic plant research and development in the future.

Because the bulk synthesis of nanoparticles is simple, they can be produced in larger quantities. Nanoparticles have a huge influence on agriculture. They play an important role in the regulation and development of plant life. Plants that are treated with nanoparticles produce a higher yield. As a result, it is possible that the food crisis may be resolved in the near future.

6 Conclusions

The use of nanofertilizers has produced encouraging results in increasing crop output and enhancing plant growth. The following are some advantages of nanofertilizers for plant growth:

1. *Improved Nutrient Absorption*: Nanofertilizers can improve nutrient uptake effectiveness, allowing plants to absorb nutrients more efficiently from the soil. This may lead to enhanced plant growth and increased agricultural yield.
2. *Increased Nutrient Use Efficiency*: Nanofertilizers can make plants more effective at using nutrients, which results in a reduction in the amount of fertilizer needed to produce the same amount of growth as conventional fertilizers. Saving money and lessening the impact on the environment are the possible results.
3. *Improved Soil Health*: By improving microbial activity and encouraging the growth of advantageous microbes, nanofertilizers can improve soil health. Improved soil structure, nutrient availability, and water retention may result from this.

4. *Lessened Environmental Impact*: By requiring less fertilizers and lowering the likelihood of nutrient runoff and leaching, nanofertilizers can lessen the environmental impact of conventional fertilizers.
5. *Greater Resistance to Stress*: Plants that receive nanofertilizers can withstand environmental stresses like pests, salts, and droughts. This may lead to enhanced plant growth and increased agricultural yield.

In conclusion, nanofertilizers have demonstrated significant promise for enhancing crop productivity and encouraging plant growth. They can improve soil health, lessen their negative effects on the environment, raise stress resilience, and improve nutrient uptake and usage efficiency. It is crucial to remember that additional study is necessary to completely comprehend the long-term impacts of nanofertilizers on both plants and the environment. To reduce any potential dangers related to the usage of nanofertilizers, correct application methods and safety precautions should be followed.

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Chapter 2
Fabricated Nanofertilizers: A Clean and Feasible Substitute for Conventional Fertilizers

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1 Introduction

The advent of advanced agricultural technologies, high-yield crop varieties, crop rotation, irrigation improvement, mechanization, utilization of fertilizers, and biopesticides has previously prevented large-scale famine. Despite the rise in population, inclining incomes, and related dietary changes, the world's food demands are anticipated to climb by 70% by 2050 (Bindraban et al., 2018). The biggest challenges to ensuring global food security are lack of agricultural land and water resources, climate change, crop pests, inefficient nutrient usage, and low crop production. The need for food is rising daily as a result of the growing world population, which has forced growers to use fertilizers extensively (Bernela et al., 2021). The use of more effective mineral fertilizers is an essential strategy to meet the rise in food production needed to feed the growing population and promote economic development, given the restricted number of fertile farmlands and limited freshwater resources globally (Zhang et al., 2015). Maintaining soil fertility, and enhancing crop quality as well as yield, depends heavily on nutrient fertilization. The nutrient utilization efficiency of conventional fertilizers applied directly to the soil or sprayed on leaves is significantly influenced by the final concentration of the fertilizers reaching the target areas. In practice, an extremely minuscular fraction, far below the requisite concentration, reaches the intended site as a result of chemical

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leaching, drift, runoff, hydrolysis, evaporation, photolysis, or even microbiological destruction. The widespread use of mineral fertilizers and organic residues has had a detrimental effect on soil and water quality around the world (Ashraf et al., 2021; Xie et al., 2019). As an outcome, the recurring use of an excessive amount of fertilizers has a negative impact on the soil's inherent nutrient equilibrium. Aside from these, aquatic habitats have been severely damaged as a result of harmful compounds leaking into rivers and reservoirs and also contaminating drinking water. Contrarily, unchecked use of chemical fertilizers and pesticides has increased food production significantly while further lowering food quality and soil fertility (Shang et al., 2019). Traditional fertilizers lead to groundwater pollution, water eutrophication, and soil quality degradation, which can be dangerous to both humans and the environment in addition to being expensive to farmers. The age of biofertilizers has commenced as a result of an imbalance and negligent overuse of chemical fertilizers. Despite the fact that numerous fields fall under the scope of agriculture, nanotechnology in agriculture has gained steam in the recent decade, thanks to generous public financing, although the rate of progress is slow (Mukhopadhyay, 2014). The scientific community is looking for environmentally benign fertilizers, especially ones that are highly nutrient-efficient, and nanofertilizers (NFs) are emerging as a potential substitute, as nanoparticles (NPs) possess tremendous physicochemical properties such as smaller dimensions, high surface area to volume ratio, excessive ionizing power, improved chemical stability, enhanced reactivity, elevated absorbability, increased pH tolerance, and enlarged thermal stability (Zulfiqar et al., 2019). The study, development, fabrication, synthesis, manipulation, and application of materials with one or more dimensions less than 100 nm constitute nanotechnology (Lee & Moon, 2020). Nanotechnology has been studied for the past two decades in order to improve nutrient use efficiency and target nutrient delivery to plants, leading to the birth of nanofertilizers (NFs). Materials with macro- and micronutrients that are delivered to crops in a controlled manner at the nanometer scale, typically in the form of nanoparticles, are referred to as nanofertilizers (NFs) (Shang et al., 2019; Das & Beegum 2022). NFs transfer nutrients to plants in an effective manner, exhibiting their superiority over bulky chemical fertilizers in terms of crop productivity and environmental viability (Babu et al., 2022). As a result, this approach results in the controlled release of active ingredients over a long period of time and prevents nutrients from leaching into groundwater, thus reducing the amount of fertilizer used. Nanofertilizers are essential for minimizing the use of inorganic fertilizers and their negative environmental impacts because they are highly reactive, can enter the epidermis, and allow delayed release and distribution. This improves the efficiency with which nutrients are utilized and may reduce abiotic stress and heavy metal toxicity (El-Saadony et al., 2021). Furthermore, nanotechnology boosts agricultural output efficiency by lowering relevant losses and making fertilizers and insecticides more efficient solutions (Shang et al., 2019). Scientific data suggest that an estimated 50–70% of conventional nitrogen fertilizers are lost due to evaporation, leaching, or degradation, which limits fertilizer efficiency and raises production costs (Miao et al., 2015; Yang et al., 2016). On the other hand, nitrogen-based nanoformulations regulate the release of N in nitrogenous fertilizers with the need for its assimilation by crops. The sustained and slow release of nanofertilizers is evident from the uniform and slow release of hydroxyapatite nanomaterial-coated urea for up to 60 days as compared to the release of conventional fertilizers in bulk form for a period of 30 days (Kottegoda et al., 2011). Thus, by preventing unwanted nutrient losses through direct uptake by crops, nanoformulations prevent nutrient interactions with soils, water, air, and microbes (Panpatte et al., 2016).

This chapter provides an insight into the prospective utilization of NFs in the agricultural sector by:

- Using nanofertilizers and nanopesticides to enhance the productivity of crops
- Using hydrogels, nanoclays, and nanozeolites to enrich the water-holding capacity of the soil
- Promoting the uptake of minerals from the soil
- Managing nutrition by using the nutrient use efficiency of the soil
- Intelligently monitoring soil and plant growth with the use of nanosensors
- Sustained and target-specific nutrient delivery

2 Application Methods

The integration of nanoparticles (NPs) with agrochemicals via various mechanisms such as capsulation, absorption, and surface ionic or weak bond attachments can improve the efficacy of fertilizer use. Nanofertilizers ensure the slow and controlled use of encapsulated nanoparticles, which consequently minimize the dosage by enhancing the efficiency of the applied fertilizer (Fatima et al., 2021). In response to environmental cues and biological demands, they could precisely release their active ingredients. The use of nanofertilizers is helpful as it minimizes the quantity of chemical fertilizer application and, consequently, soil toxicity (Dhir, 2021). Nanofertilizers can strengthen crop productivity by accelerating the process of seed germination, seedling growth, nitrogen metabolism, rate of photosynthesis, and carbohydrate and protein synthesis in vitro and in vivo.

2.1 The Soil Mode of Application

Soil is the basic medium that supports the growth and development of a plant. Over the course of time, due to intensive farming, soil becomes deficient in particular minerals, resulting in poor yield and improper growth and development (Mahil & Kumar, 2019). When NFs are applied to soil, the first physical process that takes place is aggregation that reduces the area of action. The Brownian motion in the soil directs nanoparticle movement toward the direction of the soil pores (Xu et al., 2020). The application of essential nutrients to the soil results in the uptake and, subsequently, in the transportation of nanoparticles through the soil root epidermis to further reach the vascular tissue xylem present in the endodermis. NPs can also penetrate the root tip meristem or those places where lateral roots develop. NPs must cross cell walls and plasma membranes to enter the epidermal layers of the roots. The xylem helps in the translocation of NPs along with water to the aerial parts of the plant (Avila-Quezada et al., 2022). Nanoparticles with diameters ranging from 3 to 5 nm are best known to enter through the tiny semipermeable root hairs (Lin & Xing, 2008). The soil mode of application, which is the most common mode of nanofertilizer application, has restrictions such as percolation of insoluble forms of the inorganic nutrients into the soil, leading to leaching by rain and irrigation (Alshaal & El-Ramady, 2017). Slomberg and Schoenfisch (2012) demonstrated the effective uptake of spherical silica NPs ranging from 14 to 200 nm by the roots of *Arabidopsis thaliana*. The active transport of AuNPs of size 40 nm from the roots to the shoots was observed in *Solanum lycopersicum* (Dan et al., 2015).

2.2 Foliar Mode of Application

The foliar mode of application has several advantages over the soil mode of application. The cuticle or the stomata allow nutrients to enter the leaves, where they further travel by symplastic or apoplastic pathways to other plant components (Avellan et al., 2021). Nanoparticles of size <5 nm are restricted by the cuticle present on the surface of the leaf and act as the primary leaf barrier. Environmental factors like temperature, light, pH, humidity, and deposition of wax on the leaf surface are the limiting factors for the entry of nanofertilizers through the foliar mode. Additionally, the chemical and physical properties of nanoparticles alter the entry (Oosterhuis & Weir, 2010). Roots, stems, fruits, grains, and young leaves serve as potent sinks for sap, and NPs can travel in both directions and accumulate to varying degrees as a result of vascular transport by the phloem. Wang et al. (2013) reported the entry of nanomaterials through the leaf stomata of watermelon plants and its further redistribution to plant tissues. Similar observations by Hong et al. (2014) revealed the penetration of CeO_2 NPs through leaves of hydroponically grown cucumber plants and their transport to different parts of the plant. Foliar-based nanofertilizers encounter a number of structural challenges since the nutrients are salt-based (cations/anions) and may be difficult to penetrate the interior plant tissue cells (Mahil & Kumar, 2019). Foliar application of zinc and boron nanofertilizers increased the fruit yield and quality of *Punica granatum*, including 4.4–7.6% increases in total soluble solids (TSSs), 20.6–46.1% increases in the maturity index, and 0.28–0.62 pH unit increases in juice pH without negatively impacting any physical fruit characteristics (Davarpanah et al., 2016) (Fig. 2.1).

Seed Treatment

Metal nanoparticles are increasingly being employed for seed treatment of various crops because of their reduced toxicity when compared to bulk salts and chelates. Additionally, only a small amount of nanofertilizers is necessary to accelerate

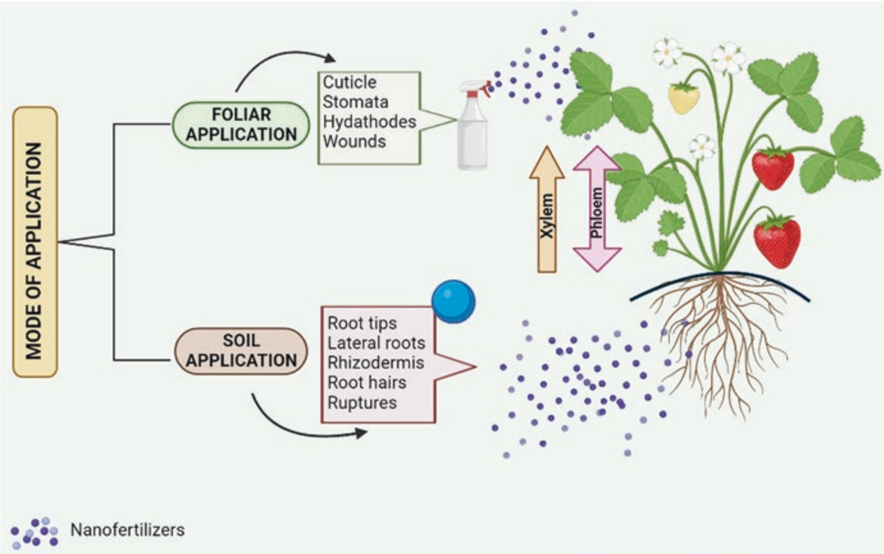

Fig. 2.1 Nanofertilizers can be applied through various modes, depending on the type of fertilizer and the target crop. Some common modes of application include foliar application, soil application, seed coating, hydroponic systems, and controlled-release fertilizers

physiological and biological development in plants (Singh et al., 2021). Nanomaterials absorbed through the seed coat may affect seed germination by regulating the emergence time of the seedling, radicle/plumule length, enzymatic activities, photosynthesis, respiration, and, ultimately, crop productivity (Ali et al., 2021). According to Monica and Cremonini (2009), after seed treatment with nanofertilizers, there is an increase in seed germination percentage, dry weight of the seedling length of the seedling, and seed health. Metal oxide nanoparticles, viz., Fe_3O_4 NPs, Co_3O_4 NPs, CeO_2 NPs, AuNPs, MnO_2 NPs, and CuO NPs are known to increase superoxide dismutase, catalase, and ascorbate peroxidase levels in plants, which ultimately enhance the defense mechanism of plants (Wei & Wang, 2013). Seed treatment provided with AgNPs are well documented to shield seeds from fungal and bacterial diseases such as powdery mildew and spot blotch in wheat plants (Park et al., 2006; Mishra et al., 2014). The ability of nanoparticles to quickly pass through seed coats and offer improved absorption and utilization by seeds is the most likely to increase the germination rates. These NPs have a positive impact on germination and on the generation of vital biomolecules and vital nutrients for plant growth, and they play a significant role in a number of enzymes (Sandeep et al., 2019). The impact of silver nanoparticles (AgNPs) was found to be positive on seed germination in the case of green beans in normal and cold temperatures. The fungicidal effects of AgNPs were found to be advantageous during seed germination in both laboratory and field settings in the case of green beans (Prażak et al., 2020). Seed treatment with ZnO NPs leads to the penetration of NPs into the cytoplasm,

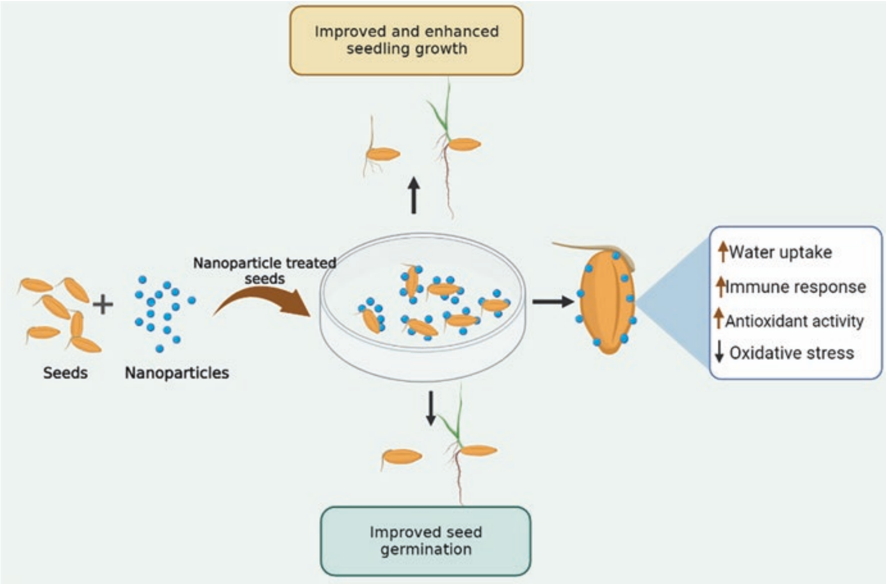

Fig. 2.2 The effect of nanoparticle-treated seeds on improved seed germination and enhanced seedling growth. There is increased water uptake, elevated immune response, and antioxidant activity, whereas an alleviation in oxidative stress in plants in response to nanoparticle-treated seeds

which alters the cell signaling pathways and the metabolic pathways and ultimately alleviates oxidative stress. The reduction in oxidative stress leads to better gaseous exchange and more photosynthesis in two oilseed crops from the Brassicaceae family, namely, *Brassica napus* L. and *Camelina sativa* (Sarkhosh et al., 2022) (Fig. 2.2).

3 The Role of Nanofertilizers in Crop Enhancement

3.1 Nanofertilizers in Plant Growth and Seed Germination

Seed germination is the foremost and delicate stage in a plant's life cycle, which promotes seedling growth, survival, and relative abundance affected by both soil toxicity and environmental and environmental cues (Shang et al., 2019). Moreover, a variety of other factors, including the environment, genetic makeup, availability of moisture, and soil fertility, have a significant impact on seed germination (Manjaiah et al., 2019). The application of nano-SiO_2, nano-TiO_2, and nano-zeolite accelerates seed germination in crop plants (Lu et al., 2002). Additionally, the utilization of multiwalled carbon nanotubes (MWCNTs) accelerates seed germination in a plethora of crop species, including barley, corn, maize, wheat, soybean, tomato, and peanut (Srivastava & Rao, 2014; Joshi et al., 2018). NFs, by the virtue of their small size and large surface area, enter the seed coat and intensify the absorption of water and nutrients, which, in turn, increase the germination and growth of the plant (Mercurio et al., 2018). Shreds of experiments indicate that there is a positive impact of nanoparticles on the process of photosynthesis, which leads to enhanced plant growth. Giraldo et al. (2014) demonstrated a three times increase in the photosynthetic activity of plants on addition of carbon nanotubes to chloroplasts as compared to the untreated ones.

3.2 Nanofertilizers in Mitigating Stress

Plants are prone to a number of abiotic and biotic stresses, which limit agricultural crop productivity and pose a threat to global food security. Drought and salinity induce both biochemical and physiological changes in plants and have been reported as damaging stressors for optimal plant growth (Zia et al., 2021). NFs provide enhanced tolerance toward abiotic stress factors (high temperatures, salinity, flooding, droughts, heavy metals, etc.) by triggering the plant's antioxidant defense system. NFs tend to enhance the photosynthetic rate and host defense mechanism in farmed plants by increasing the morphological and physiological parameters (Verma et al., 2022). Furthermore, there is a reduction in oxidative stress as nanoparticles can scavenge the reactive oxygen species (ROS) generated during the stress conditions with the action of catalase, peroxidase, and superoxide dismutase enzymes (Upadhyaya et al., 2015). NFs can regulate photosynthetic efficiency and water intake, have more effective adsorption and targeted delivery due to their ability to permeate plants, and can detoxify reactive oxygen species, which improves seed germination, growth, and crop output (Sarraf et al., 2022). Diseases and pathogens exert detrimental biotic stress on plants. Microorganisms primarily develop on or inside plant tissues, eliciting a variety of symptoms such as chlorosis, stunting, rotting, or the emergence of local lesions (Spare et al., 2021). Many plant diseases caused by *Botrytis cinerea*, *Alternaria alternate*, *Monilinia fructicola*, *Fusarium solani*, *Fusarium oxysporum*, *Phytophthora infestans*, and *Ralstonia solanacearum* could be effectively controlled by metal oxide nanomaterials such as MgO, CuO, and ZnO (Shenashen et al., 2017; Malandrakis et al., 2019).

3.3 Nanofertilizers in Enhancing Soil Fertility and Yield

Nanofertilizers enhance both soil fertility and crop yield manifold when compared to conventional fertilizers. Traditional fertilizers need to be used in bulk as chemical fertilizers have low uptake efficiency. This in turn has a negative effect on the environment, leading to soil toxicity and eutrophication (Raliya et al., 2018). Nanofertilizers allow the gradual release of nutrients over an extended period of

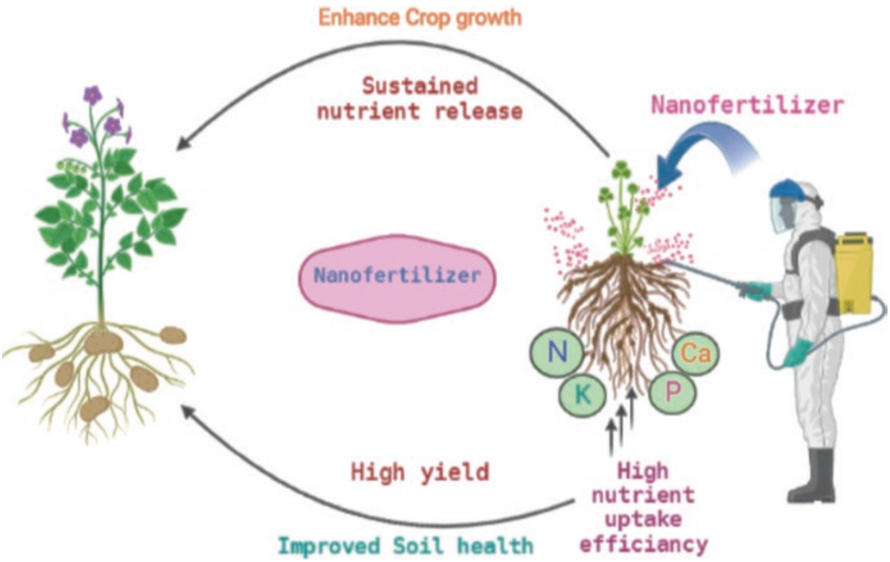

Fig. 2.3 Influence and effect of nanofertilizers on crop growth, yield, and soil health

time, which considerably reduces mineral loss, hence ensuring good soil health and environmental safety (Nongbet et al., 2022). Different macro- and micronutrients are encapsulated with NPs to synthesize nanofertilizers (NFs). Macronutrients such as carbon (C), nitrogen (N), potassium (K), calcium (Ca), magnesium (Mg), and sulfur (S) have been encapsulated by different nanomaterials to enhance crop fertilizer uptake and reduce fertilizer outflow (Kanjana, 2020). Urea is a nitrogen-rich fertilizer known for its high solubility in soil particles. In order to synthesize environmentally friendly urea, a nanoparticle matrix of hydroxyapatite was employed and urea-hydroxyapatite NPs favored the programmed and slow release of urea (Kottegoda et al., 2017). Carbon nanotubes and fullerenes, for example, have been shown to have favorable effects on plant development. Fullerenes increased hypocotyl development in *Arabidopsis* by stimulating the number of cell divisions (Gao et al., 2011) (Fig. 2.3).

4 Types of Nanofertilizers

Nutrient elements play a strategic role in all phases of plant life right from germination to growth and development. It is possible to use hydrogel and aqueous suspension forms of nanofabricated materials that contain plant nutrients to apply them safely, store them easily, and use them as a delivery mechanism. Given their strong adsorption affinity toward organic molecules and heavy metals, zero-valent iron (Fe) nanoparticles, and even iron rust nanoparticles, could be used to clean up soils contaminated with pesticides, heavy metals, and radionuclides. The development of soil micro- and macroaggregates is aided by the good soil-binding characteristics of iron nanoparticles, which are similar to those of calcium carbonate nanoparticles (Liu & Lal, 2012). The deficiency of specific elements manifests the disease, stunted growth, and low yield. Nanofertilizers can be made of a variety of NPs, including metal oxides, carbon-based NPs, and, others, based on their conjunction and compositional features. They can be created through biological, chemical, or physical (top-down) processes (Liu & Lal, 2015). The nutrients acquired from the soil and released by these nanofertilizers have an impact on how plants react. Various types of nanofertilizers, such as macronutrient nanofertilizers, micronutrient nanofertilizers, and fertilizers enriched with nanomaterials, can be created according to the available nutrient sources (Duhan et al., 2017). Green nanotechnology or biofabrication is a clean, nonhazardous, and especially ecologically friendly technique that can be used to synthesize nanofertilizers in place of the current chemical and physical processes used to create nano-products (Saratale et al., 2018). NFs synthesized by using different metals are described below.

4.1 Copper Oxide/Copper Nanofertilizers

Copper oxide has been considered to be a highly promising inorganic material for nanofertilization, due to its better efficacy since its higher surface area/volume allows better absorption within the plant tissues. Among its beneficial effects are increased metabolite production, a stronger ability to withstand abiotic stresses, a rise in radical elongation, and an increase in net photosynthesis (Leonardi et al., 2021). Without exposing customers to excessive Cu, nano-based CuO fertilizers have been considered a good alternative to protect and lengthen the shelf life of sweet potato roots (Bonilla-Bird et al., 2018). The recent uses of nano-copper (nano-Cu) compounds in agrosystems have demonstrated their potential to enhance the physiological performance and agronomical parameters of crops. A nanowire was homogenized in Milli-Q water, which was then sonicated for 30 min. The obtained mixture was used to amend the potting mix. It has been observed that a CuO oxide nanofertilizer acts as a highly potent fertilizer in the potting mix, increasing the physiological and molecular responses in alfalfa plants (Cota-Ruiz et al., 2020). Simultaneously, a biologically synthesized Cu nanofertilizer has been utilized in foliar application on basil. The biosynthesis method included the reduction of Cu ions in the presence of basil extract. The synthesized nano-Cu particles were characterized through scanning electron microscopy (SEM) and X-ray diffraction (XRD) analysis to study the shape, size, and chemical identity of the nanoparticles. According to the findings, CuNPs significantly increased the majority of morphological characteristics. Chlorophyll a, chlorophyll b, total chlorophyll, and carotenoid concentrations in basil plant leaves were significantly affected by CuNP application. Thus, the study confirms that a biofabricated Cu nanofertilizer helps increase the quality and quantity of basil through foliar application. In a study, CuO nanoparticles were released from a biodegradable shell that was made of a chitosan and sodium alginate mixture. Scanning and transmission electron microscopies (SEM and TEM, respectively) were used to analyze the morphological features, and X-ray diffraction, thermogravimetric analysis, Fourier transform infrared spectroscopy, dynamic light scattering, and inductively coupled plasma optical emission spectrometry were used to characterize the chemical composition of the synthesized CuO nanofertilizer. In the study, the impact of the fabricated nanofertilizer on the germination of *Fortunella margarita Swingle* (kumquat tree) seeds, which are members of the Rutaceae family and whose genus is connected to the most significant citrus species, has been investigated. It was observed that after providing the seeds with 15 ml of the treatment, the seedlings grew more successfully along with the development of the epigean and hypogean portions (Leonardi et al., 2021). In the latest study by Saffan et al. (2022), biologically synthesized copper nanoparticles of 350 nm–500 nm were tested on tomatoes in a greenhouse under water salinity stress. It was concluded that bio-nano-Cu improved the tomato fruit output and quality despite inadequate irrigation water quality. Therefore, it was stated that to increase the yield and quality of farmed crops, particularly in times of stress, the use of a nanobiofertilizer is promising.

4.2 Iron Oxide Nanofertilizers

Almost every part of contemporary life now uses nanomaterials, including agriculture. To replace conventional Fe fertilizers, which have several drawbacks, research was conducted to determine how effective iron oxide nanoparticles (Fe_2O_3 NPs) are as fertilizers. In a pot experiment, the effects of Fe_2O_3 NPs on the growth and development of the crop peanut (*Arachis hypogaea*), which is highly susceptible to Fe shortage, were investigated. The findings demonstrated that the peanut plant's root length, plant height, and biomass values were all increased by Fe_2O_3 NPs. By controlling the concentration of phytohormones and the activity of antioxidant enzymes, the Fe_2O_3 NPs stimulated peanut growth. In comparison to the control group, Fe contents in the peanut plant treated with Fe_2O_3 NPs were higher (Rui et al., 2016). Palchoudhury et al. (2018) carried out research to evaluate the impact of iron oxide-based nanofertilizers on embryonic root growth in legumes. On an FEI Tecnai F-20 transmission electron microscope, the size and shape of the iron oxide NPs were examined. The size of the iron oxide NPs was determined to be about 16 nm. It was confirmed through statistical analysis that iron oxide nanoparticles were able to increase root growth by 88–366% at low concentrations of 5.54103 mg/L. Therefore, given that a rise in plant development was seen with iron oxide nanoparticles for a variety of seed types, this accurately foretells the vast potential of iron oxide nanoparticles as nanofertilizers. In an experiment, the growth, production, and quality of squash plants were examined in two growing seasons, 2017 and 2018, using the foliar application of micronutrient iron oxide nanoparticles. Using a green microwave-assisted hydrothermal process, ferric nitrate analytical grade salts were used as a precursor for the creation of the iron oxide nanofertilizers. The produced sample's XRD patterns were obtained using a diffractometer with the Bragg–Brentano geometry and a copper tube. The collected results demonstrated that the squash fruits sprayed with iron oxide nanoparticles had the highest value in terms of their organic matter, protein, lipids, and energy content (Shebl et al., 2019). The biogenic synthesis of iron nanofertilizers was conducted using the marine algae *Chaetomorpha antennina.* Green synthetic iron oxide nanoparticles were used to cure drought-stressed *Setaria italica* plants. These FeNP helped the plants resist drought stress in addition to acting as a nano nutrient for them. There has been an overall acceleration in plant (*Setaria italica*) growth. Additionally, it was found that as FeNP (Fe_3O_4) concentrations increased, the amount of soluble sugar and chlorophyll in the seedlings also increased. This finding suggests that the iron the plants took up was used up for the production of photoassimilates. The latest study by Dola et al. (2022) investigated the effects of foliar spray of nano-iron at different doses (0, 100, and 200 ppm) on the soybean's physiology, yield, and seed nutritional quality under both drought and well-watered states. The foliar spray of nano-iron significantly increased plant growth under both controlled well-watered and drought circumstances, under which 200 ppm of nanoparticles boosted soybean seed output by 40.12 and 32.60%, respectively. In addition, when compared to the untreated controls, nano-iron raised the oil content of soybean seeds by 10.14 and 7.87% in drought- and well-watered situations, respectively. Finally, it could be said that exogenous foliar sprays of 200 ppm nano-Fe_3O_4 were more successful than the alternative, according to the results, because they increased drought tolerance, yield, and seed quality in soybean.

4.3 Titanium Dioxide Nanoparticles

It has been confirmed that plants can quickly absorb nanoformulated fertilizers, as they have a prolonged effective duration of nutrient supply in the soil or in the plant. According to the study, TiO_2 nanofertilizers do not exhibit any significant phytotoxicity and can increase the chlorophyll content, vegetative growth, and yield component of barley in semiarid regions with Mediterranean climates (Rameshaiah & Jpallavi 2015; Janmohammadi et al., 2016). It has been observed that low concentrations of TiO_2 NPs enhance the physiology and stress response of plants. After applying foliar TiO_2 NPs, it has been seen that plant yields have increased. At specific wavelengths, TiO_2 NPs also work as functional photocatalysts and promote photosynthesis and plant growth. It has been confirmed that a TiO_2 NP-treated variant enhanced the nutritional and quantitative characteristics of sunflowers, including oil content. With all dependent physiological indices, the TiO_2 NPs provided unexpectedly early plant maturation (Kolencik et al., 2020). Research work also compared the production of TiO_2 NPs using *Trianthema portulacastrum* and *Chenopodium quinoa* plant extracts and the traditional chemical (sol–gel) approach. High-tech methods such as X-ray diffraction (XRD), Fourier transform infrared

(FTIR) spectroscopy, scanning electron microscopy (SEM) with energy-dispersive X-ray (EDX) spectroscopy, SEM–EDS spot analysis, and elemental mapping were used to investigate the synthesized TiO_2 NPs. To test the antifungal effectiveness of synthetic TiO_2 NPs against harmful plant diseases, they were treated with wheat rust (*Ustilago tritici*). It was observed that both the sol–gel and green techniques of NP preparation showed good antifungal responses against *U. tritici*, but the TiO_2 NPs prepared using green techniques were found to exhibit the best antifungal activity against wheat rust, especially NPs made with *C. quinoa* extracts (Irshad et al., 2020). The exploratory study examined the potential impact of biosynthesized titanium dioxide nanoparticles (TiO_2 NPs) utilizing the seed extract of *Cuminum cyminum* on seed germination and germination indices of mung bean (*Vigna radiata*). The successful synthesis of TiO_2 NPs was determined by the optimal outcomes of several characterization procedures, including ultraviolet (UV), XRD, FTIR, SEM, and TEM. These were capped with several phytochemicals found in the *Cuminum cyminum* extract. The mechanism impacting both grain germination and growth rate is affected by the TiO_2 NPs penetrating mung bean seeds. As seeds were effectively treated with TiO_2 NPs, the germination indices for *Vigna radiata* significantly improved when compared to untreated seeds (Fox et al., 2020). Hydroponic growth and biochemical and physiological responses of *Nigella arvensis* were studied to assess the hormetic effects of TiO_2 NPs at concentrations ranging from 0 to 2500 mg/L. Scanning and transmission electron microscopies (SEM and TEM, respectively) were used to study the translocation of TiO_2 NPs in plant tissues. Inductively coupled plasma atomic emission spectroscopy was used to measure the bioaccumulation of total titanium. It was observed that 100 mg/L of TiO_2 NPs considerably aided in the elongation of roots and shoots as well as in the expansion of the entire biomass. Overall, the study highlighted the physiological and biochemical changes brought about by TiO_2 NPs in a medicinal plant.

4.4 Cerium Oxide Nanoparticles

Due to their unique chemical and biophysical characteristics, cerium oxide nanoparticles (CeO_2 NPs) have captured the attention of researchers in particular. It has been observed that corn root and leaf biomass showed significant variations, after the application of CeO_2 NP fertilizers (Fox et al., 2020). According to research, cerium oxide nanoparticles (CeO_2 NPs) can operate as direct antioxidants and free radical scavengers, depending on the size, surface characteristics, exposure time, and age of the plant. Low concentrations of CeO_2 NPs have a favorable impact on growth and photosynthesis, increasing growth metrics and chlorophyll levels (Abdulhameed et al., 2021). The research was carried out to evaluate how fertilizing with chemical nitrogen–phosphorus–potassium (NPK) and nano-NPK fertilizers affects cabbage growth and yield. While CeO_2 NPs were created using laser ablation, nanofertilizers (N, P, and K) were purchased. The findings revealed that in terms of plant height, head weight, external leaf weight, and overall plant yield, nanofertilization treatments outperformed chemical fertilization treatments. The CeO NP treatment had the highest total plant production (72 tonnes per hectare) (Abdulhameed et al., 2021). The effect of cerium oxide nanoparticles on the nutritional value of tomato (*Solanum lycopersicum*) fruits growing in *Fusarium oxysporum*-infested soil was examined in a study. After being transplanted into pots containing a soil mixture contaminated with the *Fusarium* wilt pathogen, 3-week-old seedlings of tomato plants were exposed to foliar and soil routes to CeO_2 nanoparticles at concentrations of 0, 50, and 250 mg/L. Fruit characteristics such as biomass, water content, diameter, and nutritional value were assessed. It was found that foliar exposure to CeO_2 NPs at a concentration of 250 mg/L increased the fruit dry weight (67%) and lycopene content (9%) in infested plants as compared to the infested, untreated controls (Adisa et al., 2020). The purpose of the study was to investigate the potential of cerium oxide nanoparticles (CeO_2 NPs) in reducing salt stress in grapevine (*Vitis vinifera*) cuttings. By testing a variety of agronomic, physiological, analytical, and biochemical parameters, it was specifically determined how CeO_2 NPs (25, 50, and 100 mg L^{-1}) and salinity (25 and 75 mM sodium chloride (NaCl)) interacted. Treatments with CeO_2 NPs generally reduced the negative effects of salt stress (75 mM NaCl), significantly improving the relevant agronomic traits of grapevine. Under conditions of high salinity, CeO_2 NPs significantly reduced chlorophyll damage. Furthermore, grapevine damage brought on by salinity was lessened by the presence of CeO_2 NPs (Gohari et al., 2021). Global food security and agricultural productivity are gravely threatened by salinity stress. A recent study has examined how cerium oxide nanomaterials (CeO_2 NPs) in maize reduce salt stress. Deionized water or a 100-mM NaCl solution was used to water soil-grown maize plants as a salinity stress treatment or a control. On maize leaves, foliar applications of CeO_2 NPs (1, 5, 10, 20, and 50 mg/L) with antioxidative enzyme-mimicking activities were conducted for 7 days. The morphological, physiological, biochemical, and transcriptome responses of maize were observed in the study. CeO_2 NPs at 10, 20, and 50 mg/L increased the maize's ability to tolerate salt by 69.5%, 69.1%, and 86.8%, respectively. Additionally, in salt-stressed maize leaves, 10 mg/L CeO_2 NPs reduced reactive oxygen species (ROS) levels by 58.5%, increased photosynthetic efficiency by 30.8%, and preserved Na^+/K^+ equilibrium. After the application of CeO_2 NPs, transcriptomic analysis showed that the antioxidative defense system-related genes returned to the normal control level, proving that CeO_2 NPs removed ROS through their inherent antioxidative enzymatic activities. Figure 2.4 describes a variety of nano-based fertilizers and their impact on plants.

4.5 Selenium Nanoparticles

In a study undertaken, the molecular, developmental, and physiological responses of tomato plants to foliar treatments of selenium nanoparticles (nSe) at 0, 3, and 10 mg l^{-1} or corresponding dosages of sodium selenate (BSe) were investigated. It was observed that BSe /nSe treatment at 3 mg l^{-1} boosted the shoot and root

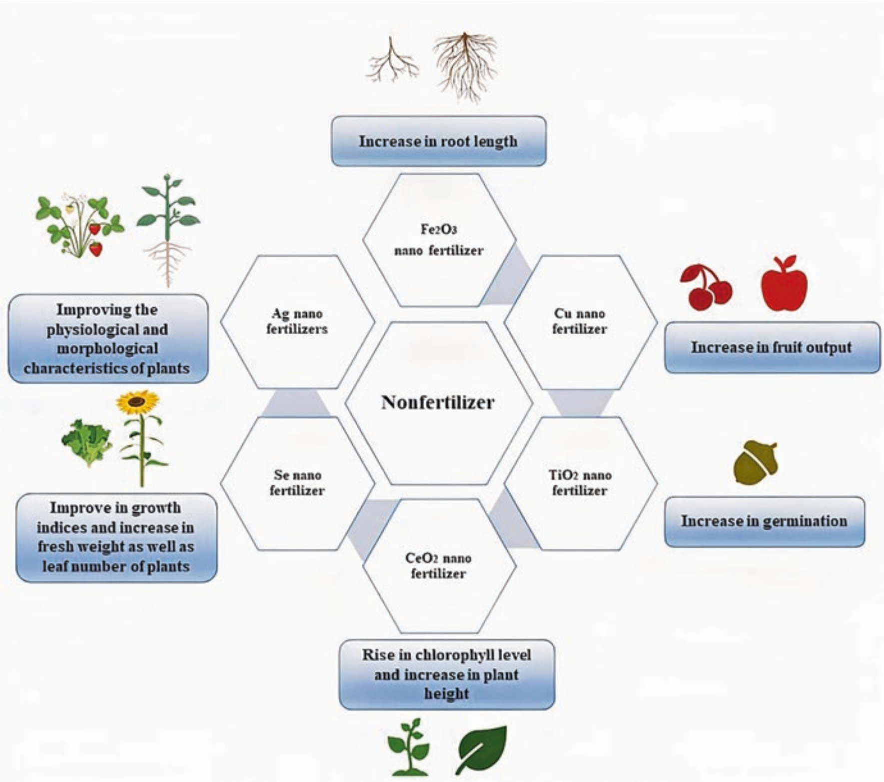

Fig. 2.4 Different types of nanofertilizers and their effect on plants

biomass. Fruit yield and postharvest longevity were increased by foliar BSe/nSe spray, especially at a lower dose (Neysanian et al., 2020). Another research was undertaken to evaluate the effect of glycol chitosan-coated selenium nanoparticles (SeNPs) on the ginsenoside accumulation in *Panax ginseng*. It was observed that 20 mg l^{-1} of GC SeNP administration significantly increased the expression of genes involved in the ginsenoside biosynthesis pathway (*PgHMGR*, *PgSS*, *PgSE*, and *PgDDS*). Ginsenoside accumulated up to 217.47 mg/mL and 169.86 mg/mL after treatment with 20 mg L^{-1} GC SeNPs, mostly as a result of the elevated proportion of Rb1 and Re ginsenosides. The overall findings suggested that environmentally acceptable GC conjugation with SeNPs might be utilized as a biofortifier to improve the ginsenoside profile and raise the caliber of ginseng roots (Abid et al., 2021). Significant attention has been paid to the use of green nanotechnology in agriculture, particularly in the creation of novel nanofertilizers and nanoinsecticides. Here, selenium ions are reduced by the metabolites released by the fungus *Penicillium chrysogenum* to form selenium nanoparticles (SeNPs). The study investigated the effectiveness of SeNPs in inhibiting the cutworm (*Agrotis ipsilon*) and improving sunflower (*Helianthus annuus L.*)'s growth performance. In particular, at 20 ppm, the field experiment showed SeNPs to have the potential to improve sunflower growth indices and carotenoid content. Responses to SeNP concentrations included a considerable promotion of the amounts of free proline, phenolic compounds, carbohydrates, proteins, and chlorophylls (Amin et al., 2021). Application of exogenous selenium (SE) during the cultivation of lettuce (*Lactuca sativa* L.) may prevent Se deficiency. Low levels of Se have positive effects on plant cell metabolism, and Se treatment can boost growth, production, and quality while lowering the level of nitrate in lettuce. In this study, selenium (Se) nanoparticles (NPs) were biosynthesized by reducing selenium (Se) ions when exposed to a rosemary (*Salvia rosmarinus* Spenn.) extract. The size and form of the SeNPs were evaluated using scanning electron microscopy (SEM). It was observed that the majority of nutrient solutions, in particular, 2 mg L^{-1} SeNPs, increased plant height, leaf number, fresh weight, chlorophyll a, total chlorophyll, and nitrate reductase activity (Mohammadi et al., 2022).

4.6 Nanosilica

Over the past few years, the study of plants has seen a significant uptick in the use of nanobiotechnology. To promote growth, increase production, and improve crop protection methods, several metal oxide nanomaterials have been used. Nanosilica has distinguished itself as one of them, playing a crucial role in directing plant development and granting resistance to a variety of biotic and abiotic challenges. Reactive oxygen species (ROS) buildup and membrane lipid peroxidation are decreased by the uptake of nanosilica in the roots and leaves. It is well recognized to limit the uptake of heavy metals such as sodium ions by plants. Additionally, the deposition of nanosilica on leaf tissues strengthens the plant's protection against diseases (Mathur & Roy 2020). While nitrogen fertilization can boost the amount of chlorophyll, silica fertilization can make maize plants more resilient to the effects of drought. The effect of nanosilica–NPK fertilizers and manure–nanosilica on chlorophyll a, b, and the overall amount of chlorophyll present in sweet corn plants is compared in the study. The study found that whereas chlorophyll levels in nanosilica–manure fertilizers tend to decline with time, they grow from the 10th to the 60th day in nanosilica–NPK fertilizers (Prihastanti & Subagio, 2019). Two open-field tests were conducted to evaluate the impact of the application of silicon nanoparticles on the agro-physiological characteristics and biochemical components of potato plants grown in saline soil. The findings demonstrate that, in comparison to untreated potato plants, the application of a nanofertilizer significantly increases plant height, fresh and dry biomasses, the number of stems per plant, the relative water content of leaves, the chlorophyll content of leaves, the photosynthetic rate (Pn), leaf stomatal conductance (Gc), and tuber yields (Mahmoud et al., 2022).

4.7 Silver Nanofertilizers

To create a nanobiofertilizer, onion silver nanoparticles (AgNPs) were green-synthesized from an onion extract. AgNPs were characterized using Fourier transform infrared (FTIR) spectroscopy, UV–visible spectrophotometry, and scanning electron microscopy. It has been confirmed that for tomato and brinjal plants, the synthetic nanobiofertilizer made from onion extracts is efficient. Such sorts of nanobiofertilizers can assist in cutting down the overuse of chemical fertilizers, environmental pollution, and farm management costs (Gosavi et al., 2020). Due to their excellent capacity to boost nutrient utilization efficiency, nanofertilizers are advantageous for nutrition control. The purpose of this study was to ascertain how some growth characteristics of radish cultivated under deficiency irrigation circumstances were impacted by silver nanoparticles (AgNPs). Four distinct irrigation water levels and four different nano-silver dosages were used in this investigation to achieve this goal. The results demonstrated that in deficit irrigation, root length, root diameter, root fresh weight, and root dry weight considerably reduced. Ag nanoparticle applications considerably enhanced the root characteristics but had no statistically significant effect on the number of leaves. In a full irrigation application with Ag, the highest root height (33.21 mm) was found (80 ppm). Thus, it can be concluded that, compared to the control application of non-silver nanoparticles, radish plant development in silver nanoparticles can be greatly improved even under deficiency irrigation conditions (Çakmakci et al., 2022). It has been investigated how different Ag-containing NP concentrations (0, 2.5, 5, 10, and 25 mg/L) affect tomato (*Solanum tuberosum* L.) seed germination rates, biomass buildup, phenolic compounds, total protein, enzymatic activity, and total soluble sugar in vitro. The collected results showed that the tomato seed germination rate, germination speed index, and the emergence of stem and root systems are significantly influenced by Ag-containing nanoparticles, along with total protein, enzymatic activities, phenolic compounds, and total soluble sugar as well as photosynthetic pigments (Salih et al., 2022). Table 2.1 Illustrates different nano-based fertilizers and their positive impact on a variety of crops.

5 Nanofertilizers vs. Conventional Fertilizers

NFs distribute nutrients to plants in a clever manner that boosts crop yield and preserves the environment in comparison to cumbersome chemical fertilizers. Plants can absorb NFs through their roots or their foliage, depending on the application techniques and particle characteristics. NF-carrying plants have improved resistance to biotic and abiotic stressors. Furthermore, it lessens the environmental impact and production costs. NFs' many benefits provide new opportunities for promoting sustainable agriculture and halting climate change (Babu et al., 2022). Nanofertilizers are essential for minimizing the use of inorganic fertilizers and their negative environmental impacts because they are highly reactive, can enter the epidermis, and

Table 2.1 The impact of different nanofertilizers on a variety of crops

Nanomaterial	Crops	Effects	References
CuO ZnO MnO Fe_2O_3	*Lactuca sativa*	Significantly enhanced plant growth	Liu et al. (2016)
ZnO Fe_2O_3 TiO_2	*Hordeum vulgare*	Increase in the yield components of barley	Janmohammadi et al. (2016)
Fe	*Glycine max*	High shoot fresh weight	Cieschi et al. (2019)
Ag	*Allium cepa*	Increase in the yield	Fouda et al. (2020)
SiO_2	*Zea mays*	Increased plant growth and soil fertility by increasing the enzymatic activities of microbes	Kukreti et al. (2020)
ZnO Fe_2O_3	*Triticum aestivum*	Increase in proline, soluble sugars, and enzymatic activities Increase in the plant yield	Seyed et al. (2020)
Fe_3O_4	Tomato	Increased plant growth and yield	Raiesi-Ardali et al. (2022)
Se TiO_2	*Stevia rebaudiana*	Helps in combating high levels of salinity	Sheikhalipour et al. (2021)
Se	*Mentha suaveolens*	Improved pineapple mint growth and secondary metabolite profile under saline conditions	Kiumarzi et al. (2022)
Se	Mustard	Improved germination	Sarkar et al. (2022)
SiO_2	Maize	Increase in the photosynthetic rate	Yao et al. (2022)

allow delayed release and distribution. This improves the efficiency with which nutrients are utilized and may reduce abiotic stress and heavy metal toxicity (El-Saadony et al., 2021). Nanoparticles are so small that they can even pass through plant cells, which is the fundamental clue to delivering the desired product at the cellular level, which also makes NFs superior to traditional fertilizers (Meghana et al., 2021). Their smaller size, large surface area, and high surface area to volume ratio contribute to the slow, sustained, and targeted release of nanofertilizers as compared to conventional fertilizers. Modern nanofertilizers in particular, which are extremely effective (50–70%) in terms of controlled nutrient release compared to conventional fertilizers (40–50%), may be crucial for plant nutrition and human health (Table 2.2).

6 Future Perspectives

Crop yield and soil fertility are both greatly influenced by fertilizer use. Increased nutrient use efficiency by nanofertilizers enables effective nutrient management. Nanoparticles are an inventive fertilizer delivery technology because of their large

Table 2.2 Comparison between conventional fertilizers and nanofertilizers

S. No.	Characteristics	Conventional fertilizers	Nanofertilizers
1.	Bioavailability and solubility of minerals	Low bioavailability and reduced solubility due to large particle size	Enhanced and improved bioavailability by virtue of nano size
2.	Nutrient uptake efficiency	Nutrient uptake efficiency gets decreased because the roots are not able to absorb the minerals effectively	Increase in nutrient uptake ratio as roots and roots hair because of nano dimensions.
3.	Nutrient release	The bulk release of nutrients causes toxicity and ecological imbalance	Nanofertilizers have better absorption by roots
4.	The loss rate of minerals	The mineral loss rate is high due to leaching, heavy rainfall, and drift	A low mineral loss rate due to effective uptake by the plant
5.	Duration of the release of minerals	No controlled release of minerals	Controlled release of minerals by nanofertilizers
6.	The release rate of minerals	Excess release of minerals leads to toxic issues	By encapsulation, there is a controlled rate of mineral release

surface area, high sorption capacity, and controlled-release kinetics. According to a number of laboratory-scale studies, the use of nanofertilizers can accelerate and increase photosynthesis, nitrogen, carbohydrate, and protein metabolisms, seed germination, and seedling development. When used in conjunction with microorganisms, nanofertilizers also improve abiotic stress tolerance (nanobiofertilizers). Although there are now more possibilities for sustainable agriculture, thanks to nanofertilizers, there are still numerous uncertainties and restrictions that need to be carefully studied before being put into practice on the ground. In the fertilizer industry, nanofertilizers are viewed as promising future developments with the potential to considerably improve nutrient retention for the best crop output. The main issue facing the world is how to produce more food with the limited resources that are available while using the least amount of fertilizers and pesticides possible without harming the environment. Numerous nanomaterials have been tested against seed germination, shoot/root development, and crop production. Traditional farmers deal with a variety of problems, including chemical toxicity brought on by the excessive use of fungicides and pesticides, the emergence of resistance to these products, and, occasionally, the high cost of these products, which is out of the reach of marginal farmers, especially in developing countries.

7 Conclusions

Due to the obviously growing global population, there are stipulations of ever-increasing food and grain supply, when resources are depleting. A customized nanofertilizer was developed as a breakthrough in material design and consumer product development. Although the implementation of these methodologies in agriculture is still in its infancy, it has the potential to revolutionize agricultural systems, particularly with relation to manure application issues. The use of various nanofertilizers can have a significant impact on agricultural output by reducing fertilizer costs and emission hazards. Nanofertilizers offer targeted dispersion and controlled release due to their improved solubility, reactivity, and ability to penetrate the cuticle. Additionally, managing the soil's fertility and nutrients for crops will be the biggest challenge in the coming years due to the widespread use of chemical fertilizers and modern agricultural practices. Furthermore, by lowering abiotic stress and heavy metal toxicity, nanofertilizers can improve crop growth, yield, quality, and nutrient usage efficiency. However, rather than its benefits and efficacy, attention is being brought to the problems associated with consuming and using technology in limited ways. In order to boost all levels of productivity in our agricultural system, synthetic fertilizers must be replaced with cutting-edge and environmentally friendly nanofertilizers. According to the data, the impact of NPs varies with plant type and is influenced by their application method, size, shape, and concentration. Crop yield can be considerably boosted once the proper dosage and plant requirements for nanofertilizers are determined. Future crop plants may considerably profit from greener nano nutrition, especially given the nanotoxicological impacts of nanomaterials and nanoparticles. Green nanomaterials/NPs could thus be employed as a nutrient source for crops, greatly contributing to more ecologically friendly nano nutrition. Attention has recently been drawn to the use of nanohybrid structures, particularly nanofertilizers, to increase agricultural yields while also protecting the environment through clever pesticide administration. Thus, the search for sustainable alternatives to boost food production is becoming more and more important. This chapter has provided an overview of the creation and uses of nanofertilizers as well as any potential concerns to the environment and public health.

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Chapter 3
Nanofertilizers: Types, Synthesis, Methods, and Mechanisms

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1 Introduction

The projection of the world's human population reaching 9.6 billion by 2050 poses a significant challenge in terms of food production. To meet the needs of this growing population, a 50% increase in food production is required by 2050 (UNDESA, 2015). The use of conventional fertilizers and pesticides has been on the rise in recent years, resulting in increased yields and poverty reduction. However, the long-term consequences of the Green Revolution have become apparent, as extensive use of chemical fertilizers has disrupted soil mineral content and depleted soil fertility (Mahapatra et al., 2022; Padhan et al., 2021a). This overreliance on chemical fertilizers has also led to environmental degradation and pollution. In order to protect the environment and reduce the excessive use of chemical fertilizers, improving fertilizer absorption efficiency in crop plants is crucial (Liu et al., 2020). The ultimate goal is to minimize the use of plant protection materials, reduce nutrient losses during fertilization, and maximize revenue in the agricultural sector (Servin et al., 2015). Nanofertilizers (NFs) offer a promising solution to achieve these objectives.

Nanofertilizers (NFs), as a groundbreaking innovation, hold immense potential for addressing the growing concerns of global food security and sustainable agriculture. With the world's population on the rise, there is an urgent need to develop efficient and eco-friendly approaches to maximize crop yields while minimizing the

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negative impacts on the environment (Escribà-Gelonch et al., 2023). Traditional fertilizers, although effective in enhancing plant growth, have posed challenges such as nutrient runoff, soil degradation, and contamination of water bodies (Mahapatra et al., 2022). The emergence of nanotechnology has provided a remarkable solution to overcome these hurdles. One of the key advantages of NFs lies in their ability to precisely control the release of nutrients, ensuring that plants receive them when needed the most. This controlled-release mechanism allows for better nutrient absorption, reducing wastage and increasing nutrient use efficiency. By delivering nutrients directly to the root zone, NFs minimize leaching and volatilization, thus preventing nutrient loss and environmental pollution. Moreover, the nanoscale size of these fertilizers facilitates their easy uptake by plant roots, enhancing nutrient availability and uptake rates.

The types of NFs available offer diverse approaches to nutrient delivery and release. Nanostructured fertilizers, composed of nanoparticles or nanocomposites, provide a high surface area for nutrient encapsulation, resulting in slow and sustained release over an extended period. This controlled nutrient release aligns with the crop's growth stages, ensuring that plants receive a continuous supply of essential elements (Nongbet et al., 2022). On the other hand, nanoencapsulated fertilizers protect nutrients from degradation and leaching, allowing for their gradual release and improving their stability in the soil. Nanocomposite fertilizers, formed by combining nanoparticles with traditional fertilizers, offer a synergistic effect by enhancing nutrient availability, reducing losses, and optimizing plant uptake (El-Saadony et al., 2019; Reda et al., 2020). The synthesis of NFs involves various methods, each with its advantages and considerations. Physical methods, such as high-energy ball milling and sol–gel synthesis, enable the production of nanostructured materials by manipulating particle size and morphology. Chemical methods like precipitation and coprecipitation facilitate the formation of nanoparticles and nanoencapsulated fertilizers through controlled chemical reactions. Additionally, biological synthesis methods, employing microorganisms or plant extracts, provide a sustainable and environmentally friendly approach to produce nanoparticles with specific properties (El-Saadony et al., 2020, 2021; Reda et al., 2021).

Understanding the mechanisms of action of NFs is crucial to grasp their impact on plant growth and soil health. The improved solubility of nutrients due to nanosized particles enables better absorption by plant roots, resulting in enhanced nutrient availability and uptake efficiency. The increased diffusion rates of nutrients in the soil matrix ensure a wider distribution, benefiting plant roots beyond their immediate vicinity. Furthermore, NFs can stimulate beneficial microbial activity in the soil, promoting nutrient cycling and improving soil fertility (Tyagi et al., 2022). These multifaceted mechanisms work in tandem to optimize plant nutrition, leading to improved crop growth, increased yield, and, ultimately, food security. The advent of NFs opens up new avenues for sustainable agriculture, offering a promising solution to the challenges faced by conventional fertilizers. The efficient utilization of nutrients, reduced environmental impact, and enhanced crop productivity make NFs a compelling choice for farmers and agricultural practitioners. However, further research is needed to explore the long-term effects, safety considerations, and cost-effectiveness of NFs on a larger scale (Chhipa & Joshi, 2016).

Therefore, NFs commonly termed "smart fertilizers" (Wang et al., 2021) represent a cutting-edge technology that holds immense potential for transforming the agricultural landscape. With their ability to provide controlled release, improved nutrient uptake, and targeted delivery, NFs offer a pathway to sustainable agriculture, ensuring food security while minimizing environmental degradation. Continued advancements in nanotechnology and rigorous scientific research will pave the way for the widespread adoption of NFs as a key tool in global efforts toward a more sustainable and productive future in agriculture.

2 Comparative Analysis of Conventional Fertilizers vs. Nanofertilizers

Fertilizers play a vital role in modern agriculture by providing essential nutrients to plants, enhancing crop productivity, and ensuring food security. However, conventional fertilizers have raised concerns due to their adverse environmental impacts and inefficient nutrient utilization (Kah et al., 2018; Tarafdar et al., 2020). The advent of nanotechnology has introduced a new era in agriculture, offering the potential to revolutionize nutrient management through the development of NFs (Monreal et al., 2016; Feregrino-Pérez et al., 2018). This chapter aims to provide a comprehensive analysis of the differences between conventional fertilizers and NFs, exploring their composition, mode of action, benefits, and environmental implications (Solanki et al., 2015).

2.1 Composition and Structure

Conventional fertilizers typically consist of macronutrients, such as nitrogen (N), phosphorus (P), and potassium (K), in their readily available forms. These fertilizers are often derived from nonrenewable sources and are formulated to release nutrients rapidly upon application (Navarro et al., 2008). In contrast, NFs are nano-sized materials designed to efficiently deliver nutrients to plants. They can be classified into different types based on their composition, namely, nanostructured fertilizers, nanoencapsulated fertilizers, and nanocomposite fertilizers. Nanostructured fertilizers consist of nano-sized materials, such as nanoparticles or nanocomposites, that encapsulate or deliver nutrients to plants. Nanoencapsulated fertilizers involve the encapsulation of nutrients within nanoscale structures, providing controlled release and targeted delivery. Nanocomposite fertilizers combine nanoparticles with conventional fertilizers to enhance nutrient release and improve efficiency.

2.2 Nutrient Release and Uptake Efficiency

Conventional fertilizers often release nutrients rapidly into the soil, leading to inefficient nutrient utilization by plants. This rapid release can result in nutrient leaching, volatilization, and runoff, causing environmental pollution and wastage (Dan et al., 2015; Padhan et al., 2021b). In contrast, NFs offer controlled-release mechanisms, allowing for gradual and sustained nutrient release. This controlled release aligns with the crop's growth stages, ensuring that plants receive a continuous supply of nutrients when needed. By providing steady nutrient availability, NFs enhance nutrient uptake efficiency, minimizing nutrient losses and maximizing plant utilization.

2.3 Targeted Delivery and Nutrient Availability

Conventional fertilizers are typically broadcasted or applied uniformly across the field, resulting in uneven nutrient distribution. This can lead to overfertilization in some areas and underfertilization in others. In contrast, NFs enable targeted delivery of nutrients, ensuring precise placement and efficient utilization. The nanoscale size of these fertilizers allows them to penetrate the root zone more effectively, increasing nutrient availability to plants (Wesołowska et al., 2021). By delivering nutrients directly to the roots, NFs reduce nutrient losses through leaching and improve nutrient uptake by plants.

2.4 Environmental Impacts

Conventional fertilizers have significant environmental implications due to their excessive and inefficient use. Nutrient runoff from fields can contribute to water pollution, leading to eutrophication in lakes and rivers. Moreover, the production and transportation of conventional fertilizers require considerable energy inputs, contributing to greenhouse gas emissions. In contrast, NFs offer the potential to reduce environmental impacts (Pérez-de-Luque A., 2017; Rochette et al., 2018). The controlled-release and targeted delivery mechanisms of NFs minimize nutrient losses, thus reducing the risk of water contamination. Additionally, the enhanced nutrient uptake efficiency of NFs results in lower fertilizer application rates, potentially reducing energy consumption and greenhouse gas emissions (Table 3.1).

The key differences between conventional fertilizers and NFs lie in their composition, nutrient release mechanisms, and environmental implications. NFs offer controlled release, targeted delivery, and improved nutrient uptake efficiency, resulting in reduced nutrient losses and enhanced crop productivity. The potential environmental benefits of NFs include minimized water contamination, reduced energy

Table 3.1 Comparative analysis of conventional fertilizers vs. nanofertilizers

Particulars	Conventional fertilizers	NFs	Explanation
Composition	Macro- and micronutrients	Nano-sized particles or composites	Conventional fertilizers consist of macro- and micronutrients in their original form, whereas NFs are composed of nano-sized particles or composites that enhance nutrient availability and absorption (Navarro et al., 2008)
Nutrient release	Rapid release	Controlled release	Conventional fertilizers release nutrients rapidly upon application, whereas NFs offer controlled release, thus ensuring a steady and prolonged nutrient supply to plants (Slomberg & Schoenfisch, 2012)
Nutrient absorption	Less efficient	Enhanced absorption and utilization by plants	NFs enhance nutrient absorption and utilization by plants, resulting in improved nutrient use efficiency and crop yield. Conventional fertilizers are often less efficient in nutrient absorption (Wesołowska et al., 2021)
Environmental impact	Potential pollution	Reduced leaching and environmental impact	Conventional fertilizers can contribute to pollution and nutrient leaching, leading to environmental concerns. NFs, on the other hand, have reduced leaching and environmental impact due to their controlled-release mechanisms (Rochette et al., 2018)
Efficiency	Variable effectiveness	Improved nutrient use efficiency and crop yield	Conventional fertilizers' effectiveness can vary based on factors such as soil conditions and application rates. NFs have been shown to improve nutrient use efficiency, leading to enhanced crop growth and productivity
Application	Soil application	Multiple application modes (soil, foliar, seed coating)	Conventional fertilizers are typically applied to the soil. In contrast, NFs offer multiple application modes, including soil application, foliar spray, and seed coating, thus providing flexibility in nutrient delivery
Toxicity	Potential toxicity	Proper design minimizes toxicity risks	Conventional fertilizers may have potential toxicity risks if misused or overapplied. Proper design and formulation of NFs minimize toxicity risks while maximizing the nutrient uptake by plants

(continued)

Table 3.1 (continued)

Particulars	Conventional fertilizers	NFs	Explanation
Cost	Relatively low cost	Higher initial cost, but long-term benefits	Conventional fertilizers are generally more affordable compared to NFs, which may have a higher initial cost. However, the long-term benefits of improved nutrient utilization and reduced environmental impact can offset the initial investment
Sustainability	Environmental concerns	Promotes sustainable agricultural practices	Conventional fertilizers raise concerns regarding environmental pollution and sustainability. NFs promote sustainable agricultural practices by reducing nutrient losses, optimizing nutrient absorption, and minimizing environmental impacts

consumption, and lower greenhouse gas emissions (Fleischer et al., 1999; Monreal et al., 2016; Feregrino-Pérez et al., 2018). However, challenges such as safety considerations, cost-effectiveness, and regulatory frameworks need to be addressed. With further research and advancements, NFs hold immense potential for revolutionizing nutrient management in agriculture and contributing to sustainable food production systems.

3 Diverse Types of Nanofertilizers: An Overview

NFs have emerged as a promising solution to address the challenges of conventional fertilizers in modern agriculture. By harnessing the unique properties and functionalities at the nanoscale, NFs offer improved nutrient delivery, controlled-release mechanisms, and enhanced nutrient uptake efficiency (Singh et al., 2020).

3.1 Nanostructured Fertilizers

Nanostructured fertilizers are a type of NF that consist of nano-sized materials, such as nanoparticles, nanocomposites, or nanocoatings, which encapsulate or deliver nutrients to plants (Iravani et al., 2014; Chakraborty et al., 2023). These materials provide a high surface area for nutrient encapsulation and controlled-release mechanisms. Examples of nanostructured fertilizers include:

3.1.1 Nano-Sized Nitrogen Fertilizers

Nitrogen is an essential nutrient for plant growth, and nanoscale nitrogen fertilizers, such as nano-sized urea or ammonium-based fertilizers, offer improved efficiency and reduced losses through leaching and volatilization (Zhang et al., 2015).

3.1.2 Nanocomposite Phosphorus Fertilizers

Phosphorus is another critical nutrient for plant development, and nanocomposite fertilizers, composed of nanoparticles and conventional phosphorus fertilizers, enhance nutrient availability and uptake by improving solubility and reducing phosphorus fixation in the soil.

3.1.3 Nanocoated Potassium Fertilizers

Nanocoatings on potassium-based fertilizers help in controlled release, extending the availability of potassium nutrients to plants over a longer period, thus optimizing plant uptake and minimizing losses.

3.2 Nanoencapsulated Fertilizers

Nanoencapsulated fertilizers involve the encapsulation of nutrients within nanoscale structures, providing controlled-release and targeted delivery mechanisms. This type of NF protects the nutrients from leaching, volatilization, and degradation while enhancing their solubility and availability. Some examples of nanoencapsulated fertilizers include:

3.2.1 Nanoencapsulated Slow-Release Nitrogen Fertilizers

These fertilizers utilize nanostructures, such as polymer coatings or nanocapsules, to encapsulate nitrogen nutrients, ensuring their gradual release and prolonged availability to plants.

3.2.2 Nanoencapsulated Micronutrient Fertilizers

Micronutrients, such as iron, zinc, and copper, are essential for plant growth in small quantities. Nanoencapsulation of micronutrients enhances their stability, solubility, and targeted delivery, ensuring efficient uptake by plants.

3.3 Nanocomposite Fertilizers

Nanocomposite fertilizers combine nanoparticles with conventional fertilizers, resulting in hybrid materials that exhibit enhanced nutrient release properties and improved efficiency. By integrating nanoparticles, these fertilizers offer synergistic effects and improved nutrient utilization (Feng et al., 2019). Examples of nanocomposite fertilizers include:

3.3.1 Nanoparticle-Enhanced Controlled-Release Fertilizers

In this type, nanoparticles are incorporated into controlled-release fertilizers, enhancing their nutrient release properties. For instance, nanoparticles like clay minerals or zeolites can be added to urea-based fertilizers, resulting in improved nitrogen release patterns.

3.3.2 Nanoparticle-Blended Organic Fertilizers

Organic fertilizers, such as compost or manure, can be blended with nanoparticles to improve nutrient availability, release, and plant uptake. Nanoparticles like biochar or clay minerals aid in nutrient retention and slow-release mechanisms.

3.4 Other Types of Nanofertilizers

Apart from the aforementioned types, there are ongoing research and developments exploring additional NFs. These include:

3.4.1 Nanosensors for Nutrient Monitoring

Nanotechnology enables the development of nanosensors that can detect and monitor nutrient levels in soil in real time (Kadhum Alghanimi & Hadi, 2021). These nanosensors provide valuable data on nutrient availability and enable precise nutrient management practices.

3.4.2 Nanoparticles for Seed Coating

Nanoparticles can be applied as seed coatings to enhance seed germination, root development, and nutrient uptake. These coatings can provide controlled release of nutrients, protect seeds from pathogens, and improve the overall plant performance.

Table 3.2 Types of nanofertilizers along with their composition, method of synthesis, and examples

Nanofertilizer type	Composition	Synthesis method	Examples
Nanostructured fertilizers	Nano-sized materials (e.g., nanoparticles, nanocomposites) encapsulating or delivering nutrients to plants	Physical synthesis methods (e.g., high-energy ball milling, sol–gel synthesis)	Nano-sized nitrogen fertilizers, nanocomposite phosphorus fertilizers, nanocoated potassium fertilizers
Nanoencapsulated fertilizers	Nutrients encapsulated within nanoscale structures, facilitating controlled release and targeted delivery	Chemical synthesis methods (e.g., precipitation, coprecipitation)	Nanoencapsulated slow-release nitrogen fertilizers, nanoencapsulated micronutrient fertilizers
Nanocomposite fertilizer	Hybrid materials combining nanoparticles with conventional fertilizers for improved nutrient release and efficiency	Biological synthesis methods (e.g., microbe-mediated synthesis)	Nanoparticle-enhanced controlled-release fertilizers, nanoparticle-blended organic fertilizers
Nanosensors for nutrient monitoring	Nanoscale sensors for real-time detection and monitoring of nutrient levels in soil	Physical and chemical synthesis methods tailored for sensor development	Nanoparticle-based nutrient sensors for nitrogen, phosphorus, and potassium
Nanoparticle seed coatings	Nanoparticles applied as coatings on seeds to enhance germination, root development, and nutrient uptake	Surface modification techniques (e.g., layer-by-layer deposition)	Nano-coated seeds with iron nanoparticles for improved iron uptake
Nano-based soil amendments	Nanoparticles integrated into soil to improve structure, water retention, and nutrient-holding capacity	Physical mixing or application techniques	Nanoclay amendments for enhanced soil structure and water retention

3.4.3 Nano-Based Soil Amendments

Nanoparticles, such as nanoclays or nano-hydrogels, can be used as soil amendments to improve soil structure, water retention, and nutrient-holding capacity. These nano-based amendments enhance nutrient availability to plants and promote healthy root development (Table 3.2).

4 Synthesis Methods of Nanofertilizers

The synthesis of NFs involves various methods, each with its advantages and considerations. These methods are elucidated in the following sections.

Methods of Synthesis of Nanoparticles

The methods of synthesis can be broadly divided into two aspects: synthesis based on raw materials and synthesis based upon the nature of the driving forces.

4.1 Classification of Synthesis Methods Based on Raw Materials

This encompasses two approaches: the bottom-up approach and the top-down approach.

4.1.1 The Bottom-Up Approach

The concept of constructing nanoparticles or nanoclusters atom by atom or molecule by molecule is referred to as bottom-up synthesis. This approach involves the use of chemical or biological methods to gradually build up nanoparticles (Escudero et al., 2021). Wet chemical procedures are the traditional and widely adopted techniques for synthesizing metallic nanoparticles (Baig et al., 2021). The process begins with the formation of nanoscale structures, followed by the incorporation of desired nutrients. The bottom-up approach allows precise control over particle size, morphology, and composition, resulting in tailored NFs with improved nutrient release and plant uptake. These procedures typically involve the growth of nanoparticles in a liquid medium containing specific reactants, including reducing agents like sodium borohydride, potassium bitartrate, methoxy polyethylene glycol, or hydrazine. To prevent nanoparticle agglomeration, a stabilizing agent such as sodium dodecyl benzyl sulfate or polyvinyl pyrrolidone is incorporated into the reaction mixture. Once the synthesis is complete, the nanoparticles undergo physical, chemical, and mechanical characterization to assess their solubility, dispersibility, and stability, among other functionalities (Lin et al., 2014).

The major advantages of the bottom-up approach are as follows:

- *Controlled Nutrient Release*: The bottom-up approach enables the encapsulation of nutrients within nanoscale structures, providing controlled and sustained release. This ensures that nutrients are released gradually, matching the specific requirements of plants during different growth stages (Baig et al., 2021). Controlled nutrient release minimizes nutrient losses and improves nutrient use efficiency, leading to enhanced crop productivity.
- *Tailored Properties*: With the bottom-up approach, NFs can be precisely engineered to possess desired properties, such as size, shape, surface charge, and composition. By manipulating these parameters, researchers can optimize the performance of NFs for specific crops and soil conditions, maximizing nutrient uptake and utilization (Lin et al., 2014).

- *Improved Nutrient Stability*: NFs synthesized using the bottom-up approach exhibit enhanced stability compared to conventional fertilizers. The encapsulation of nutrients within nanoscale structures protects them from leaching, volatilization, and chemical reactions in the soil. This improves nutrient availability to plants and reduces environmental pollution.
- *Synergistic Effects*: The bottom-up approach allows the incorporation of multiple nutrients or additives into a single nanofertilizer formulation. This enables the creation of synergistic effects, where the combined presence of different elements or compounds enhances nutrient uptake, plant growth, and stress tolerance (Chakraborty et al., 2023). Synergistic NFs can provide comprehensive nutrient solutions and address specific nutrient deficiencies.

Demerits of the Bottom-Up Approach

- *Complex Synthesis Procedures*: The bottom-up approach often involves intricate synthesis procedures, requiring specialized equipment and expertise. Chemical synthesis methods may involve multistep reactions, precise control over reaction parameters, and purification steps. These complexities can increase the cost and time associated with nanofertilizer production.
- *Safety Concerns*: The synthesis of NFs using the bottom-up approach may involve the use of hazardous chemicals or high-temperature reactions. Ensuring the safety of researchers and the environment during synthesis and handling of NFs is of utmost importance. Adequate safety protocols and risk assessments are necessary to mitigate potential hazards.
- *Long-Term Effects and Regulation*: As NFs are a relatively new technology, their long-term effects on soil health, ecosystem dynamics, and human health are still being investigated. Additionally, the regulatory frameworks for NFs vary across different regions, posing challenges in terms of standardization, labeling, and commercialization.
- *Cost Considerations*: The bottom-up approach, with its intricate synthesis procedures and specialized equipment, can contribute to higher production costs compared to conventional fertilizers. The cost-effectiveness of NF needs to be explored for its better applicability.

4.1.2 The Top-Down Approach

The process of segmenting large materials into smaller particles using physical or chemical methods is employed in this approach. It involves breaking down a bulk material into its respective nanoparticles. Physical synthesis methods, such as attrition and pyrolysis, are commonly utilized for the production of metallic nanoparticles (Borges et al., 2017; Chen et al., 2017). Attrition involves grinding macro- or microscale particles using a size-reducing mechanism, such as an ordinary or planetary ball mill. The resulting particles are then air classified to separate oxidized nanoparticles. Various factors, including the milling time, material properties, and atmospheric conditions, critically influence the characteristics of the nanoparticles obtained. On the other hand, pyrolysis entails the high-pressure combustion of an organic precursor (liquid or gas) forced through an orifice. The resulting ash is subsequently air classified to recover oxidized nanoparticles. The top-down approach allows for precise control over particle size and shape, leading to the production of NFs with specific properties and controlled-release mechanisms.

Merits of the Top-Down Approach

- *Particle Size Control*: The top-down approach enables precise control over particle size, allowing researchers to tailor NFs to specific requirements. By manipulating the size of nanoparticles, nutrient release rates and plant uptake efficiency can be optimized, resulting in improved nutrient utilization and reduced environmental impact.
- *Rapid Production*: The top-down approach offers a relatively faster production process compared to other synthesis methods. The ability to rapidly reduce bulk materials into nanoparticles allows for efficient production at a larger scale. This scalability makes the top-down approach suitable for commercial applications in agriculture (Chen et al., 2017).
- *Uniformity and Homogeneity*: With the top-down approach, nanoparticles can be produced with a high degree of uniformity and homogeneity. This uniformity ensures consistent nutrient distribution within the NFs, leading to more predictable and reliable nutrient release patterns. Uniform nanoparticles also facilitate their application and interaction with plants and soils.
- *Utilization of Existing Materials*: The top-down approach often involves the transformation of existing bulk materials into nanoparticles. This utilization of available materials can contribute to the sustainable use of resources and reduce waste. It provides an opportunity to repurpose and enhance the properties of conventional fertilizers, making them more efficient and environmentally friendly.

Demerits of the Top-Down Approach

- *Limited Control over Composition*: The top-down approach may have limitations in terms of controlling the chemical composition of NFs. Breaking down bulk materials into smaller particles does not allow for precise manipulation of the internal structure or elemental composition (Chen et al., 2017). This lack of control can restrict the incorporation of specific nutrients or additives, limiting the versatility of nanofertilizer formulations.
- *High Energy Requirements*: The top-down approach often involves energy-intensive processes such as grinding, milling, or fragmentation to reduce the size of particles. These processes require significant energy inputs, which can contribute to higher production costs and environmental impacts. Energy-efficient techniques need to be developed to mitigate these challenges.
- *Risk of Agglomeration and Inhomogeneity*: Nanoparticles produced through the top-down approach may be prone to agglomeration or uneven distribution, which can impact their performance and nutrient release properties. Ensuring the dispersion and stability of nanoparticles throughout the nanofertilizer formulation requires careful attention and appropriate techniques.

- *Environmental Considerations*: The top-down approach may involve the use of chemical processes or high-energy mechanical methods, which can result in the generation of waste products and potentially harmful by-products. Proper waste management and environmental impact assessments are crucial to minimize any adverse effects on ecosystems and human health.

The top-down approach in nanofertilizer synthesis offers distinct merits and demerits that need to be carefully evaluated. While this approach provides control over particle size, rapid production, uniformity, and utilization of existing materials, it also presents challenges such as limited control over composition.

Hybrid Nanofertilizers Hybrid nanofertilizers combine an organic matrix, typically a polymer, with a dispersed inorganic phase consisting of evenly distributed nanoparticles in nano size. A study conducted by Tarafdar et al. (2020) demonstrated the prolonged release of hybrid nanofertilizers for a duration of 14 days in *Abelmoschus esculentus*. In their research, the authors synthesized hydroxyapatite modified with urea, which serves as a nitrogen, calcium, and phosphate source. Additionally, copper, iron, and zinc nanoparticles were incorporated into the modified hydroxyapatite. The inclusion of these nanoparticles resulted in a significant enhancement of the overall absorption of copper, iron, zinc, and other essential nutrients in the fruit.

4.2 Classification of Synthesis Methods Based on the Nature of the Driving Forces

The various synthesis methods of nanofertilizers can be summarized into the following categories depending upon the nature of the driving forces.

1. Mechanical methods
2. Physical methods
3. Chemical methods
4. Physicochemical methods
5. Biological methods

4.2.1 Mechanical Methods

NFs have gained significant attention in agriculture due to their unique properties and potential to enhance nutrient management and crop productivity. Among the various methods available for synthesizing NFs, mechanical methods offer a straightforward and effective approach. These methods utilize mechanical forces to break down bulk materials into nanoparticles, allowing for precise control over particle size, morphology, and composition.

Grinding-Based Synthesis

Grinding-based methods involve the application of mechanical forces through abrasion or impact to reduce the particle size of bulk materials. This approach is commonly used for synthesizing metallic and oxide nanoparticles.

(a) *Ball Milling*: This is a widely utilized technique in nanofertilizer synthesis. It involves the use of grinding balls within a rotating cylindrical container to facilitate the breakdown of bulk materials (Barhoum et al., 2017). The collision and grinding action between the balls and the material result in the formation of nanoparticles. Ball milling allows for control over particle size and distribution, making it suitable for producing NFs with specific characteristics.

(b) *High-Energy Milling*: This refers to a specialized form of ball milling where the mechanical forces are intensified through the use of high-speed rotational mills or vibrating mills. This method enables rapid and efficient particle size reduction, leading to the production of nanoscale particles (Jin et al., 2018). High-energy milling is particularly useful for synthesizing NFs with enhanced reactivity and controlled-release properties.

Attrition-Based Synthesis

Attrition-based methods involve the rubbing or friction between particles to break them down into smaller sizes. These methods are suitable for producing oxide nanoparticles and composites.

(a) *Attrition Milling*: This relies on the collision and rubbing between particles to achieve size reduction. It typically involves the use of a rotating impeller or grinding media to create a turbulent environment within a container (Belaiche et al., 2021). The particles are subjected to repeated impacts and shear forces, resulting in the formation of nanoparticles. Attrition milling offers advantages such as simplicity, scalability, and the ability to control the particle size distribution.

(b) *Jet Milling*: This utilizes high-velocity gas streams to propel particles against each other or solid surfaces, leading to particle size reduction. In this method, micron-sized particles are accelerated by supersonic gas jets, causing collisions and fracturing. Jet milling enables the production of fine nanoparticles with narrow size distribution (Angelidis et al., 2015). It is a versatile technique suitable for various materials and can be used for large-scale production.

The mechanical methods of nanofertilizer synthesis offer several advantages and find applications in diverse fields:

(i) *Precise Control*: Mechanical methods allow precise control over particle size, shape, and distribution, facilitating the production of NFs with tailored properties for specific agricultural applications.

(ii) *Scalability*: These methods are generally scalable, enabling the production of NFs on a large scale to meet agricultural demands.

(iii) *Cost-Effectiveness*: Mechanical methods often involve simple equipment and fewer processing steps, resulting in cost-effective nanofertilizer synthesis.

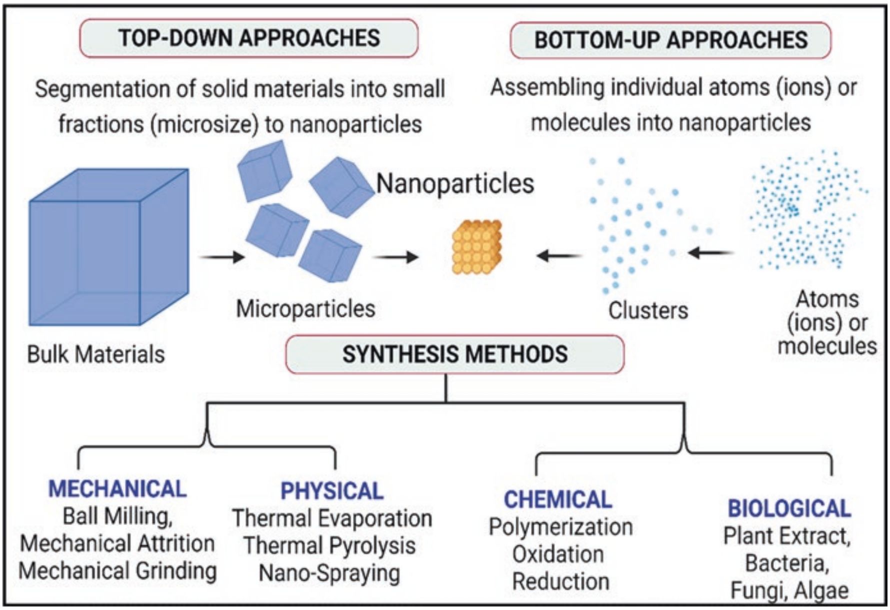

Fig. 3.1 A schematic demonstration illustrating the synthesis of nanoparticles. (Modified from Barhoum et al., 2022)

(iv) *Controlled Release*: NFs synthesized through mechanical methods can exhibit controlled-release properties, allowing for efficient nutrient delivery to plants and reducing nutrient loss.

(v) *Environmental Compatibility*: Mechanical methods are generally environmentally friendly, as they eliminate the need for toxic chemicals and involve fewer energy-intensive processes.

The mechanical methods of nanofertilizer synthesis, such as grinding and attrition-based techniques, provide a versatile and efficient approach to producing nanoparticles with precise control over particle size and morphology. These methods offer advantages in terms of scalability, cost-effectiveness, and controlled-release properties, making them suitable for various agricultural operations (Fig. 3.1).

4.2.2 Physical Methods

Various synthesis methods are employed to produce NFs, including physical methods that harness physical phenomena to generate nanoparticles. Some of the prominent physical methods are described as follows.

Vapor-Phase Condensation

Vapor-phase condensation is a widely used physical method for synthesizing nanoparticles. It involves the vaporization of precursor materials followed by their condensation into nanoparticles. The vapor is created either through thermal evaporation or chemical reactions, and, then, it is rapidly cooled to induce condensation. This method allows for precise control over particle size and composition.

(a) *Chemical Vapor Deposition (CVD)*: CVD is a vapor-phase condensation technique that involves the reaction of gaseous precursor compounds in a reactor chamber to form nanoparticles (Nikam et al., 2018). The precursors decompose or react to generate nanoparticles on a heated substrate. CVD offers excellent control over particle size, composition, and morphology, making it suitable for the production of complex NFs.
(b) *Physical Vapor Deposition (PVD)*: PVD is a vapor-phase condensation technique where materials are evaporated under vacuum conditions and the resulting vapor condenses on a substrate to form nanoparticles. Techniques such as evaporation, sputtering, and laser ablation are commonly employed in PVD. PVD allows for the synthesis of highly pure and well-defined nanoparticles.

Laser Ablation

Laser ablation is a physical method used to generate nanoparticles by irradiating a target material with a laser beam (Barhoum et al., 2017). The high-energy laser pulse vaporizes the target material, creating a plasma plume that rapidly cools and condenses into nanoparticles. Laser ablation offers control over particle size, composition, and surface properties, making it suitable for producing tailored NFs (Janas & Koziol, 2016).

Electrospray and Electrospinning

Electrospray and electrospinning are electrohydrodynamic techniques that generate nanoparticles through the application of an electric field to a liquid precursor solution or melt.

(a) *Electrospray*: This involves the dispersion of a liquid precursor into fine droplets using an electric field. The droplets undergo solvent evaporation, leading to the formation of nanoparticles. Electrospray enables the production of monodisperse nanoparticles with controlled size and morphology.
(b) *Electrospinning*: This is a technique used to produce nanofibers that can be further processed into NFs. It involves the application of a high voltage to a polymer solution, creating a charged jet that elongates and solidifies into nanofibers upon solvent evaporation. Electrospinning offers versatility in controlling fiber diameter, composition, and structure (Panigrahi et al., 2004).

Laser ablation and spinning are commonly utilized physical techniques employed in the synthesis of nanoparticles (Barhoum et al., 2017; Jin et al., 2018). For instance, one approach involves the generation of plasma using radio-frequency heating coils. The process involves placing the metal in a pestle and transferring it into a vacuum chamber surrounded by radio-frequency heating coils. The metal is then heated above its evaporation point using helium, resulting in the formation of plasma (Sánchez-Ahijón et al., 2020). The metal vapor subsequently nucleates on helium gas atoms and diffuses to a cold collector rod, where nanoparticles are collected and passivated by oxygen gas (Belaiche et al., 2021). In the case of laser ablation, the starting material is exposed to the intense energy emitted by a pulsed laser. This causes volatilization of the material particles and formation of plasma, which is then deposited on a support to form thin films (Amendola & Meneghetti, 2009). Laser ablation synthesis in solution involves preparation of colloidal solutions of nanoparticles using various solvents (Janas & Koziol, 2016).

Regarding the spinning method, the bulk material is subjected to low pressure, resulting in its deposition on a cold base. Subsequently, a magnetic field is applied to remove smaller particles that have been deposited on a support, forming a thin film (Pesheck & Lorence, 2009). Another method for the synthesis of nanoparticles in solution involves irradiation-induced synthesis, typically utilizing high-energy (1.5 MeV) electron beam irradiation. Additionally, microwave irradiation, which is a form of electromagnetic irradiation with mobile electric charges, is frequently employed with emulsion systems (Panigrahi et al., 2004).

By employing these physical methods, researchers can manipulate the synthesis process to achieve the desired characteristics and functionalities in the resulting nanoparticles. These methods offer control over particle size, morphology, and composition, allowing for the development of tailored NFs with specific properties for agricultural applications. As research in nanofertilizer synthesis continues to advance, further exploration and optimization of physical methods will contribute to the development of innovative and efficient NFs that can significantly enhance nutrient management and crop productivity in agriculture.

4.2.3 Chemical Methods

Chemical techniques play a significant role in the fabrication of nanomaterials by facilitating nucleation and growth of precursor species. These techniques involve various chemical reactions, including those that occur in the vapor state. In vapor-state reactions, the material vapor is introduced into a chemical vapor deposition (CVD) reactor. Within this reactor, the resulting particles combine with other gases on a base at a specific temperature, leading to the formation of a solid film. This method offers the advantage of preparing quasi-particles that mimic the desired nanostructure. One of the key advantages of chemical methods is their ability to precisely control the size and morphology of the nanomaterials, thereby enabling the production of highly stable nanostructures (Nikam et al., 2018). Various synthesis methods are employed to fabricate NFs, including chemical methods that involve the manipulation of chemical reactions to produce nanoparticles with desired properties.

Precipitation Methods

Precipitation methods are widely employed in the synthesis of NFs, utilizing chemical reactions to precipitate nanoparticles from solution. These methods involve the controlled mixing of reactants to induce the formation of nanoparticles (Tadic et al., 2019). Common precipitation methods include:

(a) *Coprecipitation*: This involves the simultaneous precipitation of multiple elements or compounds to form composite nanoparticles. This method allows for the incorporation of various nutrients or additives into the nanofertilizer matrix, providing a platform for tailored nutrient release.
(b) *Sol–Gel Method*: This involves the conversion of a sol (a stable colloidal suspension) into a gel by a chemical reaction. The gel is subsequently dried and calcined to obtain the desired nanofertilizer (Pesheck & Lorence, 2009). This method offers precise control over the composition and structure of the nanofertilizer.

Hydrothermal and Solvothermal Methods

Hydrothermal and solvothermal methods involve the synthesis of nanoparticles under high-temperature and high-pressure conditions. These methods allow for the controlled growth of nanoparticles through chemical reactions occurring in a solvent. Key methods include:

(a) *Hydrothermal Synthesis*: This involves the reaction of forerunners in an aqueous medium under elevated temperature and pressure. This method enables the formation of well-defined nanoparticles with precise size and morphology.
(b) *Solvothermal Synthesis*: This follows a comparable principle to hydrothermal synthesis but employs organic solvents as the reaction medium. Solvothermal methods offer the advantage of controlling the solvent properties to influence the growth and properties of the resulting nanofertilizer.

Solvent Evaporation

Solvent evaporation is a simple and widely used method for synthesizing nanoparticles. It involves dissolving the precursor materials in a suitable solvent and subsequently evaporating the solvent to induce nanoparticle formation. The rate of solvent evaporation influences the particle size, with slower evaporation leading to larger nanoparticles. This method is advantageous for producing NFs with controlled size and composition.

Electrochemical Methods

Electrochemical methods are based on electrochemical reactions to fabricate NFs. These methods involve the use of electrodes and electrolytes to induce chemical reactions that result in nanoparticle formation. Electrochemical methods offer precise control over the size, shape, and composition of nanoparticles. Key techniques include electrodeposition and electrochemical etching (Panigrahi et al., 2004).

However, it is important to note that chemical methods may require the use of hazardous chemicals during the fabrication process. These chemicals pose potential risks to the environment, and safety considerations must be taken into account. Despite this drawback, the advantages of chemical methods, such as size and morphology control, and the production of stable nanomaterials, make them valuable techniques in nanomaterial synthesis. Chemical methods offer significant benefits in the fabrication of nanomaterials through precise control over size, morphology, and stability. These methods utilize various chemical reactions, including vapor-state reactions and the use of liquid mediums. While the advantages of chemical methods are notable, caution must be exercised due to the involvement of hazardous chemicals. Continued research and development in chemical synthesis techniques will contribute to the advancement of nanomaterials and their applications in various fields.

4.2.4 Physicochemical Methods

Physicochemical approaches are employed in the synthesis of nanomaterials, combining both physical and chemical processes (Tadic et al., 2019; Jhung et al., 2007). An example of a physicochemical method is the electrochemical approach used for fabricating metal nanoparticles, where a metallic anode dissolves in an aprotic solvent. Hydrothermal and solvothermal methods, templating CVD, microwave irradiation, combustion, thermal decomposition, and pulsed laser deposition are also considered physicochemical methods (Tadic et al., 2019). These approaches allow for the modulation of specific nanoparticle properties such as size, shape, crystallinity, and stability. Additionally, the combination of biological and chemical methods can be classified as a physicochemical approach, further expanding the range of techniques available (Komal et al., 2019; Barhoum et al., 2014).

Physicochemical processes offer the advantage of reducing reaction time while enabling control over the desired characteristics of the nanoparticles. Researchers can tailor the size, shape, crystallinity, and stability of the nanoparticles to meet specific requirements. However, the implementation of physicochemical methods often involves the use of sophisticated and costly equipment, and it may also require the use of hazardous chemicals (Komal et al., 2019; Barhoum et al., 2014). Therefore, proper handling and disposal of chemicals are essential to ensure safety and minimize environmental impact.

4.2.5 Biological Methods

Biological methods of nanofertilizer synthesis involve the use of biological entities such as microorganisms, plants, and enzymes to produce nanoparticles. These methods offer several advantages, including their eco-friendly nature, mild reaction conditions, and ability to produce nanoparticles with controlled size and shape.

Microbial Synthesis

Biological methods offer environmentally friendly approaches for the fabrication of nanomaterials by harnessing the unique capabilities of certain microbes and plants (Parsons et al., 2007; Sharma et al., 2023). These methods have distinct advantages, including the elimination of expensive chemicals, reduced energy consumption, and the generation of environmentally benign products and by-products. Plant-based approaches, utilizing plant extracts, are particularly advantageous due to their low-maintenance requirements. The use of plant extracts for the reduction of metal ions to nanoparticles has been known since 1900, whereas the production of nanometals using plant extracts and the synthesis of nanoparticles using living plants have been more extensively studied in the past 30 and 10 years, respectively (Willner et al., 2006). In these biological methods, enzymes and other biomolecules, such as DNA, telomers, and actin filaments, serve as catalysts for nanoparticle growth, whereas various biological organisms, including fungi, bacteria, and cells, act as active units for nanoparticle production.

By leveraging the catalytic properties of enzymes and biomolecules, biological methods enable precise control over the size, shape, and composition of nanoparticles. This control allows for the tailored design of NFs with specific properties that enhance nutrient availability and absorption in plants. Moreover, the utilization of biological organisms as active units for nanoparticle production offers scalability and cost-effectiveness, as they can be easily cultivated and maintained (Chakraborty et al., 2023). Microbes and plants possess inherent mechanisms for the reduction and stabilization of metal ions, which facilitate the synthesis of nanoparticles. Through their metabolic activities, these biological entities mediate the transformation of metal ions into nanoparticles, resulting in the production of NFs. The choice of microbes or plants depends on factors such as their ability to accumulate and convert metal ions, their compatibility with the desired nanoparticle properties, and their ease of cultivation. The biologically mediated methods involved in nanofertilizer synthesis are as follows:

(i) *Plant-Mediated Synthesis*: Plants, including their various parts, such as leaves, stems, and roots, can act as biofactories for the synthesis of nanoparticles. The process involves the uptake of metal ions from the surrounding environment by plants, followed by their reduction and subsequent formation of nanoparticles within plant tissues. Plant-mediated synthesis offers several benefits, such as accessibility, abundance, and the ability to produce nanoparticles using simple reaction conditions (Raliya et al., 2017). Additionally, the resulting nanoparticles tend to be more stable and exhibit enhanced bioactivity, making them suitable for agricultural applications.

(ii) *Enzymatic Synthesis*: Enzymes are highly specific catalysts that can facilitate the synthesis of nanoparticles with precise control over their size, shape, and composition. Enzymatic methods often involve the use of specific enzymes capable of reducing metal ions and facilitating nanoparticle formation. Enzymatic synthesis offers advantages such as high reaction specificity, mild reaction conditions, and the ability to produce nanoparticles with desired characteristics (Parsons et al., 2007). Moreover, enzymes can be easily obtained from natural sources or through recombinant DNA technology, allowing for efficient and sustainable synthesis processes.

(iii) *Alga-Mediated Synthesis*: Algae, including microalgae and macroalgae, have gained attention as potential agents for nanofertilizer synthesis. These organisms possess inherent capabilities to sequester and transform metal ions into nanoparticles through their metabolic activities. Alga-mediated synthesis is environmentally friendly, sustainable, and can be performed in aqueous solutions without the need for high temperatures or toxic chemicals. The resulting nanoparticles exhibit good stability and can be tailored to possess specific properties for agricultural applications.

(iv) *Yeast-Mediated Synthesis*: Yeast, a type of fungus, can be utilized for the synthesis of nanoparticles. Certain strains of yeasts have the ability to reduce metal ions and facilitate the formation of nanoparticles. This method offers advantages such as simplicity, cost-effectiveness, and scalability. Yeast-mediated synthesis can be performed under ambient conditions and does not require elaborate equipment or toxic chemicals, making it a favorable approach for nanofertilizer production.

(v) *Plant Extract-Mediated Synthesis*: Plant extracts containing various biomolecules, such as polyphenols, flavonoids, and proteins, can serve as reducing and stabilizing agents in the synthesis of nanoparticles. These biomolecules present in plant extracts have the capability to convert metal ions into nanoparticles. Plant extract-mediated synthesis is a versatile and environmentally friendly method that allows for the synthesis of nanoparticles with controlled properties. Additionally, plant extracts are readily available and offer a wide range of options for nanoparticle synthesis.

(vi) *Genetic Engineering*: Advancements in genetic engineering techniques have paved the way for the synthesis of nanoparticles using genetically modified organisms (GMOs). By introducing specific genes into microorganisms or plants, researchers can enhance their ability to accumulate and convert metal ions into nanoparticles. Genetic engineering offers precise control over the synthesis process, allowing for the production of nanoparticles with desired characteristics (Sharma et al., 2023; Panigrahi et al., 2021). This method holds great potential for tailoring NFs to meet the specific nutrient requirements of different crops.

(vii) *Microbial Enzyme-Assisted Synthesis*: Microorganisms produce various enzymes that possess the capability to reduce metal ions and participate in nanoparticle synthesis. By utilizing these microbial enzymes, researchers can enhance the efficiency and specificity of nanofertilizer synthesis. Microbial enzyme-assisted synthesis provides advantages such as high catalytic activity, substrate specificity, and the ability to control the size and shape of nanoparticles. This method enables the production of NFs with improved nutrient availability and absorption efficiency.

(viii) *Mycorrhiza-Mediated Synthesis*: Mycorrhizal fungi form a mutualistic association with plant roots, enhancing nutrient uptake and promoting plant growth. Recent studies have explored the potential of mycorrhizal fungi in nanoparticle synthesis. These fungi possess the ability to transform metal ions into nanoparticles, offering a novel approach to produce NFs. Mycorrhiza-mediated synthesis holds promise for developing sustainable and plant-friendly NFs that can improve nutrient utilization and enhance crop productivity.

The biological synthesis of NFs not only offers environmental benefits but also holds potential for improving nutrient management in agriculture. These NFs can enhance nutrient uptake, promote plant growth, and mitigate the adverse effects of nutrient deficiencies. Furthermore, biological methods enable the utilization of natural, renewable resources, reducing the reliance on chemical-based approaches.

They provide sustainable and eco-friendly approaches for the synthesis of NFs (Sharma et al., 2023). Through the activity of microbes and plants, these methods offer precise control over nanoparticle properties and provide opportunities for tailoring NFs to meet specific agricultural requirements. The ongoing advancements in biological nanofertilizer synthesis hold great promise for addressing global food security challenges and promoting sustainable agricultural practices while minimizing environmental impacts (Table 3.3).

Table 3.3 List of important approved and commercially available nanofertilizers

Nanofertilizer	Constituents	Manufacturer country
Nano Ultra	Organic matter, N, P, K, Mg	Taiwan
Nano-calcium (magic green)	Ca, Si, Na, Al	Germany
Nanocapsule	N, P, K, Fe, Mg, Na	Thailand
Nano micronutrient (EcoStar)	Zn, B, Cu, Fe, EDTA-Mo, Mn	India
PPC nano	M protein, Na_2O, K_2O, $(NH_4)_2SO_4$	Malaysia
Nano Max NPK fertilizer	Multiple organic acids chelated with major nutrients, amino acids	India
TAG nanofertilizer	Proteino-lacto-gluconate chelated with micronutrients, vitamins	India
Nano green	Extracts of corn, grain, soybeans, potatoes	India
Biozar nanofertilizer	Organic materials, micro- and macromolecules	Iran
Nano-urea (liquid)	Urea particles	India
Plant nutrition powder (green nano)	N, P, K, Fe, Mg, Na	Thailand
Hero Super Nano	Organic matter, N, P, K, Mg	Thailand
Supplementary powder	Fe, Na	Thailand
Zinc oxide	Zinc	Taiwan
Titanium dioxide	Titanium	Taiwan
Silicon dioxide	Silicon	
Manganese dioxide	Manganese	
Selenium colloid	Selenium colloid	
NanoCS™ of NanoShield®	NPK, Zn	USA
NanoGro®	NPK	
NanoN+™	N	
NanoK®	K	
NanoPhos®	P	
NanoZn®	Zn	
NanoPack®	S, Cu, Mn, Fe	
NanoCalSi®	Ca, Si	
NanoFe™	Fe	
Nano-Ag answer®	NPK, other ingredients 93.4%	USA
Hibong biological-produced fulvic acid	Nanofertilizers, chitosan oligosaccharides	China
Humic acid-embodied granular fertilizer	Humic acid and organic matter	
Seaweed nanofertilizer	NPK, seaweed extract	

5 Mode of Application of Nanofertilizers

NFs offer innovative solutions for efficient nutrient management in agriculture. Their unique properties and enhanced nutrient delivery capabilities make them promising tools to improve crop productivity and reduce environmental impact. The application of NFs can occur through various modes, each with its own advantages and considerations. In this section, we will explore the different modes of NF application and their implications.

5.1 Soil Application

Soil application is the most common mode of NF deployment. NFs can be incorporated into the soil during soil preparation or applied directly to the root zone around the plants. The nanoparticles released in the soil gradually release nutrients, ensuring a sustained nutrient supply to the plants. This mode allows for efficient nutrient absorption by the root system and minimizes nutrient losses through leaching or volatilization.

The uptake of nanoparticles by plants is influenced by plant physiology, with absorption occurring through various structures such as trichomes, stomata, stigma, and hydathodes. Once absorbed, nanoparticles are transported within the plant through the phloem and xylem (Schwab et al., 2016; Wang et al., 2016; Padhan et al., 2021c). Two main routes facilitate the translocation of nanoparticles: the apoplastic pathway and the symplastic pathway. In the apoplastic pathway, macromolecules, including water, move through the apoplast, which consists of cell walls and intercellular spaces. However, the movement of macromolecules in this pathway is constrained by the size exclusion limits (SELs) of the cell walls, typically ranging from 5 to 20 nm (Bernela et al., 2021). In contrast, the symplastic pathway involves the movement of macromolecules from one cell to another through the plasmodesmata, which are small channels connecting the cytoplasm of adjacent cells. This pathway allows for direct transport within the plant's tissues (Šamaj et al., 2004; Etxeberria et al., 2006). The entry of nanoparticles into plant cells can occur through endocytosis from the cell wall, facilitated by the diameter of the stomata (ranging from 5 to 20 nm) or the base of trichomes, and subsequently transferred to other tissues.

The symplastic route relies on the SELs of the plasmodesmata, which typically range from 3 to 50 nm in diameter (Lucas & Lee, 2004; Heinlein & Epel, 2004). The Casparian strip, a specialized cell layer, acts as a barrier to transport into the plant's vascular system (Aubert et al., 2012). Interestingly, there are instances where nanoparticles larger than the SELs of cell walls, plasmodesmata, and the Casparian strip (such as 50 nm nanoparticles) have been internalized, potentially influenced by enzymatic activity. Nanofertilizers can also be combined with nanoparticles to control phytopathogens. When plant pathogens attack, the stress enzymes within plant cells can break the chemical bonds in the nanocapsules of the polymer wall, thus triggering the release of mucilage to prevent infection (Ropitaux et al., 2020). Additionally, the accumulation of nanoparticles on leaf surfaces may lead to foliar heating, which can impact gas exchange due to obstruction of the stomata (Ma et al., 2010).

5.2 Foliar Spray

The size of nanoparticles plays a crucial role in their interaction with plant cells. Nanoparticles ranging from 3 to 8 nm can penetrate the root epidermis and reach the xylem through osmotic pressure, allowing their transport to the aerial parts of the plant (Tripathi et al., 2017; Lin & Xing, 2008; Du et al., 2011; Rajput et al., 2020; Ali et al., 2021). Once they cross the cell walls, nanoparticles are transported apoplastically through extracellular spaces until they reach the central vascular cylinder, enabling their unidirectional upward movement through the xylem. To enter the central vascular cylinder, nanoparticles need to traverse the Casparian strip barrier. This occurs by binding to carrier proteins on the endodermal cell membrane through mechanisms like endocytosis, pore formation, and transport. Subsequently, nanoparticles move from one cell to another via the plasmodesmata, becoming internalized in the cytoplasm (Jha et al., 2011). Aggregated nanoparticles that fail to internalize accumulate on the Casparian strip, while those that reach the xylem are transported to the shoots and then redistributed through the phloem back to the roots (Dimkpa et al., 2012; Josko & Oleszczuk, 2013).

Within plants, nanoparticles can be found in various locations, including the epidermal cell wall, cortical cell cytoplasm, and nuclei (Josko & Oleszczuk, 2013). Nanoparticles that do not enter the root surface of soil aggregates can influence nutrient absorption. Direct absorption of nanoparticles in seeds can occur by entering the coat through parenchymatic intercellular spaces and diffusing into the cotyledon. Nanoparticles can also enter through the root tip meristem or at points of lateral root formation, taking advantage of wounds in the Casparian strip. To enter the epidermal layers of roots, nanoparticles must penetrate cell walls and plasma membranes, with the cell wall pores typically ranging from 3 to 8 nm in size (Carpita & Gibeaut, 1993). Although this size poses a challenge for nanoparticles to enter, it has been observed that nanoparticles can induce the formation of larger pores in cell walls, facilitating their internalization (Navarro et al., 2008).

Conventional fertilizers often result in nutrient leaching and pollution of soil and water, while certain agrochemicals contribute to greenhouse gas emissions and climate change (Rochette et al., 2018; Wesołowska et al., 2021). Controlled release of nanoparticles can address these issues. For example, Torney et al. (2007) demonstrated the controlled intracellular release of desired chemicals in protoplasts using mesoporous silica nanoparticles. To mitigate nitrogen leaching, treatments with polyolefin-coated urea, neem-coated urea, and sulfur-coated urea have been employed to control the release of nitrogen (Preetha & Balakrishnan, 2017). Studies have also explored the use of double-layered hydroxide nanocomposites for controlled nutrient release (Benício et al., 2017) as well as the slow release of integrated superabsorbent fertilizers to enhance soil moisture conservation (Wang et al., 2021). Furthermore, plants can exhibit responses to nanoparticles. For instance, the application of bentonite and titanium dioxide (TiO_2) nanoparticles led to a reduction in the diameter of *Zea mays* seedling root cell wall pores from 6.6 to 3.0 nm (Asli & Neumann, 2009).

5.3 Seed Coating

Another mode of NF application is seed coating, where nanoparticles are coated onto the surface of seeds before planting. This approach ensures that the nutrients are readily available to the germinating seedlings, providing them with a nutrient boost during early growth stages (Chakraborty et al., 2023). Seed coating with NFs improves seedling vigor, enhances root development, and promotes uniform plant establishment.

5.4 Drip Fertigation

NFs can also be applied through drip irrigation systems. By adding NF suspensions to the irrigation water, nutrients are directly delivered to the root zone. This mode enables precise control of nutrient application and minimizes nutrient losses due to runoff or evaporation (Fatima et al., 2020). Drip irrigation with NFs ensures targeted nutrient supply and efficient water usage, making it suitable for both field and greenhouse applications.

5.5 Controlled-Release Systems

Controlled-release systems involve encapsulating NFs within polymer coatings or matrices. These coatings control the release rate of nutrients, providing a sustained and controlled nutrient supply to the plants over an extended period. Controlled-release NFs offer improved nutrient use efficiency, reduce nutrient losses, and minimize the frequency of fertilizer application (Zulfiqar et al., 2019).

5.6 Nano-Hydrogel Application

Nano-hydrogels, which are nanoscale three-dimensional networks of hydrophilic polymers, can be used as carriers for NFs. These hydrogels can absorb and retain water and nutrients, acting as reservoirs that release the nutrients gradually to the plants. The application of nano-hydrogels loaded with NFs improves water retention in the soil, reduces nutrient leaching, and enhances nutrient availability to plants.

5.7 Nanocoating on Substrates

NFs can be coated onto various substrates, such as organic materials or inorganic carriers like zeolites or clay minerals. These coated substrates can be incorporated into the soil or used as top dressings. A nanofertilizer coating provides a controlled nutrient release and protects the nutrients from leaching or immobilization in the soil, ensuring their availability to plants over an extended period.

5.8 Hydroponic Systems

NFs can be used in hydroponic systems, where plants are grown in nutrient-rich water solutions without soil. The nanoparticles can be added directly to the hydroponic nutrient solution, providing a controlled and precise nutrient supply to the plants' root systems (Fatima et al., 2020). Hydroponic systems combined with NF application offer efficient nutrient uptake, water conservation, and optimal nutrient management for soilless agriculture.

5.9 Biodegradable Nanoparticles for Root Coating

Biodegradable nanoparticles can be coated onto the root systems of plants. These nanoparticles gradually release nutrients as they degrade, providing a localized nutrient supply to the plants' roots. Root coating with biodegradable NFs promotes nutrient absorption, enhances root development, and reduces nutrient losses to the surrounding environment.

5.10 Nanoencapsulation

Nanoencapsulation involves enclosing NFs within protective shells or capsules. These encapsulated nanoparticles can be applied through various modes such as soil application, foliar spray, or seed coating. The encapsulation protects the nanoparticles from degradation and enhances their stability, ensuring a controlled release of nutrients over an extended period. Nanoencapsulation enables precise nutrient delivery, reduces nutrient losses, and improves nutrient use efficiency (He et al., 2019; Chakraborty et al., 2023).

5.11 Nanofertilizer Incorporation in Compost

NFs can be incorporated into composting processes to enhance the nutrient content and quality of compost. By adding NFs to the organic waste during composting, the resulting compost becomes enriched with essential nutrients (Raliya et al., 2017). This nutrient-rich compost can then be applied to the soil, providing a slow-release source of nutrients for plants.

5.12 Nanofertilizer Application via Biodegradable Mulches

Biodegradable mulches, such as films or sheets made from biodegradable polymers, can be coated with NFs. These mulches are then laid on the soil surface around plants, slowly releasing nutrients as they degrade. Nanofertilizer-coated mulches offer controlled nutrient release, weed suppression, moisture conservation, and improved soil fertility (Zulfiqar et al., 2019).

It is important to note that the selection of the appropriate mode of NF application should consider factors such as crop type, growth stage, specific nutrient requirements, environmental conditions, and local farming practices. Additionally, proper application techniques, dosages, and timing should be followed to ensure effective nutrient uptake, minimize waste, and mitigate any potential environmental risks (Figs. 3.2 and 3.3).

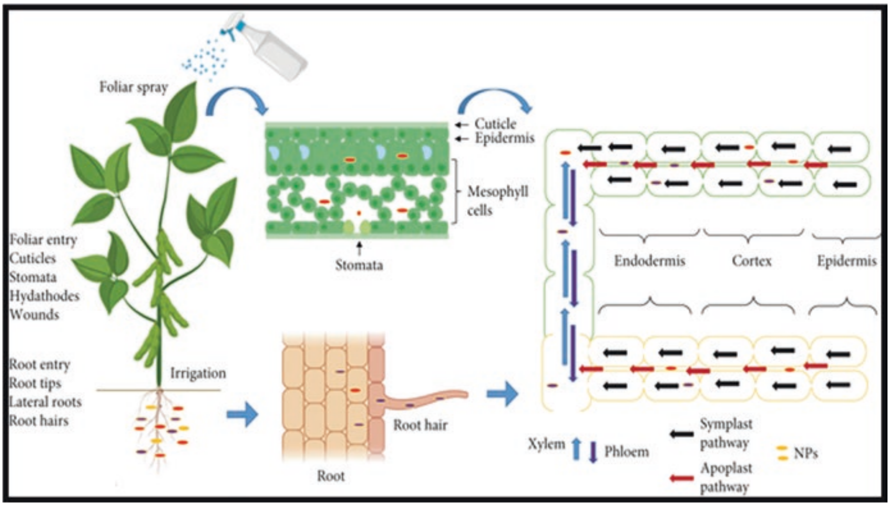

Fig. 3.2 Schematic visualization of the uptake of nanoparticles via various routes and their translocation pathways in various plant sections

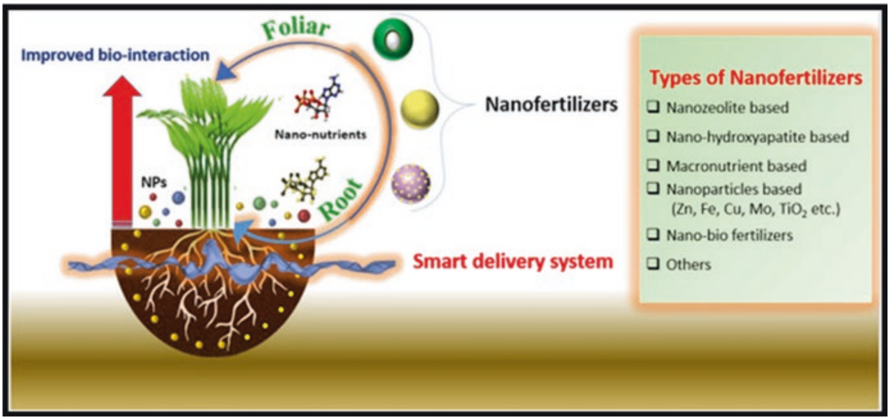

Fig. 3.3 Various approaches of application of NFs (Md. Rashid Al-Mamun et al., 2021)

6 The Mechanisms of Action of Nanofertilizers

Nanofertilizers have gained significant attention in the field of agriculture due to their unique mechanisms of action, which offer potential benefits in nutrient uptake, plant growth, and crop productivity. These mechanisms can be attributed to the physicochemical properties and nanostructured nature of the fertilizers.

The reactivity of nanomaterials facilitates efficient nutrient absorption in plants, leading to greater utilization and minimal losses compared to conventional fertilizers (Prasad et al., 2017; Pérez-de-Luque, 2017). The effectiveness of nanofertilizers in nutrient absorption, distribution, and accumulation depends on various factors, including soil pH, organic matter content, soil texture, and nanoparticle properties such as size and coating (El-Ramady et al., 2018; Ma et al., 2018). Nanofertilizers can be absorbed by plants through roots and leaves, affecting their behavior, bioavailability, and absorption within the plant (El-Ramady et al., 2018). Numerous studies have demonstrated the superior efficacy of nanofertilizers compared to conventional fertilizers. For example, nanofertilizers enriched with macronutrients have shown a 19% increase in plant development compared to conventional fertilizers, whereas those containing micronutrients have exhibited an 18% improvement (Kah et al., 2018). Furthermore, nanofertilizers with carriers for macronutrients have resulted in a remarkable 29% growth enhancement compared to conventional fertilizers. Nanofertilizers based on nano-chitosan, combined with nitrogen (N), phosphorus (P), and potassium (K), have been found to increase the sugar content and improve wheat properties (Abdel-Aziz et al., 2016). In another study focusing on wheat, Salama (2012) observed that the application of silver nanoparticles led to increased shoot and root length, leaf area, and the contents of chlorophyll, carbohydrates, and proteins. Moreover, nanofertilizers have the advantage of slow release, with nutrients being released over a period of 40–50 days, compared to the conventional fertilizers' release duration of 4–10 days (Chen & Wei, 2018).

(i) *Increased Nutrient Availability and Uptake*: Nanofertilizers exhibit a large surface area and high reactivity due to their nanoscale dimensions. This increased surface area allows for better contact and interaction with plant roots. The nanoparticles can release nutrients gradually, ensuring a sustained supply to the plants. The small particle size and high surface energy of nanofertilizers facilitate their penetration into the root tissues, enhancing nutrient uptake efficiency (Sharma et al., 2020). Additionally, the nanoparticles can overcome barriers such as soil pH, nutrient imbalances, and antagonistic reactions, thereby improving nutrient availability to the plants.

(ii) *Enhanced Nutrient Use Efficiency*: Nanofertilizers can improve nutrient use efficiency by reducing nutrient losses through leaching and volatilization. The controlled release of nutrients from nanofertilizers ensures that they are available to plants when needed, minimizing wastage and maximizing utilization (Mahapatra et al., 2022). The nanoparticles can also promote the conversion of nutrients into forms that are readily absorbable by plants, optimizing nutrient utilization and reducing environmental pollution (Shyam et al., 2021).

(iii) *Stimulated Plant Growth and Development*: The unique properties of nanofertilizers can stimulate plant growth and development. The nanoparticles can act as signaling molecules, triggering specific plant responses that promote root growth, shoot development, and overall plant vigor. Nanofertilizers can also enhance photosynthesis, chlorophyll synthesis, and enzymatic activity, leading to improved plant growth, increased biomass production, and enhanced crop yields.

(iv) *Enhanced Stress Tolerance*: Nanofertilizers have shown potential in improving plant tolerance to various abiotic and biotic stresses (Fatima et al., 2020). The nanoparticles can act as antioxidants, scavenging reactive oxygen species and protecting plants from oxidative damage caused by stress factors such as drought, salinity, and heavy metals. Nanofertilizers can also enhance a plant's defense mechanisms, leading to improved resistance against pests, diseases, and pathogenic infections.

(v) *Soil Health Improvement*: The application of nanofertilizers can positively influence soil health and fertility. The nanoparticles can enhance soil aggregation, improve water-holding capacity, and promote the growth of beneficial soil microorganisms (Chakraborty et al., 2023). Nanofertilizers can also mitigate soil degradation and nutrient depletion by replenishing essential nutrients and restoring soil nutrient balance.

(vi) *Nanoparticle Uptake and Translocation*: Nanofertilizers can enter plant cells through various uptake mechanisms. They can be taken up directly by root hairs, penetrating the cell walls and membranes. The small size of nanoparticles enables them to move easily through cell compartments, facilitating their translocation to different plant parts, including shoots, leaves, and reproductive organs (Raliya et al., 2017). This efficient uptake and translocation of nanoparticles ensure a uniform distribution of nutrients within the plant, contributing to balanced growth and development.

(vii) *Controlled-Release and Slow-Release Mechanisms*: One of the advantages of nanofertilizers is their ability to release nutrients gradually and in a controlled manner (Fatima et al., 2020). The nanoparticles can be engineered to have specific coatings or encapsulations that regulate the release of nutrients over an extended period. This slow-release mechanism ensures a steady supply of nutrients to the plants, reducing the frequency of fertilizer applications and minimizing nutrient loss through leaching or runoff.

(viii) *Nano-Enhanced Nutrient Uptake Pathways*: Nanofertilizers can enhance nutrient uptake by promoting the expression of specific transporters and channels in plant roots. The nanoparticles can interact with the cell membranes, modifying their permeability and facilitating the transport of nutrients into the cells. This nano-enhanced uptake pathway enables efficient nutrient absorption and assimilation, leading to improved plant nutrition and growth.

(ix) *Hormonal Regulation*: Nanofertilizers can influence plant hormone signaling pathways, leading to hormonal regulation and physiological responses (Fatima et al., 2020). The nanoparticles can modulate the biosynthesis, metabolism, and distribution of plant hormones such as auxins, cytokinins, and gibberellins, which play crucial roles in plant growth and development. By manipulating hormone levels and their transport, nanofertilizers can stimulate root branching, shoot elongation, flowering, and fruit development.

(x) *Gene Expression and Genetic Regulation*: Nanofertilizers can modulate gene expression patterns in plants, influencing the activation or repression of specific genes involved in nutrient uptake, stress responses, and growth regulation. The nanoparticles can interact with DNA, RNA, and proteins, altering their conformation and activity. This genetic regulation induced by nanofertilizers can enhance nutrient acquisition, stress tolerance, and overall plant performance.

(xi) *Rhizosphere Modification*: Nanofertilizers can modify the rhizosphere, which is the soil region surrounding the plant roots. The nanoparticles can alter the microbial community composition, promoting the growth of beneficial microorganisms that enhance nutrient availability and plant health. Nanofertilizers can also improve the soil structure and water-holding capacity, creating a favorable environment for root growth and nutrient absorption.

(xii) *Synergistic Effects*: Nanofertilizers can exhibit synergistic effects when combined with other agricultural inputs, such as conventional fertilizers, organic amendments, or biostimulants (Kalwani et al., 2022). The nanoparticles can enhance the efficiency and effectiveness of these inputs by improving their absorption, translocation, or utilization by plants. This synergy can lead to enhanced nutrient uptake, growth promotion, and overall crop productivity.

The understanding of the mechanisms involved in the uptake, translocation, and effects of nanoparticles within plants is crucial for optimizing the application of nanofertilizers and ensuring their safe and effective utilization in agriculture. It is important to note that the precise mechanisms of action of nanofertilizers can vary depending on the specific formulation, nanoparticle characteristics, and plant species (Raliya et al., 2017). The interplay between physicochemical properties of nanofertilizers and plant physiological processes is a complex and dynamic interaction that requires further research and understanding.

7 Challenges and Future Prospects

NFs have emerged as a promising technology in the field of agriculture, offering potential benefits such as improved nutrient absorption, controlled release, and reduced environmental impact (Mahapatra et al., 2022; Raliya et al., 2017). However, their widespread adoption and commercialization face several challenges.

7.1 Challenges

- *Safety and Environmental Concerns*: One of the primary challenges associated with NFs is the potential risk to human health and the environment. The nanoscale particles used in NFs may have unknown toxicity effects. It is crucial to conduct comprehensive safety assessments and evaluate the environmental impact before their large-scale deployment.
- *Regulatory Framework*: The regulatory framework for NFs is still evolving, with limited guidelines and standards in place. The development of clear regulations and standards specific to NFs is necessary to ensure their safe and responsible use as well as to facilitate their market acceptance.
- *Scalability and Cost*: The production of NFs on a large scale can be challenging, resulting in higher production costs compared to conventional fertilizers. To promote the widespread adoption of NFs, there is a need for scalable and cost-effective manufacturing processes that can meet the demands of agricultural systems.
- *Integration with Existing Agricultural Practices*: Integrating NFs into existing agricultural practices and supply chains poses logistical challenges. Compatibility with the existing equipment, application methods, and formulation compatibility need to be addressed for seamless adoption of NFs in different farming systems.
- *Knowledge and Awareness*: There is a need to enhance knowledge and awareness among farmers, agronomists, and stakeholders about the benefits and potential risks associated with NFs. Education and training programs can play a crucial role in ensuring the responsible and effective use of NFs.

7.2 Future Prospects

Despite the challenges, NFs hold significant promise for the future of agriculture (Abd El-Azeim et al., 2020). Here are some potential future prospects:

- *Enhanced Nutrient Management*: NFs have the potential to revolutionize nutrient management in agriculture. By fine-tuning the composition, structure, and release mechanisms, NFs can provide targeted and efficient nutrient delivery to plants, reducing nutrient losses and increasing crop productivity (Abdelsalam et al., 2019).
- *Controlled-Release Systems*: Advancements in nanotechnology can lead to the development of advanced controlled-release systems that respond to plant nutrient demands, environmental factors, and soil conditions. These systems can optimize nutrient availability, reduce leaching, and minimize environmental pollution.
- *Precision Agriculture*: The integration of NFs with precision agriculture techniques, such as remote sensing and data analytics, can enable site-specific nutrient management (Raliya et al., 2017; Mahana et al., 2022). This approach can optimize nutrient application based on crop requirements, leading to improved resource-use efficiency and sustainable farming practices.
- *Functional NFs*: Future research may focus on developing functional NFs that go beyond nutrient delivery. These NFs could incorporate additional functionalities such as disease resistance, stress tolerance, and enhanced plant growth promotion, contributing to the overall crop health and resilience.
- *Nanotechnology-Enabled Smart Farming*: The convergence of nanotechnology with other emerging technologies like sensors, robotics, and artificial intelligence can pave the way for smart farming systems (Chakraborty et al., 2023). NFs can play a vital role in such systems by providing precise and timely nutrient delivery, optimizing resource utilization, and enabling real-time monitoring of plant health.

While NFs face challenges in terms of safety, regulations, scalability, and integration, their prospects are promising. Addressing the challenges will require collaborative efforts from researchers, policymakers, industry, and farmers. By overcoming these hurdles and leveraging the potential of nanotechnology, we can harness the benefits of NFs to meet the increasing global demand.

8 Conclusions

From the abovementioned scenarios, it can be concluded that NFs represent a promising approach for enhancing plant nutrient uptake, improving crop productivity, and reducing environmental impacts. They can be synthesized through various methods, including chemical, physical, and biological approaches, with each offering distinct advantages and limitations. Chemical methods allow for precise control over particle size and morphology, while physical methods offer simplicity and scalability. Biological methods, on the other hand, provide environmentally friendly alternatives using plant extracts and microorganisms.

The mechanisms of action of NFs involve their size-dependent entry into plant cells, transport through the vascular system, and interactions with cellular components. Nanoparticles can be absorbed through root and leaf surfaces, where they are translocated via both apoplastic and symplastic pathways. The size and surface properties of nanoparticles influence their uptake and translocation within the plant, affecting nutrient absorption and physiological responses. Furthermore, nanoparticles can induce oxidative stress, alter membrane integrity, and interact with genetic material and cellular organelles. It is important to consider factors such as particle size, shape, surface charge, and interactions with plant cell components when designing and utilizing NFs. Understanding the mechanisms of nanoparticle uptake, distribution, and physiological effects in plants is crucial for maximizing their potential benefits and minimizing any potential risks. Further research is needed to elucidate the specific molecular mechanisms involved and optimize the synthesis and application of NFs for sustainable agriculture.

Overall, NFs hold great promise for revolutionizing agricultural practices, offering targeted nutrient delivery, reduced environmental impact, and enhanced crop productivity. Continued research and development in this field will pave the way for effective and sustainable nanofertilizer strategies, contributing to global food security and environmental sustainability.

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Chapter 4
The Potential of Nanocomposite Fertilizers for Sustainable Crop Production

Bhagwan Toksha, Shravanti Joshi, and Aniruddha Chatterjee

1 Introduction

A nanofertilizer is a product that serves the purpose of fertilizers at nano-scale. It is a product that transports nutrients to crops by modified means of transportation. The modified mean of transportation can be encapsulation, coating with thin layer or emulsion. Nanocomposite fertilizers are the formulations synthesized by combining two or more materials at nanoscale. The properites of starting materials gets curated as the composition of several nanomaterials gets captured within a material matrix. Nanocomposites evolve as an inorganic matrix hosting the organic phase, or vice versa, from an organic matrix hosting the inorganic phase. The design of Nanocomposite phase may aim at permeation of the desired component simultaneously preventing the other ill-favored components. Nanocomposites are heterogeneous or hybrid materials in a solid framework that can enhance the properties of the final product compared to those of conventional composites with individual phases. In this solid framework, at least one of the constituents has nanoscale dimensions (Neitzel et al., 2012; Sen, 2020). A variety of nanoparticles (NPs), including metals, metal oxides, zeolites, carbon-based materials, etc., are available. Nanocomposite fertilizers are used in almost every sector of agriculture. Various applications of nanocomposite materials influencing agricultural practices are depicted in Fig. 4.1.

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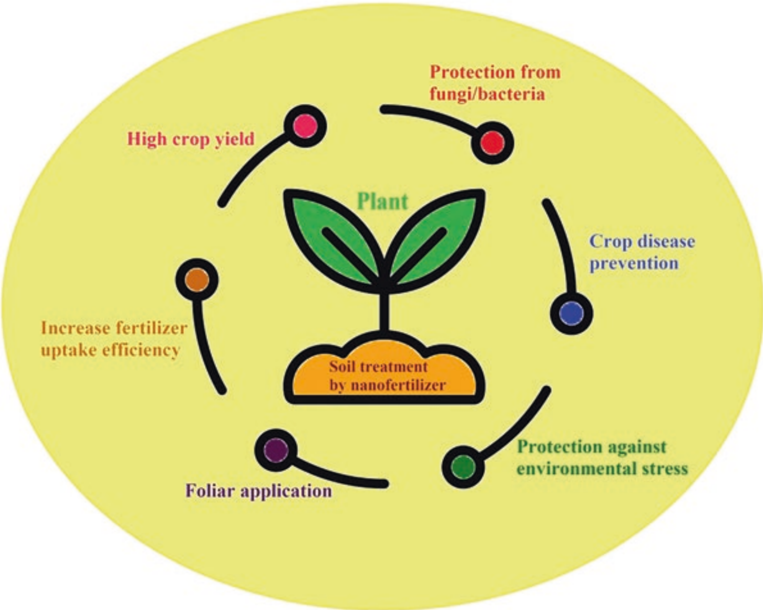

Fig. 4.1 Nanocomposite materials influencing agricultural practices

There is a lot to cover in the recent developments in nanotechnology for agriculture that have aimed to overcome the disadvantages of using conventional fertilizers. The role of nanocomposites in the fertilizer sector is particularly of interest here, as revealed by the expected increase in the use of nanofertilizers, which led to a compound annual growth rate (CAGR) exceeding 17% at a valuation of nearly USD 1.6 billion by 2030 (Jha et al., 2023). The characteristic advantages of nanotechnology, such as the extremely small size of nanoparticles, their extremely high surface area, and their high aspect ratio, provide potential solutions to address environmental concerns by replacing conventional fertilizers with nanocomposite fertilizers (Toksha et al., 2021). The various possible alterations to nanoparticle morphology, such as nanotubes, nanofilms, and nanoporous structures, enable the delivery of an optimal amount of the intended fertilizer via controlled or sustained release (Liang et al., 2022; Lohmousavi et al., 2020; Shaghaleh et al., 2022). Abiotic stresses, such as soil salinity, affect plant growth and crop production.

In India alone, salinity, alkalinity, and acidity are major factors that adversely affect food security (Kumar & Sharma, 2020). Salinity stresses roots and creates an ionic difference in the plant cell due to the buildup of Na^+ and Cl^-, which diminishes nutrient uptake thus inhibiting plant growth. This buildup of Na^+ and Cl^- in plant leaves reduces the photosynthetic area of leaves, affecting plant growth. Most crops commonly counter the harmful effects of salinity with the overproduction of a set of organic compounds. Such organic compounds act as osmolytes to counteract stress.

Additionally, crops also contain dynamic antioxidant enzymes, which are able to minimize the damage caused by environmental stressors. Such a natural defense, however, is inefficient in countering environmental stresses such as salinity. This situation demands taking economically viable and effective actions to minimize adverse effects and avoid the further increase in soil salinity. Soil salinity also changes plant physiology by disrupting its ionic balance and water homeostasis. It is also the root cause of damage in cellular-level redox homeostasis, which is caused by the escalated buildup of reactive oxygen. The losses due to saline soil have been estimated to cost over USD 27 billion dollars per year (Shahid et al., 2018).

The physiology of plants—i.e., the various functions of plant parts—enables photosynthesis and germination. Various phases of nanocomposites involving minerals and metal-based nanomaterials, such as oxides and ferrites, carbon matrices (e.g., graphene), carbon nanotubes, and biogenic materials, are synthesized for their possible applications in plant sciences. Table 4.1 presents the critical role and usage of nanocomposites in plant growth, plant physiology, crop quality, and sustainability on the basis of a few recent studies.

Their novel characteristics make nanocomposite products significantly different from their original forms of molecules and their bulk counterparts. Because of their unique properties, nanocomposites are garnering attention in research on agricultural processes, products, and applications. Nanocomposites include exciting alternatives to the existing synthetic chemical approaches to agricultural practices. These highly effective nanocomposites also modify application strategies, enable a slow-and-steady release, and improve target specificity. Nanocomposites endure over a prolonged period, which is also a vital characteristic for their applications in crop cultivation. This property influences their cost-effectiveness in that the desired activity can be achieved at a lower dose. Both lower-dose, target-oriented delivery and higher bioactivity will contribute to ecofriendly agricultural practices in the future. In-depth research in this area will ensure that the implementation of nanocomposite policies in crop sustainability and pest control will be useful and will help minimize environmental degradation and harm to humans. The aim of nanocomposites is to enhance the efficiency of the main matrix material by improving its physical, chemical, and biological properties. This ability to enhance physicochemical and biological properties also widens the application areas of newly produced nanocomposites in comparison with singly applied nanomaterials. Nanocomposites can be considered useful in the formation of nanocarriers, which are employed to carry and deliver the intended material by adopting both controlled- and slow-release modes. This improves the precision of farming practices such that it increases crop production and improves the nutrient values of consumable plant parts. Of course, this must be achieved without harming water and soil resources. The continuous reduction of dietary diversity and the increase in the consumption of staple crop-derived products have led to micronutrient deficiencies. Nanocomposites are expected to overcome such deficiencies by supplying micronutrients directly to plants. This problem of micronutrient deficiency is severe in areas where fertile soil lacks micronutrients.

Table 4.1 Applications of nanocomposite fertilizers in plant growth, plant physiology, crop quality, and sustainability

Aspect for improvement	Nanocomposite	Target	Mode of application	Critical role and usage	References
Plant growth	Bioinoculant + CeO_2	Fenugreek	Seed treatment	Increase in the uptake of essential micronutrients, improving to plant growth	Mary Isabella Sonali et al. (2022)
	Ag + graphene	*Stevia rebaudiana*	Green house foliar application	Increases in chlorophyll content, soluble sugars, and total phenol by 25–33% Higher flavonoids and total protein over 50%	Nokandeh et al. (2021)
Crop quantity and quality	Copper chlorophylline/ Silver and Copper chlorophylline /grapheme	Onion	Foliar application	Increased uptake of essential nutrient, improving crop quantity and quality	Merghany et al. (2019)
Crop quantity and quality	Ag + graphene	Melissa officinalis L	Foliar application	Higher plant productivity	Soraki et al. (2021)
Crop yield	Silica/Graphene + FeO + ZnO	Rice	Foliar application	Higher grain yield and increase in Zn and Fe uptake efficiency	Durgude et al. (2022)
Plant sustainability	GO-Ag	Wheat	In vitro— microdilution method In vivo—leaves	Crop disease prevention: antimicrobial agents against pathogenic fungi or bacteria	Chen et al. (2016)
	GO-CuO	Tomato, Pepper	In vitro and in planta	Reduction in *Fusarium* root rot and wilt diseases	El-Abeid et al. (2020)
	GO + chitosan/ethylene diamine tetra-acetic acid	Eggplant	In vivo—greenhouse	Improved plant immune response and nematocidal potential against *Meloidogyne incognita*	Attia et al. (2021)
	Mg + Chitosan	Rice	–	Antimicrobial activity against pathogens such as *Acidovorax oryzae* and *Rhizoctonia solani*	Ahmed et al. (2021)
	ZnO + $ZnFe_2O_4$	Guava	Through leaf extract	Improvement in plant immune response and prevention of transpiration, improving plant growth	Sahoo et al. (2021)

	$TiO_2/Cu_2(OH)_2CO$	Agar Medium	Agar medium under laboratory conditions	Antimicrobial activity against pathogenic fungal and bacterial infections	Liu et al. (2020)
	Montmorillonite + dimethyl silicone oil	Wheat	By spraying on leaf surface	Protection against powdery mildew infection in wheat crop via alleviation of physiological and biochemical stresses	Zhang et al. (2022a, b)
	Montmorillonite + peptide aptamer	*Stylosanthes*	By spraying on leaf surface	Protection against fungal anthracnose with improved antifungal activity through a secondary structure change Longer water retention achieved via hydrophobic interaction	Xu et al. (2022)
	Biopolymer arabinogalactan hosting Se NPs	Potato	Laboratory conditions	Antimicrobial activity against *Clavibacter michiganensis* ssp. sepedonicus	Perfileva et al. (2017)
	TiO_2 + N + and F	Tomato	Laboratory conditions	Antifungal activity against *Fusarium oxysporum*	El-Kahky et al. (2021)

NPs nanoparticles, *GO* graphene oxide

Recent studies have evaluated the role of nanoformulations in various aspects of plant growth and crop yield (Chakraborty et al., 2023; Jakhar et al., 2022; Sharma et al., 2022). A study aiming to determine the role of nanostructured materials in the variation of photosynthetic efficiency using a sustainable horticulture model was reported by Tighe-Neira et al. (2018). Other reports have shown that nanocomposites play roles in one of the growth phases of plants and in their variations, such as silica and its nanocomposites and copper and its nanocomposites. Also, Antul Kumar et al. and Matias Menossi et al. have elaborated on the inclusion of nanocomposites and bionanocomposites in sustainable agriculture.

The process that maintains the quality of crop yields is termed *biofortification* (Aziz et al., 2019; De Steur et al., 2017). There are a few well-known approaches to enhancing micronutrient content and bioavailability in edible staple crop tissues during plant growth (Carvalho & Vasconcelos, 2013). Using fertilizers; improving soil content so that all the required micronutrients reach the plant, known as agronomic biofortification; and practicing genetic engineering via plant breeding modification all improve the quality of crops (Dhaliwal et al., 2023). Using nanocomposite-based approaches for improving biofortified staple crop yields is a promising alternative to remediate micronutrient deficiencies (Achari et al., 2019). Food crops supplemented with micronutrients seem to have positive impacts on nutrition and human health (Dutta et al., 2022). A recent review has updated the approaches that use nanoparticles to overcome nutrient deficiencies. The fortification of micronutrients in plants will in turn fulfill humans' nutrient requirements (Kapoor et al., 2022).

The objective of this chapter is to present an up-to-date understanding of nanocomposite fertilizers. What has been recently carried out in the field of nanocomposite fertilizers and how these findings will be helpful in developing overall fertilizer policies, including those for nanocomposites, are summarized in this chapter. This chapter also aims to provide a readable synthesis of the recent standard resources of nanocomposite fertilizers available in the literature. Moreover, this chapter reviews and provides updates on the contemporary knowledge on and the future of nanocomposites for promoting sustainable crop cultivation under the dynamic global climate.

2 Nutritional Nanocomposites

The role of nanocomposites encompasses plant growth, plant physiology, crop quantity, and crop quality. Nanocomposite fertilizers are promising alternatives to their bulk and conventional counterparts thanks to their enormous potential. Various factors, such as the conditions in which the nanocomposites are applied, are considered and evaluated for each plant. As a result of efforts taken for sustainable agriculture, world cereal production is expected to increase by the end of the 2020s. The main crops that will benefit from this growth include maize, wheat, and supplementary coarse grains. Increased research on seed varieties and superior agricultural modifications have contributed the most to increasing crop yields. However, these attempts have fallen short in alleviating the impacts of climate change and production constraints. In the majority of developing countries, production constraints such as investment financing and land-tenure issues are quite serious. The price of fertilizer is a vital consideration in agricultural financial investments. The causes of the dynamic changes in cereal prices include seasonality, financial constraints such as transport costs (which depend on energy/oil prices), and agricultural commodity price volatility (Kwas et al., 2022).

A greener approach to increased agricultural productivity could lead to possible pathways to reduce the carbon emissions of agriculture and to increase the area for crop production. Of these pathways, the area for crop production is almost at its limit and arguably cannot be extended further. Increasing the food production index is necessary to increase cereal food production while reducing agricultural carbon emissions. Alternate designs include using ecofriendly, effective fertilizers that can enhance crop yield in healthy, ecological settings (Koondhar et al., 2021). Cereals and other food grains are important because of their nutritional contributions and low costs (Beyer, 2010). Understanding the natural functionalities and modifications of a given crop could be vital in designing nanocomposite fertilizers (do Nascimento et al., 2022). For example, alterations in the germination process lead to the increased bioavailability of nutrients such as carbohydrates and proteins (Poole et al., 2021). Another example of this kind is bioactive compounds' leading to increased levels of antioxidants and fiber (Erenstein et al., 2022). The nanocomposite fertilizers enriching crop products can reduce many severe medical conditions due to malnutrition by increasing the intake of bioactive food components, particularly dietary fiber. The hidden hunger problem, due to food containing low levels of mineral elements, could be solved by using nanocomposite fertilizers. While aiming to meet humans' nutritional requirements, ecological boundaries must not be crossed and resources must not be overexploited because those would further exacerbate environmental degradation and water scarcity. Climate changes and crises further compound problems such as crop adaptation and crop losses. The application of nanocomposite fertilizers has been adopted as a novel agricultural practice to overcome difficulties in maintaining worldwide cereal production, enhancing crops' crucial nutrients, and reducing the levels of poisonous elements in the edible parts of agricultural crops. However, these materials' deleterious effects on crops' physiologies, antipathogen activities, and action mechanisms remain challenges for the scientific community to overcome. Generating nanocomposite fertilizers via a green synthesis method would reduce the potential toxicity of the nanocomposite fertilizers in comparison with those obtained via conventional approaches that use environmentally degrading precursors (García-Ovando et al., 2022). The improvements in nutrient availability thanks to nanocomposite fertilizers, as compared to conventional fertilizers, is discussed in the following section. Its subsections are as follows:

2.1 Plant growth
2.2 Plant physiology
2.3 Crop quantity and quality

2.1 Plant Growth

More than 14 mineral elements—in the form of micro- and macronutrients, including oxygen, carbon dioxide, and water—are required for a plant to grow (Mengel et al., 2001; White & Brown, 2010). The physiological and biochemical processes of plants can be improved by using nanocomposite fertilizers to increase nutrient availability. This in turn contributes to the plant's overall growth. The dynamics of including nanophase materials for plant growth have been focal points of research over the past decade (Amer et al., 2021; Sigmon et al., 2021; Verma et al., 2018, 2019). Industrialization has long contaminated soil and water resources, and such contamination has spread all over the planet. The main concern here is that heavy metal stress conditions hamper the metabolic, physiological, and biochemical characteristics of plants and plant growth. Heavy metal stresses also affect other indications of plants' life spans, such as seed germination, photosynthetic activity, root length and size, root-tip mitosis, and micronucleus induction. Heavy metals accelerate aging and cause roots to be shorter, thinner, and less developed overall. Nanocomposites formed under gamma irradiation involving chitosan, Ag, and Mn-Mg ferrite improved plant growth in cabbage under Cd stress. The Cd content was reduced in leaves and roots, and the chlorophyll values increased. Including this nanocomposite also reportedly improved the antioxidant and nonantioxidant enzymes of the target plant (Abdel Maksoud et al., 2022). The environmental hazards of urea rise from urease hydrolyzation. Urea's leaching into the nearby environment reduces nutrient-uptake efficiency. A fertilizer synergist (FS) of sodium humate transported by a hydrogen-bond nano-network leading to high biosafety and a decrease in agricultural pollution was reported by Linglin Zhou et al. (2017). Images from field experiments on potato, corn, and rice crops are depicted in Fig. 4.2.

The term *micronutrients* in the context of agriculture refers to elements that are abundant in soil. Elements such as Cu, Fe, Mn, and Zn are subsumed under this class, and they are required in smaller amount but play critical roles in plant growth and development. Micronutrients enable healthy plant growth, whereas their deficiency causes abnormal growth in plants, and higher concentrations may hamper plant growth. One role of micronutrients in plant growth and development is to maximize crop yields (Chrysargyris et al., 2022; Tripathi et al., 2015). The routes that micronutrients take in plants, including soil broadcast spreaders and foliar sprays, suffer from conventional drawbacks such as volatilization, leaching, and surface runoff. In addition to this disbursement of micronutrients through the soil, seed treatment is useful for early critical plant growth and for crop yields. The fixation or unavailability of these nutrients is sensitive to many climatic and edaphic conditions.

Copper in trace amounts is one such micronutrient that is essential for plant growth. Besides exhibiting antibacterial, antifungal, and insecticidal activities at the nanosize, it also inhibits plant growth in higher concentrations (Jampílek & Kráľová, 2022). Chitosan/polyacrylic acid/copper nanocomposites obtained via

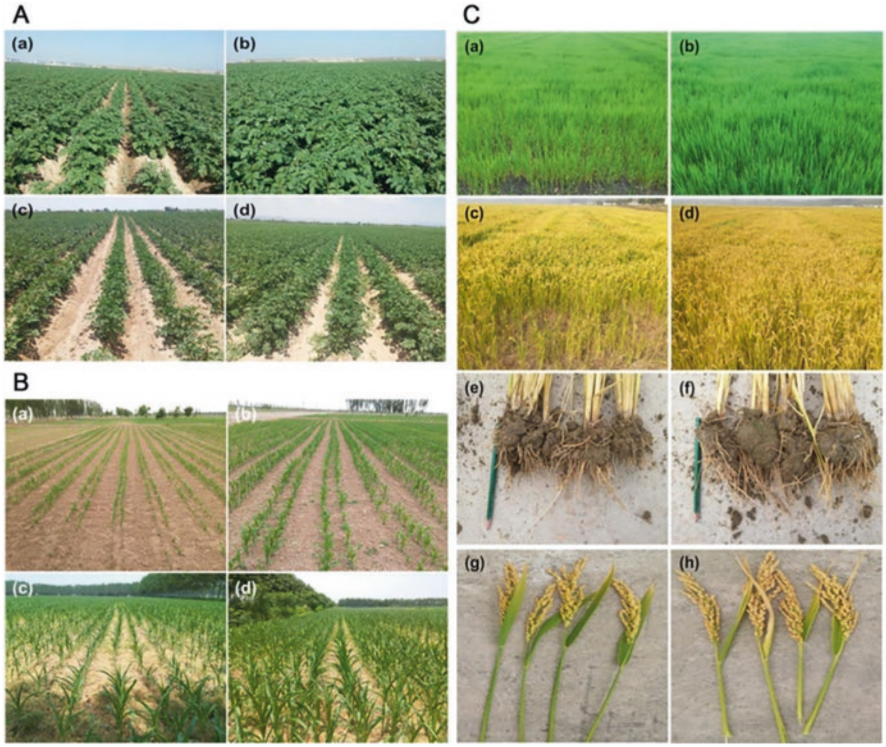

Fig. 4.2 Field photographs of (**a**) potato, (**b**) corn, and (**c**) rice at their seedling and mature stages, including rice roots and ears. (Reprinted with permission from Zhou et al., 2017)

copolymerization were provided through foliar method to onion plants (Abd El-Aziz et al., 2019). This experiment demonstrated the antibacterial activity of synthesized nanocomposites and resulted in the higher growth and yield of onion bulbs.

Zinc is a metal to which a large number of proteins are bound and is used in all six enzyme groups (Osman et al., 2021). Nanocomposites, such as zinc NCs, have proven to be beneficial to plants grown under salinity or drought stress (Batista et al., 2020). Improvement along various indicators—such as enhanced plant growth, chlorophyll content, and fewer aborted seeds per pod with better antioxidant enzyme activity—and the accumulation of osmolytes are attributed to the use of zinc NCs (Kheir et al., 2019). When provided to maize crops, urea-based nanocomposites, including $ZnSO_4$ or ZnO NCs, in fertilizer stimulated plant development in a nutrient-poor sand. When several fertilizer nanocomposites were applied simultaneously, it improved root morphology characteristics, such as increased root length and surface area, which improved nutrient uptake from soil (Giroto et al., 2022). In a study of cotton plants, zinc NCs in fertilizer improved several physiological parameters, namely chlorophyll content and antioxidant activity, which are indicators of plant quality and quantity (Hussein & Abou-Baker, 2018). Plants treated with foliar applications of Zn NC fertilizer and humic acid markedly increased plant growth and dry biomass (Najafi Vafa et al., 2015). Additionally, the contents of plant growth–promoting hormones were increased with the use of Fe and Zn NC fertilizers (Sharifi, 2016). Layered double hydroxide (LDH) and multi-walled carbon nanotubes (MWCNTs) with zinc have also been explored to improve micronutrient release and distribution. One study on onion plants under arid conditions used MWCNTs as micronutrient distributors and a nutrient stabilizer, which resulted in improved plant growth (Kumar et al., 2018). Nanocomposites of Zn and Al in a layered double-hydroxide matrix maintained the pH level via a controlled release of α-naphthalene acetate, which acted as a plant growth regulator (bin Hussein et al., 2002).

Iron (Fe) is an essential micronutrient for plant growth. It contributes to photosynthesis, chloroplast development, and dark respiration. Iron-deficit plants exhibit reduced photosystems and lipid composition and altered chlorophyll ratios (Alidoust & Isoda, 2013; Ghasemi et al., 2014). *Gum kondagogu*, a natural biopolymer, has been used in a nanocomposite material for mungbean plant growth. This nanocomposite, which includes highly monodispersed Fe nanoparticles and *Gum kondagogu*, has been reported to improve plant growth. The increased radial length and biomass were attributed to increased water uptake that was facilitated by the use of Fe nanoparticles (Raju et al., 2016). Zeolite/Fe_2O_3 nanocomposites synthesized by using low-cost and low-energy natural materials were reported as a fertilizer formulation that improved plant growth and yields (Jahangirian et al., 2020).

Macronutrients such as nitrogen (N), phosphorus (P), and potassium (K)—together referred to as NPK—are required in adequate amount for plants to efficiently reach their genetic yield potentials. NCs have well-known benefits, such as the ease of penetration, that enhance the application of NPK. The increase in the growth of wheat leaves, for example, was achieved by increasing NPK nutrient availability, thanks to a nanosize formulation that penetrated the leaves' stomata via gas exchange, as reported by Abdel-Aziz et al. (2018). Many biopolymers are in the nanocomposite formulations used in the agricultural sector (Kassem et al., 2021; Menossi et al., 2022; Olad et al., 2018; Pimsen et al., 2021). In the exploration of sustainable agricultural practices, chitosan-based nanocomposites (ChNCs) could be ecofriendly alternatives that contribute to plant growth (Jain et al., 2022). Chitosan, a natural polymer extracted from the chitin deacetylation of crustaceans, insects, fungi, etc., is used as one of the types of NPK nanocomposites. Chitosan has a natural affinity for metals, making it an efficient encapsulating agent. Efficient nutrient utilization ensures plant growth and can be achieved by using chitosan-based nanocomposites (Sharma et al., 2022). ChNCs are some of the prime candidates for improving crop growth, crop physiology, and crop protection. ChNCs are often sourced from biofood waste in cost-effective, biodegradable, biocompatible, and benign ways. These formulations regulate plant growth, antimicrobial activities, and stress-inhibitory activities. Recently, researchers designed and tested various recipes involving several types of ChNCs (Sangwan et al., 2023). Overall, ChNCs contributes towards a wide range of enhancements of plant morphology.

However, there are mixed reports about the role of chitosan on the growth of the roots, shoots, and leaves of various plants. One study on the use of chitosan + NPK nanocomposites for the growth of wheat plants in sandy soil reported positive results at harvest along crop and mobilization indices, along with a shorter life cycle (Abdel-Aziz et al., 2016). By using the slow-release method, nanocomposites formed with zeolite and chitosan and combined with sago starch reported to result in better growth indicators. Such nanocomposites also helped in maintaining the water level, proving their use as slow-release fertilizers (Pimsen et al., 2021). A superabsorbent nanocomposite revealed that the slow-release process facilitated water uptake. This nanocomposite was produced by using an Fe and NPK agrochemical formulation based on maize bran and montmorillonite (Gharekhani et al., 2018). In another formulation, poly (vinyl alcohol) + cellulose nanocomposites were developed such that the cellulose nanocrystals were derived from hemp stems through chemical treatments. The poly (vinyl alcohol) + cellulose nanocomposites were used to coat NPK-compound fertilizers by using a fluidized bed-coating machine. Improvements in release behavior and moisture content in soil were reported after using these formulations (Kassem et al., 2021).

2.2 Plant Physiology

Plant physiology parameters include fresh/dry weight, root–shoot ratios, root biomass and shoot biomass. Leaf area, crop yield, the reproductive index, photosynthetic pigment content, and chlorophyll α fluorescence are some of the other important plant physiology parameters (Füzy et al., 2019). Because the inclusion of nanosize minerals as nutrients and stimulants in plant fertilizer strategies has improved the physiological and biochemical attributes of plants, research on the use of nanocomposites for improving plant physiology has accelerated. Additionally, nanoparticles also reduce oxidative damage and improve water and nutrient uptake, resulting in increased crop yields.

Biochar, a charcoal-like substance, is synthesized in a controlled environment by burning the organic waste from agriculture and forestry to reduce contamination and ensure the safe storage of carbon. In the pursuit of increasing of crop yields, the harmful effects of various environmental stresses, such as salinity, must be minimized (Hessini et al., 2019). Any imbalance in the conventional practice of using mineral fertilizers reduces plant growth potential and nutritive quality instead of achieving higher yields (Kumar et al., 2021). Moreover, it worsens soil conditions and pollutes the environment.

Salinity affects plant growth potential, reduces the output of photosynthesis, and adversely impacts water and ion statuses in affected plants. Researchers have aimed to improve plants' salt tolerance under saline conditions by increasing the electron transport rate and reducing sodium accumulation and reactive oxygen species (ROS) generation (Chrysargyris et al., 2019). Salt toxicity leads to stomatal conductivity, which generates high levels of reactive oxygen species (Egamberdieva et al., 2019; Kapoor et al., 2022). This high level of reactive oxygen species disrupts plants' cellular structures and causes cell death. To enable plant survival under saline conditions, ample concentrations of nutrients must be made available to plants; this is because nutrients help regulate physiological pathways under saline stress (Sheldon et al., 2017).

The use of biochar nanocomposites with magnesium and manganese has been reported to increase the contents of potassium, manganese, and magnesium in plant tissues, photosynthetic pigmentation, and leaf water content and to reduce sodium accumulation, together increasing plant biomass when compared with control plants (Ghassemi-Golezani & Farhangi-Abriz, 2021). Nanocomposites such as biochar and metal oxides might compound the benefits of biochar and nanomaterials. Nanocomposites made from a combination of magnesium and manganese metal oxides with biochar improved chlorophyll content, root growth, and the overall productivity of safflowers (Ghassemi-Golezani & Farhangi-Abriz, 2021). This nanocomposite also contributed to maintaining optimal concentrations of nutrients and optimal water content in plant cells and enhanced nutrient absorption rates (Farhangi-Abriz & Ghassemi-Golezani, 2021).

The physiological and biochemical parameters of crops improve with the application of nanocomposites. In the case of sunflowers, a Fe_3O_4 + H_2O biocompatible magnetic nanofluid improved the total chlorophyll content of leaves at a low concentration, namely > 0.75% (Pîrvulescu, et al., 2015). Barley plants were hydroponically subjected to a recipe of Co and Nd doped in Fe nanoparticles that were produced via the sonochemical synthesis method. This resulted in an increase in biomass, chlorophyll content, and carotenoids at certain concentrations (125, 250, 500, and 1000 mg/L); that study concluded that the improvement in plant physiology showed a positive correlation between magnetic nanoparticles (MNPs) and photosynthetic machinery (Tombuloglu et al., 2020). After foliar applications of nanosize TiO_2 ($nTiO_2$), increases in yield, chlorophyll content, carotenoids, and anthocyanin content were reported in maize plants by Morteza et al. and in barley plants by Janmohammadi et al. (Morteza et al., 2013; Janmohammadi et al., 2016). Other studies have reported improvements in the structure of chlorophyll, the ability to capture sunlight, pigment production, ribulose-1,5-bisphosphate carboxylase/oxygenase (RuBisCo) activity, and photosynthesis efficiency after applications of $nTiO_2$ (Gohari et al., 2020; Satti et al., 2022; Yang et al., 2006). A study using perlite NPs and TiO_2/perlite NCs claimed that biologically synthesized NPs were more benign than chemically synthesized NPs. While no significant change in chlorophyll or carotenoid contents was reported in that study, valuable secondary metabolites, such as volatile compounds, hypericin, and pseudohypericin, significantly increased after the treatment using TiO_2/perlite NCs. The experimental steps involved in that study are depicted in Fig. 4.3 (Ebadollahi et al., 2019).

The benefits of Zn and Si nanoparticles could be advantageous to plant physiology (Song & Kim, 2020; Sturikova et al., 2018). A Zn-Si nanocomposite could bring the functionalities of separate phases together. Zn plays a critical role in various crops in that it improves chlorophyll content, plant biomass, and yield quantity. The functionality of Si controlling root to leave transportation of Na^+ ions and increasing the level of K^+ ions in leaves is useful in minimizing the negative impacts of oxidative, salinity, and drought stresses (Naaz et al., 2022; Rastogi et al., 2019).

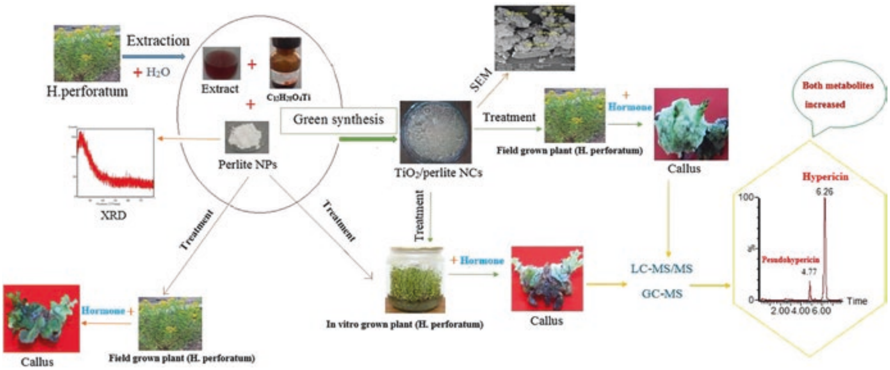

Fig. 4.3 Flowchart showing the role of TiO_2/perlite NCs on the plant physiology of *Hypericum perforatum*. (Reprinted with permission from Ebadollahi et al., 2019)

These features become useful under soil salinity, arid, and semiarid conditions. A foliar spray containing Zn-Si nanocomposites that was used on soybean plants in saline soil that contained plant growth–promoting microbes significantly diminished the detrimental effects of water stress and soil salinity on soybean crop physiology (Osman et al., 2021). The changes to plants after a water application led to deeper root penetration, heavier nodules (according to dry weight), and higher leaf K^+ content. A metal nanocomposite of magnesium and manganese based on biochar was evaluated for soil quality and salt toxicity in safflowers. The study emphasized the role of NCs in enriching plant physiology when the water level of plant tissues was maintained. The NCs affected the required exchangeable sodium concentration in soil and enhanced the nutrient absorption rate of plants. Osmotic stress is a consequence of salinity which reduces the abosorption rate of the plants. A reduction in the osmotic stress was observed after the application of NCs.

Our current gap between food demands and agricultural production requires scientific approaches that bring about uniform seed germination and seedling development to ensure proper crop growth. The process of germination initiated via imbibition—i.e., mature dry seed taking up water from soil moisture—completes the life cycle in a way that lengthens the embryonic axis, typically the radicle, from the seed envelope. The degradation of starch during the germination of crop seeds and the consequent seedling establishment lead to enzymatic actions. α-amylase is the enzyme that initiates the hydrolysis of starch granules naturally synthesized during the germination of seeds. The α-amylase augmentation during seed germination is vital for efficient plant growth. Seed priming is one of the standard modern agricultural practices advantageous for increasing seed germination efficiency, seedling growth, and protection against pathogens (Chakkalakkal et al., 2022). Including NCs in priming, which achieves the slow uptake of intended nutrients to the developing plant, standardizes the antioxidant defense system, leading to enhanced germination competence and plant growth (Szőllősi et al., 2020). Various parameters, such as comparable size, stability, and coatings of nanocomposite materials, are advantageous for plants to take up nutrients through the root epidermis (Zhang et al., 2022a, b). These nanocomposites are bio-altered into their ionic forms and are distributed throughout the rest of the plant parts (Szőllősi et al., 2020). The NCs work as a stimulus in seed germination by reducing seed dormancy, which eventually accelerates the germination rate and seedling development. Reductions in cell division in the apex roots, leading to root shortening, and increases in the levels of lipid peroxidation, leading to chromosomal aberrations and mitotic abnormalities, need to be properly addressed before systematically using NCs.

Crop seed germination is vulnerable to diverse environmental stresses. A nanocomposite recipe that preserves germination activity at desired levels while helping seeds adapt to adverse environmental conditions is needed. Coating reagents in nanocomposites have effectively improved wheat seed germination and subsequent seedling establishment under manifold environmental stresses. The carbon dioxide generated in the process of seed respiration and gradually emitted oxygen may accelerate seed germination activity and reduce germination time. Coating reagents can be critical in water absorption and retention because they effectively absorb carbon dioxide. Nanocomposite materials using natural clays help to establish a suitable soil-moisture-conserving matrix. Supplementing crops with nutrients such as zinc (Zn) and iron (Fe) may also improve moisture retention (Nada & Blumenstein, 2015). This eventually enhances crop yields and quality by improving the physical and biological parameters of soil. A silica and calcium peroxide nanocomposite matrix used as an environmentally friendly seed coating approach for wheat crops maintained high seed germination activity, as reported by Jun Ni et al. (2022). A constant rate of generating hydrogen peroxide at smaller dosages has been recognized as a mechanism for protecting seeds from microbial infection during seed germination and seedling establishment.

2.3 Crop Quantity and Quality

Nanocomposites (NCs) are readily absorbed and internally distributed by plants in such a way that they improve crop quantities and yields. NCs also demonstrate better abilities to provide nutrients because they possess large surface areas, high reactivity rates, compatible pore sizes, and desirable particle morphologies. The antimicrobial characteristics of nanoparticles can be exploited in nanocomposite formulations to protect plants. Bacteria and fungi are the main causes of infestations that lead to various crop diseases. These infections seriously threaten crop growth, reduce crop yields and quality, and can even lead to health risks to humans upon consumption. Metallic nanoparticle-based nanocomposites play significant roles in inhibiting pathogenic bacteria and fungi. More research on metallic nanoparticle-based nanocomposites needs to be carried out to assess the interactions between nanoparticles and pathogens, and the indirect effects of inducing plant susceptibility to infection also needs to be considered. Ferrite materials and their composites have a wide range of applications (Shaikh et al., 2021; Toksha et al., 2008, 2017). Most of the elements, in addition to iron, that are included in ferrite matrices are essential nutrients for plant growth and yields (Shebl et al., 2020). In one study, Mn-Zn nanosize ferrites at varying concentration levels that were applied through the foliar method to squash plants (*Cucurbita pepo L.*) resulted in yield increases as high as 50%, along with increases in organic matter content and total energy in squash leaves (Shebl et al., 2020). In the case of wheat crops, a Ce-Mn ferrite nanocomposite has been reported to improve photosynthesis efficiency and total crop yields. Realizing the potential of NC applications as fertilizers, one study reported increases in the uptakes of Fe and Mn micronutrients in plant shoots (Zarinkoob et al., 2021).

Crop quantity varies as a function of the size of nanoparticles, their compositions, and their concentrations. It also depends on the physical and chemical properties of the NCs and the targeted plant species. Fertilization efficiency is critically affected by changes in pore size distribution. Thus, the choice of synthesis method becomes important because it controls the properties of NC fertilizer, such as surface morphology, pore structure, and particle size and shape. This in turn determines crop yields. When nanocomposite fertilizers with chitosan and NPK fertilizers are used in low concentrations under clayey and sandy soil conditions, they have been reported to increase plant growth rates in wheat crops (Abdel-Aziz et al., 2016). The important characteristics of crop yields include seed weight, seed yield, seed height, and the number of branches produced. One study reported that crop quantity and quality were ensured through growth-promoting action and the simultaneous application of Fe + Zn with NPK (Drostkar et al., 2016). This beneficial effect on crop quantity and quality contributes to cumulative growth hormone production and metabolic process augmentation. In one study, seed treatments of Fe_3O_4–urea nanocomposites on rice plants under hydroponic conditions resulted in enhanced growth and yields (Guha et al., 2022). The NCs enhanced photosynthetic efficiency and nitrogen infusion by making the nitrogen and iron readily available to the plant. The slow release of urea achieved through these NCs improved the nitrogen use efficiency of the plant.

The yield and subsequent storage of crops must be considered because crops are prone to growing mildew, owing to their rich nutrition (Li et al., 2021; Rodríguez-Félix et al., 2021). Pathogens such as mildew lead to declines in quality and germination rate and can even harm human health (Wang et al., 2020; Wawrzyniak et al., 2018). Crops that have relatively large embryos easily absorb moisture and carry large numbers of bacteria. This makes them susceptible to producing pathogenic microorganisms. Postharvest moisture content provides a suitable growth environment for microorganisms during transportation and storage. This leads to the development and reproduction of pathogenic microorganisms and causes safety problems such as the mildew and excessive mycotoxins (Kimanya, 2015). The quality parameters of a crop include its color, taste, nutrition level, and processing characteristics. Moreover, seeds lose their reproductive value with the excessive growth of microorganisms, which hampers the germination rate (Walker et al., 2018). Combinations of fertilizer NCs and pesticide NCs are parts of recent approaches used to maximize plant growth potentials. Such nanocomposites are synthesized with a multiple target approach of sustained foliar retention weeding and providing nourishment to the plants. Yanzheng Ji et al. reported one such nanocomposite involving zinc, mesoporous silica, and

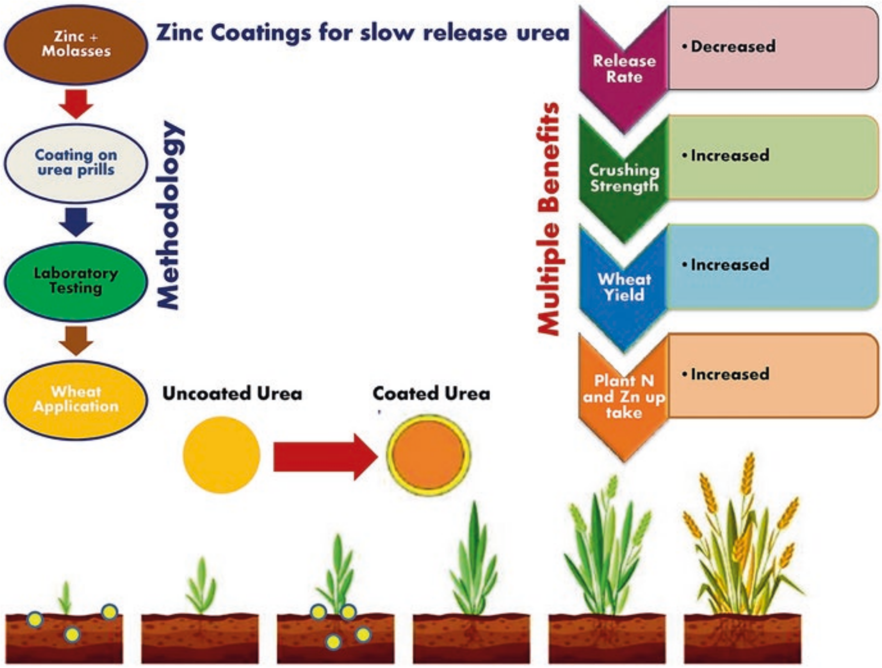

Fig. 4.4 Flowchart of steps for using nanosize zinc coatings to enhance wheat crop yields. (Reprinted with permission from Beig et al., 2022)

polydopamine working as combinations of pesticide NCs and fertilizer NCs (Ji et al., 2020). Nanocomposites used to implement or modify a slow-release mechanism has been recently explored (Dimkpa et al., 2022; Olad et al., 2018). Nano-bentonite supplemented with Zn and ZnO NPs formed a nanocomposite that was encapsulated in stearic acid, paraffin wax, and oil. A coating material binding the Zn and N achieved a slow-release mechanism, thus showing the nano-bentonite to be an ecofriendly and cost-effective material (Umar et al., 2022). The dual role of zinc as a source of micronutrients and a coating material of slow-release urea was reported by Beig et al. (2022). That study reported that the nanosize zinc coating was more effective in increasing N uptake and Zn uptake in wheat crops, resulting in higher yields compared with using bulk zinc coatings. The steps to follow when using nanosize zinc coatings to improve wheat crop yields are listed in Fig. 4.4.

3 Plant Sustainability

The overall wellbeing of crops is vital for food security. In any country's economy, agriculture creates jobs, increases GDP, and provides food, feed, and biofuels. Efforts to maintain the current rate of crop yields are failing to meet global demands.

There is currently at least a 15% gap between the global demand for agricultural products and the crop yields across the globe (Zhao et al., 2022). That crops fall victim to plant diseases and pests only exacerbates the food scarcity problem. On a global scale, the estimated average rates of crop losses caused by pathogens and by pests are 14% and 32%, respectively, for wheat, rice, maize, soybean, and potato crops (OECD-FAO, 2022). The agricultural losses due to pests amount to USD 36 billion annually in India alone (Dhaliwal et al., 2015). Age-old practices, such as tillage, crop rotation, and polycultures, and new practices, such as genetically modifying plants, have been tried and have worked to certain extents at reducing losses from disease outbreaks. Limitations on the availability of arable land and challenges facing maintaining the quality of the environment are the main concerns with these approaches. Moreover, crops may suffer from problems such as lower nutrition values, toxicity, immunosuppression, and allergic reactions (FAO-UN, 2022). In this situation, stable nanocomposites with novel properties, such as cation-exchange capacity and complexation, elevated reactivity, unusual structural phases, large ion-adsorption ratios, and the ability to aggregate, can be effectively used. Polysaccharide nanocomposites have been explored in agricultural research for sustainability (Gamage et al., 2022). These nanocomposites include a wide range of formulations, such as biopolymers, nanosize cellulose, chitin, and clay (Ge et al., 2018). Sathiyanarayanan Anusuya et al. reported the antifungal activity of β-d-glucan nanoparticles against *P. aphanidermatum*, a pathogenic fungus that distresses many prominent greenhouse crops and field crops (Anusuya & Sathiyabama, 2014). A review of the glucan biopolymer was updated by Somnath Chavanke et al., who elaborated on its effective use in mitigating the effects of climate change on crop plants by enhancing their immunity levels (Chavanke et al., 2022).

Crop storage is a pressing issue in that all efforts made to reduce hunger by following sustainable agricultural practices have not worked. The limited shelf life of crops and food waste together account for the one-third of food that is produced but not consumed. Biologically sourced multifunctional nanocomposites can be effective in addressing these concerns because they can reduce the rate of food decay by retarding ripening, reducing dehydration, and preventing microbial infections. A sustainable nanocomposite including inexpensive or waste materials such as egg-derived polymers and cellulose nanomaterials was reported by Seohui Jung et al. The food coating was palatable and washable (Jung et al., 2020).

Nanocomposites also contribute to plants by developing sensors for crop pathogen detection and mitigating environmental stresses, both of which help promote crop sustainability (Kumar et al., 2023). Crop diseases reduce physiological growth potentials and yields, causing around 40% of crop yields to be lost every year and might destroy the whole crop (Nagarajan, 2007). Crop diseases are the main challenges to overcome in achieving high yields and healthy crops. Different crops are susceptible to one or more specific diseases, hampering their quality and yields. *Fusarium* head blight (FHB) is a major disease affecting wheat and barley crops, causing as much as 50% of crop yields to be lost (Leplat et al., 2013). *Fusarium* head blight disease causes *F. graminearum* to survive for several years in soil or on dead organic matter, particularly crop residues. Its dangers are multifold because it adapts to a wide range of environmental conditions and produces extracellular enzymes that feed on diverse crop residues. Protection or resistance against pathogenic fungi or bacteria could be achieved by using nanocomposites. Graphene oxide (GO) and silver nanocomposites have shown threefold and sevenfold surges in inhibition efficiency, even at relatively low concentrations, compared to using silver and GO suspensions alone (Chen et al., 2016). Plant diseases such as *Fusarium solani* root rot and wilt diseases occur in many plants, such as soybeans, tomatoes, and peppers. While *Fusarium* root rot causes seedling stunting, root decay, stem staining, and plant death, wilt diseases disrupt water flow in the xylem, causing leaves to wilt and rapidly killing affected plants. Abeid et al. reported copper oxide–coated GO nanosheets to be effective against such diseases (El-Abeid et al., 2020).

Rice is one of the crops that is widely consumed as an essential food worldwide. Rice crops suffer numerous biotic stressors, including microbial infections, pests, and weeds. Temoor Ahmed et al. reported that the use of chitosan-iron nanocomposites controlled a bacterial leaf blight disease in rice crops by modifying plant resistance to this pathogen and improved the nutritional values of those crops (Ahmed et al., 2022). The *Plasmopara viticola* pathogen causes downy mildew disease in grapevine plants. Xiuping Wang et al. reported that GO-Fe_3O_4 nanocomposites were highly effective in treating grapevine plant infections (Wang et al., 2017). According to the above literature, there is a wide scope for research to be conducted on NCs in the fields of plant diseases and plant sustainability.

4 Conclusion

This chapter emphasized the need to study nanocomposite fertilizers. A novel overview of vital crop parameters, such as plant growth, plant physiology, and crop quantity and quality, was presented. Using NCs as nanofertilizers for the enhancement of bio-factors, NC–plant interactions, the safety of using NCs on plants, and NCs' activities in attenuating the adverse effects of abiotic stresses and heavy metal toxicities were discussed. In this context, the toxic effects of NCs on crops, such as those on crop cell structures that increase the oxidative stress indicators, remain major concerns to address. As supported by recent research publications, the conventional benefits of composites, such as enabling the product to meet nutritional requirements, are also available in the case of nanocomposite fertilizers. Improvements in the delivery mechanisms of fertilizers and slowly releasing micronutrients are among the primary benefits of using nanocomposite fertilizers. NCs are vital to reducing the use of conventional fertilizers and consequently their averse environmental effects. NCs are crucial in alleviating abiotic stresses and heavy metal toxicity. Nanocomposite formulations allow the controlled release and targeted delivery of nutrients, reducing nutrient losses. Nanocomposite formulations also positively contribute to increasing parameters such as solubility, dispersion, nutrient uptake, and nutrient availability. Plant responses to the NCs varies depending on the type of plant species, their growth stages, and the nature of the nanocomposite. This chapter laid out the role of nanocomposites in improving the wellbeing of crop, as alternatives to conventional fertilizers.

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Chapter 5
Environmentally Benign Synthesis of Metal Nanoparticles for Fertilizer Applications in Agriculture

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1 Introduction

The global population has been growing steadily over the past few centuries. According to the Food and Agriculture Organization of the United Nations (FAO, 2009), the global population will grow by 2.3 billion, between 2009 and 2050, and to feed a world population of 9.1 billion people in 2050, food production will have to increase by 70%. However, the productivity of crops has been decreasing due to biotic and abiotic stresses, climate change, and lack of water. As a result, agricultural development is being severely affected worldwide (Vijayakumar et al., 2022). As such, world agriculture is beset with a wide range of challenges, such as stagnating crop yields, low nutrient utilization efficiency, declining soil organic matter, deficiencies of several nutrients, shrinking arable lands, less water availability, shortage of labor, etc. (Raliya et al., 2017). Moreover, with a declining rural labor force and increasing food and fiber needs, agriculture is facing multiple challenges in the twenty-first century, which include producing more food and fibers to feed a growing population, producing more feedstocks for a growing bioenergy market, contributing to the overall development of many agriculture-dependent developing countries, adopting more sustainable and efficient production methods, and adapting to climate change (FAO, 2009). To resolve these issues, farming communities have been using chemical fertilizers and pesticides and genetically modified or disease-resistant crop varieties for the past five decades (Chhipa, 2017).

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Although the use of chemical fertilizers and pesticides significantly enhance food production, food quality and soil fertility are negatively impacted. Moreover, the application of fertilizers and pesticides is not efficient from the standpoint of economy. Most of the applied agrochemicals are lost via different processes such as leaching, mineralization, and bioconversion (Bollag et al., 1992). From an estimate, 40–70% nitrogen (N), 80–90% phosphorus (P), and 50–90% potassium (K) fertilizers were found to be either lost or fixed in soils, leading to economic losses (El-Saadony et al., 2021). Additionally, the overuse of pesticides and artificial fertilizers has disrupted many ecosystems and created several health risks. Therefore, a different solution is required for precision farming and improving the existing circumstance. Nanotechnology is a key strategy for resolving this problem.

After biotechnology, nanotechnology is the fifth breakthrough technology of the century. It has demonstrated a broad range of applications in many fields, including agriculture, medicine, biology, physics, chemistry, electronics, energy, materials science, and environmental science (Chhipa, 2017). The Greek term "nano" signifies "one billionth of something." One nanometer is defined as one billionth of a meter. The science of nanotechnology focuses on creating and modifying materials with sizes between one and one hundred nanometers (1–100 nm) (Vijayakumar et al., 2022). With a focus on protecting soil and promoting environmental sustainability, nanotechnology is quickly becoming the essential enabling technology that helps boost agricultural output. The major drivers for motivating the scientific community to concentrate on advancing the expansion of nano-agrotechnology are challenging climatic conditions and increased global food security (Sangeetha et al., 2017). The improvement in nanotechnology has gained momentum through the innovation of nanoparticles (NPs). Surface area, pore size, particle shape, and reactivity are some of the distinct physical and chemical characteristics that define nanoparticles (NPs). Because of their widespread use in the agricultural sector, NPs are also known as "magic bullets." Nanoparticles can be employed as nanofertilizers, nanopesticides, and nanoherbicides, which can help crops grow more productively, reduce the overuse of chemical fertilizers, and improve their ability to withstand biotic stress. They control plant growth and boost metabolic activity. Depending on the type and concentration employed, NPs may have a beneficial or detrimental impact on the growth and yield of different plant species (Goswami & Mathur, 2019).

Site-directed delivery and controlled delivery of functional components are two features of nano-enabled agrochemicals that increase their efficiency and capacity for managing pests and illnesses. As a result, they present a fresh method of lowering the toxicity of agrochemicals to human health by minimizing their long-term consequences and reducing environmental pollution by lowering their volatilization, leaching, and drainage. Such nano-enabled agrochemicals improve crop nutrient uptake, solubility, and stability and also provide a workable alternative for managing pests and diseases (Rodrigues et al., 2017; Duhan et al., 2017; Aranaz et al., 2010; Sarkar et al., 2022).

2 Synthesis of Metal Nanoparticles

For the creation and stabilization of metallic nanoparticles, a variety of physical and chemical techniques, including electrochemical changes, chemical reduction, and photochemical reduction, are frequently used. The choice of metallic nanoparticle preparation technique is crucial because processes used in nanoparticle synthesis, such as the kinetics of metal ions' interactions with reducing agents, the process by which stabilizing agents adhere to metal nanoparticles, and various experimental techniques, have a significant impact on the stability, physicochemical properties, and morphology (structure and size) of the nanoparticles (Jamkhande et al., 2019). Metal nanoparticles can be produced using a variety of techniques. However, their synthesis can be roughly categorized into two approaches: (i) the top-down approach and (ii) the bottom-up approach.

2.1 Top-Down and Bottom-Up Approaches

2.1.1 Top-Down Approach

In the top-down method, bulk materials are split to create nanostructured materials. Top-down techniques include electro-explosion, mechanical milling, laser ablation, etching, and sputtering (Baig et al., 2021). The major drawbacks of the top-down method include elevated levels of contaminants in the finished product and poor control over the size and surface structure of the resultant NPs (Zulfiqar et al., 2019; Ndaba et al., 2022). Inadequacies in the surface structure indicate a significant disadvantage of the top-down method. Due to their high aspect ratio, these surface structure restrictions can have a considerable negative impact on the physical characteristics and surface chemistry of metallic NPs (Saratale et al., 2018a, b).

2.1.2 Bottom-Up Approach

The bottom-up method entails creating NPs from much smaller units like atoms and molecules. This method involves common chemical processes along with biological processes. Since the procedure provides for better control of particle size and reduces the quantity of contaminants in the finished product, NPs manufactured utilizing the bottom-up method are more homogeneous (Ndaba et al., 2022).

The fundamental distinction between the two approaches is the raw material used to prepare the nanoparticles. While atoms or molecules are the starting material in bottom-up approaches, top-down methods start with bulk material and use various physical, chemical, and mechanical processes to reduce the particle size to nanoparticles (Jamkhande et al., 2019). These two methodologies primarily rely on diverse physical, chemical, and biological techniques. Most of the physical

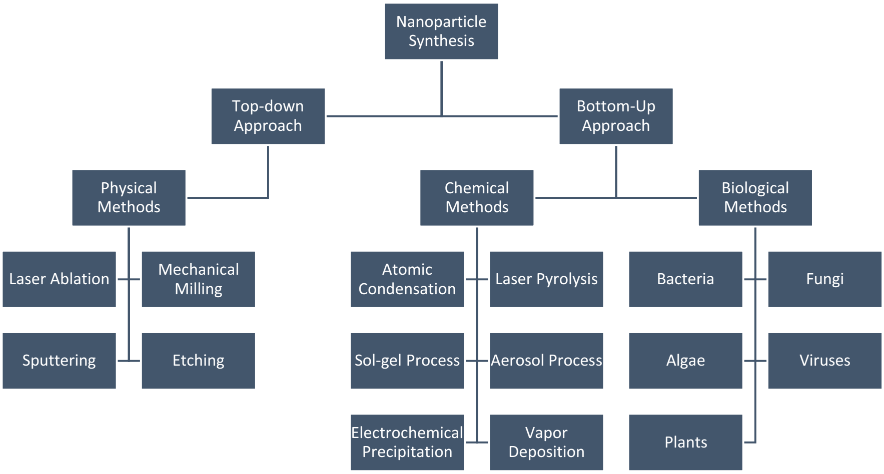

Fig. 5.1 There are two main methods for synthesizing nanoparticles: top-down and bottom-up. (1) Top-down strategy: Using mechanical or chemical methods, the top-down strategy breaks down large materials into smaller nanoparticles. Starting with a huge piece of material, this method often includes shrinking it down to the desired nanoparticle size range using physical or chemical procedures. Top-down techniques include milling, lithography, and etching as examples. (2) Bottom-up strategy: In the bottom-up strategy, individual atoms or molecules are put together to create nanoparticles. In this method, the required nanoparticle structure is built up from individual atoms or molecules using chemical or physical processes. Chemical vapor deposition, sol–gel synthesis, and coprecipitation are a few examples of bottom-up techniques

approaches, along with some chemical ways, are included in the top-down strategy; meanwhile, the bottom-up approach primarily concentrates on chemical and biological processes to synthesize metal nanoparticles. Figure 5.1 depicts the top-down and bottom-up approaches.

2.2 Physical, Chemical, and Biological Methods

2.2.1 Physical Methods

Top-down is a physical procedure dependent on material milling. This method's drawbacks include a lack of control over nanoparticle size and a higher level of contaminants. Mechanical milling, laser ablation, sputtering, and other typical physical processes are utilized to create metal nanoparticles.

Mechanical Milling

A feasible method for creating materials at the nanoscale from bulk materials is mechanical milling. It is a useful technique for creating mixtures of various phases and is useful in the creation of nanocomposites (Baig et al., 2021). It involves the structural decomposition of coarser particles into smaller ones. In this technique, a container is filled with bulk powder and numerous large balls. With the aid of a high-speed spinning ball, high mechanical energy is imparted to bulk powder material. Various high-energy mills can be used for particle size reduction. According to Rajput (2015), these high-energy mills include:

- Attrition ball mill
- Planetary ball mill
- Vibrating ball mill
- Low-energy tumbling mill
- High-energy ball mill

In each of these methods, large, freely moving, high-energy balls can either fall freely and strike the powder or can roll down the surface of the chamber housing the bulk powder material in a succession of parallel layers. It is a commonly used technique for mechanical alloying to create amorphous alloys for a variety of uses, including metal–metal, transition metal–metalloid, and metal–carbon systems.

Laser Ablation

The laser irradiation employed in the laser ablation method causes the particle size to be reduced to the nanoscale. After being covered by a thin layer, the solid target material is exposed to pulsed laser irradiation. The most used lasers are copper vapor lasers, titanium-doped sapphire lasers, Nd: YAG (neodymium-doped yttrium aluminum garnet) lasers at 106 m output, and their harmonics. When a material is exposed to laser energy, it breaks down into tiny pieces called nanoparticles (Jamkhande et al., 2019). This method is used to produce aluminum oxide (Al_2O_3) metal nanoparticles and other metalloid nanoparticles.

Sputtering

Ion sputtering is a technique that involves vaporizing a material by sputtering with a stream of ions from an inert gas. It involves bombarding solid surfaces with high-energy particles, such as plasma or gas, to create nanomaterials. Sputtering is believed to be a useful technique for creating thin nanomaterial films (Baig et al., 2021). It can be carried out in a variety of ways, including using radio-frequency diodes, magnetrons, and direct current (DC) diodes. Recently, employing magnetron sputtering of metal targets, this technique has been used to create nanoparticles from a variety of metals.

2.2.2 Chemical Methods

Sol–Gel Process

Compared to regular molecules or nanoparticles, colloidal particles are significantly bigger. However, colloids become bulky when mixed with a liquid, whereas nanoscale molecules always appear transparent. It involves the development of networks through the production of colloidal suspension (sol) and gelatin to create a network in a continuous liquid phase (gel). Metal alkoxide and alkoxysilane ions serve as the precursor to the synthesis of these colloids. Tetramethoxysilane (TMOS) and tetraethoxysilane (TEOS), which create silica gels, are the most often utilized. Alkoxides cannot be mixed with water. They are silica, aluminum, titanium, zirconium, and many more organometallic precursors. Alcohol is utilized as a mutual solvent. An initial homogeneous solution of one or more chosen alkoxides is used in the sol–gel procedure. These serve as organic precursors to materials like zirconia, titania, alumina, silica, and more. The catalyst controls pH and initiates the reaction. Four phases are involved in sol–gel formation: 1. hydrolysis, 2. condensation, 3. growth of particles, and 4. agglomeration of particles (Rajput, 2015).

Electrochemical Precipitation

This strategy uses an arrested precipitation mechanism to manage size. The fundamental strategy is to create and study the nanomaterial in situ, or in the same liquid media, to prevent physical changes and the accumulation of microscopic crystallites. Double-layer repulsion of crystallites utilizing nonaqueous solvents at lower temperatures for synthesis was used to control thermal coagulation and Oswald ripening. The synthesis involved constituent materials reacting with one another in an appropriate solvent. Prior to the precipitation reaction, the dopant is incorporated into the parent solution. A surfactant is employed to keep the produced particles apart. The resulting nanocrystals are centrifuged apart, cleaned, and vacuum dried. The dried material is then subjected to ultraviolet (UV) curing to see whether the surfactant capping coating on the nanocluster's surface could polymerize and provide real quantum confinement (Rajput, 2015).

Vapor Deposition

A solid is deposited on a heated surface through a chemical reaction from the vapor or gas phase in a process known as chemical vapor deposition (CVD). In thermal CVD, a high temperature of more than 900 °C activates the process. An exhaust system, a deposition chamber, and a gas supply system make up a typical apparatus. Plasma at temperatures between 300 and 700 °C initiates the reaction in plasma CVD. Pyrolysis takes place in laser CVD when a heat-absorbing substrate is heated by a laser's thermal energy. Ultraviolet radiation that has enough photon energy to break the chemical bond in the reactant molecules is used to trigger the chemical reaction in photo-laser CVD. This method involves photon activation of the reaction, and deposition takes place at room temperature. Nanocomposite powders can be synthesized using CVD (Rajput, 2015).

2.2.3 Biological Methods

The biological method involves various biological entities such as microbes (bacteria, algae, fungi, viruses), plants, organic wastes, etc.

3 Why Environmentally Benign Synthesis of Metal Nanoparticles (NPs) Is Necessary

Although physical and chemical processes have been employed for decades to produce nanoparticles, there are still many issues with them. The basic drawbacks of physical procedures are (i) excessive production cost, (ii) consumption of large amounts of energy, and (iii) low manufacturing yield (Shedbalkar et al., 2014).

According to Gahlawat and Choudhury (2019), chemical methods result in more uniform NPs in terms of size and shape, and the reduction step does not require as much energy. Therefore, the most preferred method of NP synthesis throughout the past decade has been chemical synthesis. However, chemical techniques of NP synthesis entail the use of toxic chemicals that are associated with cytotoxicity, carcinogenicity, and genotoxicity, contributing to the notion that such processes are environmentally hazardous.

In contrast, NPs produced by biological means are regarded as clean, safe, economical, and nontoxic when compared to conventional ways; as such, they are suggested as potential environmentally friendly substitutes for chemical and physical processes. Plants and microbes have the ability to gather and absorb metallic ions from their surroundings, making them suitable candidates for the synthesis of nanomaterials. Although a wide variety of biological entities are utilized in the production of NPs, plants, algae, fungi, yeast, bacteria, actinomycetes, and viruses are the most frequently used bioorganisms (Saratale et al., 2018a).

3.1 Green Synthesis of Metal Nanoparticles

The biological synthesis of metal NPs has advanced significantly and is currently being developed as an alternative environmentally friendly procedure. The environmentally benign biological synthesis of NPs is commonly referred to as “green synthesis” or “green chemistry” processes. Using entire cells, metabolites, or extracts from plants and microbes as environmentally friendly raw materials, the green synthesis of nanoparticles creates metallic nanoparticles. It has advantages over chemical and physical processes in that it is secure, straightforward, cost-effective, reasonably reproducible, and it frequently produces more stable materials (Adelere & Lateef, 2016).

Plants and plant parts have been extensively used recently in the synthesis of numerous nanoparticles due to the rich biodiversity of plants and their potential secondary metabolites. Alkaloids, flavonoids, saponins, steroids, tannins, and other beneficial natural chemicals are prevalent in plant extracts. These items can be made from a variety of plant parts, including leaves, stems, roots, shoots, flowers, barks, and seeds. In the bioreduction technique used to create metallic nanoparticles, they serve as reducing and stabilizing agents. Many greener nanoparticles, including cobalt, copper, silver, gold, palladium, platinum, zinc oxide, and magnetite, have been successfully synthesized using plants (Adelere & Lateef, 2016).

A wide range of materials, including plants and plant products, algae, fungi, yeasts, bacteria, and viruses, can be used in the biological production of NPs. Precursors of noble metal salts are combined with biomaterials to begin the production of NPs. Proteins, alkaloids, flavonoids, reducing sugars, polyphenols, and other substances are present in biomaterials and act as reducing and capping agents for the synthesis of NPs from their metal salt predecessors. The color shift of the colloidal solution can be used to visually check the reduction of the metal salt precursor to its subsequent NPs. In the recent past, several research documented the synthesis of Ag, Au, Cu, Pt, Cd, Pt, Pd, Ru, Rh, etc. utilizing different biological agents (Dikshit et al., 2021). Figure 5.2 describes the general steps in the biosynthesis of metal nanoparticles both using microorganisms and plant elements.

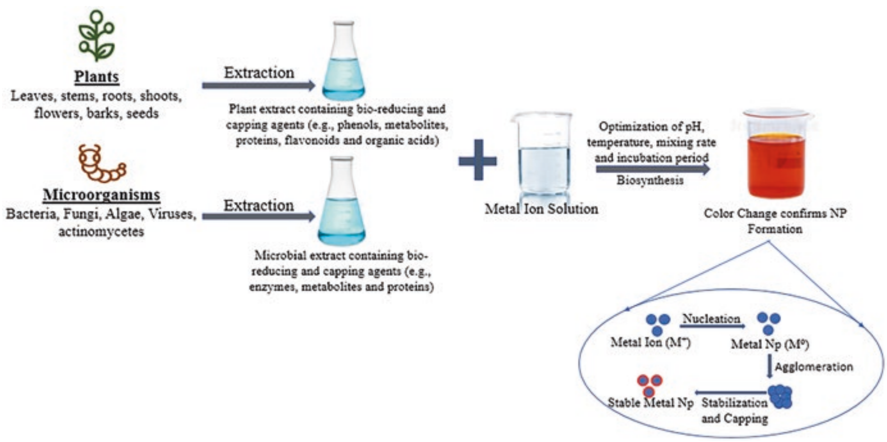

Fig. 5.2 A schematic representation of metallic nanoparticle biosynthesis. (Modified from Kumari et al. (2020), Ndaba et al. (2022), and Dikshit et al. (2021))

3.2 Microbial Synthesis of Metal NPs

Various microorganisms are involved in the production of metal nanoparticles because of their properties. Among the microorganisms, bacteria, fungi, algae, and viruses are the most common. Bacteria and viruses can survive in various adverse environments, and, owing to their ease of culture and less production costs, they can be broadly used to produce MtNPs.

3.2.1 Bacteria-Mediated Synthesis of Nanoparticles

Diverse groups of bacteria were used to synthesize various metal nanoparticles. As they can grow faster and can adapt to different adverse environments, bacteria are used nowadays for production, although the mechanism is not yet fully understood.

A *Bacillus subtilis* EWP-46 cell-free extract was used for the reduction of nitrate in silver NP (AgNP) production. Several variables, including hydrogen ion concentration, temperature, silver ion (Ag^+ ion), and time, influenced the formation of AgNPs. More AgNPs were found to be produced when the conditions were held constant at pH 10.0, 60 °C, 1.0 mM Ag^+ ion, and 720 min. AgNPs were tested against Gram-positive (*Staphylococcus aureus*) and Gram-negative (*Pseudomonas fluorescens*) bacteria to determine their primary inhibitory focus and least bactericidal convergence (Velmurugan et al., 2014).

In another study, *Bacillus licheniformis* cell-free extract (BLCFE)-coated silver nanoparticles were produced by the organism with an average particle size of 18–63 nm, and the synthesized nanoparticles resulted in disintegrated biofilm production of *Vibrio parahaemolyticus* (Shanthi et al., 2016).

Ghorbani (2017) used *Salmonella typhimurium* for the fast production of AgNPs. Table 5.1 summarizes some of the past research studies that were conducted involving the green synthesis of metallic nanoparticles using bacteria.

3.2.2 Fungi-Mediated Synthesis of Metal Nanoparticles

For the biological synthesis of metal nanoparticles, several fungal families have been investigated, including *Alternaria*, *Amylomyces*, *Aspergillus*, *Bipolaris*, *Candida*, *Cladosporium*, *Colletotrichum*, *Coriolus*, *Cylindrocladium*, *Fusarium*, *Ganoderma*, *Helminthosporium*, *Humicola*, *Lecanicillium*, *Mucor*, *Neurospora*, *Penicillium*, *Pestalotiopsis*, and *Phanerochaete*. The *Aspergillus* and *Fusarium* fungus families have been the most thoroughly studied for the nanosynthesis of the following metals and their metal oxides: Au, Ag, Ti, Zn, Ce, Fe, Mg, P, and Pt (Chhipa, 2019).

Trichoderma reesei, among the *Trichoderma* species, is used for the mycosynthesis of AgNPs. The ability of this fungi to detoxify microclimates makes them eligible for the biosynthesis of nanoparticles. These AgNPs have antimicrobial or

Table 5.1 Metallic nanoparticles synthesized using bacteria and the size and morphology of the synthesized nanoparticles

Bacteria	Metallic nanoparticles	Size (nm)	Morphology	Cellular location	References
Bacillus subtilis	Ag	3–20	Spherical	ND	Alsamhary (2020)
Bacillus licheniformis	Ag	40	ND	ND	Kalishwaralal et al. (2008)
Pseudomonas stutzeri	Ag	200	Triangular	ND	Klaus et al. (1999)
Actinobacteria	Ag	13.2	Spherical	ND	Wypij et al. (2017)
Ochrobactrum anthropi	Ag	38–85	Spherical	ND	Thomas et al. (2014)
Pantoea ananatis	Ag	8.06–91.31	Spherical	ND	Monowar et al. (2018)
Corynebacterium sp. SH09	Ag	10–15	ND	Intracellular	Narayanan and Sakthivel (2010)
Escherichia coli	Ag	50	Irregular	ND	Gurunathan et al. (2009)
Morganella sp.	Ag	20 ± 5	Spherical	Extracellular	Parikh et al. (2008)
Bacillus cereus	Ag	4–5	Spherical	Intracellular	Babu and Gunasekaran (2009)
Bacillus licheniformis	Ag	50	Irregular	Intracellular	Kalimuthu et al. (2008)
Corynebacterium glutamicum	Ag	5–50	Irregular	Extracellular	Sneha et al. (2010)
Lactobacillus sp.	Ti	40–60	Spherical	Extracellular	Prasad et al. (2007)
Desulfobacteraceae	ZnS	2–5	Spherical	Intracellular	Labrenz et al. (2000)
Desulfobacteraceae	ZnS	2–5	Biofilm	ND	Labrenz et al. (2000)
Aquaspirillum magnetotacticum	Fe_3O_4	40–50	Octahedral prism	Intracellular	Mann et al. (1984)
Magnetospirillum magnetotacticum	Fe_3O_4	47.1	Cuboctahedron	Intracellular	Philip (2009)
Magnetospirillum magnetotacticum (MS-1)	Fe_3O_4	~ 50	Cuboctahedron	Intracellular	Lee et al. (2004)
Shewanella oneidensis	Fe_3O_4	40–50	Rectangular, rhombic, hexagonal	ND	Suresh et al. (2011)
Lactobacillus acidophilus	Se	2–15	Spherical	ND	Alam et al. (2020)
Lysinibacillus sp. ZYM-1	Se	100–200	Cubic	ND	Che et al. (2017)

Modified from Dikshit et al. (2021) and Saratale et al. (2018a, b)
ND not defined

antibacterial abilities, which work against Gram-positive and Gram-negative microorganisms like bacteria (Vahabi & Dorcheh, 2014).

The fungal strains of *Aspergillus flavus* SP-3, *Trichoderma gamsii* SP-4, *Talaromyces flavus* SP-5, and *Aspergillus oryzae* SP-6 were treated with silver nitrate to produce AgNPs in an experiment by Anand et al. (2015). The synthesized nanoparticles had an average size of 20–60 nm and had antimicrobial properties against both Gram-positive and Gram-negative bacteria.

An *Aspergillus terreus* filtrate was used for AgNP production in an experiment conducted by Li et al. (2011). The synthesized particle size ranged from 1 to 20 nm. NADH was present in the fungal filtrate, and it acted as a secondary metabolite to convert metal precursors to metal nanoparticles.

Pestalotiopsis longiseta was used for the extracellular production of AgNPs. The particle size ranged from 123 to 195 nm (Vardhana & Kathiravan, 2015). Table 5.2 summarizes the names of the fungi that were used to produce MtNPs.

3.2.3 Algae-Mediated Synthesis of Nanoparticles

Spirogyra varians is utilized for the production of AgNPs and is considered the most feasible method. The produced nanoparticles can be effectively used as an antibacterial agent (Salari et al., 2016). Table 5.3 summarizes the algae used for MtNP production.

3.3 Plant-Mediated Synthesis of Nanoparticles

Anogeissus latifolia, a protein-rich edible gum is used to produce AgNPs. The gum extracts are used to convert metal precursors to metal nanoparticles. The synthesized particles are size controlled and easy to handle. The gum encapsulates AgNPs and increases their efficiency as the reaction time increases and it gets more time to get involved in various biological and antimicrobial activities (Kora et al., 2012) (Table 5.4). Table 5.4 summarizes the use of some plant extracts for the synthesis of various MtNPs.

4 Characterization of Metal Nanoparticles

The exploration of nanoparticles' uses, absorption, and toxicology depends heavily on their characterization. Nanoparticles are characterized using a variety of techniques depending on the matrix, analyte, concentration, complexity, and intrinsic qualities (Singh et al., 2021). The characterization of metal nanoparticles can be divided into two parts: (i) structural characterization and (ii) morphological

Table 5.2 Metallic nanoparticles synthesized using fungi and the size and morphology of the synthesized nanoparticles

Fungi	Metallic nanoparticles	Size	Morphology	Cellular location	References
Fusarium oxysporum	Ag	5–50	ND	Extracellular	Senapati et al. (2004)
Fusarium solani USM 3799	Ag	16.23	Spherical	Extracellular	Ingle et al. (2009)
Coriolus versicolor	Ag	25–75	Spherical	Extracellular	Sanghi and Verma (2009)
Aspergillus niger	Ag	20	Spherical	Extracellular	Gade et al. (2008)
Phoma glomerata	Ag	60–80	Spherical	Extracellular	Birla et al. (2009)
Penicillium brevicompactum	Ag	58.35 ± 17.88	ND	Extracellular	Shaligram et al. (2009)
Cladosporium cladosporioides	Ag	10–100	Spherical	Extracellular	Balaji et al. (2009)
Penicillium fellutanum	Ag	5–25	Spherical	Extracellular	Kathiresan et al. (2009)
Aspergillus fumigatus	Ag	5–25	Spherical	Extra cellular	Bhainsa and D'souza (2006).
Fusarium oxysporum	Ag	5–15	Variable	ND	Mohammadian (2007)
Fusarium semitectum	Ag	10–60	Spherical	ND	Basavaraja et al. (2008)
Verticillium sp.	Ag	5–50	Spherical	ND	Senapati et al. (2004)
Yeast strain MKY3	Ag	2–5	Hexagonal	Extracellular	Kowshik et al. (2002a)
Yeast strain MKY3	Ag	9–25	Irregular	ND	Kowshik et al. (2002a)
Fusarium oxysporum	Si	5–15	Quasi-spherical	Extracellular	Bansal et al. (2005)
Fusarium oxysporum	Ti	6–13	Spherical	Extracellular	Bansal et al. (2005)
Fusarium oxysporum	Zr	3–11	Quasi-spherical	Extracellular	Bansal et al. (2004)
Fusarium oxysporum	TiO_2	6–13	Spherical	ND	Bansal et al. (2005)
Fusarium oxysporum	ZrO_2	3–11	Spherical	ND	Bansal et al. (2004)
Schizosaccharomyces pombe	CdS	1–1.5	Wurtzite-hexagonal	Intracellular	Kowshik et al. (2002b)
Yeast	CdS	3.6	Spherical	ND	Prasad and Jha (2010)
Torulopsis sp.	PbS	2–5	Spherical	Intracellular	Kowshik et al. (2002b)
Yeast	Fe_3O_4	<100	Wormhole-like	ND	Zhou et al. (2009)
Saccharomyces cerevisiae	$^{Sb}2^{O}3$	2–10	Spherical	ND	Jha et al. (2009)

Modified from Saratale et al. (2018a, b)

Table 5.3 Metallic nanoparticle synthesized using algae and the size and morphology of the synthesized nanoparticles

Algal species	NPs	Size of NPs (nm)	Morphology	References
Cystophora moniliformis	Ag	50–100	Spherical	Prasad et al. (2013)
Caulerpa racemosa	Ag	05–25	Spherical, triangular	Kathiraven et al. (2015)
Chaetomorpha linum	Ag	03–44	Clusters	Nuraje et al. (2014)
Scenedesmus sp.	Ag	15–20	Spherical, crystalline	Jena et al. (2014)
Gracilaria corticata	Ag	18–46	Nanospheres	Kumar et al. (2012)
Leptolyngbya valderianum	Ag	02–20	Spherical, intracellular	Roychoudhury and Pal (2014)
Pithophora oedogonia	Ag	25–44	Cubical, hexagonal	Sinha et al. (2015)
Porphyra vietnamensis	Ag	13 ± 03	Spherical	Venkatpurwar and Pokharkar (2011)
Sargassum tenerrimum	Ag	20	Spherical	Kumar et al. (2012)
Sargassum wightii	Ag	08–27	ND	Saratale et al. (2017)
Spirogyra varians	Ag	35	Quasi-spheres	Salari et al. (2016)
Ulva lactuca	Ag	–	Spherical	Murugan et al. (2015)
Sargassum muticum	Ag	43–79	Spherical	Madhiyazhagan et al. (2015)
Gelidium amansii	Ag	27–54	Spherical	Pugazhendhi et al. (2018)
Laminaria japonica	Ag	31	Spherical to oval	Kim et al. (2018)
Chlorococcum sp. MM11	Fe	20–50	Spherical	Vigneshwaran et al. (2006)
Sargassum bovinum	Pd	05–10	Octahedral	Momeni and Nabipour (2015)

Modified from Saratale et al. (2018a, b)

characterization. Researchers mostly employ Fourier transform infrared (FTIR) spectroscopy, X-ray diffraction (XRD), and X-ray fluorescence (XRF) techniques for the structural characterization of nanomaterials. Scanning electron microscopy (SEM), transmission electron microscopy (TEM), and energy-dispersive X-ray spectroscopy (EDS) techniques can all be used to analyze the morphology of nanomaterials (Samaddar et al., 2018).

4.1 Structural Characterization

FTIR spectroscopy is used to characterize the vibrational modes of the precursors and synthesized nanoparticles. The presence of impurities in the final product can also be determined using an FTIR spectrogram. If the product's spectrogram shows

Table 5.4 Metallic nanoparticles synthesized using plant extracts and the size of the synthesized nanoparticles

NPs	Plants	Parts	Extractants	Precursors	Size (nm)
AuNPs	*Butea monosperma*	Leaf	Water	$HAuCl_4$	10–100
	Pelargonium graveolens	Leaf	Water	$HAuCl_4$	20–40
	Salix alba	Leaf	Water	$HAuCl_4 \cdot 3H_2O$	50–80
	Guazuma ulmifolia L.	Bark	Water	$HAuCl_4 \cdot 3H_2O$	20–25
	Nerium oleander	Bark	Methanol	$HAuCl_4$	20–40
	Rubia cordifolia	Fruit	Ethanol	$HAuCl_4$	5–20
	Litsea cubeba	Fruit	Water	$HAuCl_4 \cdot 3H_2O$	8–18
	Piper longum	Fruit	Water	$HAuCl_4$	20–200
	Hibiscus sabdariffa	Flower	Water	$HAuCl_4 \cdot 3H_2O$	15–45
	Coleus forskohlii	Root	Water	$HAuCl_4$	5–18
	Stachys lavandulifolia	Overground part	Overground part	$HAuCl_4$	34–80
AgNPs	*Lotus garcinii*	Leaf	Water	$AgNO_3$	7–20
	Morinda citrifolia	Leaf	Methanol	$AgNO_3$	10–100
	Prunus mume	Fruit	Water	$AgNO_3$	~30
	Eugenia stipitata McVaugh	Fruit	Water	$AgNO_3$	15–45
	Aconitum toxicum Reichenb.	Root	96% ethanol	$AgNO_3$	53–67
	Catharanthus roseus	Bark	Water	$AgNO_3$	1–26
CuNPs	*Ocimum sanctum*	Leaf	Water	$CuSO_4 \cdot 5H_2O$	50–70
	Hibiscus rosa-sinensis	Flower	Water	$Cu(CH_3COO)_2 \cdot H_2O$	0.115–1.1 μm
PtNPs	*Costus speciosus*	Leaf	95% ethanol	Platinum 2,4-pentanedionate	10–50

Modified from Bao et al. (2021)

peaks at a different level than the precursor's, then this indicates that there might be some impurities present in the final product. The features of MtNPs, including chemical concentration, surface chemistry, surface functional groups, and atomic organization and transmission, are measured using Fourier transform infrared (FTIR) spectroscopy.

The crystalline structure of synthetic nano-samples is investigated using X-ray diffraction (XRD).

The content of different particles contained in the produced nanomaterials is identified using X-ray fluorescence (XRF) analysis. According to an experiment by Li et al. (2016), produced α-Fe_2O_3 contained various impurities such as 0.898% SiO_2, 0.486% TiO_2, and 0.112% MgO.

4.2 Morphological Characterization

Scanning electron microscopy (SEM) is used to morphologically characterize metal nanoparticles. Since the application of metallic nanoparticles is largely dependent on the particle size and shape of the NPs, SEM is used to characterize the internal dispersion of the NPs.

Energy-dispersive X-ray spectroscopic analysis is performed alongside SEM imaging to investigate the distribution pattern of other metal species on synthesized NPs (Samaddar et al., 2018). In an experiment by Fang et al. (2011), the EDS analysis showed that the amount of nickel (Ni) and Zn on zero-valent FeNPs was too low to be detected. Energy-dispersive X-ray spectroscopy (EDS) is typically used to analyze the elemental composition of MtNPs.

Transmission electron microscopic images are used to determine the particle size or pore size of NPs. Since the synthesis of nanoparticles is size-dependent, a change in temperature can cause alterations in NP size. Therefore, TEM images are used to identify any size change during the synthesis process (Samaddar et al., 2018). The position, size, and shape of MtNPs can be seen using transmission electron microscopy (TEM), scanning electron microscopy (SEM), and atomic force microscopy (AFM).

UV–visible (UV-vis) spectroscopy is another method that is used for structural characterization. MtNPs are typically tested for stability and synthesis using UV–visible spectroscopy.

The size of the NPs at an extremely low level can be estimated using a dynamic light scattering (DLS)/zeta potential size analyzer. Zeta potential describes the surface condition of a nanoparticle and predicts its stability over time (Singh et al., 2021). The size and surface charge of MtNPs is mostly assessed using the dynamic light scattering (DLS) method.

5 Use of Metallic Nanoparticles in Sustainable Agriculture

The primary issue with excessive and prolonged use of chemical fertilizers in agriculture is the decline in soil fertility, which ultimately has an impact on the output of agricultural goods. According to the literature, weeds cause 13% damage, plant infections cause 13% loss, and insect pests cause 14% loss globally. The loss value of crops has been calculated to be USD 2000 billion annually. As a result, it is crucial to increase crops that are resistant to pests and droughts to enhance crop productivity (Rai & Ingle, 2012; Saratale et al., 2018a). Nanomaterials can be applied to soil systems as both nanofertilizers and nanopesticides. The term "nanofertilizers" refers to nanomaterials that are either nutrients themselves or act as carriers or additions for the nutrients (by, for example, combining with minerals) (macro- or micronutrients). Nutrients can also be enclosed within nanoparticles to create these types of fertilizers (Saleem & Zaidi, 2020).

Nanomaterials that can provide one or more nutrients to plants to promote their development and production are known as nanofertilizers. One of the possible methods for boosting plant growth and productivity to meet the world's rising food demand is the use of nanoparticle fertilizers. The distribution of chemicals to the desired places is made possible by the nanofertilizers' extremely high sorption capacity, surface area, and regulated chemical release kinetics (Snehal & Lohani, 2018). With higher nutrient use efficiency, nanofertilizers can boost crop output and quality while lowering production costs, resulting in sustainable agriculture. Nanofertilizers are organic fertilizers or smart fertilizers that provide plants tiny but potent doses of nutrients. Encapsulating nanofertilizers can increase nutrient uptake, which eventually lowers nutrient loss, promotes healthy plant development, and enhances crop quality. By preventing nutrients from interacting with soil, water, air, and microbes, nanoformulations minimize the risk of environmental degradation by providing progressive and controlled release of nutrients to the target regions. The usage of MtNP-based nanofertilizers was found to have a great potential to boost crop productivity (Bahrulolum et al., 2021). The effects of metal nanoparticles as nanofertilizers can be discussed in two pathways. The produced nanoparticles can be applied directly on soil or can be used through foliar application.

MtNPs, which include silver, gold, cadmium, copper, zinc, iron, and selenium (Se), have a variety of uses in agriculture, including promoting plant development, having antibacterial and antifungal effects, and acting as nanofertilizers and nanobiosensors (Bahrulolum et al., 2021). Zn and Fe, two nanonutrients produced by biosynthesis, help plants cope with stress and avoid cell damage. Different microbially produced nanonutrients, such as those containing boron, iron, sulfur, molybdenum, magnesium, nitrogen, phosphorus, and potassium, improved grain yield by 12%–54% and dry matter yield by 18%–34% in crops of cauliflower, capsicum, castor, cluster beans, chickpeas, maize, mung beans, pearl millet, rice, tomatoes, and wheat, depending on the nutrient ratios (Chhipa, 2019).

Acid phosphatase, alkaline phosphatase, aryl sulfatase, cellulase, dehydrogenase, esterase, hemicellulase, lignase, and nitrate reductase had an increase in rhizosphere activity between 18% and 283%. Nutrient usage efficiency was also enhanced by 3- to 20-fold by nanofertilizers. Smart nanonutrients' large surface area and targeted delivery could drastically reduce the amount of nanofertilizers used at the field level from kilograms to milligrams, thus reducing fertilizer leaching and eutrophication (Chhipa, 2019).

NPs' actual functionality is determined by how they interact with the substrate on which they have been used. The uptake and distribution of NPs in crops directly affect their actual influence and impact (Singh et al., 2021).

5.1 Silver Nanoparticles (AgNPs)

Silver ions make up a significant portion of these nanoparticles (10–20 nm in size). Inside living systems, these particles are highly active and effective. Various harmful microorganisms have been fought off using silver nanoparticles. Silver nanoparticles, for instance, have been used to treat spot blotch disease. They are also used to break seed dormancy, boost seed vigor index, and raise seedling fresh weight, among other things. Silver nanoparticles are simple to synthesize and safe for the environment. Research on the ability of plants to withstand stress brought on by silver nanoparticles is still ongoing (Singh et al., 2021).

5.2 Zinc Oxide Nanoparticles (ZnO NPs)

Due to the lower availability of zinc and its restricted amount in calcium carbonate-enriched soils due to their alkaline pH, both soils and plants commonly suffer from zinc deficiency. Zinc sulfate fertilizers are used as an alternative to lessen this. Despite this, plants still experience zinc deficiency. Due to their tiny size and wide surface area, zinc oxide nanoparticles are the ideal solution to treat zinc deficiency since they are quickly absorbed by plants. The 100-nm size of zinc oxide nanoparticles makes them particularly effective. In order to synthesize zinc oxide nanoparticles, zinc sulfate heptahydrate is typically dissolved in water. Concomitantly, a bioactive extract is obtained from desirable living organisms such as plants and animals. Water or ethanol are used to prepare the extract. The two prepared solutions are then combined at the proper pH to produce the desired zinc oxide nanoparticles. These nanoparticles may offer a low-cost, environmentally safe, and long-lasting solution to a few plant-related issues, including pathogenic invasions and zinc shortages (Singh et al., 2021).

5.3 Titanium Dioxide Nanoparticles (TiO_2 NPs)

Titanium dioxide nanoparticles (TiO_2 NPs), which range in size from 5 to 30 nm, are widely produced and applied owing to their photocatalytic properties. Therefore, they are utilized in pigment formation. These nanoparticles help plants grow and photosynthesize more. Broad beans (a common leguminous crop) had their soil salinity reduced by titanium dioxide nanoparticles ($nTiO_2$) (Abdel Latef et al., 2018). Additionally, it is applied via roots or foliar spray at extremely low concentrations to promote plant growth, enzymatic activity, photosynthesis of chlorophyll content that promotes nutrient uptake, and stress tolerance and to increase crop yield and quality (Singh et al., 2021).

5.4 Iron Oxide Nanoparticles (Fe_2O_3 NPs)

Due to their ability to substitute conventionally ineffective Fe fertilizers, iron oxide nanoparticles (Fe_2O_3 NPs) are vital oxide nanomaterials that are extensively used in agriculture. They typically range in size from 10 to 20 nm and exhibit a unique sort of magnetism. They can take on a variety of forms, including rods, spheres, cubes, self-oriented flowers, etc. Fe is naturally abundant mostly in the form of Fe^{3+}, whereas plants and other living things can only take up Fe^{2+} (Singh et al., 2021). Fe mediates a few physiological responses in plants, including leghemoglobin generation in nodules, chlorophyll synthesis, redox reaction, respiration, etc. However, Fe must be applied in optimum amounts, as both deficiency and excess are harmful to plants. Fe deficiency is a common problem in various crops. According to Sánchez-Alcalá et al., *Arachis hypogaea* (peanut) is extremely susceptible to Fe deficiency. As demonstrated by the peanut, soybean, and wheat crops, studies have shown that iron oxide nanoparticles have a good impact on plant development and productivity (Sánchez-Alcalá et al., 2014).

5.5 Copper Nanoparticles (CuNPs)

Due to characteristics such as their extremely small size and high surface area to volume ratio as compared to materials formed from bigger particles, CuNPs perform better than bulk copper particles. CuNPs have several uses in agriculture due to their antifungal and antibacterial actions against Gram-positive and Gram-negative bacteria as well as harmful fungi. CuNPs show antifungal efficacy against plant pathogenic fungi such *Phytophthora infestans*, *Fusarium oxysporum*, *Fusarium culmorum*, and *Fusarium graminearum*. At doses under 100 ppm, they have also been shown to behave as germination promoters and growth stimulants in several plants. CuNPs have been synthesized thus far using a variety of chemical, physical, and green synthesis techniques in diverse quantities, configurations, and morphologies (Bahrulolum et al., 2021).

5.6 Selenium Nanoparticles (SeNPs)

Most living things require selenium, which is present in soil, water, seeds, animals, and food. Se fertilizers must be added to the soil to enhance the Se content in plant nutrients, and Se levels in food must be balanced, as SeNPs boost the plant's capacity to suppress infections and activate antifungal characteristics. Se-balanced food processing is a quick procedure that aids in resolving the Se imbalance problem in agriculture. It is crucial to ensure the optimum amount of selenium in the soil, and fertilizers made of pure selenium compounds are employed to achieve this. However, Se fertilizers only last for one or a few harvests in rich topsoil, and, over a short time, inorganic Se compounds are washed away by rain into the infertile horizons beneath the soil. Organic Se compounds are not actively leached, but they are readily broken down after application. SeNPs have the benefit of not slowly leaching from the soil and not dissolving in water or aqueous solutions, making them excellent nanofertilizers (Bahrulolum et al., 2021).

6 Other Uses

In addition to agriculture, nanoparticles are employed in plasmonics, optoelectronics, surface-enhanced Raman scattering (SERS), biological sensors, catalysts, sorbents, energy production, and DNA sequencing. The easy growth of fungi and their abundant production of reducing and stabilizing agents make mycosynthesis of nanomaterials an efficient method in industrial manufacturing. At the laboratory scale, new cutting-edge nanotechnology offers a superior answer to sustainable agriculture. Nanoparticle applications are still in their infancy, including those such as nanofertilizers, nanopesticides, nanofungicides, nanoherbicides, nanosensors for pathogen detection, and nanomaterials for pesticide sorption. In addition to this, nanoparticles utilized in the food packaging sector are also widely accepted. Many packaged food products have longer shelf lives owing to nanocoating and wrapping in wrappers that include nanomaterials (nanofilms) (Chhipa, 2019).

6.1 Nanopesticides

The widespread use of chemical pesticides is a major global concern since they can cause serious problems like biomagnification. Many organophosphate insecticides build up in the animal adipose tissue and affect the food chain. The creation and application of nanoparticles with an organic origin and pesticidal characteristics is a practical remedy for this issue (Singh et al., 2021).

With regard to fungi that cause fungal plant diseases, silver nanomaterials have shown antifungal activity against *Alternaria alternata*, *Botrytis cinerea*, *Bipolaris sorokiniana*, *Magnaporthe grisea*, *Sclerotium*, *Sclerotium cepivorum*, *Candida tropicalis*, *Candida parapsilosis*, *C. albicans*, *Colletotrichum gloeosporioides*, and *Raffaelea* sp. Similar to this, ZnO exhibits antifungal action against *Penicillium expansum*, *B. cinerea*, and *A. niger.* The cell wall is damaged by nanopesticide's interaction with fungus hyphae, which prevents conidial germination and fungal growth (Chhipa, 2019).

In recent studies, a *Taraxacum officinale* leaf extract has been used to produce AgNPs, which exhibited significant antibacterial action against two significant phytopathogens, *Xanthomonas axonopodis* and *Pseudomonas syringae*. A tetracycline-containing nanoformulation demonstrated increased antibacterial activity against phytopathogens. Additionally, it was discovered in this study that synthetic AgNPs had a stronger antibacterial impact than those sold in stores. In order to manage phytopathogens, these AgNPs may be used as a less expensive substitute for commercial pesticides (Saratale et al., 2018a).

Cu-based nanoparticles (Cu/Cu_2O NPs, Cu_2O NPs, and CuO NPs) have been identified as promising agro-fungicides and have been shown to be effective against a variety of phytopathogens, including *Fusarium* sp., *Phoma destructiva*, *Cochliobolus lunatus*, *A. alternata*, *F. oxysporum*, *Penicillium italicum*, *Penicillium*

Digitatum, and *Rhizoctonia solani*). Giannousi et al. (2013) reported the use of Cu_2O NPs as agro-fungicides to control the important plant pathogen *Phytophthora infestans*. It is interesting to note that CuNPs cause oxidative stress, which can function differently depending on the species of fungus.

6.2 Nanosensors

In addition to the use of nanopesticides and nanofertilizers, nanosensors were created to identify plant diseases, plant hormones, soil moisture, and residual pesticides. Nanosensors are useful in providing real-time information on field conditions and soil health. Chemical sensors based on carbon nanomaterials were created to detect pesticide residues in plants. Additionally, *Xanthomonas axonopodis*, the causative agent of the bacterial spot illness, was targeted for detection using nanoprobes. To find the pathogen, they combined anti-rabbit secondary antibodies with silica nanoparticles (Chhipa, 2019).

7 Conclusions

Considering the growing population demand for food and the critical environmental issues, precision farming is an obvious solution. The application of metal nanoparticles is essential for achieving precision farming. Typical production processes of metal nanoparticles are fraught with a number of problems, including the use of hazardous solvents, the generation of toxic by-products products and the consumption of high energy. As a result, environmentally friendly production routes, such as "green synthesis," are being adopted more and more for metal nanoparticles. The green synthesis process has a variety of environmental benefits, including its efficiency, cost-effectiveness, and eco-friendliness. The green synthesis process is likely to play an enormous role in achieving sustainable agriculture. Metal nanoparticles produced via green synthesis are not only eco-friendly but are also capable of being delivered to specific sites over a long period of time. As a result, these nanoparticles are good candidates for slow-release fertilizers. Metal nanoparticles offer advantageous qualities that can be used to improve plant growth through both soil and foliar applications. High germination rates, high growth rates, etc. are only a few of the plant growth indices that are improved by the usage of metal nanoparticles. In addition to their use as fertilizers, metal nanoparticles can also be used as nanosensors, soil and water amendment tools, and other applications that can be crucial for achieving increased and sustainable agricultural output.

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Chapter 6
Plant Nanonutrients for Sustainable Agriculture

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1 Introduction

Agriculture is essential for basic human development and sustenance (Mahapatra et al., 2022). The world of agriculture is currently facing several difficulties, including a changing climate brought on by the greenhouse effect and global warming, urbanization brought on by changes in lifestyles, the careless use of nonrenewable resources like petroleum, natural gas, high-quality rock phosphate, etc., and environmental problems like runoff and eutrophication associated with the application of more chemical fertilizers than necessary (Ditta & Arshad, 2016). The world's population is growing at an alarming rate, which exacerbates these issues. The gap between the supply and demand for food has grown significantly as a result of rising food demands and declining nutritional deposits, and this will only become worse in the years to come. Increased use of synthetic fertilizers on lands has led to physicochemical conditions, environmental contamination, and long-lasting changes in the ecology of soil. Due to this, soil's natural fertility has significantly decreased, which has a negative impact on agricultural output, human health, and cleanliness. According to researchers, the following strategies can be used to meet the demand for food grains for the world's expanding population: (a) innovative farming; (b) circular bioeconomies through agri-technologies, (c) precision farming, and (d) smart nano-interventions or nanonutrients for sustainable and climate-smart agriculture (Devaney et al., 2017; Lokko et al., 2018; Wreford et al., 2019; Naveen et al., 2017). Nanonutrients are regarded as prospective contenders in the fertilizer

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sector and show great promise for enhancing nutrient retention for optimum crop yield. Because nanonutrients or nanoparticles (NPs) have special physicochemical properties, such as high surface area, high reactivity, tunable pore sizes, and particle morphology, nanotechnology opens a wide range of novel applications in the fields of plant nutrition, needed to meet the demands of the world's growing population (Ditta & Arshad, 2016). Optimal nutrient management for sustainable crop production is a research priority in agriculture. Application of nanomaterials along with improved farming system is a great strategy for achieving sustainable agriculture, as shown in Fig. 6.1 (Shang et al., 2019). The provision of nutrients at the nanoscale for sustainable crop development has proven to be the most fascinating field of research in this regard. We can boost the effectiveness of plants' macro- and micronutrients by using this technique. Moreover, the development of nanonutrients and their biofortification has the potential to improve the bioavailability and effectiveness of nutrients, resulting in a multifold rise in productivity (Mahapatra et al., 2022). In comparison to other fertilizers, nanonutrients have been shown to be more effective because they reduce nitrogen loss from leaching, emissions, and long-term assimilation by soil microorganisms. Additionally, controlled-release fertilizers may improve soil quality by reducing the negative side effects linked to excessive

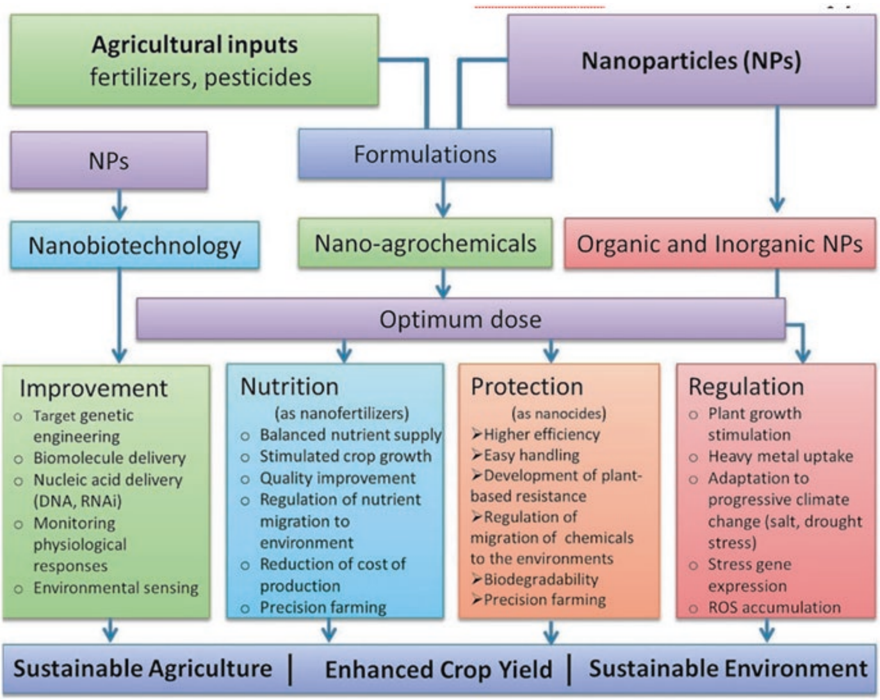

Fig. 6.1 Prospects of nanomaterials in sustainable agriculture production (Shang et al., 2019, under Creative Commons license, MDPI)

use of conventional chemical fertilizers. This review aims to draw attention to nanonutrients and their effects on crop yield.

2 Nanonutrients

Nanonutrients have high reactivities due to their small size, a high surface area to volume ratio, and improved productivity (Shalaby et al., 2022). Due to their novel mechanisms of action, improved nutrient use efficiency, less nutrient loss, and minimal environmental degradation, nanonutrients have been shown to be more effective than standard chemical fertilizers (Adisa et al., 2019). The intensive use of traditional or chemical fertilizers resulted in a number of issues that had severe effects on agroecosystems, including low crop nutrient use efficiency and significant nutrient losses to groundwater. As mentioned above, the controlled-release method of feeding cultivated plants with nanonutrients is an emerging strategy in the revolution of agricultural systems (Hong et al., 2021). The enormous increase in surface area made possible by the small size of nano nutrients that allows for efficient absorption by plants. Moreover, nanotechnological interventions have improved not only the bioavailability of minerals to crops for greater agricultural yield but also contributed to a decrease in pathogenic infections (Adisa et al., 2019). There are various methods that are employed for the synthesis of nanomaterials, as shown in Fig. 6.2. The chemical and physical techniques for the synthesis of nanoparticles are very costly and employ the application of poisonous and dangerous chemicals responsible for different biological hazards. However, green methods for the synthesis of nanoparticles are cost-effective, safe, eco-friendly, and rapid. Prathista Industries Limited has successfully developed a fourth-generation (4G) nanotechnology-based biofertilizer by incorporating biosynthesized nanonutrients into the third-generation (3G) lacto-gluconate technology for sustainable agriculture. The various products mentioned in Table 6.1 work just at the ppm (parts per million) level to meet the nutrient requirements of crops, and the cost of these nanonutrient-based fertilizers is similar to those of traditional fertilizers (Sairam & Gangurde, 2015).

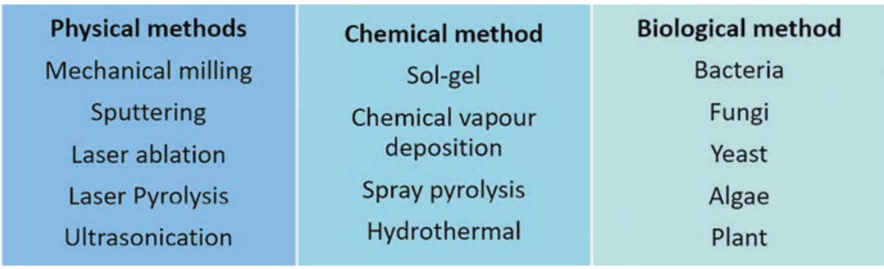

Fig. 6.2 Methods of metal nanoparticle synthesis

Table 6.1 Nanotechnology-based biofertilizer developed by Prathista Industries Limited

Name of the product	Details
Aishwarya®	This is NPK nanonutrients formulation, which fulfills the nitrogen, phosphorus, and potassium need and enhances root growth, photosynthesis, etc.
Biozinc®	This formulation addresses zinc deficiency for all crops
Biophos®	This is a nanotechnology-based formulation to address phosphorus deficiency in all crops
Biopotash®	This is a formulation of potash nanonutrients with lacto gluconates, which promotes the growth of healthy green leaves and increases plant resistance to diseases
Megacal®	This contains nanonutrients of calcium, magnesium, potassium, zinc, manganese, iron, copper, boron, and all other macro- and micronutrients, except nitrogen in organic form, which help in achieving a higher crop yield

2.1 Nano-nacronutrients

Nano-macronutrients are made up of one or more of enormous quantities of N, P, K, Ca, Mg, and S that agricultural plants need. With the growing demand for more food to feed the world's expanding population, the need for macronutrients by agricultural plants is expanding as well. Scientists and technicians from all over the world have created nanonutrients comprising macronutrients, and these have demonstrated a significantly higher efficiency in boosting the growth and productivity of crops. As a result, they are an affordable alternative to the currently available traditional chemical fertilizers because they not only boost efficiency but also lower costs (Ditta & Arshad, 2016). Moreover, it is well established that traditional fertilizer sources pose a threat to agroecosystems by causing excessive buildup. Their runoff can contaminate water bodies, causing eutrophication, and ultimately harm the aquatic biota. Use of nanonutrients as the replacement of traditional fertilizer sources may minimize environmental effects by reducing the overall application levels of these elements. Numerous studies have assessed the impact of various nano-macronutrients on the growth, development, and nutritional improvement in plants. Moreover, the application of nanonutrients are reported to shorten the life cycle and grain yield of plants. For example, Abdel-Aziz et al. (2016) demonstrated that foliar exposure of an NPK–nano-chitosan composite at a rate of 10–100 mg/L to wheat considerably reduced the plant's life span by 40 days and boosted its grain yield by 51 and 56% in comparison to the controls and standard NPK fertilizers, respectively. A significant improvement in potato yield by the application of NPK nanofertilizers compared to NPK chemical fertilizers has been reported by Abd El-Azeim et al. (2020). They found that foliar application of NPK nanofertilizers produced the maximum yield and the best quality of potatoes as well as the highest profit-to-cost ratio for potato production. Furthermore, compared to soil treatments, their study suggests using foliar sprays of nanofertilizers in potato cultivation to boost both yield and quality. Use of lower rates of nanofertilizers as foliar applications has been demonstrated to be an economical and environmentally friendly alternative to recommended amounts of chemical fertilizers with a notable boost in potato output and quality (Abd El-Azeim et al., 2020). The effectiveness of a nanocomposite of urea-modified hydroxyapatite encapsulated under pressure within *Gliricidia sepium* was demonstrated by Kottegoda et al. (2011). The nanocomposite released about 78% more nitrogen than the commercial fertilizers. When compared to a standard fertilizer, this temporal release pattern could greatly increase the efficiency of N uptake by plants. The results of the study mentioned above reveal a viable macronutrient composition based on nanotechnology that optimizes nutritional dose by releasing N slowly and sustainably over time. Rathnayaka et al. (2018) also reported that nano-nitrogen fertilizers could be used as an alternative to urea for rice cultivation as they significantly increase the growth and yield performance of the rice cultivar "Bg 250." Application of nano-potash (K) increased shoot length, stem diameter, yield, and the number of flowers per plant in *Narcissus tazetta* (Asgari et al., 2018).

2.2 Nano-micronutrients

Micronutrients are those elements that are required by plants in only trace amounts but play a vital role in their metabolism and stress tolerance (Zulfiqar et al., 2019). They are essential for many different metabolic processes of plants. Deficiency of these micronutrients may cause severe damage to plants and, sometimes, consumption of micronutrient-deficient food items exerts ill effects on humans (Rana et al., 2019). However, even slight variations in pH, soil structure, and organic matter have a significant impact on their accessibility. Nanonutrients containing these micronutrients might solve these problems and attain their optimal availability. Micronutrient fertilizers provide the necessary nutrients that plants need in relatively smaller amounts than macronutrient fertilizers, which is often less than 10 mg/kg of soil. Nanoscale nutrient forms can increase the availability of these critical nutrients by encouraging plant metabolism and consequently boosting growth, development, and nutritional quality (Adisa et al., 2019). Nano-micronutrient fertilizers exhibit high efficiency and functionalities, are convenient and easy to apply, and, due to their small size, the required elements can be rapidly delivered to different subcellular parts of the plant (Janmohammadi et al., 2016). Fe, Mn, Zn are considered the most essential micronutrients, which play an extremely important role in plant growth and development by regulating plant metabolism. These micronutrient nanoparticles have enhanced the growth of many crop plants much more efficiently than have bulk micronutrients (Makarem et al., 2019). Al-juthery et al. (2019) also reported that foliar application of nano-micronutrients (iron, zinc, and copper) improved the growth parameters of wheat plants. Soil application of a combination of nano-micronutrients such as Si, Zn, B, and nanoparticle zeolite efficiently mitigated the toxic effects of soil salinity on potato plants by enhancing plant growth, leaf stomatal conductance, chlorophyll content, and leaf photosynthetic rate and increased the contents of endogenous elements (N, P, K, Ca, Zn, and B), proline and gibberellic acid hormone (GA3) in leaf tissues, and proteins, carbohydrates, and antioxidant enzymes (polyphenol oxidase (PPO) and peroxidase (POD) in tubers) (Mahmoud et al., 2019). Mahmoud and Taha (2018) also reported that a combination of chicken manure, nano-iron (nano-Fe), and nano-zinc (nano-Zn) boosted the growth parameters and yield of *Eruca sativa* plants. This enhancement of plant growth by nano-micronutrients is associated with high level of growth promoter indole acetic acid (IAA) and low level of abscisic acid (ABA). Moreover, in nano-treated plants, an increase in sulfur, ascorbic acid, crude protein, glucose, and fructose contents and antioxidant compounds such as total phenolics, total flavonoids, and carotenoids is also observed. Biochar is widely used in agriculture to enhance the quality of soil. Mahmoud and El-Tanahy (2022) prepared water-soluble dried carbon powder nanoparticles (wsCNPs) from biochar obtained from leftover biomass of agricultural land. Foliar spray of this CNP along with sulfur significantly improved the vegetative growth parameters, photosynthetic pigments, yield, bulb quality, and phytochemical compounds of onion (*Allium cepa* L.) plants.

2.3 Uptake of Nanonutrients by Plants

There are a number of potential ways for plants to receive nanonutrients, including through their leaves, roots, or endocytosis (Ghosh & Bera, 2021). Plants take in NPs either through foliar exposure or root exposure and then transport them to different parts of the plants via apoplastic or symplastic pathways as shown in Fig. 6.3. The amount of nutrients that can build up in the soil during cultivation can be significantly limited by absorption by plant roots due to the size of pores and the absorbent component. According to studies, the uptake mechanism of nutrient release through plant roots that is mediated by nanofertilizers is more effective (Abobatta, 2019; Adhikari & Ramana, 2019). In plants, roots, stomatal apertures, leaf hydathodes, trichomes, and other structures mediate the uptake of nanoparticles. When nanoparticles are present in the soil, the roots that remain in direct contact with them absorb them from the soil and carry them to various plant parts. Additionally, the porous and thinner root cuticles and the cell walls of the root hairs enhance the uptake of nanoparticles by the roots (Galway, 2006). Additionally, root pore size influences the uptake of nanoparticles (Zhao et al., 2012). Foliarly applied nanonutrients are deposited on foliar surfaces and are directly able to infiltrate the plant system through the stomata, hydathodes, trichomes, etc., due to their nanoscale size and gaseous uptake by plants (Wang et al., 2013). Additionally, there is a possible positive link between the rate of water absorption and the uptake of nanoparticles by transpiration (Rico et al., 2013; Zhai et al., 2014). Moreover, foliarly applied greater-sized nanonutrients were discovered to flow in the vascular system, epidermal cells, and cortex (Aubert et al., 2012). Nanonutrients taken up from the external

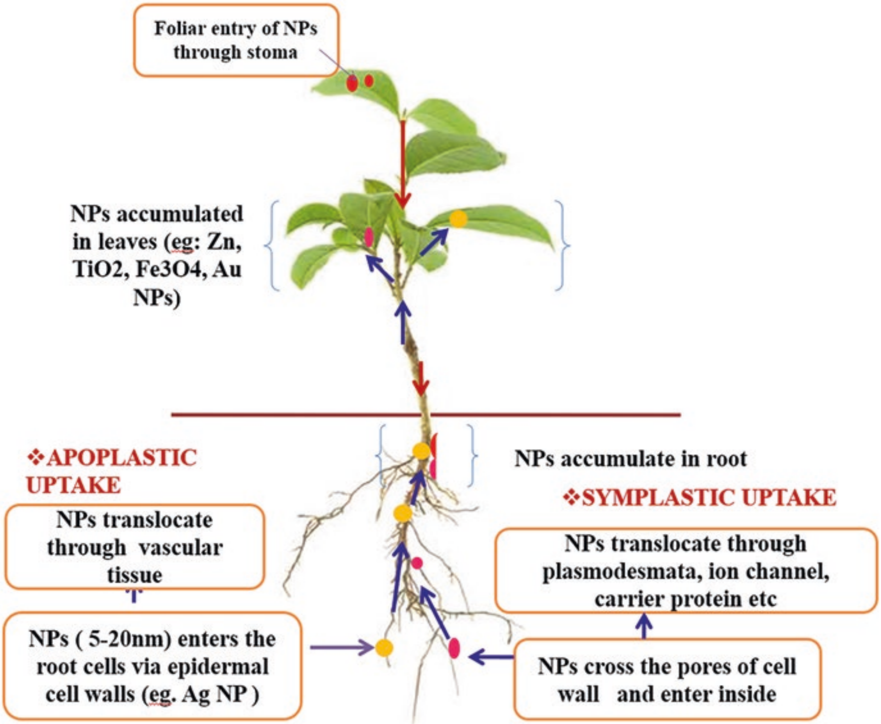

Fig. 6.3 Uptake of NPs in plants. NPs can enter plants through their roots, leaves, and flowers, although their roots are the main route for NP uptake. Passive diffusion and active transport are the two main methods of NP uptake through roots. Smaller NPs (10 nm) can pass through cell membranes by passive diffusion, whereas bigger NPs (>10 nm) must be ingested through endocytosis. NPs can build up in the roots, stems, leaves, and flowers of a plant in addition to being transferred by the xylem and phloem

environment can enter plant cells using a variety of mechanisms, including aquaporin-mediated transport of water molecules, ion channel transport, passive transport, association with organic matter, etc. (Yang et al., 2017). A nanoparticle's size or diameter, its surface chemistry and charge, plant growth stage, cell wall structure, pore size, biochemical makeup, etc., are the factors that influence their uptake and translocation (Bidhendi & Geitmann, 2016). The uptake of nanoparticles also varies depending on the type of plant or crop (e.g., maximum in pea, lettuce, and rice) (García-Gómez et al., 2018; Margenot et al., 2018; Da Costa & Sharma, 2016).Studying the uptake, transport, and accumulation of nanonutrients is a great need of the time in order to receive the fruitful effects of nanonutrients on plants. More studies are needed to understand the mechanisms of uptake and signaling of nanoparticles inside plants.

3 Application Strategies

The mode of application of nanonutrients is just one of the several variables that determine their complicated effects. Numerous research studies have discussed the different ways that nanonutrients can be applied, including soil application, foliar application, seed priming, etc., as presented in Fig. 6.4.

3.1 Seed Priming

Priming of seeds is a well-known treatment for improving the quality of seeds, which enhances the yield as well as resistance to various biotic and abiotic stresses. Priming is carried out by soaking the seeds in nanosuspension with subsequent drying (Galaktionova et al., 2020). By changing the expression of genes that modulate metabolic processes, nanoparticles can act directly against pathogens and alter the metabolism of seeds and plants. This increases the effectiveness of the innate immune system, changes hormone production, and increases plant resistance to pests, diseases, and abiotic stresses (Malik et al., 2020). The initial phase of seed germination is the imbibition phase, which involves water exchange. Aquaporin gene expression can be induced by seed priming with nanoparticles during this germination process, thus enhancing water uptake in seedlings (Nile et al., 2022). During the germination process and even over time, seed nano-priming can activate or change a variety of gene expression patterns and metabolic

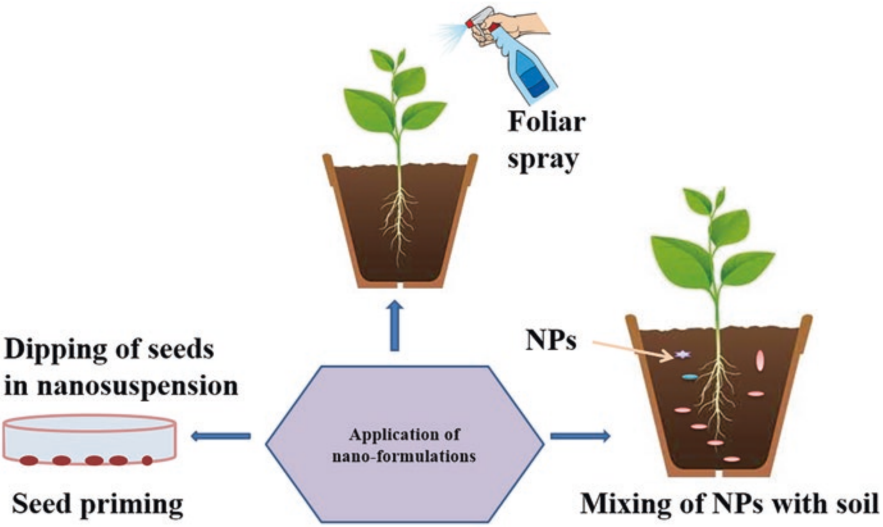

Fig. 6.4 Application strategies of nanonutrients. Nanonutrients are a type of nanoparticles that are used to deliver essential nutrients to plants, with the aim of improving plant growth, yield, and nutritional quality

pathways (Wu et al., 2020). Since many nanoparticles have antimicrobial properties and can load antimicrobial compounds, seed nano-priming can also be employed to protect seeds. Additionally, biofortification of seeds by nano-priming can be employed to encourage an improvement in food quality and production (Sundaria et al., 2019). Seed nano-priming has been proven to boost germination, since such technologies are able to maintain reactive oxygen species (ROS) levels in the ideal range, comprising an oxidative window that promotes seed germination. The uptake of nanoparticles under seed coating can encourage the generation of ROS by influencing various metabolic pathways, elevating the level of active gibberellins, and mobilizing storage proteins (Chandrasekaran et al., 2020). Because seed nano-priming has favorable impacts on plant metabolism and development, it can boost the yield of several crop species. Faster growth of the leaf area and roots boosts the ability of plants to acquire nutrients and water, which, in turn, increases the use of light energy for plant growth (Pereira et al., 2021).

3.2 Foliar Application

Foliar application, the most applied method by the researchers, involves direct spraying of liquid nanoformulation onto the leaf surface (Mahapatra et al., 2022). It increases the efficacy of plant protection technologies compared to the conventional soil root application method (Hong et al., 2021). Foliar NPs can enter plants through the stomata or leaf epidermis, water or ion pores, ion channels, protein carriers, endocytosis, stigma, wounds, and trichomes before moving through the apoplast or symplastic pathway (Zahedi et al., 2020). While the main locations of NP accumulation are the vacuoles and cell walls, the xylem and phloem also play significant roles in the transport of NPs (Hong et al., 2021). Controlled release of nanonutrients at specific sites, quick biofortification, increased absorption and assimilation of nanonutrients, and a reduction in the lack of some key elements in crops are only a few benefits of foliar application of nanonutrients (Budke et al., 2020). Moreover, nanonutrients with either a positive or negative charge can be absorbed by the leaves and transported to the roots (Su et al., 2019). Due to this, reactive oxygen generation was decreased, agricultural produce had a longer shelf life, better defences and resilience to abiotic stresses, pests, and enhanced yield and quality of crops (Lu et al., 2020). Furthermore, it also reduces the absorption of heavy metals by plants due to the promotion of antioxidant enzymatic activity and improved stress tolerance. The parameters that affect the absorption of foliar nanonutrients include leaf hair, cuticular wax, particle size, epidermal structure, leaf area, development stage, light, temperature, humidity, and the physical and chemical properties of NPs. Wax and cell walls can serve as physical barriers to stop the uptake of nanonutrients (Dappe et al., 2019). One study showed that foliar application of nanonutrients such as nano-N, nano-Zn, and nano-Cu at three different stages such as the vegetative stage, flowering stage, and fruiting stage, respectively, increased the yield in capsicum plants (Ruban et al., 2021).

3.3 Soil-Based Application

The application of nanonutrients to soil is one of the important strategies for obtaining its benefits. In this method, the nanoformulation is mixed with the soil in which the plant is grown. When nanonutrients are applied to the soil, they come in touch with exudates and can easily deposit on or stick to the surface of the roots (Gao et al., 2018). As a result, the root exudates and, occasionally, humic acids specifically or randomly interact with the adsorbed nanonutrients, causing considerable physicochemical modifications (Rico et al., 2011). The degree of bioaccumulation and fate of nanoparticles in the soil or plant system can be altered by the physicochemical changes caused by plant exudates. Mucilage can also help nanoparticles adhere to the root surface. The initial phase in the bioaccumulation process is the adsorption of NPs by plant roots from the soil, which may be impacted by the NPs' characteristics and the surrounding environment (Nair et al., 2010). Numerous researchers have looked at various NPs and hypothesized that accumulation in plants take place by adsorption in roots, dispersion in plant tissues, and other modifications like the breakdown of the crystal phase, biotransformation, and bioaccumulation. The presence of microbial siderophores and root exudates is one of the mechanisms for increased bioavailability of NPs in the rhizosphere. The production of organic ligands by plants and microorganisms for the solubilization of minerals from insufficiently accessible sources is well recognized (Chen, 2018). Furthermore, soil application of nanonutrients also has some limitations. For example, only negatively charged nanonutrients are absorbed by plant roots because positively charged particles cause the development of mucilage, which prevents plant roots from absorbing them. Therefore, other methods are also employed to obtain the fruitful effects of nanonutrients.

4 Effects on Plants

4.1 Copper (Cu) Nanoparticles

Cumplido-Nájera et al. (2019) reported that foliar application of Cu nanoparticles enhanced the defense mechanism by triggering the synthesis of antioxidative enzymes in tomato plants. The treatment of copper nanoparticles (CuNPs) on plants boosted anthocyanin, chlorophyll, and carotenoid concentrations in comparison to water-treated plants under drought stress conditions, as reported by Van Nguyen et al. (2022). Their study showed that CuNP regulation of plant defense mechanisms related to drought tolerance is a promising strategy for production of drought-tolerant crop plants. The higher leaf water content, plant biomass, seed number, and grain production under drought as compared to water-treated plants showed that the CuNP-priming plants had improved drought tolerance. According to the findings of Thakur et al. (2022), applying CuNPs to wheat seedlings caused noticeable changes in their metabolic profiles. Total flavonoid content (TFC) and carotenoid content significantly increased at 5 ppm and 2 ppm, respectively, of CuNP compared to controls, whereas total phenol content (TPC) and total ascorbic acid (TAC) were at their maximum levels at 100 ppm. Moreover, with an increase in CuNP concentration in contrast to the controls, chlorophyll content declines. Another work on CuNPs demonstrated the possibility of using biogenic CuNPs to either restrict or stimulate seedling growth. Chlorophyll a, chlorophyll b, and total chlorophyll contents were increased by foliar application of 0.06 mg/mL of CuNPs after 21 days of treatment. Moreover, a higher concentration of CuNPs (0.43 mg/mL) decreased the number of pigments in the leaves. Additionally, biogenic CuNPs had a higher copper uptake than commercial CuNPs, which had a negligible impact on seedling growth (Essa et al., 2021). Copper oxide (CuO) nanoparticles act as a good source of nutrition for plants and exhibit excellent antimicrobial property. Elakkiya et al. (2021) showed that green-synthesized CuO NPs acted as a potent antimicrobial agent against the plant pathogens *Phoma destructiva* and *Curvularia lunata* at 40 µl concentration and also improved plant growth in *Brassica nigra*.

4.2 Iron (Fe) Nanoparticles

Many studies have suggested that the application of nano-iron oxide is a significant method to cope with Fe deficiency in crop plants. Application of this nanonutrient at 2 g L^{-1} has been found to be more effective than other sources of iron nanofertilizers, resulting in increased activities of peroxidase (POX), catalase (CAT), and ascorbate peroxidase (APX), the total contents of chlorophyll a and b, and the quality of bread wheat grain (Ghafari & Razmjoo, 2013). Li et al. (2021) also confirmed that a low dose of zero-valent iron (ZVI) and Fe_3O_4 NP treatments significantly mitigated the symptoms caused by Fe deficiency in rice plants. These NP treatments alleviated oxidative stress and regulated phytohormone levels and Fe accumulation in plants by regulating the Fe transport genes to improve rice growth under Fe-deficient conditions. Likewise, the study by Singh et al. (2021) also revealed that iron oxide nanoparticles (IONPs) functioned as nano-supplements for enhancing the shoot growth of *Eucalyptus tereticornis* by boosting the gene expression of different antioxidant enzymes and synergistically improving the activity of catalase and peroxidase enzymes. Additionally, their findings demonstrated the ability of IONPs to restore soil iron deficiency, while also having a higher tolerance to salt stress, should open up new avenues for regulating abiotic stresses in agroforestry. Kokina et al. (2021) conducted an experiment on three genotypes of barley (*Hordeum vulgare* L.) to investigate the effect of Fe_3O_4 NPs at low concentrations (0, 1, 10, and 20 mg/L). The results show that Fe_3O_4 NPs at low concentrations could be successfully used as nanonutrients for enhancing the growth and yield of barley and other crop plants. Besides the growth parameters, Fe_3O_4 NPs have the potential to enhance the resistance against serious fungal diseases, such as powdery mildew in crop plants, by increasing the miR159c expression (Kokina et al., 2020). Again, according to Sreelakshmi et al. (2021), FeNPs help plants resist drought stress in addition to acting as a nanonutrient for it. There has been an overall acceleration in the growth of plants (*Setaria italica*). Additionally, it was found that with increasing FeNP (Fe_3O_4) concentrations, the amount of soluble sugar and chlorophyll in the seedlings is also enhanced. Their finding suggests that the iron the plants took up was used to produce photoassimilates. No harmful effect on the plants was noticed during the experiment. This demonstrates the potential of green-synthesized FeNPs to function as an environmentally benign fertilizer even in drought-stressed environments. The results of the study by Bidi et al. (2021) authenticate the contribution of FeNPs to reducing As phytotoxicity on rice by promoting the accumulation of chelating substances (proline, glutathione, and phytochelatins) and the sequestration and immobilization of As in the vacuoles and cell walls. FeNPs reduce buildup in the roots and leaves of As-stressed plants by downregulating the expression of the genes involved in As absorption and translocation (Lsi1 and Lsi2). By modifying the expression of the genes that control Fe absorption and its transport to leaves (*IRT1*, *IRT2*, *YSL2*, *YSL13*, *FRDL1*, *DMAS1*, *NAS2*, and NAS3), FeNPs also enhanced the accumulation of Fe in the roots and leaves, resulting in the restoration of photosynthetic pigments and the growth of plants.

4.3 Magnesium (Mg) Nanoparticles

Magnesium (Mg) is an essential macronutrient, which plays an important role in several physiological processes to support plant growth and development (Chaudhry et al., 2021). Shinde et al. (2018) reported that green-synthesized magnesium hydroxide nanoparticles could be used for enhancement of seed germination and seedling growth promotion of *Zea mays* at concentrations of 500 ppm. Cai et al. (2018) confirmed that MgO NPs serve as an outstanding Mg supplement for plants. Results have shown that MgO NPs were easily taken up by the roots of tobacco plants and well distributed throughout the whole plant, which resulted in an increase in the chlorophyll content and stimulation of plant growth. Similar results were obtained when 60 ppm of an MgO NP was applied on cotton plants. Foliar application of this NP solution significantly enhanced growth parameters like plant height, the number of leaves, leaf area and leaf area index of cotton, chlorophyll content (Soil plant analysis development (SPAD) chlorophyll meter value), the number of opened bolls per plant, boll weight, and seed cotton yield (Kanjana, 2020). The probable role of MgO NPs as nanofertilizers has been indicated by the morpho-biochemical alterations in horse gram (Sharma et al., 2022). They discovered a considerable increase in the shoot–root length, fresh biomass, and chlorophyll content of horse gram exposed to MgO NPs. Additionally, after exposure to MgO NPs, the accumulation of protein and carbohydrates increased by 4–20 and 18–127%, respectively. The increase in the accumulation of total polyphenolics following NP treatment increased the antioxidant potential by 5–19%. Moreover, antioxidant enzymatic activity and total phenol and flavonoid contents were enhanced in the presence of MgO NPs. Ahmed et al. (2021) evaluated the role of MgO NPs through their application at a rate of 200 mg/kg in arsenic (As)-polluted soil and found dramatic enhancement in plant biomass, antioxidant enzymatic levels, and lowered ROS compared with the control plants. According to the findings of the study, biogenic MgO NPs could be employed as a potent nanofertilizer for rice cultivation in metal-contaminated soils. Similarly, MgO NPs also play a role in reducing lead (Pb) stress in plants by increasing the concentration of iron, manganese, copper, and zinc as well as antioxidant enzymatic activity (Faiz et al., 2022).

4.4 Calcium (Ca) Nanoparticles

Nanoparticles can also be used as nanocarriers of commercial fertilizers, which minimize the use of chemical fertilizers, thus causing less damage to soil. For example, through a field experiment on *Tempranillo grapevines*, Pérez-Álvarez et al. (2020) investigated the efficiency of amorphous calcium phosphate (ACP) nanoparticles as nanocarriers of urea (U-ACP). The results have suggested that foliar application of such nanofertilizers significantly increased the amino acid content than those of the controls. Anand et al. (2021) synthesized calcium oxide nanoparticles from marine molluscan shells, which enhanced the germination and seedling vigor in green mung, and suggested that they could be used as a nutrient source for plants. Under salt stress, the impact of calcium phosphate NP (CaP NPs) application as a soil fertilizer on the production of bioactive components of broad bean plants has been established. The findings of their research justify the use of CaP nanofertilizers in place of conventional fertilizers that contain Ca^{2+} or P to increase plant productivity and resilience to salt stress. The results demonstrated that when exposed to salt stress, CaP NPs significantly increased plant production by 30% compared to standard fertilizers. This improvement may be explained by a noticeably larger increase in total soluble sugars, antioxidant enzymes, proline content, and total phenolics when using nanofertilizers under salt stress compared to conventional nanofertilizers. Additionally, plant growth metrics, photosynthetic pigments, and oxidative stress markers all showed greater mitigating effects with nanofertilizers (Nasrallah et al., 2022). The study by Badihi et al. (2021) evaluated the functional potential of the nano-macronutrient calcium nanoparticle (CaNP) (1 g/L) along with putrescine (1 mM) to boost the growth and phytochemical qualities in *Crocus sativus*. Putrescine and CaNP treatment had a greater combined impact on the morphological parameters than either treatment alone. However, the findings of the high-performance liquid chromatographic (HPLC) analysis revealed that CaNP treatment alone has a greater impact on the concentration of crocin, picrocrocin, and safranal than do CaNP and putrescine together.

4.5 Zinc Oxide (ZnO) Nanoparticles

Nano-ZnO is one of the most efficient nano-micronutrient fertilizers widely used in agriculture. Different studies have confirmed the potentiality of ZnO nanoparticles as an efficient nanofertilizer. Khalid et al. (2022) conducted an experiment to study the comparative effects of different conventional fertilizers, such as $ZnSO_4.7H_2O$, $FeSO_4.7H_2O$, and $MgSO_4.7H_2O$, and nano-enabled fertilizers on *Caesalpinia bonducella* plants. The results indicated that the highest increase in growth and nutrient and chlorophyll contents of plants were achieved at the dose concentration of 100 ppm ZnO NP treatment. Similar results were obtained when zinc sulfate ($ZnSO_4$) and zinc nanofertilizers (ZnO NPs) were applied to coffee (*Coffea arabica* L.) plants by foliar spray. The results indicated that the application of ZnO NPs improved the growth and physiology of the plants more efficiently than did conventional Zn salts because of better penetration of the NPs through the leaves (Rossi et al., 2019). The study of Yusefi-Tanha et al. (2020) concluded that ZnO NPs are efficient nanonutrients for boosting seed yield up to 160 mg/kg and enriching Zn-deficient soil with Zn. Awad et al. (2021), in an experiment, applied zinc oxide nanoparticles (ZnO NPs) along with ascorbic acid (ASA) on sweet potato (Beauregard cv.) plants grown in calcareous soil. The results showed that foliar treatment with NPs maintains the nutritional status and yield of tuber roots of sweet potato plants grown under stressful conditions of high soil $CaCO_3$ content. ZnO NP treatment could efficiently ameliorate drought stress in eggplant (Semida et al., 2021), cucumber (Ghani et al., 2022), and rice (Upadhyaya et al., 2020), by preventing chlorophyll degradation and cell membrane damage, thus increasing the acquisition of macro- and micronutrients, relative water content (RWC), total phenolic content (TPC), and antioxidant activity of the plants. The effectiveness of ZnO NPs as a foliar treatment on the growth performance of cucumber plants subjected to drought stress was evaluated in a pot experiment. Plants exposed to ZnO NPs showed a decrease in the lipid peroxidation and ROS buildup caused by drought stress. The improvement in enzymatic and nonenzymatic antioxidant components led to a significant decrease in oxidative damage. Due to drought stress, both phenol and mineral concentrations were decreased. Additionally, under both normal and drought conditions, ZnO NPs caused an increase in proline, glycine betaine, free amino acids, and sugar levels. Additionally, foliar application of ZnO NPs prevented the drop in phenol and mineral nutrient content caused by drought (Ghani et al., 2022). According to the study of Venkatachalam et al. (2017), ZnO NPs have the immense potential to reduce Cd and Pb toxicity in *Leucaena leucocephala* seedlings. Many studies have shown the antimicrobial property of ZnO NPs due to which they can protect plants by suppressing various diseases. For example, green-synthesized ZnO NPs inhibited the growth of plant pathogenic fungi, such as *Fusarium graminearum* (Lakshmeesha et al., 2019), *Fusarium oxysporum*, *Phomopsis azadirachtae* (Begum et al., 2020), *Alternaria alternata*, *Aspergillus niger*, *Botrytis cinerea*, *Penicillium expansum* (Jamdagni et al., 2018), etc.

4.6 Sulfur (S) Nanoparticles

Sulfur (S) is an essential nutrient for plant growth and development, and nano-sulfur can be used as an agricultural amendment to enhance crop nutrition and provide crop protection from various diseases and abiotic stresses (Yuan et al., 2021; Wang et al., 2022). Sulfur NPs, at a concentration of 300 ppm, enhance the root and shoot growth in tomato plants (Salem et al., 2016). Najafi et al. (2020) showed that green-synthesized sulfur NPs, at a concentration of 1 mg/ml, significantly improved the growth and photosynthetic parameters of lettuce plants. Moreover, this NP treatment increased phytochemicals such as anthocyanin, total phenol, flavonoids, proline, glycine betaine, and soluble sugar and reduced the malondialdehyde (MDA) and hydrogen peroxide (H_2O_2) content in the plants. Yuan et al. (2021) also showed that sulfur nanoparticle (SNP) treatment increased the macronutrients (K, Ca, P, Mg) and micronutrient (Zn, Mn, Fe) concentrations in roots and shoots, shoot height and root length, and plant biomass in *Brassica napus* L. under mercury (Hg) stress conditions. Seed priming with nano-sulfur alleviated Mn toxicity in sunflower seedlings by enhancing the antioxidative defense system of the plant (Ragab & Saad-Allah, 2020). Foliar and seed treatment with SNPs significantly decreased the disease incidence in tomato plants caused by the fungal pathogen *Fusarium oxysporum* and enhanced the shoot biomass through the activation of salicylic acid-dependent systemic acquired pathway and upregulation of pathogenesis- and antioxidant-related genes of the plants (Cao et al., 2021). Starch-capped sulfur nanoparticles exhibited anti-phytopathogenic activity against the potato ring rot pathogen *Clavibacter michiganensis* subsp. *Sepedonicus* (Lesnichaya et al., 2021). Athawale et al. (2018) also showed that sulfur nanoparticles in combination with bavistin inhibited the pathogen *Fusarium oxysporum*, causing soft rot of ginger.

4.7 Silicon (Si) Nanoparticles

Si is one of the most common elements present in the soil. Although the essentiality of Si in plants has not yet been established, many reports have suggested Si as a "quasi-essential" element for plants, which play an important role in physiological processes and plant protection against many biotic and abiotic stresses (Siddiqui et al., 2020). Many studies have explored the impact of nano-Si on plants. Treatment with 20 mg L^{-1} of SiO_2 NPs increased the number of flowers and flower buds, accelerated flowing, and enhanced flower longevity and flower color indices of gerbera (*Gerbera jamesonii* L.) plants growing under hydroponic conditions (Alikhani et al., 2021). SiO_2 NP treatment also induced seed germination, seed vigor index, and seedling fresh weight and dry weight in tomato plants (Siddiqui & Al-Whaibi, 2014), wheat grass (Azimi et al., 2014), rice (Adhikari et al., 2013), and *Helianthus annuus* (Janmohammadi & Sabaghnia, 2015). Mushtaq et al. (2018) developed a controlled-release fertilizer (CRF) by combining NPK and SiO_2 NPs inside the core, with chitosan as the inner layer coating and sodium alginate and kaolin as outer coating. This controlled-release fertilizer was capable of releasing nutrients slowly and withholding a large quantity of water in the soil, which could help plants growing under salinity and drought conditions. Alsaeedi et al. (2019) showed that SiNPs at rate of 200 mg kg^{-1} had a significant positive effect on the vegetative and yield characteristics of cucumber and successfully mitigated both water and salinity stresses. The positive impact of SiO_2 nanofertilizers on the growth and yield of cucumbers and their potential to limit salinization incursion were also described by Yassen et al. (2017). The results showed that NP treatment increased the K^+ content in roots and was involved in maintaining ion homeostasis and regulating the osmotic balance, which helps plants adapt to salinity and water-deficit stresses. Moreover, NP treatment also induced silicon content in leaves, which regulates water losses. Manivannan and Ahn (2017) described that SiNPs enhanced stress tolerance in plants through the upregulation of the expression of osNAC proteins that are responsible for the upregulation of genes for stress tolerance, proline synthesis, soluble sugar biosynthesis, and redox homeostasis.

4.8 Selenium (Se) Nanoparticles

Excellent biological responses have been found to be possible with selenium (Se) and its compounds. González-Lemus et al. (2022) suggested that NPs of Se could be an excellent alternative for Se fertilizers to improve the production of higher-quality forage crops. The results of their study showed that foliar application of NPs increases the biomass and bioactive compounds such as proteins, phenols, flavonoids, tannins, and antioxidants of the plant. The production of efficient forms of Se using sustainable means has become important due to its low bioavailability and rising toxicity, and this has led to the production of nanoforms of selenium or selenium nanoparticles (SeNPs). Se NP possesses several advantages compared to elemental Se or bulk Se due to its higher surface area to volume ratio and high solubility. Application of selenium nanoparticles (SeNPs) has been reported to enhance plant growth and decrease heavy metal uptake and toxicity in plants. To enhance the impact of nanoparticles, researchers use different compounds to functionalize or produce composites of nanoparticles. For example, Farooq et al. (2022) investigated the role of melatonin selenium nanoparticles (MT-Se NPs) in *Brassica napus* plant growth and arsenic (As) tolerance. The phytotoxic effects of the treatment (80 μM) were ameliorated by melatonin selenium nanoparticle (MT-Se NP) administration and resulted in a significant increase in leaf chlorophyll fluorescence, biomass accumulation, and reduced ROS in comparison to As-stressed plants. The application of MT-Se NPs to As-stressed plants decreased photosynthetic inhibition and oxidative stress, increased MDA and H_2O_2 concentrations, and increased the activities of antioxidant enzymes. Overall, MT-Se NP treatment enhanced plant development more successfully than MT and Se alone treatment. The purpose of this study was to investigate how melatonin and selenium can work together to increase plant enzymatic activity and exert synergistic effects. Ghazi et al. (2022) monitored the impact of salt stress on the germination of wheat seeds. When 100 mg/L of SeNP was employed, the final germination percentage, mean germination time, vigor index, and germination rate index all improved by 25, 25, 39.4, and 11%, respectively, under salt stress conditions. The results from a gnotobiotic sand system, on the other hand, show that the vegetative growth parameters of shoot length, root length, fresh weight, and dry weight were improved by 22.8, 24.9, 19.2, and 20%, respectively, compared to untreated controls treated with 100 mg/L SeNPs. Babashpour-Asl et al. (2022) studied the effects of foliar application of SeNPs on the yield, water content, proline concentration, phenolic content, lipid peroxidation, and essential oil (EO) properties of coriander (*Coriandrum sativum*) under Cd stress. SeNP treatment increased shoot and root weight, chlorophyll (Chl) content, and relative water content (RWC) under Cd stress.

4.9 Manganese (Mn) Nanoparticles

Manganese is one of the micronutrients that serves as a cofactor of different enzymes of plant metabolic processes. The impact of varying concentrations (0, 10, 20, 30, and 40 ppm) of MnO_2 NPs was examined on the common dry bean plant parameters, yield, chemical quality of leaves and seeds, genomic DNA, and several genes encoding proteins (Salama et al., 2022). The outcomes demonstrated that MnO_2 NPs, at a concentration of 30 ppm, improved the growth standards and the yield percentage of the common dry bean by 45.2 and 48.9% over the course of two seasons, respectively. Additionally, MnO_2 NPs, at concentrations of 30 and 40 ppm, dramatically altered the genomic DNA and several genes that code for proteins in the plants compared to other concentrations. Different chemical characteristics of seeds and leaves responded differently to MnO_2 NPs. The study of Dimkpa et al. (2018) assessed the impact of nano-Mn on wheat production and nutrient uptake in comparison to bulk and ionic manganese (Mn). Their research showed that using nano-Mn as a foliar treatment could provide more control on plant responses. Significant differences between foliar exposure to nano-Mn and soil were observed, including higher shoot (37%) and grain (12%) Mn contents, lower soil nitrate-N levels, and higher soil (17%) and shoot (43%) P levels. These results recommend exercising caution in its usage in agriculture since exposure to nanoscale Mn in soil may have subtle effects on plants that are different from bulk or ionic Mn. Shebl et al. (2020) prepared manganese zinc ferrite ($Mn_{0.5}$ $Zn_{0.5}$ Fe_2O_4) NPs by hydrothermal green synthesis, which increased the growth and yield of squash plants at a concentration of 10 ppm. Ye et al. (2020) showed that seed priming with manganese (III) oxide nanoparticles alleviated salinity stress in *Capsicum annuum* L. during germination at 100 mM NaCl through the redistribution of macro/micronutrients among the roots and shoots.

4.10 Molybdenum (Mo) Nanoparticles

Molybdenum (Mo) is one of the essential micronutrients of plants, serving as a cofactor of many enzymes such as nitrate reductase (NR), sulfite oxidase, xanthine dehydrogenase, aldehyde oxidase, and the mitochondrial amidoxime reductase (Mendel, 2011). The potential effect of molybdenum disulfide nanoparticles (MoS_2 NPs) on the physiological index and transcriptomic profiles was studied on marine microalgae *Dunaliella salina* by Luo et al. (2020). The results revealed that NP treatment increased the chlorophyll, protein, and carbohydrate contents by upregulating the genes related to porphyrin synthesis, glycolysis/gluconeogenesis, and the tricarboxylic acid cycle (TCA) cycle. Li et al. (2018) also showed that MoS_2 NP treatment enhanced the growth of rice seedlings by improving the chlorophyll synthesis and the expression of aquaporin genes. Foliar sprays with green-synthesized MoNPs significantly reduced the NO_3^- accumulation by increasing nitrate reductase (NR) activity in spinach (*Spinacia oleracea* L.). Moreover, the MoNP treatment also increased plant height, fresh and dry weights, and chlorophyll content (Abbasifar et al., 2019). Similar results were obtained by Sutulienė et al. (2021). They showed that 50 and 100 ppm MoNP treatment enhanced pea plant height, fresh and dry biomass, and chlorophyll content and increased the P, Ca, Mg, and Fe contents by twofold. Thomas et al. (2017) synthesized molybdenum nanoparticles from the fungus *Aspergillus tubingensis* TFR-29, and application of this NP at a concentration of 4 ppm significantly increased the root area, length, perimeter, the number of tips, root diameter, biomass, and grain yield of chickpeas. Ahmed et al. (2022) investigated the impact of synergistic interaction of plant growth–promoting rhizobacteria (PGPR), *Bacillus* sp. strain ZH16, and biogenic MoNPs on wheat plants. The results showed that co-application of bacteria and the MoNPs enhanced the morphological parameters of the plants by improving nutrient acquisition and by maintaining the ionic balance. Furthermore, this NP treatment reduced the translocation in plants by 30.3%. Taran et al. (2014) also studied the combined effect of colloidal solution of MoNP and microbial preparation on the microbial composition in the rhizosphere of *Cicer arietinum* L. The results showed that this NP treatment increased the number of nodules by two times and the antioxidant activity of chickpea plants and enhanced the formation of "agronomically valuable" microflora. Raj et al. (2021) synthesized hexagonal molybdenum trioxide (h-MoO_3) NPs and Ag-doped h-MoO_3 NPs and studied their effects on seedlings of foxtail and finger millet plants. Both NPs increased the seed germination percentage and enhanced seedling growth. Zhang et al. (2022) reported that MoO_3 NPs improved the growth of rice plants without exerting any phytotoxic effect. This study showed that MoO_3 NPs enhanced NO_3^- assimilation by promoting the activity of nitrate reductase, glutamine synthetase, and glutamate synthase and increased the root exudates that helped in the uptake and utilization of the MoO_3 NPs. Therefore MoNPs could be used as an efficient nanofertilizer for crop plants.

5 Ecotoxicological Entanglement

In the past few decades, many nanoformulations, which offer smart solutions toward more sustainable and efficient agriculture, have been developed, but we need to explore the impact of nanomaterials on the environment. Nanoparticles impart toxicity either by direct interaction with the cell surface, causing membrane or cell damage, or by dissolution of NPs releasing toxic ions, which interact with the DNA of organisms. NPs also damage cellular content by generation of reactive oxygen species (ROS) in cells (Buchman et al., 2019). Application of NPs in agriculture has led to an increase in NP content in soil, which may cause toxic effects to the soil flora and fauna. The toxic effects of various NPs are mentioned in Table 6.2. CuNPs decrease soil bacteria by causing membrane damages and cell lysis (Concha-Guerrero et al., 2014). Lee et al. (2022) studied the toxic effects of silver nanoparticles (AgNPs) and zinc oxide nanoparticles (ZnO NPs) on zebrafish embryos in

Table 6.2 Toxic effects of different nanoparticles

Nanoparticles	Effect	References
MgO	Increases chromosomal aberrations and decreases the mitotic index (MI) of cell root tips	Mangalampalli et al. (2018)
	Reduces root length, antioxidant potential, carbohydrate and protein accumulation, chlorophyll and fresh biomass in black gram	Sharma et al. (2021)
	Induces cytotoxicity by glutathione (GSH) depletion in human lung epithelial cells	Akhtar et al. (2018)
CuO NPs	Significantly decrease the microbial activity associated with C and N cycling in agricultural lands	Simonin et al. (2018)
	Decrease the cell viability in human lung epithelial cells	Ahamed et al. (2010)
	Inhibit the root and shoot lengths; induce ultrastructural changes in chloroplasts, the mitochondria, vacuoles, and the stomatal structure in spring barley	Rajput et al. (2018)
ZnO NPs	Decrease the metabolic activity and cell number as well as increase the rate of apoptotic and dead cells in two human intestinal cell lines, namely, Caco-2 and LT97	Mittag et al. (2021)
	Reduce the activity of the fungi community associated with leaf litter decomposition	Du et al. (2020)
	Cause damage to fungal cell walls and vegetative and reproductive structures of coffee fungi *Mycena citricolor* and *Colletotrichum* sp.	Arciniegas-Grijalba and Guerra Sierra (2019)
	Result in DNA damage and functional impairment of human umbilical vein endothelial cells	Poier et al. (2020)
γ- Fe_2O_3 NPs	Induce several cardiotoxic effects on zebrafish embryos	Pereira et al. (2020)
SeNPs	Reduce the growth of wheat plants at high concentrations	Ikram et al. (2020)
	Decrease growth and biomass production and induce oxidative stress in *Lactuca sativa* at a concentration of 10 mg/ml	Najafi et al. (2020)

aquatic environments. The results reveal that AgNPs and ZnO NPs lead to cytotoxicity by inducing programmed cell death, excessive oxidative stress, and dysfunctional autophagy and increased the mortality of zebrafish embryos and delayed hatching time. Shah et al. (2022), in a study, reported the toxic effect of ZnO NPs on soil organisms and carbon as well as nitrogen cycling of manures in the soil–plant system. This study revealed that a high dose 1000 mg kg^{-1} of ZnO NPs decreased the microbial colony-forming units (CFUs), which resulted in the reduction of mineralization of organic N and C emission from poultry manure (PM) and farmyard manure (FYM). A concentration of 100 μg mL^{-1} of SiNP caused significant DNA damage in the root meristem cells of *Allium cepa* (Liman et al., 2020). Lei et al. (2023) in a review explained the transformational behavior and potential toxicity of iron-based nanoparticles (NPs), especially high concentrations of zerovalent iron nanoparticles (nZVI). Physical, chemical, and biological transformations of iron-based NPs in the environment induce toxicity in aquatic animals *Daphnia magna* (Keller et al., 2012) and *Oryzias latipes*, bacteria, algae, and plants. This nanotoxicity is due to NP-induced ROS, which results in disruption of membrane integrity, cell death, and disturbance in the ionic transport chain. Many studies have reported the adverse effects of nanomaterials on biological systems. The toxicity of nanoparticles mostly depends on the physical properties of the particles such as morphology, size, and density. In addition to this, nanotoxicity also depends on particle concentration, frequency, and duration of exposure (Buzea & Pacheco, 2019). Researchers are still working on how to reduce the nanotoxicity. By manipulating morphology and by adding capping and chelating agents, the toxicity of nanoparticles could be reduced. NPs could easily enter the human body by food chains and may cause cellular damage. Therefore, extensive research is needed in this field.

6 Conclusions and Future Trends

Nanotechnology-based processes provide effective solutions in the fields of agriculture and precision farming, plant breeding, and plant genetic engineering. Application of slow-release nanofertilizers can improve the growth of crop plants and ecological environment of agricultural land soil. Nanofertilizers containing macro- and micronutrients not only improve plant nutrient access but also protect plants from several biotic and abiotic stresses. Nanofertilizers perform better than conventional fertilizers in terms of nutrient uptake, solubility, and efficiency. Application of nanofertilizers helps regulate the migration of nutrients into the environment and to improve the water-holding capacity and microbial activity of soil. Therefore, mass production and application of nanofertilizers is needed to avoid the harmful effects of chemical fertilizers and to restore the natural environment. In the future, nano-enabled strategies will perform well to achieve smart and sustainable agriculture and to maintain global food security. However, long-term deposition of nanomaterials in soil and water bodies may pose a threat to living beings and, hence, there is a need for proper study to evaluate the responses of plants and animals to nanomaterials. Both positive and negative impacts of nanomaterials on plants should be explored felicitously before commercialization of any nanobioformulation. Furthermore, biosynthesis or green synthesis methods must be utilized for production of nanomaterials because of their environment-friendliness, feasibility, and cost-effectiveness. The application of nanotechnology in agriculture is a new approach; therefore, efficient rules, regulatory laws, and restrictions are necessary for the safe use of nanomaterials.

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Chapter 7
Synthesis, Characterization, and Uses of Nanofertilizers and Nano-Agrochemicals for Sustainable Agriculture

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1 Introduction

One of the most essential industries for supporting a nation's economy is agriculture. The fragmentation of land use caused by population increase, the movement of agricultural workers to other industries, and the scarcity of natural resources are among the issues that limit the agricultural sector's growth (Frona, 2019). Nanofertilizers (NFs) have recently gained popularity in modern agriculture, for maximizing crop production, improving nutrient uptake efficiency, reducing chemical fertilizer applications, reducing wastage, and decreasing cultivation costs. Developing innovative approaches for appropriate formulations and delivery mechanisms is extremely important to ensure optimal nutrient uptake (Verma et al., 2022). The application of nanofertilizers in the frame of a sustainable agriculture system has indicated it to be a novel way for improving soil quality and plant growth

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performance (Godfray et al., 2010). Because of rising food crop demand, the global nanofertilizer market is rapidly expanding. The rapidly growing global population and the need to feed everyone will propel the global nanofertilizer industry forward over the next 5 years. The global nanofertilizer market was valued at USD 353.9 million in 2021 and is expected to grow at a significant compound annual growth rate (CAGR) of 17.9% from 2022 to 2030 (source: https://www.precedenceresearch.com/nanopesticides-market) (see Fig. 7.1).

Although fertilizers are necessary for agriculture to feed the world's growing population, the excessive use of chemical fertilizers pollutes the environment (Mahapatra et al., 2022; Srivastav, 2020). Scientists have developed nanotechnology to be used in agriculture to improve the sustainability of crops by reducing agricultural inputs such as fertilizers and pesticides or by reducing outputs that can harm the environment and/or human health. One of the main problems in agriculture is the low use efficiency of fertilizers. Annually, hundreds of millions of tons of conventional fertilizers are lost to the environment without benefiting crop plants worldwide. For example, nitrogen (N) is one of the most heavily applied nutrients in crop production, but plants use only 30–50% of the applied amount and about 50–70% is lost from the root zone due to processes such as nitrogen leaching, volatilization of ammonia, and emission of nitrous oxide (Ditta et al., 2016). When nitrogen fertilizers are added to soil, nitrogen is transformed into ammonium followed by conversion to its nitrate form (NO_3^-), which is a highly mobile form that does not get adsorbed because of the negative charge of clay particles in the soil. Nitrate leaching is a serious problem for natural ecosystems, and its high levels are associated with such diseases as methemoglobinemia in infants, gastric cancer, birth defects, and heart diseases. An investigation in China revealed that 80% of the 67 main lakes have been polluted to a level that is unhealthy for human contact. Verma

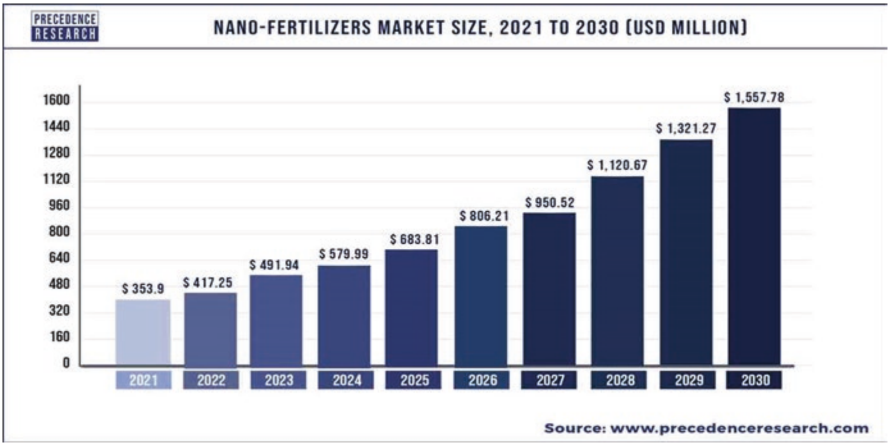

Fig. 7.1 The value of the global nanofertilizer market from 2021 to 2030 is estimated to be billions of US dollars. (Source: https://www.precedenceresearch.com/nanopesticides-market)

Table 7.1 Commercial nanofertilizers (NFs) that are available worldwide

S. No	Nutrients (essential/ functional)	Company/firm
1	Nitrogen (N)	NanoUrea, IFFCO, India
2	Phosphorus (P)	TAG Nano Phos, SK Organic Farms, India
3	Potassium (K)	NanoMax Potash, JU Agri Sciences, India
4	Zinc (Zn)	Geolife Nano Zn, Geolife Agritech India Ltd., India; Silvertech Kimya Sanayi veTicaret Ltd., Turkey; AFME Trading Group, UK
5	Calcium (Ca)	Nano Calcium Chelate Fertilizer, AFME Trading Group, UK; Nubiotek®Ultra Ca, Bioteksa, Mexico; Fertile Calcium 25, HPL Agronegocios, Brazil; Lithical, Litho Plant, Brazil
6	Iron (Fe), magnesium (Mg)	Nubiotek® Hyper Fe+Mg, Bioteksa, Mexico
7	Magnesium (Mg), molybdenum (Mo), zinc (Zn)	Nanovec TSS 80, Laboratories, Bio-Medicin, Brazil
8	Boron (B)	Nano Bor20%, Alert Biotech, India
9	Silver (Ag)	Nano-Ag Answer®, Urth Agriculture, USA
10	Silicon (Si)	Nano Land Baltic, Lithuania; potassium and phosphorus, Fosvit K30, Kimitec Group, Spain

et al. (2022) provided a list of commercial nano-fertilizers (NFs) that are available worldwide (Table 7.1).

Nanofertilizers (NFs) are intended to be more efficient than conventional fertilizers as they supply available elements with low bioavailability, such as phosphorus (P) and zinc (Zn), while also reducing the loss of mobile nutrients to the soil, such as nitrate (Kah et al., 2018; Tarafder et al., 2020). NFs can be divided into nanomaterials (NMs) that act as nutrients themselves and are made of macronutrients or micronutrients and NMs that act as carriers of macronutrients loaded with nutrients or enhanced fertilizers (Liu & Lal, 2015). Crops can absorb nutrients slowly and sustainably because the nanostructure of NFs provides a high surface-to-volume ratio (Feregrino-Pérez et al., 2018; Monreal et al., 2016), leading to a greater number of active sites for biological activity. There are high expectations about the applications of nanotechnologies in the agricultural sector. Apparently, the nanotools deliver agricultural inputs in an efficient and controlled manner, providing long-term solutions to climate change and pollution (Solanki et al., 2015).

Moreover, in calcareous and alkaline soils, some of the applied N fertilizers such as urea and ammonium convert to NH_3, causing its volatilization. Some of it may also oxidize and get converted into nitric acid, which forms acid rain, thus causing damage to vegetation and acidifying lakes. In addition, N fertilizers contribute to increased greenhouse gas (GHG) emissions of nitrous oxide. Though N_2O constitutes only 5% of all greenhouse gas emissions, it is 300 times as potent as carbon dioxide.

1.1 Advantages of Nanofertilizers

There is increasing pressure on the agricultural sector to meet the ever-increasing demands of the ever-increasing human population. Nutrient fertilization is essential for preserving soil fertility and increasing crop productivity and quality. Exact nutrient management of horticultural crops is a major challenge around the world because it is heavily reliant on chemical fertilizers. Traditional fertilizers are not only expensive for the producer but are also potentially harmful to humans and the environment (Zulfiqar et al., 2019). Furthermore, slow-release nitrogenous fertilizers, such as UF-30 and urea super granules (USG), and others have recently been developed. Their application is intended to combat flooding. Ordinary urea is rapidly converted into its gaseous form in flooded conditions, rendering it unavailable to plants. USG and UF-30, both forms of urea, release nitrogen very slowly, thus reducing nitrogen loss. Nitrification inhibitors, a recent discovery, have also been found to slow down the rate of nitrogen release from urea. Before being applied to the flooded field, urea is treated with these chemicals. Deep urea placement in the root zone, whether in the form of USG or mud balls (briquettes), is a time-consuming and thus costly technique. However, these fertilizers have been on the market for some time. These formulations typically consist of tiny capsules containing nitrogen, phosphorus, and other desired nutrients. The outer shell slows down both the rate at which water can enter the inner contents of the capsule to liberate nutrients and the rate at which end products escape from the capsule. Recently, fertilizers that fit the description of “controlled-release” have more fully been developed and made possible by sophisticated materials and manufacturing techniques that can tune the shells so that they alter nutrient release rates in desired ways as the soil’s temperature, acidity, or moisture changes.

Although controlled-release technologies improve fertilizer efficiency, they do not eliminate all of the disadvantages of fertilizer use. Ammonia, urea, and potash are still among the products; however, producing these substances is energy-intensive, which means that their production can contribute to greenhouse gas production and climate change. However, this effect could be mitigated using more environmentally friendly nitrogen sources and incorporating microorganisms that improve the efficiency of nitrogen and phosphorus uptake by plants. There is no evidence that the materials used to make the shells are harmful to the environment, but this risk must be monitored whenever new substances are introduced in large quantities.

As a vivid example of slow-release fertilizers, using coated urea fertilizers (Fig. 7.2) can be considered as the least expensive way to boost urea efficiency in flooded rice fields. Coating treatment also aims to slow down the rate at which nitrogen is released from ordinary urea. The two most common coating materials are sulfur and neem cakes. Due to the high cost of sulfur, neem-coated urea (NCU) is less expensive than sulfur-coated urea (SCU). Making sulfur-coated urea is also a difficult process, whereas farmers can make neem-coated urea. NCU has shown promising results in maize, potato, sugarcane, and cotton trials.

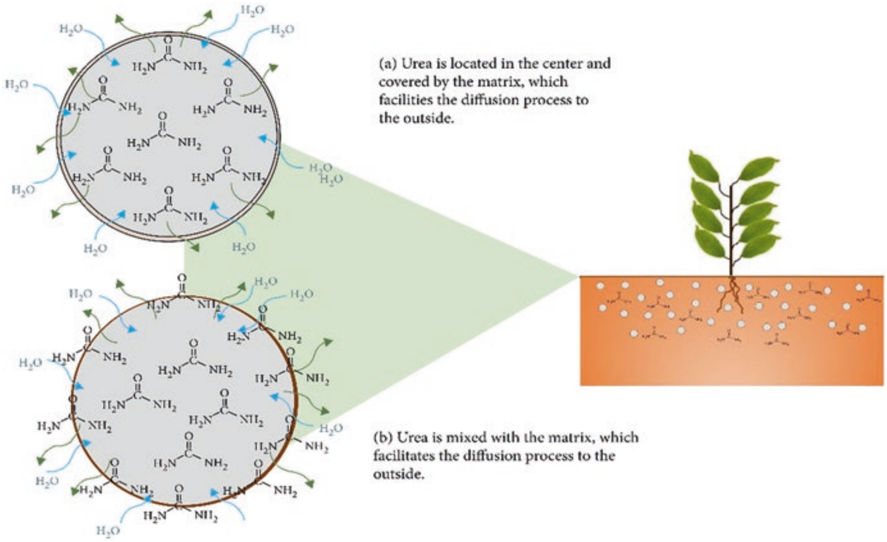

Fig. 7.2 The release of coated urea into the soil is a complicated process impacted by numerous factors. Coated urea's slow-release qualities make it more efficient than ordinary urea fertilizers since it decreases the risks of overfertilizing plants and causing environmental damage. However, correct management methods, such as suitable application rates, timing, and positioning of coated urea in the soil, are critical to maintaining optimal plant uptake and minimizing potential environmental losses. (Reprinted from Tapia-Hernández et al., 2022 with Creative Commons License)

Nanofertilizers have advantages in nutrition management due to their excellent ability to improve nutrient utilization efficiency. Unlike traditional fertilizers, nutrients applied alone or in combination are bonded to nano-dimensional adsorbents, which slowly release nutrients. This strategy reduces fertilizer loss into groundwater while increasing nutrient utilization efficiency. Furthermore, nanofertilizers can be used to boost resistance to abiotic stress, and, when combined with microorganisms, these nanobiofertilizers provide a slew of additional benefits. Even though nanofertilizers have unquestionably opened up new avenues for sustainable agriculture, their drawbacks must also be carefully evaluated before they are placed on the market (Precedence Research, 2022). Aside from slow release, the nano-carriers deliver nutrients to the correct location, reducing the amount of active chemicals deposited in the plant (Avila-Quezada et al., 2022).

Nanofertilizers are seen as perfect solutions to tackle the problems of conventional fertilizers because of their capability to increase yield, improve soil fertility, increase nutrient efficiency and uptake in plants, and reduce environmental pollution by releasing nutrients into the soil gradually in portions and in a controlled manner, as shown in Fig. 7.3 (Tapia-Hernández et al., 2022).

The low solubility of some conventional fertilizers (e.g., calcium sulfate ($CaSO_4$)) can be overcome by developing nanoformulations with higher solubility and dispersion.

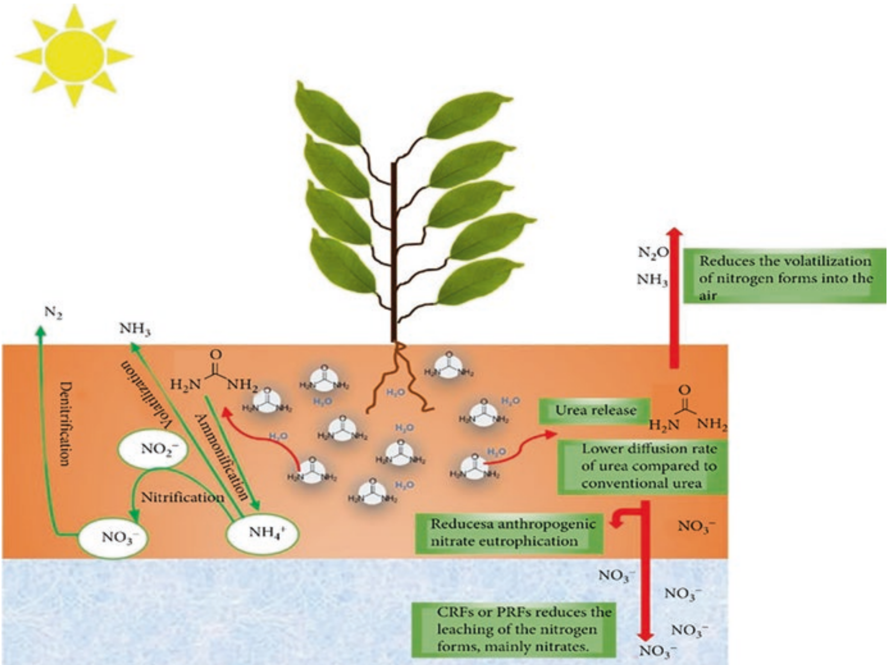

Fig. 7.3 Slow-release fertilizers gradually release nutrients into the soil in sections, ensuring a steady supply of nutrients to support plant growth and development. They can be organic or inorganic and come in a variety of forms. To promote optimal plant growth and output, the appropriate product and application technique must be chosen. Good management methods can help avoid overfertilization and reduce environmental repercussions. (Reprinted from Tapia-Hernández et al., 2022 with Creative Commons License)

The excess release of nutrients for water-soluble fertilizers of conventional technology may produce toxicity and upset the ecological balance in the environment. Nanofertilizers can tackle this problem by regulating the release pattern of nutrients with encapsulation and coating nanomaterials with polymers etc.

Some nutrients may be used by plants at the time of delivery, whereas the remaining nutrients are transformed into insoluble salts in the soil. The effective duration of fertilizer input into the soil can be increased using nanostructured formulations.

2 Preparation of Nanofertilizers

(a) Introduction

A nanometer (nm) is a length unit of 10^{-9}, or a billionth of a meter, in distance. To visualize a nanometer, consider the diameter of a human hair is roughly 75,000–100,000 nanometers, whereas the breadth of the little finger's nail is about 10 million nanometers. The ability to observe, measure, manipulate, and manufacture things at nanoscale size is known as nanotechnology. The physical, chemical, and biological properties of the matter change, compared to the bulk volume of the same material, because of the great surface area per unit of volume and also the decreased size of matter to the nano-size range. The changes in the properties of nanomaterials and their significant surface area have allowed nanotechnologists to use nanomaterials in different fields that they could not think of earlier. Nanotechnology has become a promising field to help humanity achieve its goals in many other fields.

Nanofertilizers can be categorized into three main groups based on the active part of nanomaterials. The first group is nanoparticles (NPs) containing nutrients such as hydroxyapatite, copper oxide, and zinc oxide. All nanomaterials in this group are either considered essential nutrients for plants or include essential nutrients in their composition, for example, hydroxyapatite contains both calcium and phosphorus, which are both considered macronutrients. The second group includes nanomaterial-enhanced fertilizers where the nanomaterials such as nanoclay minerals (zeolite, bentonite, montmorillonite), mesoporous silica, and biochar act as carriers or vehicles for nutrients. The third category includes plant growth stimulation nanomaterials such as titanium dioxide which has been noted to have a high impact on plant growth and productivity despite not being an essential nutrient.

(b) Synthesis of Nanofertilizers and Nanoparticles

Nanofertilizers like any other nanomaterials have two methods of synthesis. The first is the physical method (top-to-down approach), which involves breaking down bulk materials into smaller particles at the nanoscale level using the ultrasonic method or milling with a ball mill machine. The second method is to chemically synthesize nanoparticles (bottom-to-up approach) by means of chemical reactions among materials under certain conditions, leading to creating the desired nanofertilizer. For example, to synthesize hydroxyapatite, a source of calcium, such as calcium hydroxide, and a source of phosphorus, such as phosphoric acid, are both needed. A reaction between these two materials in a Ca:P ratio of 1.67 and raising the pH to 10 will make the calcium bond with phosphorus.

The formation of the formatting nucleus of hydroxyapatite in the reaction, grading accumulation, and dispersion to nano-size would form nanoparticles of hydroxyapatite. The chemical method has an advantage over the physical method as it makes it possible to control the shape and size of nanoparticles by controlling the synthesis conditions or using some chemical materials that act as molds. The physical method cannot control the shape of the resulting nanomaterials and usually produces irregular shapes, but it is useful in converting natural bulk materials, which exist in abundance and are used as fertilizers or vehicles for nutrients into nanomaterials.

After the synthesis of nanomaterials, if they have low solubility or they can be used as foliar fertilizers, then they can be used without any modifications. On the other hand, if the synthesized nanomaterials have high solubility, or if they can be used as a vehicle for highly soluble fertilizers such as urea, or if they can be added directly to the soil, then they need to be coated with a hydrophobic layer to facilitate slow-release nutrients and also to give the fertilizers a proper form (beads or pellets) for soil application. Coating and encapsulation of slow-release fertilizers have been extensively studied using a variety of materials. Coating sulfur with petroleum-based polymers to control the release rate has been found to have lesser environmental impacts due to better release, longer persistence, and low biodegradability.

Nowadays, researchers have endeavored to develop renewable sources and biodegradable coating materials such as lignin, cellulose, thermoplastic starch, sodium alginate, chitosan, and carboxy methyl cellulose to decrease the environmental hazards of using petroleum materials and to achieve sustainable resource use.

3 Characterization of Nanofertilizers

Different techniques and analyses are used for the synthesis of nanofertilizers so that the desired products have the desired characteristics that meet the conditions laid out. For example, X-ray diffraction (XRD) helps in characterizing the synthesized materials by elaborating the crystal structure of the materials. It can distinguish between materials that have the same chemical composition. For example, if calcium and phosphorus ions react with each other, obtaining mono-, di-, tri-, or octa-calcium phosphate or hydroxyapatite can be expected. Which one of these is synthesized will depend on the process condition, and XRD can help us identify that material.

Another commonly used procedure is the Fourier transform infrared spectroscopy (FTIR) to study the functional groups that exist on the surface of nanomaterials and to confirm any modification that may have happened in the nanomaterial. For example, urea has two functional groups, namely, carbonyl and amine, and hydroxyapatite has P–O and OH. After hydroxyapatite modification with urea, both carbonyl and amine groups will appear in the hydroxyapatite graph, as shown in Fig. 7.3. It also helps us realize the difference between coating materials, which are extracted using different methods. For example, lignin is the most abundant polymer on the earth, and it can be extracted from plants, paper manufacturing wastes (biorefinery residues), or any other resources, and its composition differs not only by the extracting method but also from one plant to another as well as plant age. Using FTIR spectroscopy will help in studying its functional groups to determine the differences between them and the best source to use (Fig. 7.4).

In addition, transmission electron microscopy (TEM) is one of the most important techniques to determine both the particle size and shape of the synthesized nanomaterials, which greatly influences their characteristics. This determines the nanomaterials' ability to be used in different fields, e.g., mesoporous materials can be used as adsorbent materials because of their large surface area. Scanning electron microscopy (SEM) can be used to study the morphology of fertilizer beads and coating layers to observe cracks, holes, and roughness that may exist in the coating layers, which affects the release behavior of the nanofertilizers (Helal et al., 2023b). These characteristics allow the water and soil solution to enter through the coating layers and reach the nutrients, which help increase the release rate of the nutrients in the soil solution (Fig. 7.5).

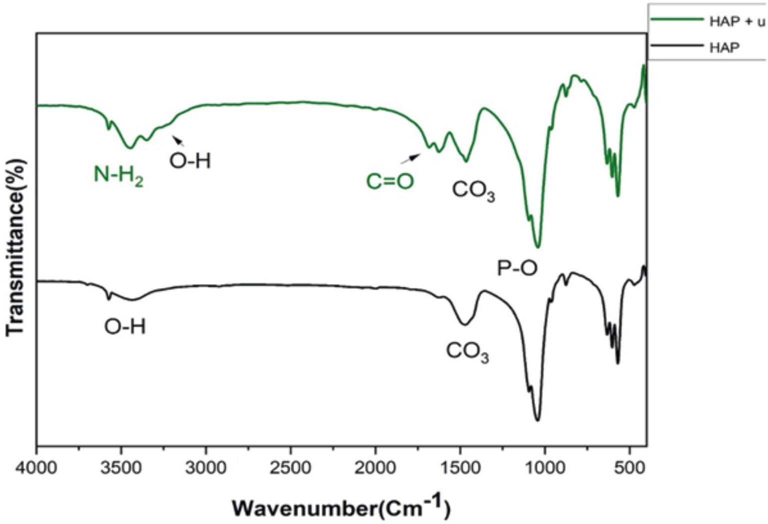

Fig. 7.4 Fourier transform infrared (FTIR) spectroscopy to study the functional groups in nanomaterials

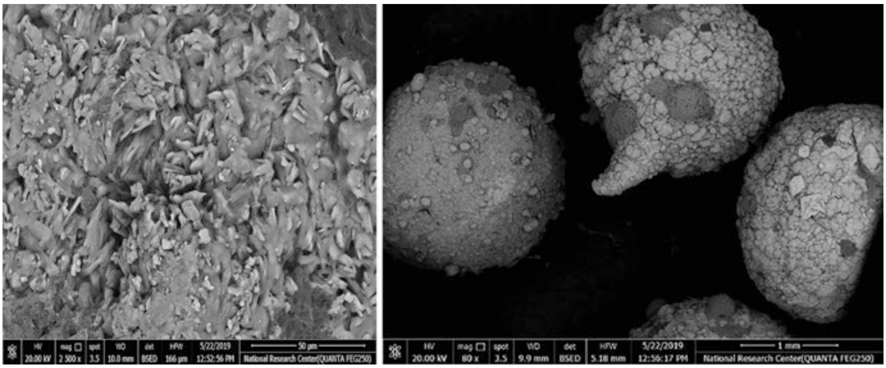

Fig. 7.5 Scanning electron microscopy (SEM) to study the morphology of fertilizer beads and coating layers to observe cracks, holes, and roughness

4 Nutrient Release Characterization and Stimulus Responses

After the preparation of a nano-coated fertilizer, it is necessary to study its reactivity with water and soil as well as the release rate of nutrients, as shown in Fig. 7.6. This is carried out by measure several leaches at different times. Each leach is considered as irrigation. By determining the amount of nutrients released in each leach, the total time needed to release the nutrients from the fertilizer can be calculated. The release behavior of the nutrients from the beads of the coated nanofertilizer depends on experiment conditions such as pH, the cation types existing in the soil, and

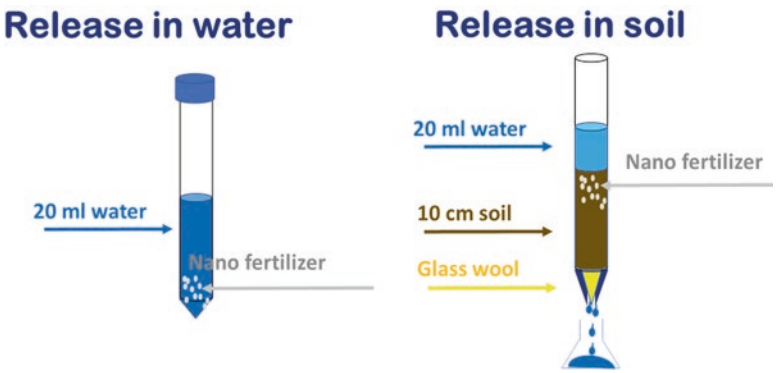

Fig. 7.6 A schematic of procedures to determine nutrient release

irrigation water quality. All of the experimental conditions have to be similar to the field conditions because the release of nutrients will differ from one soil to another, and, so, if a controlled-release fertilizer is supposed to be used in alkaline soil, then the release behavior should be characterized in the same soil.

Many researchers have recorded a slow-release rate for different types of nanofertilizers. A lignin–clay nanohybrid used as a carrier for urea showed an excellent release behavior with full release taking 20 days, whereas conventional urea released completely in the first few days (Shugang Zhang et al., 2020). Urea-modified hydroxyapatite encapsulated in *Gliricidia sepium* wood showed a full urea release duration of 60 days in acidic soil and still released only 80% of its total amount (kottegoda et al., 2011).

5 Plant Behavior with Nanofertilizer Applications

Nanofertilizers have recently gained popularity in modern agriculture, for maximizing crop production, improving nutrient uptake efficiency, and reducing chemical fertilizer waste and cultivation costs (Helal et al. 2023a). Developing innovative methodologies for developing appropriate formulations and delivery mechanisms is essential for providing optimal uptake of nutrients (Verma et al., 2022). Nanofertilizer application in the frame of a sustainable agriculture system has been demonstrated to be a novel way for improving soil quality and plant growth performance (Godfray et al., 2010). Nanofertilizers play an important role in improving the growth, morphology, and physiology of plants (Gohari et al., 2020). Besides stimulus responses and release rates, the mechanisms also include changes in the physiological characteristics of plant features through a change in the formation of reactive oxygen species (ROS), peroxidase, superoxide dismutase (SOD), catalase (CAT) enzymatic activities, and amendments to the leaves' protein, chlorophyll, and total phenolic content (TPC) (Chung et al., 2018). Indeed, the key to the successful application of nanotechnology in sustainable agriculture is the detection of optimal concentrations of nanofertilizers for optimal effectiveness while maintaining the nontoxicity of various nanoparticles to nontarget species (Tariq et al., 2022).

As water molecules play a crucial role in the germination of seeds, several nanofertilizers have also been found to regulate the water imbalance in the seed coat, which has an impact on seed germination (Verma et al., 2020). It has been discovered that the use of nanofertilizers reduced the impact of salt stress during the bitter almond seed's germination period by forming new pores inside the seed coat, which, in turn, increased the biological activity of the stored food and, consequently, triggered the emergence of the embryo from dormancy (Badran et al., 2018).

Seed priming, the technique of treating seeds before planting, causes a physiological change in the seed and speeds up germination. A potential seed priming method called nano-priming increases seed germination, seed growth, and yield by giving the seed resilience to biotic and abiotic stresses (Bruce et al., 2007). Nano-priming promotes the formation of nanopores in the shoot, aids in water absorption, activates reactive oxygen species (ROS) and antioxidant mechanisms in plant seeds, and forms hydroxyl radicals that loosen cell walls quickly and encourage the rapid hydrolysis of starch. For example, silver (Ag) nanoparticle priming has been found to help in the formation of nanopores on the seed coat; Ag nanoparticles are gentle ROS stress-persuaded agents and act as nanocatalysts for increasing the activity of starch-hydrolyzing enzymes (Singh et al., 2020).

Titanium dioxide (TiO_2) nanoparticles (NPs) are known for their photocatalytic activity, high stability, and low costs and have found commercial applications for sustainable crop production. Exposure to TiO_2 NPs has significantly changed germination rates in many plants. The photocatalytic activity of NPs with different sizes and shapes may be the cause of the variation in the germination rate of seeds (Ma et al., 2012). TiO_2 NPs affect plant growth, cell division, cell size, callus induction, and hormone rates (gibberellins and cytokinins) (Golami et al., 2018). TiO_2 NPs, at lower concentrations, enhance seed germination, the promptness index, and seedling growth of onion plants. However, concentrations over and above 50 μg mL^{-1} can be inhibitory for seed germination and seedling growth in onions. Clement et al. (2013) observed that flax seeds treated in a suspension of TiO_2 anatase NPs at a concentration of 100 mg L^{-1} favorably altered root growth and seed germination. They attributed these advantageous benefits to the antimicrobial properties of the crystalline structure of TiO_2, which may strengthen plants' tolerance to stress.

Under hydroponics, 50 mg L^{-1} of nano-TiO_2 slightly enhanced the root and shoot fresh biomass compared to the untreated controls. At a concentration of 100–400 mg L^{-1}, the antioxidant defense system in the plant was stimulated to alleviate oxidative stress. However, the highest concentration (400 mg L^{-1}) significantly decreased root fresh biomass. So, the ideal concentration of TiO_2 NPs can improve the nutritional content of edible tissues without being hazardous to plants or endangering consumers' health (Hu et al., 2020). Silver nanoparticles (AgNPs) have been recently demonstrated to have good, strong antibacterial properties, making them an attractive choice for usage in the food and agricultural industries for packaging and disease detection (Quardos & Mar, 2010). When applied to the soil at a dosage of

100 mg kg^{-1}, AgNPs had a beneficial impact on maize biomass. On the other hand, the same treatment noticeably affected the bacterial communities in the rhizosphere and resulted in less enzymatic activities, and considerable changes in carbon use and community composition profiles were also noted (Sillen et al., 2015). In another study, silver nanoparticles, at the rate of 25 ppm, significantly enhanced the different growth parameters and N, P, and potassium (K) uptake efficiency of wheat. However, AgNPs, at the rate of 75 ppm, increased chlorophyll content effectively (Jhanzab et al., 2015).

Silicon (Si), a quasi-essential plant micronutrient, supports the growth of plants, particularly in dry environmental conditions. Additionally, silicon fertilization causes the plant's shoot system to become more erect, improves the plant's ability to photosynthesize, increases its chlorophyll content, and increases the quality of output (Kah et al., 2018). By treating the soil with SiO_2-NPs (up to 10 g kg^{-1}) in combination with mineral NPK, an enhancement in photosynthesis, production, and productivity of maize plants was observed (El-Naggar et al., 2020). Foliar spraying on cocoa clones with SiO_2 NPs increased both photosynthetic and electron transport rates, which could be related to significant enhancement in nutrient content and plant growth (Gómez-Vera et al., 2021). The application of copper nanoparticles (CuNPs) has the potential to improve the physiological performance and agronomical parameters of alfalfa. The root contents of iron (Fe) and Zn) and the Fe content in leaves has been noted to increase compared to the control treatment (Cota-Ruiz et al., 2020). Moreover, nano-copper application augmented leaf superoxide dismutase expression.

The effectiveness of using chitosan nanoparticles (CNPs) in agriculture has been widely noted. CNMs are simple to apply to leaf surfaces, and because they enter through the plant's stomata, there is no contact with the soil system (Abdel-Aziz et al., 2016). For instance, a 10% foliar application of nano-chitosan significantly increased the growth and yield metrics, photosynthetic pigments, and potato tuber productivity – chemical contents at harvest, and macronutrients in potato leaves and tubers – compared to the control treatment (Elshamy et al., 2019). The effect of different types of nanofertilizers on plant growth and productivity is presented in Table 7.2.

6 Nanotechnology for Phytopathogen Control

Both plant pests and pathogens are natural habitants of a plant's surrounding environment and are responsible for dramatic crop losses of up to 20–40% annually (Savary et al., 2012). Although the application of chemical pesticides has a rapid effect on phytopathogens, their extensive use and long-term persistence in soils can have negative impacts on soil fertility, and undesirable disturbances in the natural micro and macro soil biota have been observed (Shahid et al., 2018). During recent decades, nanoparticles/nanoformulations have found a significant role in plant

Table 7.2 The effect of different types of nanofertilizers on plant growth and productivity

Types of NPs	Concentration	Plants	Impacts on plants	References
SiO_2 NPs	8 gL^{-1}	*Solanum lycopersicum* L.	Induce seed germination	Siddiqui et al. (2014)
SiO_2 NPs	10 g kg^{-1}	*Zea mays*	Enhance the photosynthetic rate, yield, and productivity of plants	El-Naggar et al. (2020)
SiO_2 NPs	300 ppm	*Saccharum officinarum L.*	Increase leaf photosynthetic responses, chlorophyll fluorescence yield, photosynthetic pigments, and photosynthetic apparatus during chilling stress	Elsheery et al. (2020)
AgNPs	2 mg L^{-1}	*Zea mays*	Maximize the biomass of plants	Sillen et al. (2015)
Fe_2O_3 NPs	4 to 12 μg mL^{-1}	*Triticum aestivum*	Enhance the different growth parameters and N, P, and K uptake efficiency	Jhanzab et al. (2015)
AgNPs	100 mg kg^{-1}	*Coriandrum sativum* L.	Enhance the nutrient quality of edible tissues	Hu et al. (2020)
AgNPs	25 ppm	*Lens culinaris*	Improve the germination rate and early growth of seedlings under salt stress conditions	Sabaghnia and Janmohammadi (2015)
TiO_2 NPs	50 mg L^{-1}	*Medicago sativa*	Enhance the physiological performance and agronomical parameters of plants	Cota-Ruiz et al. (2020)
SiO_2 NPs	1 mM	*Zea mays*	Maximize the biomass of plants	Sillen et al. (2015)
CuNPs	80 mg kg^{-1}	*Triticum aestivum*	Enhance the different growth parameters and N, P, and K uptake efficiency	Jhanzab et al. (2015)

disease management strategies as bactericides, fungicides, nematicides, and/or nanofertilizers to stimulate plant health and overall productivity (Kumar et al., 2022). Metal nanoparticles, viz., copper, silver, zinc oxide, and titanium dioxide, have been widely studied for their antibacterial, and antifungal properties (Kim et al., 2017). In soil systems, some nanofertilizers can also be applied as nanopesticides due to their toxic effect on plant pathogens (Adisa et al., 2019)

(a) Nano-Hydroxyapatite (nHAp) Against Plant Diseases

Hydroxyapatite (HA) is a naturally occurring calcium phosphate mineral, and nano-scale HA (nHA) has been introduced to soil as an amendment for the reduction of the buildup of heavy metal accumulation in crops. These amendments were discovered to have favorable effects on the soil microbiota. For instance, the addition of nHA and microsized HA to Cu-contaminated soils at 1% (w/w) concentration increased both bacterial diversity and abundance (Zhang et al., 2019). The role of nano-scale hydroxyapatite in the disease suppression of *Fusarium*-infected tomatoes has been proved by Ma et al. (2021), as the content of salicylic acid in the shoot was increased by 10–45%. This study demonstrated the potential relationship between the antioxidant and phytohormone pathways in nHA-promoted defense against *Fusarium* infection. The study conducted by Almutairi and Alharbi (2015) showed that a treatment with hydroxyapatite nanoparticles in combination with mycorrhizal fungi was effective in reducing the total population of root-knot nematodes infecting tomato plants. This may conducted by indirect mechanisms via increasing the uptake of essential nutrients and water by plants and stimulating the internal plant defense system against nematode infection.

(b) Silver Nanoparticles Against Plant Diseases

The use of silver nanoparticles (AgNPs) in the management of pathogens is well-recognized in both agricultural and health sectors. The physical characteristics, i.e., sizes, shapes, and coating agents of AgNPs, as well as the type of target pathogen, are important factors that affect the effectiveness of AgNPs as successful pesticides (Mansoor et al., 2021). There are numerous mechanisms via which AgNPs can act against plant pathogens, including the disintegration of the fungal cell wall, surface protein damage, nucleic acid damage by the production and accumulation of ROS and free radicals, and blockage of proton pumps. It has been hypothesized that AgNPs lead to the accumulation of silver ions, which blocks respiration by efflux of intracellular ions and thus damages the electron transport system (Du et al., 2012). Unlike synthetic pesticides, green-synthesized silver nanoparticles can be prepared using eco-friendly approaches. For example, *Serratia* sp., a plant growth-promoting rhizobacterium, has been used for biosynthesizing silver nanoparticles, which showed promising antifungal activity against the spot blotch pathogen of wheat, *Bipolaris sorokiniana* (Mishra et al., 2014).

Fusarium graminearum is the causal agent of *Fusarium* head blight (FHB) disease in cereal crops, resulting in huge yield damage and mycotoxin contamination in food and feed. Jian et al. (2022) introduced AgNPs with a diameter of 2 nm as a promising fungicide for their string behavior fungicide-resistant strains of *F. graminearum*. The application AgNPs has remarkable potential to impair the development and metabolic pathways of such fungi. The activity of AgNPs against sclerotium-forming fungal pathogens was also investigated by Min et al. (2009). AgNPs were efficient in inhibiting fungal hyphal growth in a dose-dependent manner and in sclerotial germination with distinct morphological malformations even at low doses. The nematicidal potentiality of AgNPs has been proven in several studies. For instance, in vitro application of AgNPs at a 0.1 μg ml^{-1} concentration caused irreversible nematode mortality by 100% after 12 h of exposure. The dosage of 3 μg ml^{-1} of AgNPs was effective when applied under field conditions for the management of *Meloidogyne graminicola* infecting rice (Baronia et al., 2020). Another field study demonstrated the role of AgNPs in mitigating damage caused by root-knot nematodes in Bermuda grass, as a notable reduction in gall formation was achieved over 2 years without any sign of phytotoxicity (Cromwell et al., 2014). *Meloidogyne incognita* was more susceptible to different doses of AgNPs than were *Pratylenchus penetrans* and *Tylenchulus semipenetrans* in all the treatments (Shoaib et al., 2021). Furthermore, the insecticidal activity of AgNPs has been proven against *Sitophilus oryzae* L. (Bhandari et al., 2014), *Spodoptera litura* F., and *Tribolium castaneum* and *Trogoderma granarium* (Yasir et al., 2012; Abbas et al., 2020).

(c) Zinc Oxide Nanoparticles Against Plant Diseases

Zinc is widely used to control plant diseases, especially those caused by fungi. However, zinc oxide nanoparticles (ZnO NPs) are more effective in controlling the growth of plant fungal pathogens (Khan et al., 2019). ZnO NPs exert direct suppressive action on fungal growth by destroying the growing mycelia and by eliminating mycotoxins such as fusaric acid (Yehia & Ahmed, 2013). Lakshmeesha et al. (2019) stated that the fungicidal activity of ZnO NPs may be related to an upraise in lipid peroxidation, reactive oxygen species (ROS) levels, and alternation in the ergosterol content that changed the membrane integrity and morphology of conidia. An in vitro test was carried out to screen the nematicidal activity of ZnO NPs, and the results reported significant distribution and accumulation of ZnO NPs in nematode juveniles under direct exposure (Elansary et al., 2021).

(d) Titanium Dioxide Nanoparticles Against Plant Diseases

Titanium dioxide (TiO_2) nanoparticles have been formulated worldwide at large-scale production for several applications, including pesticide, pigment, and cosmetic manufacturing. Recently, titanium dioxide nanoparticles (TiO_2 NPs) have been proven to be promising pesticides when applied at the optimum recommended dosage (Boxi et al., 2016). TiO_2 NPs have triggered the activity of many vital enzymes and enhanced nitrate absorption, accelerating the transformation of inorganic to organic nitrogen, making it available for plants and hence increasing crop yield and productivity (Capaldi Arruda et al., 2015). In addition, they have been shown to exhibit fungicidal and bactericidal activities against various important fungi and phytopathogenic bacteria (Huang et al., 2012). TiO_2 NPs exerted a high insecticidal effect in concentrations above 100 ppm against *Bactericera cockerelli* second instar nymphs (Gutiérrez-Ramírez et al., 2021). TiO_2 NPs exerted toxic effects on *Fusarium oxysporum*, *Sclerotium rolfsii*, and *Rhizoctonia solani*, the causal agents of damping off and root rot disease of sugar beet (El-Argawy et al., 2016). In addition, TiO_2 NPs showed nematicidal potentiality against root-knot nematodes (Ardakani, 2013).

7 Short- and Long-Term Effects on the Environment

The absorption of nanoparticles by plants and their food parts may be the most serious of the issues. The accumulation of nanoparticles is determined by a variety of factors, the most important of which are species of plants, tissues/organs that will be used immediately as food or for food processing, and nanoparticle type and size. Because of the variability in NP–plant interactions, nanomaterials used in nanofertilizers can accumulate in plants and, in some cases, cause toxicity issues not only for plants but also for humans (Lowry et al., 2012). Multiwalled carbon nanotubes, for example, cause phytotoxicity in red spinach (*Amaranthus tricolour* L.), causing growth inhibition, reactive oxygen species production, and cell death (Pullagurala et al., 2018). Cerium oxide (C_eO_2) nanoparticles can accumulate and inhibit the nitrogen fixation potential of soybean (Priester et al., 2012), endangering not only the future of leguminous crops in agriculture but also causing human health issues.

The expansion of cropping systems and the use of fertilizers have undoubtedly contributed to the reduction of world hunger, particularly in Asia and Africa, but this was not without its negative side effects, including decreased nutrient use efficiency (NPK), decreased soil quality, and extremely harmful effects on the environment. Drinking water sources have become contaminated and poisoned over time by the large-scale accumulation of these nutrients caused by runoff and the leaching of mineral nutrients into water bodies (surface and subsurface sources). Additionally, the enrichment of surface water bodies with these plant nutrients results in eutrophication and algal bloom. The primary cause of eutrophication is over usage of phosphate fertilizers (Morari, 2011; Hazra, 2016). Meanwhile, agriculture is responsible for around 11% of the world's anthropogenic greenhouse gas (GHG) emissions, which are mostly attributable to the production of synthetic fertilizers, particularly nitrogen fertilizers, as well as the usage of fertilizers during crop cultivation.

In agriculture, nanotechnology has emerged as a more effective and potentially sustainable way to accomplish production goals and maintain environmental quality using fewer raw materials and active chemicals, improving plant nutrient uptake, and reducing nutrient losses to the environment (Bhardwaj et al., 2022). Nanofertilizers can improve nutrient availability for plants, minimize nutrient losses through leaching, and have a minimal environmental impact. In general, the goal is to minimize energy consumption and reduce nutrient losses to the environment, and this is without a loss (or rather improvement) in plant productivity. Nanoparticles/nanomaterials not only provide beneficial uses in tested doses but also pose an undesirable risk when used in large quantities. Studies have shown that nanoparticles are transported from the surrounding environment into soil-inhabiting organisms (Gupta & Xie, 2018). Some studies have also pointed to nanoparticles moving from crop to crop and from crop to food (Koo et al., 2015), raising concerns about their possible negative effects on soil, plants, and animals. The loss of nutrients from agricultural fields through the leaching process or via gaseous emissions causes environmental contamination and helps climate change (Shalaby et al., 2022).

In this direction, nanofertilizers (along with better water management) will significantly help reduce pesticide pollution (Chai, 2019; Mohanraj, 2019). Many researchers have reported that the use of nanofertilizers has a noteworthy effect on reducing the amount of nanofertilizers (Abdel-Aziz et al., 2016; Ramírez-Rodríguez et al., 2020; Tarafdar et al., 2020), and 10% chitosan-NPK fertilizer use resulted in reducing GHG emissions (Mohanraj, 2017, 2019). Thus, the environmental issues exacerbated by conventional fertilizers and agrochemical use may be mitigated by applying nanofertilizers, even under stress conditions (Astaneh et al., 2021; Bhardwaj et al., 2022). The employment of this technology in agricultural production systems may be constrained by new environmental and unanticipated health safety problems (Ashkavand et al., 2018; Dimkpa & Bindraban, 2017; Mittal et al., 2020) as well as food security issues (Iqbal, 2019; Lopez-Moreno et al., 2018; Rajput et al., 2021; White & Gardea-Torresdey, 2018). Careful and precisely tested responses would help replace conventional technology with nanotechnology and its products for global benefits.

8 Conclusions

Nanofertilizers have a significant impact on agriculture by increasing productivity and resistance to abiotic stresses. As a result, promising nanofertilizer applications in agricultural biotechnology and horticulture cannot be overlooked. Besides that, the possible advantages of nanofertilizers have sparked a great deal of interest in increasing intensive agricultural production potential underneath the current climate change scenario. The primary economic benefits of using nanofertilizers are reduced leaching and volatilization associated with the application of conventional fertilizers. At the same time, such a significant outcome on the yield and quality of the product has a huge potential to increase growers' profit margins through the use of this technology. Despite the exciting results of nanofertilizers in agriculture, their marketability has not yet been prioritized. Uncertainties about nanomaterial interaction with the environment and potential effects on human health must be thoroughly investigated before commercializing nanofertilizers.

The impact of fertilizer distribution is a critical criterion that influences agricultural productivity. Numerous factors influence this phenomenon, including soil type, chemical interactions with other nutrients, leaching effect, and plant uptake efficiency. Extensive use of agrochemicals has resulted in serious deterioration of soil fertility, increased episodes of environmental hazards, pathogen resistance, and general threats to soil biodiversity. Nanotechnology has opened new doors for developing efficient nano-sized materials with better nutrients and agrochemical use efficiencies. Nanofertilizers are nutrient carriers with nano-dimensions ranging from 30 to 40 nm, which can hold many nutrient ions and slowly and steadily release them in accordance with crop demand. The synthesis and characterization of nanomaterials is an important step in achieving the desired properties for improved efficiency and stimulus responses. To achieve the best results and reduce environmental impacts, both short- and long-term responses must be evaluated. Nanofertilizers can aid in increasing utilization efficiency.

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Chapter 8
Green Synthesis of Nanofertilizers and Their Application for Crop Production

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1 Introduction

Nanotechnology is a multidisciplinary branch of science, growing quickly with numerous scientific and technological applications (Anjum et al., 2019; Gul et al., 2021; Nadeem et al., 2018; Saleem et al., 2019). Key principles from chemistry, engineering, physics, and biology are combined in this subject to create new approaches to regulating and creating nanoparticles (NPs) (Verma et al., 2022a). These NPs have dimensions between 1 and 100 nm along at least one axis (Rajput et al., 2021a). Nanotechnology focuses on the creation, study, and utilization of various nanoparticles (NPs). Most NPs are synthesized using chemical and physical methods that involve noble metals like gold, silver, or platinum; however, these procedures are not environmentally friendly (Hatami et al., 2016). There is an urgent need to create a method of producing NPs that is safe for humans and the environment. The safety-by-design philosophy has motivated the development of several green synthesis methodologies for NPs that are safe, simple, cost-effective, reproducible, and scalable. Hence, numerous biological systems are currently widely

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used in green synthesis methods to produce NPs, including yeast, fungi, bacteria, and plant extracts (Dey & Somaiah, 2022). Among these green biological approaches, the green production of NPs based on plants has emerged as the gold standard due to its versatility and relative simplicity. NPs' increased surface area-to-volume ratio enhanced their physical, chemical, and biological features and functions. By providing specific nutrients to plants in nanoparticle form, nanofertilizers boost crop yields (Dimkpa & Bindraban, 2016). Nanoparticulate fertilizers, micro-nanofertilizers, and macro-nanofertilizers are the three types of nanofertilizers based on plant nutrient requirements. With a diameter of 100 nm or less, nanofertilizers can be dispersed as a powder or a liquid (Chhipa & Joshi, 2016). They make nutrients available to plants, which increases plant uptake of nutrients and yield. Briefly described nanofertilizers have the following salient properties: (1) by foliar and soil treatments that give the right nutrients to improve plant growth; (2) being affordable and sustainable producers of plant nutrients; (3) having a high fertilization rate, and (4) playing a significant role in preventing pollution (Adelere & Lateef, 2016). In addition, nanofertilizers are a novel type of fertilizer that helps clean polluted water. In this overview, we'll look in this chapter, how nanoparticles are made, why they're useful as nanofertilizers, how they affect soil and plant quality, and how they interact with various plant tissues. As far as we're aware, this is the first time all of these ideas have been brought together in one book chapter.

2 Causes and Consequences of Nutrient Deficiency

Soil nutrient deficiency is common and has negative effects on soil health, crop yield, and farmer income. Fertilizers are used in large amounts to make crops grow better, but most macronutrients are not easy for plants to use, so they usually only use about half of the fertilizer that is put on them. Most macronutrients are also inaccessible to plants because they are insoluble in soil (Zulfiqar et al., 2019). The leaching and runoff of residual fertilizer all contribute to the aggravation of soil, air, and water pollution. Therefore, increasing productivity by using chemical fertilizers may benefit the economy in the short term, but it compromises the agroecosystem in the long run. Damage to soil health and microflora, disruption of subterranean food webs, mutations in plant and animal DNA, and shifts in ecosystem ecology are all consequences of the overuse of chemical fertilizers (Saini et al., 2021; Verma et al., 2022a, b). Numerous factors, such as nutrient immobilization, leaching, surface run-off, excessive use of pesticides and herbicides, soil erosion, poor soil fertility, temperature, and moisture, all have an impact on the plant's overall nutritional state (Kabata-Pendias, 2010; Nongbet et al., 2022). Worldwide, plant growth and development are being stymied by the excessive application of macronutrients like nitrogen, phosphorus, and potassium, as well as a wide range of micronutrients (Kabata-Pendias, 2010). In order to improve the functional value of crops and the species that live alongside them for better and more efficient nutrient usage, adding value, and cleaning up the environment, we must develop sustainable alternatives to chemical fertilizers that build on basic research and apply creativity. Agricultural domains, such as food security and productivity, can both benefit from the systematic application of nanotechnology. Both micronutrients and macronutrients play important roles in warding off disease in plants. Increased yields, stress resistance, and resistance to pathogen attack are all possible outcomes of using NPs to improve plant nutritional status (Naderi & Danesh-Shahraki, 2013). This demonstrates that nutrient insufficiency in agricultural soils requires targeted, site-specific nanotechnological interventions that release the carrier material (nutrient) in a regulated manner.

3 Nanofertilizers Versus Conventional Chemical Fertilizers

Particularly in poorer nations, chemical fertilizers are applied to plants or sprayed on them without consideration for the nutritional status of the soil or the plant. Because conventional fertilizer applications are not targeted, less fertilizer actually reaches the plant (use efficiency) than is lost through leaching and seepage from agricultural fields into water bodies and the soil beneath, resulting in losses for the economy and the environment (Nongbet et al., 2022). Soil degradation occurs when people repeatedly apply too much fertilizer, which leads to an overabundance of nutrients and, in turn, reduces N fixation, increases the number of pathogens and pests that affect soil flora and fauna, and upsets mineral homeostasis (Kabata-Pendias, 2010).

About 75% of the main N fertilizer, urea, is lost when it is used because it evaporates and gets washed away (Rajput et al., 2021b). Groundwater contamination and water body overburden with nitrates, which lengthen dead zones in water bodies and release nitrous oxide into the environment, are linked to inefficient fertilizer delivery. Nitrous oxide is the third-most common substance that depletes the ozone layer. In comparison to carbon dioxide and methane, it is a greenhouse gas (GHG) with a larger potential for global warming. The anthropogenic interference with the N cycle, which is necessary for the synthesis of proteins in all organisms, has significantly increased as a result of chemically manufactured N fertilizer. Waste is decreased by the progressive, on-demand release of nutrients made possible by nanoparticle fertilizers (Kumar & Sharma, 2020).

Nanotechnology can be used to look into nanoscale materials that can carry fertilizers or act as vectors to let smart nanofertilizers have controlled release kinetics (Zulfiqar et al., 2019). The synthesis and use of metal NPs in nanofertilizers, which is a sustainable alternative to the current, pricey, and environmentally harmful conventional chemical fertilization processes, has sparked a "Nano-Bio Revolution" in the field of nano-enabled NP synthesis technologies. Another advantage of nanobiofertilizers is the employment of biological systems to create these NPs due to the fertilizer's focused needs-based release and low waste (Fig. 8.1) (Davari et al.,

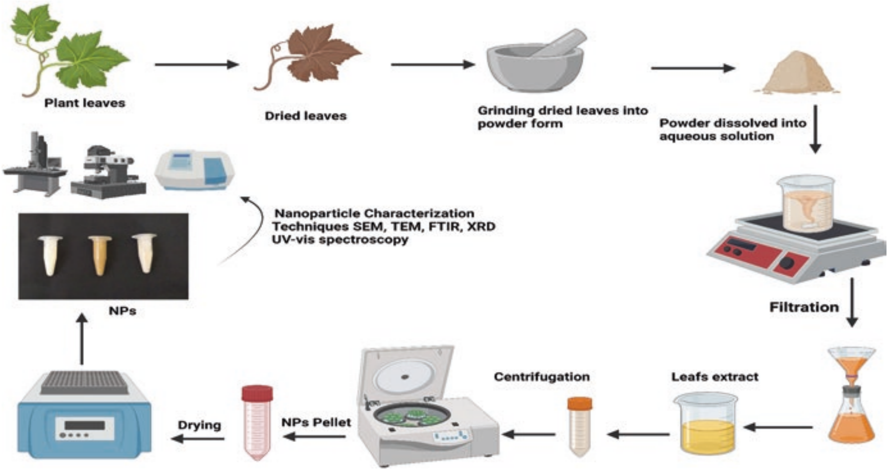

Fig. 8.1 Nanofertilizers are specialized fertilizers that consist of nanosized particles that contain essential nutrients and minerals required by plants for their growth and development. These nanofertilizers are designed to improve crop yields, enhance soil fertility, and reduce the use of traditional fertilizers, which can have negative environmental impacts

2017). NPs are small, have a large surface area, are easily soluble, and can move around. They also have a high surface tension, which helps control the release of the fertilizer. NPs can translocate rapidly in plants. They enhance protection through nanopesticides, nanofertilizers, and nanoherbicides and hasten the release of nutrients by nanofertilizers (Karthika et al., 2018).

4 Plant-Based Green NPs Biosynthesis

The importance of "Green Chemistry" to "Sustainable Development" has attracted a lot of interest over the past 10 years (Kates et al., 2012). Sustainable development is growth and development that satisfies current needs without endangering those of future generations (Kates et al., 2012). Many chemical industries depend on sustainable development because of its emphasis on minimizing the effects of pollution and making the best use of finite natural resources (Omer, 2008). The three crucial conditions for the eco-friendly production of NPs are the choice of a green or eco-friendly solvent (the most frequently used being water, ethanol, and their mixes), a suitable nontoxic reducing agent, and a safe chemical for stabilization (Rakgotho et al., 2022).

Nanoparticles have been synthesized via numerous synthetic routes, the prevalent being biosynthetic, chemical, and physical. Toxic and hazardous chemicals are typically used in chemical processes, which increases costs and poses other environmental risks (Narayanan & Sakthivel, 2011). On the other hand, green

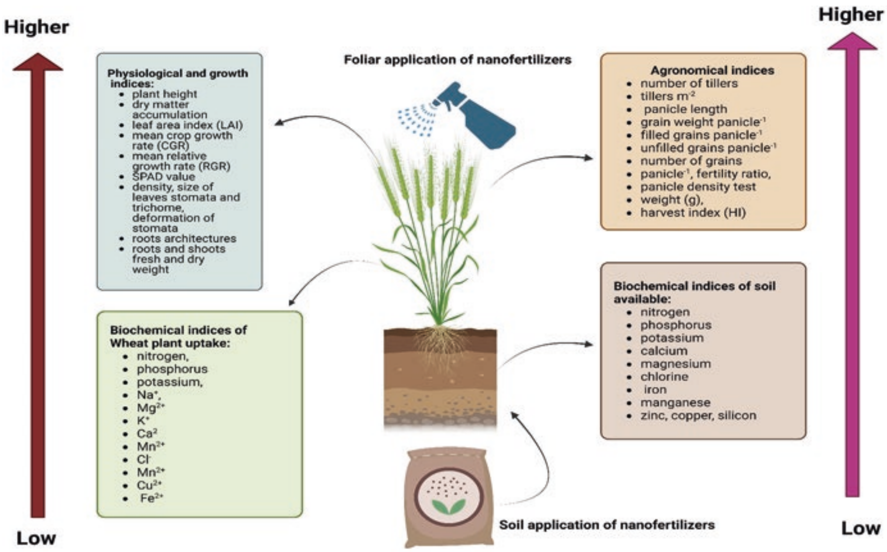

Fig. 8.2 The biosynthesis of plant-based green nanoparticles (NPs) involves several processes, starting from the selection of the plant source, extraction of bioactive molecules, and synthesis of NPs using these molecules

synthesis is a nonhazardous, biocompatible, and eco-friendly way to create NPs for uses beyond medicine (Narayanan & Sakthivel, 2011). Green synthesis is performed using fungi, algae, bacteria, and plants. However, many different NPs have been synthesized using plant components like fruits, stems, seeds, leaves, and fruits (Fig. 8.2) (Razavi et al., 2015). Indeed, NPs of tunable size, shape, and composition can be manufactured from plant extracts. Their extract contains a wide variety of phytochemicals, some of which may act as natural stabilizing and/or reducing agents in the production of NPs (Patil & Chandrasekaran, 2020). In addition to their high biological potential and a variety of possible applications in industries such as nanomedicine, cosmetics, agriculture, bioengineering, and food science, NPs derived from plants are widely acknowledged to be safer for human consumption than their chemically synthesized counterparts. To guarantee consistency in their production, safety, and biological function, these NPs must be completely and correctly specified. This is why a wide variety of physicochemical techniques are employed to precisely define the synthesized NPs. (Faisal et al., 2021). Scanning electron microscopy (SEM), transmission electron microscopy (TEM), photoluminescence analysis, attenuated total reflection, UV-visible diffuse reflectance spectroscopy, Fourier transform infrared spectroscopy, and dynamic light scattering are a few of these techniques (Stefanos et al., 2018) (Fig. 8.2).

4.1 Extracts from Fruit Waste and Vegetable Waste

Fresh fruits and vegetables make up the biggest part of food waste in stores (Eriksson et al., 2012). These can be anything from the leftover pulp from pressing fruit to the ends of cabbage (Wijngaard et al., 2009). In 2008, Americans lost $42.8 billion worth of fruit and vegetables at retail and consumer levels, or about $141.50 per person (Sagar et al., 2018). These can be made at different points in the food supply chain, from the farm to the table. This includes both pre- and post-consumer steps such as harvesting, transporting, storing, marketing, and processing (Wijngaard et al., 2009). Green and sustainable silver nanoparticle synthesis can be achieved with the help of the abundant polyphenols, dietary fibers, enzymes, and proteins found in fruits and vegetables (Wijngaard et al., 2009). Fruits such as orange peels, banana skins, apple cores, and pear cores are all examples of industrial food waste. Oranges, grapefruits, lemons, limes, and mandarins are among the world's most widely grown fruits (Shen et al., 2013). Approximately 30% (w/w) of the grapes used in wine production are likely to be wasted as solid by-products like marcs, pomace, and stems (Shen et al., 2013).

4.2 Extracts from Spent Fruit and Vegetable Peels

Fruit and vegetable peels, the most common byproduct of food processing, have been identified as a rich resource for numerous bioactive compounds. When fruit is processed, the peels are often thrown away as waste (20–30% for bananas and 30–50% for mangoes), despite their potential use in the environmentally friendly green synthesis of silver nanoparticles (Kowalska et al., 2017). Apple, white grapes, and red beet peels are also examples of food waste (Choi et al., 2015). In contrast, citrus fruits account for 115 million tons of annual production, with about 30 million tons processed commercially for juice production. Nearly half of the wet-fruit mass is the peel after industrial processing of citrus fruits (Choi et al., 2015). Orange is the most important citrus fruit, with 50 million tons, and the peel makes up 44% of waste (Rafiq et al., 2018). Some studies have been done on extracts from fruit and vegetable waste.

4.3 Extractions from Spent Cereal

Cereal wastes are produced both during and after the harvesting of the grain. Straw, stover, peelings, cobs, stalks, bagasse, and other lignocellulosic residues are the most common forms of waste produced during harvest. Somewhere in the neighborhood, 200 billion tons of lignocellulosic biomass are produced each year in the world's primary agricultural sector (Guo et al., 2010). Grain processing also results in by-products like gluten meal (GM) and dried distillers grains and solubles

(DDGS). It was estimated that the United States produced around 44 million tons of DDGS in 2018 (Chatzifragkou et al., 2015). Additionally, China annually produces over 840,000 tons of corn GM, most of which ends up as feed or in the trash (Zhuang et al., 2013). Therefore, the cereal byproducts obtained additional value as reducing agents for the synthesis of silver nanoparticles because of their high production. Waste from wheat, corn, and rice cereals could be used to make extracts that act as reducing agents. The main components of straw and husk waste are cellulose, hemicellulose, and lignin, while the primary components of GM and DDGS are proteins (Farooq et al., 2012; Li et al., 2019). Straw, husk, and bran extracts have been used as reducing agents in some studies.

5 Role of Different Green NPs in Agriculture Sectors

5.1 Silver NPs

Due to their antimicrobial properties, silver nanoparticles have found widespread application in a variety of settings, including medicine, industry, and sports (Song & Kim, 2009). Different optical, electrical, and thermal characteristics, including high electrical conductivity and antibacterial and catalytic capabilities, are present in them (Ahmed et al., 2016). Because of their chemical stability, excellent conductivity, catalytic properties, and—most importantly—their antibacterial, antiviral, antifungal, and anti-inflammatory properties (Ahmed et al., 2016). Composite fibers, cryogenic superconducting materials, cosmetics, the food sector, and electrical parts have all used them. Due to a direct interaction between the Ag ions in the silver nanoparticles and the plant's morphology and physiology, plants treated with silver nanoparticles exhibit greater resistance to fungal, bacterial, and nematode attacks (Ahmed et al., 2016). Ag nanoparticles may also hasten seed germination, according to a related theory (Kale et al., 2021).

5.2 Copper NPs

There are two types of copper oxide nanoparticles: copper (I) oxide and copper (II) oxide (Cu_2O). The CuO form has been the subject of extensive research due to its beneficial features, including high-temperature superconductivity, spin dynamics, and electron correlation. These substances are employed in solar energy conversion, batteries, high-temperature superconductors, gas-sensing devices, catalysis, and field emission (Ren et al., 2009). Because of their high surface-to-volume ratio, continuously renewing surface, and fluctuating microelectrode potential values, nanoparticles are frequently used as catalysts. They are widely used in the healthcare and wastewater treatment industries because they are efficient against germs like *Bacillus subtilis* (Ruparelia et al., 2008).

5.3 Zinc NPs

Nanotechnology is the twenty-first century's most innovative field. The commercialization of nanoproducts is the subject of a great deal of ongoing research around the globe. Nanoparticles have become increasingly significant in comparison to their bulk counterparts because of their distinctive characteristics. Nanoparticles made from zinc oxide have found widespread application in a variety of fields, including gas sensing, biosensing, cosmetics, drug delivery, and more. The extraordinary optical, physical, and antibacterial qualities of zinc oxide nanoparticles (ZnO NPs) imply that they might find wide use in agricultural contexts. ZnO NPs can be produced using a variety of chemical processes, including hydrothermal synthesis, vapor transport, and precipitation. In addition, a number of plant extracts can be used to biosynthesize ZnO NPs When compared to chemical synthesis, this green synthesis is much safer and friendlier to the environment. Zincite has become well-known because it is used in many industrial fields. ZnO NPs have been used to make solar cells, gas sensors, chemical absorbents, varistors, hydrogenation catalysts, and photocatalytic degradation catalysts. They have also been used in optical and electrical devices (Pérez-Hernández et al., 2012).

5.4 Iron Oxide NPs

In nature, iron can be found in three different oxides: magnetite (Fe_3O_4), maghemite (Fe_2O_3), and hematite (Fe_2O_3) (Kaningini et al., 2022). Due to their low toxicity, superparamagnetic properties, and easy separation methodology, magnetic iron oxide nanoparticles, such as magnetite and maghemite, have garnered a lot of attention (Kaningini et al., 2022). Their use in diagnostic magnetic resonance imaging, thermal therapy, and drug delivery are particularly intriguing biomedical applications (Ali et al., 2016). Iron oxide nanoparticles are highly magnetic and have a wide range of uses, such as magnetic seals and inks, magnetic recording media, catalysts, ferrofluids, contrast agents for MRI, and therapeutic agents for cancer treatment, among others (Teja & Koh, 2009). As a novel and promising technology, the use of iron oxide nanoparticles in agriculture still has room for development. For instance, Fe_2O_3 nanoparticles increased growth in peanuts by enhancing the availability of Fe in the soil and plant cells by regulating the contents of phytohormones and the activity of antioxidant enzymes (Ali et al., 2016). The most common methods of administering iron oxide nanoparticles to plants are soil drenching and foliar application (Teja & Koh, 2009). Many chemical, physical, and biological processes can be used to prepare iron oxide nanoparticles (Maswada et al., 2018). It has been demonstrated that biosynthesis of iron oxide nanoparticles is a more economical and environmentally friendly option than physical and chemical methods of production. These nanoparticles are safe to use because they are formed using plant-based materials like sugars, antioxidants, amino acids, and proteins (Fathi et al., 2017).

5.5 Silicon NPs

Some metal and nonmetal NPs, including SiNPs, have been shown to improve plant resilience against biotic and abiotic stress by mitigating their negative effects (Pinedo-Guerrero et al., 2020). In addition, it strengthens plants' immunity to a wide range of toxic metals (Alsamadany et al., 2022). Nanotechnology is a low-cost, nontoxic way to boost agricultural output without endangering human health or the environment. Since SiNPs are manufactured using greener concepts and will mitigate the negative effects of chemical fungicides, their use in agriculture is predicated on the idea that they will reduce hazardous environmental inputs and excessive fertilizer costs. SiNPs have the potential to be used in agriculture because of their executive characteristics, such as their large surface area and small dimension, which ensure a realistic dispersion in plant tissues (Alsamadany et al., 2022). Researchers and practitioners have investigated NPs for use as soil stabilizers. In order to deposit SiNP in the shoot, it must first be polymerized in the root tissues (Alam et al., 2022). The verified mechanism, however, has yet to be investigated (Coutris et al., 2012). Pesticides, herbicides, and fertilizers containing SiNPs were applied topically to plants (Martin-Ortigosa et al., 2014). In addition to their potential use in agriculture to improve soil water retention, SiNPs have been proposed as carriers for the transport of materials such as proteins, nucleotides, and other compounds in flora (Martin-Ortigosa et al., 2014). SiNPs' versatility stems from their many desirable characteristics, including their low production cost, hydrophobicity, high surface area/pore volume, and biocompatibility. For instance, silica nanoparticles (SiNPs) have been used to solve problems in agriculture due to their exceptional adsorption power and nontoxic nature. Recently, SiNPs have been used to increase crop yields, foster greater plant growth, and foster resistance to disease. New possible uses for SiNPs are still being explored and researched. The enhancement of agricultural output is viewed as nanotechnology's second-most important application.

6 Methodology for Application of Nanofertilizers

6.1 Uptake of NPs from Soil via Roots System

NPs pass through the root's epidermis, cross the endodermis, and reach the xylem, where they are carried to the plant's leaves. When NPs are between 3 and 8 nm, they are able to pass through the cell wall pores and enter the cell (Lin & Xing, 2008). Since the Casparian strip has wounds, NPs can also enter through the root tip meristem or at the sites of lateral root formation. NPs need to be able to cross cell membranes and cell walls in order to reach the root epidermis. They then travel through the blood vessels (xylem). Cell wall pores range in size from 3 to 8 nm (Lin & Xing, 2008), making it difficult for NPs to enter; however, it has been demonstrated that

NPs cause the formation of large pores in cell walls, allowing for their internalization. In contrast to their inability to absorb AuNP of size 18 nm (Markus et al., 2016), tomato roots can absorb AuNP of size 3.5 nm. *Arabidopsis thaliana* can absorb 14–200 nm spherical silica NPs through its roots (Kiefer et al., 2015). Furthermore, 40 nm spherical AuNPs were transported from the roots to the shoots of *Solanum lycopersicum* (Ahmed et al., 2023). Feeder root hairs are the entry point for microelements into the plant. Root exudates contain organic acids and phenols, which dissolve Ca, Mg, Fe, S, or Zn-encapsulated microspheres (Wang et al., 2020). Leaching occurs after fertilizers are applied to the soil, causing nutrient loss and pollution of both soil and water. Furthermore, greenhouse gases and climate change are attributed to the use of certain agrochemicals. The controlled intracellular release of target compounds in protoplasts using mesoporous silica nanoparticles. Treatments to reduce nitrogen leaching in the soil included the use of urea coated with polyolefin, neem, and sulfur (Younis et al., 2020). Hydroxide nanocomposites with two layers were used in a study to gradually release nutrients. The relationship between soil and water retention and the slow release of integrated superabsorbent fertilizer (Dennis et al., 2015). The surface cross-linked product performed well in terms of slow release and soil moisture conservation. Plants, interestingly enough, can respond to NPs as well. After using bentonite and TiO_2 nanoparticles, the size of the pores in the root cell walls of *Zea mays* seedlings decreased from 6.6 to 3.0 nm (Janmohammadi et al., 2016).

6.2 Uptake of NPs from Foliar via Stomatal System

Plants' physiological characteristics influence their ability to absorb nanoparticles (Alabdallah & Alzahrani, 2020). Typically, trichomes, stomata, stigmas, and hydathodes absorb NPs before they are carried throughout the plant through the phloem and xylem (Zhao et al., 2020). There are two pathways for NP translocation: apoplastic and symplastic. The apoplastic pathway involves the transport of macromolecules (such as NPs, water, and so on) across the apoplast, or cell wall, and into the cytoplasm. However, the size exclusion limits (SELs) of cell walls (5–20 nm) restrict the movement of such macromolecules during this transport (Mejias et al., 2021). In contrast, the symplastic pathway involves the transfer of macromolecules (NPs) across the plasma membrane through a process called plasmodesmata. Endocytosis is a process that allows the NPs to enter the cells from the cell wall (Schwab et al., 2016). The nanoparticles' ability to enter the plant cell wall and be transported to the tissues is dependent on the diameter of the stomata, which ranges from 5 to 20 nm (Schwab et al., 2016). The SELs of the plasmodesmata, which range in size from 3 to 50 nm (Schwab et al., 2016), control the flow of material through the symplast route. Transport into the vascular system is blocked by the Casparian strip (Schwab et al., 2016). Although SEL is necessary for the entry and translocation of NPs, some research suggests that SELs of the cell wall, plasmodesmata, and Casparian strip can be influenced by enzymes, allowing NPs as large as

50 nm to be internalized. Researchers found that cucumber leaves were able to absorb and transport CeO_2 NPs throughout the plant (Sangeetha et al., 2021). Spraying lettuce leaves with AgNPs allows them to be taken up and distributed throughout the plant (Das et al., 2018). Foliar applications of NPK NFs were more effective than edaphic applications of NPK conventional fertilizers in boosting potato yields (Drostkar et al., 2016). The use of NPK NFs has been shown to have positive effects on the environment, the economy, and the ecology. To further combat phytopathogens, NFs can be mixed with nanoparticles. Enzymes produced by stressed plant cells can release polymer wall nanocapsules from their chemical bonds. The plant secretes mucilage when it senses an onslaught from pathogens (Ha et al., 2019). Furthermore, nanoparticle accumulation on leaf surfaces can lead to foliar heating, which in turn can lead to changes in gas exchange due to stomatal obstruction (Ha et al., 2019).

7 Plant–NP Interaction

Scientific and technological progress is helping the agricultural industry by providing us with novel approaches and tools to address longstanding challenges. New nanoformulations for environmentally friendly farming are constantly being developed because of advancements in nanotechnology (Fraceto et al., 2016). This latest generation of substances has the tendency to immediately affect plant physiology upon entry into the complicated plant–soil system, and this fact may be used to comprehend the subsequent impacts. Furthermore, a crucial understanding of the positive or negative interaction of these nanomaterials (NMs) with plants is required for the controlled delivery of active chemicals. Hence, they might offer unique opportunities for creating superior products based on nanoparticles. Natural NM concentrations are reportedly significantly lower than those deemed dangerous, as well. Yet, there are still certain blanks that need to be filled in with thorough safety evaluations (Fraceto et al., 2016).

There are many barriers within plants, ranging in size from micrometers (mm) to nanometers (nm), so the size of NPs must be taken into account as a crucial factor when studying absorption (Fraceto et al., 2016). For instance, a cuticle membrane is composed of cells in the epidermis foliar. When the epidermis opens for gaseous exchange, a stoma with two guard cells forms a pore that is about 3–12 nm wide and 10–30 nm long (Avellan et al., 2021). Because of these stomatal pores, NPs can move freely among the plant tissues. The epidermis's cuticle layer and the stomata's trichrome have noticeably different permeation properties. However, the cuticle layer, which has an exclusion size limit in the nm range, is more abundant on the leaf epidermis (Ali et al., 2021). NPs in the 4–100 nm size range were described to be able to penetrate the cuticle by dissolving the waxy layer, and NPs larger than 50 nm with fluorescent tags may buildup in the epidermis just below the cuticle where there are no stomata (Larue et al., 2014). Polymeric NPs with a diameter of 43 nm can enter *Vicia faba* leaves only through the stomata, while particles of 1 m in size could not do so (Larue et al., 2014). When NPs enter the body through the stomata, they tend to settle on the substomatal cavity cell wall. TEM analysis of the *Nicotiana benthamiana* plant revealed the potential absorption of tiny NPs as 20 nm Fe_3O_4 NPs. Understanding the route that NPs take once they enter plants is crucial because it reveals potential sites of accumulation. The apoplast and the symplast are two of the plant's most vital pathways for the upward and downward movement of NPs. Both the symplastic and apoplastic pathways allow for transport through intercellular spaces, the former through the cytoplasm of neighboring cells and the latter utilizing the xylem vessels and cell walls of neighboring cells (Roberts & Oparka, 2003). Plasmodesmata acts as a cytoplasmic connection to allow the movement of particles between adjacent cells and allow for communication between the cells. They have a diameter of 20–50 nm and are encased in particles that are only 3 nm in size (Roberts & Oparka, 2003).

The uptake, absorption, and trafficking of NPs within plants confer a high degree of freedom on these particles. Plants' surface receptors, transporters, and specialized membrane proteins are all altered by the NMs' physicochemical contact with them due to their energy and surface charge (Perez-Labrada et al., 2019). In comparison with their unmodified counterparts, NPs with varying surface charges exhibit distinct differences in aggregation capacity and surface attributes (Hotze et al., 2010). An unequal distribution of permanent negative charges and hydrophobic and hydrophilic constituents (cellulose fibers and lignin have surface potentials of 15 and 45 Mv, respectively) make up the cell wall, a biological membrane present within the leaves (Santiago et al., 2013). The NPs with a positive charge are absorbed in tissues and can be facilitated by the negatively charged cell wall. The infiltration of cationic NPs instead of anionic NPs may be facilitated by ion exchange at the surface of plant cell walls, which are negatively charged (Meychik et al., 2005). Nevertheless, negatively charged NPs benefit considerably from improved transport efficiency. Zhu et al. demonstrate substantially stronger binding of NPs with a positive charge at the surface of the root, which explains how the movement and uptake of AuNPs are reliant on their surface charge. However, the internalization and translocation rates of negatively charged NPs were shown to be greater (Meychik et al., 2005). Negatively charged CeO NPs showed limited root accumulation but increased shoot internalization, possibly by overcoming electrostatic repulsion. Positively charged CeO NPs strongly bind to the surface of roots (which are negatively charged) (Lui et al., 2019).

8 Techniques for Assessing Nanoparticle Distribution and Distribution Quantification

In addition to the need for new methods to monitor plant–NM interactions, there is a pressing need for more data on the quantification of NP uptake and translocation within plants and when they are discharged into the environment. In this study, a vibrating sample magnetometer was used to measure the concentration and uptake of iron (Fe_3O_4) NPs in the roots and leaves of pumpkin (*Cucurbita maxima*) plants (Zhang et al., 2022). Similarly, the magnetization dependency of Fe_3O_4 NPs on both magnetic field and temperature allows for their detection, quantification, and tracking in various plant organs (Govea-Alcaide et al., 2016). It is difficult to discriminate between intact Fe_3O_4 NPs and leached ions, which is the principal barrier to the tracking and translocation of Fe_3O_4 NPs. This problem is overcome by combining magnetic particle spectrometry with traditional atomic absorption (Govea-Alcaide et al., 2016). In addition, translocation of multi-walled carbon nanotubes (MWCNTs) and C70 fullerene from the roots to the leaves of rice (*Oryza sativa*) was seen using electron microscopy; yet, the quantity of NPs absorbed by the plants was not measured (Lin et al., 2009). Here, Raman spectroscopy and transmission electron microscopy (TEM) were utilized to quantify MWCNT uptake in wheat and rapeseed plants (Larue et al., 2012). The detection and localization of different NMs in plants can be aided by the use of important imaging methods, including X-rays and computed tomography. Recently, a combination of improved Darkfield (DF), X-ray computed nanotomography (nano-CT), and hyperspectral (HSI) imaging was employed to pinpoint the precise location of gold NPs in *A. thaliana* roots. Better tools for characterizing and evaluating the NP–plant interaction at the cellular level can be obtained by combining two-dimensional (DF-HSI) and three-dimensional (3D) (nano-CT) approaches (Larue et al., 2012). Another noninvasive, highly sensitive method for visualizing NPs in lettuce (*Lactuca sativa*) is to combine autoradiography, positron emission tomography, scanning electron microscopy (SEM), and transmission electron microscopy (TEM) (Zhang et al., 2022). In a ground-breaking examination, scientists evaluated the effect and interaction of garlic (*Allium sativum*) with TiO_2 NPs using UV-visible spectra, laser-induced fluorescence, and time resolved. As a result, the garlic plants' leaves had more chlorophyll and were more actively photosynthesizing than the control. The ratio of the intensity of the red to far-red chlorophyll fluorescence bands dropped, but the scientists also observed an increase in the photosynthetic function and amount of chlorophyll (Bharti et al., 2018). The innovative method of two-photon excitation microscopy was used to identify MWCNTs, TiO_2, and cerium oxide NPs in wheat tissues in vivo (Wild & Jones, 2009). There are a few other crucial methods such as microscopy and spectroscopy. Microscopy techniques offer a distinct benefit for evaluating NPs in various samples, but they also have several major drawbacks, such as requiring sample preparation, analyzing just a subset of the sample, and providing only limited 3D imaging. Hence, one promising method for detecting, characterizing, and quantifying NMs is single-particle inductively coupled plasma mass spectrometry SP-ICP-MS) analysis with ICP-MS (inductively coupled plasma mass spectrometry (Wild & Jones, 2009). The uptake of CuO NPs in lettuce, collard greens, and kale is also measured using SP-ICP-MS for human consumption (Keller et al., 2018). As soon as they enter the plant, NMs easily undergo chemical changes; hence, analytical methods based on mass spectrometry are helpful for differentiating between their various forms. One method involved the use of SP-ICP-MS and ESI tandem MS to ascertain what happened to the ZnO NPs present in the lettuce (Keller et al., 2018). To study the route of uptake and accumulation of the AuNPs in watermelon plants, we used ICP-MS to quantify the NPs (Raliya et al., 2016). The combined efficacy of these methods, or their use in tandem, is where their benefits shine. Nath et al. utilized SEM, EDS, and SP-ICP-MS to investigate the concurrent absorption, retention, and dispersion of Cu, Ag, and ZnO NPs in *A. thaliana* (Keller et al., 2018). Similarly, three orthogonal techniques—SP-ICP-MS, electron microscopy, and ICP-optical emission spectrometry—are combined to study the absorption and size distribution of TiO_2 NPs in tissues of the rice plant (*Oryza sativa*).

9 Constructing Nanoscale Fertilizers

Biofabrication of NPs utilizing biological processes has drawn a lot of interest due to the growing need and desire for ecologically friendly, efficient, and nontoxic nanoparticle formation methodologies (Hininger et al., 2004; Sheiha et al., 2020). In plants and microorganisms, NPs are synthesized by compounds like alkaloids, pigments, amines, enzymes, proteins, and phenolic compounds (Abdelnour et al., 2020). Chemical processes use harmful chemicals and have harmful impacts on the surroundings, while physical processes are prohibitively expensive.

10 Function of Nanofertilizers

Application of conventional nutrients to the soil reduces the ease with which plants can access those nutrients in several ways. As a result, foliar spraying is the most effective strategy for addressing nitrogen shortages and boosting crop yield and quality (Ombodi & Saigusa, 2008). Less fertilizer use has other benefits, including less soil pollution and better nutrient use efficiency. Nano-coated compounds with a size higher than 10 nm have been reported to increase penetration across stomata (Tarafdar et al., 2014). Due to their large surface area, regulated release kinetics to the desired area, and high sorption tendency, nanofertilizers are an effective delivery approach (Tarafdar et al., 2014). In many cases, nanocarriers can schedule and place the delivery of nutrients perfectly. As a result, the best available research on the effects of nanofertilizers on crop productivity, efficiency, resistance to abiotic stress, and reduction in heavy metal toxicity should be presented.

10.1 Crop Growth and Development

Nanofertilizers boost the availability of nutrients, which is crucial for the biochemical and physiological processes involved in crop growth. The use of nano-NPK encouraged the growth of wheat leaves due to the ease with which it was absorbed by the leaves via the exchange pores or stomata. The effects on cotton and pearl millet were the same (Tarafdar et al., 2014). The growth of plants and dry biomass was significantly boosted by the foliar application of Zn nanofertilizer (Gharaei et al., 2015). As plant quality and production rise, it is feasible that physiological processes like antioxidant activity and chlorophyll concentration will also benefit (Rezaei & Abbasi, n.d.). Natural auxin (indole acetic acid [IAA]) synthesis is influenced by zinc, which also stimulates important enzymes in the metabolism of glucose and protein, growth regulators, biological membrane integrity, and pollen formation (Sharifi et al., 2016). When nano-Zn fertilizer was applied, there was a corresponding increase in the levels of hormones that stimulate plant growth. Foliar applications of nano-Fe fertilizer to both fodder corn and *Ocimum basilicum L.* followed the same pattern (Sharifi et al., 2016). TiO_2 foliar sprays also boosted plant total dry matter by encouraging N assimilation, improving photoreduction activities of photosystem II and the electron transport chain, and eliminating reactive oxygen species.

10.2 NP-Based Improvement of Crop Plant Physiology

When nanofertilizers were given to crops, a notable improvement was observed in both physiological and biochemical measurements. Biocompatible magnetic nanofluid (MNF) increased the overall chlorophyll content of sunflower leaves, but at higher amounts (>0.75% MNF), chlorophyll content decreased (Pîrvulescu et al., 2015). Foliar treatment with nTiO_2 considerably boosted the carotenoid, anthocyanin, and chlorophyll contents of maize crops, leading to a higher overall harvest (Morteza et al., 2013). Barley's anthocyanin and chlorophyll levels were shown to be elevated after spraying tiny TiO_2 particles onto leaves (Janmohammadi et al., 2016). In reality, nTiO_2 reinforces the chlorophyll structure, boosts RUBISCO activity, increases pigment production, and intensifies the chlorophyll's ability to capture sunlight. After being treated with nano TiO_2, spinach grew more and had a greater protein content and N metabolism (Cai et al., 2019). The leaf chlorophyll content of spinach treated with nTiO_2 was discovered to be 17 times larger than that of spinach treated with the control treatment, and the photosynthetic rate was found to be 29% higher (Gao et al., 2013). Nano-Zn fertilizer reduces peroxidase, catalase, and oxidase activity while increasing polyphenol content in cotton and soybean crops (Sheykhbaglou et al., 2010). An increase in plant dry biomass, chlorophyll, and total soluble leaf protein was seen after a pearl millet crop received foliar Zn nanofertilizer treatment (Tarafdar et al., 2014). The levels of chlorophyll, phosphorus, and essential oil in savory plants all rose after being treated with nano-Zn (Gharaei et al., 2015). Using nanofertilizers increased the rice crop's antioxidant capacity. Secondary metabolites known as antioxidants are produced by plants against environmental challenges like water stress, salt stress, and nutritional deficiency. The nanofertilizer delivers sufficient nutrients to increase antioxidant activity since it is better absorbed by plant cells.

10.3 Impact on Yield Quantity and Quality of Crop

In recent years, researchers have investigated whether nanofertilizers might boost agricultural productivity. Using nanofertilizer in a foliar spray significantly increased wheat harvest success (Drostkar et al., 2016). More generation of growth hormone and improvement in metabolism after foliar application of NPK nano fertilizers led to greater chickpea production and production elements (Drostkar et al., 2016). Cotton production is significantly affected by the usage of nanofertilizers. The development of chickpeas can be manipulated for the better by the use of nanofertilizers (Drostkar et al., 2016). Grain output in pearl millet was improved by 37.7% after Zn nanofertilizer was sprayed on the plant's leaves (Drostkar et al., 2016). In addition, when nano-Zn was applied to sunflower plants, the quantity of oil in the seeds increased (Rajput et al., 2018). Nano-Zn oxide improved the bioavailability of zinc in groundnut crops, leading to a higher pod yield (Prasad, 2008). Nano-Zn′s low volume-to-surface area ratio improves Zn productivity and absorption (Pérez-Hernández et al., 2012). Compared to conventional $ZnSO_4$ fertilizer, nano-Zn fertilizer only needs to be applied once every 10 years (Thounaojam et al., 2021). An increase in rice grain production and its constituents was observed after a concentration of 40 ppm of nano-Zn oxide particles was added to the soil (Ghasemi et al., 2017). After the foliar application of metal oxide nanoparticles (ZnO, MgO, and CuO), seed cotton production increased by 33%, 22%, and 18%, respectively. Nano-zinc (Zn) and boron (B) fertilizers applied by foliar spray improved pomegranate fruit production (636 mg Zn tree-1, and 34 mg B tree-1) (Davarpanah et al., 2016). By applying $nTiO_2$ to the leaves of the crop, farmers can influence the development of the crop and boost both production and production elements (Janmohammadi et al., 2016). The increase in photosynthetic activity caused by $nTiO_2$ spraying has been proven to improve yield characteristics and the quantity of photoassimilates present in leaves (i.e., source capacity). Furthermore, the application of $nTiO_2$ increased crop production and fertilizer use efficiency by a sizeable amount (Janmohammadi et al., 2016). $nTiO_2$ enhanced nitrogen metabolism and photosynthetic complexes, resulting in increased fresh and dried plant mass (Janmohammadi et al., 2016). Moreover, the nanoparticle $nTiO_2$ photocatalyst activity helped maize development and grain yield by increasing pigment formation, increasing chemical functions, and converting the energy of light into active electrons (Zahedi et al., 2021). The use of Fe nanofertilizer boosted soybean harvest output (Sheykhbaglou et al., 2010). Applying 0.5 g L^{-1} nano-Fe as a spray to black pea plants resulted in greater increases in pods per plant, 1000-seed weight, yield, and chlorophyll content compared to bulk Fe (Delfani et al., 2014). Another study indicated that, compared to the control, grain yield was improved by 23.3% after spraying nano-Fe (2%) on leaves (Jaberzadeh et al., 2013). Yield and yield components were both improved after manganese (Mn) nanoparticles were applied to *Vigna radiata* (L.) (Ghafariyan et al., 2013). Increased nutrient utilization efficiency brought about by the use of nano-Mn, nano-Fe, and nano-Zn (30 ppm) led to a rise in peanut production and quality (Mekdad, 2017). As a result of its antimicrobial effects, foliar application of nano silver (Ag) enhanced potato tuber yields, which suggests that healthier seed tubers may remain in the soil for longer, leading to more robust plants (Davod et al., 2011). Peanut plant height, lateral branching, seed weight per plant, pod maturity, pod production, seed length, seed quantity per plant, pod and seed yield, and all biological functions were improved by foliar usage of nanochelated molybdenum (Davod et al., 2011).

Improved crop quality requires the addition of nutrients. Crop quality improved when nanofertilizers were used instead of conventional fertilizers. Utilizing metal oxide nanoparticles enhanced cotton's fiber durability and uniformity ratio (Prasad et al., 2012). The protein content of peanuts grown with nanofertilizer is greater (Prasad et al., 2012). By applying foliar nano-Fe and Zn fertilizers to fodder maize, compared to bulk materials, crude protein, and soluble carbohydrate quantities were increased (Sharifi et al., 2016). Zinc is essential for the production of chlorophyll, carbonic anhydrase, starch, and photosynthesis; hence, Zn fertilizers increase levels of soluble carbohydrates, hastening the development of carbohydrates (Sharifi et al., 2016). Peanut seeds saw an increase in their total protein, oil, soluble sugars, and starch content after being treated with nanofertilizers (Zulfiqar & Ashraf, 2021). Zinc is essential for protein synthesis in plants (Pérez-Hernández et al., 2012). Root development is aided by Zn, which aids in the uptake of vital nutrients, including nitrogen (N), which is important for the formation of protein. Zinc aids in the metabolism of plant hormones, particularly indole acetic acid (IAA), carbohydrates, and proteins, which help in the synthesis of starch and seed maturity (Yu et al., 2020). The protein content of black-eyed pea seeds was more affected by nano-Fe than bulk Fe (Jiang et al., 2021).

11 Nanotechnology in Agriculture: Benefits and Risks

Nanoparticles are a promising new technology with applications in medicine, agriculture, and other vital fields. Yet, it is still unclear what dangers these compounds represent to people and ecosystems. Nanotoxicology refers to the study of the possible toxicity of nanoparticles and the discovery of techniques to use them safely (Riediker et al., 2004). Various aspects, including biological components, chemical components, shape and size, and reactions in the media of usage, can make it impossible to compare the protective or toxic character of these nanoparticles (Riediker et al., 2004). Determining the toxicological information for every nanoproduct is vital for figuring out the NP residues in the environment and/or present in the biological system (Oberdörster et al., 2005). However, there is currently insufficient proof that NPs directly cause human illness. According to Haji et al., they have been hypothesized to have DNA damage and cell inflammatory responses as their genotoxic impacts, both of which can have toxicological consequences (Oberdörster et al., 2005). Contrarily, the advantages to the environment, financial stability, and biological sustainability brought about by the use of nanogoods in crop promotion are more obvious. While nanofertilizers improve plant health, nanomaterials increase the ability of plants to withstand stress brought on by abiotic or biotic causes (Tiwari et al., 2012). The risks of nanotechnology should be assessed before it is used. The possible effects of a novel nanofertilizer on the environment and human health should be assessed, confirmed, and mitigated through regulatory control and product redesign before it can be released onto the market (He et al., 2015). Particle size, dosage, fabrication materials, etc., all play a role in making nanoparticles as dangerous elements (He et al., 2015). The findings of research by Pullagurala et al. (2018) showed that greater amounts of NPs have detrimental impacts on plants, while lesser dosages applied in specific situations have favorable effects. Higher levels of tailored nanotextiles (>500 mg L^{-1}) were found to be phytotoxic, while treatments at lesser amounts (50 mg L^{-1}) had a positive impact (Jiang et al., 2021). Higher concentrations of ZnO NPs caused the roots of plants to become clogged, which prevented them from absorbing essential nutrients (Djanaguiraman et al., 2018). By interacting with other media, NPs generated from chemicals can be poisonous and release dangerous byproducts. The trend toward synthesizing nanoparticles using biostrategies aims to overcome this issue. As NPs are toxic to marine microflora but harmless to microorganisms of soil, the environment has an impact on the safety and behavior of nanoparticles. When asked about the potential risks associated with NP goods, the US Food and Drug Administration concluded that they posed no threat to human health.

12 Natural Farming and Green Nanotechnology

By growing food without the use of chemical inputs like fertilizers and pesticides, natural farming aims to reduce human influence on the environment. The advantages of organic farming are numerous. Natural farming is more environmentally friendly than conventional farming because it protects soil quality and biodiversity, consumes less water, and requires fewer artificial pesticides and fertilizers. Natural farming practices, which place a strong emphasis on using organic and local inputs, result in more nutrient-dense food that is also free of synthetic pesticides and fertilizers that may be hazardous to human health. Because natural farming practices involve less inputs and less equipment, they are more economical for subsistence farmers. Using organic farming methods like composting, crop rotation, and cover crops can all help with soil structure, fertility, and erosion. Soil structure, fertility, and erosion are all aided by using organic farming techniques like composting, crop rotation, and intercropping. Natural farming practices are preferable because they prioritize animal welfare and encourage the ethical treatment of livestock. Natural farming, in its entirety, is an environmentally and health-friendly method of agriculture.

13 Conclusion

Green synthetic methods have been developed to create nanoparticles utilizing microorganisms, plants, and other organic sources in response to the increasing need for green chemistry and nanotechnology. Synthesizing NPs in a way that is good for the environment has been a major focus of research. Due to their inexpensive manufacture, lack of toxicity, accessibility, and ecologically friendly composition, plant extract-mediated NPs have generated a lot of interest in terms of both their prospective and possible applications. Numerous unique plant substances speed up and accelerate the production of compounds. The manufacture of green nanomaterials utilizing pants is a fascinating and expanding topic of nanotechnology that has the potential to significantly improve environmental conditions and advance the field of nanoscience over the long run. These green plant-based NPs have the tendency to be utilized in various biological fields, such as medicine, sensors, biotechnology, cosmetics, agriculture, dye degradation, bioengineering sciences, imaging, optics, catalysis, food packaging, textile engineering, and others. These NPs show promise as a drug delivery mechanism of the future for the biomedical industry. These ecofriendly NPs have several potential applications, such as combating phytopathogens in farming and cleaning up polluted water sources. Although this ecologically friendly and low-impact way of creating NPs is receiving acceptance and is anticipated to grow quickly in the years to come, concerns remain about its potential effects on people and other animals, as well as the environmental accumulation and influence of these particles. The creation of engineered nanoparticles represents a major advancement in the fields of materials science and consumer goods manufacturing. Although nanotechnology is only now being applied to farming, it has the potential to drastically alter agricultural systems, particularly in relation to issues with fertilizer application. Since they reduce fertilizer prices and emission concerns, nanofertilizers have a substantial impact on agricultural output. Nanofertilizers have the potential for targeted administration and regulated release since they are more soluble, reactive, and penetrable through the cuticle. Nanofertilizers reduce the toxicity of heavy metals, stress caused by abiotic factors, boosts crop development, production, quality, and the efficiency with which nutrients are utilized. Meanwhile, the potential downsides of overconsumption and inefficient functioning have received more attention than the advantages and usefulness of the technology itself.

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Chapter 9
Nanobiofertilizers: Applications, Crop Productivity, and Sustainable Agriculture

G. Somna, Dinakar Challabathula, and Kavya Bakka

1 Introduction

Agriculture is an inevitable sector that provides raw materials mainly for food and feed industries and other sectors like fuel, furniture, and feedstock industries. Agricultural productivity is challenged by different reasons such as unavailability of space, plant diseases, and abrupt climatic changes in environmental conditions. These severe issues demand a technique for reducing the inevitability of old techniques and developing modern practices that focus on improved agricultural productivity (Yunlong & Smit, 1994). Nanotechnology can be used for the sustainable growth of agriculture as it is a new, smart, and innovative technique with different applications (Tilman et al., 2002). The use of nanotechnology in agriculture is made possible by making necessary advancements in isolating and characterizing nanomaterials in a particular way forming nanoparticles with remarkable properties (Bandyopadhyay et al., 2013). The physical and chemical properties of NPs depend on unusual optical, physical, and biological features corresponding to materials employed in the synthesis of organic, inorganic, metal, and hybrid nanoparticles. Biofertilizers are mainly composed of live formulations of beneficial microbes that, when applied to seed, leaf, or soil, enhance plant growth by providing increased nourishment for the plants (Nanjwade et al., 2011; Thomas et al., 2013). Nanomaterials (NMs) are effective in agricultural fields with specific compositions,

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sizes, and properties that can be of natural or synthetic origin (Puri et al., 2009). Different NMs have enhanced earlier plant germination as well as plant production through the modulation of plant gene expression and associated biological pathways. It also depends on the plants and varies with different stages of plant growth, method of administration, and exposure time. Agricultural practices like the use of fertilizers and pesticides enhanced productivity but created serious and even life-threatening aftereffects. There arises the importance of practices that increase growth and yield-reducing issues like nanotechnology, where different techniques like nanoformulations of agrochemicals, nano biosensors, nanodevices, and nanoarrays are utilized (McLoughlin et al., 2011; Mir et al., 2018). The entry of metal complexes into the cell is facilitated by the movement of negatively charged compounds through the membrane with a negative charge (Tandy et al., 2006). There are different examples explaining the importance of NPs in the agricultural field. The compound aluminum (Al) oxide has a phytotoxic effect on root elongation, but loading this nano-Al with different percentages of phenanthrene reduced this inhibitory impact, suggesting slightly reduced root elongation in the presence of NP-coated phenanthrene (Yang & Watts, 2005). On the other hand, the seed treated with titanium dioxide (TiO_2) NPs enhanced the physiological properties of spinach, increasing the germination rate, chlorophyll, plant dry weight, and photosynthesis rate (Yang et al., 2006).

Biofertilizers are biological compounds with live microbes that are applied to seeds, plant surfaces, or soil and that promote plant growth through various mechanisms. Biofertilizers are products that, when added to the soil, contain microorganisms that are essential for soil fertility and plant growth. Biofertilizers colonize the rhizosphere, or interior, of plants when applied to the leaf surface, seeds, or soil and promote growth by controlling the amount or availability of primary nutrients to the plant host. Organic fertilizers contain chemicals and live microorganisms that provide nutrients to plants through natural processes such as nitrogen fixation, phosphorus solubilization, and the production of growth-promoting chemicals. They help to bring back the natural nutrient cycle, thereby increasing organic matter in the soil. Applying biofertilizers can improve soil sustainability and health while growing healthy crops. Biofertilizers may reduce the need for synthetic fertilizers and pesticides, but they cannot completely replace chemical fertilizers (Kole et al., 2013).

The process involving polymeric materials in which microbes are entrapped to produce beads that are permeable to various gases, nutrients, and metabolites to maintain cell viability is called encapsulation. Encapsulation provides good protection of the active substance against aggressive environmental influences. For the encapsulation process, different polymers like gelatine, starch, cellulose, etc., are used. Bioformulations are found in liquid and solid forms, but dry formulations are preferred over wet formulations because of their increased shelf life and ease of storage and transport. Micellar-enhanced ultrafiltration is used to separate organic compounds like thuringiensin dissolved in aqueous streams (John & Boppart, 2011).

Biofertilizers are formulations comprising one or more microorganisms that can enhance the productivity of soil by fixing atmospheric nitrogen and solubilizing phosphorus, which in turn stimulates plant growth. The integration of biofertilizers with nanoparticles to improve the growth of plants can be defined as nanobiofertilizers. Different strains of bacteria rely on different mechanisms, such as nitrogen fixation, potassium or phosphorus solubilization, phytohormone production, and degradability, in order to improve the uptake of nutrients, soil fertility, and yield improvement. The use of biological fertilizers is a mainstream scientific activity in developing sustainable agriculture, as they help overcome the shortcomings caused by chemical-based farming methods. The stability of biofertilizers can be enhanced by using nanoformulations resistant to desiccation, heat, and radiation (Zulfiqar et al., 2019).

2 Objectives

This chapter revolves around the formulation of different nanobiofertilizers involved in plant growth and stress mitigation. The mechanism of action of nanobiofertilizers employed in the application of plants and the synthesis and characterization of different nanoparticles are discussed. The entire chapter gives an idea of why application of nanobiofertilizers is helpful in sustainable agriculture and crop productivity.

3 Encapsulation in Nanoparticles

Encapsulation of microorganisms beneficial for plants has shown an increase in the availability of nitrogen, phosphorus, and potassium in the root area. In the past decade, techniques have been standardized to create beads that coat or entrap microbial cells with polymeric materials to maintain cell viability by rendering them permeable to nutrients, gases, and metabolites (John & Boppart, 2011). Encapsulation is divided by size into macroencapsulation (a few millimeters to a few centimeters in size) and microencapsulation (size 1–1000 μm, generally less than 200 μm) (Nordstierna et al., 2010). The active agent involved is protected by encapsulation using starch or cellulose from harsh environmental factors (Chang et al., 2000; Cheze-Lange et al., 2002). The utilization of different dyes also helps in increasing the viability of microbes (Cohen et al., 1990). Although wet formulations have better shelf life and storage transport properties, they are less preferred compared to dry formulations (Burges & Jones, 1998). The increasing demand for new formulations to substitute chemical pesticides and fertilizers has attracted the attention of researchers and new avenues in this direction are being explored to create cheaper and more effective technologies. Micellar-enhanced ultrafiltration (MEUF) is an example for an advanced technique used to separate dissolved organic compounds like thuringiensin from aqueous streams of Bt-based products commercially (Tzeng et al., 1999). For these plant growth-promoting bacteria-based formulations, in situ product removal (ISPR), which is biochemical product removal during the fermentation process, has been successfully applied in the removal of Bt toxin proteins (Agrawal & Burns, 1996), whereas crossflow microfiltration (CFM) has been utilized for the extraction of all kinds of proteins and the harvest of recombinant yeasts (Hwang & Chang, 2004). Macroencapsulation technology has advantages over microencapsulation (Desai et al., 2022). Encapsulation adequately protects the active ingredient from aggressive environmental influences. Cellulose gelatine, starch, and other polymers are currently used for drug encapsulation (Amiet Charpentier et al., 1998; Chang et al., 2000; Cheze-Lange et al., 2002). Protection can be improved to some extent by coating the capsule with a dye (Cohen et al., 1990; Schoebitz et al., 2013).

3.1 Nanoemulsions

A wide range of natural and synthetic ingredients such as oil, surfactants, cosurfactants, weighting agents, ripening inhibitors, thickeners, or gelling agents are used to create a simple and highly efficient pharmaceutical delivery system for encapsulation. Nanoemulsions are about ten to several hundred nanometers in size. Nanoemulsions have been shown to be beneficial for the bioavailability of some types of essential substances by increasing their bioactivity in agrochemicals. There are also stable particle aggregations and gravitational separations.

3.2 Nanolipid Carriers

Nanolipid carriers are formulations of solid lipids and oils called nanostructured lipid carriers. They are advanced lipid-based nanocarriers that perform better than classical nanoemulsions due to lower leakage of entrapped bioactive ingredients and improved control of the size and release process.

4 Formulation of Nanobiofertilizer

The formulations comprising one or more microorganisms that can enhance the productivity of soil by fixing atmospheric nitrogen and solubilizing phosphorus, which in turn stimulates plant growth, are called biofertilizers (Kole et al., 2013). Therefore, the integration of biofertilizers with nanoparticles to improve the growth of plants can be defined as nanobiofertilizers (Simarmata et al., 2016). Nanobiofertilizers can be effectively employed for improving nutrient utilization and soil fertility and thereby increasing yields through increased nitrogen fixation, potassium and phosphorus solubilization, phytohormone production, and detoxification. The advancements in biofertilizers are one of the major scientific endeavors for the development of sustainable agriculture, as they help to overcome the shortcomings associated with chemical-based farming techniques (Zulfiqar et al., 2019).

The stability of biofertilizers can be enhanced by using nanoformulations with resistant to desiccation, heat, and radiation (Jampílek & Kráľová, 2017). Hydrophobic silica nanoparticles added to the water-in-oil emulsion showed an improvement in the delivery of biofertilizers to soil and plants (Kaushik & Djiwanti, 2017). Nanobiofertilizers are capable of solving the limitations of biofertilizers, but this promising technology requires further research and development (Zulfiqar et al., 2019). Inoculation of nanoparticles and biofertilizers enhances plant growth and stress tolerance. In conclusion, nanobiofertilizers have become an economically and ecologically sustainable, highly versatile, and long-lasting agricultural tool (Sharma et al., 2023) (Fig. 9.1).

4.1 Bioformulations

A formulation is a mixture of active and inert substances, whereas a bio-preparation is a formulation of microorganisms to preserve them, deliver them to their destination, and enhance the activity of biofertilizers. Inert media include fine clay, peat,

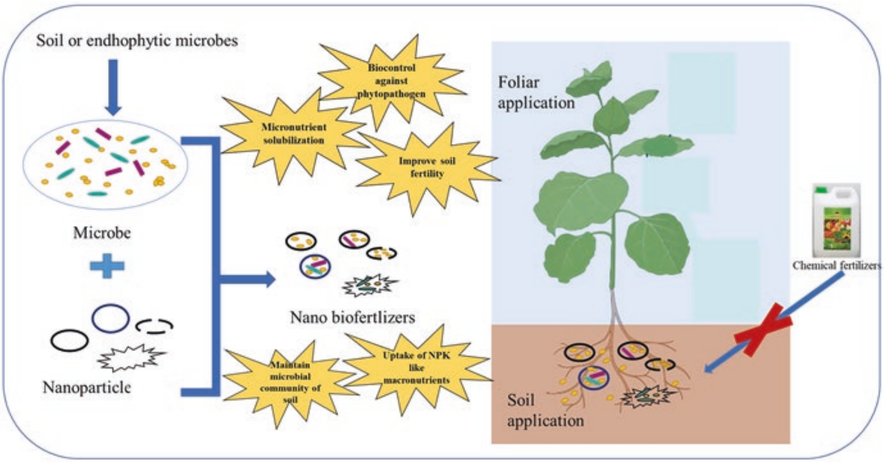

Fig. 9.1 Beneficial microorganisms, such as bacteria, fungi, and algae, are incorporated into nanoparticles in nanobiofertilizers, a category of fertilizer based on nanotechnology. These biofertilizers can aid plant growth and development in a few ways, including better nutrient uptake, increased pest and disease resistance, and increased tolerance to environmental stressors. Here are a few possible uses for nanobiofertilizer. By offering sustainable and environmentally benign substitutes for traditional fertilizers and pesticides, nanobiofertilizers have the potential to completely transform the agriculture sector

vermiculite, alginate and polyacrylamide beads, diatomaceous earth, talc, vermiculite, properties, some additives such as gums, silica gel, methylcellulose, and starch preparations are available in solid and liquid formulations.

4.1.1 Solid Formulations

Granules

Granules are dry preparations with an active ingredient content of 5–20%, a binder, and a carrier (Brar et al., 2006). They are divided into coarse particles (size range 100–1000 μm) and microgranules (size range 100–600 μm). The granules are formulated to be non-clumping, dusty, and free-flowing and break easily, releasing the active ingredient. The pellets are nonbreathable and safe and are mainly used for soil treatment. A concern with granular dosage forms is related to storage and extended shelf life (O'Callaghan et al., 2005). The most commonly used pellets are wheat flour pellets or corn flour. Granules are made from gelatinized corn starch, gluten, cottonseed, and sugars, gelatine or gum acacia, sodium alginate, and diatomaceous earth. Although granulated formulations are very effective, their use is also insufficient due to the UV inactivation of the active ingredient (Bailey et al., 1996).

Wettable Powders

Wettable powders (WPs) consist of active ingredients (50–80%), bulking agents (15–45%), dispersants (1–10%), and surfactants (3–5%) to achieve desired efficacy formulations (Brar et al., 2006). These dry formulations are readily miscible with water and can be easily added to normal water just before application. WPs have a longer shelf life by controlling moisture content, which ensure a firm marketplace. Agricultural substances and business waste by merchandise consisting of bagasse–sand–molasses mixtures, corn cob–sand–molasses, compost/farm manure mixture, cow dung–sand mixtures, diatomaceous earth, fly ash, inert charcoal, natural cakes, sawdust–sand–molasses mixtures, and wheat bran–sand mixtures also can be used to put together powder formulations (Khan et al., 2007).

Dust

Dust is also one of the oldest types of formulations, which contains a very finely ground mixture of active ingredients (usually 10%) and particles with sizes in the range of 50–100 μm. They also have a longer shelf life and are more effective, but they still have some handling and application issues.

4.1.2 Liquid Formulations

Liquid formulations, also called aqueous suspensions, consist of suspensions of biomass in water, oil, or a mixture of both (emulsions) (Schisler et al., 2004). Typical liquid formulations contain 10–40 active ingredients 1–3% suspension composition, 1–5% dispersant, 3–8% surfactant, and 35–65 °C plus liquid (oil or water) (Brar et al., 2006). The liquid formula can be the following genres.

Suspension Concentrates

Suspension concentrates (SCs) are formed from solid active ingredients with poor water solubility and reasonable stability. They are nondusty and easy to use compared to WPs.

Oil-Miscible Flowable Concentrate

This is a stable suspension of active ingredients in a fluid intended for prior dilution in an organic solvent (Singh & Merchant, 2012).

Ultralow Volume Suspension

They are ready-to-use suspensions with ultralow volume equipment, and air or soil spray equipment, and create a very fine spray (Singh & Merchant, 2012).

Oil Dispersion

Oil dispersion (OD) is a stable suspension of the active ingredients in solvents or oils that are insoluble in water (Michereff et al., 2009). OD has confirmed its growing importance over the past decade. Some protective measures are required when handling fungi containing OD formulations. As with long-term storage, the active ingredient (conidia) may be suspended or solidified at the bottom of the container (Butt et al., 2001). The oil evaporates much less, so it has a longer exposure and can be applied as an emulsion (oil in water) (Luz & Batagin, 2005) or, in some cases, as an inverse emulsion (water in oil) (Batta, 2007).

4.2 Formulations for Nutrient Uptake

Microbial inoculants serve as an effective method of supplying nutrients to plants as they greatly reduce the use of chemical fertilizers, leading to an increasing number of commercially produced biofertilizers for various crops (Berg, 2009; Trabelsi & Mhamdi, 2013).

Nitrogen is an essential plant macronutrient required in large quantities, but only a very small amount is provided by nitrogen fertilizers to the soil, and only a very small percentage of it is utilized in agricultural systems, even when the amount of application is remarkably increased (Vitousek et al., 2009). Nitrogen-fixing capability is limited to very little, and some others depend on symbiotic fixation of nitrogen by rhizobia (leguminous association) and Frankia (nonlegume association) (Franche et al., 2009). Humans are now synthetically fixing nitrogen at twice the rate of natural processes. Therefore, the role of rhizobia in sustainable crop production is confirmed, and it can be used as inoculum with nanoformulations to envisage agronomic practices for better nitrogen supply (Gupta et al., 2004; Arora & Padua, 2010). In legume inoculation, powdered granular or liquid formulations contain peat as carrier material. *Azoarcus, Achromobacter, Burkholderia, Gluconacetobacter, Herbaspirillum, Klebsiella*, and *Serratia* have been identified as potent endophytic nitrogen-fixing strains that can be used as microbial inoculum in preparation (Franche et al., 2009).

Phosphate is probably the least available plant nutrient found in the rhizosphere because it is inorganically fixed and forms organic complexes (Eswaran et al., 1997). In average soils, the phosphorus content is much lower, and only 0.1% of it is available for plants (Achal et al., 2007). It was observed that the application of phosphate fertilizers does not meet the needs of the plant. Mineralization and immobilization of the organic conversion of insoluble phosphorus into a form accessible to plants is a biological process in the soil, such as the microbial activity of phosphate solubilizing bacteria (PSB) and arbuscular mycorrhizal fungi (AMF) (Fankem et al., 2006; Khan et al., 2007). The development of microbial inoculum containing phosphate solubilizing microbes (PSM) and the use of PSM have helped increase yields in many plants. Commercialization as biopreparations has not been very successful due to quality control and the development of reliable and pollution-free bioproducts, while field performance is open to various environmental influences (Khan et al., 2009). *Pseudomonas* spp., *Bacillus* spp., *Aspergillus* spp., and *Penicillium* spp. are mainly used in PSB-based biofertilizers (Sharma et al., 2013). However, later products such as phosphobacterin, P Sol B®, and FOSFOSOL® received a lot of attention due to their success.

Potassium intake is as important as nitrogen and phosphorus for balanced plant growth. This macronutrient participates as an enzyme activator in several physiological reactions, such as protein synthesis, photosynthesis, and starch synthesis, and contributes to resistance to diseases and insects (Rehm & Schmitt, 2002). In the world, India ranks fourth in terms of total potassium consumption after the United States, China, and Brazil. It was found that "instant" K in the soil is dissolved by some bacteria with the release of organic acids, which increases the concentration of K in the soil solution (Meena et al., 2014). The ability to dissolve K-rich minerals such as mica, illite, and orthoclase is of great interest in the development of probiotics able to provide soluble K to plants. Biofertilizer K has been tested in several countries, notably China and Korea (Sheng & Lin, 2006). Most of the development of potassium-based biofertilizers has involved the use of these PSBs, which can also dissolve potassium-containing minerals. *Frateuria aurantia* has recently been recognized as a very efficient K-mobilizing bacterium and has been used in the commercial production of the biofertilizers Symbion-K, Biosol K, and K Sol B (Ahmed & El-Araby, 2012).

4.3 Formulations for Biocontrol

About 1400 biocontrol products are commercially available worldwide (Marrone, 2007), and new products are registering day by day. The formulations of different biofertilizers depend on different factors like the type of microbe, viability, and virulence of the strains, and whether the amount of inoculum is sufficient to create an impact on plants. The goal is to ensure that the agent is delivered alive, is functional, and has the potential to be effective in the field (Ash et al., 2010). Many researchers are elucidating the mechanism in detail and the methods of preparation (Burges & Jones, 1998; Couch, 2000).

4.4 Consortia-Based Inoculants

Most of the biological formulations contain a single strain; mixed cultures with other microorganisms serve as a better approach for the total growth and development of plants. In case of legumes, the use of rhizome co-inoculation with mycorrhizae gave substantial results. This co-inoculation not only upgraded the plant's nutritional status but also increased drought tolerance in alfalfa (Ardakani et al., 2009), soybean (Song et al., 2012), broad beans, chickpeas (Tavasolee et al., 2011), and pigeon peas (Bhattacharjee & Sharma, 2012). The combination of PSB and rhizobia in legumes promotes plant growth (Messele & Pant, 2012). The technique that provides a faster and more continuous supply of nutrients for growth is the integrated application of PSB with the co-culture of K-soluble bacteria. In the recent times, conjugate nanobiofertilizer formulations are being developed by researchers as sustainable agriculture practices and several patens are being awarded (Paikray & Malik, 2010). A conjugated biological formulation with nine strains from the genera *Azotobacter* spp., *Bacillus* spp., *Frauteria* spp., and *Streptomyces* spp., formulated as a wetting powder and found to be beneficial to gram black (Maiyappan et al., 2010). In a similar study, the bioconjugates of *Burkholderia* sp. MSSP and three other PGP bacteria were tested to enhance the growth of *Cajanus cajan*. In this

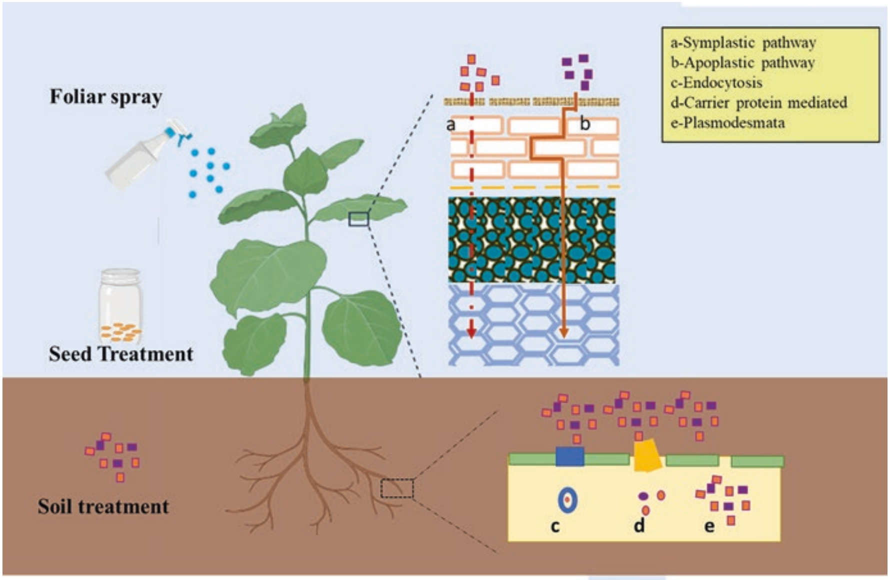

Fig. 9.2 Depending on the technique of delivery, the mechanism of action and uptake of nanoparticles can differ. In general, various parameters such as nanoparticle size, shape, surface charge, and concentration, as well as plant species and ambient conditions, can influence nanoparticle uptake and the mechanism of action. These criteria must be considered when selecting the best nanoparticle and application method for a certain crop and growing condition. Furthermore, the safety and potential environmental implications of nanoparticles must be carefully assessed in order to ensure their long-term and responsible use in agriculture

study, different materials like bagasse, sawdust, cocoa peat, rice husk, wheat bran, charcoal, rock phosphate, and whey paneer were used as liquid carriers and the results confirmed growth enhancement in pigeon pea (Pandey & Maheshwari, 2007). The combined inoculation of AMF and Rhizobium fungi facilitated a higher accumulation of N and P in the shoots of common pea plants compared with inoculation of both separately. Cyanobacteria, microalgae, and Azotobacter populations can be considered the best candidates for biostimulants and biofertilizers for plants (Zayadan et al., 2014). BioGro is a conjugated biofertilizer with *Pseudomonas fluroscens*, a soil yeast, and two PGPR Bacillus strains widely used in Vietnam (Fig. 9.2).

5 Synthesis of Nanoparticles

Nanomaterials can be synthesized by using physical, chemical, and biological approaches. The top-down approach describes physical or chemical processing that converts bulk material into nanoform, for example, by grinding, milling, etc. The other method of synthesis is the bottom-up method, in which smaller building

Table 9.1 Nanoparticle synthesis methods

Type of NP synthesis	Method
Physical synthesis	Thermal decomposition, ball milling, lithography, laser ablation and sputtering
Chemical synthesis	Sol-gel method, chemical vapor decomposition, spinning, and pyrolysis
Biological synthesis	Microbial incubation, plant-based biosynthesis

blocks are assembled together to create functional nanoscale materials. The bottom-up approach mostly involves chemical processing, while the top-down approach involves physical breaking (Raliya et al., 2018). The nanoscale fertilizer produced thus gives high productivity, nutrient enrichment, enhanced soil fertility, more microbial diversity, and nutrient mobilization, reducing the demand for fertilizers. The most common approaches used for the synthesis of nanoparticles are chemical reduction by organic and inorganic reducing agents. The chemical synthesis approaches employed in the synthesis of nanoparticles include chemical vapor deposition (CVD), chemical precipitation, and sol-gel technique (Tarafder et al., 2020). Various physical synthesis techniques, including gas condensation, planetary ball mills, vibrating ball mills, low-energy tumbling mills, and high-energy ball mills, were explored. Physical synthesis methods are commonly used method because of ease in synthesis and less time-consuming (Uhm et al., 2007). Biological synthesis is a process where different microbes, like bacteria and fungi, are utilized in green nanosynthesis. The biosynthesis of NPs uses different plant extracts or microbial extracts. It is also reported that plant waste is employed as a reducing agent for the synthesis. These green chemistry biosynthetic pathways reduce the risk of contamination at the source level, where reagents are eco-friendly (Tarafder et al., 2020).

A cost-effective and ecofriendly approach for the synthesis of nanoparticles is green synthesis, which is devoid of toxic chemical usage. The combined amalgamation of extracts of organisms and metallic salts leads to production of nanoparticles via green synthesis. This can be done through two different methods based on their composition: a) plant-based and b) microbe based methods. Plants based method is more convenient as the plant material can reduce the metallic ions quickly (Table 9.1).

5.1 Physical Synthesis or Top-Down Synthesis

5.1.1 Thermal Decomposition Method

Thermal decomposition is an energy-consuming process in which particles are chemically decomposed by heat (Salavati-Niasari et al., 2008). The temperature for chemical decomposition depends on specific temperature at which the element used for nanoparticle synthesis is chemically decomposed. As an example, paramagnetic polyethylene glycol is used to synthesize gadolinium oxide nanoparticles through thermal decomposition (Ijaz et al., 2020).

5.1.2 Ball-Milling Method

It is a simple, inexpensive mechanical method that uses large-sized substances to produce nanoparticles. In this method, kinetic energy is transferred from the medium used for grinding to the material to be destroyed. Materials with enhanced properties, like metals and alloys, are used to form nanoparticles in industrial scale. Alloys of different metals are used to increase the properties of nanoparticles according to their usage. In ball milling model, different milling techniques are used, like horizontal oscillatory milling, ultrasonic wave-assisted ball milling, and planetary ball milling (Ijaz et al., 2020).

5.1.3 Lithography

Lithographic methods are capable of making micron-sized particles, which require energy-intensive and expensive equipment. There are different lithographic techniques, like electron beam lithography, photolithography, soft lithography, focused ion lithography, nanoimprint lithography, and dip-pin lithography. Compared to typical lithography, nanoimprint lithography is a unique method. This is done through template synthesis: a template material like a latex sphere is synthesized and coated with soft polymeric material. However, top-down synthesis destructs the coating material (Ijaz et al., 2020).

5.1.4 Laser Ablation

A simple method for synthesizing nanoparticles is to irradiate various metals immersed in solution with laser light and condense plasma to produce nanoparticles (Amendola & Meneghetti, 2009). This is a traditional top-down chemical approach and differs from metal-to-nanoparticle reduction. The main advantage of laser ablation techniques is that they do not require any stabilizing agent or chemical (Ijaz et al., 2020).

5.1.5 Sputtering

Sputtering is the ejection of particles for the deposition of nanoparticles (Das et al., 2016). The easy deposition of a thin NP layer can be facilitated by annealing. The size and shape of nanoparticles are determined by factors such as temperature, layer thickness, annealing time, and substrate (Shah & Gavrin, 2006). Various types of nanoparticles are synthesized by sputtering (Ijaz et al., 2020).

5.2 Bottom-Up Method

The bottom-up method is a constructive process where the reversal of the top-down method occurs. In this method, nanoparticles are constructed from small subunits. Bottom-up methods include different techniques like chemical vapor deposition (CVD), sol-gel, spinning, pyrolysis, and biological synthesis (Ijaz et al., 2020).

5.2.1 Chemical Vapor Deposition (CVD) Method

Chemical vapor deposition involves usage of reaction chamber in which thin layering of gaseous reactant is added onto the substrate. When in contact with the heated substrate, gas combines with substrate to form a chemical reaction. As a result of this reaction, a thin film of product is produced on the surface of the substrate, which is subsequently recovered and used. The nanoparticles obtained will be hard, strong, uniform, and highly pure, making CVD a very advantageous method. The major disadvantage of CVD is the requirement of special machinery and the production of highly toxic gas as byproducts (Shah & Gavrin, 2006).

5.2.2 Sol-Gel Method

The sol-gel method is a combination of condensation and hydrolysis reactions with colloids formed from solid particles suspended in a continuous liquid, and gels are formed by dissolving solid macromolecules in a solvent. The sol-gel method is the most preferred method, where suitable chemical solutions such as metal oxides and chlorides used in the sol-gel process act as precursors. The precursor is dispersed in the host liquid by stirring, sonication, or shaking. The final product is separated from the solid phase and liquid phase by using filtration, sedimentation, and centrifugation, and nanoparticles are recovered (Saberi-Rise and Moradi-Pour, 2020).

5.2.3 Spinning

Nanoparticles are synthesized using a rotating disk whose physical parameters are controlled, called a spinning disk reactor. The reactor is made devoid of oxygen by filling it with nitrogen or inert gas to avoid chemical reactions. The liquids such as water and precursors are pumped inside the chamber or reactor. The nanoparticles synthesized through this are characterized by various factors such as disc surface, liquid/precursor ratio, disc rotation speed, liquid flow rate, and location of the feed. The particle sizes ranged from 3 to 12 nm (Smith Nigel et al., 2006).

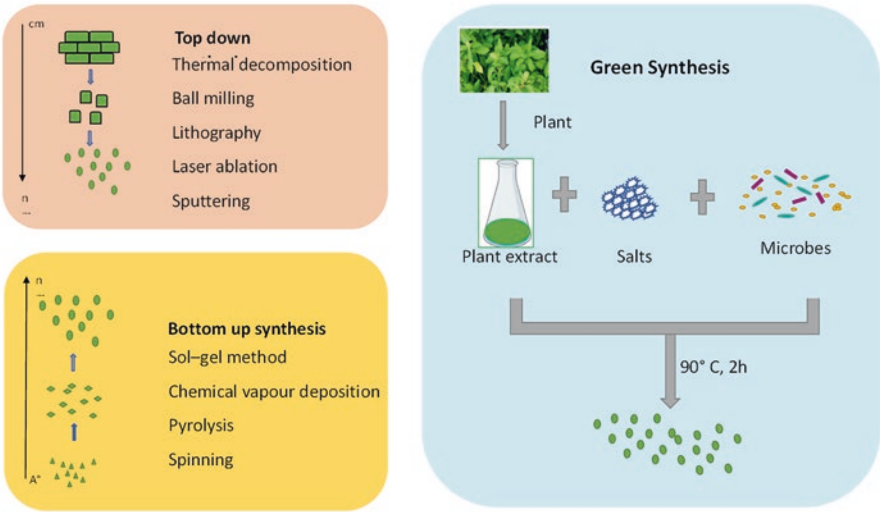

Fig. 9.3 Nanobiofertilizers are a sort of nanotechnology-based fertilizer that incorporates beneficial plants and microorganisms into nanoparticles, such as bacteria, fungi, and algae. Choosing an acceptable method is influenced by a few factors. To ensure the safety and environmental sustainability of the final nanobiofertilizers, the synthesis process must be properly developed and carried out

5.2.4 Pyrolysis

Pyrolysis is a widely used industrial method for the synthesis of nanoparticles. In this process, the precursors are burned with a flame. The precursors may be in liquid or vapor form. The precursor is transferred into the furnace at high pressure to recover nanoparticles. In order to produce a high temperature, a laser or plasma is used instead of a flame. The high temperature makes it easy to evaporate (Sourice et al., 2015) (Fig. 9.3).

6 Characterization of Nanoparticles

Nanoparticles can be characterized by qualitative or quantitative methods.

Qualitative Analysis

1. Fourier transform infrared spectroscopy
2. UV–visible spectrophotometry
3. Scanning electron microscope
4. Atomic force microscopy
5. X-ray diffraction

Table 9.2 Qualitative and quantitative characterization of nanoparticles

No	Technique	Type of analysis	References
1.	FTIR	Qualitative	Jabeen et al. (2018), Joshi et al. (2019), Kamnev et al. (2021), Khalofah et al. (2021), Rahman et al. (2021), Tarafder et al. (2020)
2.	SEM	Qualitative	Jabeen et al. (2018), Joshi et al. (2019), Kamnev et al. (2021), Rahman et al. (2021), Sotoodehnia et al. (2019), Tarafder et al. (2020)
3.	TEM	Quantitative	Saleem and Khan (2023), Sotoodehnia et al. (2019)
4.	XRD	Qualitative	Jabeen et al. (2018), Joshi et al. (2019), Tarafder et al. (2020)
5.	HAADF	Quantitative	Joshi et al. (2019), Mejías et al. (2021)
6.	UVS	Qualitative	Jabeen et al. (2018), Joshi et al. (2019)
7.	AFM	Qualitative	(Joshi et al. (2019), Rahman et al. (2021)
8.	ICP-MS	Quantitative	Rahman et al. (2021), Tarafder et al. (2020)

Quantitative Analysis

1. Transmission electron microscopy
2. Annular dark-field imaging
3. Inductively coupled plasma-mass spectrometry (Table 9.2)

7 Types of Nanobiofertilizer

Biofertilizers include different bacteria for nutrient uptake and solubilization. Nitrogen-fixing bacteria are essential for plant growth and development because plants cannot convert atmospheric nitrogen to ammonia. *Azotobacter, Rhizobium*, and *Azospirillum* are important examples of nitrogen-fixing bacteria. Azotobacter is an aerobic bacterium in alkaline soils that has found increasing application in large-scale nitrogen fixation. Rhizobium forms symbiotic bonds with the roots of legumes and is therefore a useful biofertilizer for legumes. *Bacillus, Pseudomonas*, and *Aspergillus* are primarily phosphate-solubilizing microorganisms. They accelerate plant growth by increasing plant access to phosphorus. Apart from these, the commercialized biofertilizer industry focuses on potassium-mobilizing biofertilizers, zinc-dissolving biofertilizers, and NPK-mobilizing microbes. Different forms of nanobiofertilizers and their applications can effectively alleviate plant biotic and abiotic stress and improve plant nutritional value (Giri et al., 2023). Biofertilizers in agriculture have several drawbacks, including short crop-specific shelf life, instability in the field due to lack of defined environment, need for special storage conditions, easy drying, and uncharacteristic dosage. Apart from the shortcomings of essential biofertilizers, they are helpful for sustainable agriculture, have improved stress tolerance, and enhance soil fertility, which is inevitable to remedy nutrient deficiencies. To overcome these limitations, formulations based on nanoparticles were developed. NPK can be formulated together with these nanoparticles individually or in consortia to find better ways to improve cultivation practices (Tables 9.3 and 9.4).

8 Advantage Over Conventional Methods

Nano-formulated biofertilizers are more stable than regular biofertilizers and biostimulants due to deactivation by drying, heat, and UV light. Microbial-derived nanoparticles are more stable, nontoxic, cheaper, and environmentally friendly compared to chemically derived ones. Nanobiofertilizers promoted plant growth and nutrient quality by maintaining soil fertility through nitrogen fixation, phosphate solubilization and mobilization, siderophore generation, and plant hormone synthesis. Plant yield and quality are improved by increasing photosynthesis, nutrient uptake efficiency, photosynthetic accumulation, and nutrient transfer. Depletion of soil nutrients through leaching, gasification, soil erosion, and competition with other organisms enhances nutrient uptake and assimilation by plants. A large area can be treated with a small amount of nanobiofertilizer compared to chemical fertilizers. Rhizobium, which promotes plant growth, acts as a bio-organic component in nano-biofertilizers, assists in nitrogen fixation and phosphate solubility, and aids in soil fertility restoration. Nanomaterials help release nutrients slowly and stably according to plant needs in a synchronous mode and also act as resistance agents. Nanoclay-coated *Trichoderma* sp. and *Pseudomonas* sp. are used as an antifungal agent and also provides plant resistance to abiotic stress (Ali et al., 2021) (Table 9.5).

Table 9.3 Different plant growth promoting bacteria can be used for production of biofertilizers

Nitrogen fixing	
Free living	*Azotobacter*
Symbiotic	*Rhizobium*
Associative symbiotic	*Azospirillum*
Phosphorous solubilizing	
Bacteria	*Pseudomonas striata*
Fungi	*Penicillium* spp. *Aspergillus spp*
Phosphorus mobilizing	
Arbuscular Mycorrhiza	*Glomus spp*
Ectomycorrhiza	*Amanita* spp.
Plant Growth Promoting Bacteria	
Plant Growth Promoting Rhizobacteria	*Pseudomonas, Azospirillum, Azotobacter, Bacillus, Burkholdaria, Enterobacter, Rhizobium, Erwinia, Mycobacterium, Mesorhizobium, Flavobacterium*

Table 9.4 Nanoparticles with PGPR on their respective host and influence on plant growth and stress mitigation

Sl	Nanobiofertilizers	Plant	Microbe	Response	References
1.	Silicon dioxide (SiO_2 NPs)	*Triticum aestivum*	*Azospirillum brasilense, Bacillus* sp.*, and Azospirillum lipoferum*	Drought resistance	Akhtar and Ilyas (2022)
2.	Iron/zinc oxide NPs	*Triticum aestivum*	*Azospirillum, Pseudomonas and, Azotobacter*	Enhanced yield and growth in water deficit areas	Seyed Sharifi et al. (2020)
3.	Zinc NPs	*Phaseolus vulgaris*	Rhizobium	Enhancement of nutrient uptake and plant growth	Morsy et al. (2017)
4.	Silver NPs	*Solanum tuberosum*	Mixture of Azospirillum and Azotobacter-Nitroxin	Total yield increment of tubers	Davod et al. (2011)
5.	Nano zeolite	*Zea mays*	Bacillus	Plant growth	Khati et al. (2018)
6.	Zn NPs	*T. Aestivum*	Biochar	Heavy metal stress	Bashir et al. (2020)
7.	Fe NPs	*Trifolium repens*	Pseudomonas fluorescens	Heavy metal stress	Daryabeigi Zand et al. (2020)
8.	Ti NPs	*Triticum secale*	*Azospirillum brasilense, A. caulinodans and, Azotobacter chroococcum*	Heavy metal stress	Ghooshchi (2017)
9.		*Sorghum bicolor*	*Azotobacter*	Carbohydrate and chlorophyll content	Eliaspour et al. (2020)
10.	Ag-nanoparticles	*Allium cepa*	*Bacillus pumilus and Pseudomonas moraviensis*	Salinity stress	Jahangir et al. (2020)
11.	Silver nanoparticles	*Zea mays*	*Bacillus cereus*	Bioinoculant and growth stimulator	Kumar et al. (2020)
12.	Ag-nanoparticles	*Cucumis sativus*	*Pseudomonas putida Pseudomonas stutzeri*	Enhance the antioxidant and defense enzyme activities to enable the plant in the tolerance of different stresses	Nawaz and Bano (2020)

(continued)

Table 9.4 (continued)

Sl	Nanobiofertilizers	Plant	Microbe	Response	References
13.	Gold NPs		*Pseudomonas fluorescens, Bacillus subtilis*	Plant growth promotion	Shukla et al. (2015)
14.	Ag-NP	*Withania somnifera*	*Bacillus mojavensis*	Improves growth, photosynthetic attributes, gas exchange parameters, and Alkalo-Polyphenol contents	Danish et al. (2022)
15.	Bio fabricated Ag-NPs	*Saccharum officinarum*	*Fusarium oxysporum*	Antifungal activity against phytopathogens	Amna Mahmood et al. (2021)
16.	Green nanoparticles	*Cuminum cyminum*		Restrain Restrain fusarium wilt Restrain fusarium wilt by Antioxidant defense system	Thummar et al. (2022)
17.	Silver nanoparticles	*Saccharum officinarum*	*Bacillus* sp. *Strain AW1−2*	Antifungal activity against *Colletotrichum falcatum* Went	Ajaz et al. (2021)
18.	Silver nanoparticles		*Fusarium oxysporum*	Antibacterial potential	Ilahi et al. (2022)
19.	Silver nanoparticles	*Triticum aestivum*		Strong fungicide against *Bipolaris sorokiniana*	Mishra et al. (2014)
20.	Silver nanoparticles	*Linum usitatissimum*	*Comamonas testosteroni*	Salinity stress tolerance	Khalofah et al. (2021)
21.	Silver nanoparticles	*Zea mays*	Rhizospheric bacteria	Biomass enhancement	Sillen et al. (2015)
22.	Silver nanoparticles	*Zea mays*	*Pseudomonas fluorescence, Bacillus cereus*	Growth of maize and bioremediation of heavy metals under municipal wastewater irrigation	Khan and Bano (2016)
23.	Titanium dioxide nanoparticles	*Trifolium repens*	*Bacillus thuringiensis Azotobacter chroococcum*	Promote phytoremediation of cadmium-polluted soil	Zand et al. (2020)
24.	Nano zeolite and nano chitosan	*Trigonella foenum-graecum*	*PS2-KX650178 and PS10-KX650179*	Improve soil fertility	Kumari et al. (2020)

(continued)

Table 9.4 (continued)

Sl	Nanobiofertilizers	Plant	Microbe	Response	References
25.	Titania (TiO_2) nanoparticles		*Bacillus thuringiensis*	Total plant growth promotion	Timmusk et al. (2018)
26.	Green molybdenum nanoparticles	*Triticum aestivum*	*Bacillus* sp. *Strain ZH16*	Improved growth by nutrients supply, ionic homeostasis and arsenic accumulation	Ahmed et al. (2022)
27.	Alginate – bentonite coating enriched with titanium nanoparticles	*Phaseolus vulgaris*	*Bacillus subtilis Vru1*	Against *Rhizoctonia solani*	Saberi-Rise and Moradi-Pour (2020)

Table 9.5 Advantage of nanobiofertilizers over chemical and nanofertilizers

Chemical fertilizer	Nanofertilizer	Nanobiofertilizer
Enhanced yield	Efficient usage of fertilizer	Increased nutrition status in plants
Improved quality of yield	Proper uptake from soil to increase yield	Promoted plant growth
Imbalanced fertilization	Required amount of fertilization	Slow release of nutrients
Decreased soil organic matter	Least impact on soil organic matter	Increase nutrition status in soil
Reduced yield after a period of time	Extend the duration of supply without affecting the yield	Enhanced plant resistance

9 Conclusion

Chemical fertilizers have been used for years to increase the productivity of agricultural activities. However, chemical fertilizers have been associated with adverse effects such as environmental toxicity and long-term overuse of chemical fertilizers. This has led to the need for new, nontoxic, environmentally friendly alternatives to improve agricultural productivity without the associated side effects. To ensure the biosecurity of agriculture, it is recommended to use nanobiofertilizers instead of chemical fertilizers. Biofertilizer ingredients contain beneficial microbes with PGPR properties that supplement crop nutrients by increasing nitrogen fixation and dissolving complex organic matter into simpler forms for easy plant availability. Although they have some serious problems, such as poor shelf life, external stability, and performance in various environmental conditions, nanoparticle formulations have superiority in all of them. Encapsulation of nanomaterials extended their shelf life and showed controlled release of biofertilizers when needed. It is an environmentally friendly, renewable approach that can boost nutrient use efficiency, enrich beneficial microbial communities in soil, improve the activity of related signaling cascades, facilitate improved soil fertility and yield, and contribute to crop disease resistance. Chemical fertilizers are widely used in the agricultural sector, are the most expensive inputs in agriculture, and have various negative effects on crop production, including environmental pollution. We need environmentally sustainable strategies that improve nanotechnology and offer solutions through nanobiofertilizers that have a promising future in the field of sustainable agriculture. Nanobiofertilizers are potential nutrient enhancers that allow a slow and continuous release of nutrients into plants during the plant's growing season. Nanobiofertilizer can have several advantages for plants, such as slow and targeted release of nutrients.

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Chapter 10
ZnO Nanoparticles: Sustainable Plant Production

Tapan K. Mandal

1 Introduction

Nanoparticles (NPs), because of their unique properties, have been extensively used in agriculture as fertilizer, pesticide, insecticide, and biosensors (Duhan et al., 2017; Chhipa, 2019; Hu & Xianyu, 2021). NPs have been suggested as beneficial agents in agriculture because of their implicit use as nanofertilizers, which have a greater capacity to saturate soil than ordinary fertilizers and are more easily taken up by plants (Morales-Díaz et al., 2017). NPs of metal oxide have attracted attention because of their large surface area, good adsorption, numerous reactive sites, more catalytic activity, and chemical stability. This has considerable effects on various species. Owing to their unique characteristics, NPs greatly influence higher plants' intake, accumulation, alteration, and movement in both terrestrial and aquatic environments. (Jebel et al., 2016).

Because of characteristics like small size, greater energy, high surface-to-volume ratio, superior transport, and catalyst capabilities, nanotechnology has recently garnered considerable interest. Most significantly, it was found that NPs of the same metals displayed different properties from bulk molecules (Ahmed et al., 2022). Special characteristics of NPs lead them to numerous applications, such as in the culinary, pharmaceutical, and agricultural industries (Naveed Ul Haq et al., 2017). It is quite concerning that the growing world population will lead to higher food demands and reduced output because of factors including the prolificacy of soil, climate change, and strains of biotic as well as abiotic bacteria, which will have substantial consequences on the yield of crops (FAO, 2019). Therefore, the production of food should rise in the same proportion (Kumar et al., 2006). Manures,

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insecticides, cultivars, and genetically modified organism crops have all been extensively used to combat the problem (Yadav et al., 2013). Synthetic fertilizers play a key role in boosting crop output, but their excessive and careless usage has negative outcome on food standards and soil conditions (Zamir, 2011; Conley et al., 2009; Bai et al., 2020).

Recently, chemical and engineered nanoparticles (ENPs) are being used more and more frequently as fertilizers and for pest control. Researchers are attempting to use a biological and more environmentally responsible way to create NPs to mitigate the environmental effects of chemical fertilizers and ENPs in soil systems. The biological extract explored in biosynthesis comes from many plants and microorganisms, and it is secure, economical, and contains natural capping and reducing agents as well as various photochemicals (Senthamarai & Malaikozhundan, 2022). That's why scientists are looking at different plant extracts, fruit and flower components, and cellular and microbial parts for the environmentally friendly prepared NPs. Eco-friendly and sustainable nanoparticles (NPs) are used for various purposes, such as medication transport, electrochemical and photo decomposition performances, wastewater treatment, and biofertilizers (Alshehri et al., 2018). The phytochemicals extracted from plants have been found to play a role in the synthesis of NPs (Alshameri & Owais, 2022).

ZnO NPs are presently obtaining a great deal of attention due to their benign nature, higher necessity for plant improvement, and Zn's deficit in soil (Itroutwar et al., 2020). ZnO NPs have been employed as foliar fertilizers in several studies because they improve the agromorphological characteristics, photosynthesis, biomass, and production of plants (Munir et al., 2018). Wheat germination and growth have been shown to be significantly impacted by ZnO NPs, according to a previous report (Du et al., 2017). Zn^{+2} is a crucial trace element that takes part in both human and plant metabolism. The FDA has deemed the ZnO NPs to be safe because they are far less harmful (Senthamarai & Malaikozhundan, 2022).

Zinc is a vital micronutrient for plants, and its deficiency will reduce crop yields (Rudani et al., 2018). NPs of ZnO have been explored because of their strong antimicrobial and biocompatible nature. The production of ROS, free radicals, and the deliverance of Zn^{2+} ions are all components of the process underlying its bactericidal effect (Gharpure & Ankamwar, 2020). Priyanka and Venkatachalam investigated ZnO NPs and found that they exhibit enormous potential in their application for powerful catalysis in agriculture (Priyanka & Venkatachalam, 2016). The incorporation of ZnONPs, in the presence of Cd and Pb ions, provides protective effects on cotton seedlings by mitigating heavy metal-induced phytotoxicity and enhancing physiochemical properties. This is accomplished by modulating the photosynthetic machinery and antioxidative defense mechanisms in cotton seedlings in a distinct manner (Priyanka et al., 2021). Keerthana et al. (2021) observed that the co-exposure of ZnO NPs to stressed plants with some heavy metals profoundly increased the expansion of the roots and shoots.

This chapter investigates on ZnO NPs for their application in sustainable plant production. The chapter addresses the importance of ZnO NPs and different fabrication techniques for the manufacture of ZnO NPs. It also demonstrates nanofertilization, the use of ZnO NPs in sustainable plant production, and future trends in the use of ZnO nanofertilizers.

2 Importance of ZnO Nanoparticles

ZnO NPs play a very important role in the growth of plants due to the following:

(i) Antimicrobial activity
(ii) Biosafety
(iii) Seed germination
(iv) Translocation

Jiang et al. (2016) studied the interactions among ZnO NPs, released Zn^{2+} and ROS, and *Escherichia coli* cells and concluded that ZnO NPs are "biosafe material" for organisms. ZnO NPs have been reported to induce the germination of seeds and growth of plants, as well as conquering of disease and preservation of plants, because of their antimicrobial activity. It is known that the uptake, translocation, and accumulation of ZnO NPs by plants depend upon the properties of the ZnO NPs and the physiology of the host plant (Faizan et al., 2020). Alharby et al. investigated how ZnO NPs could reduce salt stress in tomato plants. Lower concentrations of NPs (15 mg L^{-1}) were shown to be more successful in their application than larger concentrations when it came to reducing the impacts of NaCl (30 mg L^{-1}). They concluded that more research into ZnO NPs for usage as helpful stress-reducing agents in crop production was necessary. With ZnO NPs, diverse tomato cultivars showed varying degrees of salt resistance (Alharby et al., 2016). Rizwan et al. reported that ZnO NPs increased the growth of wheat plants and reduced the oxidative stress and cadmium concentration in them (Rizwan et al., 2019). They found that ZnO NPs played a prime function in the enhancement of biomass and nutrients and the reduction of cadmium toxicity in wheat. ZnO, in addition to other metal oxide NPs, is a potential tool to combat salinity stresses, according to Rizwan et al. (Zia-ur-Rehman et al., 2023).

ZnO material is selected for usage in biomedical and for the growth of plants among the several metal NMs now accessible (Hussain et al., 2016). This is due to ZnO's special properties, which include its large availability in nature, being cheap and nonpoisonous, and its ability to generate grains with a variety of forms and possible applications (Nagajyothi et al., 2015; Hussain et al., 2016). ZnO semiconductors have an extensive direct bandgap energy (3.37 eV) and a high excitation energy of binding (Nagajyothi et al., 2015). There is a lot of evidence to support the good antibacterial, antifungal, anticancer, and oxidation-resistance performances of ZnO NPs, prepared via green synthesis (Hussain et al., 2016; Kedi et al., 2018; Sharma et al., 2016; Aquisman et al., 2020; Bala et al., 2015; Senthamarai & Malaikozhundan, 2022; Khorrami et al., 2019). ZnO plays a variety of crucial physiological roles. ZnO functions as an essential part of enzymes like alkaline phosphatase. It supports structure integrity in biomembranes and is a part of ribosomes. ZnO deficiency symptoms include (1) rosetting (slowed growth due to short internodes), (2) tiny leaves, and (3) its severe deficiency results in the death of shoot apices (Aouada & de Moura, 2015).

3 Preparation of ZnO NPs

Different authors have reported the synthesis procedures of ZnO NPs using different methods. Sahoo et al. (2021) prepared ZnO NPs using green and chemical methods, and the as synthesized materials were characterized by them. Their prepared NPs of ZnO revealed a better uniform size distribution with a mean diameter that was 57% smaller. They set up a pot experiment to evaluate the effectiveness of both NP types on the green gram (*Vigna radiata* (L.) Wilczek). Green synthesized ZnO NPs were found to enhance the green gram's growth and yield factors. Compared to normal ZnO NPs, green NPs showed that seeds had a 13.3% greater seed production, a 5.6% higher protein content, and a 3.2% higher Zn content. Up to a ZnO NP concentration of 20 mg L^{-1}, the growth of seeds was found to be significantly improved. The enhanced seed production was 56.2%; zinc content was 15.6% and 25.2%, and seed protein was 25.2% when compared to the control. These findings indicate that synthesizing and employing green NPs of ZnO have a great deal of potential for increasing enhanced nutrient utilization. ZnO NPs were created with *Aloe barbadensis* Mill (Singh et al., 2019). The NPs were characterized with microscopic devices. The size of the as-prepared ZnO NPs were estimated to be of 35 nm, which is smaller compared to those obtained from the traditional method (around 48 nm). Also, these NPs have a stronger capacity to reduce and cap leaf extracts. They examined the ZnO NPs at various NP concentrations that were sufficient for wheat seedling emergence and germination (0, 15, 62, etc.). They discovered that ZnO NPs promoted superior growth compared to control seeds. Thus, they recognize the capabilities of ZnO NPs in agriculture. *Piper betleas* leaf extract, a reducing-stabilizing negotiator, was used by Goyal et al. (2022) in preparing ZnO NPs, through the green method. They calculated the band gap as 3.41 eV, which is larger compared to the bulk ZnO (E_g = 3.37 eV). Photocatalytic activity analysis inferred that green ZnO-NPs were effective for degrading harmful reactive red dye (efficiency of degradation = 96.4%). They observed the as-prepared ZnO NPs to be effective photocatalysts and antimicrobial species. Sharma et al. (2022) studied the synthesis and antimicrobial performance of ZnO NPs using *Azadirachta indica* leaf. The prepared nanoparticles exhibit good crystallinity, with an average crystallite size of 60-65 nm as determined by XRD. The average grain size, as observed through SEM, ranges from 100-200 nm. The authors investigated whether fabricated ZnO NPs are a superior choice for biological dealings. Swarna Bharathi et al. (2022) conducted the study and found that brown seaweed algae are used in the fabrication of two different metal NPs. They biomedically investigated the SiO_2–ZnO nanocomposite for antioxidant, antibacterial, and anticancer properties. The as-synthesized SiO_2–ZnO nanocomposites were found to be a promising possible treatment agents for colon cancer's HT29 cancer cell line. They concluded that the SiO_2–ZnO nanocomposite produced by seaweed may be a source for the treatment of adenorectal colon cancer cells. Their research demonstrated that the formation of SiO_2–ZnO nanocomposites, mediated by seaweed extract, exhibits excellent antioxidant activity. Using various plant parts as manufactured particles, Gharpure et al. (2022) worked on the preparation of hexagonal wurtzite-based ZnO NPs. Abel et al. (2021) used the extraction of moringa leaves. Their process is cost-effective and environmentally friendly. Their results showed a large bandgap at 350 nm wavelength. Significant antibacterial properties were observed by the authors for the as-prepared ZnO NPs. Chikkanna et al. (2019) prepared ZnO using agricultural waste products, such as sheep and goat feces. Prepared NPs were characterized to have a sponge-like texture and a flower-like structure and to have effective antibacterial action against *Bacillus subtilis* and *Salmonella typhimurium*. ZnO NPs and Mn-doped ZnO NPs were synthesized by Priyadharsini et al. (2021) through a green synthesis process applying Carica papaya extract with a wurtzite crystal structure. It is inferred by them that Mn-doped ZnO NPs showed good antibacterial performance. Al Awadh et al. (2022) synthesized ZnO NPs from *R. sativus* leaf extract through the precipitation method, with a particle size of 66.47 nm and a wurtzite structure. The prepared NPs were effective on gram-positive and gram-negative bacteria and breast cancer cells. Green-synthesized ZnO NPs by Hassan et al. (2019) from olive and marjoram leaf extract showed alternate antifungal efficacy.

Recently, *Aegle marmelos* unripe fruit extract was used to fabricate the NPs of ZnO, and the as-prepared materials were characterized via biophysical methods (Senthamarai & Malaikozhundan, 2022). ZnO NPs produced through biological means have a 19.8 -nm crystallite size. The stability of NPs was aided by the presence of several functional molecules, which were detected by FTIR at 3657, 3486, 2316, 2183, 2032, 1978, 858, 564, and 442 cm. A hexagonal wurtzite structure is observed in the SEM micrograph (particle size 22.5 nm). According to the results of the EDX, 77.91% Zn was detected. Kyene et al. prepared the nanomaterial ZnO (Kyene et al., 2023) from *Cassia sieberiana extract* (Kyene et al., 2023). Characterization of ZnO NPs was performed employing EDX and other tools. The antibacterial performance of ZnO NPs was also assessed by them. Triterpenes, polyphenols, saponins, and anthracenosides are available from the plant extract. The average particle size determined was 12.9 nm and had a spherical appearance. NPs of ZnO were made with *Tavernier glabra*, a medicinal plant, through biogenic techniques by Khan et al. (2023). It was evidenced that ZnO NPs were produced through biosynthesis, and the functioning of biomolecules has also been demonstrated by FTIR. ZnO nanostructures were examined for the inhibition of microbes and antioxidant applications. High antileishmanial activities were exhibited by the ZnO NPs, with half-maximal inhibitory concentration values of 76.3 ± 2.08 and 90.4 ± 1.031.

ZnO's manufacturing with plant use is gaining momentum. Because it doesn't require hazardous chemicals, it is regarded as an environmentally benign method (Nagajyothi et al., 2015). ZnO NPs that had been synthesized were examined by relevant tools. It is known that plants appear to be the greatest means for the large-scale use of the green production of metal-oxide NPs through plant-mediated synthesis (Naseer et al., 2020; Rajabi et al., 2020; Dobrucka & Długaszewska, 2016; Alnehia et al., 2022). Plant extract is used to create these NPs because it is ecologically friendly, cost-effective, and easy to scale up (Dobrucka & Długaszewska, 2016; Ramesh et al., 2014). Due to their distinctive characteristics and many applications, ZnO NPs are extremely important to study among metal oxide NPs. Many techniques, including chemicals (solvothermal/sol-gel), can be used to create ZnO NPs. The chemical technique is not preferred in the manufacture of NPs as dangerous compounds are generated that may be absorbed on the NPs' surface. Similar problems are connected to physical approaches, such as their high cost and need for extreme conditions of reaction (Khan et al., 2020; Yuvakkumar et al., 2014). Due to its ease, cheapness, and significant antibacterial action, biosynthesis offers an appealing approach (Gunalan et al., 2012). Aside from being straightforward, biosynthesis of pure materials frequently requires no specialized knowledge or expensive equipment. Plant use has a precious impact on the morphology of the NPs formed (Xu et al., 2021). Synthesis methods, characterizations, and property development of the nanosized ZnO material are illustrated in Table 10.1.

Among the different procedures applied for the preparation of NPs of ZnO, green synthesis, biosynthesis, and plant-mediated synthesis methods have become more popular. In these methods, different plant extracts and plant parts are used for the preparation of pure ZnO NPs. Table 10.2 demonstrates some of the plants that were used for fabricating the NPs of zinc oxide.

It can be inferred that the green synthesis and biosynthesis methods have been mostly followed recently. Figure 10.1 presents a summary of the status of the synthesis, characterization, properties, and application of ZnO NPs for sustainable plant production.

4 Nanofertilization

Nanofertilizers are fertilizer substances with a nanometer-sized dimension that are applied to plants in a regulated manner (Bedi & Singh, 2022). NPs that enhance the yield of plants are considered nanofertilizers (Liu & Lal, 2015). NPs that enable conventional fertilizers to perform better but do not directly supply nutrients to crops are also considered nanofertilizers. The former are collectively referred to as nanofertilizers. Also, there are two subcategories of nanofertilizers: macronutrients and micronutrients. Meijas and coworkers inspected the implicit use of nanofertilizers (Mejias et al., 2021). Nanofertilizers are utilized to boost soil fertility as well as plant nutrition and nutrient efficiency (Toksha et al., 2021). The physicochemical

Table 10.1 Synthesis, characterization, and property development of ZnO NPs

Material	Method	Characterization	Property development	References
ZnO NPs	Green synthesis	XRD, SEM, EDX, UV–vis	(i) Green ZnO NPs had a mean diameter that was 57% smaller in compare to normal ZnO. (ii) Compared to normal ZnO NPs, green NPs had a greater seed output of 13.3%, a higher protein content of 5.6%, and a higher Zn content of 3.2%.	Sahoo et al. (2021)
ZnO NPs	Green route (extract of *Aloe barbadensis Mill leaf*)	Optical spectroscopy, electron microscopy	(i) Particle size of ZnO NPs = 35 nm (ii) Spherical shaped particle (iii) Ability of strong reducing and capping	Singh et al. (2019)
ZnO NPs	Green route (leaf extract of *Piper betleas* explored)	XRD, FTIR, UV-vis, EDX	(i) Band gap energy of the prepared ZnO NPs = 3.41 eV (ii) Photocatalytic activity = 96.4% (for red dye) (iii) Rate constant = 1.6×10^{-2} min^{-1} (iv) Better antimicrobial	Goyal et al. (2022)
Triangular ZnO NPs	*Azadirachta indica* leaves extract	XRD, FTIR	(i) Grain size = 60–65 nm	Sharma et al. (2022)
SiO_2 ZnO nanocomposite	(i) Biosynthesis method (ii) Brown seaweed algae were used	UV-vis, SEM, FTIR, XRD	(i) Therapeutic for colon cancer's HT29 cancer cell line (ii) Exhibits excellent antioxidant activity	Swarna Bharathi et al. (2022)
ZnO NPs	(i) Biosynthesis (ii) Plant parts of *Bixa orellana* utilized	UV-vis, XRD	(i) Hexagonal wurtzite structures (ii) Band gap obtained = 3.636 eV	Gharpure et al. (2022)
ZnO NPs	(i) Biosynthesis (ii) Extraction of moringa leaves used	UV-vis, XRD	Significant antibacterial activity	Abel et al. (2021)
ZnO NPs	(i) Green synthesis (ii) Sheep/goat faecal matter were used	UV-vis, XRD, SEM	(i) Spongy-like and flower-shaped granules with irregular structures (ii) Showed effective antibacterial activity	Chikkanna et al. (2019)
ZnO and Mn NPs	(i) Co-precipitation method (ii) Carica papaya extract used	XRD	(i) Red shift in the absorbance spectrum observed (ii) Mn-doped ZnO NPs revealed better antibacterial performance than that with ZnO NPs	Priyadharsini et al. (2021)

(continued)

Table 10.1 (continued)

Material	Method	Characterization	Property development	References
ZnO NPs	(i) Precipitation method (ii) *R. sativus* leaf extract	XRD, SEM, EDX	(i) Particle size of 66.47 nm (ii) Wurtzite structure (iii) Effective with bacteria	Al Awadh et al. (2022)
ZnO NPs	(i) Green synthesis (ii) Leaves extract of olive and marjoram were used	XRD	(i) Antifungal activity of ZnO NPs were tested on sweet bell pepper	Hassan et al. (2019)
ZnO NPs	(i) Biological method (ii) *A. marmelos* unripe fruit extract	XRD, SEM, FTIR	(i) Hexagonal wurtzite structure (ii) Crystallite size = 19.8 nm, particle size = 22.5 nm (iii) Prepared NPs were stable (iv) Am-ZnO NPs had better antibacterial and antibiofilm effects on Gram-negative bacteria	Senthamarai and Malaikoz-hundan (2022)
ZnO NPs	(ii) Green synthesis method (ii) Root bark extract of *Cassia sieberiana*	XRD, SEM, EDX, TEM, FTIR	(i) TEM measured particle size as 12.9 nm (ii) Particles were spherical in shape (iii) ZnO NPs showed good antioxidant property	Kyene et al. (2023)
ZnO NPs	(i) Biogenic techniques (ii) Aqueous extract of *Tavernier glabra*	UV-vis, XRD, SEM, EDX, FTIR	(i) Surface plasmon resonance peak at 288 nm (ii) As formed ZnO NPs are antimicrobial (iii) As prepared ZnO NPs showed strong antileishmanial activities	Khan et al. (2023)
ZnO NPs	(i) Green synthesis method (ii) Usage *Polygala tenuifolia* root extract	FTIR, UV-vis, TGA, EDX, SEM, and TEM	(i) Anti-inflammatory activity (ii) Antioxidant (iii) Anti-inflammatory	Nagajyothi et al. (2015)
ZnO NPs	(i) Green synthesis method (ii) *Hibiscus subdariffa* leaf extract	XRD	Anti-bacterial activity	Bala et al. (2015)
ZnO NPs	(i) Green synthesis (ii) *Phyllanthus embilica* stem extract	XRD, SEM	ZnO NPs showed antibacterial activity	Joel and Badhusha (2016)

(continued)

Table 10.1 (continued)

Material	Method	Characterization	Property development	References
ZnO NPs	(i) Biological synthesis route (ii) Leaf/bark of carica papaya	UV-vis, FTIR, EDX, TEM, SEM	(i) Absorption peaks obtained at 365 and 370 nm (ii) Flower/petal shaped (iii) Particle diameter = 141–168 nm	Droepenu et al. (2019)
ZnO NPs	(i) Biosynthesis (ii) *Anacardium occidentale* leaf	FTIR, SEM, TEM, EDX	(i) ZnO structures were flake-like (ii) TEM measured particle size 107 nm (iii) Strong antibacterial	Droepenu et al. (2021)
ZnO NPs	Bio synthesis (leaf extract-assisted)	HRTEM, XRD	(i) Hexagonal wurtzite structure (ii) Particle size = 15.6 nm (iii) Zeta potential = −12.14 mV	Malaikozhundan et al. (2020)
ZnO NPs	Biosynthesis	XRD, UV-Vis, EDX, TEM, FTIR	(i) Hexagonal morphology (ii) SPR peak value = 370 nm	Sharmila et al. (2018)
ZnO NPs	Green synthesis	XRD, FTIR, SEM/EDX, TGA, TEM/SAED	(i) Particle size = 2.90–25.20 nm (ii) Shape: spherical/rod	Nagajyothi et al. (2014)
ZnO NPs and ZnO/CuO nanocomposite	Green synthesis	TGA, XRD, EDX, FE-SEM, TEM, FTIR, DRS, and BET	(i) Obtained size of ZnO = 12 nm (ii) Specific surface areas: (a) ZnO (W) = 29.3 m^2/g^{-1}, and (b) ZnO/CuO = 18.0 m^2/g^{-1}	Mohammadi-aloucheh et al. (2018)

qualities and soil microbial symbiosis are affected by several factors. Nanofertilizers are anticipated to considerably increase crop growth and yields, increase fertilizer usage efficiency, limit nutrient losses, and minimize negative environmental effects (Liu & Lal, 2015). NPs possess a "smart delivery strategy". Techniques like targeted distribution and controlled release of nanostructured fertilizers can improve the efficiency of nutrient usage. According to reports, nanofertilizers can increase agricultural output by speeding up photosynthesis, nitrogen metabolism, and the generation of proteins and carbohydrates.

Techniques that are used in crops through conventional fertilizers are spraying or broadcasting. This is based on the fertilizer concentration required for the plants. The repeated use of chemical fertilizers skeptically affects the balance of inherent nutrients in the soil. So, the optimal use of chemical fertilization is required for the crop, thereby minimizing the threat of pollution in the environment. Thus, to keep the environment clean and the soil structure in good shape, there is a need for alternative methods for fertilizing the soil with improved plant growth (Miransari, 2011).

With the help of nanotechnology, the fabrication of smart fertilizers with less pollution is feasible (Chinnamuthu & Boopati, 2009). The utilization of nanotechnology in agriculture is valuable for the delivery of agricultural chemicals like fertilizers that meet the required nutrients. Due to their tiny size, elevated mobility,

Table 10.2 Plant extracts used for the ZnO NPs's fabrication

Plants used	References
Aloe vera extract	Mandal et al. (2018)
Olive and marjoram	Hassan et al. (2019)
R. sativus leaf extract	Al Awadh et al. (2022)
Carica papaya extract used	Priyadharsini et al. (2021)
Extraction of moringa leaves	Abel et al. (2021)
Aloe barbadensis Mill	Singh et al. (2019)
Piper betleas	Goyal et al. (2022)
Azadirachta indica leaves extract	Sharma et al. (2022)
Brown seaweed algae were used	Swarna Bharathi et al. (2022)
Bixa orellana	Gharpure et al. (2022)
A. marmelos unripe fruit extract	Senthamarai & Malaikozhundan (2022)
(i) Extract of root bark of *Cassia sieberiana* (ii) The bark was used for the purpose of capping as well as stabilizing	Kyene et al. (2023)
Tavernier glabra extract, a medicinal plant	Khan et al. (2023)
Polygala tenuifolia	Nagajyothi et al. (2015)
Organic extract of *Cola nitida* and *Cola acuminata* leaf	Aquisman et al. (2020)
Hibiscus subdariffa	Bala et al. (2015)
Phyllanthus embilica stem	Joel and Badhusha (2016)
Carica papaya	Droepenu et al. (2019)
Anacardium occidentale	Droepenu et al. (2021)
Watercress (*Nasturtium officinale*) extract (medicinal plant)	Bayrami et al. (2019)
Syzygium cumini	Arumugam et al. (2021)
Leaf extract of *Sambucus ebulus*	Alamdari et al. (2020)
Withania somnifera	Malaikozhundan et al. (2020)
Bauhinia tomentosa	Sharmila et al. (2018)
Utilizing *Coptidis Rhizoma*	Nagajyothi et al. (2014)
Albizia lebbeck	Umar et al. (2019)
Applying *Vaccinium arctostaphylos* L. Fruit extract	Mohammadi-aloucheh et al. (2018)
Tecoma castanifolia	Sharmila et al. (2019)
Thymus vulgaris leaf	Zare et al. (2019)
Solenostemon monostachyus leaf extract	Karu et al. (2020)
Nasturtium officinale	Bayrami et al. (2019)

decreased toxicity, large surface-to-volume ratio, and raised solubility, NPs possess the characteristics required for plants (Sasson et al., 2007; DeRosa et al., 2010; Brady & Weil, 1999). Because of their large particle size and low solubility, normal fertilizers are not very bioavailable to plants. While nanofertilizers have more solubility, their larger surface areas show more bioavailability to plants. Also, the use of nanostructured formulations may improve fertilizer effectiveness and soil nutrient absorption ratios during crop production.

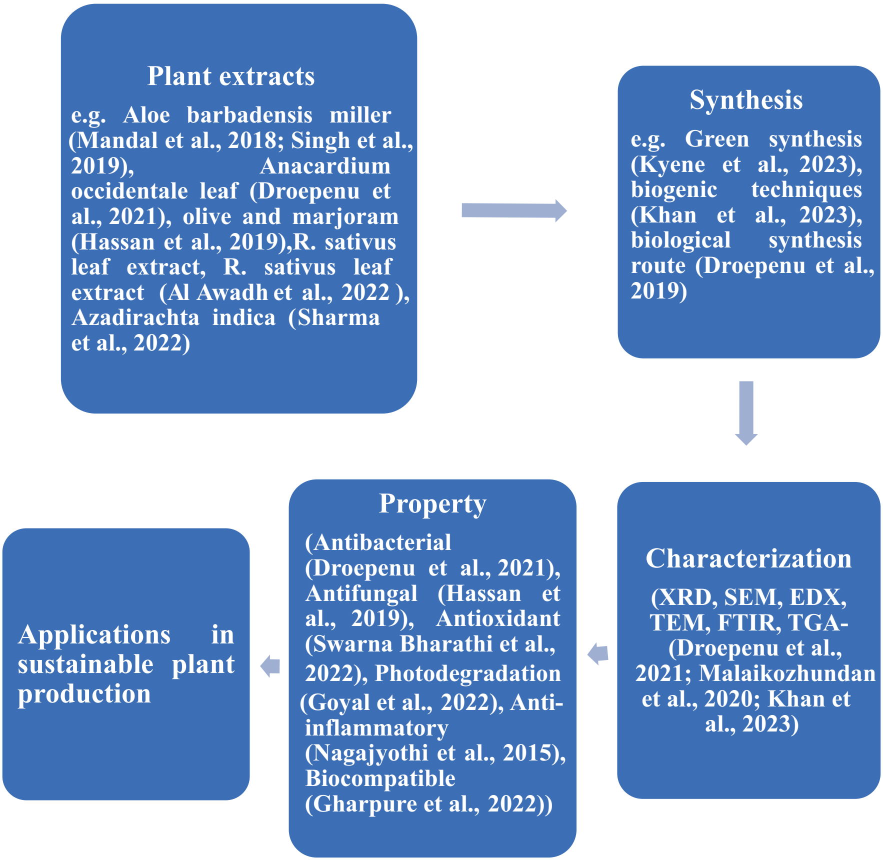

Fig. 10.1 Summary of the status of synthesis, characterization, property, and application of ZnO NPs for sustainable plant production

5 Use of ZnO NPs in Sustainable Plant Production

Nanotechnology promotes sustainable plant production and development in agriculture. Priyanka and Venkatachalam utilized ZnO NPs as fresh micronutrient catalysts to promote cotton plant development (Priyanka & Venkatachalam, 2016). The cadmium and lead phytotoxicity in cotton seedlings was mediated using ZnO NPs (Priyanka et al., 2021). The biogenesis of ZnO NPs was investigated for the revolution in agriculture by focusing on plant growth stimulation and anti-contagion (Keerthana et al., 2021). The biocompatible nature of ZnO NPs and their potential as a promising material in biomedical applications are also reported (Gharpure et al., 2022). With their biocompatible nature, ZnO NPs can be utilized as carrier molecules in applications involving medication delivery. Being antibacterial, NPs of ZnO rupture membranes and produce reactive free radicals. ZnO NPs have excellent antioxidant effects in healthy mammalian cells.

A novel, environmentally friendly approach for the treatment of filthy water is needed (Shannon et al., 2008). Since pesticides and herbicides are very toxic, chemically stable, and resistant to biodegradation, using them on agricultural land results in poisoning (Mestankova et al., 2011; Sanches et al., 2010; Tizaoui et al., 2011; Kamble et al., 2006). Water pollution is also a result of the textile industry's use of colors and the enormous amounts of dye that are discharged into the water during the production and dyeing processes as textile effluent (Zhang & Zeng, 2012). Through acts like hydrolysis and related chemical reactions that occur in wastewater, hazardous compounds are created during the breakdown of these colors. The amount of oxygen that is soluble in colored wastewater decreases, which is essential for aquatic life because of the dyes present. Moreover, it stops sunlight from entering aquatic bodies. Hence, releasing these pigments into the wastewater without proper processing results in pollution problems (Zhang et al., 2010, 2011). Eliminating these dangerous dye-containing effluents is thus becoming more and more popular.

Salt stress is a major issue in tomato and other plants. ZnO nanoparticles (NPs) have been treated with tomatoes and other plants to enhance their properties and have been observed to effectively mitigate diseases (Faizan et al., 2021a, b, c; Ahmed et al., 2022). The stress resulting from Cd has also been overcome in *Oryza sativa* (Faizan, 2021b) by the NPs of ZnO. Chilling stress in rice (Song et al., 2021) and drought-induced oxidative stress in tomato (El-Zohri et al., 2021) have been examined to be cured with ZnO NPs. Figure 10.2 depicts all these stresses in plants, and a few valuable uses of ZnO NPs are presented in Fig. 10.3.

Table 10.3 and Fig. 10.4 demonstrate the use of ZnO NPs in sustainable plant production.

Mandal et al. (2018) investigated the photodecomposition of methylene blue (MeB) using NPs of ZnO that were obtained via green synthesis. Toxic industrial effluents have prompted a lot of focus on methods to remove dangerous contaminants from wastewater. Because these contaminants affect the cultivation and reduce plant development, they cause plant diseases. Reported research by Mandal and his group supports the use of ZnO NPs for the plant's sustainable production. Figure 10.5 indicates the decrease in absorbance, that is, the concentration of pollutant MeB in water, through the ZnO photocatalyst that was prepared by Mandal et al. using aloe vera (Mandal et al., 2018).

6 Future Trends

Great challenges are associated with nanofertilizers for practical application in future crop production, biosafety, and ethical issues. The creation of affordable, nontoxic NPs is highly demanded for the efficacious implementation of nanotechnology in agriculture's future. The aim of nanoagriculture will be higher plant growth with magnificent yields. The practice of using ZnO-based and other nontoxic nanofertilizers will increase the sustainable development of plant growth and

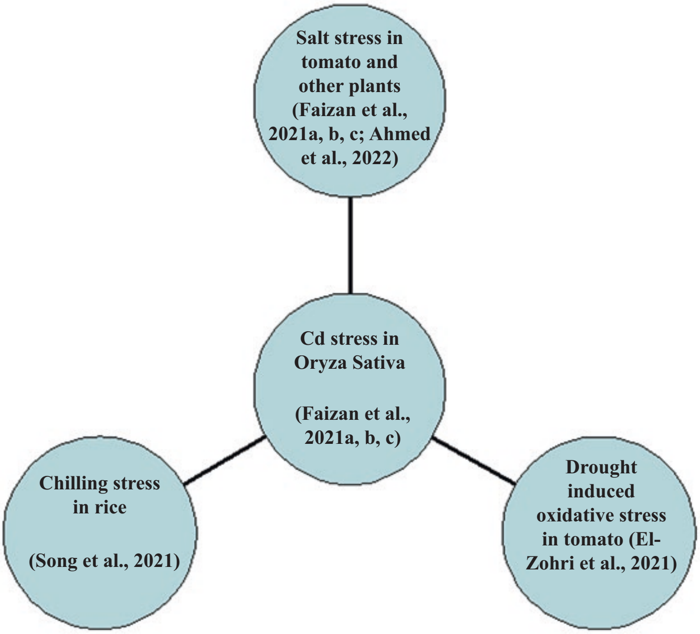

Fig. 10.2 ZnO NPs to mitigate the different stresses in plant production

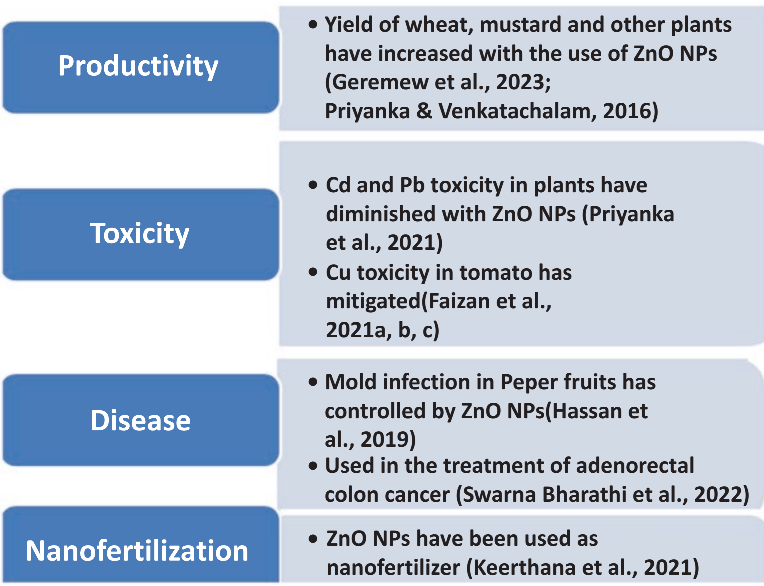

Fig. 10.3 Some applications of ZnO NPs

Table 10.3 The use of ZnO NPs in sustainable plant production

Material	Property	Application	References
ZnO NPs	Micronutrient catalyst	Surge of cotton crop productivity	Priyanka and Venkatachalam (2016)
ZnO NPs	Catalyst	Mediates cadmium and lead toxicity tolerance	Priyanka et al. (2021)
ZnO NPs	Antimicrobial	Antimicrobial activity as well as nanofertilizers	Keerthana et al. (2021)
ZnO NPs	Antifungal	Postharvest control of grey and black mold infections on pepper fruits	Hassan et al. (2019)
Triangular ZnO NPs	Antimicrobial	Antimicrobial performance – (i) *Escherichia coli* (ii) *Bacillus subtilis*	Sharma et al. (2022)
SiO_2 ZnO nanocomposites	Antioxidant activity	Shows function on adenorectal colon cancer cell	Swarna Bharathi et al. (2022)
ZnO NPS	Biocompatible	Carrier molecules used in delivery of medicine	Gharpure et al. (2022)
ZnO	Antimicrobial activity	Antimicrobial – (i) *Salmonella typhimurium* (ii) *Bacillus subtilis*	Chikkanna et al. (2019)
Mn-doped ZnO NPs	Antimicrobial	Applied for – (a) Gram positive – (b) Gram negative bacteria	Priyadharsini et al. (2021)
ZnO NPs	Photocatalysis	Degraded MB (ZnO NPs + sunlight)	Mandal et al. (2018)
ZnO NPs	Increased chlorophyll contents	Yield of wheat was increased	Adil et al. (2022)
ZnO NP (green synthesized and cow-dung mediated)	Agriculture	Germination potential of Mung bean seeds have been examined	
ZnO NP (engineered)	Agronomic productions	Production of large food and protection of environmental	Liu and Lal (2015)
ZnO NPs	Antioxidant, antimicrobial	Effective action of antimicrobial action: (a) *S. typhi* (b) *S. aureus*	Kyene et al. (2023)
ZnO NPs	Antimicrobial and antioxidant	Detected antimicrobial performances: (i) niger and (ii) subtilis, etc.	Khan et al. (2023)
ZnO NPs	Antimicrobial and antioxidant	(i) Antibacterial agents (ii) Antioxidant (normal mammalian cells)	Singh et al. (2021)

(continued)

Table 10.3 (continued)

Material	Property	Application	References
ZnO NPs	Antimicrobial and antioxidant	(i) Anti-inflammatory activity: in RAW 264.7 macrophages (ii) Antioxidant activity: 2,2-Diphenyl-1-picrylhydrazyl assay	Nagajyothi et al. (2015)
ZnO NPs	(i) Antimicrobial (ii) Antioxidant	Antibacterial activity of ZnO NPs	Aquisman et al. (2020)
ZnO NPs	Antimicrobial, antioxidant	Antibacterial activity of ZnO NPs	Bala et al. (2015)
ZnO NPs	(i) Antimicrobial (ii) Antioxidant	Antibacterial activity of ZnO	Joel and Badhusha (2016)
ZnO NPs	Antimicrobial	Antibacterial efficacy	Droepenu et al. (2019)
ZnO NPs	Antibacterial	Strong effect with infectious bacteria (Gram positive and Gram negative microbes)	Droepenu et al. (2021)
ZnO NPs	Antibacterial	ZnO NPs was treated on the *Staphylococcus aureus* and *Escherichia coli*	Bayrami et al. (2019)
	Antioxidants, nanonutrient, cytotoxic	Tested on – *Sesamum indicum*	Arumugam et al. (2021)
	Good antimicrobials, and insecticides for fighting storage pests	At 100 g mL^{1}, ZnO NPs had a stronger activity with – (i) *E. faecalis* (ii) *S. aureus*.	Malaikozhundan et al. (2020)
ZnO NPs	Suitable bactericidal species for biological uses	Effectively combated (i) *P. aeruginosa*, (ii) *E. coli*.	Sharmila et al. (2018)
ZnO NPs	Antibacterial	(i) Gram-positive (ii) Gram-negative bacteria	Nagajyothi et al. (2014)
(i) ZnO NPs (ii) ZnO/CuO nanocomposite	Antibacterial	Anti-bacterial (i) *Escherichia coli*, etc.	Mohammadi-aloucheh et al. (2018)

crop production. There will be a trend toward the development of green synthesis techniques for ZnO NP production. In future, there will be a trend toward producing a large number of plants with fewer disturbances to the environment and yielding huge amounts of crops with less environmental pollution.

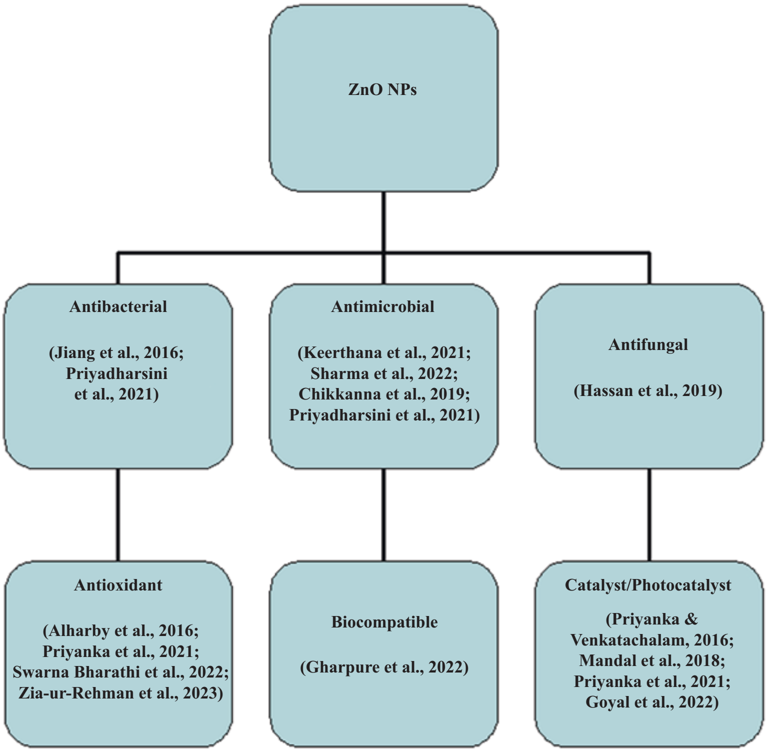

Fig. 10.4 The execution of zinc oxide nanoparticles in sustainable plant production

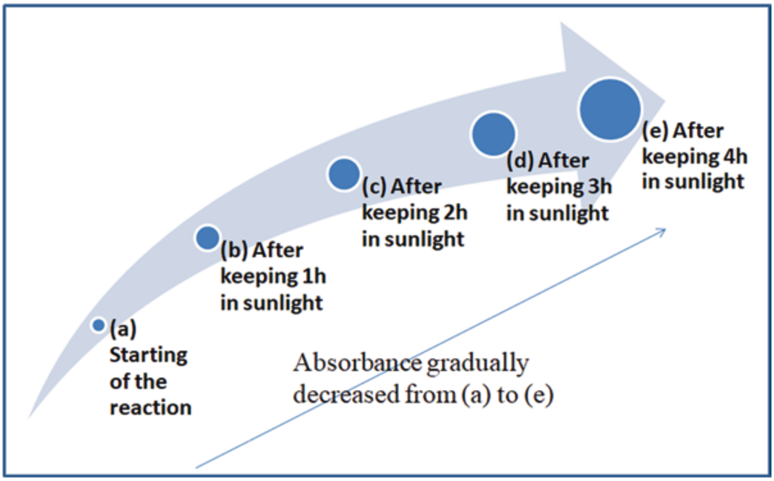

Fig. 10.5 Treatment of zinc oxide nanoparticles with methylene blue through the photocatalytic reaction. (**a**) Reaction's beginning and on keeping in the sun, for (**b**) 1 h, (**c**) 2 h, (**d**) 3 h and (**e**) 4 h

7 Conclusion

ZnO NPs could be used for sustainable agriculture, plant disease control, and crop production. However, as the properties of NPs adversely affect plants and the environment, the dose of NPs used should be well monitored. ZnO-based nanofertilizers will be able to overcome the issues of rapid degradation of ordinary fertilizers that result from photolysis, hydrolysis, and decomposition reactions. They enable the soil's gradual absorption of crucial nutrients. ZnO-based nanofertilizers can encounter challenges related to higher fertilizer consumption and soil pollution in agriculture. Nanofertilizer's application has amplified the soil's nutrient absorption and increased the productivity of crops. The influence of ZnO-based and other nanofertilizers varies with the dose, morphology, structure, duration, and solubility of the associated NPs. It is obligatory to perceive the importance of NPs of green ZnO, which have better qualities and are more environmentally benign.

More research is required to produce sustainable plants using ZnO and other NPs. Environment-friendly green synthesis routes should be explored on a large scale to produce ZnO NPs, which will increase plant production, decrease diseases in plants, and reduce the crisis in the environment. The green synthesized ZnO NPs can be used to address the inadequacies of Zn in soil for agricultural use in a cost-effective, environmentally safe, and sustainable manner.

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Chapter 11
Chitosan-Based Nanofertilizer: Types, Formulations, and Plant Promotion Mechanism

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1 Introduction

An increase in urbanization and consumption has led to increasing demand for food supply, thereby leading to the necessity of increased yield and crop production. In order to satisfy this expanding worldwide demand, high dosages of synthetic fertilizers, herbicides, and agrochemicals are delivered to plants in an effort to boost production. Synthetic fertilizers enhance crop growth but do not exert any influence on plant nutrient uptake, and their hazardous effects on the environment continue to be the same (Adnan et al., 2020). They do not seem to hold an advantage when seen from an economic perspective either. Therefore, the search continues for alternatives that are not only well suited as fertilizers but are also highly efficient under various stressful conditions, are biocompatible, and are less toxic to the environment. The emerging application of nanotechnology in agriculture is seen to bring a breakthrough advancement to the field.

Nanofertilizers that serve the above purpose can be created utilizing specific chemical, physical, mechanical, and biological processes, either from standard bulk fertilizer ingredients or by extracting different plant parts. Nanoparticles are naturally produced in nature through various mechanisms such as physiochemical weathering, volcanic eruptions, neo-formation, etc., as well as from biological

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processes with the aid of mineral-producing microorganisms (Mura et al., 2013). They are naturally found in soil minerals. Moving colloids take these nanoparticles from soil micropores, enhance their mobility, and fix them in macropores. They may readily be hindered in their motion if taken up by stationary particles. In addition to generating a complicated system of soil sedimentation with macromolecules, nanoparticles may also add soil heterogeneity, posing some challenges to leaching and transport in soil (Ben-Moshe et al., 2010; Fang et al., 2009). Nanofertilizers release agrochemicals, decrease soil toxicity, provide a target delivery mechanism, and increase fertilizer nutritional efficiency. Because of their high surface area-to-volume ratio, target specificity, better solubility, tiny size resulting in excellent mobility, and low toxicity, nanofertilizers are highly beneficial.

Preference for nanofertilizers over conventional fertilizers has already resulted in improvements in a number of agricultural issues, including declining crop yield, decline in soil organic matter, lack of soil nutrients, lack of soil heterogeneity, and loss of soil biodiversity (Jakhar et al., 2022). Keeping in mind other environmental factors such as a changing climate, a reduction in the amount of arable land due to urbanization, freshwater inaccessibility, and a manpower shortage, new-age fertilizers need to be designed to combat existing issues and prevent new ones from surfacing.

Chitosan is also nontoxic, which eliminates any potential environmental concerns. Chitosan's renewable food waste origin contributes to its biocompatibility and biodegradability. All of these characteristics combine to make chitosan nanoparticles an effective next-generation fertilizer for plant systems (Kashyap et al., 2015). The current review explores the properties of chitosan NMs as prospective next-generation fertilizers and methods for manufacturing chitosan nanoforms, as well as providing vital insights into the future directions of chitosan-based next-generation nanofertilizers (Fig. 11.1).

2 Chitosan

As the need for sustainable agriculture becomes more prominent with each passing day, the search for novel candidates with the desired turnover has intensified. Materials that are nontoxic, biocompatible, and biodegradable are most suitable, particularly those that require low capital investment but produce high yields of crops. Chitosan ticks off all these requirements. As one of the most abundant naturally occurring amino polysaccharides derived from biological wastes, chitosan find numerous agricultural and biological applications (Kumaraswamy et al., 2018). There have been a variety of chitosan types derived with many biological activities, including antibacterial and antifungal properties, but no two types of chitosan share the exact same set owing to their differing structures and physiochemical properties. Nevertheless, it only results in a wider range of applications and novel findings to cater to different needs.

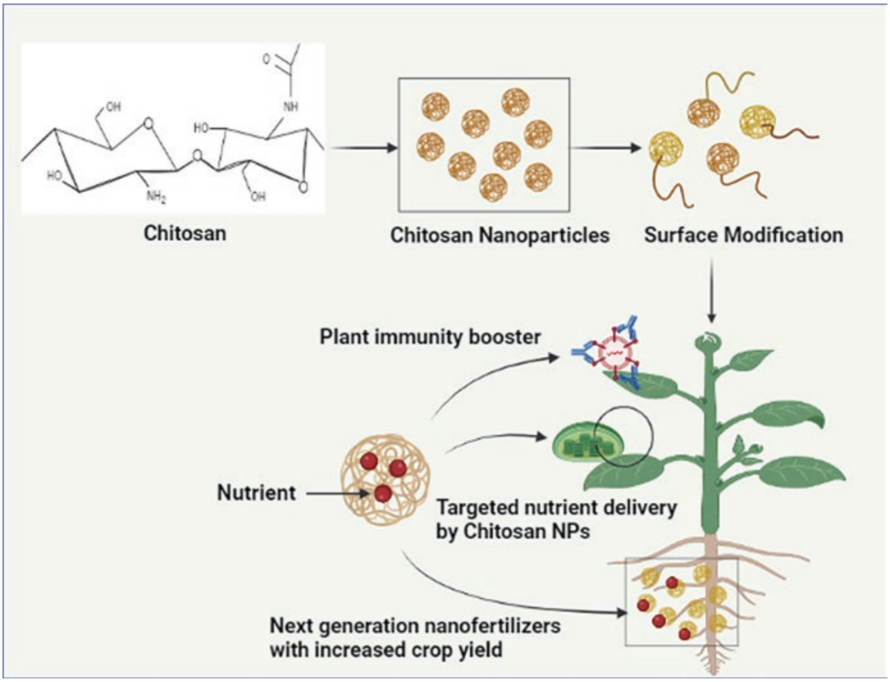

Fig. 11.1 Chitosan NMs offer significant promise as next-generation fertilizers; nevertheless, more study is required to improve their characteristics and application methods for various crops and growth situations. Field trials and long-term environmental monitoring are needed to assess the effectiveness and safety of chitosan NMs as fertilizers. Furthermore, because of the complexity of their synthesis and processing, chitosan NMs may be more expensive than standard fertilizers in terms of cost-effectiveness. In conclusion, chitosan NMs have the potential to transform the fertilizer industry by offering environmentally benign, slow-release, and effective fertilizers. However, further research is required to fully understand their advantages and disadvantages as well as to design appropriate application techniques for various agricultural systems

2.1 An Overview: Sources, Structure, and Medicinal Properties

Chitosan, a polycationic polymer, is essentially derived from chitin, the second most abundant polysaccharide available in nature, following cellulose. Chitin is an economic polymer that can be obtained from marine wastes; it is mainly found in crustacean exoskeletons and arthropods, although it is also spotted in the cell walls of fungi, yeast, and algae (Zargar et al., 2015). Chitosan and chitin are both made of numerous variations of the same two monomers: α,1-4 linked D-glucosamine and *N*-acetyl-D-glucosamine (Ibrahim & El-Zairy, 2015). Chitosan is essentially obtained from chitin through deacetylation (Fig. 11.2), and to date, three different crystallographic forms of chitin have been reported, namely: alpha (α), beta (β), and gamma (γ) chitosan, with alpha and gamma chitosan being more similar to each other in physiochemical terms (Kaya et al., 2017). These physiochemical

Fig. 11.2 Preparation of chitosan by deacetylation. (Created with BioRender.com)

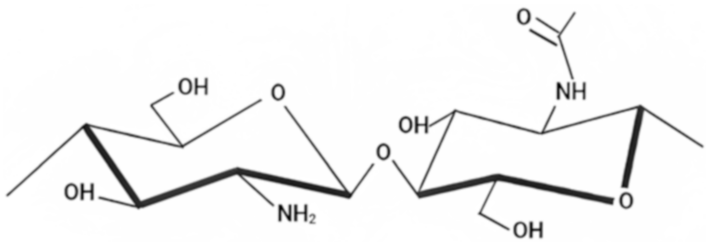

Fig. 11.3 Chitosan is a natural biopolymer formed from chitin, a polysaccharide found in crustaceans' shells and fungi's cell walls. Chitosan is created by deacetylating chitin, removing some of the acetyl groups, and converting it into a cationic polysaccharide. The resultant chitosan molecule has a linear structure with glucosamine and *N*-acetylglucosamine repeating units joined by (14) β glycosidic linkages. Chitosan's chemical structure is represented by the molecular formula $(C_6H_{11}NO_4)n$

characteristics are usually measured through Fourier-transform infrared spectroscopy, scanning electron microscopy, liquid-state nuclear magnetic resonance, etc.

Chitosan's functionality is due to the amino and hydroxyl groups on its second, third, and sixth carbons, among which the hydroxyl group at C6 is the most active owing to the minimal steric hindrance it faces (Fig. 11.3). This allows free rotation of C6-OH when compared to the hydroxyl group at the third carbon. Due to the high availability of NH_2 and OH for bonding, chitosan functions as a compound with high bioactivity (Wang et al., 2020a, b). Chitosan's ability to adhere to plant surfaces comes from the amino group it owns, which gives chitosan a net positive charge as a result of which it is able to form interactions with anionic molecules on membrane layers (Jakhar et al., 2022).

Chitosan finds various applications in the biomedical field owing to its various properties, which make it medicinally compatible. In addition to having strong antibacterial, antiviral, and antifungal effects, it also has other characteristics like nontoxicity, hemocompatibility, and mucoadhesivity (Zhao et al., 2018). One of chitosan's primary advantages as a biomedical agent is that it does not trigger a strong immune response. Its ability to adhere to mucus not only makes mucosal pathway delivery easy but also aids in the delivery of agents that lack affinity to mucus (Bugnicourt & Ladavière, 2016). Chitosan is seen to increase wound healing rates by interacting with platelets through its amino groups (Okamoto et al., 2003). It is also found to have potential antitumor activity along with its elevated antioxidant capacity (Tokoro et al., 1988; Younes & Rinaudo, 2015). On top of it all, chitosan's biodegradability is what makes it a perfect next-generation candidate as an efficient biomedical agent.

2.2 Role of Chitosan in Agriculture

The presence of numerous amino and hydroxyl group in the chitosan made its use as adsorbents to remove organic and inorganic pollutants from water (Bandara et al., 2020). Chitosan was widely used as a flocculating agent to gather pollutants as a part of the wastewater treatment process (Lichtfouse et al., 2019). Magnetic chitosan nanoparticles were also seen as promising adsorbents because of the possibility of adsorbent recycling under a magnetic field (Lü et al., 2017). Following this, chitosan's primary uses shifted from sewage and water treatment to extensive use as a fertilizer, plant growth stimulant, soil enricher, ant staling agent, etc. Chitosan not only has antibacterial and antifungal activity, but it also induces disease resistance in various plants by enhancing innate immunity (Babu et al., 2022). Chitosan application on plants reduced water loss in plant systems and restricted stomatal apertures, acting as an antitranspirant and limiting pathogen entry into plants through stomata (Bittelli et al., 2001). Chitosan is also proven to combat salinity and drought stress in plants. Several stresses occurring due to abiotic conditions are also tackled by chitosan through increased production of aldehydes, ketones, and phenols in plants, which aid in stress tolerance regulation (Bandara et al., 2020).

3 Chitosan as a Nanofertilizer

3.1 Chitosan as a Nanofertilizer: Properties and Function

Porous nanosized chitosan is considered one of the most effective candidates for micro- and macronutrient delivery in recent times. Although soil fertilization is one of the vital practices required to support crop growth, a variety of setbacks are still observed that hinder the proper functioning of said fertilizers. Conventional fertilizers used for prolonged periods in large quantities not only alter soil pH but also increase soil salinity. To combat such issues, chitosan-based nanofertilizers were researched owing to the promising properties they possess (Mujtaba et al., 2020).

Chitosan is an ideal choice for the formulation of nanofertilizers for various reasons, including its low cost, but there are certain distinct attributes that enhance its bioactivity (Yu et al., 2021). Chitosan's ability to trigger the plant's innate immune system guarantees plant redox homeostasis maintenance (Babu et al., 2022). The slow-release property of chitosan nanomaterials prolongs the availability of nutrients to the plants, thereby ensuring complete and efficient uptake of these materials (Prajapati et al., 2022). Chitosan nanomaterials possess a low dispersity index, which is essential to ensuring stability and consistent bioactivity. The zeta potential of nano-chitosan becomes extremely important due to its effect on the penetration ability of the nanoparticles and the possibility of surface interactions (Saharan et al., 2016). High zeta potential leads to high repulsion between nanoparticles, which prevents them from forming aggregates in the soil (Hu et al., 2020; Schwab et al., 2015). Size is, of course, a key consideration for elevated surface interactions. Chitosan nanoparticles with symmetric nanoarchitecture can infiltrate plant tissues with only moderate inhibition. The small size of chitosan nanofertilizer is said to facilitate its entry into plant leaf stomata, from where it is translocated throughout the plant system via phloem from the root to the shoot (Mujtaba et al., 2020). Nano-chitosan is seen to easily penetrate the stomata, stigma, cuticle, trichome, and even root connections and plant wounds (Eichert et al., 2008; Yu et al., 2021).

Structurally speaking, as a consequence of reduced steric hindrance, amino groups, and hydroxyl groups are made more available for bonding, which enables chitosan's increased bioactivity (Wang et al., 2020a, b). Interactions of chitosan with membrane phospholipids are facilitated by the amino group, which imparts a net positive charge on chitosan. On the other hand, the hydroxyl group accelerates signal transduction due to its electron-accepting nature. This innate functionality of chitosan is elevated through cross-linking a cationic amino group containing linear chitosan with anionic tripolyphosphate (TPP) (Azmana et al., 2021). The resulting chitosan nanomaterials exhibit a higher surface area-to-volume ratio. This results in an increase in the number of surface functional groups, which ultimately increases the possibility of interactions with plant surfaces. These functional groups of chitosan nanomaterials covalently or electrostatically bond with various ingredients and form several conjugates with organic and inorganic materials. The porous structure of chitosan increases these interactions even more, leading to a higher load of active materials in the nano-chitosan (Kumaraswamy et al., 2018). In addition to all these characteristics, the cationic polymer is inherently anti-inflammatory and anti-hypercholesterolemic in nature, and this can be even more enhanced by conjugation with several compounds like urea (Bandara et al., 2020; Negm et al., 2020). Chitosan is also nontoxic, which eliminates any environmental concerns that might arise. Chitosan's origin source being renewable food waste contributes to its biocompatibility and biodegradability. All these factors make chitosan nanomaterials an excellent next-generation fertilizer for plant systems (Kashyap et al., 2015).

3.2 Water Retention and Salinity Moderation Capacity of Chitosan

Stress in plants can be induced by various factors, including drought and salinity. Plant anatomy and physiology are heavily dependent on water availability, and a deficiency in this leads to a drastic decrease in yields. Water unavailability leads to the closure of plant stomata, which results in a reduced photosynthesis rate, decreased chlorophyll content in plants, and destruction of chloroplasts. High salinity levels have been proven to be detrimental to plant growth and development (Zayed et al., 2017). Chitosan nanomaterials are able to wonderfully combat these environmental stresses.

Foliar application of chitosan nanofertilizer reduced stomatal conductance and transpiration in plant systems, leading to water retention. Controlled release of nitric oxide (NO) by chitosan nanomaterials alleviates drought stress in plants more effectively than plants with free nitric oxide donor chemicals. Treated plants show high root biomass and photosynthesis rates in contrast to untreated controls. Chitosan is seen to increase the production of phenolic compounds, plant antioxidants, and osmoregulators, eventually increasing crop yield (Priyaadharshini et al., 2019; Rabêlo et al., 2019; Silveira et al., 2019).

Similar to drought stress, NO-releasing chitosan nanoparticles were more effective than free NO donors in tackling salt stress. The controlled release of NO by nano-chitosan increases the bioavailability of NO, thereby increasing chlorophyll content in treated plants. Gene coding for known detoxifying agents like superoxide dismutase (SOD) and jasmonic acid (JA) has been demonstrated in some cases to be upregulated by the application of chitosan nanofertilizer, mitigating any negative impacts of salinity stress on the plants (Hemantaranjan, 2014). Treated plants show high chlorophyll content, high protein levels, and improved metabolism, which ultimately aids better plant growth and development (Oliveira et al., 2016; Sen et al., 2020).

3.3 Chitosan Combats Temperature and Heavy Metal Stress

Extreme temperatures, constantly fluctuating temperatures, and the presence of toxic heavy metals in the cultivation soil are other environmental stresses that are induced in crops (Bandara et al., 2020). There has been a combinational use of bulk chitosan and zinc to suppress heat stress in plants (Ibrahim & Ramadan, 2015). Also, at low temperatures, priming seeds with chitosan at 15 °C did not only decrease germination time but also increase shoot height and root length (Guan et al., 2009). Additionally, chitosan is seen to possess the ability to complex heavy metal ions that might be present in the soil, making them unavailable to enter and affect plant systems, thereby preventing associated damage (Kamari et al., 2011).

4 Types of Chitosan-Based Nanofertilizers and Applications

Owing to their small size, nanoparticles have an increased ability to penetrate plant surfaces, which makes them a potential candidate for fertilizer delivery (Jakhar et al., 2022). Nanofertilizers can be classified into two types, mainly micronutrient and macronutrient nanofertilizers. Different macronutrients like calcium, phosphorus, potassium, magnesium, sulfur, nitrogen, and phosphorus that have been encapsulated with NPs minimize their overall requirements while providing the crops with the appropriate amount of nutrients (Zulfiqar et al., 2019). When combined with various metals and substances, chitosan is seen to show enhanced growth and development in plants, and the amine groups contained in chitosan that are available for bonding exhibit elevated affinity for metals; this trait is exploited for designing chitosan-based nanofertilizers (Adisa et al., 2019).

4.1 Chitosan–NPK Nanofertilizer

Chitosan is combined with nitrogen, phosphorous, and potassium by polymerization to synthesize CS-PMAA nanoparticles, to which urea, calcium phosphate, and potassium chloride are consecutively loaded (Abdel-aziz et al., 2016). When chitosan-NPK was delivered to plant systems through foliar spray, plant characteristics such as plant stem diameter and leaf area were seen to be enhanced when compared to untreated controls, which subsequently increased the overall harvest, mobilization, and crop index (Corradini et al., 2010; Khalifa & Hasaneen, 2018). α- and β-chitosan (CS) derived from shrimp wastes were characterized, produced into nano NPK fertilizers, and applied to *Capsicum annum* L. cv. The acquired results showed that, in comparison to the control and chemical fertilizer-treated plants, the nano-composite NPK with a 25% concentration considerably increased the growth, yield, and harvest of *C. annuum* (Abdel-Aziz et al., 2021). In addition to increased root and shoot height, higher starch content in the roots of treated plants was observed, and slow release of NPK was also detected with over 80% release of loaded materials through 168 h (Prajapati et al., 2022). Elevated carbon and phosphorous availability contribute to enhanced enzymatic activity of acid-alkaline phosphatases and glucosidases in the soil (Kubavat et al., 2020). A comparison drawn between nanomaterials based on their size and zeta potentials extends the conclusion that nanomaterials with greater zeta potential and smaller sizes tend to show enhanced nanofertilizer activity (Motakef Kazemi & Salimi, 2019). One notable advantage of chitosan-NPK fertilizers is that they have a strong affinity to the surface of plants due to a higher positive charge, thereby reducing runoff by a great percentage. This also contributes to a reduction in the interaction of chitosan-NPK nanofertilizer with other nutrients. These nanofertilizers additionally prove to have little to no adverse effects on plant systems (Prajapati et al., 2022).

4.2 Chitosan–Zinc Nanofertilizer

Zinc is an essential plant micronutrient and serves as a cofactor for over 300 enzymes in plants, all while playing a crucial role in maintaining cellular metabolism and homeostasis (Pereira et al., 2017; Deshpande et al., 2017). Hence, formulations of Zn-chitosan nanofertilizers were made to enhance the growth and development of plants. It was also found to have a positive effect on cellular stability and photosynthesis and to increase chlorophyll content in the plant system. The slow release of Zn is seen to contribute significantly to nanofertilizer efficiency (Kumar et al., 2021). Zinc nanoparticles and zinc nitrate were foliar sprayed at dosages of 0, 25, 50, and 100 ppm with and without chitosan. The findings show that zinc nitrate at 50 ppm and zinc nanoparticles at 25 ppm were the most effective dosages for promoting biomass production and accumulation. Particularly when mixed with zinc nitrate, the addition of chitosan improved biomass, production, and photosynthesis-related metrics (Palacio-Márquez et al., 2021). In addition to upregulating several enzymes, such as soluble starch synthase and invertase, which are crucial for plant development, Zn–chitosan NM also increases the availability of antioxidants, which in turn improves cellular stability and redox equilibrium. Due to these various factors, increased starch content in grains, along with enhanced plant survivability, can be achieved, by virtue of which crop development and yield can be significantly positively altered (Prajapati et al., 2022).

4.3 Chitosan–Urea Nanofertilizer

Nitrogen, an extremely essential macronutrient in plants, serves as a precursor for amino acids, which thereafter form various different plant proteins and enzymes. The most commonly used source of nitrogen, which is conventionally administered as a fertilizer for plants, is urea (Kalia et al., 2019). Therefore, chitosan–urea nanofertilizers will ultimately become a fertile field of research. Granular urea is encapsulated into chitosan nanomaterials and produces spherical urea–chitosan nano particles through numerous cross-links. On application, it was found that the release of urea occurs slowly over a period of one whole month, and this controlled release was seen to impact nitrogen interaction dynamics in the soil to a considerable extent (Kalia et al., 2019). When deployed on potato plants, chitosan-urea nanofertilizer was found to increase tuber size and root length, elevate levels of carbon and potassium, and alter ammonium-nitrogen and nitrate-nitrogen in the treated soil (Kondal et al., 2021). Additionally, it induced noticeable alterations in urease and dehydrogenase activity, especially decreasing the former to a large extent. Chitosan–urea nanofertilizers increased water intake in potato plants and induced improved seed germination, which ultimately led to higher potato yield (Wang et al., 2020a, b).

4.4 Chitosan–Copper Nanofertilizer

Although considered toxic for plants and the environment at higher concentrations, copper proves to be a helpful micronutrient when administered in limited quantities, and these effects are reflected in plant growth, development, and reproducibility (Zarb et al., 2002). Naturally, to exploit this effect of copper on plant metabolism, chitosan–copper nanofertilizers were proposed. Through ionic gelation, copper ions were encapsulated in the nanopores of the chitosan matrix; glutaraldehyde-cross-linked hydrogels of chitosan were prepared, which were then complexed with copper nanoparticles (Saharan et al., 2015; Juárez-Maldonado et al., 2016). Studies after application reveal that plants treated with chitosan–Cu nanofertilizers exhibited increased root length, plant height, and stem diameter. Apart from morphological enhancements, a boost in the content of various enzymes like catalase, amylase, protease, and a few defense enzymes was seen, in addition to accelerated antioxidant activity owing to an increase in the production of lycopene, superoxide dismutase, and peroxidase (Saharan et al., 2015). This increase in the growth and development of plants contributes to the controlled release of copper ions from the matrix, which extends the availability of copper for the plants over comparatively long periods of time. Also, when compared to standalone chitosan, chitosan–Cu nanofertilizers seem to have an elevated positive effect on photosynthesis and seedling development, which leads to higher protein content in seeds, thereby increasing crop yield overall (Choudhary et al., 2017; Sathiyabama & Manikandan, 2018). Rivera-Jaramillo et al. demonstrated that PVA-chitosan-nCu complex nanoparticles applied to tomato plants promoted their yield along with an increase in the number of fruits, average fruit weight, aerial fresh weight, and root fresh weight. The complex nanoparticle also improved the defense system by boosting the activity of the phenylalanine ammonia lyase (PAL) enzyme and PR1 gene overexpression (Rivera-Jaramillo et al., 2021).

4.5 Chitosan–Silicon Nanofertilizer

Even though it is not considered a conventional plant essential nutrient, silicon supplementation has proven to enhance various plant characteristics over a period of exposure. Simple silica treatment yielded stronger and thicker stems, better positioning of leaves with shorter internodes, and enhanced resistance to environmental stresses. All these benefits can be magnified if combined with the chitosan delivery system (Frew et al., 2018). Chitosan–Si nanofertilizers are produced by encapsulating silicon in chitosan–TPP matrix. As seen previously in chitosan–NPK nanofertilizers, chitosan–Si fertilizers also have a high value of zeta potential and greater affinity to plant surfaces, which contributes to their high performance. On foliar application of this nanofertilizer, it was observed that the treated plants displayed increased leaf surface area and chlorophyll content, which are naturally reflected in the plant's photosynthesis capabilities. According to a study (Kumaraswamy et al., 2021), chitosan–Si nanofertilizer is seen to influence root length, root number, shoot length, seedling length, and fresh weight significantly. By adding nano-silicon and nano-chitosan to the soil, either individually or in combination, the bioavailability of mineral nutrients is increased, which minimizes the need for huge conventional fertilizer applications. This results in more robust crops and productive plant edaphic systems (Robledo-Olivo). Elevated levels of antioxidant activity and defense enzymes were also observed in the treated plants as compared to their controls. As chitosan and silica induce great plant growth-promoting activity individually, when combined, they give enhanced results in terms of plant development (Prajapati et al., 2022). By encapsulating additional crucial nutrients alongside Si, CS–Si NF may be further customized to expand its utility in treating multi-nutrient insufficiency (Kumaraswamy et al., 2021).

4.6 Chitosan-Copper-Salicylic Nanofertilizer

Another interesting example of the enhanced results of synergistic combinations is the case of chitosan-copper–salicylic nanofertilizers. This is achieved by co-encapsulating copper and salicylic acid inside a highly porous and symmetric chitosan nanomatrix. This symmetry and porosity caused due to a low PDI were attributed to the slow release of components into the soil from the nanomatrix (Sharma et al., 2020). On administration with chitosan–Cu–SA nanofertilizer, treated plants showed increased sucrose content in growing cobs. In a study conducted by (Choudhary et al., 2017), plant height, stem diameter, root length, and root number all demonstrated significantly higher values. Plant photosynthesis and oxidative stress resistance were both elevated as a result of reduced malondialdehyde (Prajapati et al., 2022). Foliar application of Cu–chitosan nanoparticles significantly increased the antioxidant/defense enzyme activity in maize leaves. These plant leaves had SOD activity that was four to six times greater than those treated with bulk chitosan. Apart from boosting plant development, chitosan–Cu nanoparticles also reduce the severity of diseases in plants (Choudhary et al., 2017). Chitosan–copper–salicylic is the best example to support the possibility of delivering both macro and micronutrients into plants while objectively enhancing plant characteristics through the delivery of nutrients, even while inducing high stress and disease resistance in them. Chitosan nanoparticles loaded with salicylic acid at a concentration of 200–400 ppm have been used to reduce Cassava leaf spot disease. Other concentrations of CS-NP-loaded SA improved Cassava plant growth with an increase in the number of shoots, root length, and weight (Hoang et al., 2022).

5 Methods of Formulation

Chitosan micro- and nanoparticles have been prepared using a variety of techniques. While choosing a method, it is important to take into account the particle size, stability of the active component and the finished product, residual toxicity present in the finished product, and the kinetics of the drug release profile (Agnihotri et al., 200). The molecular weight of chitosan, its chemical structure, specifically the degree of deacetylation, and the preparation method all have a significant impact on the size of the generated particles when creating chitosan particulate systems. Higher molecular weight chitosan typically results in larger-sized particles (Luangtana-anan et al., 2005). There are various ways to make chitosan micro-nanoparticles, and these particles often include a drug that is primarily attached to the chitosan through hydrogen bonding, electrostatic contact, or hydrophobic coupling (Table 11.1). Chitosan micro/nanoparticles can generally be loaded with a therapeutic agent either during the preparation process or after the particles have been created. The therapeutic drug is integrated and embedded in the chitosan matrix in the first case, whereas it is adsorbed on the surface of the particle in the second. The goal is often to achieve high entrapment efficiency, which can be done by incorporating the therapeutic agent into the matrix; however, the preparation method, additives, etc. may have an impact on the therapeutic agent (Ahmed & Aljaeid, 2016).

5.1 Precipitation

This technique relies on the chitosan's physicochemical features, specifically its insolubility in an alkaline pH medium and the precipitate it produces as a result. As seen in Fig. 11.4, using a compressed air nozzle and a chitosan solution, coacervate droplets are created by blowing the chitosan solution into an alkali solution (Wang et al., 2016). The particles are then separated and purified by filtering or centrifugation, followed by multiple washings in hot and cold water. This method is used to make chitosan-DNA nanoparticles (Agnihotri et al., 2004). Allopurinol-loaded chitosan-coated magnetic nanoparticles have been used for the treatment of nephrolithiasis caused by hyperuricemic nephropathy (Kandav et al., 2019).

5.2 Sieving Method

Chitosan hydrogel containing the drug is first formed, and then a cross-linking agent, such as glutaraldehyde, is added to create a cross-linked chitosan hydrogel. This cross-linked chitosan hydrogel is then passed through a sieve of a specific size to obtain the drug-loaded microparticles (Fig. 11.5) (Ahmed & Aljaeid, 2016). The

Table 11.1 Methods and principles involved in the formulation of chitosan nanoparticles (NPs)

Methods	Principle	Application	References
Coacervation/precipitation	*Precipitation*; chitosan solution blown into alkali solution to form coacervate droplets	Chitosan DNA nanoparticles used as a nonviral vector for gene transfer and potential vaccination carrier	Garg et al. (2019); Ahmed and Aljaeid (2016)
Sieving method	*Cross-linking*; chitosan hydrogel cross-linked and passed through the sieve of definite size	Extended drug release in Clozapine microparticles, Schizophrenia treatment	Abdulla et al. (2021); Yanat and Schroën (2021)
Reverse micelles	*Covalent cross-linking*; lipophilic surfactant and an organic phase are mixed with chitosan and glutaraldehyde in an organic solvent	NPs of size less than 100 nm are used in tumor-targeted drug delivery.	Mitra et al. (2001)
Spray drying (green preparation route)	*Supercritical CO_2 assisted solubilization and atomization*; chitosan dissolved in aqueous acetic acid maintaining air temperature of 120–150 °C	Delivery of cyclosporin A	Başaran et al. (2013); Singh and Van den Mooter (2016)
Ionotropic gelation	*Cross-linking in the presence of counterions*; gelation of chitosan to produce chitosan cations	Delivery of insulin, cancer therapy Gene therapy: delivery of DNA	Al-Qadi et al. (2012); Özbaş-Turan and Akbuğa (2011)
Emulsion cross-linking	*Covalent cross-linking*; chemical interaction of the cross-linking agent with an amino group of chitosan	Gene delivery	Garg et al. (2019)
Emulsion droplet coalescence	*Cross-linking and precipitation*; mixture of chitosan and NaOH emulsion stirred at high speed forming droplets and precipitating chitosan droplets to form small particles	Gadolinium neutron capture therapy for cancer	Ho et al. (2022); Tokumitsu et al. (1999)

resulting microparticles are washed with sodium hydroxide to remove any excess glutaraldehyde and then heat-dried in an oven (Agnihotri et al., 2004).

5.3 Reverse Micelles

Mitra et al. (2001) were the first to report the production of chitosan nanoparticles from reverse micelles as a strategy for tumor-targeted delivery. In this process of reverse micellization, a lipophilic surfactant is dissolved in a suitable organic solvent, such as n-hexane, to create a W/O microemulsion. Due to the action of surfactants, reverse micelles are produced that are made up of water droplets that are

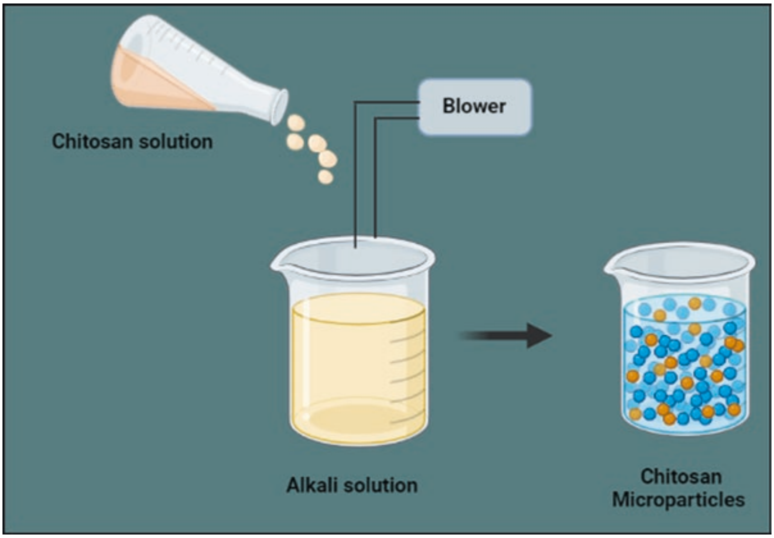

Fig. 11.4 Production of chitosan nanoparticles by precipitation method

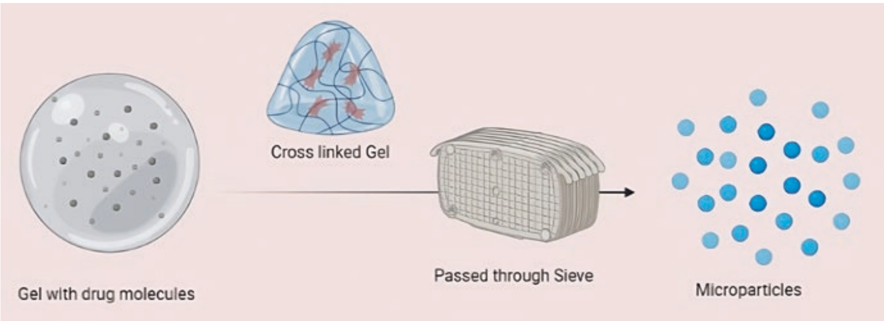

Fig. 11.5 Production of chitosan nanoparticles by sieving

dispersed in organic solvents in the nanometer range (1–10 nm) (Melo et al., 2001). These nanodroplets can be used as a reactor to create nanoparticles in their aqueous core. A cross-linking agent is added to ensure complete cross-linking. To obtain a dry bulk, the organic solvent is subsequently evaporated. The resultant dried mass is dissolved in water, a suitable salt is applied to precipitate the surfactant out, and then the drug-loaded chitosan nanoparticles are recovered by centrifugation to remove the surfactant, as shown in Fig. 11.6 (Mohammed et al., 2017). 5-Fluorouracil-loaded cross-linked chitosan nanoparticles formulated using the reverse micelles technique for effective drug delivery to a certain targeted area along with a reduction in oral toxicity and improved tolerability (Sethi et al., 2021).

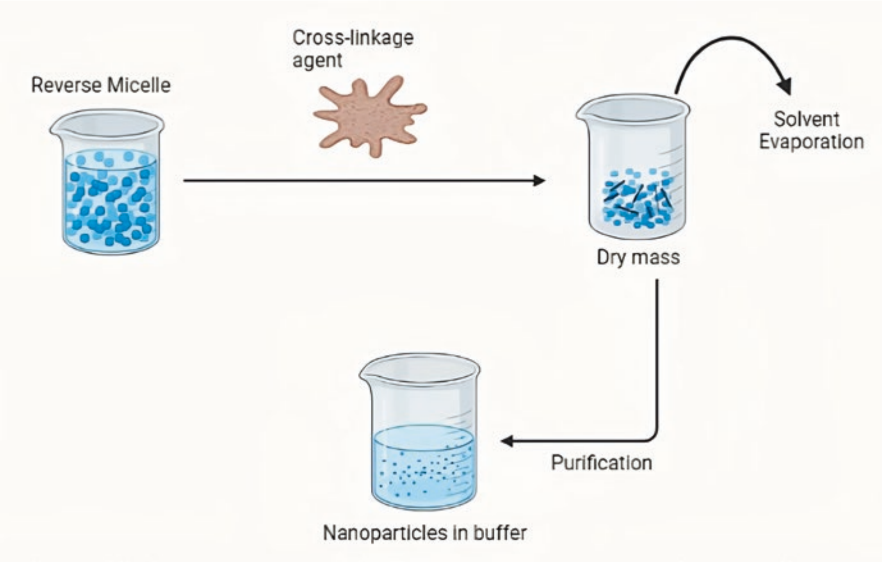

Fig. 11.6 Preparation of chitosan nanoparticles by reverse micelles process

5.4 *Spray Drying*

Spray drying has been used to produce dry powders and granules from drug-excipient mixes that are either in solution or in suspension (Chawla et al., 1994). This technique could create microparticles from various polymeric materials that were loaded with proteins, vaccine antigens, and medications (Ahmed & Aljaeid, 2016). For protein-loaded chitosan micro/nanoparticles, spray drying offers a simple, effective, one-step, and protein-friendly technique. To produce the necessary particles, an aqueous chitosan-protein solution is prepared and sprayed into a drying chamber via a nozzle (Fig. 11.7). Examples of proteins that can be loaded into chitosan microparticles using this technique include salmon calcitonin and bovine serum albumin (BSA) (He et al., 1999).

5.5 *Ionotropic Gelation*

Ionotropic gelation is based on the ability of polyelectrolytes to cross-link in the presence of counterions (Fan et al., 2012; Giri et al., 2012). The most commonly used technique for creating alginate nanoparticles is ionic gelation (Calvo et al., 1997). In a two-step process based on the ionotropic gelation of polyanion with calcium chloride and polycationic cross-linking, alginate-chitosan nanoparticles were created. Chitosan polysaccharide is dissolved in an acidic aqueous solution in the ionic gelation process to produce the cation of chitosan. The polyanionic

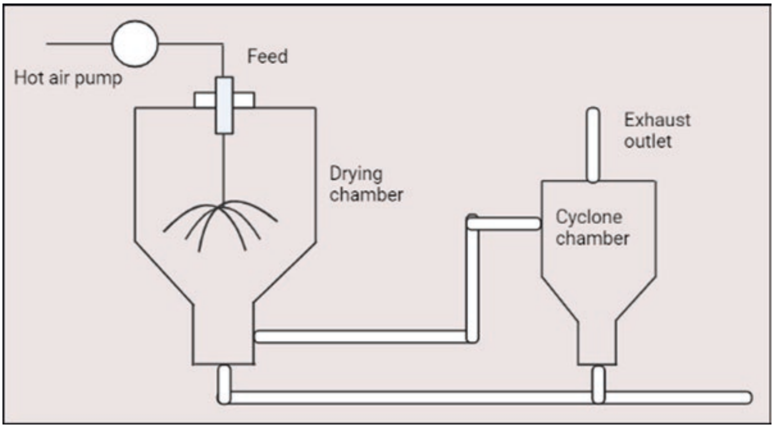

Fig. 11.7 Production of chitosan NPs by spray drying method

tripolyphosphate solution is then gradually added while being constantly stirred (Fig. 11.8). Chitosan experiences ionic gelation and precipitates as spherical particles because of the complexation between species that have opposing charges. The lipid-chitosan hybrid nanoparticles fabricated by the single-step ionic gelation method can deliver cisplatin under regulated conditions and serve as a viable platform for the prospective delivery of cisplatin to tumors, according to the characterization and in vitro release profile (Khan et al., 2019).

5.6 Emulsion Cross Linking

In this technique, a cross-linking agent interacts chemically with the main amino groups of chitosan to produce chitosan micro-/nanoparticles. Glutaraldehyde, *p*-phthaldehyde, ascorbyl palmitate, and dehydroascorbyl palmitate are typical cross-linkers (Bugamelli et al., 1998). Chemical cross-linking can occur in one or two steps. The process comprises creating an aqueous water/oil (W/O) emulsion with the therapeutic drug and chitosan which is then emulsified with an external immiscible solvent before cross-linking is gradually added (Fig. 11.9). Centrifugation, numerous washing processes (with petroleum ether, acetone, sodium metabisulfite, and water), and vacuum- or freeze-drying are frequently used to separate NPs from the emulsion. As the external oil phase prevents the therapeutic agent from escaping, the formation of these particles in the interior water phase of a W/O emulsion promotes the trapping of the therapeutic agent (Jameela et al., 1998). This technique has been used to create chitosan microparticles that contain BSA. Due to toxicity and drug integrity issues associated with glutaraldehyde, this method is no longer used (Garg et al., 2019).

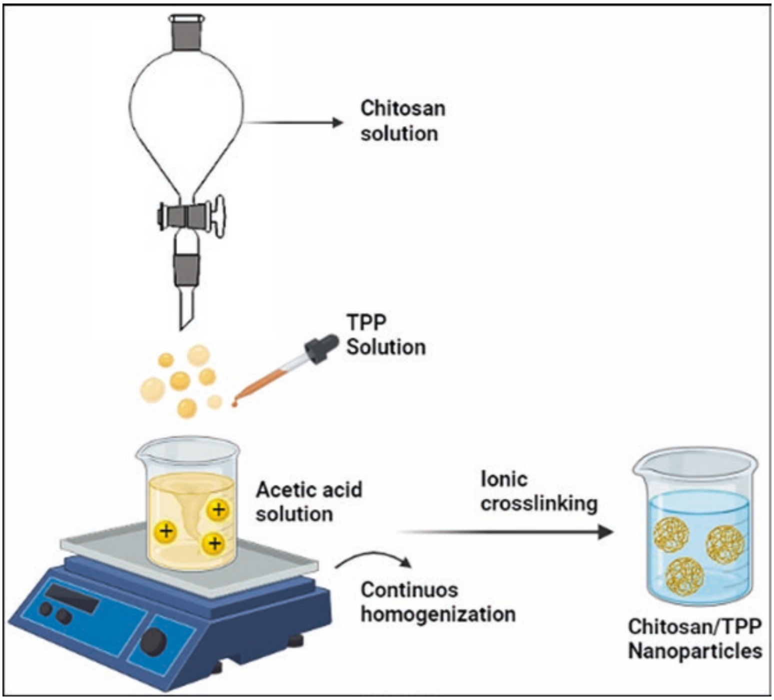

Fig. 11.8 Production of chitosan NPs by ionotropic gelation method

6 Emulsion-Droplet Coalescence

In order to create two emulsions, chitosan, and NaOH solutions were both emulsified into the same oil phase (paraffin oil). The two emulsions are combined and mixed while spinning at a rapid rate, allowing the emulsion droplets to coalesce randomly and precipitate (Fig. 11.10) (Tokumitsu et al., 1999). The advantage of this method over the emulsion cross-linking method is that it enables an electrostatic connection between the free amino groups of chitosan and the used anionic drug, allowing for increased drug loading (Agnihotri et al., 2004).

7 Controlled Release of Active Ingredients from Chitosan-Based Nanomaterials

The therapeutic effects of CSNPs are significantly influenced by the drug release from those particles. Due to their physicochemical characteristics, CSNPs come in a variety of forms and sizes, which affect how the drug is released. The ability of the components that make up the NPs to absorb water, the rate and speed of

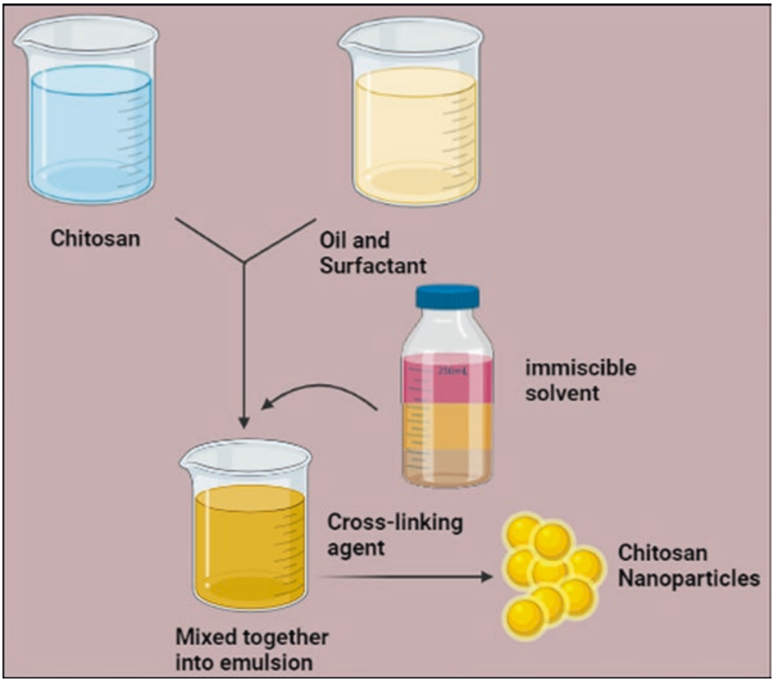

Fig. 11.9 Production of chitosan NPs by emulsion cross-linking

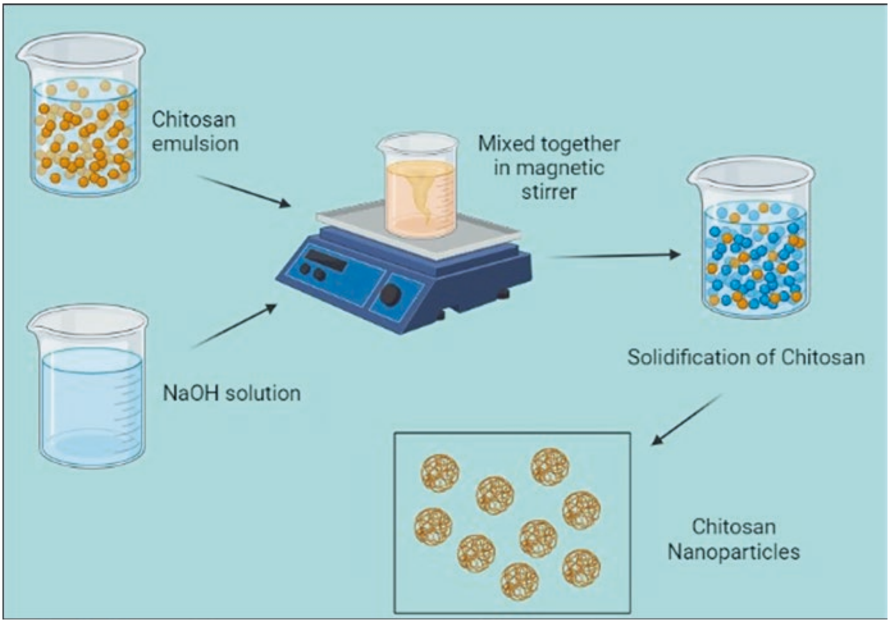

Fig. 11.10 Production of chitosan NPs by emulsion droplet coalescence

degradation, the chemical composition, MW, solubility, and crystallinity have an impact on the release of the NPs. Even interactions between drugs or between drugs and polymers seem to have a major impact on the drug's release from the delivery system (Iacob et al., 2021). One of the following methods can control the release of the drug from the polymer: (a) erosion of the polymer matrix's surface; (b) the breakdown of polymer bonds at the surface or in the bulk of the matrix; or (c) drug diffusion. Sometimes a combination of the three techniques can frequently be employed to release the drug (Herdiana et al., 2022). The release of the drug from CSNPs is also regulated by pH due to the solubility of CS. Drug release can be controlled using CS derivatives in accordance with the expected pharmacokinetic characteristics of the drug. Several mechanisms, including polymer swelling, drug diffusion via the polymeric matrix, drug diffusion through the adsorbed drug, polymer erosion or degradation, and a combination of both erosion and degradation, control the release of drugs from chitosan nanoparticles (Mohammed et al., 2017).

7.1 Diffusion-Controlled Release

The diffusion control mechanism is the most useful one for drug release. The drug or active substance flows through the polymer NP matrix, which serves as a controlled release device, and this induces the diffusion mechanism. When the active agent has a longer duration, the rate of drug release reduces (Herdiana et al., 2022). The molecule passes through the polymer matrix's interior in the direction of the release medium. Polymer chains provide the diffusion barrier, which prevents the drug from moving. Diffusion may also be related to swelling or erosion. Diffusion is mathematically explained by Fick's Law. The following assumptions must be made in order to derive the parameters of Fick's law: sink conditions are always provided by the medium surrounding the nanoparticles; a pseudo-steady state is maintained during drug release; and the drug particle diameter is lower than the average distance of drug diffusion through the polymeric matrix (Siepmann & Siepmann, 2012). The release of *Punica granatum* L. extracts in a controlled manner for antibacterial applicability and topical delivery was controlled by a Fickian diffusion mechanism (Mohamady Hussein et al., 2021).

7.2 Swelling-Controlled Release

Water is absorbed into the polymer until the polymer dissolves, which causes the polymer to swell. The solubility of the polymer in water or the surrounding biological medium acts as a chief aspect of this medication release mechanism. The polymer chains untangle when it comes into contact with the surrounding medium and begin to swell. Drug release from that region of the polymer matrix occurs next. The drug release profile is often greatly influenced by the hydrophilicity of the polymer, the swelling velocity of the polymer, and the density of the polymer chains (Fonseca-Santos & Chorilli, 2017). By using a non-Fickian diffusion technique, the active ingredient is delivered to the polymer matrix simultaneously by erosion and diffusion. Relaxation constant plays a vital role in the matrix swelling device. The slower the drug is released from the matrix, the more significant the relaxation constant's value. The release process seems to be best described by the Weibull model (Herdiana et al., 2022). This will consequently have an impact on how quickly the medication is made available for membrane transport or cellular uptake, which will have an impact on how quickly the drug is absorbed from the site of delivery in vivo.

7.3 Erosion and Degradation-Controlled Release

Polymer erosion and degradation have common characteristics. Sometimes, as bonds break due to polymer breakdown, physical erosion may result. Polymer erosion is a complicated process that includes swelling, diffusion, and disintegration. There are two types of erosion: homogeneous and heterogeneous. In contrast to heterogeneous erosion, which occurs from the surface toward the inner core, homogenous erosion occurs at the same pace throughout the matrix (Lee & Yeo, 2015). Enzymes or the medium in the region may be responsible for polymer breakdown. The copolymer composition, pH of the surrounding medium, and water uptake by the polymer are further factors that affect how quickly a polymer degrades. The type of polymer, internal bonding, additives (chitosan derivatives), the shape and size of the nanoparticles influences the drug release (Göpferich, 1996).

7.4 Oral Drug Delivery

For the development of new drugs, oral administration (OD) is the preferred dosage form due to its ease, safety, and patient tolerance. However, achieving oral delivery presents a number of difficulties, including a variation in pH (the stomach is highly acidic), the presence of enzymes, the first-pass action in the liver, and the intestinal barrier to drug absorption (Bowman & Leong, 2006). NPs are used as oral delivery vehicles for polynucleotides, proteins, and macromolecules due to their benefits over other drug delivery systems, including their small particle size, high surface area, and possibility for surface modification. Also, they make the acid-labile medicines more GIT stable (Palacio et al., 2016).

Tamoxifen is a mildly water-soluble anticancer medication that makes an excellent option for oral cancer treatment delivery. Tamoxifen was made into lecithin-chitosan nanoparticles to improve its ability to penetrate through the intestinal epithelium (Barbieri et al., 2015). Tamoxifen is more readily absorbed by the paracellular route due to the NPs' mucoadhesive properties. Additionally, Feng et al. (2013) reported on a possible method for administering anticancer medications orally. Chitosan and carboxymethyl chitosan were used to create doxorubicin hydrochloride (DOX) nanoparticles. The small intestine's ability to absorb DOX was found to be improved by these nanostructures (Feng et al., 2013).

7.5 Nasal Drug Delivery

A noninvasive method of drug administration to the brain, respiratory system, and/or systemic circulation is nasal delivery. Moreover, due to their low permeability across the nasal epithelium, hydrophilic medications, proteins and peptides, nucleic acids, and polysaccharides pose challenges. Nasal absorption is essential for the medications to work properly. *Molecular* weight, lipophilicity, and charge are examples of the physical properties of drugs that control nasal absorption. Due to its use in nasal delivery, chitosan has mucoadhesion qualities as well as low toxicity, biodegradability, and biocompatibility, which can help address this issue. Nasal absorption can occur in three different ways: through the trigeminal nerves, the paracellular pathway, and the transcellular pathway. Liu et al., 2018 proposed that carbamazepine (an antiepileptic medicine) can be delivered intra-nasally with the help of carboxymethyl chitosan nanoparticles which bypass the blood–brain barrier. They created NPs that had good entrapment efficiency (80%) and a small particle size (218.76 ± 2.41 nm). They performed in vivo and in vitro testing, and the results demonstrated improved drug absorption and brain-targeting properties (Liu et al., 2018). Leuprolide-loaded chitosan and thiolated-chitosan nanoparticles were created by Shahnaz et al. (2012). When compared to the leuprolide solution, these chitosan and thiolated-chitosan nanoparticles boosted drug transport across the porcine nasal mucosa by twofold to fivefold, respectively (Shahnaz et al., 2012). Delivering drugs to the brain in case of any brain tumor has always been a major challenge. Another study emphasized the appropriateness of lipid-core nanocapsules coated with chitosan (LNC_{chit}) as a promising method for administering simvastatin for the treatment of brain malignancies via a nose-to-brain approach (Bruinsmann et al., 2019).

7.6 Injection Drug Delivery

The term "injection administration" typically refers to administering medications intravenously, subcutaneously, intramuscularly, and intraarterially. Drugs can be administered intravenously, which ensures that they all enter the systemic circulation and start working right away. The systemic circulation is reached by intramuscular or subcutaneous injections, which have the drawbacks of low bioavailability and slow effectiveness. The primary use of arterial injection is blood transfusion for serious sickness. To provide therapeutic effects, the chitosan nanodrugs are administered via parenteral injection (Li et al., 2018).

To release doxorubicin when needed, pH-responsive nanoparticles were created that responded gradually. After being injected into the tumor-bearing animals, the DOX-loaded NPs could respond sequentially to extracellular and intracellular pH. The nanoparticles contained pH-responsive dimethylmaleic acid and urocanic acid. The tumor tissues significantly absorbed the DOX-loaded NPs in the somewhat acidic extracellular environment of the tumor. Then, the acidic endo/lysosome environment caused NPs to release DOX as necessary. The volume and pace of DOX accumulation in tumor tissue were significantly higher for the stepwise pH-responsive NPs than for free DOX. Additionally, they created gradual pH-/reduction-responsive nanoparticles for regulated DOX release by injection into the tail vein (Chen et al., 2017).

Since it treats severe or sudden sickness more quickly, injection administration has clear advantages in emergency situations. Another study evaluated the strong immunity against intranasal *Chlamydia psittaci*, which is induced by intranasal immunization with inactivated chlamydial elementary bodies formulated in VCG-chitosan nanoparticles (Zuo et al., 2021). However, the use of injections can have certain negative side effects, such as vascular injury, skin damage, and severe bacterial and viral infections (Kwon et al., 2017).

8 Mechanisms of Action

8.1 Plant Innate Immunity Booster

Over time, plants have evolved to defend themselves through various dynamic responses, such as the production of defense enzymes and antioxidants to combat stress and pathogen invasion. Despite not being specific to diseases and pathogens, they offer the plants broad protection (Iriti et al., 2006; Iriti & Faoro, 2009). This wonderful mechanism in plants is proven to be naturally elicited by chitosan through various means such as phenolic compound accumulation, synthesis of the cell wall, reactive oxygen species (ROS) generation, and gene regulation (Kumaraswamy et al., 2018).

It has been proven that negatively charged genetic materials exhibit elevated affinity for positively charged chitosan, which ultimately results in gene regulation at the chromatin level (Isaac et al., 2009; Liu et al., 2005; Xing et al., 2014). In the case of pathogen entry, chitosan competes with nuclear proteins for attachment to DNA (Hadwiger, 2008). The plant pattern recognition receptor recognizes chitosan as a pathogen-associated molecular pattern, and hence, chitosan induces receptor-like kinase and MAP kinase pathways. On recognition by receptors, chitosan further induces increased production of ROS against pathogens, upregulates pathogen-related genes and proteins such as β 1,3 glucanase and thaumatin, and increases the amounts and accumulation of NO, phenols, flavonoids, cytosolic Ca^{2+}, jasmonic acid, and abscisic acid. NO in particular leads to enhanced expression of

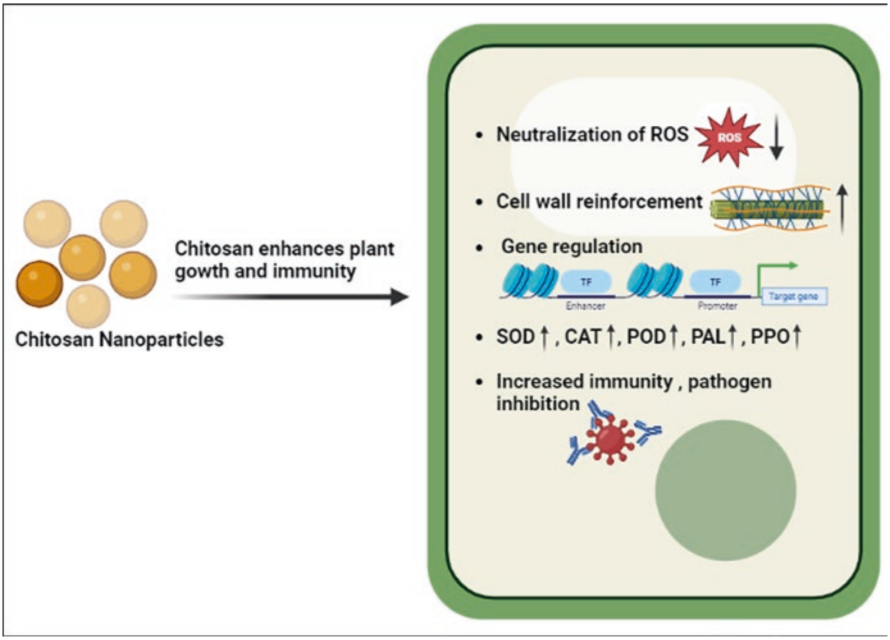

Fig. 11.11 The effects of chitosan nanoparticles on plant cells are complex and vary depending on the nanoparticles' concentration, size, and surface features, as well as the plant species and environmental conditions. Depending on the dose and length of exposure, chitosan NPs can have both helpful and negative effects on plant cells. As a result, it is critical to thoroughly assess the potential impacts of chitosan NPs on plant cells as well as optimize their concentration and administration methods for various crops and growing environments

various antioxidants and defense enzymes, including superoxide dismutase (SOD), catalase (CAT), peroxidase (POD), phenylalanine ammonia lyase (PAL), and polyphenol oxidase (PPO), due to regulation of gene expression, which in turn regulates protein expression and function (Fig. 11.11) (Hadwiger, 2013; Iriti & Faoro, 2009; Iriti & Varoni, 2014). There was a twofold to fourfold increase in the abovementioned enzyme production in treated plants in comparison to control plants (Kumaraswamy et al., 2018). Neutralization of ROS to reduce chances of oxidative stress in plants during pathogenic entry is owed to the increase in SOD, POD, and CAT due to increased gene expression, while cell wall reinforcement is seen due to elevated production of lignin, suberin, and melanin caused by the increased production of POD, PAL, and PPO (Bruce & West, 1989; Gómez-Vásquez et al., 2004; Kuźniak & Urbanek, 2000). Notably, chitin derived from fungal cell walls exhibited higher activity of chitinase (Sathiyabama & Charles, 2015). Therefore, chitosan ultimately boosts plant innate dynamic immunity in the plant systems on which it is applied through an increase in diverse reactive species scavenging enzymes, antioxidants, and cell wall thickening agents.

8.2 Plant Growth Enhancer

Plant growth can be stimulated by various methodologies, including a few that are primarily enhanced by the application of chitosan to plants. Chitosan creates a suitable environment for plants by providing ample amounts of micronutrients and antioxidant enzymes for their development. The most extensively researched application techniques for chitosan are foliar application, soil amendment, and seed treatment (Bittelli et al., 2001; Choudhary et al., 2017; Guan et al., 2009).

Remarkably, the nanosize of chitosan nanomaterials in synergy with its net positive charge makes it easy for attachment onto plant surfaces and penetration into plant systems, which ultimately results in improved seed germination, although it is also contributed by the production of antioxidant enzymes during the germination stage to scavenge reactive species (Anusuya & Banu, 2016; Kumaraswamy et al., 2018; Saharan et al., 2015; Nguyen Van et al., 2013). Chitosan is seen to degrade and mobilize food reserves through the activation of hydrolytic enzymes such as α-amylase, which make nutrients required for plant growth more available and are supplemented by enhanced root cell division and the activation of auxin and cytokinin, which help in the uptake of those immobilized nutrients (Dzung et al., 2011; John et al., 1997). Chitosan shows the ability to enhance plant development and growth even under diseased conditions. Bulk chitosan demonstrates decreased solubility in aqueous medium and requires acidic conditions, but this in turn, may cause cytotoxic effects in plants (Saharan et al., 2016); but when coupled with copper (Cu), chitosan-Cu nanoparticles have been studied to improve plant growth by a noticeable extent owing to copper's crucial role in electron transfer and its strong fungicidal activity (Mujtaba et al., 2020). In addition to these enhanced features, the slow release of Cu from chitosan prevents any possible toxicity occurring in seeds due to the Cu ions (Kumaraswamy et al., 2018). Chitosan also increases nitrogen, potassium, and phosphorous contents in plants after application. It also increases the osmotic pressure of the stomata, which leads to greater opening of stomata. In addition to this, chitosan also increases leaf area and chlorophyll content, which all synergistically increase photosynthesis in plants (Kumaraswamy et al., 2018).

These bioregulatory and bioenhancing activities make chitosan an excellent candidate for plant growth promotion, and in combination with other growth-enhancing factors, the effect on plants only seems to get stronger.

9 Future Directions and Challenges

Global agriculture has been facing numerous issues due to an increase in population, the use of more agrochemicals, nutrient deficiency, and climate change. An emerging alternative for maintaining food safety and the sustainability of agricultural production systems is biopolymer-based nano-delivery systems. One such approach that can fulfill the huge demand for food supply in the agricultural field involves chitosan-based nanofertilizers. This next-generation nanofertilizer exhibits a regulated, gradual release of encapsulated materials that can release their active components into the environment (Yahya, 2018). The higher surface charge property and the presence of functional groups on chitosan nanomaterials can be exploited for targeted delivery of nutrients in the subcellular organelles of plants. Delivery of macronutrients to various plant parts can also be possible via the targeted interaction of guiding peptides with the $OH^{-}/NH3^{+}$ groups in chitosan NMs (Santana et al., 2020). Another future prospect of chitosan nanofertilizers is complementing them with features such as supplying nutrients based on biotic and abiotic stress conditions. Therefore, chitosan nanofertilizers would help combat climate change while increasing crop yield, reducing carbon emissions, and leading to a balanced ecosystem.

Despite being both economically and environmentally sustainable, chitosan nanofertilizers face challenges to be delivered as next-generation fertilizers for agricultural applications. It is currently difficult to tailor chitosan biopolymer into useful nanoforms. The availability of raw materials (mainly chitin/chitosan) for the industrial-scale synthesis of chitosan NMs needs to be ensured, along with the scaling up of the process for large-scale distribution. Once these challenges are addressed, the production of commercially viable chitosan nanofertilizers using appropriate techniques can be done easily, leading to a future where even limited usage of such fertilizers would generate the desired higher agricultural yield.

10 Conclusion

The use of conventional fertilizers has led to harmful impacts on crop yield and on the environment. Several literature studies have proven that next-generation fertilizers, primarily chitosan-based nanofertilizers, have been able to fill this gap. Chitosan, a biopolymer that has biophysical properties that can be easily modified, has varied applications in agricultural, biomedical, pharmaceuticals, and other applied fields. Chitosan nanoparticles have gained prominence in various scientific sectors over the past two decades. Numerous techniques for the formulation of these nanoforms have emerged that prove to be more eco-friendly, easily biodegradable, and lacking any hazardous chemicals. In a variety of industries, including pharma and agriculture, chitosan nanoparticles are used primarily to achieve sustained release and high loading capacity of medications or active substances (Yanat & Schroën, 2021). Several studies have shown that chitosan nanofertilizers have led to an increase in crop yield, with enhanced leaf and shoot growth in number and size. It has also contributed to plant defense mechanisms with minimal quantity of usage. In addition to reducing nutrient runoff and inducing plant antioxidant responses for improved performance under environmental stress conditions, chitosan NMs can provide nutrients to plants in a dynamic way (Prajapati et al., 2022). Despite the difficulties involved in converting and scaling up chitosan biopolymer into commercially viable suitable nanoforms, the authors anticipate that chitosan NMs can be transformed into an effective next-generation nanofertilizer technology in the agricultural domain through further research in this area.

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Chapter 12
Selenium Nanomaterials: Contribution Toward Crop Development

Pradnya B. Nikam, Satish V. Patil, Zahoor A. Baba, and Farah K. Ahmed

1 Introduction

Among all the economic sectors, agriculture and farming are vital for the surveillance of the entire living population. The increase in population is leading to a rise in food demand, ultimately exerting high demands for crop yield (Hemathilake & Gunathilake, 2022). Along with population growth, there is a shift toward civilization, which results in the use of agricultural land and a reduction in cultivable agricultural land. Furthermore, changes in climatic and biological stressors contribute to yield reduction (Calzadilla et al., 2013). So it becomes necessary to formulate sustainable crop production solutions with affordable cost, safety, enhanced nutritional value, and resistance to biotic and abiotic stress conditions.

Chemical fertilizers are widely used in conventional agricultural methods to maintain soil fertility and conditioning. These fertilizers mainly comprise macronutrients, including nitrogen, phosphorous, potassium, calcium, sulfur, and magnesium, with other micronutrients, such as iron, copper, boron, molybdenum, manganese, and chlorine (Suhag, 2016). According to the US Department of Agriculture reports, the global use of chemical fertilizers in 2019 was 215.37 million tons, which may have increased further in the recent year (Ritchie et al., 2022) (Retrieved on December 22, 2012, from https://ourworldindata.org/fertilizers

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[Online Resource]). As it is known, overuse of any product leads to other issues; the same has happened with the excessive use of chemical-based fertilizers. Due to their physical immobilization, transformations, and lower bioavailability for the targeted crops, many of these fertilizers are left in the soil rather than absorbed by the plants. These leftover products cause soil acidification, increase salinity, and affect the soil microbial population. The excess nutrients in the fertilizer in the soil leached into water bodies and lead to eutrophication (Mansoori, 2017; Pahalvi et al., 2022). The rise of nanotechnology has favored the development of nanofertilizers to address issues caused by the indiscriminate use of chemical fertilizers. The unique property of nanomaterial of any element, such as smaller size (<100 nm) with increased surface area, leads to maximum absorption through the plant cells without causing soil and water pollution, compared to traditional chemical fertilizers. Nanofertilizers can be nutrients that have been transformed into a nanoscale form from their bulk form or nutrients that have been coated and loaded with nanoparticles. The entry and translocation of nanoparticles (NPs) within the nanofertilizers applied to plants depend on the plant type, the plant's morphology, and also on the physical properties of the nanoparticles. Through the roots, the NPs can be transported through different channels and carried by either apoplastic or symplastic pathways, which then target the vascular system. Other than this, the NPs can also enter through the cuticles and stomatal openings on the leaves when applied as foliar sprays (Shalaby et al., 2022a; Zia-ur-Rehman et al., 2023). The use of nanofertilizer reduces the high amount of wastage associated with bulk fertilizers, ultimately reducing the number of products required for plant production, enhancing stress management and the nutrient content of the crops or plants (Moreno-Martín et al., 2020).

Selenium (Se) is present in different enzymatic and nonenzymatic proteins and is, therefore, considered one of the essential elements for metabolism in humans and animals. Some examples include enzymes such as thioredoxin reductases, deiodinase, glutathione peroxidase, and some other selenoproteins (Gudkov et al., 2020; Nikam et al., 2022b). SeNPs' physiological importance has led to their inclusion in poultry and fish feed to reduce biotic and abiotic stress and increase productivity (Gupta & Gupta, 2000; Kumar et al., 2023; Sarkar et al., 2015). Just like other micronutrients (e.g., Cu, Zn, Mn, etc.), selenium (Se) also participates in maintaining plant physiology (El-Ramady et al., 2014). In the case of plants, the essential requirement of selenium has been diminished, but it still contributes to overall plant growth and development (Pilon-Smits, 2019). As it is required in trace amounts, excess selenium can lead to a toxic health condition known as selenosis. Se is available in the environment in its oxidized state, such as selenate and selenite, which are highly soluble in water and hence have higher bioavailability. The inorganic forms of Se include its sodium salts, and its organic forms include the amino acids, selenomethionine and selenocysteine. Moreover, zero-valent Se, i.e., selenium nanoparticles, are much more beneficial than their other forms due to their insolubility in water, higher surface area, and targeted bioavailability. The selenium nanoparticles (SeNPs) possess dual nature of being an antioxidant as well as a pro-oxidant, which leads to their application in reducing the oxidation stress and killing the targeted cells by inducing reactive oxygen species, respectively (Bano et al., 2021; Gudkov

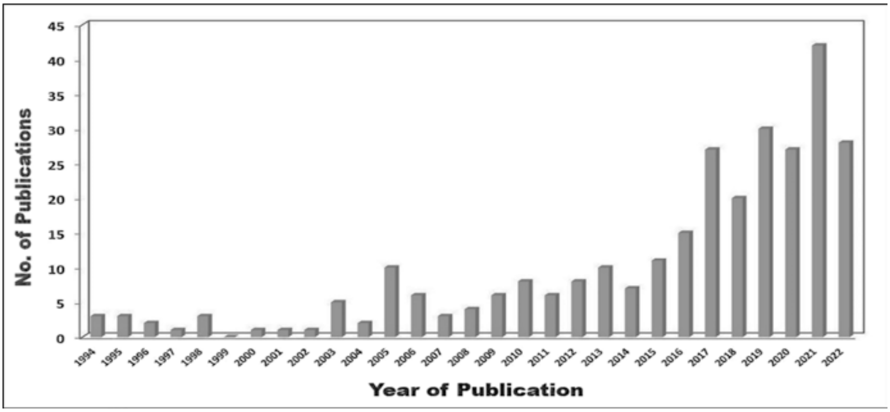

Fig. 12.1 Yearly data of several publications on the topic of selenium nanofertilizer

et al., 2020). However, in the case of plants, some evidence suggests that inorganic selenium outperforms nanoselenium. Under salinity stress, bulk selenium was more adventitious than nanoselenium on *Coriandrum sativum* (coriander) and was also found to enhance secondary metabolites within the extracted essential oils of coriander (El-Kinany et al., 2019). Figure 12.1 represents graphical data of some research articles and review articles published on the topic, selenium nanoparticles as plant fertilizers, from the year 1994 to 2022, retrieved from PubMed database (https://pubmed.ncbi.nlm.nih.gov reviewed on 7 Jan 2023). This chapter focuses on how these SeNPs can carry their properties for better application as nanofertilizers in plants.

2 Synthesis of Selenium Nanofertilizer

2.1 Synthesis of SeNPs

There are three different types of synthesis of SeNPs, which include chemical, physical, and biological methods. Some examples of the physical methods, including pulse laser ablation, microwave, electrokinetic reactions, milling, and grinding, require specific instruments and hence are expensive techniques (Bano et al., 2021; Mellinas et al., 2019). The microwave method involves heating inorganic selenium compounds using microwave radiation, which are time-sensitive reactions. Among all these physical methods, laser ablation is the most favored technique (Perfileva, 2022). The microwave treatment of bean shell extracts of *Theobroma cacao* L., in addition to sodium selenite, produced SeNPs with diameters of 1–3 nm. These SeNPs had potent antioxidant activities and remained stable for about two months without getting agglomerated (Mellinas et al., 2019). The most common methods for producing SeNPs are chemical and biological. Different chemicals, such as

L-ascorbic acid as a reducing agent, along with external stabilizers such as PVP (polyvinylpyrrolidone) or CTAB (cetyltrimethyl ammonium bromide), can be used for SeNP production from selenite or selenate (El-Ramady et al., 2014). Still, chemical methods have some drawbacks, such as the use of hazardous chemicals and the high cost, whereas biological synthesis methods for SeNP synthesis are non-hazardous and inexpensive. The biological methods include enzymes, plant extracts, microbial extracts, or whole live microorganisms (bacteria, fungi, cyanobacteria, actinomycetes, and algae). The applications of biologically synthesized selenium nanoparticles (SeNPs) as a nanofertilizer in plant protection and development have been depicted in Fig. 12.2.

In plants, the primary and secondary metabolites play a vital role in catalyzing the reducing reactions to synthesize nanomaterials (Shahbaz et al., 2022). The leaf extracts of *Hibiscus sabdariffa* reduced the selenious acid and stabilized the SeNPs by using their metabolites. The average size of SeNPs obtained was 33 nm, and these particles potentially reduced the oxidative damage in rats caused due to diabetes (Fan et al., 2020). The reaction of flower extracts of *Bougainvillea spectabilis* yielded SeNPs having a size of 24.24 nm and maximum absorbance at 326 nm, evidenced by the nanosynthesis. According to the FTIR results, this reaction was catalyzed and stabilized by functional groups such as alcohols, ketones, and amines (Ganesan, 2015). The SeNPs synthesized using *Allium sativum* (garlic) buds were in the size range of 50–150 nm and were responsible for mitigating the drought stress effects on the wheat plant (Ikram et al., 2020). Not just fresh plant extracts but dried forms such as Fenugreek seed powder can also transform the selenious acid into nanoselenium. The SeNPs formed after the reaction of fenugreek seed powder with ascorbic acid as an inducer for the reaction, and the substrate selenious acid

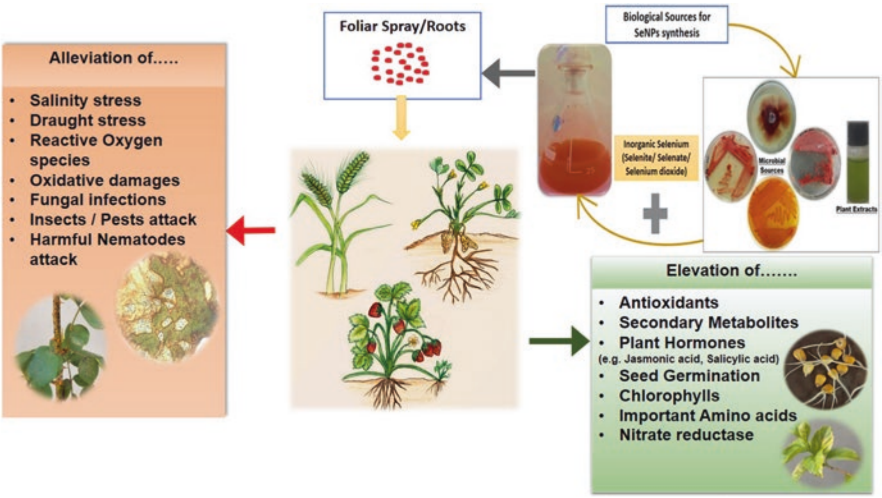

Fig. 12.2 Biogenic selenium nanoparticles (SeNPs) synthesis and their applications in plant growth promotion and protection

was of size ranging from 50 to 150 nm. The SeNPs were observed to be stabilized due to the flavanol and phenol contents of the seeds powder (Ramamurthy et al., 2013). Utilizing plant waste for nanosynthesis is one of the cheapest and safe methods. One of the studies has reported the use of extracts from the peel waste of prickly pear to produce SeNPs with spherical shapes and a broad range of particle sizes from 10 to 57 nm. These SeNPs were found to have potent, mosquito larvicidal, antibacterial, and antifungal effects against some human pathogens (Hashem et al., 2021). Another study was conducted using orange fruit peel extracts, which synthesized polydispersed, spherical SeNPs of size 16–95 nm. These nanoparticles had antibacterial activity, especially against the multidrug-resistant strain of *Staphylococcus aureus* (Salem et al., 2022). Just like plants, many microbial species have the capability of transforming inorganic selenium into nanoselenium. Extracts of green tea produced SeNPs when reacted with sodium selenite, and the size of these nanoparticles was reduced by using *Lycium barbarum* as a stabilizer (Zhang et al., 2018).

Besides plants, microbes are also the best environment-friendly hosts for producing SeNPs. Moreover, many of them are plant-friendly, which could probably help in enhancing the growth and yield of the plants through their metabolites, promoting selenium nanosynthesis. In the case of bacteria, SeNPs are the outcome of many reductases enzymatic reactions carried out within the periplasm or cytoplasm of the cell. These types of mechanisms are considered detoxification reactions, in which the bacteria perform in the presence of toxic selenium compounds and convert into less toxic and insoluble nanoselenium (Claudia et al., 2021; Medina Cruz et al., 2018). Even fungal metabolites can contribute to nanosynthesis, mostly extracellularly (Amin et al., 2021; Asghari-Paskiabi et al., 2018; Diko et al., 2020). The use of whole cells, extracts, or filtered growth material for nanoselenium synthesis, including yeast (Wu et al., 2021), *Lactobacillus acidophilus* (Alam et al., 2020), *Rhizobium pusense* (Nikam et al., 2022a), *Anabaena variabilis* (Afzal et al., 2021), and *Fusarium oxysporum* (Asghari-Paskiabi et al., 2018) has been reported in the literature. In the case of *Acinetobacter* sp. *SW30*, it was studied for the first time that the enzyme lignin peroxidase was responsible for the synthesis of SeNPs; these nanoparticles were approximately 100 nm in size (Wadhwani et al., 2018). The *Bacillus* sp. MSh.1-mediated synthesis of SeNPs resulted in spherical nanoparticles with sizes ranging from 80 to 220 nm. These nanoparticles were effective inhibitors of biofilm synthesis from several human pathogens, including *S. aureus*, *P. aeruginosa*, and *P. mirabilis* (Shakibaie et al., 2015a). Not just pure strains but also genetically modified yeast strain, such as *Pichia pastoris*, was exploited for SeNP production. This bacterium carried nanosynthesis by the cytochrome b5 reductase enzyme having metal-resisting properties. The SeNPs were 70–180 nm in size and possessed less cytotoxicity than other fates of selenium (Elahian et al., 2017). Edible fungal species, *Lentinula edodes*, were able to reduce sodium selenite and 1,5-diphenyl-3-selenopentanedione to nanoselenium with a spherical structure and an average diameter of about 180 nm (Vetchinkina et al., 2013). In this way, many biological sources can be utilized to produce SeNPs by using the reducing properties of their metabolites.

2.2 Synthesis of SeNP Nanocomposites

Nanocomposites (NCs) often consist of natural or artificial polymers in combination with synthesized elemental nanomaterials within their matrices. This process improves the physical properties of nanomaterials. Most of the nanoparticles need to undergo surface modifications to avoid agglomeration problems and reduce the nanoefficiency before being polymerized in a matrix (Kango et al., 2013; Rane et al., 2018). Various organic and inorganic polymers, such as PVA (polyvinyl alcohol), polylactides (PLA), chitosan, cellulose, nylon, polypropylene, and many others, have been used for NC production (Kango et al., 2013; Vandervoort & Ludwig, 2002; Virkutyte & Varma, 2011). Selenium nanoparticles, coated with silica and PVP, were synthesized into an NC form that had multiple biological applications. The PVP treatment increased the porosity of the material. This SeNC was effectively used for fluorescence imaging and targeted delivery of a chemotherapeutic drug, doxorubicin (Liu et al., 2018). Selenium-based NCs were tested against the pathogenic bacteria *Clavibacter sepedonicus*, causing ring rot in potatoes. The selenium nanoparticles embedded in the arabinogalactan polymer matrix inhibited this pathogenic bacterium without harming the rhizospheric bacterium *Rhodococcus erythropolis*, ultimately enhancing the potato crop yield (Perfileva et al., 2021a). A similar study was conducted on *Phytophthora cactorum,* a phyto-pathogenic fungus that infects the potato plant. These selenium NCs were prepared using natural polysaccharides, such as starch, arabinogalactan (AG), and Kappa-carrageenan (CAR). The last two NCs had more effective fungicidal effects than the starch-SeNPs. In addition to this, the CAR selenium NC inhibited the bacteria *Pseudomonas oryzihabitans* and AG selenium NCs inhibited the growth of *Acinetobacter guillouiae* (Perfileva et al., 2021b). Biopolymer-based selenium nanocomposites are gaining much attention due to their higher biocompatibility with other biological targets and ecological safety. An amino polysaccharide, Chitosan, along with selenium, can be used in different forms to design nanocomposites to achieve biomedical as well as agricultural benefits (Chen et al., 2022). Using biological species for synthesizing nanocomposites can lead to stable nanomaterials. The fungal species secrete many extracellular polysaccharides and metabolites, which can be a better measure to enhance the properties of nanomaterials and increase their performance. Such types of compounds reduce the agglomeration of the nanoparticles and enhance their reactivity, which can be a better measure for applications of nanomaterials in different fields, including agroecosystems (Tsivileva et al., 2021).

2.3 Characterization of Selenium Nanomaterials

The most essential step before the application of nanoparticles is their characterization, which helps to depict the properties of the nanoparticles. The UV–visible spectrum of the obtained SeNPs colloidal suspension can give primary confirmation of nanosynthesis based on the maximum absorption peak due to the surface plasmon resonance of the nanomaterials. For example, SeNPs synthesized using *Diospyros Montana* leaf extract maximally absorbed the 261 nm wavelength (Karuppannan et al., 2017). Electron microscopy techniques, such as SEM and TEM, along with EDAX, provide the nanoparticle's shape, size, and elemental composition. It gives details of the surface morphology of the nanoparticles. The FTIR technique gives a spectrum that reveals the presence of functional groups responsible for the transformation of the bulk form of an element into nanoparticles of that element (El-Gazzar & Ismail, 2020). Dynamic light scattering (DLS) is used to study the size distribution of the nanoparticles based on the light scattering due to the continuous Brownian motion of the nanoparticles. Along with this, Zeta potential gives the overall charge on the nanoparticles, which can help depict the stability of the synthesized nanoparticles. Other than these most followed methods, some advanced techniques can be used for characterizing and differentiating the artificially or naturally synthesized nanoparticles (Montes-Burgos et al., 2010).

3 Selenium Utilization in Plants

Selenium content in soil varies at different locations. For example, in India, the northeastern part of Punjab has been found to have high concentrations of Se in its soil, about 3.63 mg per kg, and groundwater had an average of 170 g per liter (Sharma et al., 2009). Depending on such areas, the selenium content of crops or plants varies accordingly. The hyper-accumulating plants carry higher Se content, whereas the non-accumulating plants are less likely to cause Se toxicity if consumed. Plants absorb Se from the soil or water primarily through the roots and, in some cases, the leaves. As Se has properties like sulfur (S), studies reveal that the sulfate transporters may be the route for the uptake of inorganic selenite. This accumulation also depends on pH and the amount of sulfur in the soil, as sulfate competes with selenium to go through the transporters. This selenate undergoes a cascade of reactions and is converted into selenide and selenium-containing amino acids. Some Se non-accumulator plants release the excess selenium in volatile forms such as dimethyl selenide (Sors et al., 2005; Wang et al., 2020). Similarly, selenite can be taken up within the plants trough phosphate or silicon transporters and metabolized into usable organic selenium amino acids (Li et al., 2008; Wang et al., 2020; Zhang et al., 2014; Zhao et al., 2010).

In the case of SeNPs, the absorption occurs in a size-dependent manner. Smaller-sized nanoparticles are easily absorbed and transported into the plants for further conversions in the tissues (Hu et al., 2018). Some examples of crops exposed to the treatment of SeNPs to fight against various conditions are given in Table 12.1. A few studies show that when crops such as wheat and rice were treated with SeNPs and inorganic selenite salt, the absorption of SeNPs by the plant tissues was less than that of selenite. The overall results in wheat plants suggested that the transport of SeNPs took place through aquaporin in the roots and that their absorption was size-dependent

Table 12.1 SeNPs' beneficial effects on various crops, as well as in-vitro studies on plant infections

Sr. no.	Host plant and dose of SeNPs	Effect of SeNPs on the plants	References
1.	*Brassica napus* (150 µ mol/L)	Expression of aquaporin genes Reduces oxidative damage due to salt stress Promoted seed germination	El-Badri et al. (2022)
2.	*Oryza sativa* (100 µg/ml)	Protection of crops against heavy metal stress (Cd and Pb)	Hussain et al. (2020)
3.	Chillies and tomato crops (50 and 100 ppm)	Inhibition of infection due to *Colletotrichum capsici* and *Alternaria solani*	Joshi et al. (2019)
4.	*Arachis hypogaea* (20 and 40 ppm)	Improved growth by reducing oxidative stress Enhanced oil production in the seeds	Hussein et al. (2019)
5.	*Citrus aurantifolia*	Increased germination rate, stem length, and diameter Enhanced indole production	Ahmed et al. (2018)
6.	Banana (100 mg/L)	Increased photosynthetic pigments and antioxidant enzymes Improved rooting and acclimatization of banana transplants	Shalaby et al. (2022b)
7.	*Nicotinia tobacum* (265–530 µM)	Callus development and growth of root system	Domokos-Szabolcsy et al. (2012)
8.	*Hypericum perforatum* (12 mg/L)	Enhanced secondary metabolites production for medicinal benefits	Nazari et al. (2022)
9.	Eggplant, tomato, and cucumber (10 µg/Kg)	Overall plant growth and development	Gudkov et al. (2020)
10.	*Triticum aestivum* (100 µg/mL)	Reduced the infection of *Fusarium* sp., causing root rot and crown disease in the plant	El-Saadony et al. (2021)
11.	Strawberry (10–20 mg/L)	Increased organic sugar acids and antioxidant enzyme systems to reduce the salinity stress	Zahedi et al. (2019a)
12.	*Momordica charantia* (10 and 20 mg/mL)	Antioxidant activity against salt stress Increased proline and water content	Sheikhalipour et al. (2021)
13.	Pomegranate (2 µM)	Improved overall quality of fruits (anthocyanin, antioxidants, sugars, and phenolic compounds) and crop yield	Zahedi et al. (2019b)
14.	Celery (5 mg/ml)	Enhanced antioxidant activity and flavonoid content Increased levels of nutrients like β-carotene, tryptophan, and arginine	Li et al. (2020a)
15.	Garden cress (1 mg/L)	Improved nitrate reductase activity, chlorophyll content, and nutrients Reduced nitrate accumulation	Khosravi et al. (2022)

(continued)

Table 12.1 (continued)

Sr. no.	Host plant and dose of SeNPs	Effect of SeNPs on the plants	References
16.	Tomato (100 ppm)	Inhibition of *Alternaria alternata* tomato blight disease	El-Gazzar and Ismail (2020)
17.	Potato (800 µg/mL)	Inhibited the early blight disease causing fungus *Alternaria solani*	Ismail et al. (2016)
18.	*Cyamopsis tetragonoloba* (100–500 mg)	Increase in chlorophylls, anthocyanin, carotenoids, and important amino acids Increased crop yield	Ragavan et al. (2017)
19.	*Mentha suaveolens* (pineapple mint) (10 mg/L)	Improved plant growth under salinity stress. Increased synthesis of essential oil components such as piperitenone oxide	Kiumarzi et al. (2022)
20.	*Triticum aestivum* (30 mg/L)	Increased morphological parameters (root, shoot length, number of leaves, etc.) of the crops under draught stress	Ikram et al. (2020)
21.	*Hordeum vulgare* (4.65 µg/mL)	Seed germination	Siddiqui et al. (2021)
22.	*Solanum lycopersicum* (Tomato) (10 ppm)	Anti-nematode activity	Nikam et al. (2022c)
23.	Pearl millet (1000 ppm)	Controlled the downy mildew infection due to *Sclerospora graminicola*	Nandini et al. (2017)
24.	*Cichorium intybus* (4 and 40 mg/L)	Up regulation of physiologically important enzymes Enhanced flowering	Abedi et al. (2021)
25.	*Coriandrum sativum*	Increased the essential oils in coriander	El-Kinany et al. (2019)

(Garza-García et al., 2022; Hu et al., 2018; Wang et al., 2020). Domokos-Szabolcsy et al. have performed comparative studies for the accumulation of red nanoselenium (SeNPs) and selenate on *Nicotinia tobaccum*. The SeNPs, at a concentration of 265–530 M, were accumulated by both the callus and roots of the tobacco plant. SeNPs stimulated tissue differentiation in the callus for organogenesis, and the roots of a regenerated plant also acquired these nanoparticles to develop the morphological characters. In contrast to the effect of SeNPs, selenate showed inhibitory effects on the differentiation and growth of the crop (Domokos-Szabolcsy et al., 2012).

4 Benefits of Selenium Nanomaterials (NMs) on Plants

4.1 Biofortification

Various health benefits of selenium, such as enhancing immune power, being an antioxidant, being antiviral, being antidiabetic, improving cognitive functions, and many more, make the intake of selenium in the diet one of the crucial factors (Hurst et al., 2013; Nikam et al., 2022b). The dietary intake requirement also differs according to age. The selenium requirement for children under 14 years is less than 40 mcg per day; in adults, it is 50–70 mcg per day. The maximum tolerance level for selenium consumption is 400 mcg per day; consumption above this level is known to have toxic side effects (R. Morgan Griffin, Selenium https://www.webmd.com/a--to-z-guides/supplement-guide-selenium site visited on Dec 31, 2022). The selenium deficiencies in the east of Siberia and China had a burst of two diseases named Keshan disease leading to improper cardiac functioning and Kaschin disease, which affects the bone joints and may also cause dwarfism (Lyons et al., 2003).

The Se content of plants depends on factors including the available Se content in soil and the plant's potential to accumulate it in its edible part. Consumption of such fruits and vegetables may be a good source of Se in the diet. Environmental conditions such as excess leaching of selenium from the soil, pH, and the presence of other interfering salts and ions in the soil also affect the selenium content in the crops (Abrams et al., 1990; Blaylock & James, 1994; Kaur et al., 2014; Schiavon & Vecchia, 2017; Terry et al., 2000). To overcome this problem in selenium-deficient areas, the biofortification of crops could be a better measure for fulfilling the daily selenium requirement. Durán et al. (2015) reported two endophytic bacterial species, *Bacillus* sp. E5 and *Acinetobacter* sp. E6.2 promoted selenium biofortification in wheat crops by converting 5 mM selenite into nano-Se. The inorganic selenite was also converted to organic selenomethionine and selenomethyl-selenocysteine, which were absorbed by the crop (Durán et al., 2015). A study was conducted on garlic seeds grown in hydroponic systems tested for the accumulation of inorganic selenium salts and nanoselenium, ultimately converting it into selenium-containing amino acids (Li et al., 2020b). The experiments were conducted on *Raphanus sativus* and *Brassica juncea* to increase selenium content in crops and make them available to consumers. The crops were cultivated using a hydroponic system. The SeNPs synthesis was carried out using chitosan and ascorbic acid. Application of these chitosan-modified SeNPs to plants increased the uptake of beneficial elements such as iron, zinc, copper, and selenium. The plants utilized these chitosan-based SeNPs and transformed them into metabolically active and bioavailable amino acids such as selenomethionine, Se-methyl selenocysteine, and -glutamyl-Se-MetSeCys (Moreno-Martín et al., 2020). The uptake of selenium using varying concentrations of SeNPs (20 and 40 ppm) was checked even in an oilseed plant, *Archis hypogaea* (ground nut). The treatment enhanced the yield of groundnut plants and increased the unsaturated fatty acid content in the seeds (Hussein et al., 2019). Other than fruits and vegetables, selenium fortification is also done in cereals, as they are consumed heavily throughout the world. Selenium is well-known as an antioxidant and improves thyroid metabolism; its fortification and iodine in cereal crops could prove to be better foods for proper thyroid functioning (Lyons, 2018). In oats (*Avena sativa*), a combination of selenium foliar spray and soil treatment was used, which fortified the grains with selenium while also increasing another nutrient uptake. This also increased the enzyme activities of urease and alkaline phosphatase. Consuming such fortified foods may reduce selenium deficiencies and their consequences (Li et al., 2021).

4.2 Alleviation of Abiotic Stress

The literature always highlights that Se promotes plants' growth by alleviating the environment's abiotic stress conditions such as high salinity, temperature, oxidative stress, and interference of heavy metals (El-Ramady et al., 2020; Garza-García et al., 2022). Excess soil salinity hinders plants' nutrient uptake, ultimately affecting their development. Tomato crops grown under salt-stressed conditions (NaCl 50 mM) were treated with selenium nanoparticles supplemented at 1, 5, 10, and 20 mg per liter. This treatment reduced oxidative stress, enhanced photosynthesis, and increased phenolic content. Upregulation of enzymes such as catalase, superoxide dismutase, and ascorbate peroxidase provided antioxidant potential against salt stress and enhanced the fruit quality (Morales-Espinoza et al., 2019). Similar results regarding antioxidant activities were observed in *Melissa officinalis* plants under high salt stress (50–150 mM) after spraying SeNPs at 50 and 100 mg per liter on the leaves. The treatment of SeNPs facilitated the expression of genes responsible for the biosynthesis of a phenolic compound, rosmarinic acid, and helped the plant to resist salt-induced stress (Ghasemian, 2021). The cultivation of crops in low-quality water induces different problems, including excess salt accumulation, reducing microbial interactions, and calcium carbonate in the soil. The use of combinational nanofertilizer of Se and Cu nanoparticles promoted the yield of tomato crops in all these harsh physiological conditions (Saffan et al., 2022).

Along with high soil salinity, high temperatures during cultivation are also one of the reasons behind oxidation in crops, which results in reduced productivity. The grain of sorghum gets affected by a temperature higher than the optimum temperature required for its growth and production. The foliar application of SeNPs (particle sizes of 10–40 nm) on Sorghum positively impacted the enzymatic reduction of reactive oxygen species. It also increased the foliar phospholipid content and grain production of the crop (Djanaguiraman et al., 2018). Accumulating heavy metals in soil due to excess industrialization is affecting the entire environment. Heavy metals such as arsenic (As), cadmium (Cd), lead (Pb), and mercury (Hg) harm the crops, which also results in oxidative damage and the total yield. Selenium has been studied as a mitigating factor for such heavy metal stress (Bano et al., 2021; El-Ramady et al., 2020; Yang et al., 2003). It has been well-studied that nanoparticles at moderate or lower concentrations are saviors for crops. However, at the same time, their increased concentrations may harm their physiology, ultimately affecting their productivity. The same effect was observed in the *Vigna radiate* (mung beans), which was treated with both cerium dioxide nanoparticles ($nCeO_2$) and SeNPs. The $nCeO_2$ at concentrations of 250–1000 mg/L enhanced the phosphorous, cerium, and protein content within the grains. Simultaneously at 1000 mg/L, $nCeO_2$ decreased the numbers of pods, seeds, and overall biomass production. Additionally, the photosynthesis system of the plants was also negatively affected. The use of SeNPs on these cerium-stressed crops helped in the mitigation of excess Ce accumulation in seeds and the overall negative impact of nCe on the mung plants. Moreover, the seeds were found to incorporate iron, zinc, and selenium within them

(Kamali-Andani et al., 2023). The SeNPs, combined with silicon nanoparticles, reduced the Cd content by 62% and Pb by 52% in *Oryza sativa* (rice). This increased the crop biomass and enhanced the grains' nutritional value (Hussain et al., 2020). The species *Brassica campestris* grown in chromium-contaminated soil was checked for its activity in the presence of selenite supplementation. Plants undergo all types of nutritional, physiological, and metabolic stress at higher chromium doses. Also, consuming such contaminated foods and vegetables leads to toxic effects on consumers. The use of selenite did not reduce the chromium-induced shunted growth of plants. Nevertheless, it noticeably maintained the microflora in soil contaminated with chromium (Cai et al., 2019).

Using various concentrations of bio-SeNPs and Se (IV), El-Badri and his colleagues studied the effects of Se (higher dosages) on seed germination and seedling growth of *B. napus* (0, 50, 100, and 150 mol L^1). The use of nanosolutions improved seed germination when compared to sodium selenite and the control. The molecular mechanisms and genes involved in Se detoxification during the early seedling stage, as well as the effects of bio-SeNPs and Se (IV) on morpho-physiochemical traits under normal and salt stress conditions, were observed. The findings demonstrate that the morpho-physiochemical response of rapeseed to bio-SeNPs was frequently stronger than the relative control and Se (IV) treatments under both normal and salt stress conditions. Additionally, it has been demonstrated that bio-SeNPs enhance seed germination and seedling growth as well as photosynthetic capacity, secondary metabolism, and the capability of the defense system (El-Badri et al., 2022).

4.3 Alleviation of Biotic Stress

With the changes in physical parameters, there are numerous emerging pathogenic infections in plants, including microbial and pest/insect attacks. These biological stress conditions challenge the overall plant health and adversely affect the yield of the crops. Newer techniques, including nanoparticle use, can create promising solutions for these phytopathogens, mitigating their resistance factors. SeNPs are already known for their dual nature of inducing and reducing oxidative stress, which is a primary target for reducing biological invaders (Pilon-Smits, 2019; Zohra et al., 2021). Fungal infections are dominant in crops, and the increased use of fungicides is responsible for worsening the environmental sources. One of the fungi, *Rhizoctonia solani*, causing infection in *Vicia faba (fava beans)*, was inhibited by using *Bacillus megaterium*-synthesized SeNPs. The combination treatment of soaking and spraying of SeNPs solution enhanced the concentration (0.0625–1 mM) based on the antifungal activity in the infected crops. SeNPs promoted the growth of the crop by inducing peroxidase and polyphenol oxidase antioxidant enzymes. The photosynthetic pigments and other metabolic products were also stimulated after exposing SeNPs (Hashem et al., 2021). Production of SeNPs using the bacteria *Lactobacillus acidophilus* resulted in nanoparticles of size 40 nm. These SeNPs were tested against root rot and crown disease in wheat due to the infection of

Fusarium graminearum. The 100 μg/ml concentration reduced the salt and heat stress in the crops and promoted growth by increasing antioxidants and other metabolic products (El-Saadony et al., 2021). SeNPs synthesized using *Trichoderma* sp. culture filtrate reduced the growth and spore formation of *Sclerospora graminicola*, infecting the pearl millet. Application of these SeNPs and *Trichoderma asperellum* on the infected crops helped the plant growth by reducing the condition of Downy mildew in infected pearl millet and had sporicidal activity against the pathogenic fungus (Nandini et al., 2017).

Other than Fungi, the invasion of insects is also a concern for crop production. *Agrotis ipsilon* (cutworm) attacks the crop stems and causes destruction. Amin and his team reported a cutworm infection on sunflowers. The *Penicillium chrysogenum*-mediated SeNPs effectively act against the infection. The SeNPs killed the larvae of different stages of cutworm at 25 ppm concentration. The application of SeNPs has also been found to enhance the metabolism in sunflower crops (Amin et al., 2021). Similarly, the effective control was observed against plant destructors, i.e., root-knot nematodes, belonging to *Meloidogyne* sp. The SeNPs synthesized using the laser ablation technique administered resistance mechanism in tomato crops against the nematode infection. The treatment induced expression of the PR-6 gene within the infected plants, which is responsible for producing proteinase inhibitors (acting as markers) that would act on the nematodes, ultimately killing them. The overall results improved the growth and development of tomato crops (Udalova et al., 2018). A similar result was reported by Nikam et al., i.e., SeNPs treatments lead to protecting tomato plants. The plant growth-promoting bacteria *Rhizobium* sp.-assisted SeNPs treatment was found to increase yield by reducing the nematode infestations. The foliar spraying treatment of SeNPs (10 ppm) in *Meloidogyne*-infected tomato crops was found to induce protease inhibitors in the roots and leaves of the treated plant, which results in an effective decrease in the nematode infestation as well as overall growth of plant and yield of tomato (Nikam et al., 2022c). This approach to knowing all the advantages and disadvantages of biogenic nanofertilizers will bring a revolutionary change in agriculture applications.

Do SeNPs Have Some Adverse Impact on Crops?

The uptake and accumulation of selenium in plants entirely depend on the soil Se content. Besides this, the tendency of accumulation also varies from plant to plant, i.e., nonaccumulators (<100 mg/kg), accumulators (100–1000 mg/kg), and hyperaccumulators (1500 mg/kg DW) (Perfileva, 2022; Pilon-Smits, 2019). In the case of excess uptake, plants involve a mechanism for transforming Se into volatile forms, e.g., dimethyl selenide (El-Ramady et al., 2016; Pilon-Smits, 2019). As Se is known to have dual effects of reducing and increasing oxidative stress, it becomes essential to study its required amount for exact application. Many reports state that beyond a specifically required concentration of SeNPs, there are some deleterious effects on plants that include reduced photosynthetic activities, reduced production of antioxidant enzymes, and stunted growth and yield of the crops. Se excess in plants also leads to misleading incorporation of Se-amino acids during protein synthesis, which could also be responsible for inducing phytotoxicity. (Garza-García et al., 2022; Li et al., 2020b).

When the wheat crop was sprayed with *Allium sativum*–mediated SeNPs, the difference between effect concentrations of the treatment was highlighted. At a concentration of 30 mg/L, the SeNPs enhanced the roots, shoot, and the number of leaves, photosynthesis reactions, and many other features of plant production. In contrast, increasing the concentration of SeNPs at 40 mg/L downturned these effects and harm the plant (Ikram et al., 2020). In one of the studies done on *Capsicum annum*, Sotoodehnia-Korani et al. (2020) showed that at lower concentrations of 0.5 and 1 mg/L, the SeNPs increased the expression levels of nitrate reductase to stimulate, but at higher concentrations (10 and 30 mg/L) opposite results were observed that had toxic effects by lowering the nitrogen uptake of the plant (Sotoodehnia-Korani et al., 2020). Similar results were obtained when biologically produced SeNPs were used to check salt stress and nematode-induced resistance in tomato crops. The 10-ppm concentration of SeNPs spray efficiently promoted the resistance and growth of the plant, but at 50 ppm, it faced some toxic effects, which resulted in stunted growth (Nikam et al., 2022c). SeNPs synthesized using *Trichoderma* sp. could control downy mildew caused due to *Sclerospora graminicola* infection in pearl millet. A low concentration (100 ppm) of SeNPs did not inhibit the pathogen, and the plant was also able to tolerate about 1000 ppm of SeNPs, which is considered a very high concentration compared to other reports (Nandini et al., 2017).

Another aspect regarding any unfavorable effects of SeNPs on crops is the relation between the SeNPs concentration and the soil microflora. Soil is a vast source for the diverse microbial population, which includes symbiotic as well as non-symbiotic nitrogen-fixing bacteria (*Rhizobium* sp.*, Azotobacter* sp.*, Azoarcus* sp.*, Azospirillum* sp.*, Acetobacter* sp.*,* etc.), phosphate solubilizers (*Bacillus* sp.*, Pseudomonas* sp.*, Penicillium* sp.*, Aspergillus* sp., *Serratia phosphaticum*, etc.), and other plant growth promoters (Chaparro et al., 2012; Tilak et al., 2005). There is also a well-known example of the symbiotic relation between fungi and plants, i.e., Mycorrhizae, which reduces the abiotic stress conditions in crops and enhances their nutrient uptake. Some plant growth promoting rhizobia helps the Mycorrhizal association with the plants (Hrynkiewicz & Baum, 2012). To date, there is insufficient data on the adverse effect of SeNPs on the ecologically essential soil microbes associated with plant development. However, only some reports have conducted experiments to know the antimicrobial effects of SeNPs on soil microorganisms. The indirect effect of SeNPs on some non-specific plant-associated rhizospheric bacteria is depicted in Fig. 12.3. In a study conducted by Liu et al. (2021), a comparative analysis of selenite and SeNPs was done on soil bacteria, including the two most common bacteria, *Bacillus* species and *E. coli*. It was found that due to the unique properties of nanoparticles released, the SeNPs slowly resulted in elevating the bacterial count by 171% at lower concentrations and 136% at higher SeNPs concentration. The SeNPs enhanced the probiotic bacteria in the soil, such as *Tuberibacillus, Bryobacter, Mizugakibacter,* and *Telmatospirillum.* In contrast, there was a significant decrease in the bacterial population at both higher and lower concentrations of selenite due to free radicles formation but found to stimulate some of the high stress tolerating species such as *Candidimonas.* This made SeNPs a

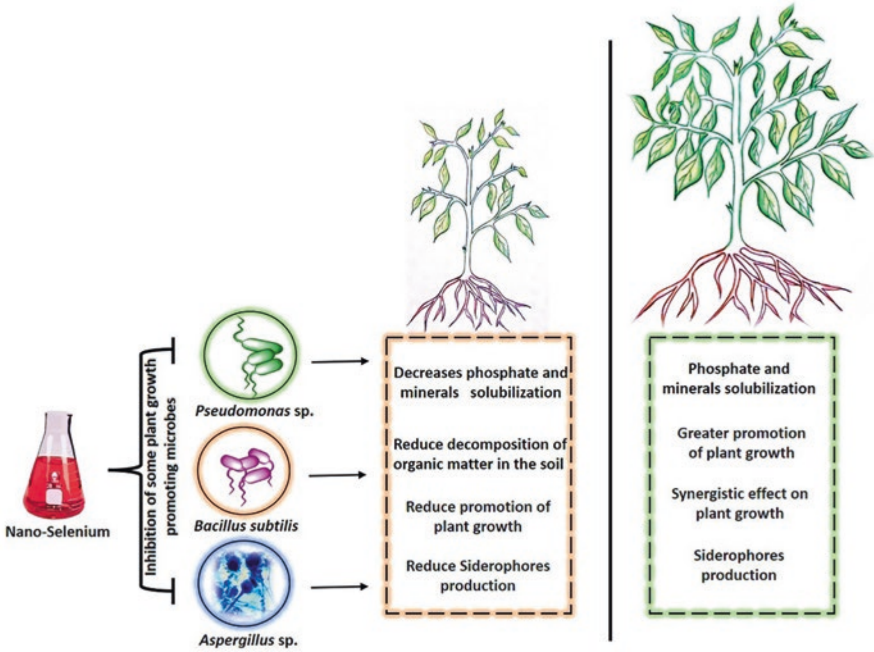

Fig. 12.3 Possible adverse effects of nanoselenium on soil microbes

good source of selenium for crops with less disturbance to rhizospheric microflora (Liu et al., 2021). A deep analysis of rhizospheric microbes affected due to selenite, selenate, *Bacillus*-mediated SeNPs, and *Yeast*-mediated synthesis of SeNPs was done on the selenium hyperaccumulating medicinal plant named *Cardamine violifolia*. The SeNPs from *Bacillus* increased the population of *Patulibacter, Leucobacter, Denitrobacter,* and *Sporosarcina* and decreased *Chlamydiae, Acidobacteria, Epsilonbacteraeota,* and *Elusimicrobia*, whereas Yeast SeNPs decreased Spirochetes in addition to above-mentioned bacterial taxa. The selenite and selenate treatments had similar results with minor changes in terms of taxon names (Guo et al., 2022). The role of Se nanofertilizer on soil microflora can be related to the antibacterial as well as antifungal effects of SeNPs on different commonly found microbes, which are also a part of rhizosphere species, for example, *Pseudomonas* sp. A few examples of the antimicrobial role of SeNPs are given in Table 12.2.

Other than this, using one of the inorganic salts of selenium (selenite) elevated the abundance of ecologically essential bacteria in the rhizospheric zone of oats crop. Some microbes belong to the decomposers categories *Chloroflexi, Bacteroidetes, Actinobacteria*, and others, including *Geobacter, Chlorobi, Nitrospirae, Holophaga, Lysobacter*, etc. It is already mentioned earlier that nanoselenium possesses lower toxic effects than other existing bioavailable forms of Se (Zhang & Spallholz, 2011), so their appropriate usage, considering their environmental effects, may be effectively practical in terms of agriculture applications.

Table 12.2 Antibacterial activity of SeNPs on some common soil microbes contributing to plant development

Sr. no.	Source of SeNPs	Inhibitory concentrations	Targeted species	References
1.	*Bacillus* sp. Msh-1	1000 μg/ml	*Aspergillus fumigatus*	Shakibaie et al. (2015b)
2.	*Anabaena variabilis* NCCU–441	20–60 μg/ml	*Bacillus subtilis* *Klebsiella pneumonia* *Escherichia coli*	Afzal et al. (2021)
3.	Bee propolis extract	250 μg/ml 100–500 μg/ml	*Bacillus cereus* *Aspergillus niger* *Aspergillus flavus*	Shubharani et al. (2019)
4.	*Emblica officinalis*	59.83 μg/ml 13.50 μg/ml 07.66 μg/ml 25.50 μg/ml 13.33 μg/ml	*E. coli* *A. flavus* *A. brasiliensis* *A. oryzae* *A. ochraceus*	Gunti et al. (2019)
5.	*Lactobacillus acidophilus*	9.4 μg/ml 3.5 μg/ml 6.54 μg/ml 4 μg/ml	*E. coli* *B. subtilis* *Klebsiella pneumonia* *P. aeruginosa*	Alam et al. (2020)
6.	*Bacillus* sp. JAPSK	25–100 μL	*Pseudomonas* sp. *E. coli* *Klebsiella* sp.	Singh et al. (2014)
7.	Ascorbic acid with stabilizers (Chitosan and BSA) Glucose	200–400 μg/ml 100–290 μg/ml 200–290 μg/ml 400 μg/ml	*E. coli* *B. subtilis* *K. pneumonia* *P. aeruginosa*	Filipović et al. (2021)
8.	*Ziziphus spina-christi* Callus extract	0.0156 mM 0.0312 mM 0.0156 mM 0.152 mM 0.312 mM 0.0625 mM 0.125 mM	*P. aeruginosa* *E. coli* *B. subtilis* *A. fumigatus* *A. niger* *A. terreus* *A. flavus*	lashin et al. (2021)
9.	*Providencia vermicola*	10 μg/ml 20 μg/ml	*B. cereus* *E. coli*	El-Deeb et al. (2018)
10.	*Ralstonia eutropha*	100 μg/ml 250 μg/ml	*P. aeruginosa* *E. coli*	Srivastava and Mukhopadhyay (2015)

5 Conclusions

Various metal nanomaterials are currently advocated as the new bio-inputs or fertilizers, like silver, gold, titanium, etc. However, these popular materials do not play any vital role in plant biochemistry and physiology. Contrastingly, selenium is a well-known element for its critical role in plant and animal physiology or life cycles. Using selenium nanomaterial conjugates as nanofertilizers for crop improvement is justifiable. As a result, selenium, as a nanofertilizer, contributes to crop productivity by increasing crop stress tolerance and nutritional value by targeting photosynthetic reactions. Simultaneously, the research, including the use of selenium nanopowder, also reveals its negative effect, leading to conditions like necrosis and chlorosis due to higher concentrations of SeNPs. Despite knowing all the benefits of using selenium nanoparticles over conventional selenite, selenate, or organic selenium fertilizers, there are still some uncertainties regarding their side effects due to the different concentrations of SeNPs for different species of plants. To overcome this, standardizing the formulations specific to plants and their respective problems could work on another level for agricultural benefits. Also, biological methods for fabricating SeNPs must be worked on for their ecologically safe options over chemical methods. These biological SeNPs in the form of Se-nanofertilizers can be a newer site for managing the biotic and abiotic stresses developing during cultivation. Also, as per the research conducted till now, it has been found that selenium in its different forms, whether it is selenite, selenate, or SeNPs, has some antimicrobial properties that completely depend on the concentrations used, which makes it favorable to be used as a biocontrol agent. However, when it comes to healthy soil microflora, which stimulates plants in many ways, it is still scarcely known. This aspect of using SeNPs as nanofertilizers needs some more attention, and the concentrations need to be produced based on dosage as per the requirements of plant species in different physiological parameters. From the overall data, we can conclude that the use of SeNPs-based fertilizers has a profitable view, but at the same time, risk management studies for using this nanoselenium for plants need more attention and evaluation (Table 12.3).

Table 12.3 Benefits of biogenic selenium nanoparticles (SeNPs) in agriculture sector

Benefit	Description
Seed germination	Biogenic SeNPs can enhance seed germination by improving the water uptake and nutrient availability of the seed. This can result in faster and more uniform germination, which can lead to higher crop productivity.
Root growth and development	Biogenic SeNPs can improve root growth and development by increasing the root surface area and root hair density. This can improve nutrient uptake and water absorption, leading to higher crop productivity.
Photosynthesis	Biogenic SeNPs can increase the photosynthetic activity of plants by enhancing chlorophyll content and photosynthetic pigment synthesis. This can improve the efficiency of light absorption and energy conversion, leading to higher crop productivity.
Nutrient uptake	Biogenic SeNPs can increase the uptake of nutrients such as nitrogen, phosphorus, and potassium by plants. This can improve plant growth and development, leading to higher crop productivity.
Stress tolerance	Biogenic SeNPs can enhance plant resistance to biotic and abiotic stressors such as pests, diseases, drought, and salinity. This can improve plant growth and development, leading to higher crop productivity.
Crop yield	Biogenic SeNPs have been shown to increase crop yield by improving plant growth and development, enhancing the photosynthetic activity, and increasing nutrient uptake. Higher crop yield means more food production, which can contribute to food security.
Sustainable agriculture	Biogenic SeNPs can promote sustainable agriculture by reducing the use of synthetic fertilizers and pesticides, improving soil quality, and increasing crop productivity. This can reduce the environmental impact of agriculture and support long-term food production.

It is important to note that more research is needed to fully understand the benefits and risks of biogenic SeNPs for agriculture. However, the existing evidence suggests that they have the potential to be a valuable tool for improving crop productivity and sustainability.

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Chapter 13
Smart Fertilizers: The Prospect of Slow Release Nanofertilizers in Modern Agricultural Practices

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1 Introduction

The world population is expected to reach the 9.7 billion mark by 2050, and the global grain requirement has been predicted to be increased by 70% to meet the demands of this rapidly growing population (FAO, 2017; World Population Prospects, 2022). Even though in the past few decades, the application of fertilizers has been influential to increase productivity up to a certain streak, the food supply chain is still facing issues due to a decline in agricultural yields and limited land availability. To overcome such concerns, farmers are imposed to use conventional fertilizers, herbicides, and pesticides (Singh et al., 2009; El-Ghamry et al., 2018). Haphazard usage of these agrochemicals is vicious as their carcinogenic and mutagenic properties may lead to hazardous effects on human health and the environment (Sarıgül & İnam, 2009). Moreover, these conventional approaches have not been demonstrated to be efficient in fulfilling the current nutritional demands of this expanding global population. For soil supplementation, huge amounts of nutrient salts like ammonium salts, urea, nitrate, and phosphate compounds are applied in the form of fertilizers, provoking higher concentrations of salts in soil that impedes crop yield (Mani & Mondal, 2016). The application of chemical fertilizers has been seen to result in the loss of nutrients as they fail to reach the targeted sites and therefore get fixed into the soil or contribute to water pollution through leaching (Liu & Lal, 2015; Feregrino-Perez et al., 2018). As mentioned in a study by Bortolin et al. (2013), most of the urea applied in soil perishes due to volatilization and leaching which leads to the accumulation of NH^{4+} increasing the soil pH

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(Bortolin et al., 2013). Some reports have stated that key macronutrients like nitrogen, phosphorus, and potassium, when applied to soil, result in a considerable loss of up to 40–70%, 80–90%, and 50–90%, respectively (Feregrino-Perez et al., 2018). The scarcity of micronutrients like iron is due to the low solubility of the oxidized ferric form in aerobic conditions (Sebastian et al., 2017). Zinc and magnesium deficiency is also very usual in neutral and alkaline soil and calcium-rich soil (Rengel, 2015). Additionally, repeated applications of these macronutrient fertilizers lead to a sharp decline in soil fertility and an increase in salt concentration in soil, thereby hampering crucial soil properties and crop productivity (Liu & Lal, 2015; Solanki et al., 2015; Feregrino-Perez et al., 2018). Therefore, modern approaches and technologies need to take over these conventional practices to fulfil the nutritional demands in an economically and ecologically feasible manner.

Nanotechnology is an emerging field that bears the promise to contribute significantly toward agricultural developments. Various nanomaterials like single or multiwalled nanotubes, magnetized iron nanoparticles, copper (Cu), aluminum (Al), silver (Ag), gold (Au), zinc (Zn), silica (Si), cerium oxide (Ce_2O_3), and titanium dioxide (TiO_2) (Raliya & Tarafdar, 2013; Raliya et al., 2015, 2016a, b; Tan et al., 2017) have been demonstrated to enhance the yield in plants. Nanoparticles provide a high surface-to-volume ratio and controlled release mechanisms that enable them to be considered as next-generation fertilizers (Feregrino-Perez et al., 2018). Nanofertilizers are nanomaterials encapsulated or functionalized with nutrients that enable the controlled and targeted delivery of one or multiple nutrients to satisfy the needs of plants (Zuverza-Mena et al., 2017). Hence, it is very essential to develop smart fertilizers to sustain agricultural productivity as well as crop quality (Iavicoli et al., 2017; Dimkpa & Bindraban, 2017). Nanotechnology has been currently exploring a new era of slow-release systems to deliver fertilizers in a targeted and controlled fashion. Slow-release can be elucidated as a permeation-regulated transfer of active substances from a modified reservoir to a targeted region accompanied by genuine maintenance of the concentration level of the active ingredient at a fixed level for an extended period (Mihou et al., 2007).

Nanofertilizers have been designed with the objective of controlled delivery of agrochemicals in the agricultural field as they possess high resilience and extended shelf life. In this connection, the implementation of slow-release systems can be regarded as one of the most promising approaches to sustainable agriculture and the improvement of nutrient availability in plants (Kuzma, 2007; Lal, 2008; Kabiri et al., 2011). This chapter provides insight into this revolutionary transition from conventional nanofertilizers to modernized smart slow-release fertilizers, their implementation in agricultural restoration, and the probable challenges against their utilization in agroindustries.

2 Nanofertilizer Application—Present Status

Nanofertilizers are micro- and/or macronutrients that are encapsulated or functionalized with nanomaterials mediating the controlled release and its successive slow diffusion into the soil. The use of nanoscale fertilizers can minimize nutrient loss reducing its fast degradation and volatility, thereby enhancing the nutrient quality and the fertility of the soil and promoting crop productivity (Nongbet et al., 2022). Nanofertilizers provide a significant role in crop production and are found to enhance the growth, yield, and quality of crops and food products for human and animal consumption (Meena et al., 2017). In the current context of sustainable agriculture, recent progress is undoubtedly witnessing the successful use of numerous nanofertilizers for achieving enhanced crop productivity (Zulfiqar et al., 2019).

Micro- and macronutrients are essential components for the healthy growth and development of plants. Lacking an adequate supply of these essential elements as well as their presence in excess amounts can impart deleterious effects on plants (Madan et al., 2016). These minerals play crucial roles throughout the phases of germination, growth, and development of plants, including the functioning of cellular components like proteins, pigments, and enzymes, and are involved in cellular signaling and metabolism (Duhan et al., 2017). Among all the essential nutrients, nitrate, phosphorus, potassium, and magnesium are majorly required by plants and cannot be absorbed directly from the atmosphere, thus being absorbed through the roots (Wang et al., 2016). In this connection, the nanoscale dimension of nanofertilizers has become a specialized solution for addressing nutrient deficiency problems.

Nanofertilizers generally include as constituents several nanoparticles, including metal oxides, carbon-based, and nanoporous materials, in varying compositions and combinations (Liu & Lal, 2015). Nanofertilizers can be synthesized by physical, chemical, and biological techniques and are equipped to provide a controlled-release function, ensuring a slow and restrained supply of imperative nutrient molecules (Zulfiqar et al., 2019; Usman et al., 2020). The modern micro- and macronutrient-based nanofertilizers and nanomaterial-enhanced fertilizers can improve the solubility, dispersion, bioavailability, and accessibility of definite nutrient molecules, conferring a secured and stable binding to the plant surface, reducing nutrient wastage (Duhan et al., 2017; Prasad et al., 2017). Nanofertilizers act as the influencers of many proteins, photosynthetic pigments, coenzymes, purines, vitamins, activators for the photosynthesis, and respiration systems of the plant (Jakiene et al., 2015). For the nanoparticles to be applied as nanofertilizers, initially they are synthesized via different approaches and then loaded or encapsulated with required nutrients to enhance target-specific plant uptake efficacy (Zulfiqar et al., 2019). In some instances, different nanoparticles are combined to develop intracellular structures in cell walls to enter and enhance the potential genetic properties (Larue et al., 2012). Thus, nano-assisted fertilizers showed excellent transport characteristics through plant tissues/cells with controlled mobility over conventional water-soluble fertilizers. The working mechanism of nanoparticles is flexible on both root entry and foliar entry (Zulfiqar et al., 2019). Therefore, nano-assisted materials in nanofertilizers play a significant role against various abiotic stresses like drought (Jaberzadeh et al., 2013), salinity (Siddiqui et al., 2014), heavy metal (Tripathi et al., 2015), temperature (Haghighi et al., 2014), etc.

2.1 Macronutrient Nanofertilizers

Conventional macronutrient biofertilizers are the chemical alloy of one or multiple nutrients like N, P, K, S, Ca, Mg, and many others that are required crucially in a higher content for plant growth and development. Among these, the chief macronutrients (N, P, and K) were found to be elusive to the plants (40–70%, 80–90%, and 50–90%, respectively), after soil application, resulting in a considerable loss of minerals (Zulfiqar et al., 2019). According to sources, overall macronutrient fertilizer ($P_2O_5 + N_2 + K_2O$) consumption is subjected to be increased from 175.5 million tons (Mt) to 263 Mt by 2050 globally (Liu & Lal, 2015). Therefore, the low efficiency and substantial application of these traditional macronutrient fertilizers can lead to their transport in huge amounts to the surface and groundwater bodies, leading to a disruption in the aquatic ecosystems, along with threats to human health. To replace conventional macronutrient nanofertilizers and to ensure sustainable food yield, highly effective and environment-friendly macronutrient nanofertilizers are required to earliest. In addition to the improved crop growth and yield, these macronutrient nanofertilizers can be an efficient tool in dispensing the required amount of nutrients to the plants, reducing the transportation cost and nutrient loss (Liu & Lal, 2015; Zulfiqar et al., 2019). These nanofertilizers are composed of one or a few nutrients encapsulated or loaded on definite nanoparticles. The efficacy of nanoparticles is regulated by several factors, including particle size, distribution, organic matter, uptake, soil texture, exposure route, soil pH, and accumulation of nanofertilizers in plants (Chhipa, 2017). Nanoparticles are favored to enter the intercellular spaces through apoplastic pathways and even into the epidermal and cortical cells to accumulate. Nitrogen nanofertilizers have been studied to show the highest seed yield and oil yield, in comparison to conventional N fertilizers. While phosphorus nanofertilizers were found to enhance biomass production in *Glycine max*. Furthermore, the application of NPK nanofertilizers was investigated to enhance the plant height, seed weight, and seed yield in *Helianthus annuus* (Baloch et al., 2015). Among the other macronutrient nanofertilizers, calcium carbonate nanoparticles ($CaCO_3$ NPs) appeared to be a handy tool in increasing the soluble sugar and protein in *Arachis hypogaea* (Bandala & Berli, 2019). Delfani et al. (2014) reported enhanced seed growth in *Vigna unguiculata*, after the combined application of magnesium nanoparticles (Mg NPs) and iron nanoparticles (Fe NPs) (Delfani et al., 2014).

Zeolites substantially improve the soil condition by increasing the water utilization efficiency and can also enhance the nutrient capacity by minimizing the volatilization of ammonia and salts (Sangeetha & Baskar, 2016). A study by Lateef et al. (2016) on composite materials of nano-zeolite (ZNC) loaded with macronutrients

(N, P, K, Ca, Mg, and S) and micronutrients (Fe, Zn, and Cu) in the form of their salts, showed an exceptional increase in water absorbency, water retention capacity, swelling ratio, and equilibrium water content of ZNC in comparison to nano-zeolite (NZ), therefore showing the environment-friendly approach of ZNC to be applied as fertilizers (Lateef et al., 2016). In another study on slow-release Zn nanofertilizer, where NZ was used as a substrate, it was observed that both zeolite and ZnO NPs significantly increased the mineral nitrogen (N) content in soil than the biogas slurry alone. This was due to the significant increase in the nutrient mobilization that was influenced by extracellular enzymes such as phosphatase and urease and soil microbiota (Yuvaraj & Subramanian, 2018).

Some of the recent studies have suggested that the traditional water-soluble phosphorus fertilizes can be substituted by nano-hydroxyapatite [nHA, $Ca_{10}(PO_4)_6(OH)_2$]-based nanofertilizer, which is a key component of human bones, teeth, and hard tissues (Gómez-Morales et al., 2013; Chhipa, 2017; Maghsoodi et al., 2020). Eutrophication caused by commercially available P fertilizers can be turned down up to a certain level by using nHA due to its less solubility and contamination risk. Besides, it forms a strong bond with urea, causing a potential slow release of nitrogen or urea (Kottegoda et al., 2011; Maghsoodi et al., 2020).

2.2 *Micronutrient Nanofertilizers*

Micronutrients are the essential elements that are required in a very minute amount ($\leq$100 ppm) but are vital for maintaining various metabolic processes in plants. Micronutrients such as iron (Fe), manganese (Mn), zinc (Zn), copper (Cu), molybdenum (Mo), and titanium dioxide (TiO_2) are often found to be added as soluble salts in NPK fertilizers (Zulfiqar et al., 2019).

Among different micronutrient nanofertilizers, iron (Fe) is one of the essential ones that can regulate optimal plant growth. Ghafariyan et al. (2013) evaluated iron nanoparticles (FeNPs) in hydroponic soybean plants to reduce chlorotic symptoms. In another research, the application of 0.5 g L^{-1} FeNPs on black-eyed pea plants increased leaf iron content, the number of pods per plant, grain weight, and chlorophyll content (Delfani et al., 2014). Zn is also a very important micronutrient that is responsible for enzyme activity, proliferation, differentiation of cells, and chloroplast development. The optimization of Zn concentration is necessary as there are reports of both positive and negative effects (Sturikova et al., 2018). In general, a concentration of 0.05 mg/L was found to be optimum for regular plant growth, above which phytotoxicity was observed (Liu & Lal, 2015). The use of Zn nanoparticles (ZnNPs) in mung bean showed some extraordinary boost in the form of increased root and shoot length and biomass (Mahajan et al., 2011). Mn is another essential micronutrient that is required for healthy plants. The application of Mn nanoparticles (MnNPs) in mung bean (*Vigna radiata*) demonstrated excellent results in terms of increased photosynthesis, as well as root-shoot length, biomass, and the number of rootlets (Pradhan et al., 2013).

Cu and TiO_2 nanoparticles (CuNPs and TiO_2NPs, respectively) were also evaluated as micronutrient nanofertilizers as both of these are required at a trace amount for the normal growth of plants (Wang et al., 2020). CuNPs-based fertilizers are much of interest nowadays as they can function both as pesticides and fertilizers. CuNPs were found to be effective in increasing the photosynthetic rate in *Elodea densa* when seeds were incubated with a concentration of less than 0.25 mg/L (Nekrasova et al., 2011). Among the photocatalytic materials, titanium dioxide (TiO_2) was found to be a sustainable model to tackle major agricultural issues, in terms of photoactivity, chemical stability, tunable hydrophilicity, and biocompatibility. TiO_2-based nanomaterials (TiO_2 NPs) demonstrated an upper hand over conventional metallic nanomaterials as it is shown not to hamper the germination in rice, lettuce, radish, cucumber, tomato, and pea, yet exalting the root elongation when applied at a lower dose of 0.5 g/Kg (Rodríguez-González et al., 2019). Moreover, molybdenum (Mo) at a very low soil concentration (0.01 mg/L) contributes to an important micronutrient for optimal plant growth. Legumes exposed to both colloidal molybdenum nanoparticles (MoNPs) and microorganism-functionalized colloidal MoNPs showed enhanced performance, yield, and disease resistance than that of the untreated plants (Taran et al., 2014) (Table 13.1).

2.3 Nano-Biofertilizers

In addition to the macro- and micronutrient fertilizers, presently, the development of nano-biofertilizers is also being reckoned as effective over conventional chemical fertilizers, due to their lesser environmental toxicity and residual effects. Nano-biofertilizers are the amalgamation of engineered nanoparticles with conventional biofertilizers, like microorganisms that can provide sufficient nutrients to plants, by fixing atmospheric nitrogen, solubilizing phosphate, restoring soil nutrient richness, and solubilizing insoluble complex organic matter into simple compounds (Dineshkumar et al., 2018; Itelima et al., 2018). In this connection, Boddupalli et al. (2017) have reported that the combined application of different plant growth-enhancing organisms (such as *Azolla*, *Azospirillum*, *Azotobacter*, *Azotobacter*, *Bacillus*, *Beijerinckia*, Cyanobacteria, *Pseudomonas*, and *Rhizobium*) and nanoparticles resulted in the enhancement in plant growth along with the alleviation of the phytotoxicity of NPs (Boddupalli et al., 2017). The use of nanoclay-coated *Trichoderma* sp. and *Pseudomonas* sp. as biofertilizers has improved the water retention capacity as well as nutrient use efficiency in crops (Mukhopadhyay & De, 2014). The application of silver (Ag) and gold (Au) nanoparticles encapsulated biofertilizer using *Pseudomonas fluorescens*, *Bacillus subtilis*, and *Paenibacillus elgii* has shown excellence in inducing plant growth in different agricultural plants (Rahman & Zhang, 2018). Biosynthesized ZnO nanoparticles incorporated with *Pseudomonas aeruginosa* have also shown broad-spectrum antimicrobial properties that can be implemented for enhancing crop protection (Barsainya & Singh, 2018).

Table 13.1 Application of various nanofertilizers in plants and their positive impacts

Nanoparticles	Crop species	Applied concentration	Positive impacts	References
Calcium borate nanoparticles	*Lactuca sativa* and *Cucurbita pepo*	30 mg/L at 10-day intervals throughout the experiment	Reduced the boron deficiency and significantly improved the productivity of both crops	Meier et al. (2020)
Carbon nanoparticles	*Zea mays*	50–800 mg/kg NPK fertilized soil	Enhanced crop growth through improved biomass yield, plant height, nutrient uptake, and nutrient use efficiency	Zhao et al. (2021)
Carbon nanoparticles loaded with nitrogen (N) and potassium (K)	*Phaseolus vulgaris*	0–40 mg/L foliar spray	Improved growth parameters (plant height, number of leaves per plant, number of flowers per plant, and plant fresh weight) along with increased yield	Salama et al. (2021)
Cerium dioxide nanoparticles	*Brassica oleracea*	Applied in combination with NPK fertilizer	Cabbage head weight increased three times higher than the control plants; chlorophyll content also increased significantly	Abdulhameed et al. (2021)
Cu-, Fe-, and N-doped titanium dioxide nanoparticles	*Vigna unguiculata*	Foliar application	Improved morphological characteristics, productivity, photosynthetic attributes, alert physiological changes; reduced lipid peroxidation and hydrogen peroxide content	Kamal and Mogazy (2021)
Graphite carbon nanoparticles	*Lactuca sativa*	1% wt CNP along with 30% commercial fertilizer	Nitrogen uptake increased, reduced nitrate leaching, but no reduction in yield than the 100% use of commercial fertilizer	Pandorf et al. (2020)

(continued)

Table 13.1 (continued)

Nanoparticles	Crop species	Applied concentration	Positive impacts	References
Hydroxyapatite nanoparticles	*Rosmarinus officinalis*	0.5 and 1 g/L foliar spray	Improved growth characteristics (thickness in the stem, lamina, midvein, xylem, and phloem) and oil production with great quality	Elsayed et al. (2022)
Iron oxide nanoparticle	*Morus alba*	10 mg/kg in soil	Promising improvement in morphological traits, photosynthetic attributes, and antioxidant defense than the control plants	Haydar et al. (2022)
NPK nanoparticles	*Zea mays*	1.5 g/L in the case of spraying and 7.5 kg/ha in the case of soil mix along with mineral fertilizer	Increased the uptake of N, P, and K elements; increased morphological traits and total yield with improved grain quality	Al-Gym and Al-Asady (2020)
Selenium nanoparticles (SeNPs)	*Solanum melongena, Cucumis sativus, Solanum lycopersicum*	1–25 μg/kg soil	Leaf plate surface area increased double than the untreated seedlings; reduction in hyperthermia stress	Gudkov et al. (2020)
Silica nanoparticles	*Cucumis sativus*	0–120 mg/L foliar spray	Enhanced plant length, leaf area, leaf number, leaf biomass, fruit weights, and quality as compared to control plants	Yassen et al. (2017)
Silica nanoparticles	*Tagetes erecta*	100–600 mg/L foliar spray	Enhanced biometrics; physiological, biochemical, and flower traits (days taken to first bud initiation, fresh and dry mass of flower, flowering duration)	Attia and Elhawat (2021)
Zero-valent iron (ZVI), Fe_3O_4 nanoparticles	*Oryza sativa*	50 mg/L foliar spray	Improved plant growth and photosynthetic attributes under iron-deficient conditions	Li et al. (2021)

(continued)

Table 13.1 (continued)

Nanoparticles	Crop species	Applied concentration	Positive impacts	References
Zinc oxide nanoparticles	*Coffea arabica*	10 mg/L foliar application	Increased fresh and dry weight of leaves and roots; Zn uptake increased; and the photosynthetic rate increased than the untreated and zinc sulfate–treated plants	Rossi et al. (2019)
Zinc oxide nanoparticles	*Oryza sativa*	0.5–5 g/L foliar spray	Significantly improved the growth and yield parameters, reverted the Zn-deficiency symptoms, enhanced the plant Zn content	Bala et al. (2019)

3 Scope of Nanofertilizers in the Improvement of Plant Growth and Development

Nanofertilizers perform a very crucial role in the physiological and biochemical functions of plants by increasing the availability of nutrients (Verma et al., 2022). In wheat, nano-NPK was observed to increase nutrient availability and stomatal dynamics along with photosynthetic parameters, thereby improving leaf growth (Abdel-Aziz et al., 2018). Zn nanofertilizers were observed to increase overall plant performance including biomass, photosynthetic pigments, and enzymatic activities (Vafa et al., 2015). Zn is also capable of activating various enzymes that are associated with metabolic processes (Rezaei & Abbasi, 2014; Hussein & Abou-Baker, 2018; Seleiman et al., 2020), as well as growth regulators, pollen production, and biological membrane integrity, via affecting the auxin production in plants (Alloway, 2008; Rajput et al., 2021; Wu & Li, 2021). Zn nanofertilizers were found to improve the photosynthetic pigments, plant length, biomass, soluble protein, and carbohydrates in maize. Moreover, they accelerated the biosynthesis of carbohydrates in maize by increasing the formation of soluble sugars (Sharifi, 2016). Groundnut seeds when treated with Zn nanofertilizers gained higher levels of starch, sugars, protein, and oil, which are important components for grain development and metabolism (Safyan et al., 2012; El-Metwally et al., 2018; El-Saadony et al., 2021). Pomegranate fruit yield was seen to be increased after the foliar application of nano-Zn and -B (Boron) (Janmohammadi et al., 2016). The foliar application of TiO_2 nanoparticles was observed to affect the growth and development of barley plants, boosting plant yield, and seed quality as well as improving fertilizer efficiency and grain production (Janmohammadi et al., 2016; Tarafder et al., 2020). In another study, TiO_2 nanofertilizers were demonstrated to increase plant biomass by uplifting the activities of photosynthetic complexes and nitrogen metabolism, thereby contributing to plant development and seed quality (Raliya et al., 2015; Janmohammadi et al., 2016; Mittal et al., 2020). The use of Fe nanofertilizers boosted the crop yield in soybean which was visible in terms of seed production (Sheykhbaglou et al., 2010). The application of Mn nanofertilizers in mung bean enhanced the nutrient utilization efficiency along with the crop quality. The photosynthetic rate was observed to be improved in groundnuts after the application of Mn nanofertilizers (Ghafariyan et al., 2013; Mekdad, 2017; El-Metwally et al., 2018; Adisa et al., 2019). In a study, the foliar application of Mo nanoparticles in groundnut was found to be enhancing the plant length, pod numbers, grain weight number, length of seeds, seed and pod output, and overall biomass (Fellet et al., 2021). Therefore, recent studies have sufficiently advocated for the beneficial attributes of different nanoparticles for plant growth and development.

4 Slow-Release Nanofertilizers

As discussed previously, several nanomaterials have contributed to healthy plant growth and development, yet the effects were not always found to be beneficial (Kah, 2015; Ma et al., 2018). Kah et al. (2018) classified all the nanofertilizers into three categories: micronutrient nanofertilizers, macronutrient nanofertilizers, and nanocarriers (Kah et al., 2018). Among them, nanocarriers were evaluated to have the highest median efficacy. These nanocarriers are designed to possess all the necessary properties like effective concentration, controlled release in response to definite stimuli, enhanced targeted delivery mechanisms, reduced ecotoxicity, and also an efficient mode of delivering agrochemicals to avoid repeated application. These nanocarriers act as carriers of beneficial compounds that ensure a properly targeted delivery without hampering plant growth and other organisms. Moreover, they can be formulated in such a way so that they release nutrients in a slow and controlled manner (Guo et al., 2018). Slow-release nanofertilizers are magnificent alternatives to conventional soluble fertilizers due to their proficiency in releasing nutrients at a slower rate throughout the growth phases of plants; therefore, plants can absorb most of the nutrients without being wasted due to leaching.

4.1 Synthesis of Slow-Release Fertilizers

Slow-release fertilizers for agricultural applications are mostly formulated in microcapsule suspensions encapsulating different agrochemicals (Hack et al., 2012). As agricultural practices require Kg-scale production, it is crucial to map out specific scalable techniques for the manufacture of slow-release fertilizers. Though the traditional bottom-up approaches assemble molecules at the molecular level, providing good control over the size and shape, they have limitations in channelizing large-scale productions. Hence, the synthesis procedure needs to be both rapid and scalable, which promotes a low-cost production of these slow-release fertilizers (Lee et al., 2022). The most common processes for the production of slow-release fertilizers are discussed as follows.

4.1.1 Nanoprecipitation

Solvent displacement or nanoprecipitation is a schematic technique for the production of nanoparticles. It is a simple and low-energy-consuming technique. In this process, dissolved solutes are precipitated as particles by rapidly changing the solvent quality that is generated by the addition of miscible antisolvent or ionic/pH gradient or temperature manipulation (Hornig et al., 2009; Zhu et al., 2010; D'Addio & Prud'homme, 2011; Zhou et al., 2017). For agricultural implementations, this technique can be scaled up to an approach called flash nanoprecipitation (FNP) (Johnson & Prud'homme, 2003; Feng et al., 2019). This method converts the conventional nanoprecipitation into a continuous process by the addition of cross flows in a confined impinging jet mixer or multi-inlet mixer or jet mixing reactor (Liu et al., 2008; Han et al., 2012; Ranadive et al., 2019). This scale-up technique can generate 3–10 kg/day of nanofertilizers and can be further enhanced by running parallel such units to maximize the output (Lim et al., 2014; Feng et al., 2019). Nanoprecipitation is commonly used for the controlled-release pesticide delivery (Boehm et al., 2003; Yearla & Padmasree, 2016). In this connection, the formulation of slow-release nanofertilizers offers higher penetration across leaves as well as increased efficacy of systematic delivery to the plant.

4.1.2 Emulsion Evaporation

Currently, emulsion evaporation is the most used method in manufacturing controlled-release fertilizers (Hack et al., 2012). In this self-assembly technique, agrochemicals, slow-release matrices, and other organic components are dissolved in a water-immiscible, volatile organic solvent like dichloromethane, chloroform, or ethyl alcohol. The water phase containing surfactants emulsifies the oil phase using an ultrasonic probe or high-speed homogenizer. This results in the formation of an oil–water emulsion, which is followed by the removal of organic solvent, thereby forming nanoparticles by self-assembly. The process shows similar encapsulation efficiency to nanoprecipitation methods (Zhang et al., 2013).

4.1.3 Ionotropic Gelation

In this technique, controlled release systems are developed through cross-linking or by electrostatic interactions between the charged matrix and oppositely charged particles. This can be done through common chemicals like cross-linking sodium alginate with calcium ions or with sodium tripolyphosphate and can be implemented for agrochemical delivery. This method has been used to demonstrate a wide variety of agrochemicals, including plant growth regulators, insecticides, herbicides, and fungicides (Namasivayam et al., 2018; Maluin et al., 2019; Valderrama et al., 2020; Ghaderpoori et al., 2020). These nanofertilizers provide sustainable release of agrochemicals ensuring their extended efficiency (Artusio et al., 2021).

4.2 Delivery, Uptake, Translocation, and Biodistribution of Slow-Release Nanofertilizers

The concept of nanomaterials customized for precise delivery to plants was initially adapted from targeted drug delivery using nanocarriers (Biju, 2014). These nanofertilizers consist of plant nutrients encapsulated on nanocarriers, delaying availability for plant uptake, thus allowing the extension of the period for the availability of fertilizer after a single application (Fu et al., 2018). Generally, agrochemicals are delivered to plants by three means—foliar spray, soil treatment, and seed treatment. Functionalized nanomaterials have several ramifications when applied to soil as the direct exposure and localized concentration of particles are much higher than those of the indirect foliar application, contributing a significantly weak amount to the plant sinks. To avoid nutrient loss due to foliar applications, a higher leaf area index and low exposure dose with multiple applications and weather-based applications are required. Yet the higher soil exposure could affect the rhizospheric microbial communities and influence the aggregation, thereby limiting plant uptake (Gajjar et al., 2009; Collins et al., 2012; Fernández & Brown, 2013; Mehta et al., 2016; Cao et al., 2016). Despite certain circumstantial factors (such as particle concentration in air, weather conditions, exposure time, and physiochemical properties of particles), aerosols of functionalized nanomaterials may cause risk to humans or other animals, if inhaled or exposed to air (Biswas & Wu, 2005). In this connection, to ensure safe foliar application, the use of suitable shield equipment and eye-protective glasses, along with masks and gloves, is necessary (Jain et al., 2018). Mesoporous silica nanoparticles with 3 nm pore size were used to deliver a gene and its chemical inducer into isolated tobacco plant cells and leaves (Torney et al., 2007). To avoid the leaching of the loaded gene and its inducer, gold nanoparticles were capped. Different specific target molecules like aptamers, oligonucleotides, and peptide molecules can be used for the surface operationalization of nanofertilizers to the nutrients in the nanocarriers get released in response to plant signals in the rhizosphere (Mastronardi et al., 2016; Monreal et al., 2016). In a study, it has been evaluated that foliar application of iron and magnesium NPs to black-eyed peas (*Vigna unguiculata*) showed comprehensive positive growth and developmental changes. Similar results were found in other experiments performed on tomatoes and watermelons (Delfani et al., 2014; Raliya et al., 2016a, b) (Fig. 13.1).

Several studies have used models to convey the mechanism of uptake and transport in different plant parts. The uptake process involves the movement of nutrient

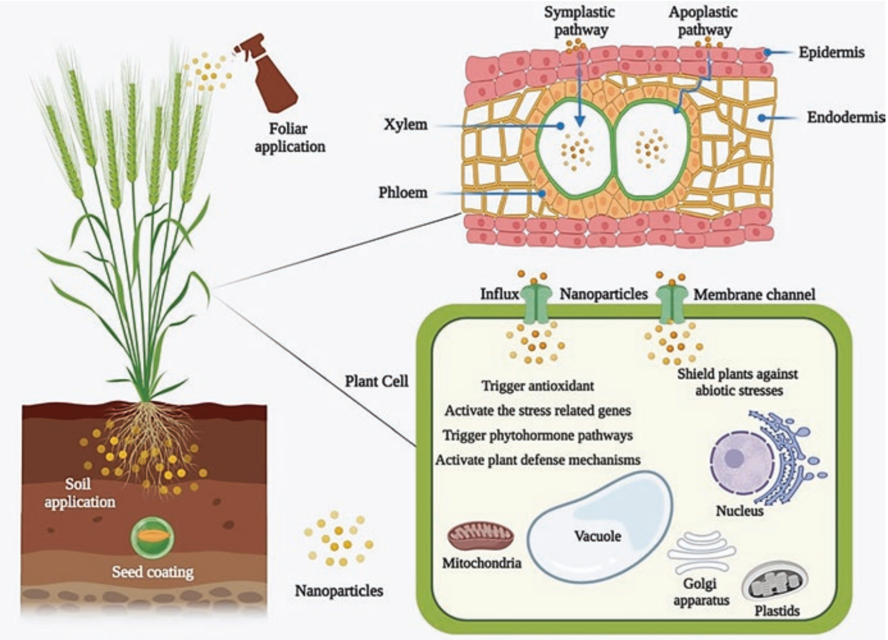

Fig. 13.1 Schematic portrayal of nanofertilizers application, uptake, and translocation of nutrients in plants. NPs delivered to plants by soil application, seed coating, and foliar spray to improve overall plant growth and development (Source: Manzoor et al., 2022)

ions through the soil toward the root xylem vessels followed by transport in the xylem and further biodistribution of ions in different plant parts (Bowling, 1976). The movement of water and solutes can be demonstrated by Richard's equation and the convection-diffusion equation in currently studied models. There are also many models where nutrient uptake has been described by the Michaelis–Menten equation (Claassen et al., 1986; Barber, 1995). It was observed that uptake enhanced with the increasing nutrient concentration in a curvilinear pattern approaching the maximum level of uptake. Still, the kinetic parameters fluctuate with plant species, plant age, soil temperature, and other important properties. Initially, the nutrient transport models in plant tissues were analyzed considering steady-state source-sink theory, where the flow was driven by an osmotically generated pressure gradient (Minchin et al., 1993). As diffusional pressure is insignificant in comparison to convective transport in the main bulk flow and thereby neglected. Although, diffusive transport is effective near the vessel boundaries as the connective flux is zero (Payvandi et al., 2014). Most of the models in the literature convey only a few aspects of fertilizer to crop translocation pathway. However, numerous models have been developed to identify nutrient uptake, but there are still some loopholes in current studies. Hence, it is much necessary to address the models of nanofertilizers uptake and transport in plants.

5 Recent Status of Different Slow-Release Nanofertilizers

In the current scenario, among the nano-enabled slow-release fertilizers for the smart delivery of nutrients, most of the systems were observed to be involved with macronutrients considering their fundamental and biological functions, larger inputs, and high loss. The carrier material studied for the delivery of such nutrients falls into different categories such as mesoporous silica, carbon-based nanomaterials, nanoclays, hydroxyapatite nanoparticles, and many more.

Mesoporous silica nanoparticles (MSiNPs) are one of the most efficient carrier molecules that have been evaluated to be very useful in the delivery of nutrients and pesticides. In this regard, the prospect of ABA-encapsulated and thiol group-dodecyl disulfide-functionalized mesoporous silica nanoparticles (MSiNPs) was considered to be effective for the alleviation of drought stress in *Arabidopsis thaliana* via increasing seed germination and internal antioxidant defense (Sun et al., 2018). In another study, the ABA-encapsulated MSiNPs were found to diminish the effects of cold stress, besides salt and drought stress (Jin et al., 2013). The use of MSiNPs as a carrier of urea fertilizer resulted in the controlled release of urea which suggested its utility as a smart delivery system for agrochemicals like pesticides and fertilizers (Wanyika et al., 2012). The rich mesoporous surface of silica enables this material to be biofunctionalized with urease for the development of a delivery system for nitrogen (Hossain et al., 2008). The uptake of MSiNPs by wheat and lupin increased plant growth by enhancing the accumulation of leaf total protein and chlorophyll pigments. This also introduces MSiNPs to be used as an effective delivery system of agrochemicals in plants in a controlled manner without hampering the plant growth and yield (Sun et al., 2016). The MSiNPs were also found to accelerate the delivery of different macro- and micronutrients like K, Mg, Ca, Zn, and Mn in *Zoysia* sp., playing an effective role in plant growth (Adams et al., 2020). Functionalized and encapsulated SiNPs and NPK were combined to synthesize controlled-release fertilizers (CRFs), meant to be implemented for the precise and well-restraint delivery of agrochemicals (Mushtaq et al., 2018). However, given the complex synthesis procedure and a shortage of field applications, further evaluation of the feasibility and applicability of MSiNPs as a nutrient carrier requires to be looked forward (Fig. 13.2).

Carbon-based nanomaterials have gained greater attention for drug delivery as well as fertilizer applications (Bianco et al., 2005; Mukherjee et al., 2016). In a study by Ashfaq et al. (2017), Cu nanoparticles-loaded carbon nanofibers (CNFs) were evaluated to show a slower release of Cu in water than that of Cu-loaded activated carbon microfibers (ACFs) (Ashfaq et al., 2017). Nanofiber formulation was observed to enhance the seed germination rate, root-shoot length, chlorophyll, and protein content of chickpeas (*Cicer arietinum*). Kumar et al. (2018) demonstrated a polymer film (PVAc-starch) with carbon nanofibers as a carrier of Cu–Zn nanoparticles on chickpeas and found that its polymeric composition prevented the rapid release of Cu–Zn nanoparticles into the soil. Moreover, the effects of Zn on reactive oxygen species (ROS) and the translocation of Cu–Zn CNFs within plant tissues

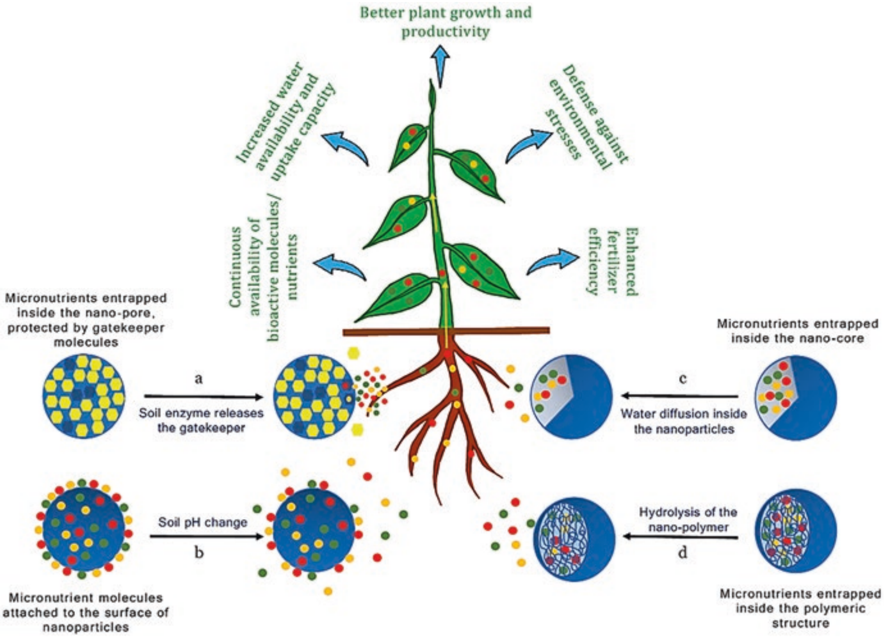

Fig. 13.2 Mechanism of controlled release of micronutrients by slow-release fertilizer. (**a**) Micronutrients entrapped inside the nanoparticle's pore and secured by some gatekeeper materials (biomacromolecules and biopolymers); (**b**) micronutrients get attached to the surface of the nanoparticles by different bonds or magnetic force; (**c**) micronutrients entrapped inside the nano-core; and (**d**) entrapment of micronutrients by some polymeric nanoparticles aided by their net-like structure, and the factors (e.g., soil enzyme, soil pH, water diffusion, hydrolysis of polymers, etc.) affecting the release of micronutrients

were also observed in chickpea (Kumar et al., 2018). Still, the mechanism responsible for plant uptake of nutrient-loaded nanocarriers in both studies was not clearly stated.

Nanoclays are layered silicates with two-dimensional platelets of a nanoscale thickness (~1 nm) and length of several micrometers (de Azeredo et al., 2011). Nanoclays have a wide range of applications including fertilizer carriers as well as in food and beverage packing (Lagarón & Busolo, 2012). Nanoclays can be both anionic and cationic (Hayles et al., 2017). The unique anion exchange capacity of these nanoclays makes them favorable to act as carriers for nitrate, phosphate, and borate (Everaert et al., 2016; Benício et al., 2017; Bernardo et al., 2018; Songkhum et al., 2018). The most frequently used cationic nanoclays used as nutrient carriers are montmorillonite, zeolite, and kaolinite (Roshanravan et al., 2015; Lateef et al., 2016; Mikhak et al., 2017). Nanoclays can protect nutrient molecules from physical barriers as well as intercalate nutrients into their layers through ion exchange or non-electrostatic interactions like H-bond (Kottegoda et al., 2014; Everaert et al., 2016; Songkhum et al., 2018). These features allow nanoclays to hold the potential of sustaining nutrients for a longer time, accelerate plant growth, improve nutrient use efficiency, balance nutrient supply, and minimize environmental pollution (Roshanravan et al., 2015; Kottegoda et al., 2014; Benício et al., 2017; Songkhum et al., 2018). Moreover, nanoclays can modify soil parameters. For instance, a study on LDH-P (layered double hydroxide phosphates) showed that pH increased in both sandy and clayey soils after cultivating maize plants 25 days after sowing. It was postulated that an increase in pH facilitates the adsorption of P by plants, although the mechanism is still unexamined (Benício et al., 2017) (Table 13.2).

Hydroxyapatite nanoparticles (nHAs) are another group of much-interested nano-enabled nutrient delivery systems. Urea-laden hydroxyapatite nanohybrids were developed by a research group and showed efficient slow release of nitrogen (Kottegoda et al., 2017). The nHA synthesized from carboxymethyl cellulose (CMC) when applied to soybean (*Glycine max*) was demonstrated to increase the growth rate by 32.6% more than that of the conventional P fertilizer-treated plants (Liu & Lal, 2014). Priyam et al. (2019) invented a novel technique of nHA biosynthesis from *Bacillus licheniformis*, a phosphate-releasing bacteria, that have similar properties to commercially available nHA, yet not having any negative impacts on soil bacterium (Priyam et al., 2019). A study by Xiong et al. (2018) revealed that the application of nHA bearing a surface charge of −13.8 can result in a higher yield of plants in comparison to conventional fertilizers (Xiong et al., 2018).

Among the polymeric nanoparticles, chitosan is a promising material as an agrochemical delivery system. Chitosan nanoparticles loaded with NPK (chitosan–NPK NPs) were compared to conventional NPK fertilizers, and after foliar application, chitosan–NPK NPs were found to accelerate growth and crop yield in wheat (Abdel-Aziz et al., 2016). Even though this polymeric nanofertilizer showed great potential, the mechanism behind it is still unknown. The enhancement possibly is a result of the slow release of NPK from chitosan NPs. Another nano-enabled fertilizer was produced by premixing montmorillonite, urea, and the polymer of polycaprolactone (PCL) or polyacrylamide hydrogel (HG), having a urea load of 75% in the final product. Among these, the HG polymer was found to enhance the mechanical strength of fertilizer and the nanofertilizer was demonstrated to show a slower release of N relative to pure urea. They also showed a significant role in the decline of N_2O emissions (Kundu et al., 2016).

Besides these majorly used nanocarriers of nanofertilizers, there are several different unconventional nano-enabled slow-release fertilizers. A nanosized Mn carbonate hollow core–shell loaded with Zn sulfate was reported to show a controlled release of Zn as demanded by rice plants (Yuvaraj & Subramanian, 2015). The result showed that the core–shell structure enhanced the nutrient use efficiency by extending the prolonged release of Zn for up to 29 days, which was more than the traditional $ZnSO_4$. Pine oleoresin and nanoscale zinc oxide or rock phosphate were used as carriers for urea and were found to decrease N_2O emissions (Kundu et al., 2016). Although there are still a limited number of studies regarding the mechanism of the controlled release of nutrients by these smart slow-release fertilizers.

Table 13.2 Different slow-release nanofertilizers and their perspective of application in plants

Slow-release component (coating/encapsulated)	Core material (carrier)	Perspective of synthesis	References
Commercial fertilizer (undefined)	Silica nanoparticles	To compete with the salinity and drought stress of plants	Mushtaq et al. (2019)
Copper nanoparticles	Carbon nanofiber	To increase water uptake capacity, germination rate, seedling lengths, and chlorophyll and protein	Ashfaq et al. (2017)
Copper oxide nanoparticles	Chitosan and sodium alginate complex	To obtain a hybrid nanocomposite for making a potential alternative to realize a smart delivery nanofertilizer using an eco-sustainable method	Leonardi et al. (2021)
Diammonium phosphate (DAP) fertilizer	Potassium ferrite nanoparticles	Phosphate and nitrogen slow release in the soil to defend their deficit	Saleem et al. (2021)
Halloysite nanotubes	Chitosan	To prepare a potential controlled-release carrier and delivery system for agricultural fertilizers	Wang et al. (2020)
Humic substances	Nanohydroxyapatites	Synergistic co-release of phosphate ions and humic substance, early plant growth, productivity under NaCl-induced abiotic stresses	Yoon et al. (2020)
NPK and silica nanoparticles	The first coating of semipermeable chitosan and the second superabsorbent coating of sodium alginate and kaolin	Slow release of NPK and silica nanoparticles withholds a large amount of water which can help a plant to survive under salinity and extreme drought stress	Mushtaq et al. (2018)
Potassium and nitrogen (urea and nitrate)	Calcium phosphate nanoparticles and nano-NPK	Enhancement in the efficacy of conventional fertilizer, controlled availability of nitrogen to plants	Ramírez-Rodríguez et al. (2020)
Urea	Nano-biocomposite of starch-g-poly(acrylic acid-co-acrylamide) superabsorbent polymer with natural char nanoparticles	To increase the soil water holding capacity and sustainability of N by slow release of urea	Salimi et al. (2020)
Zinc oxide nanoparticles	Soy-protein-based bioplastic	To study the increment in the versatility and functionality of bioplastics and nanofertilization in horticulture	Jiménez-Rosado et al. (2021)

6 Limitations and Concerns in the Commercialization of Slow-Release Nanofertilizers

In recent times, a huge increase in the number of patents issued for the synthesis of nano-based agricultural commercials and their applications has been noted (Kim et al., 2018). Research funding for nano-research is highest in the USA, followed by Germany and Japan, whereas China published the highest number of publications, and the USA obtained the highest number of patents (Dubey & Mailapalli, 2016). The global market for nanoformulation and agrochemical utilization is rapidly spreading out in the USA, Brazil, China, India, South Africa, and multiple European countries. Particularly in India, several agrochemical corporations are developing nano-based fertilizers. For instance, Tropical Agrosystem India Private Limited has launched nanofertilizers in the name TAG NANO (NPK, PhoS, Zinc, Cal, and many more). These are protein-lacto-glutamate formulations chelated with micronutrients, vitamins, seaweed extracts, humic acids, and probiotics (Elemike et al., 2019; Guha et al., 2020). Nano Green Sciences, Inc., India has also produced a colloidal nanofertilizer. Two other companies, namely, JU Agri Sciences Pvt. Ltd., Janakpuri, New Delhi, India, and Shan Maw Myae Trading Co., Ltd., have also released nanofertilizers under the name Nano Max NPK Fertilizer and Nano Micro Nutrient (Eco Star), respectively (Guha et al., 2020).

Although there are numerous research publications and patents concerning the prospects of crop production and protection, the commercialization of those nano-products is extremely limited. Specifically, due to the low expenditure on research and development infrastructure, high production value, low agricultural returns, and negligence in the transfer and imposition of technology in the agricultural sector, challenges have arisen (Huang et al., 2015; Kah, 2015). Besides, these products may pose threat to agricultural and food production by contaminating the food chain causing high risk to humans as well as to the ecosystem (Peng et al., 2017). Thereby it is very essential to gain authentic information regarding the various challenges and limitations of the facilities offered by nanobiology in the agroindustry (Iavicoli et al., 2017).

The major challenges encountered during the commercialization of nano-based agricultural products are the high valuation involved in the production, the limitations in the scalability of research and the development of trials, and the concerns related to the public's perception of the product's impacts on health and the environment (Agrawal & Rathore, 2014). Therefore, scrutinizing the issues related to expenses and returns involved in nano-agrochemical productions is very crucial for the desired levels of implementation and success of these products (Dimkpa & Bindraban, 2017).

To confront such issues, an analysis of various nano-agrochemical products, as well as production methods, is essential to be compared to discover the best-suited production path for the manufacturing of nanomaterials (Pereira et al., 2015; Dimkpa & Bindraban, 2017). Finding such a comprehensive analysis can serve as an important information tool to escort future investments from various industries.

However, the commercialization and mass production of these nano-based products need to be controlled and strictly tracked through government-devised and globally implementable standards (Agrawal & Rathore, 2014).

7 Future Perspectives

Nanofertilizers, especially slow-release smart nanofertilizers, hold great potential in the restoration of agricultural practices and production by deploying pieces of information from all cross-disciplinary fields. Studies involving the comparison among slow-release nanofertilizers, conventional nanofertilizers, and traditional nutrient fertilizers to evaluate the relative plant growth and development parameters as well as plant-protection mechanisms are highly recommended for further transparency of understanding their mode of action. The preliminary evaluation needs to be done under a controlled environment to screen and validate whether any ecological safety issues are in occurrence. This can be followed by further field trial experiments of the developed controlled-release fertilizers against the conventional ones. This will provide a more realistic approach to determining the benefits of their agricultural application in terms of their cost efficiency, effectiveness, and environmental proficiency. Moreover, to design adequate tools for their regulation and associated benefits, substantial characterization of both nano- and non-nano-fractions of these slow-release nanofertilizers is required. Additionally, an integrated analysis of these nano-based smart fertilizers can be performed to ensure further advancements and commercialization of technology. It will be a huge success if slow-release nanofertilizers can be revolutionized to pose a phenomenal impact on the environment, energy, and the economy. Further, research and technological interventions are advisable that focus on the optimization of fabrication procedures and the search for non-contaminative or biodegradable low-cost continuous matrix materials for making nanofertilizers an economically viable venture.

8 Conclusion

Slow-release nanofertilizers (SRFs) are a potential new agricultural productivity and sustainability solution. SRFs can deliver nutrients to plants in a regulated and sustained manner, reducing nutrient runoff and improving water usage efficiency. SRFs can also be programmed to target certain plant growth stages, increasing agricultural yields even more. SRFs can be more cost-effective than traditional fertilizers, in addition to providing environmental benefits. SRFs can be sprayed at lower rates, saving farmers money on fertilizer. SRFs can also be utilized to increase crop quality, potentially leading to better prices. SRFs are still in their early phases of application, but the potential benefits of this technology are evident. SRFs have the ability to transform modern agriculture methods and contribute to meeting the world's growing food needs. SRFs are an exciting new technology that has the potential to transform modern agriculture practices. More research is needed to fully understand the benefits and dangers of SRFs, although current evidence indicates that they have the potential to be a valuable tool for boosting crop yield and sustainability. Smart fertilizer development, particularly slow-release nanofertilizers, represents a bright prospect for modern agriculture techniques. These fertilizers provide various benefits, including greater nutrient usage efficiency, reduced pollution, and increased crop yields. More research is needed, however, to fully comprehend the long-term consequences of these fertilizers on soil health, plant growth, and the ecosystem. Overall, smart fertilizers have the potential to be a helpful tool for sustainable agriculture, but careful implementation and monitoring are required to assure their safe and successful usage.

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Chapter 14
Effects of Metal Nanoparticles on Plants and Related Microbes in Agroecosystems

Eman Tawfik, Mohamed Fathy Ahmed, Muthuraman Yuvaraj, and K. S. Subramanian

1 Introduction

Without the application of agrochemicals like fertilizers, pesticides, etc., sustainable production and efficiency in modern agriculture are unthinkable. However, each agrochemical has definite possible drawbacks that could affect human and environmental health, such as water contamination or residues on food products. Therefore, careful control and management of inputs may help to minimize these risks (Kah, 2015). To revolutionize agricultural methods, minimize the effect of modern agriculture on the surrounding environment, and improve both the quantity and quality of crops, a high-tech agricultural system using engineered efficient nanotools may be developed (Sekhon, 2014; Liu & Lal, 2015; Prasad et al., 2017).

One of the main areas where metal-based NPs are released into the environment is agricultural land. Understanding how metal-based NPs are transported and transformed in the agricultural environment is crucial for determining how they affect the agricultural ecosystem. The fate and transit of metal-based NPs may be significantly impacted by the quantity of dissolved soil organic matter that is frequently

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present in agricultural soil. Plants, being a vital component of agricultural activities, have exhibited intricate and dynamic interactions with nanoparticles (NPs) composed of metals. Reviews of NP stability and aggregation in the environment (Hotze et al., 2010; Chen, 2018), NP transport in environmental media (Bradford et al., 2002; Lin et al., 2010), NP interaction with plants (Thul et al., 2013), and NP bioavailability, toxicity, and destiny in ecosystems have all been published (Judy et al., 2014; Yadav et al., 2018). However, the majority of studies on the environmental effects of metal-based NPs look at the agricultural soil environment and plant system individually and rarely highlight them as integrated systems, which is important for agricultural ecosystem analysis. The stability, transformation, transport, and interactions of metal-based NPs with plants in the agricultural plant and soil system are covered in this review, along with future views. To create nanopesticides for plant protection, nanoparticles (NPs) with antimicrobial properties can be used. The two main categories of crop diseases are bacterial and fungal plant diseases. Once they become infected, they pose a serious threat to crop growth, lower yield and quality, and affect food safety, endangering human health (Li et al., 2023).

Nanotechnology is a fascinating scientific technology that is used in a variety of industries, including electronics, chemicals, pharmaceuticals, healthcare, environmental applications, agriculture, and the military. Nanoparticles or nanomaterials are discrete assemblages of atoms with a large adsorptive surface area that are measured in nanometers (10–9 m). Through cation or anionic exchanges of nutrient ions, this feature can be used to increase nutrient usage efficiency. This can be accomplished by limiting the interaction of nutrients with soil, water, and microbes and only releasing nutrients when they can be taken up by the plant directly (De Rosa et al., 2010). According to Liu et al. (2006), coating and cementing of nano- and sub-nanocomposites can be used to control how quickly nutrients are released from a fertilizer capsule. Furthermore, using transmission electron microscopes and scanning electron microscopes, the actions of nanoparticles were carefully observed (SEM). It has been demonstrated that patented nanocomposites with N, P, K, micronutrients, mannose, and amino acids improve the uptake and utilization of nutrients by grain crops (Yuvaraj & Subramanian, 2015, 2021).

Zeolites are known to have a large surface area and are capable of controlling the adsorption and desorption of nutrients, which ultimately increases crop yields. Zeolites can be used in agriculture due to their unique cation exchange, molecular sieving, and adsorption capabilities (Mumpton, 1999). Because of the decreased volatilization and leaching losses, fertilizer blends with zeolites can produce the same yield with less fertilizer used. Zeolite can store nutrients in the root zone, resulting in increased plant nutrient utilization rates. The massive storage area is provided by the honeycomb crystal structure. Water molecules and other cationic plant nutrient ions, such as potassium (KC) and zinc (Zn2C), are also stored in the zeolite crystal and are easily accessible to the plant (Yuvaraj & Subramanian, 2018).

This chapter spotted the light on the application of nanometals as nano-biofertilizers to enhance the crop productivity. Also, nanoparticles works as antimicrobial agents to inhibit the microbial growth, activity, and their enzymatic activity for the microorganisms in soil, water, or any other source related to agriculture. So, they can be considered as affortless access antimicrobial agents.

2 Nanofertilizers

Although nanofertilizers have become widely available in the market in recent years, major chemical companies are yet to shape agricultural fertilizers. “Nanofertilizers may contain nano-zinc, silica, iron, and titanium dioxide, as well as ZnCdSe/ZnS core–shell QDs, InP/ZnS core–shell QDs, Mn/ZnSe QDs, gold nanorods, core–shell QDs, and other materials. In the current decade, extensive research has been conducted on the uptake, biological fate, and toxicity of several metal oxide NPs, including Al_2O_3, TiO_2, CeO_2, FeO, and ZnO NPs for agricultural production (Dimkpa, 2014; Zhang et al., 2016). Zinc deficiency has been identified as one of the primary factors limiting agricultural productivity in alkaline soils” (Sadeghzadeh, 2013).

By direct proton bombardment or enrichment with 18O during synthesis, metal oxide NPs can be radiolabeled to produce 18F. In the presence of proteins and cell medium, the size, degree of aggregation, and zeta potential of metal oxide NPs are investigated (Llop et al., 2014; Marzbani et al., 2015). “Ion beam microscopy, transmission electron microscopy, Raman chemical imaging spectroscopy, and confocal laser scanning microscopy are additional techniques used to monitor NP uptake and intracellular fate” (Marzbani et al., 2015). “Future sustainable bio-based economies will continue to reduce and replace harmful materials in existing applications by utilizing eco-efficient bioprocesses and renewable bioresources. As a result, they will play a significant role (and represent the key strategic challenge) in the creation of the technologies needed to address 21st-century issues” (Marzbani et al., 2015). As we learn more about biology, ecology, material science, biodiversity, biotechnology, and engineering, we can use biomass and organic wastes in new ways and also make biomass more productive.

ZnO, TiO_2, SiO_2, and fullerenes are a few NPs with photochemical activity. When excited electrons are exposed to light, they directly electron transfer with oxygen to form superoxide radicals (Hoffmann et al., 2007). Therefore, when organisms are exposed to NPs and UV radiation at the same time, this ecotoxicity is caught in the act (particularly since UV light has higher energy than visible light). According to Kovochich et al. (2005) and Vannini et al. (2014), “the generation of reactive oxygen species (ROS) is an oxidative stress parameter that can be used in the context of toxicity and ecotoxicity determination. In this case, the cells respond to oxidative stress by increasing the number of protective enzymatic or genetic constitutions that are easily measurable. For instance, TiO_2 and fullerenes have been shown to produce ROS (Sayes et al., 2004). On the other hand, other writers have suggested that NPs (fullerenes and silicon NPs) may protect against oxidative stress” (Daroczi et al., 2006; Venkatachalam et al., 2017).

3 Impact on Plant

The complexity of natural systems and the environmental impact of materials are receiving more and more attention in ecotoxicological studies. To ascertain the long-term effects of environmental exposure to nanoparticles and to identify potential coping strategies, the in-depth investigation would be required (Cox et al., 2017; Singh et al., 2017) (Fig. 14.1). More research on NP bioaccumulation in the food chain and interactions with other environmental pollutants is required. When NPs enter a plant's cellular system, migrate through the shoot, and accumulate in various aerial locations, the probability that they will cycle through the ecosystem's many trophic levels increases. As NPs accumulate, they impact respiration and transpiration rates, alter photosynthesis, and block food material transit (Shweta et al., 2016; Du et al., 2017). The surface properties of both this surface and the NPs are interconnected with their respective levels of hazard. The assessment of the ecotoxicity of nanoparticles (NPs) is of paramount importance as it enables the establishment of a definitive link between the adverse impacts of NPs and various organisms across trophic levels, encompassing microorganisms, plants, and humans (Rana & Kalaichelvan, 2013; Prasad et al., 2017).

NP's have a characterized properties like: form, surface features, size, exposure period, and concentration employed, determine how beneficial they are. Crop management, plant species, age, soil type, substrate, and hydroponic conditions are some more important variables. Depending on the kind of stress they engage with,

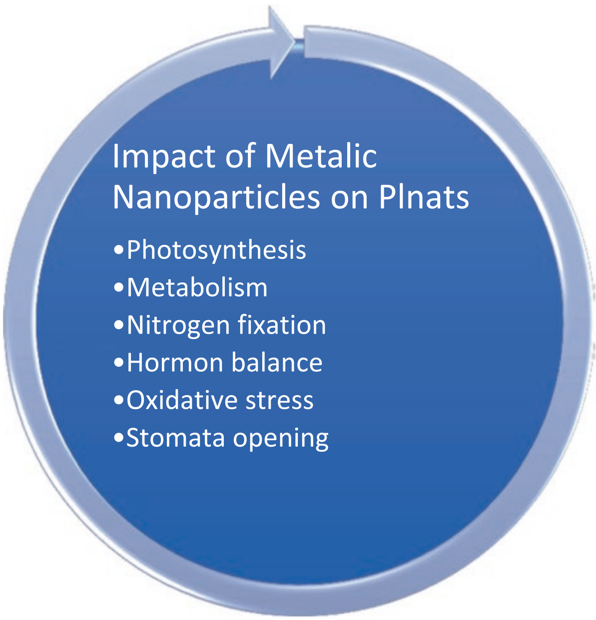

Fig. 14.1 The effect of nanoparticles uptake on plant behavior

NPs have varied impacts on plants and can produce distinct reactions. According to Tripathi et al. (2017), Singh et al. (2018), Pérez-Labrada et al. (2020), "There is a wide spectrum of consequences arising from physiological, biochemical, genetic, and morphological modifications, as well as changes in plant architecture and histology."

3.1 The Mechanism for Nanoparticle Interaction in Plants

Nanoparticles must be able to penetrate the plant and its surroundings in order to spread across the ecosystem. Nanoparticle transmission was carried out using protoplasts, plants, and organs (Wang et al., 2016). The cell wall prevents nanoparticles from entering plant cells and is mostly determined by the species of plant and the properties of the nanoparticles (Singh et al., 2015). A plant cell receives nanoparticles through an active transport process that is regulated by a number of cellular functions (Tripathi et al., 2017). Metal nanoparticle alteration, which alters their properties and fate in distinct plant species, is the main focus of dissolution. Metal nanoparticles with shifting valences undergo redox reactions in the soil, where they interact with biogenic redox processes to change the particles (Rico et al., 2015).

Nanomaterials called nanofertilizers supply one or more types of nutrients to growing plants, promoting their growth, and enhancing output. They come in two different varieties. On the one hand, the nanomaterials provide nutrients to plants to enhance their growth and yield, but on the other hand, they are nutrient carriers and only help in the transport and release of nutrients without acting as a direct source of nutrients (Nelwamondo et al., 2022).

The ways and methods of exposure of variable nanoparticles to plants are illustrated in Table 14.1.

3.2 Improving Postharvest Quality

Manufacturing and historical harvesting have benefited greatly from nanotechnology. Enhancing quality involves managing microbes, packaging, and other elements. Banana, carrot, tomato, and onion crops have all been preserved with the help of nanoparticles in the past for fungal control. Newer ranges of packing coverages, like TiO_2 and Ag NPs, are used because of their availability, physical and chemical stability, and nontoxicity. Nanosilver with a wide surface area displayed the capacity to absorb and degrade ethylene, while nano-TiO_2 with light catalytic capability was created. Nanoparticles are not only used to control disease, insects, and pests but they are also used to enhance the quality of grains, pulses, fruits, and vegetables after harvest. On the other hand, "the effect of physiochemically produced metal nanoparticles on the quality of many crops has been extensively studied. The impact of biogenic-produced metal nanoparticles on historical agricultural

Table 14.1 Different exposure methods of nanoparticles to crops

Nanoparticle	Exposure methodology	Plant studied	References
Silver	Irrigation in field	*Zea mays*	Berahmand et al. (2012)
	Hydroponic	*Oryza sativa*	Mazumdar and Ahmed (2011)
	Hydroponic	*Cucurbita pepo*	Hawthorne et al. (2012)
	Petri plates	*Zea mays*	Pokhrel and Dubey (2013)
	Growth medium	*Oryza sativa*	Mirzajani et al. (2013)
	Pots with soil	*Capsicum annuum*	Vinkovic´ et al. (2017)
Copper	Growth medium	*Phaseolus radiates*	Lee et al. (2008)
	Hydroponic	*Elodea densa*	Nekrasova et al. (2011)
	Petri plates	*Raphanus sativus*	Atha et al. (2012)
	Pots with sand	*Triticum aestivum*	Adams et al. (2017)
Titanium	Pots	*Spinacia oleracea*	Gao et al. (2008)
	Hydroponic	*Zea mays*	Asli and Neumann (2009)
	Petri plate	*Vicia narbonensis*	Castiglione et al. (2011)
	Field	*Triticum aestivum*	Jaberzadeh et al. (2013)
Zinc	Hydroponic	*Lolium perenne*	Lin and Xing (2008)
	Pots	*Arachis hypogaea*	Prasad et al. (2012)
Iron	Petri plate	*Triticum aestivum*	Iannone et al. (2016)
	Hydroponic	*Zea mays*	Li et al. (2016)
Nickle	Petri plates	*Solanum lycopersicum*	Faisal et al. (2013)
	Petri plates	*Hordeum vulgare*	Soares et al. (2016)

harvest quality has received little attention, despite this. Saffron petals are byproducts of saffron processing that are thrown away after harvesting" (Solgi, 2018; Devra, 2022).

Synthesized Ag NPs using a Citrus Sinensis peel extract showed a better antibacterial impact against *E. coli, E. aerogenes, Klebsiella* sp., and Shigella sp., according to the research by Kaviya et al. (2011). All doses of Ag NPs significantly prolonged the life of rose flowers as compared to the control group, according to the research by Hassan et al. (2014) into the effects of 25, 50, and 100 mg L^{-1} bio-produced Au NPs on rose flower quality.

4 Plant Morphological and Physiological Alterations Due to Nanoparticles Action

Plant species, particle types, and concentrations may all have an impact on the interaction of nanoparticles with plants and the physiological and morphological aspects (Lin & Xing, 2007). The root and shoot biomass, as well as the rate and percentage of seed germination, could all be increased by the nanoparticles in a variety of crop plants (Liu et al., 2009a, b; Kole et al., 2013). Increases in physiological characteristics including photosynthetic activity, N and P metabolism, and increased enzyme activity have all been linked to increases in morphological qualities (Yang et al., 2007; Khodakovskaya et al., 2009; Krishnaraj et al., 2012; Song et al., 2012).

4.1 Effect of Nanoparticles on Changes in Plant Morphology

The prior researchers' results made it abundantly evident that the impact of nanoparticles on plants differed depending on their morphological characteristics. According to a morphological inquiry on *B. monnieri*, Ag NPs generated a slight reduction in the shoot and root length by triggering the desertion of the air chamber in the cortex of root and a difference in the sizes, shapes, and distribution of the xylem elements inside the stem (Krishnaraj et al. 2012). On Lemna minor, Song et al. (2012) discovered that the application of TiO_2 NPs enhanced plant development at lower concentrations. Similar findings were made by Riahi-Madvar et al. (2021), who found that administering Al_2O_3 NPs to wheat only influences root growth at lower concentrations while maintaining control over other morphological characteristics. However, Giordani et al. (2012) reported the "effects of TiO_2 NPs and Al_2O_3 NPs on tomato seedlings after one week of treatment in the hydroponics cultural system. They came to the conclusion that, compared to control or seedlings exposed to Fe_3O_4 NPs, seedlings grown with high concentrations of TiO_2 NPs showed an aberrant proliferation of root hairs and that the plants treated with nanoparticles did not exhibit any harmful symptoms."

4.2 Effect of Nanoparticles on Changes in Plant Physiology

The application of several nanoparticles has a considerable impact on the crop plants physiology. It may have a direct or indirect effect on physiological measurements by affecting the generation of catalase, reactive oxygen species (ROS), superoxide dismutase activity, peroxidase, phenol, chlorophyll, and protein levels. Higher protein and carbohydrate levels are seen in Ag NPs-treated *B. monnieri* plants, although total phenol levels, catalase activity, and peroxidase activity are all reduced, according to Krishnaraj et al. (2012). Furthermore, it is clear from Song et al's report (2012) that "by eliminating reactive oxygen species from the plant cells, the application of TiO_2 NPs at lower concentrations (200 mg/ml) boosts the chlorophyll, peroxidase, catalase, superoxide dismutase, and malondialdehyde activities and contents on Lemna minor in comparison to bulk."

Similar findings were made by Raliya and Trafadar (2013), who discovered that applying ZnO NPs to the leaves of cluster beans at a lower dosage (10 ppm) resulted in higher concentrations of chlorophyll, phosphorus, and total soluble leaf protein. However, Sindhura et al. (2014) reported that in all of the treatments at 30 and 60 days after sowing groundnut under pot conditions, alkaline phosphatase, acidic phosphatase, and dehydrogenase activities were elevated as compared to control.

Additionally, Li et al. (2013).'s observation of the physiological properties of Fe_2O_3 NPs on watermelon demonstrated that a sizeable quantity of Fe_2O_3 NPs dispersed in a liquid media had been readily absorbed and translocated into various plant tissues. Their findings from their experiments demonstrated that different concentrations of Fe_2O_3 NPs improved the growth attributes beside seedling germination and seedling growth and enhanced physiological parameters. They came to the conclusion that adding Fe_2O_3 NPs at the right concentration (20 mg/l) could improve watermelon's physiological processes and resilience to environmental challenges, as well as increase seed germination and seedling growth. We have presented some tabular summaries of recently published papers on the effects of nanoparticles on plant physiological changes.

5 The Biological Processes of Nanofertilizers Work

Because plant cell walls include tiny pores (up to 20 nm), which increase nutrient uptake, nanofertilizers have been promoted for their increased nutrient utilization efficiency (NUE) (Fleischer et al., 1999). According to studies, "plant roots, which serve as nutrient entry points, are much more permeable to nanoparticles than standard manuring materials. By employing root exudates, molecular transporters through ionic channels, and the development of new micropores, nanofertilizer uptake can be improved (Rico et al., 2011). It has also been noted that leaf stomatal apertures and nanopores facilitate the uptake of nanomaterials and their penetration deep inside leaves. In comparison to bigger particles greater than 1.0 micrometers in size, it was shown that broad bean (*Vicia faba*) nanoparticles (43 nm) were more effective at penetrating deeply into leaf interior in large numbers (Eichert & Goldbach, 2008). Similar to this, the leaf stomatal radii of Arabian coffee (*C. arabica*) and sour cherry (*P. cerasus*) were both below 100 nm (Eichert et al., 2008), suggesting that nanofertilizers may be successful in improving nutrient uptake. It has also been suggested that nanofertilizers have higher NUE due to increased nutrient delivery and transport through plasmodesmata, which are ion-transporting channels between cells that are nanosized (50–60 nm) (Zambryski, 2004). Carbon nanotubes served as efficient molecular transporters, delivering fluorescent colors to tobacco cells through improved cell membrane penetration" (Liu et al., 2009a, b). The delivery of various goods to desired locations in various plants was also made possible by silica nanoparticles (Torney et al., 2007).

6 Nanoparticle Uptake and Transport in Plants

Lopez-Moreno et al. (2010a) discovered that "for cucumber, alfalfa, tomato, and maize seedlings, the most growth (140%) was observed at a dosage of 2000 mg/l and the least growth (50%) at a concentration of 500 mg/l. A few years later, Lopez-Monero et al. (2010b) used X-ray absorption spectroscopy to identify the uptake, storage, and distinct toxicity of CeO_2 NPs in four edible plants. According to their findings, the physical and chemical interactions of nanoparticles with root structures and exudates may be the cause of the varied toxicity. A recent study by Birbaum et al. (2010) exposed CeO_2 NPs to corn leaves in the form of an aerosol or suspension and found that about 50 g of cerium per gramme of leaves was either absorbed or integrated but that there was no evidence of cerium translocation into freshly grown leaves. These results clearly demonstrated that plant species influences CeO_2 NPs' ability to absorb and translocate. Zhu et al. (2008) observed the same impact of Fe_2O_3 NPs on the absorption, translocation, and accumulation on hydroponic pumpkin seedlings. They came to the conclusion that the uptake of nanoparticles is a species-dependent process and that the signal for the uptake of Fe_2O_3 NPs is not just limited to plant components."

Since Wang et al. (2011) could find no evidence of Fe_2O_3 NP uptake on the pumpkin, they made the assumption that the size of the applied nanoparticles would have a direct impact on the nanoparticles' ability to permeate plasma membranes and penetrate cell walls. However, Li et al. (2013) "studied the impact of suspended Fe_2O_3 NPs in a liquid medium on watermelon and reported that the suspended nanoparticles had been directly taken up and translocated into various plant parts, which may have increased physiological function and increased seedling germination to some extent. With a rise in treatment concentration, the beneficial benefits of nanoparticles first accelerated and subsequently slowed."

The ryegrass experiment supported the ZnO NPs' adsorption and deposition on the root surfaces (Lin & Xing 2007). The cytoplasm, apoplast, and nuclei of the endodermal cells as well as vascular system were all clearly visible in the cross-sectional transverse electron microscopy pictures of the ryegrass root. Later, Lopez-Moreno (2010a) showed that ZnO NPs at a concentration of 500 mg/l were taken up by and accumulated on soybean seedlings. They came to the conclusion that high nanoparticle concentrations increased the likelihood of agglomeration forms, which may obstruct nanoparticle entry through the cell pore and diminish uptake and accumulation of nanoparticles inside the tissues of plants.

7 Effect of Nanoparticles on Plant Toxicity to Cells and Genes

Tan et al. (2009) investigated the toxicity of rice cell suspensions containing multi-walled carbon nanotubes and found that both low and high quantities of these materials kill cells. "The breakdown of genetic material in Arabidopsis cells was directly related to the genetic toxicity of the nanomaterials, according to Shen et al. (2010) who stated that the concentration and size of single-walled carbon nanotubes generate the toxicity in the rice and Arabidopsis protoplast cells. Lopez-Moreno et al. (2010a) evaluated the cellular toxicity of CeO_2 and ZnO NPs on soybean seedlings and used a RAPD assay to determine the genetic toxicity of both NPs. They went on to explain that the main cause of the rise in toxicity is the interaction of genetic material with zinc ions. However, Ghosh et al. (2010) showed in a different study that superoxide radicals produced during lipid peroxidation caused TiO_2 NPs to be cytotoxic and genotoxic. Babu et al. (2008) identified the dose- and duration-dependent reactions in the root meristem of *Allium cepa*, however, as a result of a reduction in mitotic indices brought on by various kinds of chromosomal aberrations in response to Ag NPs. According to Kumari et al. (2009), treatment of *A. cepa* cells with different concentrations of Ag NPs led to chromosomes becoming sticky and breaking, which may ultimately induce genotoxicity in cells. Similar to this, Racuciu and Creanga (2009) reported that the quantity of nucleic acid was decreased by biocompatible magnetic nanoparticles coated with perchloric acid and proposed that the magnetic nanoparticles caused chromosomal abnormalities in corn cells".

Through modifications in the levels of phytohormones, TiO_2 and iron-based NPs can postpone senescence and hasten cell proliferation (Landa 2021). At the cellular and molecular levels in plants, Ag NPs can potentially be harmful. Numerous investigations revealed that changes to cell structure and cell division occur along with the restriction of plant growth following exposure to Ag NP. After being exposed to 40 mg/L Ag NPs, Yin et al. (2011) discovered that "*Lolium multiflorum* seedlings failed to form root hair, the cortical cells were extensively vacuolated and collapsed, and the epidermis and root cap were also harmed". In maize (*Zea mays* L.) and cabbage (*Brassica oleracea* var. *capitata* L.), Pokhrel et al. (2013) found that Ag NPs might decrease the size of the vacuole and result in a loss of cell turgidity and size. Similarly, Mazumdar (2014) discovered that vacuoles and cell wall integrity were impaired after Ag NPs entered the cell of *Brassica campestris*, and other organelles may also have been impacted. Similar findings were made by Mirzajani et al. (2013) who discovered that rice cells might be damaged by Ag NPs that could enter the cell wall at concentrations up to 60 g/mL. Additionally, Kumari et al. (2009) showed that Ag NP treatment dramatically reduced the mitotic index in Allium cepa and disrupted cell division, leading to chromatin bridge, stickiness, altered metaphase, multiple chromosomal breakage, and cell disintegration. A general schematic representation for mode of action of metallic nanoparticles on plant is represented in Fig. 14.2.

8 Microorganisms and Nanoparticle Interaction

According to Pajuelo et al. (2011) and Sacca et al. (2017), soil microorganisms play important roles in immobilizing nutrients, cycling carbon, and detoxifying and degrading pollutants, all of which contribute to improved soil health. About 15% of the total microbial communities in the widely dispersed heterotrophic microflora is made up of bacterial populations from various species, which either directly or indirectly promote plant growth (Govindasamy et al., 2010; Etesami & Maheshwari, 2018). These rhizosphere-dwelling bacterial communities, also known as plant

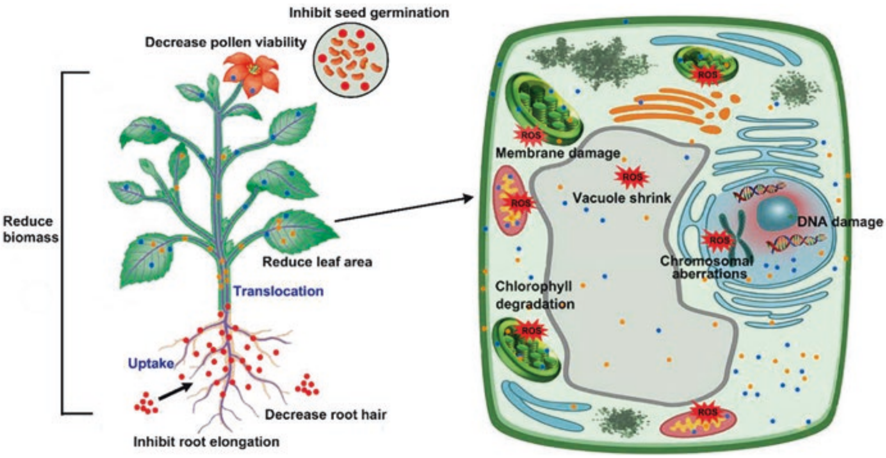

Fig. 14.2 The Uptake, translocation, and phytotoxicity of silver nanoparticles in plants. Depending on the type and concentration of nanoparticles, plant absorption can have a variety of consequences on plant behavior. They have also been proven to have an impact on plant physiology, including photosynthesis, respiration, and water use efficiency. Furthermore, nanoparticles can have an impact on plant nutrient intake and distribution, resulting in changes in nutrient buildup and plant quality. (Reprinted from Yan and Chen (2019) "Licensee MDPI, Basel, Switzerland. This article is an open-access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license")

growth-promoting rhizobacteria (PGPR), are capable of colonizing plant roots (Gopalakrishnan et al., 2015). Only 2–5% of rhizosphere bacteria has been identified as powerful PGPRs despite being such a diverse population (Jha et al., 2010). "The interactions of NPs-PGPR are essential given the significance of PGPR to plant health (Mesa-Marn et al., 2018). Similar to other xenobiotics, the detrimental impact of NPs on beneficial soil bacteria is now only becoming apparent and is still not fully understood. Due to the increasing release of agricultural goods utilizing nanotechnology, such as pesticides, fertilizers, and herbicides that are based on nanoparticles, it is essential to examine how NPs interact with bacteria (Duhan et al., 2017). For instance, Fe NPs and TiO_2 NPs used in water purification and environmental remediation both restrict and promote the growth of target organisms when introduced directly (Mueller & Nowack, 2010). However, at the same concentrations, non-target microorganisms and other living entities are also poisoned by Fe NPs and TiO_2 NPs. Instead, nZVI only had negative effects on soil microbes (Cullen et al., 2011). On pure microbial cultures and soil microorganisms, some other NPs, including FeO NPs, ZnO NPs, Ag NPs, CuO NPs, and TiO_2 NPs, have demonstrated varying chronic and acute harmful effects (Table 14.2). Other aspects affecting the interaction between NPs and bacteria are their size, surface charges, capping agent, presence of divalent anions or cations, and the makeup and charge of their cell walls" (Acharya et al., 2018).

Table 14.2 Effect of variable nanoparticles on soil microbes

No.	Nanoparticle	Microorganism	Effect	References
1	Ag NPs	*Nitrosomonas europaea*	Cell wall damage, fragmented nuclei, and size-dependent reduction of NH_3 oxidation capping	Yuan et al. (2013)
2	Fe NPs	*Paracoccus* sp.	Increased cell proliferation and NO_3 biodegradation; a dose-dependent reduction in cell density	Jiang et al. (2015)
3	CuO NPs	Soil nitrifying bacteria	The nitrification kinetics were reduced	Vandevoort and Arai (2018)
4	ZnO NPs	Aquatic microcosm experiment	Negative effect on the structure of the fungal community and the activities of microbial enzymes	Du et al. (2020)
5	MoO_3	*Aspergillus flavus* and *A. niger*	Significant growth inhibition, nuclear condensation produced by NPs, altered hyphal architecture, and metabolic alterations that resulted in apoptosis	Chaves-Lopez et al. (2018)
6	Ag NPs	*Glomus aggregatum*	Decreased glomalin content, mycorrhizal responsiveness, and mycorrhizal colonization	Abd-Alla et al. (2016)
7	ZnO NPs	*Glomus versiforme*	Harmful effects on the AMF symbiosis	Wang et al. (2016)
8	ZnO NPs	*Azotobacter*	Inhibit enzymatic activities	Chai et al. (2015)
9	TiO_2 NPs	Soil bacteria	Inhibit enzymatic activity and pose detrimental effect on microbial activity, abundance, and diversity	Buzea et al. (2007)
10	Au NPs	*Bacillus subtilis*	Affect antibacterial activities (growth inhibition zone)	Lakshmi et al. (2012)

8.1 Interaction of NPs with Bacteria

The ecosystem depends heavily on soil microorganisms, which are essential for the dynamics of organic matter and the nutrient cycle, biogeochemical cycling, the biodegradation of pollutants, and crop production. In order to exhibit antimicrobial activity, nanoparticles can interact with bacterial cells using a variety of mechanisms, such as electrostatic attraction, van der Waals forces, receptor–ligand interactions, and hydrophobic interactions. Nanoparticles, which travel from the outside to the inside of bacteria, cross the bacterial membrane, alter its structure and function, and then come into contact with DNA, lysozyme, and ribozyme enzyme, among other cell components. Numerous mechanisms, such as oxidative stress, heterogeneous changes, cell membrane permeability changes, electrolyte imbalance problems, enzyme inhibition, protein inactivation, and changes in gene expression, may occur when nanoparticles come into contact with bacteria (Çiçek, 2021).

8.2 *Interaction of NPs with Rhizobacteria*

Extracellular polymeric substances (EPSs), hormones, organic acids, and enzymes can modify the surface properties, bioavailability, and speciation of NPs in the rhizosphere in addition to plant root secretions (Fig. 14.3).

8.2.1 Ag NPs-PGPR Interactions

Ag NP concentrations in the environment are anticipated to increase during the next years as a result of the wide use (Mitrano & Nowack 2017). The Ag NPs are partially or completely sulfidized during wastewater treatment, and the converted Ag NPs are reportedly significantly less harmful than the pristine Ag NPs (Levard et al. 2013). Ag NPs undergone partial sulfidation in the presence of secretome, resulting in Ag–Ag_2S core–shell structure.

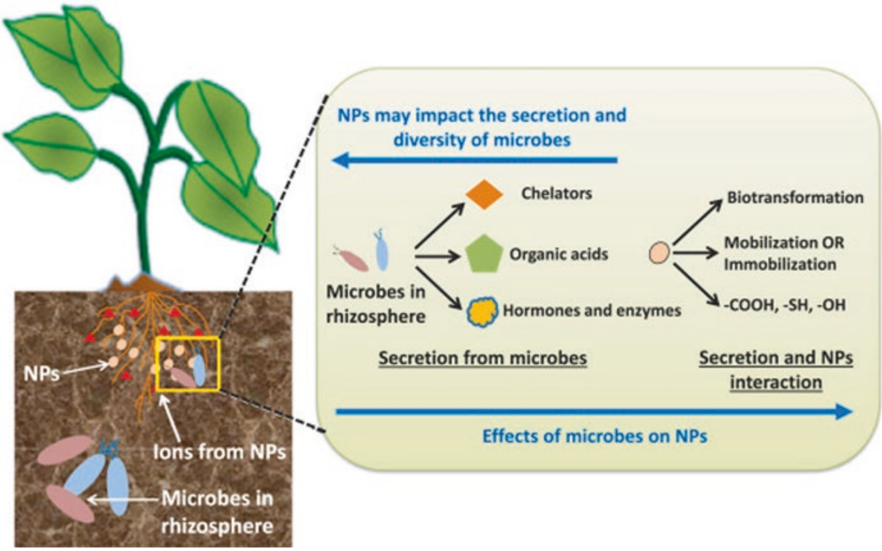

Fig. 14.3 Illustration of different interactions between NPs and soil microbes. According to studies, NPs can interact with soil microorganisms by physical adsorption, electrostatic attraction, and chemical interactions, among other mechanisms. These interactions can be affected by the NPs' surface characteristics, including size, shape, and surface charge. For instance, negatively charged microbial cell membranes can bind to positively charged nanoparticles (NPs), changing the structure and functionality of the microbes. The type and concentration of NPs, the makeup of the microbial population, and the environmental circumstances all have an impact on how NPs affect soil bacteria. According to certain research, NPs can impede microbial activity and growth, which reduces the cycling of nutrients and the breakdown of organic matter. However, other studies have shown that NPs can increase nutritional availability and drive microbial activity. (Reprinted from Ameen et al. 2021) "(This article is an open-access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license)"

8.2.2 ZnO NPs-PGPR Interactions

In addition to having a considerable negative impact on edible plants, ZnO NPs have also been found to influence soil bacterial development. For instance, in contrast to controls, acetate-stabilized ZnO NPs induced diverse global protein expression profiles in the soil bacteria *Cupriavidus necator* JMP134 (Neal et al., 2012). "In a study, it was found that 306 mM ZnO NPs fully prevented the growth of Pseudomonas species, whereas 7.7 mM ZnO NPs of a size 100 nm reduced colony-forming units of *P. chlororaphis* O6 by 12.5%. (Soni et al., 2017). Additionally, *P. aeruginosa* PAO1 and *P. putida* KT2440 were almost completely incapable of generating biofilms when exposed to ZnO NPs (50 nm). Additionally, by reducing its metabolic activity by more than 75% when exposed to ZnO NPs, the elimination of EPSs increased the anti-biofilm effect" (Ouyang et al., 2017).

8.2.3 TiO_2 NPs-PGPR Interactions

Two alternative approaches can be used to comprehend how TiO_2 NPs affect soil bacteria: "(i) toxicity assessment following photoactivation of TiO_2 NPs and (ii) without photoactivation of TiO_2 NPs". The majority of research, however, do not back up the idea that the toxicity of TiO_2 NPs results from photoactivation. Additionally, several investigations have revealed that even at greater concentrations, TiO_2 NPs are not very hazardous. For instance, Jiang et al. (2009) showed that "bacteria were unaffected by the TiO_2 NPs (50 nm) without photoactivation at a dose rate of 418 mM. In contrast, *P. putida* biofilm viability was reduced by almost 99% on glass surfaces covered with photoactivated TiO_2 NPs (5.6 nm). Recent research on the effects of TiO_2 NPs on the PGPR metabolism in soils found that inoculating *T. aestivum* with *Paenibacillus polymyxa* A26, *Alcaligenes faecalis*, *Bacillus thuringiensis* AZP2, and a mutant strain of *P. polymyxa* A26Dsfp alone or in various combinations enhanced plant development. Wheat responses to salt, drought, and pathogens were simultaneously evaluated along with the impacts of TiO_2 NPs and PGPR. It has been hypothesized that TiO_2 NPs can boost the growth of PGPR when plants are co-inoculated with *P. polymyxa* A26, *B. thuringiensis* AZP2, or *A. faecalis* based on the accumulation of shoot biomass of wheat. However, when plants were cultivated in sand, there was no growth promotion seen under exposure to TiO_2 NPs (Timmusk et al., 2018)."

8.3 Interaction of Nanoparticles with Soil Fungi

The importance of fungus in soil health has been well documented in a wealth of literature. Here, the ability of the soil to support biological productivity and plant health is defined by the overall soil health rather than the soil quality. According to research, fungal variety plays an important part in enhancing soil health, crop productivity, and the efficiency of the entire agricultural system (Nielsen et al., 2015) (Table 14.1). Fungi are merely energy consumers, but because of their extensive activity on and in the soil, they are essential to the survival of terrestrial life. The first organisms to inhabit the tissues of dead plants on and inside the soil are often soil fungus, which break down and decompose the dead plants. In fact, because of the way they are physically arranged into a network of mycelium, which is made up of branching, stiff tubes (hyphae), loaded with protoplasm, fungi are naturally equipped with the capacity to break down dead things. As a result, the fungal population breaks down the soil's organic matter while cooperating with other soil organisms to release nutrients for plant growth. When it comes to protecting crops from harmful microorganisms, this job becomes extremely crucial. For instance, "arbuscular mycorrhizal fungi (AMF) constitute the most significant family of beneficial microorganisms in agri- and horticultural soils (Gosling et al., 2006). By enhancing roots, nutrient cycling, stress tolerance, and ion uptake, AMF significantly improves plant performance and crop output. In addition to these, some fungi that are antagonistic to one another, such as *Glomus* sp. and *Trichoderma* sp., suppress fungal infections to shield crops and plants against illnesses (Dawidziuk et al., 2016). Additionally, *Trichoderma* sp. (*T. asperellum*, *T. atroviride, T. harzianum, T. virens*, and *T. viride*) is frequently found in biostimulants and biocontrol formulations for horticultural crops" (Guzman-Guzm'an et al., 2019).

Numerous important roles are played by soil yeast applications in the upkeep of sustainable agriculture. By encouraging plants to consume minerals like "N, P, and K and producing antimicrobials in the rhizosphere, soil yeast is frequently used as a biological control technique to prevent the colonization of harmful organisms" (Yurkov 2018). A suitable unicellular eukaryotic model organism for the toxicological assessment of nanoparticles is the yeast *Saccharomyces* cerevisiae in this context (Mukhopadhyay et al., 2002). In addition, after being incubated for 10–14 hours in YPD medium, a wide variety of metallic NPs, including TiO_2, Fe_2O_3, HfO_2, SiO_2, Al_2O_3, and CeO_2, showed 0% suppression of O_2 and membrane damage in *S. cerevisiae* at 1000 mg L^{-1} (Garca-Saucedo et al., 2011). "The process of removing or decomposing toxins, pollutants, or undesired substances or products from the environment (such as soil and water) using living organisms, such as microbes, is known as bioremediation. The innate ability of filamentous fungus to break down complex lignin and polysaccharide components of wood and litter on soil surfaces as well as underneath the soil is a prime example in this regard. Additionally, it has been observed that a variety of lignin-degrading white-rot fungus, including *Phanerochaete chrysosporium*, *P. sordid*, and *Trametes hirsuta*, can remove soil pollutants like pentachlorophenol (PCP) and creosote" (Lamar et al. 1994). *P. chrysosporium*, a specific member of the white-rot fungi group, is widely used in the bioremediation of lead-contaminated soil and the breakdown of other xenobiotic chemicals due to its well-known cellulolytic uses (Yildirim et al. 2011). "In order to decontaminate various contaminants, white-rot fungi are also used in bioremediation applications. On the other hand, the lignin-degrading fungi directly interact with nanoparticulate release from the NPs-based pesticide formulations and modify their metabolic activities. Various researchers have concentrated on analyzing the toxicological effects and interactions of metal nanoparticles with white-rot fungi in this context. A recent study showed that white-rot fungi were subject to low-level toxicological effects that were amplified by the direct buildup of nanodiamonds (NDs) in fungus balls due to cell wall breakdown and cytoplasm loss" (Ma et al. 2020). With regard to the mechanism of degradation, the intake of NDs decreased the production of ligninolytic enzymes such as laccase (Lac), manganese peroxidase (MnP), and ligninase in white-rot fungus. *P. chrysosporium* defends itself against reactive chemical species created by light-sensitive Au NP stressors, as demonstrated by Andries et al. (2016). In a nutshell, the study's findings showed that exposure to green, white, yellow, and blue light wavelengths increased the activity of several enzymes, including catalase, superoxide dismutase, lipid peroxidase, and malondialdehyde enzymes.

8.4 Molecular Alterations Brought on by Nanoparticle Stress in Soil Fungus and Bacteria

The transcriptome study's findings showed that genes for protein synthesis, ATP synthesis, and the ferric uptake regulator (Fur) were upregulated, while genes for electron transfer, cellular respiration, and flagellar assembly were downregulated. These findings point to *D. vulgaris* cell mobility inhibition, energy conversion, and iron deprivation. To combat the stress caused by CuO NPs, which was primarily brought on by an excess of ROS, the expression of genes involved in protein synthesis and ATP synthesis was specifically increased. Figure 14.4 illustrates a typical metal-based nanoparticle toxicity mechanism in advantageous soil bacteria and fungi based on the current literature study (Ameen et al., 2021).

9 Conclusion

Because of substantially reduced losses and a higher absorption rate, nanofertilizers used alone or in conjunction with organic materials have the potential to prevent environmental pollution. Furthermore, nanomaterials were discovered to improve fruit antioxidant content, leaf chlorophyll, plant height, root development, and root number. Furthermore, nanoparticle-coated controlled and slow-release fertilizers boost nutrient efficiency, absorb photosynthetically active radiation, and dramatically minimize nutrient waste.

Although nanoparticles have recently been employed in agriculture, researchers continue to face challenges because of their size, toxicity, and responsiveness to environmental variables. Numerous previous research have clearly demonstrated that all nanoparticles are nontoxic by nature and have a favorable influence on plant morphological or physiological properties. Other people, on the other hand, proved its damaging effects, but no one was able to determine the fundamental cause of the

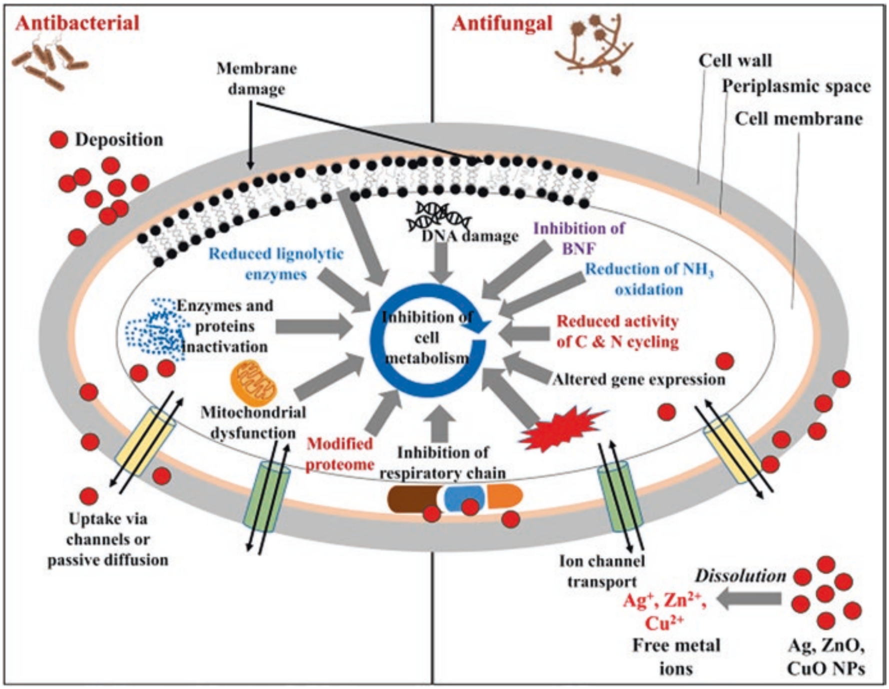

Fig. 14.4 Variable metal-based nanoparticles, including Ag NPs, ZnO NPs, and CuO NPs, as well as their ions (Ag^+, Zn^{2+}, and Cu^{2+}), have harmful effects on beneficial soil bacteria and fungus. (Reprinted from Ameen et al. (2021) "(This article is an open-access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license)"

cellular and genetic toxicity in plants. As a result, agricultural sectors continue to lag in the usage of nanoparticles as nano-biofertilizers and in the development of cutting-edge technology. More in-depth and intricate studies are thus necessary to clarify the process and causes driving this unknown research. Metal nanoparticle disposal solutions in soil agroecosystems are advocated, and safe-by-design strategies for minimizing nanoparticle interaction with beneficial soil bacteria must be developed. This is because metal nanoparticles are both physically and functionally harmful to soil bacteria. Furthermore, the agro-nanotechnology products ought to be created with a particular use in mind.

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Chapter 15
Nanostructure-Based Smart Fertilizers and Their Interaction with Plants

Rishabh Anand Omar, Neetu Talreja, Mohammad Ashfaq, and Divya Chauhan

1 Introduction

Food requirements continuously increased with the growing population and decreasing soil fertility, globally. It is estimated that approximately 9.6 billion population will increase by 2050 and the associated food requirement is also expected to increase by approximately 70–100%. Agriculture occupies a significant portion of the world's resources compared with water and energy consumption. Approximately 6–30% of the total energy consumed is agri-food chain, producing up to 20% of the greenhouse gases. Approximately 70% of the global water is consumed only for food production, which is expected to increase by ~83% by 2050 as per the increasing demand for food (Foley et al., 2011; Gahoi et al., 2021; Rodrigues et al., 2017). As a result of food waste, inefficiencies in food production are exacerbated. Approximately 30–50% of annually produced food, which is approximately 1.3 to 2 billion, is spoiled due to contamination by microbes or due to expiration of packaging which leads to waste in the supply chain (de Oliveira et al., 2014; Gerst et al., 2015; Mueller et al., 2012). The agrochemicals used for the higher production or

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higher yield of crops are avowedly insufficient. A large fraction (~2.5 million tons) of fertilizers and pesticides applied in agriculture are lost due to air loss or unable to reach efficiently to the target site, and approximately 50–70% of nitrogen is lost in a similar manner (DeRosa et al., 2010; Ghormade et al., 2011; Mejias et al., 2021). In a study by Sing et al, it was determined that approximately 90% of Indian soils exhibit low phosphorus and nitrogen content and 50% of soil samples were found with low potassium content. However, these nutrients are essential for plant growth promotion with higher yield and quality (Singh, 2008). When compared with other micronutrients, zinc (Zn) (49%) and boron (B) (33%) are the most deficient micronutrients. However, other micronutrients such as molybdenum (Mo) (13%), iron (Fe) (12%), manganese (Mn) (5%), and copper (Cu) (3%) are required in fewer amounts. A deficiency of these micronutrients decreases soil fertility and affects crop production and yield. A drastic decrease in the fertilizer ratio was recorded in the past several years. In 1970, approximately 27 kg NPK ha^{-1} was required to produce 1 ton of grain, which increase to 109 kg ha^{-1} in 2008. The ideal NPK ratio should be 4:2:1. However, the current ratio is maintained at 6.7:3.1:1 by using nitrogenous compound-enriched fertilizers (Calabi-Floody et al., 2018). The fertilizers are used to achieve the target of 300 million tons of food grains for feeding the 1.4 million people in India by 2025. The productivity and yield are still very low due to numerous reasons such as denitrification, leaching, microbial immobilization, fixation, and runoff (Rumpel et al., 2015). To achieve better crop production and yield, several fertilizers have been used in the past few years, which are mainly classified based on sources, consumption, physical state, and nature of the fertilizers. Based on the source, they were further classified into three types, in which the first one being natural fertilizers, also called traditional or organic fertilizers. They were synthesized from naturally produced substances without adding any chemicals. Fish fertilizer, potassium fertilizer, oil cake fertilizer, etc. were included in this category (Omar et al., 2022b; Randive et al., 2021). The second is chemical fertilizers, also called synthetic, inorganic, or mineral fertilizers. They are synthesized by combining several chemicals with fertilizers, which increases the nitrogen and phosphorous content in the synthesized fertilizers (Omar et al., 2019a). The third is biofertilizers which are also called microbial inoculums or microbial fertilizers. They are mainly biological substances or living organism which produces several nutrients or create a plant-beneficial environment in the soil (Abdulkarim et al., 2019; Osman et al., 2021). Based on the composition, the fertilizers were again classified into four different types, which are (1) direct fertilizers, which were directly absorbed by plants from soil, such as nitrogen and phosphorous; (2) indirect fertilizers, which were mixed into the soil to improve chemical, mechanical, and biological properties of the soil, e.g., lime and gypsum; (3) complete fertilizers, which provide NPK to plant for healthy development; and (4) incomplete fertilizers, which provide only two essential nutrients (mainly ammonia and phosphorous) to the plant (Chen et al., 2018a, b; Lawrencia et al., 2021a). On the basis of the physical state, they were classified into two different categories, which are (a) solid fertilizers, which can be present in various forms, including crystals (ammonium sulfate), prills (urea, diammonium phosphate (DAP)), powder (single superphosphate), briquettes (urea briquettes), granules, and super granules (Holland granules and urea super granules);

and (b) liquid fertilizers, which can be clear (capable to completely dissolve in water) or granular (creates a suspension of fine particles in water). Based on the nature of the fertilizers, they were classified into acidic fertilizers (used in alkaline soil to leave the acid residue) and basic fertilizers (applied in acidic soil to increase the pH of the soil by leaving basic residue). These all fertilizers are efficient for better crop production and yield. However, excessive use of these fertilizers causes a risk of destabilization of the environmental system at a planetary scale. Additionally, excessive use of chemical fertilizers causes accumulation in the soil and leads to several chronic and neurological diseases (Finch et al., 2014; Koli et al., 2019; Machell et al., 2015; Raliya et al., 2018). To overcome this problem, i.e., to prevent the excessive release of fertilizer without affecting the crop yield efficiency, there is a need for controlled-release fertilizers.

Controlled-release fertilizers termed smart fertilizers reveal different concepts and definitions. In some of the studies, smart fertilizers mean the controlled release of plant nutrients. However, some literature explains the longer/slow release of nutrients in comparison to other fertilizers (Bernardo et al., 2018; Giroto et al., 2018; Yamamoto et al., 2016). In 2016, Lu et al demonstrated the smart fertilizer as multifunctional, which was capable to reduce environmental pollution by reducing the loss of fertilizer and retaining a huge amount of water, post-fertilization (Lü et al., 2016). An ideal fertilizer should sustain numerous properties such as the release of nutrients should be matched to the crop's needs, input cost recovery maximization to maximize return on investment, and should be environmentally friendly with minimal adverse effects on soil, water, and the atmosphere (Chivenge et al., 2021; Sharma & Bali, 2018; Udvardi et al., 2021). As per the reported literature, smart fertilizers exhibit all these properties, confirming that smart fertilizers are being ideal. Therefore, the use of smart fertilizer can fulfill future food requirements without affecting soil properties or human health. Aside from the other advantages, they need to be applied to the soil in a relatively smaller quantity, reducing transportation costs and enhancing the ease of application (Udvardi et al., 2021). Like all fertilizers, smart fertilizers have limitations and disadvantages, as well as certain advantages. Figure 15.1 shows the schematic illustration of nanotechnology-based fertilizers and their effects on crops. In this chapter, we discussed the impact and application of smart fertilizers for sustainable agriculture. The later section briefly describes the types, current status, and synthesis methods of smart fertilizers. The advantage of smart fertilizers in comparison to other fertilizers and their limitations are briefly discussed. Lastly, their interaction with plants, existing challenges, and prospects of the use of smart fertilizers are outlined.

2 Current Status of the Smart Fertilizers

The new reforms in the fertilizer sector have been implanted since 2014. The new reforms include the neem coating of urea, which reduces fertilizer diversion and gas pooling, which should improve the efficiency of urea production domestically. Both

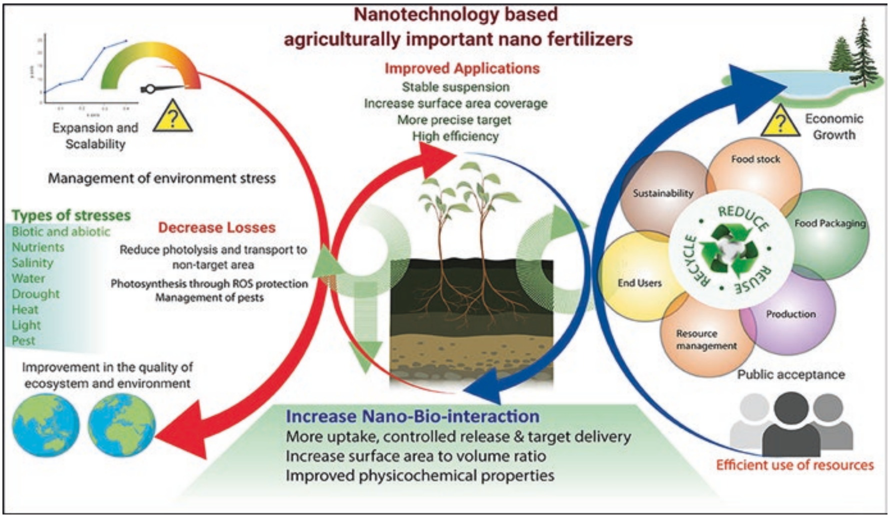

Fig. 15.1 A schematic illustration of the nanotechnology-based fertilizers and their effects on crops. The image was reproduced with permission (Reprinted from Mittal et al., 2020) "(This article is an open-access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license)"

of these things help farmers to obtain economically efficient fertilizer (Ghafoor & Habib-Ur-Rahman, 2021). In 2015–2016, the government of India budgeted ~73000 crores (approximately 0.5% of GDP) on fertilizers research. Approximately 70% of this budget is used in urea to make low-cost farming. Among all the fertilizers, urea is the most produced (~86%), most consumed (~74%), and most imported (~52%) fertilizer in India. Presently, in the global market, some smart fertilizers have been launched and used in farming applications. They are divided into two types, smart micronutrients and smart phosphate, which are available for application in pulses, oilseeds, cereals, grains, fruits, vegetables, commercial crops, etc. and available in several countries. In 2028, the global smart fertilizer market is expected to account for approximately 0.81 million USD. An environment-friendly method for synthesizing smart fertilizer is important to provide nutrient supply during crop growth, which act as nutrient reservoirs to provide nutrient supply continuously throughout the growing season. In general, these products are used to provide phosphates and micronutrients in smart form. Smart fertilizers allow the plant to control the doses of nutrients it receives, which is extremely beneficial for farmers since crops require different amounts of nutrition at different stages of growth (Ali et al., 2021; Lü et al., 2016; Naher et al., 2019; Umesha et al., 2018). Smart fertilizers' market growth is attributed primarily to a decline in arable land per capita and an increase in food demand worldwide. Furthermore, the market is expected to grow due to increased yields because plants require different quantities of nutrients at different stages of their lives. Additionally, the market's growth is boosted by the development of environment-friendly methods of improving yield (Lipper et al., 2014). Despite this, regions with lower awareness of smart agriculture and smart fertilizers hinder the growth of the smart fertilizers market (Garcia-Franco et al., 2018; Mukherjee & Batabyal, 2021; Paustian et al., 2016).

Developments in fertilizers, especially in developing economies, will create lucrative opportunities for the growth of the smart fertilizers market. On the other hand, COVID-19 is projected to disrupt the supply chain in the forecast period, which could pose a challenge to the market. The market report of smart fertilizers provides details of new trade regulations, recent developments, import–export analysis, value chain optimization, production analysis, market share, analyses of opportunities for emerging revenue of localized and domestic market players, market regulations change, growth analysis of the market, market size, category wise market growth, application dominance and niches, approval of products, launches of products, expansions in geographic ways, innovations, and technologies in the market (Azeem et al., 2014; Calabi-Floody et al., 2018; Kareem et al., 2021; Mikula et al., 2020; Rajan et al., 2021).

3 Synthesis of Nanostructured (NS) Fertilizers

There are mainly two types of processes involved in the synthesis of NS-based smart fertilizers, which are top-down synthesis and bottom-up synthesis.

3.1 Top-Down Synthesis of NS Fertilizers

The synthesis of nanostructure requires the breakdown of large materials into the nanoscale. A variety of processes are used in this approach, including grinding, milling, and physical and chemical deposition of vapors. Various NMs such as carbon beads, carbon-NPs, carbon nanofibers, carbon nanotubes, graphene, and spherical magnate were synthesized by this method. For the synthesis of carbon nanofibers (CNFs) and carbon nanotubes (CNTs), the chemical vapor deposition (CVD) process is widely used (Ashfaq et al., 2018; Sankararamakrishnan et al., 2016; Talreja et al., 2014, 2016).

CVD is widely used in the synthesis of a variety of NMs. Some of the applications of the CVD process are (i) the formation of bulky and pure powder materials, (ii) thin-film coting on a surface, and (iii) composite materials fabrication. The CVD process involves the use of several gases (as a carbon source) and surface reactions (Ashfaq et al., 2022; Omar et al., 2020). In general, the nanomaterial synthesis process is dependent on several parameters such as material composition, the temperature of the substrate, the pressure of the reactor, and the chemistry of the gaseous phase.

3.2 Bottom-Up Synthesis of NS Fertilizers

The bottom-up synthesis approach is approximately opposite to the top-down synthesis; it involves the synthesis of NMs from simple substances. The bottom-up process covers several strategies such as sol–gel, solvothermal, hydrothermal, soft templating, hard templating, reverse-micelle, and CVD process. As a result of the bottom-up approach, the material components with self-assembling processes that produce nanostructures have many advantages. NP synthesis from colloidal solutions and synthesis of quantum dots by epitaxial growth are examples of bottom-up synthesis approaches. The green synthesis process that involves the formation of NPs from plant extract or plant parts (fruit, pulp, flower, etc) also comes under the bottom-up synthesis approach (Baig et al., 2021; Cao et al., 2016; Wan et al., 2005).

4 Smart Fertilizers

Smart fertilizers are a kind of fertilizers that can release nutrients under certain control. They are produced using some nanomaterials (NMs), biodegradable material, microorganisms, or a combination of all materials. Based on their activity, smart fertilizers are divided into two groups: (1) robust release and (2) controlled-release fertilizers. A brief description of slow- and controlled-release fertilizers is provided in the next section.

4.1 Robust-Release Fertilizers

Nowadays, the most commonly used fertilizers are quick/robust-release fertilizers, which are released readily to the soil if applied properly. This kind of fertilizer is efficient for side-dressing, pre-plant applications, hydroponics, or fertigation in the farming of many crops including vegetables. They are highly effective if leaching or accumulation of high amounts of nutrients is non-effective to the soil health or can be effective if accumulation does not occur due to several circumstances. However, robust-release fertilizers are the less expensive fertilizers for crop production under favorable conditions (Burnett et al., 2016; Shrivastava & Kumar, 2015). They are available to plant at a consistent amount. However, the robust release of the fertilizers within the soil uses soil moisture. Therefore, they create a requirement for side-dressing due to the need for the replacement of nutrients as enhancement in plant growth (Möller et al., 2018). In this aspect, slow-/controlled-release fertilizers might be a promising strategy that resolves such associated issues.

4.2 Controlled-Release Fertilizers

The slow- or controlled-release fertilizers hold the nutrients in a form that delayed the plant uptake or is used post-application and/or available to the plant comparatively longer than quick-release fertilizers such as ammonium chloride, ammonium phosphate, nitrate, ammonium, urea, etc. However, none of experimental proof regarding this is reported yet. The delayed release of nutrients can be achieved by several other mechanisms including coating of a semipermeable material to control the solubility of nutrients into the water, occultation, chemicals, protein materials, and slow hydrolysis of low-molecular-weight water-soluble compounds (Beig et al., 2020; Gil-Ortiz et al., 2020; Incrocci et al., 2020; Kontárová et al., 2022; Lawrencia, et al., 2021a; Trinh & KuShaari, 2016). These kinds of fertilizers exhibit the property of slower release nutrients and provide radial availability to the plants. For example, the nitrogen products utilized by the microbe to provide accessibility to the plants are a kind of slow-release fertilizers. Some other slow-release fertilizers such as N-SURE are commercially available. The nutrient-release capability of slow-release fertilizers is completely dependent on the nature of the soil and climate. The slow-release fertilizers release the nutrients gradually in organic or inorganic form. The nutrient available in the slow-release fertilizers is inaccessible to the plants (Khan et al., 2021). However, as per the requirement of plants and soil, they started to release and make it available to the plants. Based on the source, slow-release fertilizers are two types, which are natural and artificial slow-release fertilizers (Gil-Ortiz et al., 2020; Kottegoda et al., 2017).

4.2.1 Natural Controlled-Release Fertilizers

These are mainly derived from plant manures such as green leaves, shoots, or cover crops and animal manures such as chicken, cow, poultry, and compost. They are organic and broken down into simpler or soluble forms by microbial activity. Generally, organic fertilizer takes a lot of time for being available to the plant. Therefore, they may not be available at the time of the requirement of the plant. The availability of natural slow-release fertilizers depends on the soil's microbial activity, which depends on soil moisture, temperature, and other physical parameters. These kinds of fertilizers contain both macro (N, P, K, etc.) and micro (Mn, Fe, Cu, etc.). However, nutrients' concentration in these fertilizers is relatively lower than the synthetic controlled-release fertilizers (Alori et al., 2017; Bansiwal et al., 2006; Chhowalla, 2017; Jacoby et al., 2017; Lü et al., 2016) (Fig. 15.2).

4.2.2 Synthetic Controlled-Release Fertilizers

These kinds of fertilizers are moderately soluble in water. The bioavailability of these fertilizers depends on the physical properties of the soil such as temperature and moisture content in the soil. They are prepared mainly in pellet or spike form. The

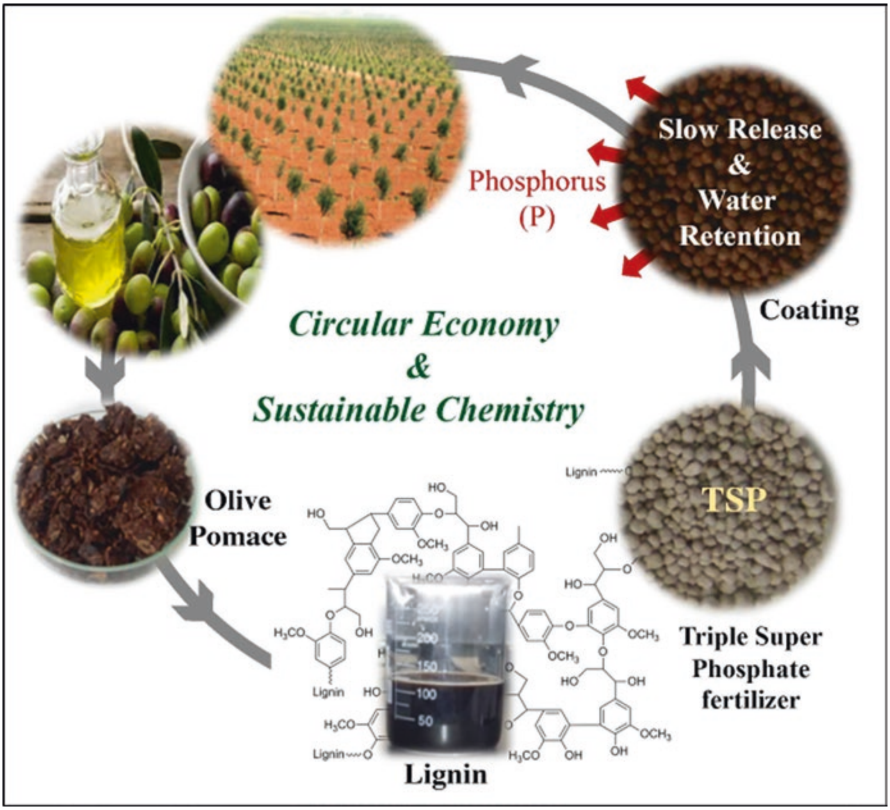

Fig. 15.2 A schematic representation of smart-coated P fertilizer for sustainable agriculture. The image was taken with permission (Reprinted from Fertahi et al., 2019) "(This article is an open-access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license)"

approximate nutrient-releasing time in synthetic slow-release fertilizers varies between 20 days and 18 months, which is dependent on the soil moisture content and temperature. Therefore, they are required in a very less amount. Sometimes due to unfavorable weather conditions, the release of nutrients is not occurring properly as per the requirements of plants. In comparison to natural slow-release fertilizers, synthetic slow-release fertilizers are rich in a single type of nutrient, such as N-SURE (a synthetic slow-release fertilizer), containing approximately 28% nitrogen (Bortolin et al., 2013; Chakraborty et al., 2023; da Rosa & dos Santos Rocha, 2013; Rashidzadeh & Olad, 2014). These fertilizers are inorganic or inorganic-material-coated or encapsulated materials having control over the release time, release pattern, and release rate of the plant nutrients. The control of release in these kinds of fertilizers is carried out by several techniques, such as coating with semipermeable material, a protein material, occultation, or other chemicals, slowing down the hydrolysis of low molecular weight water-soluble compounds. Additionally, the control-release fertilizers release their nutrients in a pattern that synchronizes with crop nutritional needs. Some examples of controlled-release fertilizers are the coating of WSP fertilizers with water-insoluble polymers (MAP, DAP, TSP - DAP-Star by Hi Fert.), polymer-coated urea, super granules of urea containing potassium and phosphorus, and ammonium polyphosphates (González et al., 2015; Jintakanon et al., 2008; Lawrencia et al., 2021b). From these main categories, some main classes of smart fertilizers are as follows:

Synthetic Polymers

Synthetic polymers are widely used in agriculture for the development of fertilizers. The smart delivery of various agrochemicals is carried out using some smart polymeric material. Various encapsulated water-soluble fertilizers are synthesized using a wide range of petroleum-based polymers, such as polyurethane, polyvinyl chloride, polyacrylonitrile, polysulfone, and polystyrene (Rivas et al., 2018; Tomaszewska & Jarosiewicz, 2002, 2006). These are biodegradable polymers; therefore, they are environmentally safe. Also, their physical properties influence the release of nutrients. Based on water vapor permeability, these fertilizers are subdivided into two categories. The first category includes polylactic acids, bipoles, and polycaprolactone, and the second category includes modified polysaccharides such as agar, alginate, and starch. These polymeric materials support the nutrient release at the time of the requirement of plants. Therefore, the efficiency of the fertilizers improved with minimal loss of nutrients and a reduction in the soil pollution related to the excessive release of nutrients (Khanra et al., 2022; Lü et al., 2016; Mohamed Salem et al., 2023; Naseri-Nosar et al., 2017; Skopinska-Wisniewska et al., 2021; Yuan et al., 2022a).

Biochar (BC)

BC is a carbonaceous material produced from biological waste. The residue of crops and byproducts of wood, paper, and pulp industries can be used as feedstock material for energy-generating pyrolysis systems. Byproducts of these systems produce BC or pyrogenic carbon. Generally, BC is synthesized using the banana stalk and corncob pomelo peel. BC has an excellent property of holding ammonium ions due to the presence of the keto or carbonyl group due to the synthesis of the material at high temperatures (~200 °C). The material can be used as fertilizer in crops for the slow release of nitrogen for the plants. Additionally, BC has a higher water-holding capacity (Barthod et al., 2016; Cai et al., 2016; Gao et al., 2022; He et al., 2022; Kocsis et al., 2022; Liu et al., 2019; Lorenz & Lal, 2014; Panwar et al., 2019; Saletnik et al., 2019). Figure 15.3 shows the graphical representation of the BC synthesis and its application in agriculture. Therefore, the use of BC for the synthesis of smart fertilizer could be beneficial to crops as a carrier material for plant nutrients and enhance soil fertility and properties due to some unique characteristics of BC itself.

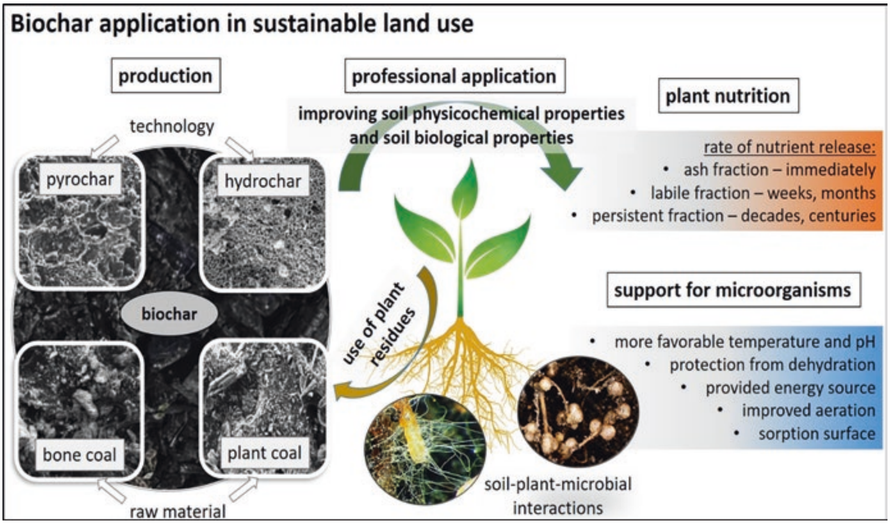

Fig. 15.3 Graphical representation of BC and their agricultural applications. The image was taken with permission. (Reprinted from Kocsis et al., 2022) "(This article is an open-access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license)"

The residuals of crops after burning can be used for the synthesis of smart fertilizers. They contain cellulose, hemicellulose, and lignin which provide mechanical strength to fertilizers. For example, wheat straw contains carboxyl, amino, ether, hydroxyl, and phosphate groups that help to formulate slow-release fertilizers with enhanced activity due to the adsorption nature of the material by these functional groups (Calabi-Floody et al., 2018; Tayade et al., 2022; Venugopalan et al., 2022). Generally, wheat straw is used for the formulation of nitrogen- and boron-doped smart fertilizers with higher water-holding capacity. Another material is cellulose, achieved from the residuals of the crops, used as a biocarrier to carry the bacterial cells with the additional property of fungal pathogen suppression of antifungal activity (Ahmed et al., 2021; Lateef et al., 2019; Mühlbachová et al., 2021). Same to cellulose, lignocellulose and compost are rapidly degrading materials on applying to the soil. Therefore, the residuals of agricultural or crops can be used alone or as a mixture with clay or BC (to provide stability) for the formulation of smart fertilizers (Bauli et al., 2021).

4.3 Nanofertilizers

These are materials at the nanoscale level with a size range of 1–100 nm. The nanofertilizers are divided into three main classes, which are (1) nanoscale fertilizers, which are mainly nanoparticles (NPs) synthesized by various methods; (2)

nanoscale additives, which are the bulk products with nanoscale additives; and (3) nanoscale coatings, also called host materials are the materials enriched with NPs. As per recent research, slow-release materials are the best alternative for quick-soluble fertilizers (Omar et al., 2019a). In nanofertilizers, the plant growth-promoting nutrients are encapsulated in NMs such as nanofibers, nanotubes, or nanorods with protective polymeric coatings (Omar et al., 2022a). The nutrient releases from these fertilizers at a very slow rate with plant growth and reduces nutrient losses. The nanoparticles used for the formulation of smart fertilizers were obtained from various synthetic or natural resources such as carbon materials, soils, plants, and microorganisms. These nanofertilizers are required in very fewer amounts. The development of smart fertilizers is mainly focused on cost-effective, slow-release fertilizers; therefore, the use of nanomaterial with some other compounds, such as clay, could be cost-effective and efficient for plant growth (Elemike et al., 2019a; Joseph et al., 2013). Using nanodevices or additives (such as aptamers, urease enzymes, nanotubes, double hydroxide NC, nanosilica particle, and nano-sized titanium oxide) with nanofertilizers, nutrient release can be synchronized with plant requirements.

5 Nanostructure-Based Smart Fertilizers

The use of NMs as smart fertilizers increases the efficiency of nutrients and reduces the environmental adverse effects caused due to other conventional fertilizers. Based on the size, morphology, and chemical properties, nanostructure-based smart fertilizers are divided into four main classes which are polymeric NC, CB-NC, metal-NPs, and hybrid-NC (Chauhan et al., 2023; Irsad et al., 2022a, b; Nongbet & Mishra, 2022; Omar, 2019b; Sasidharan et al., 2022).

5.1 Polymeric NC-Based Smart Fertilizers

Polymeric NC includes nanocapsules, nanospheres, and various other polymeric NPs. In the past few years, the NC of polymers played a key role in various fields including plant growth promotion, environmental remediation, sensors, medicine, electronics, and pollution control. The extensive application of polymeric NC is in adhesive products, coatings, and paints. The recent applications of polymeric NC were reported in several biological applications such as bioimaging, drug delivery, diagnosis of diseases, antimicrobial compounds, and agriculture. The polymer NC exhibits some unique physicochemical properties; therefore, it can be used in a variety of fields (Matei et al., 2022; Omar & Jain, 2023; Pradhan et al., 2013, 2019; Romero-Fierro et al., 2022; Sharma et al., 2021). For the application of polymeric NC, an ideal polymer should be biodegradable and placeable in agriculture. For example, chitosan is a biodegradable polymer that also exhibits the property of antibacterial and sorbent nature (Kashyap et al., 2015). These properties make it a promising material for agricultural applications. In the past study, NPK-loaded chitosan polymer was synthesized by polymerization of methacrylic acid. In comparison to other fertilizers, the loading of NPK was determined much higher in the chitosan-based NC, which enhances the plant growth and crop yield in wheat crops. The authors of the study have confirmed by TEM imaging that NC was translocated to the plant shoot through the xylem (Abdel-Aziz et al., 2016). Various other polymeric NC showed plant growth promotion. However, their mechanism is unknown. It was assumed that the growth was enhanced due to the controlled release of NPK from the polymeric NC (Guo et al., 2018; Mohammad et al., 2019; Wypij et al., 2023; Yu et al., 2021).

5.2 CB-NC-Based Smart Fertilizers

In recent times, carbon-based nanostructures (CB-NSs) such as carbon nanotubes (CNTs), carbon nanofibers (CNFs), diamond, fullerenes, and graphite received much attention in various fields, including agriculture, nanosorbents, nanocapsulation, environmental remediation, supercapacitor, fuel cells, battery separator, optoelectronic sensors, solar cells, crop improvement, and plant protection (Afreen et al., 2018). The CB-NSs exhibit some unique properties, such as electric, optical, and mechanical strength, which make them capable to be used in various applications (Afreen et al., 2022a, b; Ashfaq et al., 2019; Omar, Talreja, et al., 2022b). In agriculture, CB-NC-based smart fertilizers have fended applicability due to several reasons such as the toxic nature of CB-NC at the genetic, cellular, and physiological level, research on the genetic and nutritional effects of carbon-based nanomaterial treatments is limited, and the leaching of metal present in CB-NC into media and their stability is also not clear (Elemike et al., 2019b; Mukherjee et al., 2016). A study by Ashfaq et al., 2017 showed copper (Cu)-loaded carbon nanofibers slowly release Cu-NPs into the water in comparison to Cu loaded on activated carbon fibers (ACFs). The NC enhances the germination rate, root and shoot length, water uptake capacity, chlorophyll content, and protein content. The microscopic images captured by the authors confirm the translocation of carbon nanofibers to the plant shoot. The authors concluded that the field application of such material can be done by encapsulation of the material into a biodegradable polymer of other carrier materials (Ashfaq et al., 2017). Figure 15.4 shows the synthesis of Cu-CNFs for micronutrient delivery and their translocation ability within the plants. Gupta et al. synthesized Fe-CNFs using the CVD process for the delivery of acylated homoserine lactones (AHLs) within the plants. The data indicated that the prepared Fe-CNFs-AHLs-based composite effectively translocates within the plants from root to shoot to leaf. Moreover, Fe-CNFs-AHLs-based composite significantly improved plant growth even under stress conditions (Gupta et al., 2019). In another study of the same group, the synthesis of rhizobacteria incorporated Fe-CNFs-AHLs-based composite for growth and

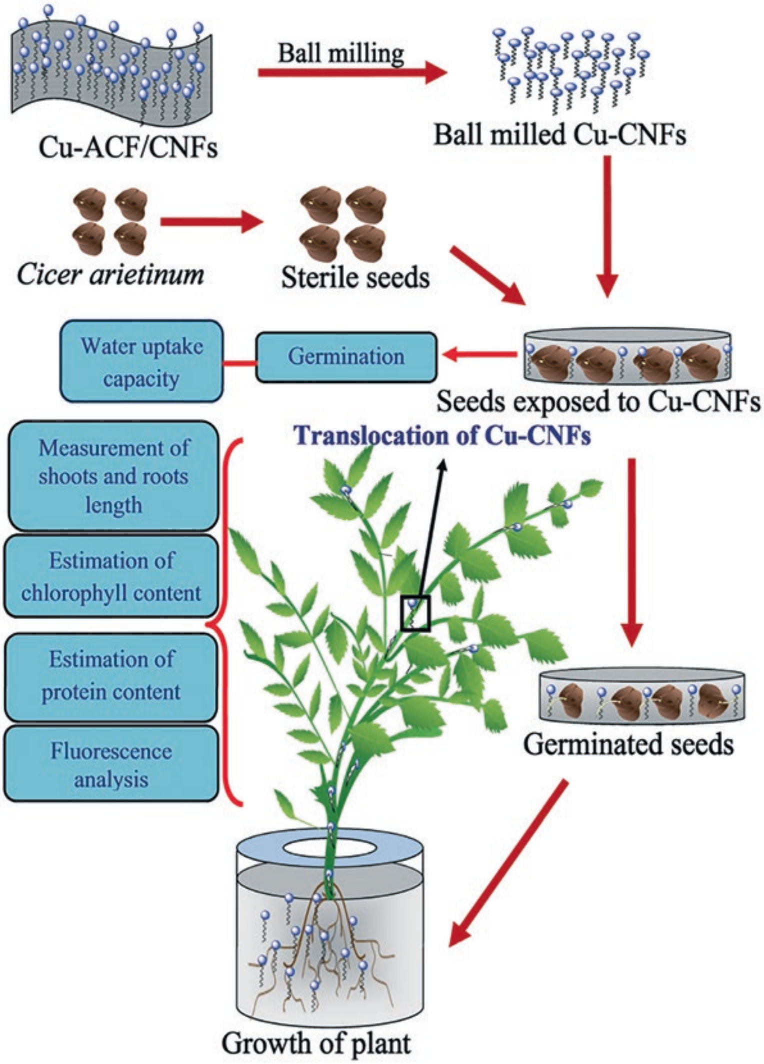

Fig. 15.4 Cu-CNFs based micronutrient delivery within the plants. The image was taken with permission. (Reprinted from Ashfaq et al., 2017) "(This article is an open-access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license)"

plant protection. The data indicate that the prepared composite effectively improves plant growth and protects against the pathogen (Gahoi et al., 2021). In general, the aforementioned literature suggested that the CB-NMs effectively enhanced the yield of crops and protect against pathogens. Interestingly, CNTs and CNFs show translocation ability within the plant that might be aided advantages for the delivery of biomolecules and micronutrients.

5.3 Metal-NP-Based Smart Fertilizers

NPs of several metals have been extensively used in engineering and biological fields in the past few years. Metal-NPs have the characteristics of surface plasmon resonance, which are entirely made up of their precursor. Some of the metal-NPs, such as Au, Ag, Zn, Fe, Cu, and minerals, have a broad band of adsorption spectrum (Chauhan et al., 2020, 2022; Irsad et al., 2020) due to advanced optical properties; the metal-NPs can be synthesized in controlled surface properties, such as size and shape (Azam et al., 2022; Bahmanzadegan et al., 2022; Kulkarni & Muddapur, 2014; Lalarukh et al., 2022; Marinescu et al., 2020; Shalaby et al., 2021). Metal-NPs are synthesized by various methods; in chemical methods, top-down and bottom-up syntheses are the main methods; however, recently, green synthesis of metal-NPs through plant extract has also been of keen interest. In agriculture, metal-NPs can bind with pesticides, agrochemicals, and fertilizers. There they enhance the efficiency of fertilizers due to their dual effect on crops, i.e., the role of fertilizers and metal-NPs (Elsayed et al., 2022; Giannousi et al., 2013; Lu et al., 2020; Ndaba et al., 2022; Noufal et al., 2021; Rajput & Minkina, 2021; Rao & Shekhawat, 2014; Rizwan et al., 2019; Rossi et al., 2019; Spielman-Sun et al., 2019; Vanti et al., 2019; Zhu et al., 2012). Metal-NPs-based smart fertilizers can enhance seed germination and plant growth. The impact of NPs-based smart fertilizers mainly depends on composition, size, surface charge, susceptibility to plants, and concentration of the NPs.

5.4 Hybrid NC-Based Smart Fertilizers

These are the inorganic/organic conjugates that bear unique properties, which make them applicable in various fields including plant growth promotion, bio-imaging, sensors, nanomedicine, drug delivery, and agriculture. A mixture of metal-NPs, polymers, and carbon-based material could be used for the formulation of hybrid NC (Guha et al., 2022; Qi et al., 2013). Kumar et al used Cu-Zn-loaded carbon nanofiber in a PVA–starch polymeric film. Application of the material in chickpeas confirms that the polymeric composition of carbon nanofibers regresses the quick release of Cu and Zn-NPs into the soil and enhances plant growth. In both the studies, the process of releasing/translocation nutrients is slow, leading to enhance the growth of plants (Kumar et al., 2018). The hybrid NC-based smart fertilizer exhibit characteristics of all NC, used as precursors. The hybrid NC is more efficient than the other NC due to its high selectivity, surface area, stability, and amenability for surface modifications. In agriculture, they release nutrients at a slow rate. Therefore, the nutrients last for the long term, and the growth of the plant as well as crop yield gets enhanced. Additionally, they are biocompatible materials and thus can be applied in the agricultural and biomedical fields as well (Ashfaq et al., 2014; Biały et al., 2022; Seddiqi et al., 2021). Instead of these NC, the nanoclays, mesoporous silica, and hydroxyapatite have taken a keen interest among the researchers in this field.

Table 15.1 summarizes the different fertilizers/nanofertilizers and their effect on plant growth. The data suggested that the fertilizers/nanofertilizers improve the development and growth of the plant by improving the thickness of the xylem, phloem, stem diameter, chlorophyll, protein content, and biomass. Moreover, these fertilizers/nanofertilizers augment the growth even under biotic and abiotic stress conditions. In general, fertilizers/nanofertilizers significantly improve plant growth, the yield of crops, and nutritional values and protect against pathogens even under stress conditions.

6 Advantages of Smart Fertilizers in Crop Production

Farming in a smart way could include bioinformatics in different sectors of agriculture. Smart fertilizers have multiple impacts on crop production and yield due to their slow-releasing or controlled-releasing nature. Due to this controlled/slow release, the plants' nutrients last for the long term and are available for the plants as per their requirements (El-Saadony et al., 2021; Nongbet et al., 2022). Some of the main advantages of smart fertilizers in agriculture are: (i) it reduces the excess accumulation of fertilizers in the soil; (ii) as per the requirements of plants, a balanced mixture of nutrients can be provided in the case of smart fertilizers; (iii) the nutrient present in the substrate does not leech into the soil, and therefore, the plants can utilize complete amount, available in the smart fertilizers; (iv) it enhances nutrient-use efficiency—leaching and runoff are reduced, ammonia is evaporated more slowly, and nutrients are used more efficiently; (v) due to slow release, the accumulation of nutrients leads to reduce the pollution; (vi) the slower rate of releasing nutrients leads to complete utilization on nutrients by plants; (vii) the smart fertilizers are not required to apply frequently, and therefore, it reduces the labor capital; (viii) it reduces the risk factors associated with the fertilizers, such as eutrophication, leaf burning, and water contaminations; (ix) it eliminates the damage of crops by avoiding the application of fertilizer in late growth stage and also reduces the labor cost and frequent applications; and (x) sometimes, it lower the pH of alkaline soil to make it normal for more availability of some of the nutrients to plants. For example, sulfur-coated urea enhances the acidity of soil due to the role of both urea and sulfur in reducing the pH of soil. Accordingly, it could make the iron in soluble form more bioavailable to the plants, enhancing the growth of plants such as sweet potatoes, blueberries, and potatoes. Also, sulfur is an essential macronutrient to the plant (Chien et al., 2009; Mastronardi et al., 2015; Mustafa et al., 2022a, b; Neina, 2019; Yuan et al., 2022b). Additionally, nanostructured-based smart fertilizers have some other benefits, such as they have higher solubility and high dispersion efficiency of micronutrients in the soil. A high amount of nutrients are present in the oxide form of NS fertilizers. Therefore, it can be converted into a soluble form by maintaining its size, shape, and solubility. Therefore, increasing the solubility of

Table 15.1 Different fertilizers/nanofertilizers and their effect on plant growth

S. no.	Nanofertilizer	Dose	Plant	Effect	Reference
1.	Hydroxyapatite	0.1 to 1 mg L^{-1}	*Rosmarinus officinalis L.*	Enhance xylem and phloem thickness and stem diameter through nanofertilizer	Elsayed et al. (2022)
2.	Fe_3O_4-urea	1:1, 1:2, and 1:3 ratio	*Oryza sativa L.*	Enhance crop yield	Guha et al. (2022)
3.	ZnO-NPs	0 to 80 mg L^{-1}	*Triticum aestivum L.*	Enhance plant growth under salinity conditions	Lalarukh et al. (2022)
4.	Nanoselenium	25 mg L^{-1}	*Cucumis sativus L.*	Promote growth at thermal and salinity conditions	Shalaby et al. (2021)
5.	ZnO-NPs	10 to 40 mg L^{-1}	*Zea mays L.*	Enhance chlorophyll and antioxidant activity	Azam et al. (2022)
6.	Nano-ZnO, FeO, and MgO	25 to 100 mg L^{-1}	*Caesalpinia bonducella*	Increase plant growth and nutrient and chlorophyll content	Bahmanzadegan et al. (2022)
7.	ZnO-NPs	15 mg L^{-1}	*Coffea arabica*	Enhance photosynthesis and biomass production	Rossi et al. (2019)
8.	Nano-ZnO	0 to 15 mg L^{-1}	*Zea mays*	Enhance phosphorous and Zn in shoots and seeds of the plant	Noufal et al. (2021)
9.	TiO_2 and SiO_2	20 to 30 mg L^{-1}	*Oryza sativa*	Enhance growth at heavy metal contamination	Rizwan et al. (2019)
10.	Ag-NPs	9 to 30 μg L^{-1}	*Vigna unguiculata*	Plant defense and plant growth promotion	Vanti et al. (2019)
11.	CuO nanoparticles	150 to 340 μg L^{-1}	*Solanum lycopersicum*	Pathogen control in plants	Giannousi et al. (2013)
12.	Zn and B-NPs	0 to 120 mg L^{-1}	*Punica granatum*	Enhance yield of pomegranate fruit	Davarpanah et al. (2016)
13.	Cu-CNF/ACF	10–500 μg mL^{-1}	*Cicer arietinum*	Increase plant growth and biomass	Ashfaq et al. (2017)
14.	Fe-CNF/ACF	75 mg L^{-1}	*Cicer arietinum*	Enhance chlorophyll content and biomass	Gupta et al. (2019)
15.	Fe-CNF/AB+ES	1 g kg^{-1}	*Cicer arietinum and Triticum aestivum*	Increase chlorophyll, protein content, biomass, and plant growth	Gahoi et al. (2021)

micronutrients and reducing their fixation in the soil can enhance their bioavailability (Basit et al., 2022; Chalk et al., 2015). The NS-based smart fertilizers enhance the nutrient use efficiency and uptake ratio due to smaller size due to smaller size, which can directly penetrate into roots and shoots of the plants. Fertilizers with nanoencapsulation offer a precise and controlled release of nutrients over an extended period and enhance nutrient use efficiency. A nanomaterial coating on fertilizer particles holds the material more firmly due to its higher surface tension than conventional surfaces. This helps in controlling the release of the material. For a controlled release of nutrients over a prolonged period, slow or controlled nanostructured formulations are ideal by encapsulating nutrients in nanofertilizers, the nutrient loss rate is greatly reduced (Basavegowda & Baek, 2021; Naz & Sulaiman, 2016; Vejan et al., 2021).

7 Interaction of Smart Fertilizers

Smart fertilizers involve many aspects of interaction with plants, which include methods by which fertilizers reach environments where plants are eventually exposed to them, environmental effect involved in the movement of fertilizers to different parts of the plants, physicochemical properties of the fertilizers, uptake and transport of fertilizers, and effect of fertilizers in the living system. These aspects are essentially needed to know for understanding the interaction and impact of smart fertilizers in plant systems (Liu & Lal, 2015; Zulfiqar et al., 2019). The use of smart fertilizers may represent a keen source of plant exposure to nutrients. In order to meet the demand for food in an ever-growing population, more efficient mineral fertilizers are a necessary approach because of the limited amount of arable lands and scarce water resources. For this reason, smart fertilizers are needed to evaluate and develop. In NS-based smart fertilizers, the NPs are the best alternative for pest control and nanofertilizers applied to the soil reach the different parts of the plants and provide benefits to the plants (Cota-Ruiz et al., 2020; Timilsena et al., 2015; Yusefi-Tanha et al., 2020). The NPs can have positive or negative effects on plants as Ag-NPs have pathogen control properties in *Bipolaris sorokiniana*, *Fusarium culmorum*, *Scalerotinia sclerotiorum*, and *Rhizoctonia solani*. On the other hand, $Cu(OH)_2$-NPs may cause an alteration of metabolism in lettuce and spinach leaves (Yan & Chen, 2019; Zhang et al., 2019).

The NS-based smart fertilizers maintain soil fertility leading to improve crop quality and productivity. This kind of fertilizers mainly enters the plants with water uptake through the xylem and reaches the different locations of plants. There, they are intact with plants and provide benefits to the crop. The transportation of fertilizers is mainly done by a symplastic pathway. Fertilizers must cross the plasma membrane and enter the symplastic pathway (Ashfaq et al., 2017; Chauhan et al., 2023; Rico et al., 2011; Schwab et al., 2016). There are many routes for entering fertilizers into the symplastic pathway of plants. Some of them are as follows: (i)

Some nanostructured smart fertilizers develop pores by disrupting the plasma membrane for crossing the plasma membrane, reaching directly to the cytosol of the plant cells without vesicle formation (Karny et al., 2018; Pérez-de-Luque, 2017; Serag et al., 2011; Wong et al., 2016). (ii) Another route is endocytosis, in which the nanoparticle enters through the plasma membrane by forming a vesicle, which can travel to the different components of the cell (Etxeberria et al., 2006). (iii) The fertilizers also enter through plasmodesmata (specialized structures in plant cells for intracellular transportation). This involves the fertilizers already present in the symplastic pathway of plants. However, the mechanism is really important in plants for translocation in the phloem (Roberts & Oparka, 2003; Zhai et al., 2014). (iv) Some of the fertilizers directly bind with carrier proteins that are similar to the plasma membrane and help in the uptake and internalization to the plant cells (Nel et al., 2009). Mainly, aquaporins involve in the transportation of fertilizers. However, aquaporins have small pore sizes (2.8–3.4 A^{O}), creating difficulties in channels for fertilizers penetration until the pore size increases or is modified (Wu & Beitz, 2007). (v) Ion channeling is also a route for the internalization of fertilizers to the plant cells. However, the size of ion channels is approximately 1 nm, which reduces the transportation of most of the fertilizers (Pérez-de-Luque, 2017; Schwabe et al., 2015). Figure 15.5 shows the translocation of NPs within the plants.

7.1 Interaction with Soil

The nanostructured-based smart fertilizers spread to the soil and enter the plants to interact with different parts of the plants. NMs have interesting properties to spread into the environment, mainly in soil (Chen, 2018). The interaction of NMs with soil changes the physicochemical properties, such as organic content, pH, water content, alkalinity, and biological properties such as microbial community, and microbial activities of soil near plants. This interaction leads to performing different processes including heteroaggregation, homoaggregation, and ionic species generation due to dissolution and sorption in the biological process. Some of the NPs, such as aluminum, have deep mobility in soil (Siddiqi & Husen, 2017). Sequestration and adsorption are the main processes involved in the movement of NPs in soil. The roots of plants uptake the nanofertilizers with water, through the xylem (Allen et al., 2017; de la Rosa et al., 2021; Dimkpa, 2018; Siddiqi & Husen, 2017).

7.2 Interaction with Plants

The impact of smart fertilizers represents a central ecosystem to fulfill the world's food demand. In this context, nanofertilizers including NPs are the better alternative to enhance crop production. The interaction of nanofertilizers with plants through

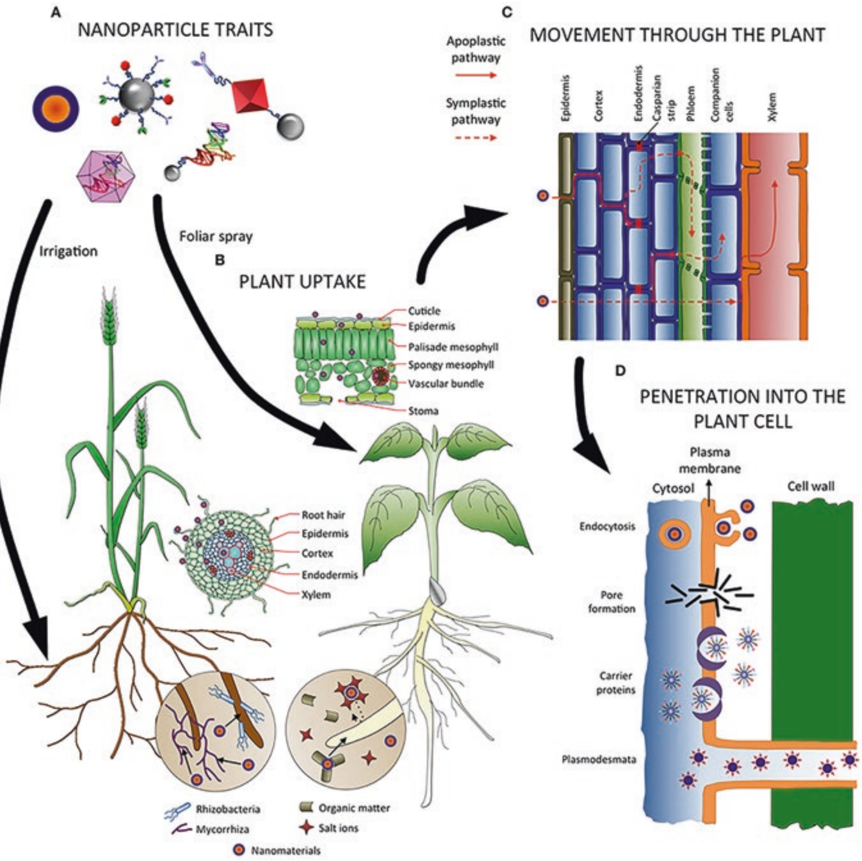

Fig. 15.5 Translocation of the NPs within the plants (The image was reproduced with permission (Pérez-de-Luque, 2017). Copyright © 2017 Pérez-de-Luque, Creative Commons Attribution License (CC BY))

different uptake, translocation, and accumulation may lead to involve in a plant. Which may lead to positive or negative effects on plants. Various studies have explained the mechanism of uptake and barrier for the uptake of nanofertilizer by plant metabolism (Avellan et al., 2019; Schwab et al., 2016). The roots of plants have rough surfaces due to the presence of root hairs. These roots produce mucilage and a variety of small molecules including organic acids (Shukla et al., 2016). In some of the studies, it was proved that encapsulation of NPs with alginic and citric acid leads to enhance uptake (Barrios et al., 2017). The roots of the plant are negatively charged, and the carboxylic acid present in alginic and citric acid provides a positive charge to the NPs that lead to attaching to the root hairs of the plants and enhances the dissolution of NPs (Zhao et al., 2012). However, it is still not known that they interact with carrier proteins or channels present in the membrane to enhance uptake. The studies also suggested that some of the NPs have smaller sizes than these pores, so they easily pass through the cell membrane (de la Rosa et al., 2021; Seo & Kim, 2020). The axial xylem system involves in the transportation of fertilizers to different parts of plants (da Cruz et al., 2019). In the presence of nanofertilizers, several tonoplastic-localized transporters are activated, which leads to enhancing the transportation of fertilizers in plants by changing the volume and content of vacuoles for nanofertilizer storage (Horaruang & Hills, 2020). In the leaf, nanofertilizers also interact with the stomata and cuticles to enter into the leaf system of the plants (Hu et al., 2020; Xiong et al., 2017). However, the specific mechanism for these interactions is unknown. The cuticle is a waxy component, hydrophobic. Therefore, it should repel the interaction of encapsulated NPs (Staiger et al., 2019). The literature proves that only a small fraction of the NPs enter the plant and some part remains in epidermis cells (Hong et al., 2016). Also, a limited number of NPs can penetrate the leaf and be transported to the other part of the plants (Hong et al., 2014). Several factors that affect the opening of pores in plants, including stomata density, location, and environmental variables still need to be known.

8 Conclusion

To fulfill the global food requirement and sustainable development, production and yield in the agriculture field have to be increased along with decreasing pollution. Our opinion is nanotechnology along with biotechnology has the potential to enhance nutrient management and crop yield. Smart fertilizers, based on slow/controlled release, and nanostructured-based smart fertilizers have shown improved soil production and crop yield with decreased nutrient loss compared with conventional fertilizers. Several materials, such as degradable polymers, clay, polymeric NPs, metal NPs, carbon nanofibers and nanotubes, agricultural waste, etc., are capable to be used as carrier materials for nutrients and bacterial inoculum for the development of smart fertilizers. NS-based smart fertilizers have been found much more efficient in plant growth due to easier transportation of nanomaterial to the different parts of the plants. The synthesis methods of NS are quite easier and environmentally friendly. There is a need to continue evaluating smart fertilizers, especially those that utilize organic wastes, and their composition, manufacture, and agronomic and environmental performance in future research. We suggested that nanostructure-based materials like CNTs, CNFs, ACF, and NPs could be more beneficial for the formulation of smart fertilizers or can be used as carrier materials for enhancing plant nutrient uptake. Interaction of such material into different parts of plants will also fulfill the nutrient requirement of plants at every location in plants. A circular economy should be used to create innovative smart fertilizers from organic wastes from agricultural harvesting residues, which are urgently needed for the sustainable intensification of agricultural systems.

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Chapter 16
Impact of Nanofertilizers for the Mitigation of Multiple Environmental Stresses

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1 Introduction

The term “abiotic stress” pertains to the harmful impact of nonliving factors on living organisms. Environmental pressures such as drought, salt, heavy metals, and extreme temperatures are among the most significant global issues. With the changing global climate caused by climatic changes and global warming, plants are becoming increasingly susceptible to abiotic stress, including heat waves, droughts, flooding, salinity, and freezing (Zandalinas et al., 2021). Human activities, such as industrialization, intensive agriculture, mining, population growth, and urbanization, indirectly harm the environment, leading to abiotic stress and the contamination of essential elements for life (Studies, 2006). Plants need to withstand various abiotic stresses like dryness, salt, and extreme temperatures (Liang et al., 2013). The response of plants to stress depends on the affected tissue or organ, and the severity and duration of the stress influence the complexity of the plant’s reaction (Munns & Tester, 2008). To enhance stress tolerance and counteract stress reactions, plants activate early stress-signaling pathways (Bhatla & Lal, 2018). Second messengers,

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such as calcium, reactive oxygen species (ROS), phospholipids, and nitric oxide (NO), along with protein kinases, are released and amplified in response to stress in plant cells (Zhang et al., 2022). SnRk1 kinases help plants recover from disturbances by modulating the expression of stress-responsive genes, reducing energy-intensive processes, and increasing resistance to stress (Zhu, 2016). Plant hormones like abscisic acid (ABA) and ethylene play significant roles as signals in triggering plant defense responses, including stomatal closure during drought (Zhu, 2016). To mitigate the detrimental effects of abiotic stress, these signaling pathways activate transcription factors that trigger a variety of stress-response genes. Excessive production of ROS due to abiotic stress can damage important physiological functions, including proteins, membranes, and other components of plant signaling (Zhu, 2016). Membrane peroxidation and damage to photosynthetic systems have been observed in various plants under stress, emphasizing the reliance of plant defense mechanisms on activating antioxidant molecules to scavenge ROS (Zörb et al., 2019). Many plant species increase their synthesis of phenolics, flavonoids, and phytochelatins in response to abiotic stress, particularly heavy metal stressors (Emamverdian et al., 2015). Additionally, plants increase their proline content to counteract osmotic effects and activate antioxidant enzymes like SOD, APX, GPX, and catalase to tolerate oxidative stress (Zulfiqar & Ashraf, 2021). Long-term abiotic stresses can negatively impact plant growth and development, leading to significant reductions in agricultural output. As plants are the primary producers in the living kingdom, the threat to plant life raises concerns about future food supplies. In fact, abiotic stresses account for up to half of the yield losses in major crops (Lowry et al., 2019). Researchers are actively investigating strategies to alleviate abiotic stress, including genetic engineering, plant breeding, and the emerging field of nanotechnology. Nanomaterials are gaining popularity as a means to protect plants from abiotic stresses such as drought, salt, heavy metals, high temperatures, and flooding (Lowry et al., 2019). The use of nanoparticles (NPs) is seen as a promising approach in sustainable agriculture to enhance crop yield by increasing plant tolerance to abiotic stress (Lowry et al., 2019). To overcome current and future production limitations in sustainable agriculture, the use of nanoparticles (NPs) is seen as a beneficial and promising strategy for changing crop yield by increasing a plant's tolerance to abiotic stress (Lowry et al., 2019).

2 Nanofertilizer Uptake and Movement in Plants

The interaction, absorption, and mechanism of nanoparticles within the plant system involve a series of processes (Fig. 16.1). The absorption of nanoparticles primarily occurs in the root epidermal regions through osmotic pressure and capillary forces. Nanoparticles with sizes ranging from 3 to 5 nm are usually well-absorbed, and they enter the plant system through tiny pores in the root epidermal cell wall (Nair et al., 2010). Despite being larger than the typical absorbing pores,

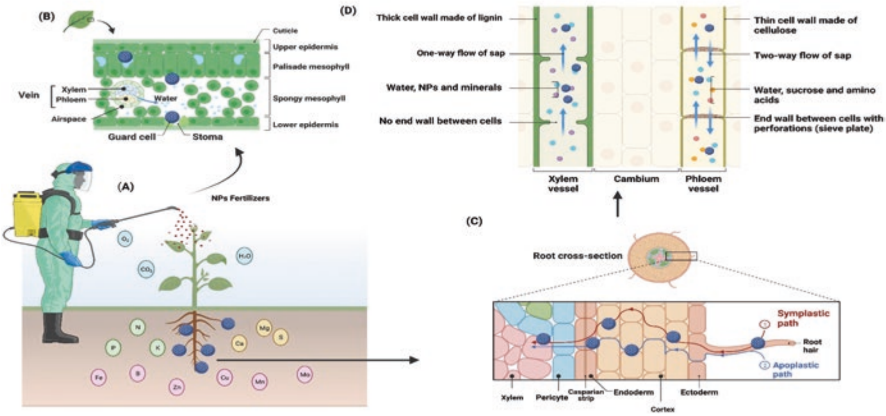

Fig. 16.1 Diagrammatic representation of (**a**) foliar application of nanofertilizer, (**b**) uptake via stomata, and (**c**) root and transport through xylem and phloem vessel into different parts of plants

nanoparticles can enhance the formation of cell wall pores, enabling their entry into the plant system. The initial interaction of nanoparticles occurs with the epidermis, and in certain cases, the particle's charge plays a crucial role in this interaction (Fig. 16.1) (Xu et al., 2022). Once inside the plant, nanoparticles can follow two routes to reach their target tissues: the apoplastic and symplastic pathways. Nanoparticles are often aided by membrane carrier proteins for transporting through the xylem channels (Pérez-de-Luque, 2017). Any aggregates present in different channel regions are transported back to the roots through the phloem. In leaves, nanoparticles can enter the internal system through both the cuticle and stomata. Particles smaller than 5 nm primarily utilize the cuticular pathway, while those larger than 5 nm take the stomatal route. The transport mechanism within leaves resembles that of roots. Nanoparticles are delivered to shoots, roots, fruits, and other plant parts via the phloem using both apoplastic and symplastic pathways (Khan et al., 2019).

2.1 *Foliar Application Pathways for Uptake Nanofertilizer*

During agricultural applications, nanoparticles are commonly sprayed onto the surface of leaves, where they adhere and enter plants through the cuticle or stomata. The waxy cuticle of the leaf epidermis, composed of wax, cutin, and pectin, acts as a natural barrier against nanoparticle entry while preventing water loss in growing leaves (Yang et al., 2015). However, the waxy cuticle has distinct hydrophilic and lipophilic channels, with diameters ranging from 0.6 nm to 4.8 nm (Avellan et al., 2019; Eichert et al., 2008). Hydrophilic nanoparticles smaller than 4.8 nm can diffuse through the hydrophilic channels, while lipophilic nanoparticles can infiltrate the cuticle surface via the lipophilic channels (Bussières, 2014). Recent studies using confocal fluorescence microscopy have shown that carbon dots smaller than 2 nm can enter cotton leaves through the cuticular pathway. It should be noted that the capacity of the plant epidermis to take in nanoparticles is limited due to the relatively small size of the cuticle pore channels (Hu et al., 2020). Consequently, nanoparticles may accumulate in the epidermis and vascular tissue after application to the leaf surface (Fig. 16.1). However, studies have also indicated that nanoparticles can be transported to other plant organs, suggesting the possibility of absorption via the stomatal pathway (Fig. 16.1).

2.2 Soil Application Pathways for Uptake Nanofertilizer

The initial interaction between nanoparticles and plant roots occurs through adsorption on the root surface. Nanoparticles with positive charges have a higher tendency to accumulate and be absorbed on the root surface due to the negative charge of the root surface caused by the release of chemicals from root hairs, such as mucus and organic acids (Hu et al., 2020). The formation of lateral roots provides a new adsorption interface for nanoparticles, enabling their entry into the root column (Peng et al., 2015). (See Fig. 16.1). The root epidermis, similar to the leaf epidermis, plays a crucial role in nanoparticle interaction. However, the epidermis of root hairs and primary/secondary roots is not fully developed, allowing direct contact and penetration of nanoparticles (Khan et al., 2019). Within the root epidermis, water can pass through the cell wall, but small pores in the wall hinder the passage of larger particles (Khan et al., 2019). When the exodermis is absent, nanoparticles can enter the xylem, the central column of the root (Su et al., 2019). Certain nanoparticles can damage the plasma membrane, leading to the formation of new pores in the epidermal cell wall, facilitating the entry of larger nanoparticles (Wu & Li, 2022). Various mechanisms are involved in the uptake of nanoparticles by plant cells upon their introduction to plant tissue (Wu & Li, 2022). These mechanisms include the ion pathway, endocytosis, protein binding to cell membranes, and physical damage.

Studies on nanoparticle uptake by plant roots indicate that the hydrophilic pathway serves as one route for nanoparticles to enter plant cells. However, due to the small pore size, this pathway is not highly effective for nanoparticle entry into cells. Endocytosis is another major pathway for nanoparticle uptake in plant cells, where nanoparticles enter cells through invagination of the plasma membrane. Nanoparticles absorbed via endocytosis do not exhibit particle size selectivity, although particles smaller than 1 μm have been shown to be taken up by plant protoplasts [41]. Endocytosis has been proposed as the mechanism for the uptake of carbon-based nanoparticles and carbon nanotubes by root cells of *Catharanthus roseus* (Grillo et al., 2021). Additionally, plants can uptake nanoparticles by binding to transport proteins in their cuticle.

3 Factors Affected Uptake of Nanofertilizer

3.1 *Size of Nanofertilizer*

Extensive research has been conducted on the size-dependent uptake of metal-based nanoparticles in plants. Studies have revealed that metal-based nanoparticles with a diameter smaller than 50 nm can enter plant leaves through the stomatal pathway [19]. The uptake ability of leaves decreases as particle size increases. Several studies have documented the foliar uptake of nanoparticles. For example, Zhu et al. applied ZnO nanoparticles (30 nm) labeled with fluorescein isothiocyanate (FITC) to wheat leaves and used confocal microscopy to observe their entry into wheat chloroplasts via the stomatal pathway and subsequent exit from the leaf epidermis (Zhu et al., 2020). The researchers also investigated how the opening and closing of stomata affected ZnO nanoparticle uptake. Wheat leaf cells exhibited lower zinc concentrations in their chloroplasts and cytoplasm when stomatal diameters were reduced. Coated gold nanoparticles of various diameters (3, 10, and 50 nm) were applied to wheat leaves, and it was found that wheat leaves were able to absorb all sizes of coated gold nanoparticles, potentially through disruption of the cuticle layer or diffusion through the stomata (Avellan et al., 2019). Transmission electron microscopy (TEM) confirmed the uptake of MgO nanoparticles (27-35 nm) by watermelon leaves (TEM). Furthermore, nanoparticles based on silica, polymer, and natural materials were found to be similarly absorbable by plant leaves as metal-based nanoparticles, with the critical size for absorption varying depending on the nanoparticle type. TEM analysis revealed that SiO_2 nanoparticles with a size of 54 nm could enter *Arabidopsis thaliana* leaves via the stomatal pathway (El-Shetehy et al., 2020). Researchers Zhao et al. demonstrated that cucumber leaves could take up FITC-labeled mesoporous silica nanoparticles (200–300 nm) (Lian et al., 2021). In another study, it was discovered that 93.6 nm polystyrene nanoplastics were small enough to enter lettuce phloem via trans epidermal transport. Recent findings have shown that rice leaves can absorb and distribute 166 nm silicon nanoparticles made from chitosan (Jia-Yi et al., 2022).

In terms of root absorption from the soil, nanoparticle size primarily influences the process. Previous studies have demonstrated the absorption of gold nanoparticles (3.5 nm) in the roots of *Vicia faba* L. and cerium oxide nanoparticles (81 nm) in maize roots (Zhao et al., 2012). Additionally, research has shown that the uptake of TiO_2 nanoparticles by wheat roots is directly proportional to the particle size. Wheat roots can absorb TiO_2 nanoparticles ranging from 36 to 140 nm, with absorption decreasing as particle size increases. TiO_2 nanoparticles larger than 140 nm are not absorbable by wheat roots (Larue et al., 2012). Generally, it is believed that metal-based nanoparticles larger than 100 nm face challenges in being absorbed by plant roots (Banerjee et al., 2019). However, it is intriguing to note that nanoparticles larger than 100 nm derived from silicon and natural polymers can still be absorbed. Arabidopsis plants treated with Si nanoparticles (200 nm) were found to have absorbed them in their roots after 6 weeks of exposure (Slomberg &

Schoenfisch, 2012). Confocal microscopy and transmission electron microscopy have shown that sugarcane roots can absorb zein nanoparticles with an average particle size of 135 nm (Prasad et al., 2018).

3.2 Surface Charge of Nanofertilizer

The ability of nanoparticles to penetrate plant mesophyll tissue is influenced not only by their size but also by their shape and charge. The shape of nanoparticles affects their surface area and contact angle with the plant surface, which in turn affects their uptake. In a study found that rod-shaped gold nanoparticles were more easily absorbed and internalized by Arabidopsis leaves compared to other shapes of nanoparticles (Su et al., 2019). Plant leaves have the capacity to take up both positively and negatively charged nanoparticles. For instance, the absorption of graphene quantum dots (GQDs) with different surface charges (NH2-GQDs and OH-GQDs) on maize leaves was evaluated. It was observed that both positively charged NH2-GQDs and negatively charged OH-GQDs were taken up by maize leaves through stomata (Sun et al., 2022). Similarly, the adsorption of positively charged FITC-labeled F-P-ZnO NPs and negatively charged F-N-ZnO NPs on wheat leaves was confirmed using confocal microscopy. The study demonstrated that positively charged nanoparticles had stronger adsorption in leaves compared to negatively charged nanoparticles (Zhu et al., 2021). The results showed that positively charged NH2-GQDs (13 nm) and negatively charged OH-GQDs (14 nm) can both be absorbed by maize leaf stomata. Confocal microscopy proved that F-P-ZnO NPs (40 nm), which are positively charged and FITC-labeled, and F-N-ZnO NPs (40 nm), which are negatively charged, accumulate at the stomata on the surface of wheat leaves. The adsorption of positively charged nanoparticles in the leaves was stronger than that of negatively charged nanoparticles, as evidenced by the electrostatic interaction between positively charged nanoparticles and negatively charged plant cell walls (Zhu et al., 2021).

Along with size, another element that affects NP's uptake by plants is its surface charge. The negative charge of plant root cell walls determines the surface charge characteristics of nanoparticles that can be absorbed by plant roots. Plant roots absorb nanoparticles somewhat less sensitively to electric charge than leaves do. Positively charged nanoparticles are electrostatically attracted to the negatively charged cell wall, which prevents them from penetrating the tissue and keeps them on the surface of the root (Bosker et al., 2019). Nanoparticles with different particle sizes (20–100 nm) and surface charges via reversible addition chain transfer polymerization. The researchers used confocal microscopy to show that both negatively and uncharged nanoparticles (22 nm) were picked up by Arabidopsis thaliana root cells and moved into the root's xylem (Parkinson et al., 2022). The negatively charged nanoparticles, on the other hand, are restricted to the root epidermis and are unable to travel farther into the Arabidopsis root (Parkinson et al., 2022).

3.3 Crop Species

Nanoparticle uptake in plant leaves is influenced by various factors, including the plant species (Ha et al., 2021). Factors such as the distribution, density, and size of pores in the leaves play a role in nanoparticle uptake. Monocotyledonous plants have more orderly and uniformly shaped stomata compared to dicotyledonous plants. The growth stage and life cycle of plants also impact the rate of nanoparticle absorption in leaves. While some plant species have stomata on both the upper and lower epidermis, this is not the norm (Zhu et al., 2020). When both sides of leaves have stomata, dicotyledon plants tend to have approximately 1.4 times more stomata per square centimeter on the lower epidermis than the upper epidermis. Monocotyledon plants, on the other hand, exhibit a similar number of stomata on both sides (Zhu et al., 2020). Abiotic environmental factors, including temperature, humidity, and light, also affect the rate of nanoparticle absorption (Rani et al., 2022). Dicotyledonous pumpkins show greater efficiency in absorbing CeO_2 NPs compared to monocotyledonous wheat (Adrees et al., 2021; Shahbaz & Ashraf, 2013). In comparison to festuca, tomatoes demonstrate a higher rate of Ce NP absorption. Recent research by Hu and colleagues reveals that the extracellular space in monocotyledonous plants like maize is insufficient for nanoparticle entry, whereas dicotyledons like cotton, with more stomata, offer greater opportunities for NP entry (Hu et al., 2020).

4 Comparing Nanofertilizers to Traditional Fertilizers

According to Singh et al. (2021), the utilization of nanoscale transporters and compounds holds promise for achieving controlled release of agrochemicals and precise delivery of macromolecules. By incorporating these technologies, it becomes possible to reduce the reliance on fertilizers and pesticides without sacrificing crop yield. Compared to nanoagrochemicals, commercial fertilizers exhibit lower efficiency due to their larger particle size and limited water penetration. Furthermore, the repeated application of chemical fertilizers can result in the accumulation of toxic heavy metals (HMs), thereby causing an ecological imbalance in the soil (Singh et al., 2021).

Soil contamination can result from the excessive use of chemical fertilizers, either through leaching or the accumulation of leftover plant waste containing surplus fertilizer. The utilization of nanoagrochemicals is crucial for achieving sustainable agriculture as it can improve fertilizer efficiency and enhance water quality control (Fraceto et al., 2016). However, prolonged exposure and bioaccumulation of nanoparticles (NPs) in plants may have detrimental effects on human health and food security (Verma et al., 2022). The edible tissues of crops can absorb and store NPs, leading to disruptions in plant physiology by interfering with cellular and subcellular structures and functions. Additionally, the natural accumulation of NPs or metal ions can alter the composition of proteins, lipids, and nucleic acids through the generation of reactive oxygen species (ROS) (Ye et al., 2020). The widespread use of NPs in agriculture raises concerns from various perspectives, including environmental, ethical, health, and safety considerations (Rajput et al., 2021). However, to date, there is only speculation and no concrete evidence supporting the idea that NPs are harmful to human health (Mosselhy et al., 2021). The application of nanotechnology in agriculture has gained popularity due to its role in developing novel NPs. However, it is crucial to thoroughly investigate the specific advantages and disadvantages associated with their use. The proliferation of NPs in the agri-environment is a direct consequence of nanotechnology development, and the safe disposal of large quantities of NPs (several hundred tons per year) raises concerns among researchers and professionals (Rajput et al., 2021). NPs can be found in various regulated entities, including air, water objects, soil, hydrobionts, algae, fungi, and the tissues of land plants and animals (Rajput et al., 2020b). Limited research has been conducted on the fate and migration of NPs in soil compared to other sources. Despite acting as a sink for NPs, soil also plays a vital role in providing essential nutrients to food crops (Ghani et al., 2022).

This analysis offers new insights into the potential impact of NPs on ecological sustainability, human health, and food safety.

5 Synthesis of Nanofertilizers

Nanotechnology involves manipulating and controlling devices at the nanometer scale, allowing for the development of "smart fertilizers" made from nanostructured materials (Sivarethinamohan & Sujatha, 2021). These nanofertilizers offer several advantages, such as improved nutrient uptake, enhanced soil fertility, increased absorption rates, higher photosynthesis and production rates, reduced soil toxicity, fewer applications, better plant health, and minimized environmental pollution (Rajput et al., 2020a). Examples of nanomaterials used in these fertilizers include gold nanorods, ZnCdSe/ZnS core–shell quantum dots, InP/ZnS core–shell quantum dots, and Mn/ZnSe quantum dots. The effectiveness of nanomaterials as nanofertilizers depends on factors like size, content, concentration, chemical properties, and the specific crop being grown. When nanofertilizers, containing nanoparticles (NPs), come in contact with water, they release their nutrients into the soil (Vishwakarma et al., 2018).

To prevent nutrient losses, NPs in nanofertilizers can be encapsulated in polymers or thin coatings. Utilizing nanofertilizers that leverage the unique characteristics of NPs is a way to increase crop productivity while minimizing input costs. Producing nanofertilizers involves combining or adding single nutrients to nanoscale adsorbents. Cationic nutrients are loaded unmodified, while anionic nutrients undergo surface adjustment during the production of nanomaterials using physical and chemical methods (Panpatte et al., 2016). Scientists have developed three main methods for encapsulating fertilizers within NPs: delivering the nutrient as nanoscale particles or emulsions, coating it with a thin polymer layer, or enclosing it within nanoporous materials (Mittal et al., 2013). Nanofertilizers have a wide range of applications, including measurement control at the nanoscale (1–100 nm), virtual forecasting modeling, and manipulation of nanoscale matter. Solid NPs also have impacts in agricultural areas. The demand for environmentally friendly, efficient, and nontoxic nanofertilizer synthesis technologies has led to interest in biofabrication of NPs using biological processes (Al-Mamun et al., 2021). There are three types of nanofertilizers that can be prepared according to plant nutrient needs: nanoscale-coating fertilizers, nanoscale additive fertilizers, and nanoporous materials. Nanofertilizers containing hydroxyapatite, a crucial mineral, have a high surface area to volume ratio and can provide both calcium and phosphorus to plants. Examples of potential nano-encapsulated fertilizers for controlled nitrogen release include urea-loaded hydroxyapatite nanohybrids (Yasmin et al., 2021). Mesoporous silica nanoparticles (NPs) with properties like large surface area, mesoporous architecture, biocompatibility, and nontoxicity have the potential to improve crop quality and support sustainable agriculture. Silica NPs have been shown to have beneficial effects on plant growth under salinity stress (Pan et al., 2022). Carbon-based nanomaterials such as carbon NPs, carbon nanotubes (CNTs), fullerenes, and fullerols are important plant growth regulators that enhance germination, chlorophyll, and protein levels. The process of creating nanofertilizers from organic and inorganic nanomaterials involves various physical or chemical methods, resulting in a diverse range of products. Examples of organic nanomaterials include lipids, polymers, and carbon nanotubes (CNTs), while inorganic nanomaterials encompass metal oxides like AgO, MgO, ZnO, and TiO_2. Polymeric NPs, such as chitosan, are a type of alternative fertilizer chemical that utilizes biodegradable, natural, and agriculturally safe carriers. Chitosan, with its polymeric cationic properties and ability to interact with negatively charged molecules or polymers, shows great potential as an agrochemical carrier.

6 Nanoparticle-Mediated Mechanism of Action in Plants to Mitigate Abiotic Stresses

From the studies that were done to find out how NPs work, several ideas have been put forward. Depending on the concentration of the NPs used, several studies have shown that they can either be hazardous to plant growth at greater concentrations or advantageous when supplied in appropriate doses (Naderi & Danesh-Shahraki, 2013). NPs enter cells by a variety of pathways in the cellular membrane, including direct penetration. It is possible that NPs act as stress signaling molecules, leading to an increase in the expression of genes related to stress. When faced with stress, the body responds by increasing its defense mechanisms, including the expression of regulatory factors. Metal-based NPs can keep ROS levels above what is considered safe, thereby activating the plant's defense system in response to stress. A meta-analysis was conducted to compare the reaction of several plant species with metal-based NPs, which revealed that root architecture change, activation of antioxidant mechanisms, and involvement of a unique signaling pathway of phytohormones were common responses to stress induced by NPs signaling (Rakgotho et al., 2022). Nevertheless, the effects were found to be modified by the nature of the NPs and the length of exposure. The downregulation of genes involved in trichoblast development, for instance, may explain the root architectural change observed following NP exposure. Trichoblasts are a subset of specialized epidermal cells that are located in the region where new root hairs originate. In addition, it has been demonstrated that genes responsive to indole acetic acid (IAA) and ethylene (ET) are positive regulators of root hair formation (Li et al., 2022). The use of NPs typically causes changes in defense-related cellular processes (Li et al., 2022). The treatment with NPs also causes an upregulation of genes encoding proteins crucial to maintaining a healthy ROS balance, including NADPH oxidase, glutathione S-transferase (GST), superoxide dismutase (SOD), and peroxidases (POX) (Li et al., 2022). NPs increase the expression of genes that turn on antioxidant enzymes (Massange-Sánchez et al., 2021). Onion seedlings revealed that TiO_2 NPs boosted the activity of the SOD enzyme and that this effect was compounded with an increase in NP concentration (Janmohammadi et al., 2016). Onion seedling growth and seed germination were both enhanced by TiO_2 NPs at low concentrations but were inhibited at high concentrations (Janmohammadi et al., 2016). TiO_2 and SiO_2 NPs were found to improve germination and growth in Glycine max seeds (Hatami et al., 2016). NPs can act as cytoplasmic signaling molecules or be detected by the calcium-binding protein (CaBP) complex (Jiang et al., 2021). As NPs reach plant cells, they are identified by NP-specific proteins, which in turn activates the transcription of genes involved in responding to stress (Jiang et al., 2021). As a result, a series of intracellular signaling pathways is activated, leading to the upregulation of genes whose expressions ultimately boost the plant's tolerance responses to abiotic stress. The sensitive to desiccation (RD20) gene was upregulated in Arabidopsis thaliana in response to salinity, drought, or ABA (Jiang et al., 2021). Additionally, it has been proposed that nanoparticles can activate antioxidant enzymes by scavenging reactive oxygen species (ROS). ZnO NPs greatly boosted the expression of Cu/Zn SOD, Fe/Mn SOD, catalase (CAT), and ascorbate peroxidase (APX) in plants under drought stress. Several transcriptomics and proteomics analyses have been carried out to better understand the interaction between plants and nanomaterials. (Hussain et al., 2016). Transcriptomics analyses demonstrated that Cu-based NPs (50 nm) influence oxidative stress-responsive genes, genes involved in brassinosteroids production, and genes involved in root development (Mittler, 2002). Studies on the metabolome of the cucumber (*Cucumis sativus*) using 40 nm-sized Cu NPs revealed an increased accumulation of secondary metabolites (such as acetyl glucosamine, phenyl lactate, and 4-aminobutyrate) involved in cell signaling and defense responses and a decreased accumulation of metabolites of flavonoid and fatty acid synthesis, as well as riboflavin and amino acid metabolism. (Mohamed et al., 2022). Additionally, transcriptome analysis revealed that tobacco plants treated with TiO_2 NPs had considerably higher transcript levels of the miRNAs 399 and 395, which are thought to be involved in the regulation of plants' adaptive responses to nutritional stress. When *A. thaliana* seedlings were exposed to carbon nanodots of 3 nm, transcriptomics analysis revealed that genes involved in cellular response to phosphate starvation, UDP-glycosyltransferase activity, and stimulus response were upregulated and genes involved in chloroplast structure and function were downregulated, leading to dose-dependent root elongation (Baig et al., 2021). Activation of the defensive response has been connected by metabolomics research to an increase in the cell wall's carbohydrate components.

7 Application of Nanofertilizers for Mitigation of Abiotic Stresses

Drought, submergence, and flooding, as well as chilling, freezing, and heat stress, are just a few examples of the stresses that are being studied in relation to plants and their resilience. The role of plant natriuretic peptides in maintaining the salt and water balance in the plant is just one of the many topics that have recently been discussed in relation to the multiple stresses on plants. Natural variations in multiple abiotic stresses in a hyper-seasonal edaphic savanna and the potential of a transcriptomic analysis under various stresses all contribute to plant boron deficiency and toxicity (Lutts et al., 2016). In addition to nanofertilizers, many other materials play important roles in reducing the combined stresses and boosting plant productivity. So far as we can tell, the agricultural sector's management of nanofertilizers is still in its infancy because it depends on a wide variety of soil and environmental factors. Figure 16.2 provides a quick look at how different stresses react on cultivated plants

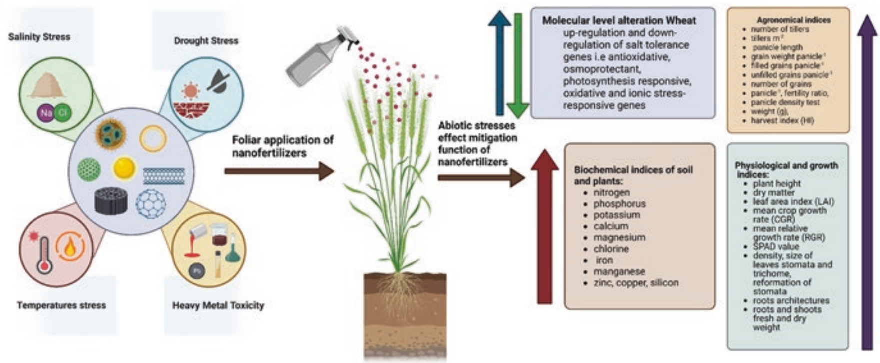

Fig. 16.2 Diagrammatic representation of mode of action of nanofertilizers to mitigating the effect of abiotic stress. The mode of action of nanofertilizers involves several mechanisms that allow plants to overcome abiotic stress by enhancing nutrient uptake, improving water retention, providing antioxidant activity, regulating plant hormones, and improving soil quality. Nanofertilizers are a promising tool for sustainable agriculture and can mitigate the negative effects of abiotic stress on plant growth and yield

when nanofertilizers are used. The stresses depicted here can be broken down into three distinct types: singular, combined, and multiple. Salinity, drought, heavy metals, water stress, and nutrient deficiency are all examples of individual stresses that could be alleviated by supplementing the soil with nanonutrients like copper oxide (CuO), selenium oxide (SeO_2), zinc oxide (ZnO), silicon dioxide (SiO_2), iron oxide (FeO_3), and sulfur (S) (Grillo et al., 2021). There are a variety of potential combinations of stresses, such as heat stress and drought, salinity and heat, heat and salinity, salinity and heavy metals, and heat and drought (Lowry et al., 2019; Rani et al., 2022). Applied nano-Si for drought and salinity, nSe for salinity and heat stress, nSi for salinity and drought [125], nSi for salinity and HMs, nZn for drought and heat stress, and nZn for drought and HMs are examples of nanonutrients that could help with the second type of problem (Younis et al., 2020). There is a lack of literature on the application of nanofertilizers in situations involving multiple stresses.

7.1 Drought Stress

Drought, characterized by water scarcity, elevated temperature, and reduced water uptake by plants, is a common stress condition (Fig. 16.2) that significantly affects plant development, including seed germination and seed setting stages (Seleiman et al., 2021). Silica nanoparticles (NPs) have been demonstrated in various studies to enhance drought tolerance in plants, although other types of NPs also exhibit this effect. Application of silica NPs resulted in improved growth and physiological parameters of hawthorn seedlings even under drought stress conditions. *Triticum aestivum* also exhibited similar positive outcomes, including increased starch and gluten contents, leading to enhanced growth and yield under drought stress (Jaberzadeh et al., 2013). The efficacy of TiO_2 in promoting germination and plant growth contributes to its positive influence on drought tolerance. Plants exposed to drought stress benefit from TiO_2 by increasing biomass, maintaining relative water content (RWC), and stimulating antioxidative enzymes (Faraji & Sepehri, 2020). Treatment with hydroxyapatite nanoparticles (CaNP) in jute seeds resulted in enhanced drought tolerance by regulating proline levels through proline biosynthesis (Das et al., 2016). Maize seedlings typically experience inhibited growth under drought stress; however, a study found that treatment with yttrium-doped Fe_2O_3 NPs improved the photosynthetic machinery, as indicated by increased chlorophyll and carotenoid content. Moreover, these NPs exhibited efficacy in mitigating the negative impacts of drought on *B. napus* (Palmqvist et al., 2017).

7.2 Salinity Stress

Salt stress is a significant challenge that adversely affects crop growth and productivity worldwide. Excessive sodium (Na+) and chloride (Cl-) exposure triggers osmoregulation in plants as a response to maintain normal physiological functions

(Fig. 16.2). However, this process can lead to the generation of reactive oxygen species (ROS) and nutrient imbalances, resulting in oxidative stress. To counteract these effects, plants accumulate organic compounds like amino acids, polyols, sugars, glycine betaine, and quaternary ammonium compounds during osmoregulation. Furthermore, maintaining ion homeostasis is crucial for reducing Na+ concentration and increasing K+ concentration in cells, which helps mitigate the effects of ROS and activate enzymatic machinery (Isayenkov, 2012). Nanoparticles (NPs) contribute to the alleviation of environmental stresses through various mechanisms, including the activation of specific genes, accumulation of osmolytes, and provision of free nutrients and amino acids. Treatment with SiO_2 NPs increased transpiration rate, water use efficiency (WUE), carbonic anhydrase activity, and salinity stress resistance in *Cucurbita pepo* (Siddiqui et al., 2022). TiO_2 (anatase) interferes with linolenic acid in the electron transport chain (ETC) and modifies photoreduction activity (Siddiqui et al., 2014). Thus, TiO_2 (anatase) interferes with linolenic acid in the ETC and modifies photoreduction activity (Su et al., 2009). In *Abelmoschus esculentus*, the application of ZnO NPs to the leaves enhanced photosynthetic functionality and enzymatic machinery, thereby mitigating the adverse effects of salinity stress.

The application of certain nanoparticles (NPs) has been found to have beneficial effects on plant development and photosynthesis, particularly in mitigating the negative effects of salinity stress. For example, ZnO NPs and Si applied together as a foliar spray improved growth in mango seedlings by enhancing carbon assimilation and nutrient uptake, leading to increased photosystem II activity and maintaining relative water content (RWC) to reduce membrane damage (Alabdallah & Alzahrani, 2020). ZnO and Si applied together as a foliar spray improved growth in mango seedlings by increasing carbon assimilation and nutrient uptake (Alabdallah & Alzahrani, 2020). Application of SiO_2 NPs in plants like *Solanum lycopersicum,* strawberry, and *Ocimum basilicum* resulted in increased vegetative growth, enhanced epicuticular wax layer, accumulation of proline, and regulation of salt stress-related genes, thereby alleviating the negative effects of salinity stress (Oprica et al., 2021). Silver nitrate nanoparticles (AgNPs) have also been proposed as potential nanoagents for mitigating salinity stress. AgNPs treatment in *Triticum aestivum* increased the accumulation of peroxidase (POD), proline, and sugar, leading to improved germination (Isayenkov & Maathuis, 2019). Other NPs such as CeO, carbon nanotubes (CNTs), and graphene NPs applied to cotton and *Catharanthus roseus* increased protein and amino acid content during the reproductive stage, enhancing tolerance to salinity stress (Isayenkov, 2012). ZnO NPs were found to enhance salt tolerance in lupine plants by reducing malondialdehyde (MDA) and Na+ contents, while also improving germination in cumin seeds. The use of ZnO NPs helped restore normal osmoregulation, improve the photosynthetic system, and decrease MDA and Na+ levels, thereby mitigating the harmful effects of NaCl (Torabian et al., 2016).

7.3 Temperature Stress

Temperature stress can have detrimental effects on plants, leading to cellular disruptions and even plant death. Heat stress, in particular, triggers physiological and biochemical responses aimed at protecting cellular structures and restoring homeostasis. This includes the production of heat shock proteins (HSPs) and activation of antioxidant mechanisms to counteract oxidative stress (Zhu, 2016). Nanoparticles (NPs) have shown promise in alleviating the impacts of heat stress on plants. For instance, treatment with selenium NPs improved antioxidant mechanisms in sorghum plants, enabling them to scavenge reactive oxygen species (ROS) generated during heat stress (Djanaguiraman et al., 2018). Similarly, selenium NPs conferred tolerance to high- and low-temperature stresses in *Lycopersicon esculentum*, enhancing the plants' ability to cope with temperature fluctuations. Silver nanoparticles (AgNPs) were found to improve various growth parameters in wheat plants under high-temperature stress, including root shoot length, root number, fresh and dry weights, leaf area, and leaf number (Iqbal et al., 2019). Additionally, the application of zinc oxide (ZnO) NPs under chilling stress in *Oryza sativa* helped modulate the antioxidative system and chilling response transcription factors, potentially enhancing the plant's ability to tolerate low temperatures (Song et al., 2021).

7.4 Heavy Metal Toxicity

Phytoremediation, which refers to the use of plants for sustainable cleanup of polluted areas, has gained popularity in the field. Nanoparticles (NPs) have emerged as effective tools in phytoremediation due to their interaction with plant metabolism and metal ions (Fig. 16.2) (Morales-Díaz et al., 2017). NPs have been found to reduce oxidative stress caused by heavy metals and promote the growth of various plant species even in toxic environments (Iqbal et al., 2019). For example, the application of silicon dioxide NPs enhanced the tolerance of *Acorus pygmaeus* to heavy metal stress by increasing biomass accumulation and the activities of biocatalysts in the plant (Iqbal et al., 2019). Furthermore, silicon dioxide NPs facilitated the absorption and accumulation of heavy metals in roots, preventing their translocation to the leaves and minimizing toxicity (Rajput et al., 2020a). NPs can immobilize toxic metal ions, and nanofibrous composite membranes based on polyvinyl alcohol and polyacrylonitrile exhibit efficient metal chelation, aiding in the removal of metals such as chromium and cadmium (Lew et al., 2021). The effectiveness of NPs in metal chelation is influenced by their surface charge [136]. NPs have also been shown to protect the membranes of stressed plants, as indicated by reduced malondialdehyde (MDA) accumulation. Zinc oxide (ZnO) NPs increased the activity of antioxidant enzymes, such as superoxide dismutase (SOD), catalase (CAT), and ascorbate peroxidase (APX), while lowering MDA content in *Leucaena leucocephala* under cadmium and lead stresses (Venkatachalam et al., 2017). Wheat seedlings exposed to heavy metals experienced reduced MDA accumulation when supplemented with magnetic nano-Fe_3O_4, which also enhanced the activity of SOD and peroxidase (POD) (Konate et al., n.d.). Iron (Fe) NPs increased the accumulation of phytochelatins and glutathione in rice, leading to upregulated activity of antioxidant enzymes and glyoxalase, thereby enhancing the plant's tolerance to arsenic (Bidi et al., 2021). In finger millet and *Gossypium hirsutum* exposed to NPs, mineral acquisition and biosynthesis of photosynthetic pigments were restored, aiding in Cd and Pb stress tolerance. Additionally, ZnO NPs showed potential in removing heavy metal-contaminated media in rice (Sinha and Verma, 2021).

8 Toxicity Concern of Nanofertilizers

The safe and responsible use of nanoparticles (NPs) requires comprehensive risk assessments and nano-toxicological evaluations to guide their development (Fig. 16.3). Although toxicological evidence suggests that the nanostructure of a substance may pose greater risks than its non-nano form, further research is needed to confirm this hypothesis (Manjunatha et al., 2016). Developing scientific approaches to manage the toxicological effects of NP interactions with the environment and biological systems is imperative (Bayat et al., 2020). The protein corona (PC) plays a crucial role in regulating interactions between NPs and living systems or cells, and incompatible NP–PC interactions can lead to cytotoxic, genotoxic, and pathophysiological effects (Rajput et al., 2018). The type of protein forming the PC,

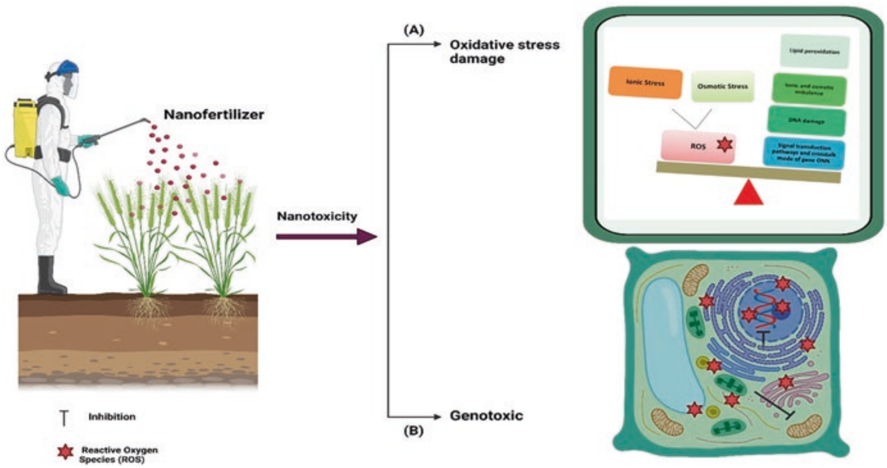

Fig. 16.3 The accumulation of nanoparticles in plant tissues can have adverse effects on plant growth and development due to the phytotoxicity effect in various plants part that leads to oxidative damage and genotoxic effect on DNA, chloroplasts and mitochondria and other cellular organelles. Therefore, the use of nanoparticle-based fertilizers should be carefully managed to minimize their potential toxicity to plants and to ensure sustainable agriculture

as well as the hydrodynamic size and charge of the protein, can positively or negatively influence the biocompatibility of NPs (Rajput et al., 2020a). NPs can exhibit phytotoxicity, leading to morphological and physiological effects on plants, such as shorter roots, damaged root tips, reduced biomass, and degraded chlorophyll. The response to NPs can vary among different plant species. For example, cucumber and guar showed an increase in chlorophyll content when exposed to titanium dioxide (TiO_2) NPs and zinc oxide (ZnO) NPs, respectively, while pea and tomato exhibited a decrease in chlorophyll content when exposed to ZnO NPs and silver (Ag) NPs, respectively (Tenzer et al., 2013). NPs can stimulate the generation of reactive oxygen species (ROS) in biological systems, disrupting normal biophysical functions and abiotic stress response mechanisms. NP exposure can also lead to genotoxic effects by influencing stress-related genes (Mirzajani et al., 2013). NP penetration results in various harmful effects, such as ion leakage and cell death, in addition to oxidative stress and anomalies in cell membranes brought on by ROS-induced lipid degradation. *Zea mays* lipid peroxidation was thought to be caused by ion leakage from CeO_2 NPs, whereas *Oryza sativa* did not exhibit this behavior at the same NP concentration (0.05–0.500 mg/L) (Rico et al., 2013). Plant–NP interactions can interfere with secondary plant metabolism, hormonal balance, and plant growth and development. NP treatment decreased the expression of genes related to phosphate loss, infections, and stress response in *Arabidopsis thaliana*, which may have affected the plant's capacity toward off diseases and form healthy roots (Rico et al., 2013). Additionally, NPs might change how nutrients are distributed, which hinders growth and development. The plant's access to nitrogen was reduced as a result of CeO_2 NPs' inhibition of rhizobacterial N_2-fixation, which slowed down normal growth and development (Schwabe et al., 2013). On the other hand, P and K were rendered more accessible in *Cucumis sativus* by TiO_2 NPs. When plants received 500 mg kg^{-1}, K and P levels increased by 35% and 34%, respectively (Servin et al., 2013). The accumulation of NP metal components in the environment and excess application of certain nutrients can have toxic effects on plants. Mechanisms to mitigate the stress caused by these factors include upregulation of antioxidant compounds and downregulation of genes responsible for metal transport to prevent further metal uptake by plants (Taylor et al., 2014). Recent studies on rice, tobacco, and wheat cultivars employing omics data in a systems' biological manner showed that metal NPs induce a generalized stress response, especially the oxidative stress response (Ruotolo et al., 2018). Even in the absence of phenotypic toxicity, high-throughput investigations of genetic and metabolic responses brought on by NP exposure are required to elucidate elements of NP phytotoxicity (Majumdar et al., 2015). Uncertainty exists regarding the effectiveness of the activated detoxification mechanisms in reversing the biomolecular stress brought on by NP exposure as well as the precise influence of NP type and interaction on nanotoxicity. Before examining the impacts of synthesized NPs in the plant system, it is crucial to fully understand their properties in order to avert any potential hazards, both to human health and the environment (Pradhan & Mailapalli, 2017). The toxicities brought on by NPs at the proteome level will be clarified by proteomic studies aimed at finding protein indicators (signature).

To ensure the effective utilization of nutrients with little to no associated toxicity, comprehensive in vitro and in vivo phytological testing is necessary before any nano-agriproducts can be commercialized (Pradhan & Mailapalli, 2017).

9 Conclusion

The worldwide threat of abiotic stress on green plants and agricultural crops, resulting from factors like urbanization, extreme weather conditions, pollution, and habitat loss, has led to the exploration of nanotechnology as a potential solution. This review focuses on the protective effects of nanoparticles (NPs) on crops and their mechanisms of accumulation in plants. NPs, which can be in the form of fertilizers, herbicides, or pesticides, are easily taken up by plants due to their small size and reactivity. Their chemical composition, particle size, surface area, and sensitivity influence their interactions with plants, resulting in various changes such as morphological, anatomical, and physiological alterations. These interactions have been found to enhance plant growth, biomass production, chlorophyll content, sugar levels, accumulation of osmolytes and antioxidants, expression of stress-related genes, and promotion of nitrogen metabolism. However, concerns have been raised regarding the accumulation of NPs in edible parts of plants and their potential adverse effects on the environment. Therefore, it is important to develop reliable evaluation methods to assess the impacts of NPs on both biotic and abiotic components of ecosystems. Additionally, studies are needed to determine safe exposure levels for humans and to develop cost-effective, nontoxic, ecologically safe, and biodegradable NPs before nanotechnology can be effectively implemented in agriculture.

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Chapter 17
Nanofertilizers: A Promising Approach to Boost Plant Health and Yield

Boudhyayan Chatterjee and V. Ravishankar Rai

1 Introduction

The soil and, consequentially, the entire ecosystem in most modern farming locations are under enormous pressure due to drastic increases in global food demand and our methods to cope with this demand so far. To keep their supply chains functional, popular agritech companies have continued to develop methods to exploit the soil to its maximum extent within production limits for several decades now. This ever-increasing bioburden has become a serious challenge for food processing companies, farms (food producers), and the various food regulatory authorities. The global population index currently predicts population growth to hit a target of approximately 11.2 billion by the end of the twenty-first century. Consequentially, millions of people will be automatically pushed below the poverty line, with serious consequences including an expected global food crisis, as officially predicted by the United Nations (2017). Hence, the present scenario brings much concern about the upcoming surge in global food demand and the agri-food industry expected to fulfill this demand, which has already surpassed the benchmark of being a 5-trillion-dollar industry (Lutz et al., 2015; Adisa et al., 2019).

Native agricultural practices need to improve if a more sustainable model of production is to be achieved. There is a growing consensus that nanotechnology will have a considerable influence on the agri-food sector, particularly in terms of food safety and sustainability, i.e., boosting the nutritional quality of the supply, and in agricultural production (Fig. 17.1) to ensure food security. Nanotechnology has been employed in the agricultural and food industries since 2003, where it has been used in food processing and preservation, crop production, animal feed improvement, and environmental monitoring (He et al., 2019). Although FDA-approved

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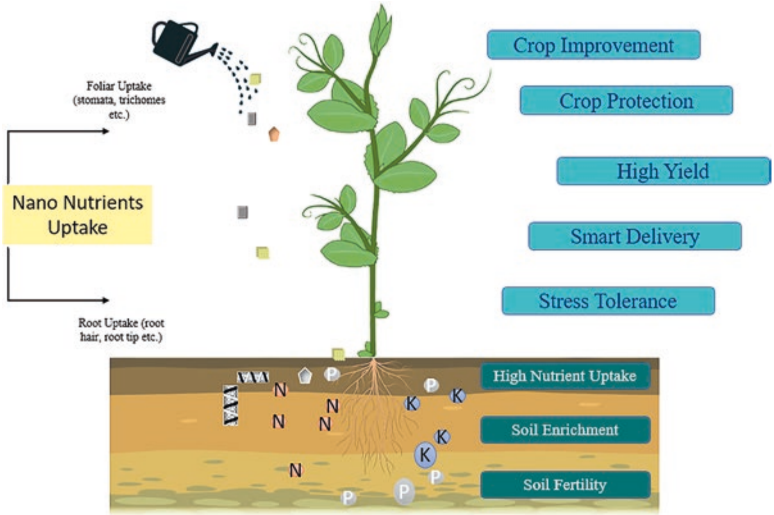

Fig. 17.1 Impact of nanofertilizers and its effect on crop

engineered nanomaterials (ENMs) are currently used in a few consumer items, their use in the agri-food industry has yet to be accepted or applied widely.

The primary goal of employing nanomaterials in agriculture is to increase agricultural yields through effective pest management and fertilization using various nanosensors, nanopesticides, and nanofertilizers (Prasad et al., 2017). Though nano-enabled herbicides, insecticides, and sensors are still in the early stages of research and development, a few commercial products containing mostly nanoparticles of micro- and macro-nutrients for plant growth, such as NanoPhos, NanoK, NanoZn, and Kocide 3000, are currently available on the market. Thus, this present article is aimed at featuring a comprehensive knowledge study about the current understanding and development in this field, which might help develop a compilation of the various factors of NFs that determine their role as sustainable, futuristic agricultural solutions.

2 Comparison of Biofertilizers, Chemical Fertilizers, and Nanofertilizers

There is a profound need to improve soil health to increase agricultural productivity which can cater to the ever-increasing global population. That's why farmers, particularly small-scale producers, often fail to keep up with the production requirements to earn a healthy profit. To increase the yield "per hectare of land," they use chemically synthesized fertilizers to improve the soil's vital nutrient contents like sulfur, nitrogen, phosphate, potassium, etc. The use of these chemical fertilizers seems to have become more prominent in the past few decades, but as the scope of research in the agriculture field has progressed, its long-term adverse effects on the soil, the wider ecosystem, and food quality have begun to surface. The primary concern of using these chemical fertilizers is that they are administered in large quantities, and most of the surplus remains unused by the plants (crops). The over-saturation of these surplus chemicals through fertilizers further leads to air, water, and soil contamination at various levels. Moreover, the overuse of such chemical fertilizers has damaged the soil profile by disrupting its natural microflora and underground food webs, with the result of inducing genetic mutations in various microorganisms, ecosystems, and biodiversities essential to a healthy ecology (Solanki et al., 2016; Raliya et al., 2018; Mandal & Lalrinchhani, 2021).

Biofertilizers are organic fertilizers made from living organisms such as bacteria, fungi, and algae. They provide essential nutrients to the plants (crops) while improving soil fertility by increasing the availability of nitrogen, phosphorus, and other minerals in the soil (Kole et al., 2013). Biofertilizers can be applied directly or indirectly through seed coating or inoculation with beneficial microorganisms, which help intensify crop yields compared to traditional chemical fertilizer administered alone (Malusa & Vassilev, 2014). In addition, they may also be sprayed onto leaves as a foliar spray, which helps increase the nutrient uptake efficiency and water retention capacity of the soil. Additionally, they reduce environmental pollution due to their organic nature and natural composition (Singh et al., 2016).

Nanofertilizers (NFs), on the other hand, are composed of nanomaterials that can be synthesized using physical (top-down) or chemical (bottom-up) methods of production, as well as biological approaches using plants, fungi, and bacteria. These particles gradually release nutrients over a period of 40–50 days, allowing for more efficient use by crops compared to traditional chemical fertilization that only lasts for 4–10 days. Due to the smaller size of the nutrient particles, they reduce the bio-transportation costs and enhance the abiotic stress tolerance when used with micro-organisms viz. nano-biofertilizers (Simarmata et al., 2016).

3 Advantages and Disadvantages of Nanofertilizers

Advanced and smart delivery systems with modern technologies made it possible to synthesize fertilizers that have enhanced nutrient uptake efficiency (NUE) with the usage of metallic nanoparticles for agro-industrial, physiological, and agronomical purposes (Fig. 17.2). With newer possibilities of nanobiotechnology toward improving agriculture in the years ahead, nanoparticles (NPs) can be used as NFs on plants and in the soil to boost crop performance (yield) by supporting the nutrients' delivery system and uptake with a more targeted approach facilitating multifunctional benefits and features. The gradual delivery of NFs extends soil health and fertility and reduces nutritional losses while maintaining the vital nutrient balance since there is a reduction in surplus chemicals leaching into groundwater, which consequently checks the toxicity concern and contamination

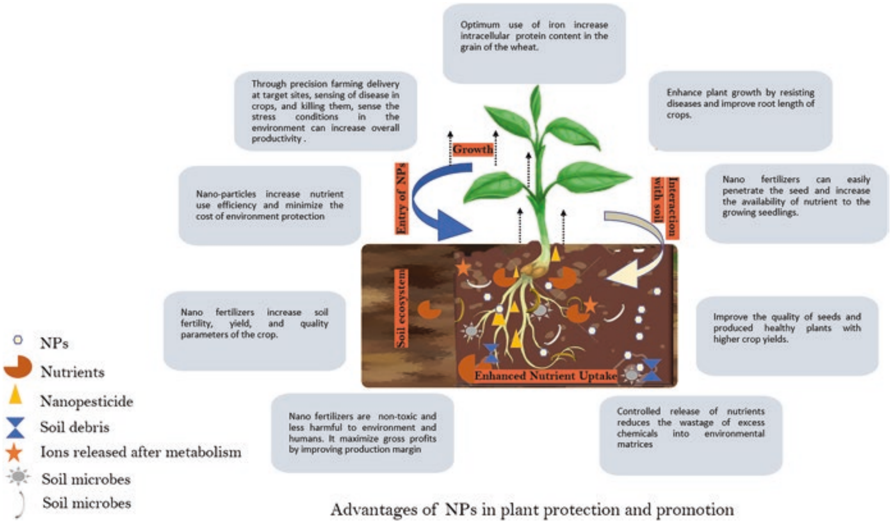

Fig. 17.2 Advantages of NPs in plant promotion

in the ecosystem. The high selectivity of zeolites allows them to deliver vital minerals in a gradual, regulated, and consistent manner as optimally needed by the plants for improved nutrient availability. However, its overall life cycle in agriculture was 24% shorter than when using traditional chemical fertilizers through the stages from sowing to maturity.

Though chemical fertilizers are still considered indispensable for high yields and overall crop productivity, nutrient materials are not retained within the biocycle. Studies have shown that almost 70% of the nitrogen content is lost by volatilization during field application, leaving only 20% available for the plants. Due to inadequate knowledge and improper vigilance, farmers use double the required quantity of fertilizer, which eventually gets washed out of the fields into water bodies, causing toxicity. The unrestricted usage of these chemicals to attain better yields is eventually detrimental to soil health, crop productivity, and agricultural performance. Thus, fertilizers with nanoscale particles are currently finding ground as an alternate choice over conventional fertilizers (Fig. 17.2). In comparison to conventional fertilizers, the nutrient release cycle of NFs continued over 6–7 weeks, whereas synthetic fertilizers release the same nutritional gross within a week. Such a rapid release of surplus nutrients in the soil without retention eventually reaches water bodies and leads to bioaccumulation. NFs afford balanced nutritional release and combat various environmental parameters to enhance the physiological fitness and performance of plants and crops. Comparatively, nanoscale fertilizers result in higher yields against a lesser use of natural resources, produce foods with higher nutritional values, enhance the soil's microbial diversity, enhance native nutrient mobilization, and reduce the demand for fertilizer quantity (Raliya et al., 2018).

4 Synthesis of Nonfertilizer

Nanoparticles containing nutrients and essential growth-promoting components for plants at the 'nanoscale' is the major approach of NFs. The two major synthesis approaches are called "top-down," wherein materials are broken down to nanoscale through grinding, etching, and milling, and "bottom-up," whereby small molecules work as a precursor material and self-assimilate to create a functional nanoscale material (Abbasifar et al., 2020). Furthermore, these two approaches can be categorized into different functional domains according to their chemical, physical, or biological synthesis methods. While physical synthesis and biosynthesis methods mostly have a "top-down" approach, but chemical synthesis techniques typically have a "bottom-up" approach (Cota-Ruiz et al., 2020; de França Bettencourt et al., 2020; Ramírez-Rodríguez et al., 2020). It has been reported that both the methods hold up well for creating NFs. A few of these have been mentioned by Shebl et al. (2019), wherein manganese, zinc, and iron NFs were obtained via the green microwave-assisted hydrothermal method using nitrate precursors with a size distribution between 20 and 60 nm. When used for squash plant growth, a similar synthesis method for the manganese–zinc ferrite NF resulted in significant improvement in overall plant's quality, as reported by Shebl et al. (2020). The gradual and controlled release of nutrients to reduce chemical waste and environmental hazards is also a contemplation for researchers in NF synthesis. In view of this conception, an ionotropic gelation method when applied to silicon-encapsulating chitosan NFs resulted in a better seedling vigor index and overall well-being of the crops when supplemented to maize plants (Kumaraswamy et al., 2021). Furthermore, carbon nanofibers delivered by Cu–Zn micronutrients encased on PVA-starch substrates were used to design slow-release NFs.

However, such methods need sophisticated high-end equipment to combine multistep synthesis methods. In synthesis, the micronutrients and carbon nanofibers were dispersed in situ on the substrate during the stage of polymerization. This process involves both acid and heat treatments, followed by a chemical vapor deposition stage, and the product is finally achieved through the top-down approach called ball milling (Kumar et al., 2020a). An ideal example of formulating NFs devoid of any hazardous materials can be seen in the study carried out by Jahangirian, where nanocomposite was formulated using a quick green synthesis method to combine zeolite and iron oxide (Fe_2O_3) nanoparticles by loading in Fe_2O_3 nanoparticles onto the Zeolite surface (Jahangirian et al., 2020).

4.1 Physical Synthesis of Nanofertilizers

Physical synthesis processes consume less time and have been used for a long time in the production of several nanoparticle-oxide complexes of cobalt, aluminum, titanium, and chromium (Nisar et al., 2019). Some widely used physical synthesis methods are the vibrating ball mill (Campbell et al., 1970; Maissel & Glang, 1970), the planetary ball mill (Nieman et al., 1989), the high energy ball mill (Konrad et al., 2001; Qazi & Javaid, 2016), the low-energy tumbling mill (Garrigue et al., 2004), the attrition ball mill (Qazi & Javaid, 2016), and the gas condensation method (Uhm et al., 2007). While being basic and technically simple synthesis technique, this top-down approach has certain drawbacks, such as source–precursor incompatibility, more scope for impurities, uncontrolled size distribution, and the need for high-cost equipment, etc., often restrict its scalability.

4.2 Chemical Synthesis

The most common bottom-up approach for synthesizing nanoparticles is through chemical synthesis via various organic and inorganic reducing agents. Chemical precipitation, vapor deposition, solid–gel techniques are some of the mainstream chemical synthesis methods employed to produce various metal oxides, sulfides, borides, and other nanoparticles (Toksha et al., 2011; Rajonee et al., 2016; Qureshi et al., 2018; Tarafder et al., 2020). Compared to the physical synthesis approach, chemical synthesis ensures more uniform particle sizes during production, reduces the chance of impurities, involves lower temperatures, and is a comprehensively more controlled approach to the total synthesis process (Belal & El-Ramady, 2016).

4.3 Biological Synthesis of Nanoparticles

Biosynthesis processes are more ecologically benign, thus the current nanobiotechnological sciences is giving much attention on its scalability for wider acceptance (Saratale et al., 2018). Here, living biological entities such as bacteria, fungi, and algae are employed to develop nanoscale synthesis processes through biomanufacturing. Biological synthesis of nanomaterials is a bottom-up approach, whereby various biobased precursor materials are used as primary reducing materials that lower environmental toxicity. Various plant parts, including the leaves, roots, fruits, and extracts, are used in the synthesis of nanoparticles or nanomaterials (Makarov et al., 2014). The synthesis of NPs through biological organisms is the key to eventual agricultural sustainability. The underexploitation of the natural potential of these tiny little organisms has severely delayed our approach to eco-friendly agriculture. However, mankind is gradually unraveling remarkable natural possibilities within the scope of the nanotechnology field. The biological synthesis of NPs has proven to be ecologically safer, far less toxic, and more cost-effective compared to all other nanomaterial synthesis techniques in agricultural applications.

Bacteria
Currently proposed bacterial NP synthesis mechanisms include metal-resistant bacteria with unique biomolecular feature that enable metal ions to be bio-transported from the extracellular environment via metal-binding proteins and delivered internally to the cytoplasm of bacterial cells (Marooufpour et al., 2019; Nasrollahzadeh et al., 2019). Positively charged metal ions from the external environment attach to negatively charged polyanionic functional groups that form the structural and functional components of bacterial cell walls (Ali et al., 2020) and is referred to as biosorption, whereby metal binding via processes like electrostatic interactions, ion exchange, physical adsorption, or complexation occurs (Mukherjee & Nethi, 2019). Biomolecular agents like enzymes (reductases) synthesize stable NPs by reducing and stabilizing metal ions either on the cellular surface or within the cytoplasm.

Fungi
Synthesis of NP via fungi is similar to bacterial synthesis processes. Synthesized NPs vary in size and shape depending on the type and amount of fungal starter culture used. They either get synthesized by biosorption through the mycelia (extracellular) or vide various intracellular enzymes and complex proteins (Jeevanandam et al., 2016; Akther et al., 2019; Feroze et al., 2020; Noor et al., 2020). Extracellular synthesis of NPs tend to be more advantageous, since it eliminates additional processes like extracting NPs from the fungal biomass and purification before application. A major setback of fungal-driven NP synthesis compared to bacterial synthesis is its higher duration of culturing (between 24 and 120 h) (Neethu et al., 2019).

Algae
Algae are widely available, simple to cultivate, and are potentially sustainable source of biological nontoxic reducing agents (Ali et al., 2020). Both living and dead microalgal biomasses can be used to synthesize metallic NPs. Alternately, boiling or heating the cultures can be used to extract biomolecules from microalgal cells. The extract is further incubated after combining them with precursor metal salt solutions to create NPs (LewisOscar et al., 2016). However, compared to other biological techniques, research investigating algae-driven synthesis of NPs is few. Further research should examine this organisms' capacity to synthesize metallic NP as eco-friendly sources of reducing agents.

5 Types of Nanofertilizers

5.1 Macro Nanofertilizers

5.1.1 Phosphorus Nanofertilizer (P-NF)

The average user experience regarding the efficiency of traditional version of P-fertilizer is not satisfactory enough to meet the need (15–20%). On the other side, P-NFs have much higher P-use/uptake efficiency (PUE) which reduces unregulated wastages. Study has shown that, using the wet chemical process synthesis method, hydroxyapatite NFs can be manufactured which considerably improves the release of NFs in soil in a controlled manner.

The application of these hydroxyapatite NF on surface-coated zeolite has been reported to contribute a significant amount of growth improvement of *Adansonia digitata* plant (Soliman et al., 2016), and showed enhanced productivity of soybean plant (*Glycine max*) (Liu & Lal, 2014) over conventional P fertilizers. Compared to the conventional fertilizers, NF, like apatite, results in lesser amount of environmental damage. The weaker interaction of NFs with the soil components prevents it from getting absorbed by the soil itself and maintains it's available in the soil solution and root rhizosphere for plant uptake. Whereas the charged compounds ($HPO4^{2-}$, Ca^{2+}, and $PO4^{3-}$) present in traditional fertilizer shows stronger interaction with soil components. Apart from productivity boosting of the crops, these P-NFs are extremely less bioavailable for toxic fungus present in water bodies, which pose far less risk of eutrophication for extended period.

5.1.2 Potassium Nanofertilizer (K-NF)

Potassium (K) regulates water transport, carbohydrate and enzyme production, cell and tissue strengthening, photosynthetic capacity enhancement, nitrate absorption, blooming, and better crop response (Nido et al., 2019). With the help of nanotechnology, agriculture is predicted to reach its highest potential. In a few studies, the outcome of K-based NF application to different plants like basil, summer squash, and garden peas has been reported. All these studies exhibited massive possibilities in boosting leaf area, chlorophyll content, intensifying leaf number, improving product quality, developing resistance to pests and drought, and also in biomass production. They are effective either via foliar spray, direct application in soil (at a dosage concentration of 1/1000), or in a form called Lithovit for boosting photosynthesis (Ghahremani et al., 2014; Gerdini, 2016). A K-based NF composed of methacrylic acid NFs with chitosan vividly promotes root elongation in pea plants when tested over conventional fertilizer (Khalifa & Hasaneen, 2018).

5.1.3 Calcium Nanofertilizer (Ca-NF)

Calcium (Ca) is a crucial component for seed growth, mineral retention in soil transportation, neutralization of dangerous chemicals, and cell wall stability. To examine the ability of $CaCl_2$, which is used as a traditional calcium supplement, foliar spraying during post-harvest stages on apple plants improves the overall quality of the fruit (Ranjbar et al., 2020). Also, a higher yield was noticed in the pomegranate plants after the application of Ca-NFs (Davarpanah et al., 2018). A 500 mg/L Ca-NFs spray accelerated blooming by 15 days and floriation by 56.3% in comparison to the control treatment (Seydmohammadi et al., 2020). In the experiment with groundnut crops, $CaCO_3$-NFs of different sizes (20–80 nm) at 160 mg/L concentration were used to test against Ca $(NO_3)_2$ at a concentration of 200 mg/L Ca, and the results showed improvement in fresh biomass production in plants, Ca absorption, and transport from root to shoot (Liu & Lal, 2015). Moreover, when urea was added to calcium phosphate nanoparticles (Ca_3 $(PO_4)_2$ nH_2O) to control the amount of nitrogen, grapevine production increased and overall plant health improved, as reported by Gaiotti et al. (2021).

5.1.4 Magnesium Nanofertilizer (Mg-NF)

Magnesium (Mg) is an integral part of the structure of chlorophyll. Due to its high mobility and leaching nature, it is difficult to hold magnesium in soil. Thus, over conventional Mg-based fertilizers, magnesium hydroxide NPs at 500 ppm showed improved seed germination along with better plant growth in maize (Shinde et al., 2020). Due to a slight better soil retention property of these NFs compared to traditional ones, even direct field application also exhibited higher photosynthetic efficiency and productivity in cowpea plants after applying 0.5 g/L Mg-NPs combined with Fe-NPs (Delfani et al., 2014).

5.2 Micro Nanofertilizers

The minerals which plants use less than 100 ppm for maintaining overall plant and soil health such as zinc (Zn), iron (Fe), molybdenum (Mo), nickel (Ni), Copper (Cu), etc. are considered as micronutrients These micronutrients (<5 mg/L) along with macronutrients can be applied as composite fertilizers in a form of soluble salts.

5.2.1 Iron (Fe) Nanofertilizer (Fe-NF)

Iron is involved in diverse biological processes inside plants. But, iron is mostly present in an insoluble form in soil, and the bioavailability for plants is less than what is required. This concern of scarcity can be resolved by applying NFs made up of various iron derivatives. Many reports of NF application in terms of iron uptake, yield, productivity, and seed generation after using Fe-based NFs have come to surface. A considerable increase in growth indices, photosynthetic pigment, and total protein content after using iron oxide NFs with a size distribution of 30 μm was reviewed by Askary et al. (2017). Nanotechnology-based Fe-oxides and salts are free from any unnecessary growth hormones to cause premature senescence. These are capable of functioning in a wide range of pH, providing a gradual and continuous release of Fe. The activities of these NFs in very low concentrations have decreased the overall wastage of chemicals. A study by Ghafariyan et al. (2013) showed that low concentrations of superparamagnetic Fe-NPs have increased the chlorophyll contents in sub-apical leaves of soybeans in a greenhouse test under hydroponic conditions, suggesting that soybean could use this type of Fe-NPs as a source of Fe and reduce chlorotic symptoms of Fe deficiency. A similar result was observed in the study with hematite NFs (α-Fe_2O_3-NFs) and ferrihydrite ($5Fe_2O_3 \cdot 9H_2O$) NFs in a hydroponics system for maize and soybean cultivation as well (Ghafariyan et al., 2013; Pariona et al., 2017). A biocomplex of Fe-NFs (Fe O_3) with Cornelian cherry fruit extract also resulted in increased biomass of longer roots and shoots in barley plants (Rostamizadeh et al., 2020).

5.2.2 Manganese NFs (Mn-NF)

It has been demonstrated that Mn-NFs are a more effective source of Mn micronutrients than the $MnSO_4$ salt that is sold commercially (Elmer et al., 2018). Mn is essential for the anabolic process of photosynthesis, the catabolic process of respiration, and the metabolism of nitrogen in plants, resulting in better N acquisition over bulk fertilizers (Pradhan et al., 2013). In a study, Mn-NF was used over commercially available $MnSO_4$ salt, and increased shoot (38%), and root growth (52%), were observed in the mung bean plant, which augmented its photosynthetic index (Pradhan et al., 2013). The application of these NFs also develops resistance against infection and promotes productivity. Elmer et al. (2018) demonstrated with watermelon plants after Mn-NF treatment suppressed disease infection and promoted productivity by 22% over commercially available fertilizer. Also, the application of Mn nano-oxide either individually or even combined with Fe nano-oxide on summer squash results in a significant improvement in production quantity (Shebl et al., 2019).

5.2.3 Cupper NFs (Cu-NF)

In plenty of physiological processes inside plants, such as mitochondrial respiration, cellular transport, antioxidative activity, protein trafficking, and hormone signaling, copper (Cu) is a vital mineral in demand, which can be effectively met with Cu-NFs (Rawat et al., 2018). While testing with actively dividing onion cells, biosynthesizing Cu-NF from a fruit-based extract of “citron” at a concentration of 20 μg/mL improved the mitotic index (Nagaonkar et al., 2015). Tomato growth and productivity were enhanced by chitosan hydrogel-combined Cu-NFs also, which improved the nutritional makeup and lycopene pigment level of fruits (Juarez-Maldonado et al., 2016). Cu-NF-treated seeds had increased protein levels, which improved wheat’s ability to withstand stress (Yasmeen et al., 2017). According to Shah and Belozerova (2009), the addition of metallic Cu-NPs to the soil (130 mg/kg) considerably enhanced the growth of 15-day lettuce seedlings by 40%; however, higher Cu accumulation can eventually cause phytotoxicity.

6 Nanobiofertilizers

To enhance soil productivity one or more microorganism, biofertilizers are being used. Fixing atmospheric nitrogen, solubilizing phosphorus for plant uptake, and simulating plant growth are some of the major functionalities achieved by the application of biofertilizers instead chemical synthetic fertilizers. With time, a few major drawbacks of biofertilizers have been observed, which include the following:

(a) Shelf life of biofertilizers is less.
(b) Stability of biofertilizers in the field declines over time drastically.
(c) Excessive heat can cause mechanistic damage to the biofertilizer components.
(d) Deteriorating microbial load after the field application is limiting its use.

To increase plant growth and also to address all of these emerging concerns, a combination of biofertilizers in miniaturized nanoparticles was made, which is known as nanobiofertilizer (Simarmata et al., 2016). The gold nanoparticles with plant growth-promoting rhizobacteria during a test to examine the effect of nanobiofertilizer were reported to exert positive effects on overall plant growth and productivity (Malusá et al., 2012; Shukla et al., 2015). Coatings with polymeric nanoparticles can also be used to develop desiccation-tolerant formulations, which will eventually improve the life span of products as reported by Kaushik & Djiwanti, 2017. Further, to improve the delivery patterns and release of bioactive materials used in plant promotion, a coating of hydrophobic silica nanoparticles on the water-in-oil emulsion has shown effective improvement in shelf-life elongation by reducing desiccation (Kaushik & Djiwanti, 2017). In addition to improving delivery strategies, *Trichoderma* and *Pseudomonas* species coated with nanoclay are effective in preventing fungal and nematode infections in rabi crops, giving rise to an abiotic stress tolerant crop variety (Mukhopadhyay & De, 2014). Outreaching the potential of nanobiofertilizers has enabled farmers to decrease seedling rates with "smart seed" technology. Smart seed is a nano-encapsulated material (alginate and starch) containing specific bacterial strains inoculated together. These seeds, after spreading over the field, get a primary barrier of protection from the environment and germinate upon achieving the desired germination temperature, soil pH, and moisture conditions (Chinnamuthu & Boopathi, 2009).

Though the application of nanotechnology has largely affected modern-day agricultural practices positively, a few fundamental problems in the production of nanobiofertilizers have remained a concern for researchers. By and large, using nanobiofertilizers has almost circumvented all the limitations of traditional biofertilizers. Still, further research in terms of manufacturing material, dosage, time of exposure, etc. needs further investigation. The NFs of macroscopic filter walls are made of radially aligned carbon nanotubes, which are capable of absorbing *Escherichia coli* only and need further investigation to capture other bacteria as well (Vandergheynst et al., 2007; Simarmata et al., 2016).

7 Effects of Nano-/biofertilizers

Lack of chemical handling awareness in terms of usage, dosage selection, and application mode has caused some of the major limitations for these scientific products. Mostly, the slow response of biofertilizers compelled the farmers to use chemical-based fertilizers to keep up with the supply of the ever-growing food market. Continuous use of harmful fertilizer leads to long-term damage for both producers and consumers. Biofertilizers use live microorganisms as their major functional components. Thus, the proper administrative conditions are crucial and should be maintained for obtaining a consistent rate of growth, like an amiable pH, temperature, storage conditions, etc. Herein, we have summarized the effect of nanomaterials on crop growth and productivity, germination, soil and set treatment.

7.1 Nanotechnology on Plant Growth and Productivity

The investigation about the effect of nanotechnology as a nanofertilizer for direct usage has shown remarkable development in different reports. NPs in the form of multiwalled carbon nanotubes or oxides of different metals like Si, Ti, Fe/Si, and zeolite, when examined on different cereal crops such as wheat, barley, maize, groundnut, and soyabean, led to higher yields and improved plants health (Changmei et al., 2002; Najafi Disfani et al., 2017; Joshi et al., 2018; Manjaiah et al., 2019). Furthermore, these metal oxide NPs and hydroxy fullerenes responded well to quality and growth enhancement in different plants as reported in studies (Gilbertson et al., 2020; Shang et al., 2019; Shojaei et al., 2019).

7.2 Nanotechnology in Promoting Crop Yield

The application of calcite-NF at a concentration of 30 ppm via foliar application has shown an improved flow rate, pollen viability and quality, and also rate of germination compared to the control, as found in a study with *Vitis vinifera* plant (Sabir, 2015). These NFs can be administered in different ways instead of direct usage. Spraying at a concentration of 50 mL/L on mango plants has improved the number of panicles and prevented mango malformation (Zagzog et al., 2017). Foliar application of a mixture of zinc (120 ppm) and boron (6.5 ppm) on pomegranate plants uplifted fruit production per unit plant by 15–38% and the overall output of pomegranate production by 17–44%, as reported by Davarpanah et al. (2018). The date palm's yield and branch weight rose after a combined application of boron nanoparticles (B-NPs) (0.05%) and wheat seed sprout extract (1.0%) (Refaai, 2014), which aided in enhanced fertilization of the date palm. When used as a foliar spray of

(0.005–0.04%) Zn, Fe, Mn, and B NPs, they increased the fruit output and quality of date palms as compared to the control (El-Sayed, 2018).

7.3 Nanotechnology in Soil and Set Treatment

There are two distinct methods used to treat soil: either the biofertilizers are combined evenly with compost or these composites are directly spread on the ground before planting (Debnath et al., 2019). A foliar spray on the plants is another way to apply it indirectly. It was noted that nanofertilizers aid in facilitating the free movement of nutrients in the soil, which further enhances the absorption of nutrients by roots. Due to the continuous supply and controlled release of nutrients, soil gets enriched with vital minerals and nutrients, higher enzyme concentrations, and microbial diversity, as found in green pepper production. Teng et al. (2018) reported a 30% higher rate of dehydrogenase and catalase enzyme activity than the control plant. To evaluate the soil quality, Sahar et al. (2020) used nanofertilizers along with compost materials consisting of NPK (sodium, phosphorus, and potassium) and applied them through the foliar technique. The findings suggest that Fe has a greater effect on determining the seed weight than other materials in the test mixture. To cure any cut pieces in the plant set, treatment is carried out, where banana sucker is used as a base and sugarcane set is used in combination with a cut piece of potato and mixed with culture solution. To prepare the culture suspension, 1 kg of biofertilizer with 40–50 L of water is mixed before application (Wahane et al., 2020) for a set treatment.

7.4 On Biomass

The total assimilated organic matter above and below the ground surface at any given point of time is considered as the total biomass of the plant. Gathering biomass and yielding higher productivity are often used interchangeably, but in terms of improvement in both cases, the application of NP in fertilizers resulted in a positive effect on productivity. A study by Yuan et al. (2018) reported that photosynthesis has been positively affected in capsicum plants by the application of FeNPs. Even at the molecular level, TiO_2 NPs can exhibit changes that facilitate growth-promoting factors in switchgrass (Boykov et al., 2019). Likewise, a study by Mehrangiz et al. (2014) showed enhanced productivity of *Arachis hypogaea* when applied with nano-chelated molybdenum. The combination of nano-Zinc chelate and nanobiofertilizer through foliar application in the ground soil was reported to improve maize production. Among different NFs tested by Ibraheem et al. (2021), NFs containing K, Zn, and Fe produced noteworthy results compared to other combinations.

8 Abiotic Stress Tolerance

8.1 Drought

Various nonbiological stressors such as drought, salinity, temperature, etc. are known as abiotic stress factors for plants, which are usually detrimental to their productivity and performance (Wang et al., 2003; Rajput et al., 2021). The applicability of synthesized nanomolecules in a nanofertilizer form has been well discussed in many studies. In response to different abiotic stresses, studies have been conducted in various pilot projects using test plants like wheat, strawberries, cotton, maize, etc. Ghassemi and Farahvash (2018) found that ZnO NPs (100 ppm) by foliar application positively affected plant height with increased leaf relative water content (LRWC) and productivity in wheat during its flowering period or anthesis. Moreover, a study demonstrating the capability of salicylic acid (SA) and Fe NPs in a limited water supply during the vegetative growth of strawberry plants came up with better plant performance and yield (Mozafari et al. (2018)). The morphological characteristics and total biomass yield in a water-deficit condition of a cotton plant were carried out by Shallan et al. (2016), where a foliar application in a mixture of SiO_2 at 3200 ppm and TiO_2 at 50 ppm boosted the plant's growth and improved its survival. The composition of CeO_2 NP (10 ppm) has also proven its efficacy on sorghum plants by increasing its photosynthetic efficiency (38%), grain yield (31%), and pollen germination (31%), and reduced drought-stimulating factors like the accumulation of superoxide radical (41%) and H_2O_2 (36%), as reported in a study by Djanaguiraman et al. (2018a). Within experimental setups severe water stress-conditioned plants administrated with, TiO_2 and Zn NPs separately promote gluten and starch levels in wheat and maize plant and enhance nutritional value paved the usage of NPs against stress management (Mittal et al., 2020; Fellet et al., 2021).

8.2 Salinity

Most food crops are threatened by salt water, and despite surplus water bodies all over the globe, only less than a few per cent of water can be used in cultivation. The presence of salt in water hinders the water absorption capacity of the plant by impairing plants' cellular network. High salt content produces ionic and osmotic stress on plants, that leads to membrane injury and deactivation of vital enzymes (Hasanuzzaman et al., 2013; Adisa et al., 2019). Studies have demonstrated few insights where the cocultivation of plants with NF under saline stress showed reduced detrimental effects. The use of Cu-NP along with chitosan-polyvinyl alcohol hydrogels in the tomato plant boosted the antioxidant and ionic capacity to promote overall productivity of the plant by reducing saline stress responses (Hernández-Hernández et al., 2018b). These NPs are even effective in germination stages, as shown by Alsaeedi et al. (2017) which decreased the Na^+

stress on the common bean *Phaseolus vulgaris.* Zn-Fe oxide NPs were also found effective in seed germination at increased salinity compared to control by 17% (Babaei et al., 2017). Another metal oxide of Zn, in ZnO-NP, developed salt resistance in the treatment at callus culture of many tomato cultivars (Alharby et al., 2017; Adisa et al., 2019). Increased tolerance for salt was also noticed in squash plants by applying silicon-NPs, as shown by Siddique et al. (2014). Furthermore, NPs in developing morphological features under high salt conditions can be observed in maize, resulting in the growth of stem height (4.8-fold) and biomass (1.2-fold) compared to untreated (Mutlu et al., 2018).

8.3 Temperature

Abiotic heat stress occurs when the temperature of the environment is too high for the plant to survive and leads to changes in the characteristics of the plant, such as its lipid structure and protein–lipid interactions (Younis et al., 2020). To survive under excess light intensities, plants must balance between photosynthetic efficiency and homeostasis, a strategy to maintain a stable internal environment and remain fully functional. Many reports have discussed the effects of nanofertilizers on plants under abiotic stress conditions like high temperatures and light intensities. In the report of Younis et al. (2020), it was shown that Si NPs can maintain morphological traits by boosting root (5–5.4%) and stem length (22–26%) in a wheat plant as a characteristic of protection during temperature stress. Interestingly, a study by Djanaguiraman et al. (2018a) exhibited that even under extreme light and temperature conditions (32/22 °C), the consistency of pollen germination, fruit production, and even intracellular plant hormones (antioxidant hormones) can be maintained at their active states by using a foliar spray of Se NPs (selenium) after testing on a sorghum plant. High temperatures for an extended period decrease total oxidative content, which impacts cellular damage. To counter this abiotic stress threat, NPs were employed and tested against maize plants. The ZnO-NPs during excess light and at 25 °C maintained the plants' performance at regular APX activity (24–57%) López-Moreno et al. (2017). The effect of nano-TiO_2 on electron transport rate, known as Fv/Fm values of tomato leaves, was studied. Fv/Fm, which stands for the maximum quantum efficiency of photosystem II (PS II) and measures how efficiently plants can convert light energy into chemical energy during photosynthesis, was found to have positive implications for the NP administration (Qi et al., 2013).

9 Nanofertilizer in Crop Protection

The food and agricultural industries are the economic backbone of countries. The massive growth in the global population, along with the effects of climate change, low agricultural production, deterioration of natural resources, and substantial post-farm losses, put further strain on the food and agriculture sectors. Agro-nanotechnology might be a potential technique for addressing agricultural and food-related issues such as disease control, effective herbicides and pesticides, nutrition management, plant breeding, soil feature modulation, and waste management. Consistent development in the field of nanotechnology, especially in agricultural techniques, has forecast its great potential. An eco-friendly approach with nano-technological interventions like nanofertilizers, nanoencapsulation, seed germination, and nanosensors has been proven to be beneficial in various studies (Shang et al., 2019). The prospective use of these nanoscale materials might help forge a radical transformation of the traditional age-old processes into a more value-added, efficient system. A few of the reported nanofertilizers used in various crops are given in Table 17.1.

9.1 Crop Protection

Plants under stress often fail to produce their desired yield, maintain productivity, and increase their net output. Abiotic salt stress aggravates the accumulation of harmful reactive oxygen species (ROS), and as a result, intensification of hydrogen peroxide, hydroxyl ions, and superoxide anion weakens the plant cells, leading to premature death. In protection against such a stress factor, nanobiofertilizer in the form of AgNP was used to counter this threat on wheat plants, which regenerated the yield by reducing the oxidative stress (Shang et al., 2019). It was also reported that even nanoenzymes, i.e., polyacrylic-coated cerium oxide NPs (nanoceria), are also capable of scavenging hydroxyl ions, providing antioxidant properties (Wahid et al., 2020). The applications of nanotools in agricultural management and the implementation of nanobiosensors have demonstrated enormous potential for agricultural usage (Sivarethinamohan & Sujatha, 2021; Duhan et al., 2017). In terms of consistent monitoring of plant disease and precision farming, nanoforms of silver, carbon, alumino-silicates, and silica can be used, which are reported as sustainable tools for crop protection (Chinnamuthu & Boopathi, 2009).

9.2 Pest Management

The major advantages of using these nanomaterials as pesticides are their ability to be absorbed easily, on-target delivery, and activity at extremely low dosages. Several reports have mentioned the self-effectivity of these nanoparticles with broad-spectrum infective properties. Different NPs have different modes of activity based on size and surface charge. The nano-sized metal oxides, while encountering pathogens, promote cell wall degradation, causing a nick, which eventually accumulates ROS at the cellular level, causing a breakdown of a cell organelle, degrading biomolecules, and altering genetic material, leading to apoptosis and cell necrosis.

Table 17.1 Applications of nanofertilizers in agriculture

Sl. no	Name	Nanomaterials	Plant	Advantages	References
1	Nanozeolite-based composite *fertilizer*	NZCF	Lettuce (*Lactuca sativa*)	Enhanced nutrient availability in soil, great potential for promoting plant growth	Khan et al. (2021)
2	Chitosan-silicon nanofertilizer	CS-Si NF	Maize (*Zea mays*)	Higher growth and yield, increased seedling vigor index, induced antioxidant-defense enzymes' activities	Kumaraswamy et al. (2021)
3	Nanochitosan nitrogen, phosphorus, and potassium (NPK) fertilizer	Nanochitosan-NPK	Wheat (*Triticum aestivum*)	Increased yield variables	Mohammad Abdel-Aziz et al. (2018)
4	Iron-based nanofertilizer	Fe_2O_3	Peanut (*Arachis hypogaea*)	Increased the biomass, chlorophyll content, and total Fe content	Rui et al. (2016)
5	Iron-based nanofertilizer	Fe_3O_4	Cucumber (*Cucumis sativus*)	Reduction of biomass and enzyme activities; increase in biomass, antioxidant enzymes superoxide dismutase and peroxidase	Konate et al. (2018)
6	Iron-based nanofertilizer	Fe	Bell pepper (*Capsicum annuum*)	Low concentrations promote plant growth, altering the leaf organization and increasing the chloroplast number and grana stacking at high conc. NPs aggregate and block the cell wall	Yuan et al. (2018)
7	Iron-based nanofertilizer	Fe_3O_4	Barley (*Hordeum vulgare*)	Enhanced the plant growth; increased some phenological parameters, such as chlorophyll, total soluble protein, number of chloroplasts, and dry weight	Tombuloglu et al. (2019)

(continued)

Table 17.1 (continued)

Sl. no	Name	Nanomaterials	Plant	Advantages	References
8	Iron-based nanofertilizer	Fe_2O_3	Moldavian balm (*Dracocephalum moldavica*)	Increased leaf area, length, and fresh and dry weight of the shoot and root under salinity stress	Moradbeygi et al. (2020)
9	Iron-based nanofertilizer	Organically coated Fe_3O_4	Tomato (*Solanum lycopersicum*)	Increased plant growth and yield, plant height, fresh shoot biomass	Raiesi-Ardali et al. (2022)
10	Copper-based nanofertilizer	CuO, $Cu_3(PO4)_2 \cdot 3H_2O$	Watermelon (*Citrullus lanatus*)	Reduced *Fusarium* wilt disease and also increased total wet mass, an important measure of plant growth	Jaya Borgatta et al. (2018)
11	Copper-based nanofertilizer	Cs-PVA, Cu NPs	Tomato (*Solanum lycopersicum*)	Enhanced plant growth under salt stress, activates the antioxidant defense mechanisms	Hernández-Hernández et al. (2018a, b)
12	Copper-based nanofertilizer	Cu	Cucumber (*Cucumis sativus*)	Carbon and nitrogen metabolism are significantly disturbed, affecting the levels of amino acids, carbohydrates, and other important biomolecules	Zhao et al. (2016)
13	Copper-based nanofertilizer	Cu	Onion (*Allium cepa*)	Produced significantly higher root length, shoot length, germination percentage, chlorophyll content, fresh weight, and dry root weight and enhanced growth	Bhanushali Mansi et al. (2017)
14	Copper-based nanofertilizer	Cu	Kidney bean (*Phaseolus vulgaris*)	Diminished chlorophyll production and nutrient element accumulation	Apodaca et al. (2017)

(continued)

Table 17.1 (continued)

Sl. no	Name	Nanomaterials	Plant	Advantages	References
15	Copper-based nanofertilizer	CuO	*Oryza sativa*	Germination rate, root and shoot length, and biomass decreased Photosynthetic rate, transpiration rate, stomatal conductance, maximal quantum yield of PSII photochemistry, and photosynthetic pigment contents declined	Da Costa and Sharma (2016)
16	Copper-based nanofertilizer	CuO	Lettuce (*Lactuca sativa*)	Modification in photosynthesis system with increased transpiration rate and higher stomatal conductance	Wang et al. (2019)
17	Copper-based nanofertilizer	CuO	Rice (*Oryza sativa*)	Cultivar-dependent responses upon exposure to Cu-based materials in grain. The decrease of nutritional elements was mainly found in wild rice, but not in cultivated rice	Deng et al. (2022a)
18	Copper-based nanofertilizer	CuO	Soybean (*Glycine max*)	Foliar application increased yield but soil application did not. The nutrient quality of soybean seeds was not affected by nano-Cu-based foliar exposure	Deng et al. (2022b)
19	Copper-based nanofertilizer	Cu	Soybean (*Glycine max*)	Improved the plant height and biomass, decreased the root nitrogen and phosphorus contents	Xiao et al. (2022)

(continued)

Table 17.1 (continued)

Sl. no	Name	Nanomaterials	Plant	Advantages	References
20	Copper-based nanofertilizer	CuO	Mustard (*Brassica juncea*)	Increased the chlorophyll content, net photosynthetic rate, leaf proline content, and antioxidant enzymes activity. Increased the growth and enhanced the photosynthetic efficiency	Faraz et al. (2022)
21	Copper-based nanofertilizer	CuO	Cucumber (*Cucumis sativus*)	Larger translocation factor, higher nutrient element content in fruits, and lower oxidative damage	Zong et al. (2022)
22	Copper-based nanofertilizer	CuO	Dragonhead (*Dracocephalum moldavica*)	Increased shoot biomass, photosynthetic pigments, and essential oil content. Yielded more medicinally valuable secondary metabolites	Nekoukhou et al. (2023)
23	Titanium-based nanofertilizer	TiO_2	Litchi (*Litchi chinensis*)	Promoted reproductive processes, especially the rate of pollen germination and pollen tube length, impact on fruit set and quality, notably increasing fruit weight, fruit color	Huang et al. (2022)
24	Titanium-based nanofertilizer	TiO_2	Wheat (*Triticum aestivum*)	Enhanced seedling dry weight, relative water content, catalase activity, ascorbate peroxidase activity, and proline content. Enhanced total chlorophyll, carotenoids, stomatal conductance, and transpiration under severe drought stress	Faraji and Sepehri (2020)

(continued)

Table 17.1 (continued)

Sl. no	Name	Nanomaterials	Plant	Advantages	References
25	Titanium-based nanofertilizer	TiO_2	Chickpea (*Cicer arietinum*)	Increased cold tolerance	Mohammadi et al. (2013)
26	Titanium-based nanofertilizer	TiO_2	Tomato (*Solanum lycopersicum*)	In promoting photosynthesis in leaves under mild heat stress	Qi et al. (2013)
27	Titanium-based nanofertilizer	TiO_2	Annual medics (*Medicago scutellata*)	Increased crop yield	Dolatabadi et al. (2015)
28	Titanium-based nanofertilizer	TiO_2	Barley (*Hordeum vulgare*)	Increased the chlorophyll content, vegetative growth, and yield component under supplemental irrigation condition	Janmohammadi et al. (2016)
29	Titanium-based nanofertilizer	TiO_2	Corn (*Zea mays*)	Increased chlorophyll carotenoids and anthocyanins content. Maximum amount of pigment was recorded, facilitate an increase in crop yield	Morteza et al. (2013)
30	Titanium-based nanofertilizer	TiO_2	Wheat (*Triticum vulgare*)	Reduced phytotoxic effect. Increased N, P, Zn, and Cu concentrations in plant body	Daghan et al. (2020)
31	Titanium-based nanofertilizer	TiO_2	Coriander (*Coriandrum sativum*)	Increased height, fruit yield, and number of branches. Increased amino acids, total sugars, total phenols, total indols, and pigments	Khater (2015)
32	Titanium-based nanofertilizer	TiO_2	Rice (*Oryza sativa*)	Increased level of phosphorus contents in roots, shoots, and grains. Decreased organic acid, fatty acid, and sugar contents	Zahra et al. (2017)

(continued)

Table 17.1 (continued)

Sl. no	Name	Nanomaterials	Plant	Advantages	References
33	Titanium-based nanofertilizer	TiO_2	Flax (*Linum usitatissimum*)	Improved the morphological and physiological traits. Enhanced chlorophyll and carotenoids contents. Increased the drought tolerance with improvement in physiological process.	Aghdam et al. (2016)
34	Cerium-based nanofertilizer	CeO_2	Grapevine (*Vitis vinifera*)	Improved agronomical, physiological, and biochemical defense responses under salt stress condition	Gohari et al. (2021)
35	Cerium-based nanofertilizer	CeO_2	Wheat (*Triticum aestivum*)	Improved the plant height, biomass, and grain yield and modified the amino acid and fatty acid	Rico et al. (2014)
36	Cerium-based nanofertilizer	CeO_2	Barley (*Hordeum vulgare*)	Improved the plant height, biomass, and chlorophyll content but reduced the spike production, modified the stress levels in leaves without apparent signs of toxicity	Rico et al. (2015)
37	Cerium-based nanofertilizer	CeO_2	Sorghum (*Sorghum bicolor*)	Protected photosynthetic rates and grain yield under drought conditions. Improved pollen germination and seed yield	Djanaguiraman et al. (2018b)
38	Cerium-based nanofertilizer	CeO_2	Cotton (*Gossypium hirsutum*)	Impact on seedling morphological, physiological, biochemical, and transcriptomic traits under salinity stress	An et al. (2020)

(continued)

Table 17.1 (continued)

Sl. no	Name	Nanomaterials	Plant	Advantages	References
39	Silver-based nanofertilizer	Ag	Pepper (*Capsicum annuum*)	Plant height and biomass decreased, whereas overall biomass increased. Cytokinin levels in the leaves increased significantly	Vinković et al. (2017)
40	Silver-based nanofertilizer	Ag	Mustard (*Brassica juncea*)	Improved the growth of seedlings by improving their antioxidant status	Sharma et al. (2012)
41	Silver-based nanofertilizer	Ag	Fenugreek (*Trigonella foenum-graecum*)	Increased plant growth, photosynthetic pigments, IAA contents, and yield quantity and quality	Sadak (2019)
42	Silver-based nanofertilizer	Ag	Wheat (*Triticum aestivum*)	Protected against heat stress and improved morphological growth mainly plant root length, shoot length, root number, plant fresh weight, and plant dry weight	Iqbal et al. (2019)
43	Silver-based nanofertilizer	Ag	Rocket (*Eruca sativa*)	Morphological and proteomic changes induced	Candida et al. (2013)
44	Silver-based nanofertilizer	Ag	Wheat (*Triticum aestivum*)	Inhibited growth and delayed the ripening, significant reduction of crop yield	Yang et al. (2018)
45	Silver-based nanofertilizer	Ag	Tomato (*Solanum lycopersicum*)	Improved germination percentage, germination rate, root length, and seedling fresh and dry weight. Alleviated the adverse effects of salt stress	Almutairi (2016)
46	Zinc-based nanofertilizer	Zn	Pearl millet (*Pennisetum americanum*)	Improved the grain yield at crop maturity	Tarafdar et al. (2014)

(continued)

Table 17.1 (continued)

Sl. no	Name	Nanomaterials	Plant	Advantages	References
47	Zinc-based nanofertilizer	ZnO	Coffee (*Coffea arabica*)	Positively affected the fresh weight and dry weight of roots and leaves, net photosynthetic rate increased	Rossi et al. (2019)
48	Zinc-based nanofertilizer	ZnO	Rice (*Oryza sativa*)	Increased grain yield and its components	Ghasemi et al. (2017)
49	Zinc-based nanofertilizer	ZnO	Wheat (*Triticum aestivum*)	Significant reductions in plant pigments, increased plant growth under salty stress conditions	Lalarukh et al. (2022)
50	Zinc-based nanofertilizer	Zn	Cotton (*Gossypium barbadense*)	Improved growth and yield under abiotic stress (salinity condition)	Hussein and Abou-Baker (2018)
51	Zinc-based nanofertilizer	ZnO	Mango (*Mangifera indica*)	Improved growth, nutrients uptake, and carbon assimilation Flower malformation decreased, and the fruit yield and physiochemical characteristics improved under salinity stress conditions	Elsheery et al. (2020a)
52	Zinc-based nanofertilizer	ZnO	Okra (*Abelmoschus esculentus*)	Enhanced the contents of the photosynthetic pigments. Increased activity of the antioxidant enzymes under salinity	Alabdallah and Alzahrani (2020)
53	Zinc-based nanofertilizer	ZnO, Zn	Lettuce (*Lactuca sativa*)	Increased biomass, chlorophylls, and antioxidant compounds	Garza-Alonso et al. (2023)
54	Gold-based nanofertilizer	Au	Pearl millet (*Pennisetum glaucum*)	Improved germination and increased seedling plant biomass. Affected the height parameters. Leaf chlorophyll content virtually unchanged in the seedling	Parveen et al. (2016)

(continued)

Table 17.1 (continued)

Sl. no	Name	Nanomaterials	Plant	Advantages	References
55	Gold-based nanofertilizer	Au	Mustard (*Brassica juncea*)	Increased the number of leaves per plant, enhancing growth and yield	Arora et al. (2012)
56	Platinum-based nanofertilizer	Pt	Wheat (*Triticum aestivum*)	Changed the morphological and physiological indexes	Astafurova et al. (2015)
57	Selenium-based nanofertilizer	Se	Maize (*Zea mays*)	Helped plants to cope with drought stress conditions by inducing a higher drought tolerance, increase in proline, K concentrations, and nitrogen metabolism in aerial parts	Bocchini et al. (2018)
58	Selenium-based nanofertilizer	Se	Wheat (*Triticum aestivum*)	Enhanced growth and micronutrient levels. Effectively stimulated wheat productivity	Yasin et al. (2015)
59	Nanosilicon dioxide nanofertilizer	SiO_2	Cucumber (*Cucumis sativa*)	A positive effect on the growth of plant and yield	Yassen et al. (2017)
60	Nanosilicon dioxide nanofertilizer	SiO_2	Mahaleb (*Prunus mahaleb*)	Alleviated the common physiological deleterious effects of drought on plants	Ashkavand et al. (2018)
62	Nanosilicon dioxide nanofertilizer	SiO_2	Strawberry (*Fragaria ananassa*)	Reduced the concentration of nitrogen and phosphorus, increased the concentration of potassium, calcium, magnesium, iron, manganese, and silicon in shoots	Yousefi and Esna-Ashari (2017)
63	Nanosilicon dioxide nanofertilizer	SiO_2 ZnO	Sugarcane (*Saccharum officinarum*)	Promote chilling tolerance, enhancing photosynthesis and improving photoprotection mechanisms	Elsheery et al. (2020b)

(continued)

Table 17.1 (continued)

Sl. no	Name	Nanomaterials	Plant	Advantages	References
64	Nanosilicon-based nanofertilizer	Si	Rice (*Oryza sativa*)	Attenuated the detrimental physiological and biochemical effects of NaCl on plants	Abdel-Haliem et al. (2017)
65	Nanosilicon dioxide nanofertilizer	Si	Marigold (*Tagetes erecta*)	Improved the plant biometrics and plant physiology, enhanced the flower's characteristics and flowering period	Attia and Elhawat (2021)
66	Carbon nanotubes	CNTs	Tomato (*Solanum lycopersicum*)	Increased the germination percentage and enhanced the growth of seedlings, produced two times more flowers and fruit	Khodakovskaya et al. (2009, 2013)
67	Multiwalled carbon nanotubes	MWCNTs	Mustard (*Brassica juncea*)	An increasing germination rate. Higher rate of plant growth (both root and shoot growth) and higher vigour	Mondal et al. (2011)
68	Multiwalled carbon nanotubes	MWCNTs	Barley (*Hordeum vulgare*), soybean (*Glycine max*) Corn (*Zea mays*)	Proved as regulators of germination and plant growth. Stimulated expression of water channel genes	Lahiani et al. (2013)
69	Water-soluble carbon nanotubes	wsCNTs	Gram (*Cicer arietinum*)	Increased growth rate in every part of the plant and better water absorption	Tripathi et al. (2011)
70	Multiwalled carbon nanotubes	MWCNTs	Hopbush (*Dodonaea viscosa*)	Improved seed germination percentage, mean germination time (MGT), root and stem lengths, as well as fresh and dry weights of root and stem	Yousefi et al. (2017)

(continued)

Table 17.1 (continued)

Sl. no	Name	Nanomaterials	Plant	Advantages	References
71	Magnetic iron oxide	Fe_2O_3	Watermelon (*Citrullus lanatus*)	Increased seed germination, seedling growth, and enhanced physiological function	Li et al. (2013)
72	Magnetic iron oxide	Fe_2O_3	Soybean (*Glycine max*)	Increased chlorophyll levels, enhanced the chlorophyll content in sub-apical leaves	Ghafariyan et al. (2013)
73	Manganese-based nanofertilizer	Mn	Mung bean (*Vigna radiate*)	Affected the assimilatory process by enhancing the net flux of nitrogen assimilation	Pradhan et al. (2014)
74	Manganese-based nanofertilizer	Mn	Soybean (*Glycine max*)	Affected shoot height, biomass, antioxidant system, and mineral element content	Jiang et al. (2023)
75	Magnesium-based nanofertilizer	MgO	Tomata (*Solanum lycopersicum*)	Induced systemic resistance responses against bacterial wilt disease, caused by Ralstonia solanacearum	Imada et al. (2016)
76	Molybdenum-based nanoparticles	Mo	Chickpea (*Cicer arietinum*)	Increased the number of nodules	Taran et al. (2014)
77	Potassium-based nanoparticles	K	Squash (*Cucurbita pepo*)	Promoted antioxidant and photosynthetic machineries, minimize oxidative stress biomarkers and Na^+ levels, boost tolerance to salt stress, and improve yield	Rady et al. (2023)

Nanoparticle–protein complexes form through electrostatic and covalent interactions in the gastrointestinal lining of insects and pests, which weaken the stomach lining, leading to hunger and eventual death (Sharma et al., 2022).

Tobacco plants are prone to different *Phytophthora* spp. by nature, but the application of AgNPs with mefenoxam (SubdueMaxx) when tested in vitro for 5 days resulted in complete inhibition without hampering the original plant growth (Ali et al., 2015). The usefulness of spherical-shaped AgNPs for its nematicide property (killing nematode) against *Meloidogyne incognita* in carrot plants was reported. Even against various plant pathogens like *Phytophthora tropicalis*, *P. capsici*, *P. tropicalis*, *P. infestans*, *P. cinnamomi*, *P. katsurae*, *P. palmivora*, and *P. parasitica*, the effectivity of AgNPs remained consistent (Fabiyi, 2021), furthermore in control of *Stromatinia cepivora* causing white rot diseases, antifungal activity was also observed after application (Darwesh & Elshahawy, 2021).

Gold nanoparticles (AuNPs) when tested against deep fungal infection in tea tree leaves, after penetrating deeper into leaf (190 μm of thickness) inhibition of fungal growth within 1 h of treatment was observed (Hou et al., 2016). The attachment of the SH group of amino acids and nanoparticles through electrostatic covalent interaction was found to be effective in developing an eco-friendly pest management system using insecticidal and nematicide properties of these NPs (Patil et al., 2016).

Conventional fungicides are used in agricultural fields often result in a hamper of native plant growth, whereas CuNPs are a safer alternative against *Fusarium* wilt infection and, at the same time promoting plant growth (Lopez-Lima et al., 2021). Antifungal properties of NPs are in direct use for agricultural sectors. Studies have shown the fungicidal properties of CuNP against different stains. Through *Eichhornia*-mediated synthesis of CuONPs, inhibition of *Fusarium culmorum and Aspergillus niger*, which are notorious fungal species infecting plants and hampering growth and productivity, was observed (Vanathi et al., 2016).

These NPs were also tested for their antimicrobial properties on *Xanthomonas axonopodis*, causing bacterial blight of pomegranate and its scanning electron microscopic (SEM) analysis revealed complete disruption of the cell wall with CuNP treatment (Thakur et al., 2018; Mondal & Mani, 2012). Sulfur nanoparticles (SNPs) by far are the most widely used conventional antimicrobials for crop protection. Compared to ordinary sulfur pesticides, nanomaterial form of sulfur contributes more. It is highly effective against powdery mildew disease causing *Erysiphe cichoracearum* at very low dosages; *Aspergillus niger* the most notorious fungal species can also be controlled by SNPs (Choudhury et al., 2010). Its effect was studied against *Fusarium solani*, *Fusarium oxysporum*, and *Venturia inaequalis*, which cause infection in tomatoes and apples, and found that the small-sized (30 nm) SNP materials are depositing on the cell wall and leading to retardation of the infection, which strengthen the belief of its effectiveness in crop protection.

Nanoemulsion have also been used extensively in pathogenic research. These are complex, non-equilibrated, optically isotropic colloidal systems with diameters in between 20 and 200 nm. Here, the active and functional chemicals are enclosed in an aqueous solution as droplets (Srilatha, 2011). They are surfactant in nature consisting of spherical aqueous droplet of functional NP suspension (Vega-Vásquez et al., 2020). The functioning and features of nanoemulsions vary depending on their production method and chemical composition. Due to its physicochemical instability, these nanoemulsions during longer storage were converted into a lyophilized form by eliminating water from the aqueous environment (Srilatha, 2011). Nanoemulsion can withstand harsh environmental condition such as extreme pressure, higher temperatures, and salinity than normal. By changing the ratio of oil and aqueous, these nanoemulsions can be maintained in constant morphology (Sun et al., 2017). For instance, cypermethrin, which is a water-insoluble pesticide, was formulated into a nanoemulsion that showing increased stability on plants. Another formulation consisting of neem tree oil demonstrated a stronger larvicidal activity despite having a smaller droplet size (Anjali et al., 2012).

9.3 Nanobiosensor, Ensuring Crop Safety

Nanobiosensor is formed when a biosensor is fabricated with nanomaterials. Biosensors can detect biological components like enzymes, antibodies, harmful pathogens, etc. This tool is a perfect amalgamation of bioelectronics, and it creates signals by two different segments: first, it detects, analyzes the biological entity, and then generates the electrical signal through the physicochemical process. This promising technique has been already employed for the identification of *E. coli and Salmonella typhi*, with bio-conjugated dye-dopped SiNPs and AuNPs using amperometric detection (Narayanan et al., 2013). In pesticide detection, single-walled carbon nanotubes (CNTs) using *Arabidopsis thaliana* as a test plant were capable to detect nitric oxide. Phytoalexin compounds in different plants using fluorescence resonance energy transfer (FRET)-based nanosensors, detection of DDT and methyl parathion using Au-based sensor and carbon-based sensors are few noteworthy examples of nanobiosensors' efficacy (Baker et al., 2017; Ali et al., 2020).

Semiconductor nanoparticles known as quantum dots have a diameter of less than 10 nm and have the ability to detect extremely low cell count (Christian et al., 2008). For instance, the Candidatus *Phytoplasma aurantifolia* that causes the Witches' broom disease in lime plants can be detected using a quantum dot-based nanosensor in the presence of extremely low cell count, such as five *Phytoplasma* cells per liter. Yang et al. (2014) created an electrochemical device based on nanotechnology principles that use palladium nanoparticles (PdNPs) as a catalyst to detect the chitinase enzyme up to 17 pg/mL specific to *Magnaporthe oryzae* during its early infection stages. Likewise, NPs combined with fluorescent silica and antibodies were used to detect spot disease by *Xanthomonas axonopodis*, on Solanaceae plants like tomatoes and pepper (Alghuthaymi et al., 2021; Maluin et al., 2021).

Different nanoparticles (NPs) consisting of copper and silver were employed for detecting various biological threats. Through CuNP, the detection of *Sclerotinia sclerotiorum*, a dominant fungal pathogen of oil seeds, can be possible (Wang et al., 2011). Also, CuNP in the form of a nanowire was employed for detecting papaya ring spot virus, *Aspergillus niger* fungus, and cauliflower mosaic virus. Using AgNPs in the detection of *Phytophthora* species have also drawn much attention for promoting sustainable agricultural practices (Schwenkbier et al., 2015). Interesting to note that few of the plant pathogens remained undercover to detect them directly, but in the infection state, plants produce a response mechanism through different phytoconstituents and plant hormones, using this level of phytochemical imbalance as an indicator CuNP combined with Au can detect salicylic acid, which is a primary indicator of *Sclerotinia sclerotiorum* contamination in oil seed plants (Wang et al., 2011).

9.4 Nanotechnology in Seed Priming

In seed priming process, the target seeds are moistened under regulated temperature and osmotic potential to activate the metabolic processes for germination followed by redrying to their original moisture content (Shelar et al., 2021). Such seeds when planted, germinate instantly since the process has already begun. This approach shortens the germination time while increasing germination rate and uniformity. The most susceptible moment for seeds is during the germination stage. As a result, seed priming can shorten the germination period while increasing the rate of the germination.

As seed priming agents, inorganic salts, fertilizers, plain water, and polyethylene glycol are employed in traditional procedures. But the current idea for increasing seed viability can be achieved using nanotechnological processes. During seed priming, NPs like C, Cu, Zn, TiO_2, etc. are used. Onion and watermelon seed priming with Au and Ag NPs offered an increased germination rate. Furthermore, nano-seed priming of fenugreek, beetroot, and spinach using nano-iron pyrite for 12 and 14 h was reported for much higher yield (Shweta et al., 2021). This technique of seed nanopriming uses nanoformulations present in the medium that are retained by the seed coat. These nanoparticles are classified into two types: active nanoparticles and sustained-release nanocarrier systems, where NPs with or without active components are retained through the seed coat and released over time (do Espirito Santo Pereira et al., 2021), whereas active nanoparticles are metal-based nanoparticles (zinc, iron, and manganese) with a diameter of 100 nm. Chili seeds primed with zinc oxide (ZnO) NPs exhibited increased germination and seedling development; in the case of bean plants and watermelon, nanopriming with Cu NPs and Fe NPs boosted plant biomass and improved seedling growth and germination (Kasote et al., 2019; Kumar et al., 2020a, b).

9.5 Nanotechnology in Postharvest Loss Reduction

According to the data obtained from FAO, nearly 40% of the harvested crops are lost in the trading and at customer stages, whereas in developing countries, this number gets accelerated for mismanagement, transport, and processing stages (FAO, 2019). Freshly harvested crops have higher moisture content which makes them vulnerable to microbial contamination. The application of advanced nanotechnological intervention is believed to be capable of reducing such postharvest losses. For instance, designing functional packing ingredients using the least quantities of bioactive molecules with improved water vapor transmission rate and mechanical properties without imparting additional flavour on the sensory properties of vegetables and fruits is presently being investigated (Flores-López et al., 2016).

Edible nanocoatings are some of the noteworthy application where freshly harvested food products are dipped or coated with nano-enabled coating materials, this can prevent excess moisture loss, reduce the rate of respiration, and create a barrier to gas exchange while at the same time, delivering original flavors, and color. Enzymes, responsible for antioxidants, and anti-browning activity are also presently being used to enhance the shelf life of food products (Zambrano-Zaragoza et al., 2018). Ag, SiO_2, and TiO_2 nanoparticles are used in food packaging materials to impart antibacterial and hygroscopic qualities for food preservation. The usage and demand for this material still depend upon several factors, including pricing, applicability, tensile properties, etc., but the anti-infective properties of NPs certainly give an extra layer of protection against any kind of microbial spoilage (Falguera et al., 2011). Since, AgNP combined with PVP material was used in a study to monitor post-harvest changes in asparagus-coated nano-fabricated packaging material. Its application considerably delayed microbial growth, reduced weight loss, and decreased skin color changes (An et al., 2008).

Another study with gelatin-derived edible coatings with cellulose nanocrystals exhibited a considerable improvement in the shelf life of fresh strawberries (Fakhouri et al., 2014). Using chitosan-assisted nanosilica coating of a semi-permeable packaging film significantly improved the physicochemical and physiological values of fruits in an ambient storage temperature, compared with that of other treatments (Shi et al., 2013). Few more instances, viz. alginate- or lysozyme-based nanolaminate coatings (Medeiros et al., 2014), chitosan film-based nano-SiO_2 (Yu et al., 2012), and Nano-ZnO coating were found preserving the value of fresh diets during prolonged storage from microbial infection and kept the post-harvest value of some fruits intact throughout the storage time (Sogvar et al., 2016).

Nanosensors in monitoring the grain quality have shown exemplary results, this can sense external changes like temperature, humidity, water content, and oxygen content in the grain (Bouwmeester et al., 2009). They can also check microbial contamination, fungal infection, and impart insecticidal properties in the stored grains (Axelos & De Voorde, 2017). The sensors can even capture the volatile agents in the environment and analyze the cause and kind of decomposition (Neethirajan & Jayas, 2011).

10 Safety and Regulatory Aspects Nanofertilizer for Agricultural Sustainability

Scientific discoveries always have two perspectives for being judged, imparting complete attention to the technical improvements for synthesis, distribution, energy conservation, and application of NFs often led to the aftermath unnoticed. It's completely undeniable that nanomaterials possess various new propositions, in an industrial setting and have the potential to capture the world market worth of billions of dollars (Rajput et al., 2020), but certain factors and risk assessments need to be studied in detail to prevent any further complications in future (Fig. 17.3).

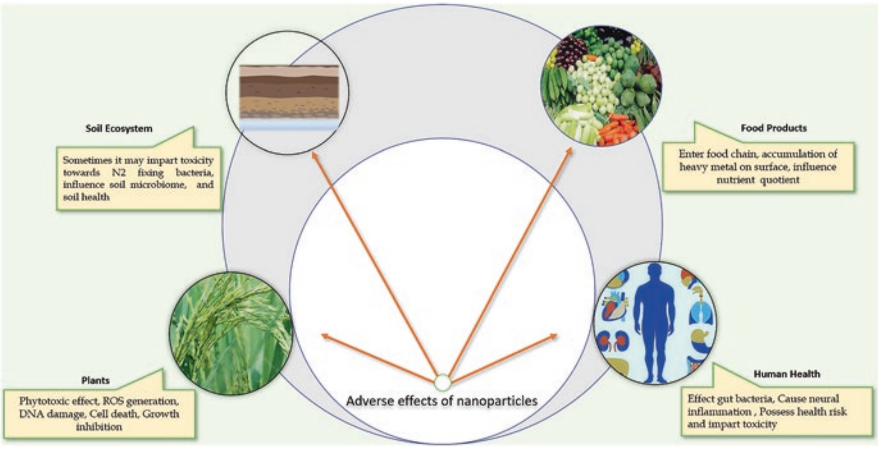

Fig. 17.3 Adverse effects of nanofertilizers on food products, soil ecosystem, plants, and human

10.1 Soil Becoming Sink

Nanoparticles reaching out to the soil can be classified into two different categories: anthropogenic sources of releasing NPs (caused directly by any human), which can also be termed "point sources," where the actual source is traceable; and nanowaste generated from a factory or wastewater treatment plant, which comes under "non-pointed sources," which cannot be traced to a single source. Dispersion of free NPs into the environment can happen either through direct factory outlets or through the degradation of surface-bound NPs and nanosized coatings. In the case of wastewater treatment plants and landfills, they often discharge a large number of concentrated NPs as effluent. Other sources of environmental exposure include spillage or leakage during the production and transport of NPs fuels unnecessary NP accumulation in soil. In a few reports on environmental toxicity caused by different nanoparticles, it has been mentioned that the total accumulated Cu content in soil is up to 500 g/kg (Keller et al., 2017), and in the case of ZnO and CeO_2, the accumulated levels reached 16 g/kg and 4.3 mg/kg of soil tested (Feng et al., 2016; Boxall et al., 2007). This fortifies the need to clean up nanowastes before they get into the process of dissolutive transformation in soil, creating a potential risk of being bioavailable.

10.2 Uptake and Accumulation Inside Plant Tissue

Adsorption is the process of two different substances getting adhered to the surface of one another. In this case, the NPs are sticked to the surface of the plant roots depending upon the characteristics features of both plants and the adhered NPs. Based on further study, the Au NPs could accumulate in *Oryza sativa* shoots, but they cannot accumulate in the shoots of *Raphanus raphanistrum* and *Cucurbita pepo*. Though positively charged NPs have a better affinity toward the plant root, the negatively charged ones can easily translocate through plant shoots (Zhu et al., 2012).

It is alarming that, through physical and mechanical forces like adhesion and friction, accumulation of NPs in the edible parts of the plant can be an initiator of bioaccumulation process. To elaborate further, the CuO NPs which stuck to the root surface cannot be desorbed during the exchanges of ions and minerals, which means that the NPs are not easily removed from the root surface (Rajput et al., 2020). Such similar instances were reported with *Brassica juncea* and *Medicago sativa* plants where the presence of ZnO-NP at the roots and shoots was observed by Bandyopadhyay et al. (2015) and Rao and Shekhawat (2016).

Treatement with conventional potassium chloride and ammonium thiosulfate fertilizer builds up the Ag-NPs in soil leading to accretion in root and shoot development (Doolette et al., 2015). Accumulation of NPs in soil and inside plants creates a negative impact on the protein, lipid, and nucleic acid profile, and cause structural impairment of the plant cells. This destabilization of structural barrier allows translocation of NPs across different plant parts through shoots and often gets deposited in developing seeds (Rico et al., 2011; Tripathi et al., 2017).

10.3 Regulatory Affairs of Nanoproducts for Commercialization

Nanotechnology and its allied sectors have already penetrated the agri-market in various aspects in terms of pest management, growth promotion, soil health improvement, plant germination, etc. It is therefore crucial to elucidate any possible detrimental effects of these products on living bodies. The foremost and primary aim should be to find the permissible dosage of any agri-nanoproduct with proper guidance for the end users. As far as human health is concerned, these products should be eyed with proper vigilance by more than one regulatory sector to analyze their social acceptability, ethical concerns, economic viability, and biosafety. It is important that before commercializing any nano-enabled product, the applicant confirms the safety measures of the product for consumers and its environmental application before market approval. China, Germany, France, Japan, Switzerland, South Korea, and the United States are the seven listed countries in the NAAS (National Academy of Agricultural Sciences) report that are largely interested in nanotechnology and its products. As a result, organizations such as the European Union Scientific Committees and Agencies (EUSCA), the Organization for Economic Cooperation and Development (OECD), the International Standard Organization (ISO), and the United States Food and Drug Administration (FDA) have established standards for testing and verification. The US government takes a "case-by-case" approach for manufacturing, but the European Union (EU) follows a legal framework of NPs in the agricultural application (Arora et al., 2022).

10.4 Toxicity Concerns of Nanofertilizers (Environmental and Health Impacts of Nanotechnology in Agriculture)

Reports regarding the toxicity of these nanointerventions are well distributed among the literature, but proper scientific implementation of this knowledge is necessary to bring about the best possible outcomes. As of now, a few reports from different studies have shown nanomaterials to have good soil compatibility in the upliftment of malnourished soil health through several in vitro tests. It is essential to understand that a nanomaterial, by definition and by characteristics, is a nano-sized product, and it is no wonder that it will be able to penetrate any physical surfaces where conventional elements will fail. This brings a further need towards the complete elucidation of nanofertilizer elements and all of their essential handling measures. As per a few earlier reports, it does not have any adverse side effects (Batley et al., 2013; Karimi & Mohseni Fard, 2017; Sengul & Asmatulu, 2020), but further studies about whether the accumulation might affect phytochemistry and other allied characteristics of the plant need to be rigorously reviewed in the future.

11 Public Awareness and Acceptance (People's Perceptions, Awareness, Ethical, and Market Concerns

The present development in terms of product manufacturing from prototypes has largely been controlled by its practical implementation. Nanotechnology and its direct application in the agricultural field, or any nanomaterial-encountering food products, come with a major challenge of consumer acceptance. Few products have already stepped into the market, such as Smartcap by BASF, Amblyline cu by Syngenta for the controlled release of pesticides, and nano-enabled supplements like Nutralease, but they need more public attention. A few of the commercially available products that have already been commercialized are listed in Table 17.2. According to many market surveys, consumers still possess more confidence on biologically synthesized or directly derived nanopolymers. Considering the larger scopes of this nano-enabled agroeconomy, it can only be sustained if, from the beginning, every possible aspects and future consequences are documented, studied, and recorded with proper scientific evidence. To earn the confidence of general public on this futuristic technology for the greater good, the toxicity concern must be scrutinized. Owing to its nanosized structure, its chemical properties also differ from those of its conventionally larger counterparts. Thus, present testing methods might not be suitable to analyze the product completely, which necessitates finding a solution for revamping. Thus, it is important to revisit the legislative framework and regulations to address the expanding number of nano-based goods

Table 17.2 Some important commercially available nanofertilizers in the market

Sl. no	Company name	Commercial product	Crops suitable	Benefits	References
1	IFFCO. India	Nano urea (liquid)	Cereals, pulses, vegetables, fruits	Increases crop yield	https://www.iffco.in/en/nano-urea-liquid-fertilizer
2	Indogulf BioAg USA	Hydromax	Trees flowers, vegetables & fruits and hydroponics	Nutrient supplement in liquid form	https://www.indogulfbioag.com/nano-hydromax-fertilizers
3		Nano Anpeekay	Corn, soybean, fruits, rice, vegetables, sugar cane, wheat, cotton, tobacco	Improves plant health; increases the level of energy, water, and nutrient-holding capacity; improves plants' resistance against pests and diseases	https://www.indogulfbioag.com/nano-anpeekay-fertilizers
4		Nano Pufa	Seasonal crops	Assists in enhancing quantity and quality of yield; better shelf life of the produce	https://www.indogulfbioag.com/nano-pufa-fertilizers
5		Nano Chito	Aquaculture and agricultural applications	Reduces fungal disease incidence and bacterial pathogen; promotesplant growth and improves the development and quality of flowers and fruits	https://www.indogulfbioag.com/nano-chito-fertilizers
6		Nano Micromax	Ruminants, poultry, fish, prawn, agricultural crops	Helpful in cases of malabsorption conditions; improves plant health	https://www.indogulfbioag.com/nano-micromax-fertilizers
7	Agro Nanotechnology Corporation, USA	Nano-Gro		Improves crop yield and product quality and boosts plant immunity against diseases and extreme weather conditions	https://www.internano.org/node/1285
8	Fanavar Nano-Pazhoohesh Markazi Company, Iran	Biozar nanofertilizer	Crop and non-productive trees or grass	Increases production and reduces the consumption of nitrogen and phosphate fertilizers	https://www.nanotech-now.com/news.cgi?story_id=51321

(continued)

Table 17.2 (continued)

Sl. no	Company name	Commercial product	Crops suitable	Benefits	References
9		Nano calcium (magic green)	Rice, fruit and vegetables	Very good for plants that lack calcium and key to the formation of sugar and starch, especially for strengthening roots, growth and greening of leaves, and fruiting	https://www.tokopedia.com/kebunkumart/magic-green-pupuk-daun-nanocalcium-60gram?utm_source=google&utm_medium=organic&utm_campaign=pdp-seo
10	Tropical Agrosystem India (P) Ltd., India	Tag nano fertilizer	AgricultuAll crops	Improves overall growth and yield of the crops; increases rate of photosynthesis and reduces the intensity of chlorosis	https://www.skorganicfarms.com/products/tag-nano-npk-4g-nano-fertiliser
11	Nano Green Sciences, Inc, India	Nano green	Macadamia nut trees to lettuce and wheat	Increases the level of sugar production as it photosynthesizes	https://product.statnano.com/product/4646/nano-green-fertilizer
12	JU Agri Sciences Pvt. Ltd., Janakpuri, New Delhi, India	Nano max NPK fertilizer	All crops	Nutritional fertilizer	https://www.indiamart.com/proddetail/nano-max-npk-fertilizer-12188041548.html
13	Shan Maw Myae Trading Co, Ltd., India	Nano micronutrient (Ecostar)	Vegetables, fruits, spices, cotton, flowers, plantation crops, cereals and pulses	Prevents micronutrient deficiencies of plants Increases photosynthesis and helps in more flowering. Tolerant to stress. Stops flowers from dropping and improves fruit set	https://shanmawmyae.com/agriculture/
14	JU Agri Sciences Pvt. Ltd., Janakpuri, New Delhi, India	Nano max NPK fertilizer	All crops	Nutritional fertilizer	https://www.indiamart.com/proddetail/nano-max-npk-fertilizer-12188041548.html
15	Bion Tech Taiwan	Nanomax	All crops	Helps to absorb and utilize nutrients, increases movement and availability of nutrients within the crop	http://www.biontech.com.tw/news_show.php?id=5

16	Lazuriton Nano Biotechnology Co., Ltd., Taiwan	Nanofertilizer	Vegetables and all crops	Nano protective layer on leaf surface to prevent pest infect., yield and quality of crops can be greatly enhanced, reduces the soil acidification	https://product.statnano.com/product/6270/nano-fertilizer
17	Smart Agri-Tech Co. Ltd., Thailand	Nano amino tablet	Rice, vegetable, fruit tree	Helps the healthy leaf and body system of plants, increases the quality of budding and young leaves to revive the plant, increases the yield of crops	https://thailandfertilizer.trustpass.alibaba.com/search/product?SearchText=nano

on the market. Furthermore, to impart some knowledge about the nanoingredients present in the feed-products, adequate labelling and listing of all the components might help in users' understanding.

11.1 Limitation of Nanofertilizers

Despite having so many potential applications distributed in various fields, it has not yet entered the mainstream. Nanotechnology is a relatively new approach, and its entire prospects are still unknown (Fig. 17.3). It is essential to keep a transparent approach to implementing this technology in the human lifestyle, which needs extensive study on toxicity. The lack of knowledge regarding investment and profit in a simulated field condition limits the estimation of the actual cost of nanofertilizers, which can provide robust information on large-scale industrial production methods. This present scenario is still fuzzy as to what extent nanofertilizers can acquire the existing chemically synthesized fertilizer markets. But still, few reports have tried to compare the growth yield and investment on different plants (Delfani et al., 2014; Dimkpa & Bindraban, 2016). There is no denying that a full economic study, along with dosage patterns and application strategies, of nanofertilizers against traditional fertilizers can provide important information for potential nanofertilizer investment by businessmen and farmers alike.

12 Conclusion

To feed an ever-increasing population, agricultural productivity must be increased while maintaining the ecosystem intact. Increased usage of fertilizer is causing environmental deterioration, soil health depletion, and pollution (air and water). Sustainable agriculture practices are the key to address such difficulties. To successfully apply these nanomaterials in the postharvest management of vegetables and fresh produce and to cater extremely nutrient-dense food for people, further study and understanding are required. Nanotechnology in agriculture might help us achieve sustainable goals by lowering the input amount of fertilizer, keeping a check on price, enhancing efficiencies, and reducing environmental pollution and toxicities caused by the chemical fertilizers. By using nanotechnology in agriculture, newer dimensions in agricultural practices, such as precision agriculture, integrated nutrient management, and nanosensing, can be easily achieved. It is anticipated that nanotechnology will increase its capacity for offering workable agricultural solutions and significantly contribute to the development of sustainable alternatives.

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Chapter 18
Complex Study of Foliar Application of Inorganic Nanofertilizers in Field Conditions: Impact on Crop Production and Environmental–Ecological Assessment

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1 Introduction

In the last century, prof. Dr. Richard P. Feynman presented a lecture titled "*There's plenty of room at the bottom*" with the concept of material manipulation at the miniature-atomic level (Feynman, 2011). This idea was not only inspiring for theory of physics but it also pushed the boundaries of material chemistry, electronics,

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and other scientific disciplines. One area of focus in academic circles was nanosized objects, specifically nanomaterials (NMs) and nanoparticles (NPs), which generally have at least one dimension in the range of 1 to 100 nanometers (Mittal et al., 2020; Rumble et al., 2015). Objects with nanosized dimensions have significant differences in physical, chemical, and biological properties compared to their macrosized or soluble counterparts, despite having a similar chemical composition (Mousavi Kouhi et al., 2014; Nagarajan, 2008).

Nanomaterials and nanoparticles can be classified according to several aspects. They are often classified based on their chemical composition into (i) *organic nanomaterials*, e.g., various organic substances, such as nanobiological fertilizers (Wang et al., 2009), humic acids (Wei & Ji, 2003), or agropolymers (Prasad, 2013), and (ii) *inorganic nanomaterials* with pure—Au, Ag, Cu NPs, or various types of oxides, sulfides, sulfates, carbonates, phosphates, silicates, etc. (Ameen et al., 2021; Mittal et al., 2020).

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The next categories address the mechanisms of nanosized formation, primarily the *bottom-up* and *top-down* principles of production. A special class of NMs and NPs belongs to drug delivery systems for therapeutic treatments (Tiwari et al., 2012) or is used as quantum dots (QDs) with unique optical, magnetic, catalytic, or electro-optical properties, often achieved through the use of sulfides and sulfosalts with metals or metalloids (Bera et al., 2010). NMs and NPs are currently making advancements in various fields, including electronics (Chen & Mao, 2007; Pištora et al., 2015), magnetic and magneto-optic equipment (Illa et al., 2019), biologically compatible implants (Vandana et al., 2019), in food industry, or biotechnology applications (Holišová et al., 2019, 2021; Omanović-Mikličanina & Maksimović, 2016).

According to the World Health Organization (WHO), the global population is expected to exceed 9 billion by 2050 (Mcguire, 2013) and implementation of NMs and NPs has become an attractive point of interests nowadays. To avert a potential food crisis, food production must be increased by about 50% in the coming decades. Given the limited time frame to meet the projected 50% increase in food production, the field of agronomy has been exploring ways to enhance food production through either conventional or traditional methods. In this context, the utilization of NMs and NPs is being considered as a potential alternative solution to address the impending food crisis. New concepts of utilizing nanotechnologies and nanobiotechnologies are being integrated into many agricultural areas, including precision agriculture, agrochemicals (nanofertilizers), food production, water management, forestry sectors, and environmental remediation strategies (Kumar et al., 2019; Singh et al., 2021), with the goal of creating precise and sustainable solutions.

Current agricultural research has shifted its attention toward the utilization of NMs and NPs, aiming for a more direct and smarter application of already existing agrochemicals and fertilizers by using them in their nanoforms (Liu & Lal, 2015). The "nano" prefix refers to a large surface-to-volume ratio and distinct morphology compared to conventional agents, which results in either more efficient use or higher effectivity of nanofertilizers, nanopesticides, nanosenzors, etc. (Prasad et al., 2014, 2017; Mittal et al., 2020). In agronomical context, unique properties of nanosensors allow for the real-time monitoring and analysis of soil and environmental conditions in situ (Abdel-Aziz & Heikal, 2021), providing opportunities for immediate and appropriate agronomic management.

In the realm of agriculture, the use of INPs has gained attention, e.g., metals Au, Ag, Cu, oxides of metals ZnO, TiO_2, SiO_2, Al_2O_3, CuO, Fe_2O_3, FeO, and occasionally sulfides or rare-earth NPs (Ameen et al., 2021). These NPs are applied in colloidal solutions, and their stability and effectiveness depend on their surface and the properties of ambient solutions (Kolenčík et al., 2021). For example, they have been shown to have great disinfection properties against pathogens (El-Gazzar & Ismail, 2020) and to support higher plants' vitality (Mittal et al., 2020). There are a variety of physical, chemical, and biological procedures, or their combinations, for the creation of NPs and their colloidal dispersions (Nasr, 2019; Jamkhande et al., 2019). The biological synthesis of inorganic NPs can be achieved through the utilization of various types of bacteria, fungi, yeasts, or extract from plants (Chaudhuri & Malodia, 2017; Mittal et al., 2020).

However, when considering potential applications of inorganic NPs through foliar or soil application, several important questions and impacts must be considered. For example, the way NPs enter the plant depends on the species; the magnitude and speed of the response can vary; what concentration range is appropriate for the whole crop production, physiology, or quantitative, nutritional values of the final product quality. Furthermore, there is a question of where NPs or their residues could by accumulate and how they may interfere, synergically or antagonistically with environmental sub-systems and ecological, or agro-ecological assemblages, potentially affecting factors such as insect diversity, and their abundance or plant reproductive abilities.

Despite the growing interest in the utilization of NPs in agriculture, the knowledge related to their interaction with plants is still limited and mainly derived from laboratory and greenhouse studies. Most often, the study of plant–nanofertilizer interaction focuses on the germination process or first developmental stages of plants. Research oriented on real-field conditions with complex interactions and mutual relationships with other agroecological subsystems is largely absent in the literature. Due to aforementioned reasons, this chapter aims to (i) examine agronomic classifications of nanofertilizers, their commercial potential, and their behavior in colloidal systems, including reactions inside the soil system and their foliar dispersal; (ii) examine the applications of metal, e.g., Au, Ag, or various metal oxides, such as ZnO, TiO_2, and Fe_2O_3, or other inorganic NPs in agriculture; (iii) evaluate the NP entrance and uptake by plants, the changes in leaf surface structures, the interactions, and redistribution of inorganic NPs in the plant tissues; (iv) examine the impact of NPs on plant production based on quantitative parameters, including yield, final fruit quality, or physiological parameters of selected crops; and lastly, (v) explore the interaction of NPs and NMs with reproductive organs, flowers, and flowering, including their impact on the quality of pollen and pollinators in real-field conditions, based on agroecological assessment of epigeic insect communities.

2 A Current Overview of Commercially Available Nanofertilizers

2.1 Agronomical Classification Systems for Nanofertilizers

Large part of the manuscript focuses on nanofertilizers and nanoagrochemicals, which have fine stoichiometry, with a crystalline nature that is thermodynamically stable in inorganic or organic forms or suspended in colloidal solutions. From an agronomic perspective, nanofertilizers can be categorized based on several aspects, such as their essentiality to (i) *macronutrients*, (ii) *micronutrients*, (iii) *growth-enhanced stimulators*, and (iv) *nanomaterials*, that increased the crop production, however, their mode of action is not understood (Liu & Lal, 2015); or others NMs corresponding to fertilizers with various functions, and quantities. Here, Karunanayaka (2021) further classifies nanofertilizers into three main categories: *nanoscale nanofertilizers* with higher content of NPs and NMs, *nanoadditives*, i.e., common fertilizers with NPs as additives, and *nanocoated (encapsulated) fertilizers* with functional embedded layers that exhibit different physical, chemical, and biological behavior, reactivity, bioavailability, and potential toxicity in comparison without the nanocore.

2.2 Commercially Available Nanofertilizers and Their Behavior in Dispersion Systems

Generally, fertilizers are substances that either contain plant nutrients or with their physical, chemical, and biological properties can indirectly improve plant nutrition or increase soil fertility (Fecenko & Ložek, 2000). Fertilizers, including nanofertilizers, can be classified, according to their effectiveness, into "direct" and "indirect". "Direct" fertilizers contain one or a combination of plant nutrients in inorganic or organic forms necessary for plant production. "Indirect" fertilizers do not provide plant nutrients directly but improve the conditions for plant nutrition, for example, by modifying the soil environment, enhancing the soil structure, promoting the gradual release of nutrients, or positively impacting the whole environmental compartment. Based on their production, fertilizers could be divided into inorganic or organic form; both types are usually formed industrially and can be in a solid, liquid, or mixed states (Fecenko & Ložek, 2000).

Currently available nanofertilizer products on the commercial market use the term "nano" very informatively. However, based on our understanding, the presence of NPs in fertilizers does not necessarily guarantee full effectiveness. For instance, the product NANOgro contains a combination of inorganic elements such as Fe, Mn, Mg, and Co together with pharmaceutical grade sugar (Mastronardi et al., 2015), but it is not possible to determine the solubility sequence or activity of the nano-related substances in this product. Also, Agro Genesis Pte Ltd. markets their products as biologically active substances under the poetic term "homeopathic plant medicine", or Agro silica product with absence of precise knowledge related to "silica" mode of action (Agro-Genesis, 2023). On the other side, Lithovit company presents a basic concept of naturally modified limestones through "tribodynamic activation" (Lithovit, 2023) which is claimed to increase the concentration of CO_2 derived from limestone ($CaCO_3$) in leaves, thus encouraging photosynthesis. The product, Lithovit, is applied in the form of an aqueous suspension to various crops like potatoes, fruits, vegetables, wheat, maize, and claims to increase yield by 12–50%. The Geolife company offers a range of nano-related nutrients, macronutrient supplements under the name Nano fert, and Nano-Mg, micronutrient supplements involving the Nano-Zn, Nano-Fe, or balance Nutri containing Zn, Fe, Mn, Ca, B, and Mo, which should be combined with humified organic matter (Geolifegroup, 2023).

Global International LTD has developed the NanoGreen product, which is applied in the form of a spray dispersion. The product contains nonionic surfactants, organic compounds based on amino and fatty acids, alkyl amines, corn oil, and organic alcohols (Nanogreensciences, 2023). It is intended to promote more intense penetration into the plant through the leaf stomata, with several beneficial modes of action such as an increase in photosynthesis, higher resistance to plant pathogens, improved crop quality, and higher yield. Nanonutrients company offers six different products labeled as nano.10^{-9}, mostly containing macronutrients. In the case of products containing amino groups, they are intended to promote more effective nutrient uptake for more intensive crop growth (Nanonutrients, 2023). Another product, Nanosilica, is intended to eliminate pest activity by terminating them. Also, the product should increase the chances of the plant's protection against subsequent diseases. Moreover, the manufacturer of Nanosilica claims that the application leads to the development of a larger and longer stem, resulting in an increased weight of the final fruits. Another of the product is Nanoiron, where the manufacturers declare more harvest light energy when spray application is done with more intensive chlorophyll production. Other companies offering commercial products of nanofertilizers are listed in Table 18.1.

From a theoretical perspective, nanofertilizers and nanoagrochemicals primarily belong to dispersion systems, which can be described by various principles of surface, physical chemistry, and electrochemistry. A dispersion system is a system composed of a dispersed phase, such as NPs, that are thermodynamically stable entities in a dispersing environment, most commonly in aqueous solution (Hiemenz & Rajagopalan, 2016). Nanoparticles with a predominant size of up to 100 nm from a physicochemical nature pose into colloidal dispersions at a size of $10^{-9} < d < 10^{-6}$ m and correspond to a surface-to-volume ratio of 60 m^2cm^{-3} (Lidén, 2011). The size range, chemical integrity, examination methods, and characteristic properties of individual dispersion systems are shown in Table 18.2.

The commercial formulations used in agriculture can be applied through various types of dispersions. Spray-applied aerosols and colloidal dispersions containing surfactants or NPs show less thermal movement and diffusion and gradually release nutrients on the surface of the leaves (Choi et al., 2003) in comparison with true solutions, which have a more rapid uptake (Li et al., 2019). On the other hand, coarse dispersions with pore-like structures, such as diatomite, can serve as carriers of NPs or other soluble substances with the goal of delivering them to a specific target site (Lodriche et al., 2013). Additionally, due to their lower thermal movement and diffusion, emulsions containing polymer substances associated with NPs or enzymes exhibit better adhesion ability and a gradual releasing effect into the soil environment. In this context, encapsulated NPs are also important, and emulsion and NPs can exhibit different solubilities with a dual nutrient effect on the root system of plants. There is some evidence that processes of aggregation can reduce the

Table 18.1 Several types of commercially available nanofertilizers widely applied in agriculture production

Company name	Applied nanomaterials	Product name	Desired properties and applications
Aqua-Yield Hub	Encapsulated K	NanoK™	Nanofertilizers and growth regulators
	Encapsulated Zn	NanoZn™	
	Combination of nanomaterials	NanoRise™	
	Combination of nanomaterials	NanoPro™	
Silvertech Kimya	ZnO	NANOFERTILIZERS	Nanofertilizer
Sanayive Ticaret Ltd.	TiO_2	NANOFERTILIZERS	Nanofertilizer
Bio Nano Technology	Protected by patent	HYPER FEED 19-19-19	Nanofertilizer and nanoargrochemical
Land Green & Technology Co.	Cu, Fe, Mn, N, Mo, and Zn	Nova L and-F	Nanofertilizer and algicide
		Nova L and Nano-Mn, Cu, Fe, Zn, Mo, and N	
Bioteksa	Fe nanoparticles, powder, Mn (encapsulation)	NUBIOTEK ® HYPER Fe + Mg	Nanofertilizer
HPLA gronegocios	Ca nanoparticles, powder	FERTILE CALCIUM25	Nutrient regulator
Litho Plant	Ca nanoparticles, powder	Lithocal	Growth stimulator and nutrient regulator
	Mg nanoparticles, powder	NANOPOWER CaMag	
Tropical Agrosystem India (P) Ltd.	Zn	TAGNANO ZINC	Growth stimulator and nutrient regulator
	Ca	TAGNANOCAL	
Alert Biotech	Zn nanoparticles, powder	Nano zinc (chelated)	Nanofertilizer and pH stabilizator
	Zn nanoparticles, powder	Nano zinc (soil application 21%)	
	B nanoparticles, powder	Nano Bor 20%	

active surface-to-volume ratio, thus decreasing the effectiveness of the dispersion. One of the advantages of microemulsion containing nanoformulation from the polyvinyl alcohol–polyacrylamide support is a gradual release under conditions of soil drought (Liu et al., 2006) or slow acquisition of nutrients (Lin, 2008). Polymers integrated into foam formulations in agricultural applications can improve the adhesion of soil nutrients (Zhang et al., 2005), in the pectin compound could promote the creation of easily absorbable gel forms (Nonomura, 2006), and many advantages also affiliate with suspension coexistence (Wang et al., 2005).

Table 18.2 Differentiation of dispersion systems according to particle sizes and their resulting properties

Analytical dispersion	Colloidal dispersion	Coarse dispersion	References
Define size range $d < 10^{-9}$ (m)	$10^{-9} < d < 10^{-6}$ (m)	Macro $d > 10^{-5}$ (m) Micro $10^{-6} < d < 10^{-5}$ (m)	Bergeret and Gallezot (2008)
Methods of analysis			
Particles cannot be analyzed even by electron microscopic methods, the character of true solutions	They are observable by electron microscopic methods such as transmission electron microscopy (TEM) and *scanning electron microscopy* (SEM), often opalescence appeared	They are easily observable with a binocular microscope and with the naked eye	Hiemenz and Rajagopalan (2016)
Mobility and filtration ability			
They are not able to catch on membranes or filter paper	They are able to pass through filter papers, but not through some types of membranes	They are usually heterogeneous composition and do not pass through membranes or filter paper	Silva et al. (2011)
Characteristic behavior in colloidal systems			
They are characterized by Brownian motion, and unpredictable thermal movement, do not sediment, have a great diffusion capacity, show considerable osmotic pressure	They do not show high thermal movement and diffusion, gradually lose colloidal stability with sedimentation ability, and have less osmotic pressure	They show weak thermal movement, strong tendency to sedimentation, do not diffuse, and have almost no osmotic pressure	Birdi (2009), Silva et al. (2011)

2.3 Agronomical Progressive Nanofertilizes and Perspectives of Their Future Development

From an agronomic perspective, combining nanomaterials (NMs) is promising due to the synergistic effects and capabilities of the materials within their specific nanodomains, as well as their unique mechanisms. Various substances, *both inorganic and organic*, have been licensed for use in soil environments, such as carbon NPs (Liu et al., 2012c), carbon nanotubes, and other NMs (Liu et al., 2012c; Lewis, 2013; Xie & Liu, 2012), nano-leucite (Farrukh & Naseem, 2014), transient metal silicates (Prasad, 2013), nanobentonite (Liu et al., 2012), carbonaceous siliceous rock-enriched selenium (Yin et al., 2009), nanoclays (Li et al., 2002), kaolinite (Zhang & Wang, 2005), nanohalloysite (Price & Wagner, 2008), palygorskite (Cao et al., 2007), clinoptilolite (Barati, 2010), hydroxyapatite (HAP) (Kottegoda et al., 2014; Wei et al., 2011), boric-coated metallic NPs including Au, Ag, Cu, and metal oxides ZnO, TiO_2, Fe_3O_4 (Deb, 2013), ZnO NPs (He et al., 2009), TiO_2 (Wu, 2004b), nanoGips (Yang & Wang, 2008), or zeolites functionalized with Fe NPs (Vempati & Hegde, 2011). Some examples of *inorganic materials with biological origin* include diatomite (Lodriche et al., 2013), diatomite with zeolite, and ceramic materials (Yu, 2005). *Biological and organic nanomaterials* include biological nanoselenium (Tian et al., 2012), nanobiological fertilizers (Wang et al., 2009), humic acids (Wei & Ji, 2003), plant extracts (Lee et al., 2007), and fermented organic fertilizer with cotton and Fe-based NPs (Liu et al., 2012b). *Inorganic materials with plastic-type medium, and polymers*, such as agropolymer with amorphic silica (Prasad, 2013), or carbon NMs with hydrophilic polymer (Biris & Khodakovskaya, 2011), and *pure plastic, and polymers* NMs such as mixed polymer, and polyvinyl alcohol (Liu et al., 2006) are also used (Table 18.3).

In the soil environment, researchers have found that NMs can play a unique role in improving soil properties in ways that are not yet fully understood. For example, Prasad (2013) found that silicates of transient elements coated with micronutrients such as Cu, Zn, Ag, Zr, and Mn can improve soil nutrition. Lodriche et al. (2013) have patented two types of siliceous diatomite with comb-like structures that can be used to absorb biologically active molecules such as pesticides and herbicides and to release them at the target side. Selenium-enriched siliceous carbonate rocks are also being studied for their potential to improve soil properties over the long term, especially the buffering capacity of the soil (Yin et al., 2009). Additionally, inorganic fertilizers consisting predominantly of minerals and rocks, e.g., natural selenium-rich silicate or carbonate rock that have been thermally modified and activated with alkaline solution with a mixture of sand, can be used for soil improvement purposes (Xuebin et al., 2009). Pure ZnO NPs accompanied with a wetting agent have been used to increase the yield of fruit trees (He et al., 2009). Vempati and Hegde (2011) created a complete plant growth medium based on natural zeolite coated with nanoiron oxides and plant nutrients augmentation. The growth medium performed several key soil functions, such as providing a reasonable cation and anion exchange capacity for nutrients, enhancing water filtration and water retention, supporting soil structure, and increasing the availability of water for crop production. The use of nanobentonite in combination with macro- and micronutrients has been shown to provide their slow release for soybeans (Liu et al., 2012). Moreover, halloysite with tabular crystals has a similar gradient of release of nutrients (Price & Wagner, 2008). The use of halloysite nanotubes coated with polysaccharide with a sulfhydryl modifier has also been proposed as a gradual dissolution nanofertilizer (Chao et al., 2020). Kaolinite and illite can be combined with polymers and nano-grade marsh dregs-gangue compounds to create coatings with controlled release (Zhang & Wang, 2005). Additionally, a multiphase fertilizer containing diatomite, montmorillonite, or kaolinite that concentrates Mg, K, and P extracted from seawater was designed to increase wheat yield by 30–60% (Zuo, 2007). Cao et al. (2007) applied the nanosized-space structure of palygorskite with composites, incorporating nitrogen as a macronutrient for its direct release into the soil environment. Also, Barati (2010) used a nanocomposite superabsorbent polymer carbohydrate graft copolymer fluid/water absorption and retention capacities, in combination with clinoptilolite and zeolite. Nan et al. (2018) published a study

Table 18.3 Overview of licensed and patented nanofertilizers and related products with potential application in agricultural practices

Types of fertilizers with potential agricultural effects	Product name or type of application	References
Active nanograde organic humic acid, where mode of action with the beneficial effect is based on functional groups included in humic acids	Active organic fertilizer	Wu (2004a)
Hydroxides of rare-earth elements in nanoforms	Nanopriming, spray-dispersion integrated into organic, or microsized fertilizers, or composite materials	Fan et al. (2007)
Fertilizers with rare-earth elements (REE) in the oxide chemical forms applied as plant growth enhancer	Nanopriming, spray-dispersion, or part of organic, or micro-fertilizers	Fan et al. (2005)
Carbon-based nanoparticles from 5 to 200 nm, and by mixing with soil nutrients, e.g., ammonia bicarbonate, urea, etc., show the synergistic effects of both counterparts	Soil application	Liu and Zhang (2010)
Silicon-titanium nano-fertilizers containing SiO_2 and TiO_2 as their primary constituents a (for both ~20%), with micromolecular silica ~4%, and nanosilver or phosphoric acid (~1%). Inventors declare the huge biomass growth for crops like wheat, rice, etc., decreasing stress tolerance, phytotoxicity, or increasing pesticide activity	Foliar application	Lai and Lai (2022)
Silica with biological origin such as diatomite, where the special thermal treatment was done and modified them to the ceramic substances	Soil application	Yu (2005)
Materials based on silicates, nano-leucite (microcline), contain K and Al tectosilicates enriched with calcium ammonium nitrates as a source of macronutrients for the gradual release of nitrogen to root system	Soil application, nanofertilizers are integrated into pellets forms	Farrukh and Naseem (2014)
Hydroxyapatite encapsulated with sulfate lignin–iron mixture as active responsive smart nanofertilizers which encourage plant's vitality under enormous environmental stress	Soil application	Jeon et al. (2022)
Nanoclays, phyllosilicates from Ximaxi locality mixed with selected micronutrients and applied as additives	Granule application	Li et al. (2002)
Amorphous silica as, agropolymers which contain carbohydrates are used for rice, millet, sunflower, etc., where carbohydrates gradually release plant-growth substances such as proteins, tannins from the surface of silica grains	Variable application, liquid formulation to treatment for roots, seedling, soil, and foliar application, or granules formation	Prasad (2013)

(continued)

Table 18.3 (continued)

Types of fertilizers with potential agricultural effects	Product name or type of application	References
Silica-based materials, or different natural and artificial polymers constructed as a composite-type structure with anchored functional Ag NPs which play antibacterial and antifungal roles	Colloidal dispersion vs. HeiO®, AGS-20	Jaynes et al. (2012)
Struvite $(NH_4)Mg(PO_4)\ 6H_2O$ with nanowire morphology contains easily soluble nitrogen, phosphorus, and magnesium and is an "ideal" nanofertilizer obtained from contaminated waters	Potential soil application	Zhou et al. (2018)
Ag NPs manifest enormous antifungal and pesticide activity	Colloidal dispersion	Liu et al. (2007)
ZnO NPs covered with chitosan potentially applied for the reduction of soil pathogen bacteria	Aquatic media application	Mohapatra and Limayem (2020)
Copolymer structure contained humic acid and ammonium polyphosphate with ZnO NPs as new type of nanofertilizer for more effective growth of plant roots	Soil application	Wang et al. (2022)
Organic-based fertilizer (bionutrients) extracted as amino acids from animal organs, plants, and enzymes; gained NMs have around 20 nm which principally support plant physiology and yield reach up to 45%	Organic spray	Kumar et al. (2013a)
Carbon nanotubes encourage water uptake in seed, germination, and plant growth, effective concentration ranges between 10 and 200 μg/ mL^{-1}, the mode of action is based on penetration through cell walls and fully highlighted the concept smart-treatment delivery system in plants	Nanopriming	Biris and Khodakovskaya (2011)
Carbon nanotubes as single, multiwalled, or water-soluble biostimulators, and nanofertilizers. They could be incorporated into soil, seeds, plants, compost, or water for increase of anion or cation exchange capacity or encourage soil microflora	Soil application or use into cultivation media	Lewis (2013)
Nanofertilizers containing macro-, and micro-fertilizers (NPK and others) with synthetic polymer like polyethylenimine (PEI) to encourage bioavailability of nutrients. Mode of action is based on polymer nanoparticles-attached molecules as carried medium in environment of plant	Aqueous solution, spray application	Dedhia et al. (2022)

on nanosilicon fertilizer incorporated into regular granular fertilizers, which showed improved application and soil absorption without redundant ion exchange. The nanosilicon fertilizer consisted of 10–30% SiO_2 (in the size range of 10–200 nm), 50–89% palm oil, and 10–20% epoxy resin. Nano-gypsum with zeolites and composite fertilizers was shown to stabilize soil properties under wide soil conditions (Yang & Wang, 2008).

In comparison to traditional fertilizers, the nitrogen, phosphorous, and potassium (NPK) fertilizers, (Kottegoda et al., 2014) proposed the use of HAP NPs that encapsulate nitrogen-containing macronutrients, which are then released into the soil environment with a range of beneficial impacts. The nitrogen can be applied in several forms, but most commonly as urea and in these proportions to HAP: 1:1, 1:3, 1:4, 1:5, and 1:6. Concept of nanofertilizer that utilizes the fermented organic fertilizer with cotton and contains Fe NPs as an insecticide was published by Liu et al. (2012b). Moreover, it also improves various soil properties and helps with the gradual release of nutrients. The synergistic effect of carbon nanotubes together with NPK fertilizer increases the yield of tobacco and reduces the loss of fertilizers (Xie & Liu, 2012). Additionally, combination of peat with metal oxide species including TiO_2, Fe, and $CaCO_3$ NPs encouraged crop yields (Wu, 2004b).

Microbial fertilizers or nanofertilizers that apply bacteria, urea, NPK, and plant antibiotics as NMs have been shown to increase yield-related parameters while not contaminating the soil and improving the soil structure and its overall vitality (Wang et al., 2009). The use of a biologically synthesized nanoselenium fertilizer has also been shown to improve the quality of fresh blueberry fruit (Tian et al., 2012).

Plant extracts have long been a commercially attractive alternative for agronomical practices. The pure stevia extract, or its combination with NPs of selenium, rare-earth elements, or organic chitosan, organo-Ca, or fermented stevia extract can be used to improve penetration properties into plants. The mixture of these substances with NPs applied as a seed coating agent to watermelon and tomato in soil environment has been shown to increase root growth, the whole development of plants, sugar content, and greatly reduce pests and other disease (Lee et al., 2007). Deb (2013) applied metallic NPs such as Au, Ag, Cu, Al, Ni, or metal alloys that were encapsulated and stabilized with micronutrient-boron compounds, which stimulated several plant-related functions and led to higher yield in potatoes (*Solanum tuberosum*). These increases were reflected in quantitative parameters such as plant height, leaf number, total fresh and dry biomass, chlorophyll content, and qualitative parameters such as decreases in soluble and reduced sugar while starch content increased. These encapsulated metals were applicable for different treatments including foliar application, hydroponics, seed treatment, seedling root dipping, soil application, nutrients for tissue culture, and in vitro cultivation. Here, one of the advantages of coated metals is that they can be transported more easily across plant membranes without consuming excessive ATP energy from the plant.

Soil enrichment is currently being accomplished using natural or artificial polymers, which also serve the purpose of slow or controlled release of nutrients (Lin, 2008). For example, the polymers are based on encapsulation in mixed polymer and polyvinyl alcohol (Liu et al., 2006) or lignosulfonate polymer integrated as a coating (Zhang et al., 2003). The fertilizer delivery containing a polymeric mixture from waste polystyrene foam has been shown to improve adhesive capabilities and encapsulation (Zhang et al., 2005), while nanopolymers containing olefin–starch blends encourage the adhesive or strengthening function of soil granules (Zhang, 2004).

Several types of NMs and nanofertilizers have been utilized in spray applications on plant leaves including micronutrients and macronutrients (Huang et al., 2021), biological NMs including amino acids (Kumar et al., 2013a), nanoselenium amino acid (Wei et al., 2012), carbon nanotubes (Li & Guan, 2011), rare-earth oxides (Wang et al., 2005), pure elements, e.g., sulfur (Xia, 2020), Ag (Malshe & Malshe, 2009; Levard et al., 2012; Yoon, 2005), metal oxides, TiO_2 (Bignozzi et al., 2008; Choi et al., 2003), ZnO, SiO_2, and other non-/metallic materials with applied transient and noble metals such as Cu, Ni, Ag, Pd, Pt, Os, Ru, and Rh (Malshe & Malshe, 2009), as well as other types of innovative and agronomically attractive nanofertilizers (Table 18.3).

The application of nanometals provides the opportunity to use not only the individual pure zero-valent NPs but also the formulation with core–shell structure. These pure metals can be integrated into either the core or applied as NP coating and can contain various types of metals alone or in combination with other compounds to provide the widespread antibacterial, antiviral, antialgal, and antifungal activity. Also, a non-metallic core composed of materials such as $CaCO_3$ or barium sulfate, encapsulating NMs within emulsions with polyvinyl chloride or various porous polymers, can exhibit several combined effects.

Upon initial dissolution of encapsulation layer, which may contain, for instance, Ag, a combined photocatalytic effect can be achieved through nanoparticle domain effects mediated with TiO_2, ZnO, or SiO_2 (Malshe & Malshe, 2009). Conversely, the cores of NPs can also be prepared with metals or other compounds and serve as a pesticide (Yoon, 2005). In the case of commercially popular Nano-argentum 10, the manufacturer not only declares high sensitivity and stability during NP treatment, which is highly effective against pathogens, including the elimination of insects, but also carries the risk of silver-soluble species manifesting hazardous, toxic, and non-degradable nature that can harm the environment (Levard et al., 2012). Another nanocomposite from the same toxicological category, based on TiO_2, was brought to the forefront by Bignozzi et al. (2008), which exhibits exceptional antibacterial, antimicrobial, antiviral, antimycotic, germicidal, and photo-remediating properties.

Huang et al. (2021) proposed a strategy for precise agriculture that involves the use of NPs with well-defined crystallinity and size for spray application on plant leaves. Also, the strict morphology of the NMs is crucial, since it has been shown that NMs entity with tabular-like shape maximized absorption and adhesion to the leaf surface, as well as great and positive zeta potential of functional NPs, was important. The study highlighted the use of micronutrients and macronutrients such as Zn, Mn, Mo, Mg, Fe, Cu, B, K, and Ca. The release of these nutrients is facilitated through the gradual release of their more soluble and reactive components in a mixture with soluble nitrates or organic acid salts, such as zinc or manganese oxalates. The effectiveness of the approach was confirmed in experiments on *Capsicum annum* plants. Xia (2020) introduced NPs of elemental sulfur (up to 50 nm) in colloidal systems together with various “dispersion-promoting” agents accompanied with anti-aggregation, deflocculation, antistatic, and surfactant properties. The aim of dispersion-promoting agents is to improve the physical properties of colloids, dispersions, and emulsion with their longer-term stability. Also, for spray application, it is important to not degrade the existing counterparts, encourage great adhesion, and absorption during foliar application. It is recommended to apply these compounds in preferential ratio of nano-sulfur vs. anti-agglomerating agents, or solution with boric acid, thiosulfate, Tween 60, acetic acid, or water. Li and Guan (2011) used carbon nanotubes in foliar treatment, which improved leaf permeability and stress tolerance. In the case of foliar application of TiO_2 NPs, individually or in combination with other fertilizers, it increased photosynthetic activity by improving the sunlight energy conversion for rice plants (Choi et al., 2003). Kumar et al. (2013a) and Wei et al. (2012) demonstrated the effectiveness of nanofertilizers based on extracted amino acids from animal organs, plant parts, and enzymes. When deposited on the leaves as foliar nutrition, they resulted in increased plant growth and improved absorption ability, particularly when combined with nanoselenium.

The mechanism of action of nanofertilizers made of rare-earth elements, such as scandium and yttrium, and lanthanides (La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu) is not fully understood. These elements are often in an oxidation rate of $^{+3}$ and are considered relatively strong oxidants. They are associated with several mineralogical formulas and are predominantly found in phosphates (monazite, xenotime), carbonates (bastnaesite), oxides (loparite, euxenite), or fluorites (parisite). Mediated uptake and translocation of rare-earth elements can initiate an increase in the plant's intake of nitrogen and potassium, while the intake of phosphates is limited. However, these elements also perform other supportive physiological and biochemical functions (Hu et al., 2004). The spray application of rare-earth elements is most probably based on a more intense quantum effect of NPs or on their unique photocatalytic properties (Wang et al., 2005). Other potential applications of nanofertilizers in the context of hydroponic, aquaponic media, or nanopriming during germination or initial growth of plants are listed in Table 18.3.

There is ongoing debate about the concepts of using nanofertilizers in the near future. One of the possibilities is to initiate the release of "agricultural active ingredients" by means of external stimuli. These external stimuli activate the reactions under the influence of electromagnetic or magnetic fields or changes in temperature and chemistry. The concept is based on the release of "active ingredients" in response to changes in pH, barometric and osmotic pressures, exposure to water, solvents, bacteria, or enzymes. One example is Al NPs coated with polymers that contain polyelectrolytes and functional organic components containing agronomically important acaracides, fungicides, bactericides, herbicides, etc. (Li et al., 2010). Similarly, organosilane-coated magnetic NPs associated with one or more attractive agriculture chemicals including pesticides, herbicides, fungicides, rodenticides, etc. were activated by an external magnetic field (Boday et al., 2013). Microcapsule architecture (Fig. 18.1a) and the basic process of germination and plant development under initialization of magnetic field are illustrated in Fig. 18.1b.

In the near future, one of the agriculture challenges will involve the use of nanosensors and electro-optic nanotechnology for real-time, in-situ monitoring of environmental conditions, as well as the integration of drone devices into actual field experiments and practices.

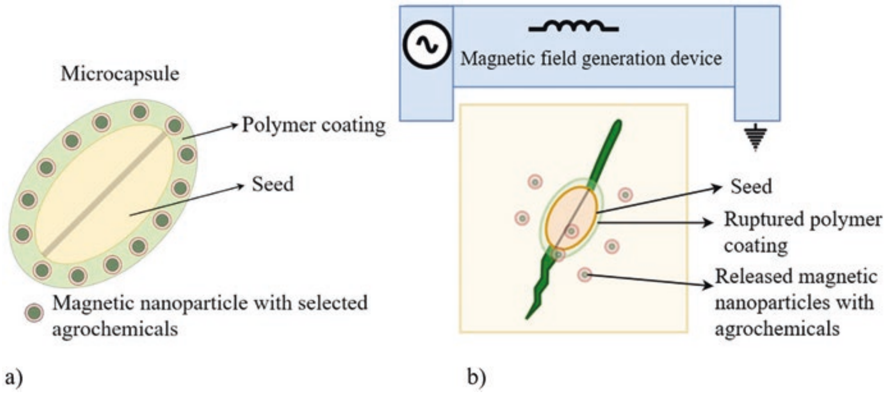

Fig. 18.1 (**a**) Cross-sectional illustration of encapsulated seed, the integrated magnetic NPs are coated with various agrochemicals (fertilizers, pesticides, herbicides, etc.) for controlled release, and "activation" are initiated under magnetic field stimuli; and (**b**) cross-sectional view of sprouted seed planted in soil (or growth medium) with released magnetic NPs and agrochemicals under magnetic field treatment

3 Effect of Foliar Application of Selected Inorganic Nanofertilizers on Crops Under Field Conditions

The entry of nanofertilizers based on INPs into the plant can affect several of their functional properties. The activity of these foliarly applied NPs changes the leaf surface anatomy and its ambient structures, where the NPs are gradually absorbed, transported, and distributed until they "reach" the targeted location (Li et al., 2019).

The leaf organs of a plant contain two basic types of trichomes: non-glandular trichomes (NGTs) and glandular trichomes (GTs). The function of the trichomes may vary depending on the organ that bears them (Werker, 2000). Trichomes create a protective barrier against herbivores, ultraviolet (UV) irradiation, pathogen attacks, and excessive water loss through transpiration (Wang et al., 2021).

Studies have shown that the application of Fe_3O_4 NPs can result in changes in trichome density and occurrence (Askary et al., 2016). The application of iron oxide NPs caused a decrease in hair density and number of some kinds of trichomes on the leaf surfaces of *Mentha*. However, the application of Fe_3O_4 NPs increased the essential oil amount in *Mentha piperita* (Askary et al., 2016). Opposite effect on hair density *Oryza sativa* was found by Da Costa and Sharma (2016) who observed that osmotic stress resulting from the application of CuO NPs manifested itself in morphological changes of the leaves, which increased the size and number of trichomes. According to Li et al. (2021), NGTs play an important role in the absorption and translocation of foliar-applied ZnO. Increased concentrations of Zn were found in the basal areas of NGTs after foliar application; however, this role of trichomes was not confirmed after root application of NPs in sunflower. Cifuentes et al. (2010) observed that the different rate of transport and accumulation of NPs also depend on the plant species. The slowest transport of magnetic carbon-coated NPs from roots to leaves was observed in sunflower. Higher accumulation of NPs was found in leaf trichomes of wheat plants, lower in the other species from the group of dicotyledonous plants, including the sunflower.

Plant trichomes play an important role in pathogen defense as well as in stress conditions due to the accumulation of various substances within their cells. For example, sunflower is very tolerant of high manganese concentration due to the accumulation of Mn in and around trichomes (Blamey et al., 1986), ornamental sunflower 'Sunbright' accumulates Si in leaf trichomes (Zanão Junior et al., 2017). Nanosilica provides higher tolerance of plants to abiotic and biotic stress. The nanosilica uptake in the leaves reduces the accumulation of reactive oxygen species (ROS) and membrane lipid peroxidation. Besides that, it restricts the entry of sodium ions and other heavy metals in plants and nanosilica deposition in the leaf tissue enhances the plant defense against pathogens (Mathur & Roy, 2020).

The epidermis of leaves is an important pathway for the entry of NPs (or nutrients) into the plant. Epidermal cells are often covered with a cuticle, which contains long-chain aliphatic waxes and cutin. Read et al. (2020) stated that due to that fact, differences in leaf surface characteristics between wheat and sunflower did not affect Zn absorption. Therefore, the cuticle is probably the main pathway of Zn absorption. However, the entry of NPs into the plants is limited by their size, due to the various sizes of cuticular pores in different plants.

The opening size of stomata, which is in the range of micrometers, is more likely to serve as an entrance for engineered NPs than trichomes or pores in cuticle (Wang et al., 2013b; Larue et al., 2014b; Hong et al., 2016; He et al., 2022). Larue et al. (2014a) suggested that Ag NPs and TiO_2 NPs travel through stomata into lettuce leaves after foliar application. He et al. (2022) investigated the role of stomata in the internalization of Ag NPs in *Arabidopsis thaliana*. The amount of Ag NPs (surface attachment and internalization) in the leaves positively correlated with the stomatal aperture. When ABA (abscisic acid) triggered stomatal closure of ABA-responsive ecotypes, the amount of Ag NPs in *Arabidopsis* leaves decreased. There was no difference in the amount of Ag NPs in the leaves of ABA-insensitive mutants with or without ABA due to similar stomatal apertures. Khai et al. (2022) found out that SeNPs exhibited a positive effect on the formation and development of gerbera stomata. The increase in the concentration of SeNPs from 0.1 to 0.7 $mg.L^{-1}$ was proportional to the increase in stomatal density, whereas at concentrations 1, 1.5, and 3 $mg.L^{-1}$, the stomatal frequency decreased significantly. SeNPs also influenced the morphology and the opening of the stomata. The increase in SeNPs concentration from 0.1 to 3 $mg.L^{-1}$ was followed by a decrease in stomatal opening. According to Landa (2021), iron-based and CeO_2 NPs enhance stomata opening which causes a better gas exchange and CO_2 assimilation rate. Kim et al. (2015) found that exposure of *Arabidopsis thaliana* to nano-zerovalent iron (nZVI) triggered high plasma membrane H^+-ATPase activity. The increase in activity caused wider stomatal aperture. This study showed that nZVI enhances stomatal opening which leads to the possibility of increased CO_2 uptake. Similarly, Yoon et al. (2019) did a research on *Arabidopsis thaliana* and found out that CO_2 assimilation rate, intracellular CO_2

concentration, transpiration rate, and stomatal conductance were significantly higher for nZVI-exposed plant leaves than control plants. Alidoust and Isoda (2013) found a positive effect of Fe_2O_3 NPs on *Glycine max* in the form of increase in photosynthetic rates following spraying. It was attributed to an increase in stomatal opening. More pronounced positive effects of NPs were observed via foliar application.

Other leaf structures can also be affected by the application of NPs. Using the technique of transmission electron microscopy, foliarly deposited NPs were shown to be localized in the cell walls and plasmalemma (Li et al., 2017), near or entrapped within the plasmodesmata, and also in the cytoplasm (He et al., 2022) of soybean and rice leaves, and leaves of *Arabidopsis thaliana*, respectively. The safe entry of NPs into cells and their specific intracellular compartments is an important step in achieving high-yield prognostic efficacy of foliar application (Behzadi et al., 2017). Endocytosis, ionic, or aqueous molecular pathways, formation of carrier protein complexes, physical damage or binding to organic substances have been recognized as the main mechanism for NPs entrance into the plant cells (Hong et al., 2021). The first cell-level barrier to entry NPs is the cell wall having pores with the size of 5 to 20 nm, allowing NPs smaller than 20 nm in size to easily penetrate. Larger sized NPs (>20 nm) are transported through other above-mentioned routes, i.e., ion channels, endocytosis, and aquaporins, or via new pores created in the cell wall (Hashemi, 2019).

The number of NPs applied foliarly has a crucial impact on the overall effects they have on the plant, its tissues, and the organization and architecture of its cells and whether it will be positive or negative. The results obtained by Raliya et al. (2015) revealed the critical concentrations (250 $mg.kg^{-1}$) of TiO_2 and ZnO NPs up to which the plant growth and development was stimulated, with no improvement beyond it. Unfortunately, the number of studies dealing with actions (especially positive ones) of foliar-sprayed INPs on plant subcellular components are very limited and scarce. By contrast, destructive ultrastructural modifications of plant cellular organelles including cell walls, cell membranes, chloroplasts (thylakoids), peroxisomes, and mitochondria (swollen cristae), as well as abnormal nucleus and abnormal size of plastoglobules and starch granules as a result of NPs phytotoxicity irrespective of exposure route, are demonstrated in many reports (Ranjan et al., 2021). Considering foliage spraying, TEM observations performed by Larue et al. (2014b) suggested that foliarly applied agglomerates of TiO_2 NPs can damage cuticle and cell walls in lettuce leaves. Also, it is known that NPs are able to generate reactive oxygen species (ROS) (oxidative stress), which in turn can cause lipid peroxidation (Paciorek et al., 2020). Since the unsaturated fatty acids in the cell membranes and biomembranes are major targets for ROS (Hashemi, 2019), disruption of cytoplasmic membrane and mitochondrial damage can occur. In many research studies, chloroplasts have been found to be the cell organelles most sensitive to the harmful impacts of NPs (Olchowik et al., 2017; Aleksandrowicz-Trzcinska et al., 2018). In *Capsicum annuum*, NPs absorbed in roots were then transported and utilized by the leaves. Low concentrations of iron NPs caused an increase in the number of chloroplasts, number of the mesophyll cells, and grana stacking which contributed to the improvement of plant growth (Yuan et al., 2018). The opposite effect on the assimilation tissue of wheat leaves was observed after application of CeO_2 NPs particles, which were transported from roots to shoots, where the exposure of leaf mesophyll to CeO_2 NPs led to chloroplast damage (Du et al., 2015). In the context of the photosynthetic apparatus, ultrastructural changes of chloroplasts with abundant and larger osmiophilic granules have been observed by TEM in foliarly exposed soybean and rice leaves to AgNPs (Li et al., 2017). Similarly, disturbances in the shape of chloroplasts with markedly increased plastoglobules and the presence of large osmiophilic globules in the cytoplasm (as an indication of the final stage of chloroplast disintegration) of oak leaves and pine needles after their foliar treatment with 50 $mg.L^{-1}$ of Cu and Ag NPs have been reported by Olchowik et al. (2017) and Aleksandrowicz-Trzcinska et al. (2018), respectively. Interestingly, ultrastructure of other organelles, such as cell walls, mitochondria, and vacuoles, remained unchanged in both studies.

Furthermore, the size of the leaf surface can also be influenced by the type, size, and concentration of NPs. Alkhatib et al. (2019) proved that the leaf area of tobacco plants treated with 5 nm iron oxide was significantly reduced, whereas plants treated with 20 nm iron oxide had a larger leaf area compared to control. In addition, the number of leaves on plants can vary. Foliar application of GA-Ag NPs (gum arabic-coated silver NPs) up to 60 $mg.L^{-1}$ significantly increased the number of leaves per plant and the area of leaves of two bean varieties. Increasing the applied concentrations of GA-Ag NPs and $AgNO_3$ up to 60 $mg.L^{-1}$ increased the uptake of both forms of silver in different parts, especially the leaves (El-Batal et al., 2016). It is logical to assume that certain relationships exist between the entry of NPs into the plant environment and the functional properties of field crops, such as increase or decrease in quantitative parameters, yield, and final fruit quality.

3.1 Evaluation of Quantitative, Qualitative, and Physiological Indicators of Crop in the Application of Inorganic Nanoparticles

In field agronomical studies, strategies are currently being developed to adapt to the effects of climate change during the main growing vegetation season (Ditta & Arshad, 2016; Fincheira et al., 2021). This is because gradual drought can negatively impact crop production, particularly in terms of quantitative and physiological indicators (Ndlovu et al., 2020; Farooq et al., 2023). Several studies have now confirmed that these adverse effects can be partially mitigated through the application of nanofertilizers and nanoagrochemicals (Fig. 18.2).

It is well established that the application of various metal and metal oxides NPs can increase the leaf chlorophyll content, encourage photosynthesis, improve water stress index, enhance nutrient uptake, and increase crop yields (Achari & Kowshik, 2018; Rajiv et al., 2018; Fincheira et al., 2021; Ain et al., 2023). Positive effects are

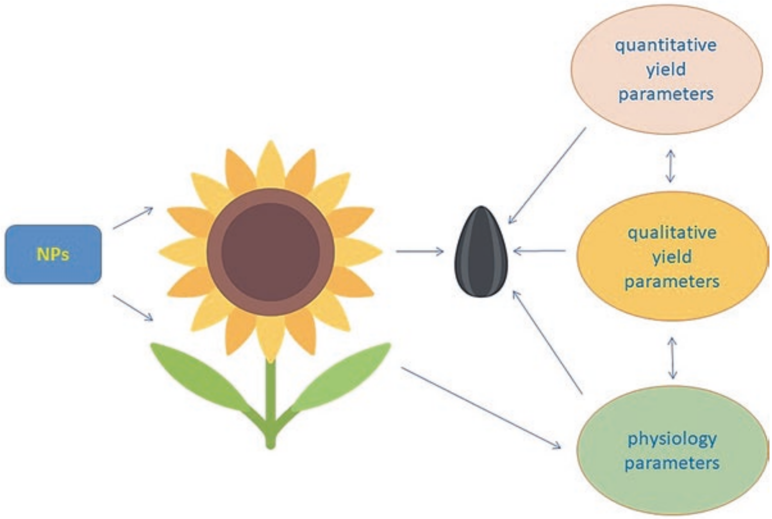

Fig. 18.2 Schematic representation of the influence of inorganic nanoparticles on quantitative and qualitative parameters, as well as physiological responses in plants

primarily observed with direct spray deposition of NPs on plant leaves (Corpas et al., 2021; Zuccarelli et al., 2020), while soil application seems to be less effective (Servin et al., 2015). However, the field of nanofertilizer use still presents new challenges that require further intensive research, including understanding potential negative effects on plants, soil, ecosystems, and humans (Javed et al., 2019; Shaban et al., 2019; Karunanayaka, 2021).

3.2 *Influence of Nanofertilizers on the Quantitative Parameters of Crops*

Nanofertilizers have gained attention in recent years as a potential solution to improve crop productivity and quality. The use of nanofertilizers can potentially increase the bioavailability of nutrients to plants, leading to improved growth and yield. Among the different types of nanofertilizers, metal and metal oxide NPs, such as zinc oxide (ZnO) and titanium dioxide (TiO_2), have been extensively studied for their effects on crop production. The advantage of zinc nanofertilizers, specifically ZnO NPs, has been found to be advantageous due to their ability to achieve similar effects as conventional ($ZnSO_4$) ionic fertilizers at a tenth of the content (Dapkekar et al., 2018; Khanm et al., 2018). The efficacy of ZnO NPs on crop production in field conditions has been well-established for crops such as wheat, corn, or rice. For example, studies by Singh et al. (2019) and Rizwan et al. (2019a) have demonstrated positive effects of ZnO NPs on the quantitative parameters of wheat and found similar positive effects for maize (Rizwan et al., 2019b). Furthermore, research has also shown the positive effects of ZnO NPs on the downy mildew of pearl millet. For these crops, Nandhini et al. (2019) found that ZnO NPs had particularly beneficial effects on the stage of germination and initial growth stages of downy mildew.

Studies on the effect of ZnO on downy mildew of pearl millet in field conditions have been conducted infrequently. One such study, by Kolenčík et al. (2019), found a relative increase in plant height and seed head length at a concentration of 2.6 mg.L^{-1} by spray dispersion. Moreover, Tarafdar et al. (2014) observed similar effects on pearl millet (*Pennisetum americanum*). Lin and Xing (2007) discovered that the root growth of radish and rape was intensified when treated with a concentration of 2 mg.L^{-1} of ZnO NPs in comparison to the control experiment. The authors also observed a significant improvement in the growth parameters of ryegrass at the same concentration. Additionally, it has been found that another oilseed, sunflower, responds positively to low concentrations of ZnO NPs (2.6 mg.L^{-1}) (Kolenčík et al., 2020), where a significant increase in production parameters such as head diameter, weight of dry seed head, weight of 1000 seed, and grain yield was observed. The mechanism of ZnO NP's effectiveness in comparison to chelated bulk $ZnSO_4$ suspension (common zinc supplement) has been found to be responsible for increases in pod yield of peanut plants (Prasad et al., 2012). Mahajan et al. (2011) found that the optimal concentration of ZnO NPs was 20 mg.L^{-1}, which significantly increased growth parameters and yield of beans. At the aforementioned concentration, an increase in the length of roots by 42% and stems by up to 98% was recorded. Rezaei and Abbasi (2014) found that the spray application of chelated form of ZnO NPs intensively stimulated cotton production by increasing the number and weight of bolls per plant. Study of the effect of ZnO NPs on rice has shown that a concentration of 40 mg.L^{-1} can significantly support the crop-yielding parameters as well as yields (Ghasemi et al., 2017). Additionally, the combination of Zn and B nanofertilizers applied through foliar application has been shown to increase the yield of pomegranates (*Punica granatum* cv. Ardestani) (Davarpanah et al., 2016). The growth-promoting effects of ZnO NPs have also been observed at higher concentrations, such as doses of 400 and 800 mg.L^{-1}, which caused a significant increase in the yield of cucumber by 10% and 60%, respectively, compared to the control variant (Zhao et al., 2013).

Inorganic nanofertilizers, like any fertilizer, can demonstrate a toxic effect on plants when applied at inappropriate concentrations. The phytotoxicity of ZnO NPs primarily depends on the specific plant species, but it is generally observed within the range 1500–2000 mg.L^{-1} (Ditta & Arshad, 2016).

There are considerably fewer studies on the effect of gold nanoparticles (Au NPs) on plant production compared to studies focused on metal oxide NPs of macro- and microelements. However, in general, the positive effects of Au NPs outweigh the negative agronomical outcomes in the academical literature (Khan et al., 2019). Several studies confirmed that Au NPs enhance the production of plants, e.g., they improve the germination activity of *Gloriosa superba* (Gopinath et al., 2013) or induce growth and yield in *Arabidopsis thaliana* (Kumar et al., 2013b). Shah and Belozerova (2009) found that low concentrations of Au NPs in combination with Cu NPs positively affected the germination and growth parameters of lettuce, or quantitative parameters of barley plants (Feichtmeier et al., 2015). Hussain et al. (2017) observed an inhibition effect on in vitro seed germination inhibition of *Artemisia absinthium* when exposed to Au NPs. Paradoxically, this finding can be considered positive information because in many countries worldwide, *Artemisia absinthium* is considered a dangerous weed commonly hazardous for crops production.

Titanium-based NPs, such as crystalline modifications of TiO_2, have been shown to have both positive and negative effects on plants, depending on the concentration and stages of growth phase of the plant species (Zahra et al., 2020, 2019). These NPs have been found to play an important role in increasing the uptake of phosphorus by the plants and promoting growth under water-deficient soil conditions. Additionally, the NPs play an important role in nitrogen metabolism, which in turn can affect the final yield of crops. These finding are supported by the study published by Kolenčík et al. (2020), which demonstrated that spray deposition of TiO_2 NPs with a concentration of 2.6 $mg.L^{-1}$ led to a greater head diameter, weight of dry seed heads, weight of 1000 seeds, and grain yield in sunflower. Other studies also reported similar outcomes for various crop plants as well (Gao et al., 2013; Morteza et al., 2013; Tarafdar et al., 2014; Janmohammadi et al., 2016). Similar to other reactive metals, silver in nanoparticulate forms exhibits a diverse and unpredictable mode of actions compared to its ionic or macro forms. Studies have shown that at a lower concentration of Ag NPs, positive effects on the root length of barley were observed in hydroponic media. However, at higher concentrations, a reduction in the root system was observed (Gruyer et al., 2013). The effect of Ag NPs on the growth of maize and beans was similarly evaluated, with results showing that growth was inhibited at higher concentrations and enhanced at lower concentrations, compared to the control experiment (Salama, 2012).

The effect of Ag NPs on plants appears to be highly dependent on the concentration at which they are applied, as evidenced by the presented studies. Also, it is well-established that Ag NPs possess strong antibacterial properties, making them an interesting option for use in crops that are susceptible to bacterial diseases such as potatoes. For example, Davod et al. (2011) found that the combined effect of nanosilver and nitroxin biofertilizer resulted in an increase in yield components mainly due to strong fitness of potato minitubers.

The role of elemental iron during plant photosynthesis is well known, and its application in the form of NPs has been shown to support plant physiological conditions that subsequently resulted in an incerase in yield and yield-related parameters. Studies have found positive effects on soybeans (Sheykhbaglou et al., 2010) and black-eyed pea (Delfani et al., 2014) when Fe NPs were applied at a concentration of 0.5 $mg.L^{-1}$; more precisely increases in number of pods per plant, weight of 1000 seeds, and yield were observed. Similar qualitative results were observed in forage corn (*Zea mays*) when seed priming was done together with foliar application of Fe NPs (Sharifi et al., 2016). The application of combinations of metals including nanoiron, zinc, and manganese under sandy soil conditions resulted in significantly increased yield of pods of peanut plants due to improved utilization of nutrients (El-Metwally et al., 2018). The foliar deposition of Fe, Zn, and NPK nanofertilizers on chickpea leaves under rainfed conditions has been shown to positively affect seed yield (Drostkar et al., 2016). The application of Mn-based NPs has also been shown to support yield and yield-related parameters of mung beans (*Vigna radiata*) when grown on a plant agar medium (Ghafariyan et al., 2013). Similarly, the study of the effects of the spray application of chelated Mo nanofertilizer on peanut plants was observed by Manjili et al. (2014) where the application of the nanofertilizer resulted in increased plant height and branching, number of pods per plant, weight of 1000 seeds, number of seeds per plant, seed size, and seed yield of peanut.

The effects of different types of nanofertilizers, including metal and metal oxide NPS, on quantitative crop parameters are presented in Table 18.4.

3.3 Effect of Inorganic Nanoparticles on the Quality of Final Agricultural Products

To achieve high seed quality, field crops require adequate levels of both micro- and macronutrients. Proper nutrient management can enhance the bioavailability of these nutrients, which is essential for optimal growth, yield quantity, and quality (Improved Crop Nutrition) (Ahmed et al., 2021). Several studies have indicated that the use of nanofertilizers leads to improved seed quality. This is likely due to the lower concentrations of nutrients used, the gradual release of nutrients, and the more targeted activity of nanofertilizers compared to conventional fertilizers (Liu & Lal, 2015).

Elementary zinc is a regulatory cofactor and a structural component of many enzymes, lipids, and proteins. It plays a crucial role in the metabolic pathways of plants, particularly in photosynthesis, the biosynthesis of phytohormones, the antioxidant defense system, the metabolism of nucleic acids, and the development of the root system, which allows crops to take up key nutrients, especially nitrogen, necessary for protein synthesis (Sturikova et al., 2018), and also encourage yield, and quality crop production (Chattha et al., 2017; Sturikova et al., 2018). For agricultural purposes, it is important to apply the correct dosage of zinc to avoid negative effects on the plants that can result from a deficiency or excessive dosages (Impa et al., 2013).

The unique properties of zinc containing NPs make them a promising option for maintaining adequate zinc levels in plants (Umair Hassan et al., 2020), improving soil fertility and soil properties, and enhancing crop production and food processing (Sheteiwy et al., 2021). Sabir et al. (2020) found that the protein content of corn grains (*Zea mays* L.) was increased by 77.3% at a concentration of 8 $mg.L^{-1}$ when treated with zinc NPs. Higher protein content is beneficial for photosynthesis, viability, and the healthy development of crops. El-Metwally et al. (2018) also observed increased protein content in peanuts (*Arachis hypogaea* L.) treated with ZnO NPs.

Table 18.4 Quantitative parameters of crops evaluation against several type of metallic-based nanoparticles

Type of NPs	Concentration	Species	Effect	References
Ag	0, 44 $mg.L^{-1}$	*Solanum lycopersicum*	Increase of plant biomass, height, and shoot length	Noshad et al. (2019)
Ag	0, 2000 $mg.L^{-1}$	*Triticum aestivum*	Decrease of plant biomass, height, and grain weight	Yang et al. (2018)
Au	0, 62, 100, 116 $mg.L^{-1}$	*Cucumis sativus, Lactuca sativa*	Positive effect on germination index	Barrena et al. (2009)
Ca	0, 160 $mg.L^{-1}$	*Arachis hypogaea*	Increase of plant biomass, height, shoot length and yield	Liu et al. (2005)
CeO_2	0, 100, 200, 400, 800 $mg.L^{-1}$	*Helianthus annuus*	Accumulation of Ce in sunflower roots with very low translocation to the upper plant parts, and no significant effects on production parameters	Tassi et al. (2017)
Fe_3O_4	0, 5, 10, 15, 20 $mg.L^{-1}$	*Triticum aestivum*	Increase of plant height, spike length, weight of shoots, roots, spikes, and grains	Rizwan et al. (2019a)
Silica NPs	0, 250, 1000 $mg.L^{-1}$	*Arabidopsis thaliana*	The size-dependent uptake by roots; no toxicity even at doses	Slomberg and Schoenfisch (2012)
TiO_2	0, 750 $mg.L^{-1}$	*Oryza sativa*	Increase of shoot length, grains, shoots, and roots	Zahra et al. (2017)
TiO_2	0, 400 $mg.L^{-1}$	*Raphanus sativus*	Increase of germination parameters	Haghighi and Teixeira Da Silva (2014)
TiO_2	0, 0.05, 2 $mg.L^{-1}$	*Brassica oleracea*	The higher concentrations had negative impact on shoot length, whereas positive impact on root length	Singh et al. (2012)
TiO_2	0, 2.6 $mg.L^{-1}$	*Helianthus annuus*	Increase of head diameter, weight of dry seed head, weight of thousand seeds, and grain yield	Kolenčík et al. (2020)
ZnO	0, 500 $mg.L^{-1}$	*Glycine max*	Decrease of root length and stem length	Yoon et al. (2014)
ZnO	0, 25, 50, 75, 100 $mg.L^{-1}$	*Triticum aestivum*	Increase of plant height, spike length, weight of shoots, roots, spikes, and grains	Rizwan et al. (2019a)
ZnO	0, 50, 75, 100 $mg.L^{-1}$	*Zea mays*	Increase of shoot length, number of leaves, shoot dry weight, root dry weight	Rizwan et al. (2019b)
ZnO	0, 15, 62, 125, 250, 500 $mg.L^{-1}$	*Triticum aestivum*	Significant enhancement of seedling growth and seed germination activity	Singh et al. (2019)

(continued)

Table 18.4 (continued)

Type of NPs	Concentration	Species	Effect	References
ZnO	2.6 mg.L^{-1}	*Setaria italica*	Increase of plant high and seed head length	Kolenčík et al. (2019)
ZnO	2.6 mg.L^{-1}	*Helianthus annuus*	Increase of head diameter, weight of dry seed head, weight of thousand seeds, and grain yield	Kolenčík et al. (2020)
ZnO	0, 1 mg.L^{-1}	*Lens esculenta*	Decrease of plant height, increase of number of pods per plant, weight of thousand seeds, and seed yield	Kolenčík et al. (2022)

In addition to higher protein content, these NPs also increased the concentration of chlorophyll, carotenoids in leaves, total carbohydrates, soluble sugars, oil, and nutrients such as N, P, Fe, Mn, and Zn in the seeds at an effective concentration of 30 mg.L^{-1}. Singh (2015) observed a positive effect on the oil quality of sunflowers (*Helianthus annuus* L.) under field conditions when treated with ZnS NPs, while Singh et al. (2019) found that the grain quality of spring wheat (*Triticum aestivum* L.) was improved with ZnO NPs treatment. Kolenčík et al. (2019) observed higher levels of oil and starch in foxtail millet (*Setaria italica* L.) treated with ZnO NPs, and Kolenčík et al. (2020) shown the increased oil content in sunflowers (*Helianthus annuus* L.) treated with ZnO NPs compared to the control group without nanoparticles.

The application of ZnO NPs to lentil plants (*Lens esculenta* L.) resulted in changes to the mineral nutrient content of the seeds, including a statistically insignificant increase in potassium, where higher levels of potassium are often associated with better taste properties. Moreover, the control group had a slightly higher content of phosphorus, which may act as an anti-nutrient in humans (Kolenčík et al., 2022). Similarly, Ernst et al. (2023) investigated that sunflower (*Helianthus annuus* L.) treated with ZnO NPs had lower levels of phosphorus and higher levels of linoleic acid compared to the nanoparticle-free control. In line with these results, Sham (2017) evidenced that the spray deposition of ZnO NPs increased the quality parameters, including oil content, of sunflowers (*Helianthus annuus* L.). Studies on peanuts (*Arachis hypogaea* L.) and corn (*Zea mays* L.) treated with ZnO NPs also obtained higher levels of proteins, carbohydrates, and oil in peanuts, as well as Zn content, chlorophyll concentration, and photosynthesis intensity in corn (Rizwan et al., 2017, 2019b; Subbaiah et al., 2016).

Higher photosynthesis intensity is typically associated with improved final fruit quality, such as increased oil, starch, crude protein content, or higher biomass (Bellesi et al., 2019) and reduced physiological water stress (Kolenčík et al., 2019). The improvement of photosynthesis intensity of zinc-based NPs can be inferred from the application of the conventional ionic forms. The nutritional composition of the final products can also be significantly affected by the application of $ZnSO_4$. For example, Singh et al. (2022) investigated that cherry tomatoes (*Solanum lycopersicum* L.) treated with $ZnSO_4$ had increased levels of vitamin C and total soluble solids (TSS), and Sardar et al. (2021) observed that the highest values of vitamins A, B, vitamin C, flavonoids, carotenoids, and phenols were found in tomatoes (*Solanum lycopersicum* L.) treated with $ZnSO_4$ at a concentration of 30 mg.L^{-1}. Similarly, ZnO NPs can improve photosynthesis by increasing chlorophyll concentration. For example, by increasing the concentration of chlorophyll, ZnO NPs increased the efficiency of photosynthesis and improved plant growth of wheat (*Triticum aestivum* L.) under salt stress (Adil et al., 2022).

Zinc NPs in combination with saponins have been shown to enhance crop growth and protect plants against phytopathogens and fungal diseases (Zabrieski et al., 2015; El-Argawy et al., 2017; Jamdagni et al., 2018; Nandhini et al., 2019). These NPs have demonstrated antibacterial activity against a range of bacteria, including *Escherichia coli* (Zhang et al., 2007; Padmavathy & Vijayaraghavan, 2008), *Klebsiella pneumonia, Staphylococcus aureus*, *Candida albicans,* and *Penicillium notatum* (Janaki et al., 2015; Thi et al., 2020), as well as *Salmonella enterica, Typhimurium, Aspergillus flavus, A. fumigatus,* and *Candida albicans* (Kaushik et al., 2019). Research has also shown that plants that are not infected with fungal pathogens maintain higher grain quality criteria (Schmidt et al., 2016).

Iron is an essential micronutrient that plays a vital role in enzymatic reactions, photosynthesis, DNA translocations, RNA synthesis, and auxin activity (Sheykhbaglou et al., 2018). However, due to the limited availability of iron minerals, iron-based NPs have been suggested as an alternative method of supplying this deficiency (Askary et al., 2017). The application of iron-based NPs (Fe_3O_4) with zinc dioxide has been shown to increase the total chlorophyll content (15.9–17.3%), as well as the concentration of Fe and Zn in the fruit and seeds of cucumber (*Cucumis sativus* L.) by 5–30.5% and 2–58.5%, respectively. Additionally, foliar application of these NPs has been found to increase the content of starch, soluble proteins, soluble sugars, and oil in the seeds of cucumber (Gupta et al., 2022). Analogical results have been observed by Tawfik et al. (2021) in *Moringa oleifera* plants (*Moringa oleifera* Lam.), where the application of iron oxide NPs (Fe_2O_3 NPs) at a concentration of 40 mg.L^{-1} resulted in significant increases in proline, indole acetic acid (IAA), photosynthetic pigments, crude protein, amino acids, and total soluble sugars. The Fe_2O_3 NPs also promoted growth in peanut (*Arachis hypogaea* L.) by regulating phytohormone and antioxidant enzyme activity (Rui et al., 2016).

The application of titanium dioxide (TiO_2) at concentrations of 100–200 mg.L^{-1} has been found to enhance the development of total phenols and flavonoids in sage (*Salvia officinalis* L.) (Ghorbanpour, 2015). In addition, the concentration of monoterpenes, the main constituent of essential oils in sage, increased significantly after the application of 200 mg.L^{-1} of TiO_2. This increase in monoterpenes is thought to be a key factor in the plant's protection mechanism against free radicals generated by NPs. The combination of silver NPs and methyl jasmonate has been shown to improve the medicinal properties of pot marigold (*Calendula officinalis* L.). This treatment significantly increased the content of saponins by 177% compared to the control. Moreover, it also led to an increase in the content of anthocyanins and flavonoids versus the control variant (Ghanati & Bakhtiarian, 2014).

Similar to silver, gold also does not belong to plant nutrients necessary for the regular growth and development of plants, not even in trace concentrations (Siddiqi & Husen, 2016). Hence, Alloway (2012) classified gold as an ultramicronutrient for plant environment. Several studies have shown its positive effects, where the effectiveness primarily depends on the concentration, and form of gold occurrence, or plant species. In the case of Au NPs ranging in size from 0.5 to 100 nm, they have been identified in various plant tissues (Siddiqi & Husen, 2016). The transport of Au NPs is likely influenced by their oxidation into mobile, ionic chemical species such as Au^{+} and Au^{3+}, and after successful accumulation, they are recrystallized back into nanoparticulate forms through reduction processes. In plant physiological context, Au NPs could be playing a crucial role of "energy generation centers" (Shah et al., 2014) under sunlight radiation (Li et al., 2020). Most likely, this energy transfer is evoked by different types of changes in plants, for example, Arora et al. (2012) confirmed a more intense chlorophyll production and fixation of CO_2 resulting in higher number of pods and seed yield in comparison with control. These outcomes were obtained at a spray dispersion of Au NPs (10 $mg.L^{-1}$) applied to mustard (*Brassica juncea* L.). A similar relationship between a more intense physiological reaction and agronomic yield-related parameters such as weight of dry seed head during foliar application of Au NPs concentration of 0.1 $mg.L^{-1}$ and biosilica composite at 10 $mg.L^{-1}$ was published by Ernst et al. (2023). In addition, the authors also observed that the final quality of sunflower seeds was improved in terms of mineral nutrient content, with a lower concentration of the human antinutrient phosphorus and a relatively higher concentration of silicon compared to the control. There was no statistically significant difference in the other analyzed nutrients, including Fe, K, Ca, and Mg, and transportation of Au NPs was not found to negatively affect grain quality. Moreover, Au NPs were not detectable in either grains or hulls. Additionally, the treatment with Au NPs was found to result in higher content of linoleic acid and lower content of oleic acid, compared to the control variant, for the examined fatty acids that humans cannot synthesize.

Overall, several studies have shown that inorganic NPs can have a positive impact on the quality of edible plant parts, including fruit and contribute to the safety of the food chain and environment (see Table 18.5 for the effects of various INPs on the quality of selected crops). However, the use of nanotechnologies also raises concerns about potential unknown side effects or impacts on the quality of final food products. One concern is the potential for persistent INPs to translocate from foliar or soil application to the final fruit and affect its antinutrient profile.

3.4 Effect of Inorganic Nanoparticles to Crop Physiology

One of the most significant processes in plant food production is photosynthesis, which is highly sensitive to external environmental stress conditions. Plants naturally respond to stress by activating antioxidant systems, but other potential

Table 18.5 Selected types of inorganic nanoparticles and their effects on crops that may influence the quality of the final products

Type of NPs	Concentration range	Crops	Effect	References
ZnO	0, 2, 4, 8, 16 $mg.L^{-1}$	*Zea mays* L.	Increase of protein content	Sabir et al. (2020)
ZnO	30 $mg.L^{-1}$	*Capsicum annuum* L.	Increase in the content of N, P, Mg, Mn, Zn, Fe, ascorbic acid, total phenols, proteins, antioxidant capacity, and fruit hardness	Uresti-Porras et al. (2021)
nSe	3, 4.5 $g.L^{-1}$	*Festuca arundinacea* Schreb.	Higher content of crude protein, lipids, crude fiber, carbohydrates, total phenols, flavonoids, tannins, and selenium, and increase in antioxidant activity	González-Lemus et al. (2022)
Fe_2O_3	0.75, 1 $g.L^{-1}$	*Glycine max* L.	Detected greater content of lipids, proteins, chlorophyll, mineral nutrients such as Fe, Mg, Ca, and P, changes in the profile of fatty acids (palmitic, oleic, linoleic, and linolenic acid)	Sheykhbaglou et al. (2018)
Fe_2O_3	30 M	*Mentha piperita* L.	Increase in dry matter content, mineral nutrients including P, K, Fe, Zn, and Ca under haline condition	Askary et al. (2017)
TiO_2	150 $mg.L^{-1}$	*Mentha piperita* L.	Increase of content of essential oil about 105%	Ahmad et al. (2018)
Ag	60 $mg.L^{-1}$	*Trigonella foenumgraecum*	Huge amount of protein content, flavonoids, phenolic acid, and vitamin C content	Sadak (2019)

mechanisms also come into play. The application of nanofertilizers has been shown to be an effective approach for regulating stress (Khan et al., 2017; Farooq et al., 2023). When NPs are applied to plants, various reactions occur at different levels and depend on the physicochemical properties of the NPs, their concentration, etc. resulting in either positive or negative effects on plants. The knowledge about the effects of NPs on plants is still growing with many knowledge gaps still present in the field of plant physiology. Future research will likely focus on increasing chlorophyll concentrations, reducing water stress, analyzing stomatal conductance reactions, and other functional properties, which remain key areas of interest in plant physiology (Shi & Huang, 2023).

In recent studies, the application of NPs based on zinc, iron, silicon, titanium, or gold have been investigated as a means of improving photosynthesis in various crops including sunflower, chickpea, bean, lentil, corn, wheat, foxtail millet, pumpkin, cucumbers, and others (Khan et al., 2017; Kolenčík et al., 2019, 2020; Du et al., 2017). However, some types of metal or metal oxide NPs, including ZnO, TiO_2, CuO, and CeO_2, have been shown to have negative impact on various parameters of photosynthetic activity. Monocot plants, such as barley, wheat, or rice, seem to be particularly sensitive at the stage of one to three true leaves (Du et al., 2017) raising concerns about the agronomic safety of applying metal-based NPs in their early growth stages. Research is also currently being conducted on the concept of the so-called "*hybrid photosynthesis*" or "*artificial photosynthesis*", which aims to enhance photosynthesis on the genome level by utilizing the NPs. This approach has shown promise, as it has led to an increase in the rate of photosynthesis by up to three times, along with higher levels of photosynthetic pigments (chlorophyll a) and the regulation of genes that encode it, as well as an increase in the activity of photosystem II. For example, the application of TiO_2 NP to wheat has been found to affect the metabolism of jasmonic acid, and the expression of SOD and GPX genes has been observed to be regulated in tomato plants after the application of ZnO NPs (Ghosh & Bera, 2021). The physiological impacts of INPs on crops are also shown in Table 18.6.

Table 18.6 The effects of different inorganic nanoparticles on various physiological indicators in several crop plants

Type of NPs	Concentration	Plants	Effect	References
Ag	0, 20, 40, 60 $mg.L^{-1}$	*Trigonella foenum-graecum*	Increase of photosynthetic pigment (chlorophyll a, chlorophyll b, and carotenoids)	Sadak (2019)
Fe	0, 0.25, 0.5 $mg.L^{-1}$	*Vigna unguiculata*	Increase of chlorophyll content	Delfani et al. (2014)
Mn	0, 0.1, 1 $mg.L^{-1}$	*Vigna radiata*	Increase of photosynthesis efficiency	Mahajan et al. (2011)
TiO_2	0, 2.6 $mg.L^{-1}$	*Helianthus annuus*	Increase of normalized vegetation index, photochemical reflectance index, and crop water stress index	Kolenčík et al. (2020)
TiO_2	0, 150 $mg.L^{-1}$	*Triticum aestivum*	Decrease of chlorophyll a content, increase of efficiency of PSII, net photosynthetic rate, transpiration rate, and stomatal conductance	Dias et al. (2019)
ZnO	0, 250 $mg.L^{-1}$	*Helianthus annuus*	Increase of chlorophyll a and chlorophyll b content	Dias et al. (2019)
ZnO	0, 2.6 $mg.L^{-1}$	*Helianthus annuus*	Increase of normalized vegetation index and photochemical reflectance index, decrease of crop water stress index	Kolenčík et al. (2020)
ZnO	0, 1 $mg.L^{-1}$	*Lens esculenta*	Decrease of plant temperature and crop water stress index and increase of stomatal conductance index	Kolenčík et al. (2022)

4 Assessment of Eco-Environmental Hazards with the Application of Inorganic Nanoparticles

4.1 Impact of Inorganic Nanoparticles on the Reproductive Organs of Plants

Nanoparticles used from various spheres of industry and agriculture come into direct or indirect interactions with plant parts and affect their functionality. Positive and negative effects of INPs on plant reproductive structures are shown in Fig. 18.3.

In relation to generative organs, the reproductive phase is the most sensitive period in the life of plants. The health and development of generative organs of plants are largely dependent on the condition and performance of the vegetative organs. In all likelihood, the time of application of INPs also plays an important role. Based on the findings so far, it is advisable to carry out the application of NP-based fertilizer before the plant enters the reproductive phase.

4.1.1 Impact of Inorganic Nanoparticles to Flowering Phase and Flowers

The onset and duration of crop flowering are agronomically important factors that affect the fruit ripening period. Positive effect of Ag NPs manifested in the acceleration of flowering in *Lilium* (Salachna et al., 2019) and *Tulipa gesneriana* (Byczyńska et al., 2019). Earlier flowering was also induced after the application of ZnO NPs in

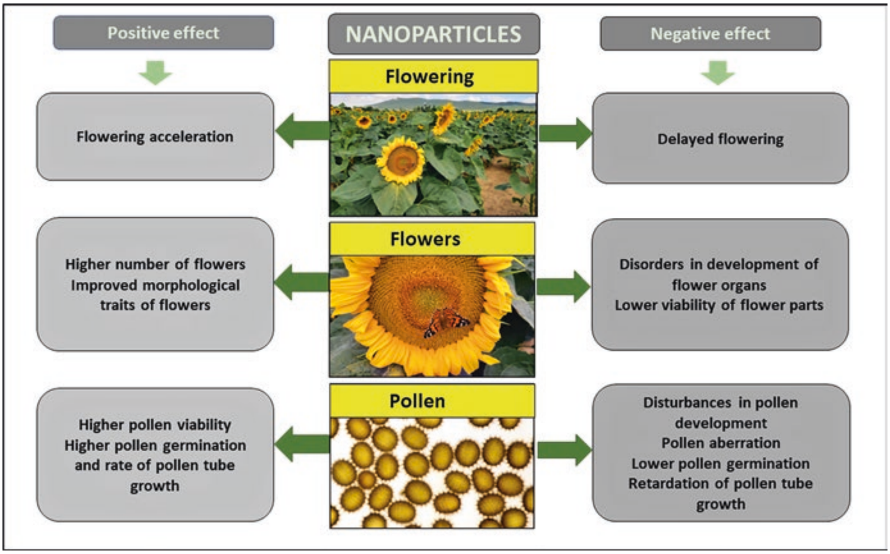

Fig. 18.3 The impact of nanoparticles on the plant generative organs and pollen

Allium cepa (Laware & Raskar, 2014). The opposite effect on the onset of flowering occurred in the model species *Arabidopsis thaliana* after the application of Ag NPs (Ke et al., 2020) as well as in wheat treated with CeO_2 NPs (Du et al., 2015), when the transition to the generative phase of growth was delayed. There are several reasons for different reactions related to the time of entry into the reproductive phase after application of INPs. It has been shown that higher seed germination, early seedling growth, seedling performance, and an increased vegetative growth generally induce earlier flowering. In the case of geophytes, the disinfecting effect of NPs was positively manifested after the treatment of vegetative reproduction diaspores, which was reflected in better growth properties and acceleration of flowering. The delay in flowering can be caused by the deterioration of physiological indicators due to stress after application of INPs. Internal causes involved in the retardation of flowering can be linked to a decrease in the expression of floral pathway integrators.

The production of a higher number of flowers is associated with a higher yield in cultivated plants. Better morphological characteristics of flowers are desirable for ornamental species. Quantitative and qualitative characteristics of flowers often depend on the condition on vegetative organs. Inhibition of vegetative growth due to Ag NPs application had a negative effect on viability of flower parts of *Arabidopsis*, while the offspring were also damaged (Ke et al., 2020). However, better characteristics of *Tagetes* flowers appeared after silica accumulation in leaves after foliar application of hydrophilic Si NPs (Attia & Elhawat, 2021). Zinc belongs to the elements necessary for the normal development of flowers and inflorescences. When supplied to plants in the form of conventional fertilizers, it increases the flowering characteristics of crops such as maize (Sharma et al., 1987), lens (Pandey et al., 2006), etc. A positive effect on the number of *Lycopersicum esculentum* flowers was also found after the foliar application of ZnO NPs, which is even more effective compared to the root application (Raliya et al., 2015). The same impact on flower formation was observed after foliar application of zinc NPs in peaches (Mosa et al., 2021). The better condition of the plants due to the antimicrobial properties of Ag NPs was also reflected in the higher production of lilium (Salachna et al., 2019), tulip (Byczyńska et al., 2019), and peach flowers (Mosa et al., 2021). Likewise, antimicrobial properties of titanium-based NPs together with higher resistance to stress had a positive effect on the number of petunia flowers (Kamali et al., 2018) and improved flower diameter of *Rosa* × *damascena* (Selahvarzi & Kamali, 2021). The preservative and protective effect of INPs can also contribute to the prolonging of viability of cut flowers (El-Serafy, 2019; Manzoor et al., 2020).

4.1.2 Impact of Inorganic Nanoparticles Against Pollen and Pollinators

Pollen grains are haploid male gametophytes participating in the fertilization process of offspring formation. Disturbances during the development of pollen grains and reduced pollen viability have a negative impact on the fruit set. NPs can negatively affect pollen and cause changes in the morphology of pollen grains. Disturbances during microsporogenesis and microgametogenesis occurring after the application of CeO_2 and ZnO NPs in *Phaseolus* resulted in pollen damage (Salehi et al., 2021, 2022). Likewise, ZnO NPs induced pollen aberrations of *Prunus persica* (Mosa et al., 2021), and adverse morphological changes in kiwifruit pollen are caused by Pd NPs (Speranza et al., 2013). Pollen abortion in *Arabidopsis* also occurred after the application of Ag NPs (Ke et al., 2020) as well as negatively charged iron NPs (Bombin et al., 2015). Damaged pollen grains are characterized by low viability. However, even the germination of morphologically normally developed pollen can be directly affected by the interaction of pollen with INPs. Adhesion of INPs to the exine surface and blocking of the germination pores of pollen grains cause inhibition of pollen germination (Aoyagi & Ugwu, 2011; Speranza et al., 2010; Dutta Gupta et al., 2020). In addition to the negative effect on pollen vitality, the capture of INPs on the surface of pollen grain can be an environmental risk of spreading contaminated pollen. The interaction of pollen with INPs also depends not only on the type of pollen grains, their size as well as the shape and size of the germination pores but also on the structure of the exine. Pollen grains with pollenkitt on their surface can be particularly susceptible to INPs sticking. Decrease in the growth rate and deformation of the pollen tube because of INPs action can reduce the chances of successfully reaching the ovule. Mechanisms causing the retardation of pollen germination and pollen tube elongation differ depending on type, size, and concentration of INPs. INPs of smaller size can enter pollen grains through pores and affect their functionality. The acidic properties of GO NPs reduce pollen germination of *Corylus avellana* and cause disturbances of *Nicotiana* pollen tube (Carniel et al., 2018). Continuous release of zinc from ZnO NPs inhibits pollen germination and pollen tube elongation in *Lilium* (Yoshihara et al., 2021). Ag NPs nanotoxicity is caused by damage of cell membranes and decrease in endogenous Ca^{2+} necessary for the growth of the pollen tube (Dutta Gupta et al., 2020). However, the surface treatment of INPs can reduce their toxicity. PVP-coated Ag NPs do not have a negative effect on kiwifruit pollen germination (Speranza et al., 2013). Initiation of pollen germination occurs after interaction with the stigma of the pistil. Although GO NPs have been shown not to damage the stigma, both pollen adhesion and germination on the stigma decreased (Zanelli et al., 2021). However, not all types of NPs have a phytotoxic effect on pollen germination. Particles of organic origin such as carbon nanosheets from a nettle fiber, even though they form an aggregate around pollen grains, did not have an impact on tobacco pollen germination (Shah et al., 2021). Even after the application of some NPs, a positive effect on pollen viability was demonstrated. Induction of vegetative nucleus activity after Au NPs application had a positive effect on onion pollen germination (Alharbi et al., 2017). Gold NPs also supported *Gloriosa superba* pollen germination (Gopinath et al., 2013). The same positive effect of Ag NPs manifested in better pollen germination as well as larger pollen grains was obtained by the application of Ag NPs in peaches (Mosa et al., 2021), as well as higher viability potential induced by Nagro organic nanofertilizer (Georgieva et al., 2017). Improving the germination of grapevine pollen can be achieved using calcite NPs (Sabir, 2015).

Most plant species are known to be pollinated by insects. Flowers offer pollinators pollen or nectar. In addition to the fact that insects can consume pollen, they also transfer pollen grains on the surface of the bodies. Ingestion of contaminated pollen poses a health risk to pollinators. In one study, TiO_2 NPs promoted sublethal effects against the gut microbiota of bees (Papa et al., 2021). Exposure to sublethal concentration of CdO and PbO NPs caused neurotoxic effect to honeybees (Al Naggar et al., 2020). Similar effect was observed for ZnO NPs when zinc was released from the NPs (Milivojević et al., 2015). Significant negative changes in the biochemical parameters of bees also occur after the exposure to CeO_2 NPs (Kos et al., 2017). The iron released from Fe-based NPs was captured on bodies of worker bees (Wang et al., 2013a). The collection, transport, and consumption of contaminated pollen by bees can pose a potential risk of transfer through honey into the food chain with human health risk (Hooven et al., 2019).

4.2 Application of Inorganic Nanoparticles as Insecticides and the Impact on Agrobiological Diversity

In insecticides, INPs play a double role. On the one hand, INPs exposure leads to a toxic effect on a target organism (Arumugam et al., 2016); on the other hand, INPs may also positively enhance the growth of crops on top of their insecticide activity (Badawy et al., 2021; Shahzad & Manzoor, 2021). INPs may enter insects and other invertebrates through ingestion, inhalation, or direct physical contact (Raj et al., 2017; Raliya et al., 2017). After the application of NPs, changes in pigmentation or integrity on surface structures are often observed in invertebrates, while in the internal environment, several reactions appear at the gene expression level leading to a negative alteration in the structure of proteins, lipids, and carbohydrate metabolism. It results in the disruption of the developmental and reproductive functions, as well as disturbances in the intake and processing of nutrients uptake with subsequent death (Shahzad & Manzoor, 2021).

Depending on their origin, INPs used as insecticides should promote functional cover, for example, through biosynthesis procedures (Badawy et al., 2021), and are able to easily adhere, penetrate, or transport within the insect. Most often, NPs are used in the form of colloidal dispersion, polymers, gels (Kah & Hofmann, 2014), or combined with chemical compounds involving silica, chitosan, alginate, polyethylene glycol (PEG), or others (Luo et al., 2016; Shahzad & Manzoor, 2021; Solè et al., 2012). Some selected types of INPs with major effects against insects and other invertebrates are shown in Table 18.7 and Fig. 18.4.

A rich and complex network of trophic interactions helps to maintain homeostasis in ecosystems and regulate the populations of all integrated organisms. The quality of the environment can be evaluated using model organisms. The diversity of arthrofauna allows for the investigation of a wide range of agroecological functions and the identification of the ecological characteristics of organisms that are most sensitive to environmental change. The species of Carabidae family are often used as a bioindicator of the quality of the environment in ecological and agricultural

Table 18.7 Type of insecticides and pesticides based on inorganic NPs and their major impact

Type of NPs	Insect species	Size, concentration, and exposition against the insect	Observed effects	References
Au NPs	*Blattella germanica*	15–30 nm, 65.58 mg.L^{-1}, orally applied	Reduced viability, reduction in the number of hatched nymphs and their overall occurrence	Small et al. (2016)
Au NPs	*Aedes aegypti, Helicoverpa armigera, Callosobruchus maculatus, Callosobruchus chinensis, Maconellicoccus hirsutus*	20–50 nm, 100 µg.L^{-1}	Inhibition of catalytic potential of trypsin, Au NPs interact with proteins via binding of SH group of amino acid are resulted to decreasing trypsin activity.	Patil et al. (2016)
Biosynthesized Ag NPs	*Aedes aegypti*	20–30 nm, 15–75 mg. ml.L^{-1}, direct physical contact of solution with larvae	Damage to the cuticular layers and the mosquito larvae, loss of hair on the head and abdomen	Ishwarya et al. (2017)
Polyvinylpyrrolidone-coated Ag NPs (PVP-Ag NPs), citrate-coated Ag NP (Cit-Ag NPs)	*Caenorhabditis elegans*	Cit-Ag NPs, 5–15 nm, PVP-Ag NPs 5–60 nm, ~35 mg.L^{-1}, direct physical contact with suspension.	The entry into the organism, transgenerational transmission, and growth inhibition	Meyer et al. (2010)
TiO_2 NP	*Bombyx mori*	5–6 nm, 5 mg. L^{-1} Orally applied	Induced mitochondrial damage, apoptosis, gradual inhibition of acetylcholinesterase, and gene expression due to oxidative stress	Xie et al. (2014)
TiO_2 NPs	*Lumbricus terrestris*	10 × 50 nm, 0 to 100 mg. kg^{-1} Direct physical contact within soil system	No mortality or bioaccumulation appeared, occurrence of apoptosis in various organs is proven	Lapied et al. (2011)

(continued)

Table 18.7 (continued)

Type of NPs	Insect species	Size, concentration, and exposition against the insect	Observed effects	References
TiO_2 composite with Al_2O_3	*Eisenia fetida*	14–16 nm, 25 $mg.L^{-1}$ Direct physical contact within solution	Oxidative stress, changes at the cellular and molecular level	Bigorgne et al. (2011)
ZnO NPs	*Eisenia fetida*	30 ± 5 nm, 50–1000 $mg.L^{-1}$ NPs encapsulated with agar	The earthworm mortality decreases with increasing ZnO NPs concentration and bioaccumulation occurrence	Li et al. (2011)
ZnO NPs with plane extract	*Aedes aegypti*	5–50 $mg.L^{-1}$	Modification of the thorax; disturbed midgut; loss of side hairs, oral and anal organs	Banumathi et al. (2017)
Fe^0 NPs adhere *Beauveria brongniartii*	*Spodoptera litura*	≤100 nm, 59–500 $mg.L^{-1}$	Reduction of glutathione-S-transferase activities during the infection period while antioxidant enzymes activities decreased	Xu et al. (2020)
Cu NPs	*Sitophilus granarius*, *Rhyzopertha dominica*	14.0–47.37 nm, 50 $mg.L^{-1}$ and 100 $mg.L^{-1}$	Activity of CuO NPs after entering the cuticle, which block pores respiratory opening with resulted poisoning, and appetite reducing. Also causes oxidative stress, blood clots, and lymphatic vessels	Badawy et al. (2021)

settings. These species are able to reflect both biotic and abiotic conditions, as well as the ecological sustainability and "health" of ecosystems (Rainio & Niemelä, 2003; Hendrickx et al., 2007).

In this context, Ernst et al. (2023) used foliar application of low-level concentration of AuSi NPs, Fe_3O_4 NPs, and ZnO NPs with control (NPs-free variant) to *Helianthus annuus* during vegetation season 2019 in field experimental locality in middle Europe (Dolná Malanta-Nitra, Slovakia). Twenty taxonomic groups of invertebrates were observed with unequally spaced distribution that decreased with

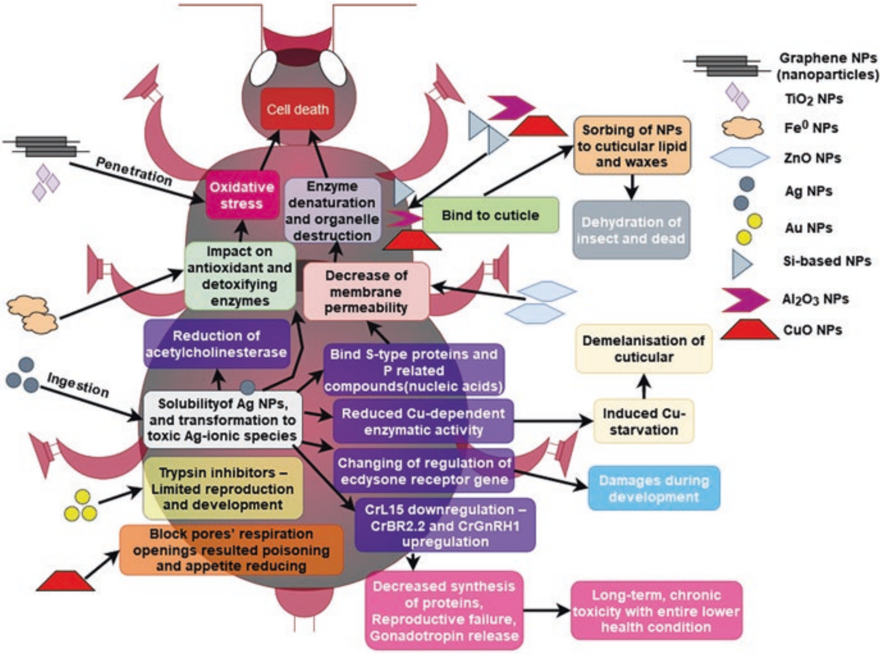

Fig. 18.4 Schematic illustration of mechanisms of interaction between inorganic nanoparticles with invertebrates. (Illustration was modified according to Benelli (2018))

time. Individual abundance of epigeic groups had corresponding order: Coleoptera > Collembola > Acarina > Formicidae > Araneida > Opilionida > Orthoptera > Larvae (nondetermined development stages of local epigeic groups) > Diptera, and abundance of other 11 groups did not exceed 1%. Faunistic similarities between individual variants according to Jaccard (Begon et al., 1997; Begon & Townsend, 2020) and dominance in compliance with Rennkonena (Begon et al., 1997; Begon & Townsend, 2020) are shown (Table 18.8).

From biodiversity of epigeic groups, the most appropriate conditions were surprisingly provided by AuSi-variant followed by control (NP-free variant) and oppositely the most ineffective variants were given by Fe_3O_4 NPs variant and ZnO NPs variant (Ernst et al., 2023). On the other hand, according to Shannon-Weaver (Begon et al., 1997; Begon & Townsend, 2020) at the locality where these two NPs were applied, a higher diversity index of insect species was observed (Table 18.9).

There was no observed negative effect on morphological and anatomical changes associated with low-concentration range of ZnO NPs for model insect species *Harpalus rufipes* (Fig. 18.5).

Also, similar observation with no significant changes when INPs spray deposition was applied to various crops was empirically recorded with other insects during

Table 18.8 Faunistic similarities assessed according to Jaccarda (**I_J**) and dominance calculated in compliance with Rennkonena **I_D**

I_J	
NPs-free control – AuSi NPs = 50.00%	**AuSi NPs – ZnO NPs =** 83.33%
NPs-free control – ZnO NPs = 62.50%	**AuSi NPs – Fe_3O_4 NPs =** 40.00%
NPs-free control – Fe_3O_4 NPs = 45.45%	**ZnO NPs – Fe_3O_4 NPs =** 50.00%
I_D	
NPs-free control – AuSi NPs = 95.41%	**AuSi NPs – ZnO NPs =** 69.51%
NPs-free control – ZnO NPs = 69.56%	**AuSi NPs – Fe_3O_4 NPs =** 79.21%
NPs-free control – Fe_3O_4 NPs = 87.75%	**ZnO NPs – Fe_3O_4 NPs =** 70.90%

I_J – the mutual similarity of the species composition of individual variants ranged from 40 to 83.3%. The highest mutual similarity was confirmed by the 83.33% similarity of the AuSi NPs – ZnO NPs variants despite their different abundance. So, the applied NPs did not negatively affect the occurrence of species and the calculated values of I_J. **I_D** – dominance representative index which comparing populations within variants. Its values ranged from 69.51 to 95.41%. The maximum value fitted for co-occurring insect species was recorded with NPs-free control and AuSi NPs variant

Table 18.9 Index diversity according to Shannon-Weavera (Begon et al., 1997; Begon & Townsend, 2020)

D	NPs-free control	AuSi NPs Variant	ZnO NPs Variant	Fe_3O_4 NPs Variant
	0.462191	0.368008	1.003723	0.557837

several vegetation seasons (no published data). Currently, the most suitable bioindicator species in the region of Central Europe is the previously mentioned *Harpalus rufipes* since it is a widespread and generally common species. Additionally, this species belongs to predator for other insects in agroecosystems; it is relatively sensitive against anthropogenic input.

In the future, the role of INPs influence on insects and invertebrates will be discussed in the trend of nanotoxicology and related disciplines, which primarily deal with NPs as a new generation of pesticides. INPs have shown promising potential as a new generation of pesticides, due to their ability to target and kill pests with high efficiency and low toxicity to non-target organisms. However, the long-term effects of INPs on insects and invertebrates are not yet fully understood. Further research is needed to determine the potential risks and benefits of using INPs as pesticides (Kah & Hofmann, 2014).

One area of particular interest is the potential for INPs to accumulate in the environment and affect the food chain. For example, if NPs are ingested by herbivorous insects, they may then be passed up the food chain to predatory insects and other invertebrates. It is important to understand the potential impacts of this process on the overall ecosystem. Additionally, the potential for INPs to affect the behavior and

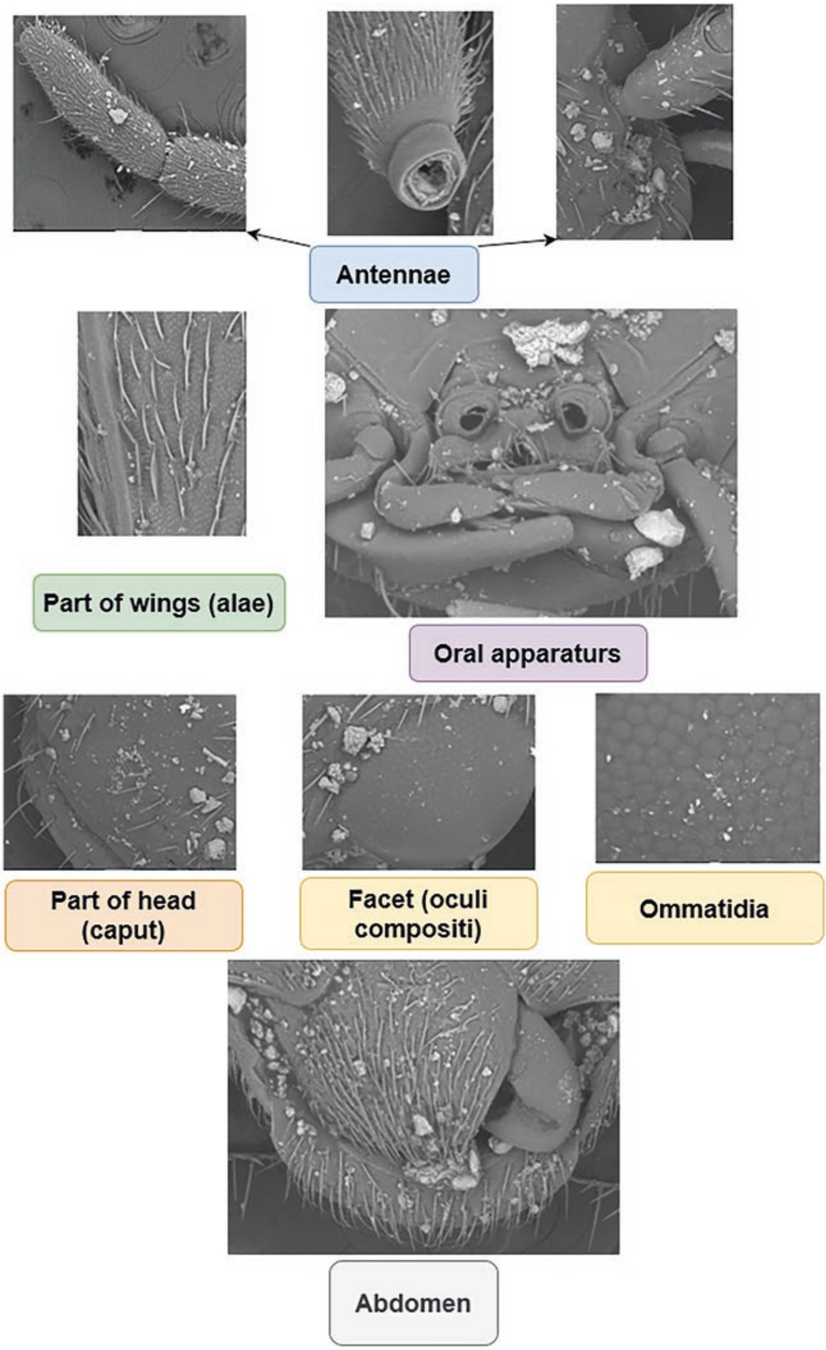

Fig. 18.5 A representative organism, *Harpalus rufipes*, showed no observable morphological or anatomical changes in various body parts, such as antennae, wings, oral apparatus, head, facets, ommatidia, and abdomen, when subjected to foliar application of ZnO NPs during the 2019 vegetation season

reproduction of insects and invertebrates should also be studied in greater detail in order to fully assess the risks and benefits of using these substances as pesticides (Kah & Hofmann, 2014; Shahzad & Manzoor, 2021; Hooven et al., 2019).

5 Conclusion and Future Perspective

The development of agronomy is being impacted by the changes in the climate and its effects on the environment, making the adoption of new technologies, such as nanotechnology, seem necessary. The main role in the dynamical development of this field is played by nanofertilizers, their innovativeness based on various concepts, but the main orientation being foliar and soil application in field crops. In their application, various methods can be utilized that take advantage of the characteristics of nanodomain materials including quantum dots effects, the principles applied in pharmacology, such as a drug delivery system with governed transport and distribution of NPs to targeted site of plant, and a regulated release of nutrients and other agrochemicals utilizing a combination of materials with specific, precisely manipulated properties, and also external stimuli.

Nanofertilizers, such as Au, Ag, or TiO_2, often called plant growth stimulants that do not have obvious essential nature and metal oxides, concretely ZnO, or Fe_2O_3 applied as micronutrients, hold promise as innovative solutions in agriculture. The precision agriculture approach, using integrated nanosensors and unmanned aerial vehicles, can monitor changes in environmental conditions in real time during the vegetation seasons. Although the entry of nanofertilizers into the plant through roots and leaves is better understood, questions remain about their effects on other plant functions, including alterations of leaf surface anatomy, the role of trichomes and stomata, etc. In addition, these factors impact the plant's ability to absorb, transform, transport, and ultimately dispose of nanofertilizers, potentially affecting the quantity, yield and yield parameters, final fruit quality, or even human health. The physiological reactions of individual crops to nanofertilizer treatment are also equivalently important and may vary with changes in local climatic conditions during vegetation season.

It is clear that nanofertilizers contain metals and metal oxides, which can present potential hazardous effects due to their physical and chemical nature. Factors such as changes in NP distribution, mobility, bioavailability, or potential toxicity to the environment should be taken into consideration. Despite several positive indicators, a heated debate about the long-term environmental and ecological impacts of nanofertilizers is ongoing. So far, there is limited knowledge about the real-field effects of nanofertilizers on individual plant development, including flowers, flowering, pollen viability, and the impact on agroecological changes as related to distribution and abundance of the epigeic insect community.

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Chapter 19
Nanofertilizers: Challenges and Future Trends

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1 Introduction

Nanotechnology has advanced significantly in recent decades and has found multiple uses in a variety of industries, including agriculture. Many of the problems that traditional chemical fertilizers confront, such as environmental issues and the need for more effective nutrient delivery to crops, are addressed by nanofertilizers (Yadav et al., 2023). However, there are some obstacles and issues to solve in their production and use (Basavegowda and Baek, 2021). One of the most difficult difficulties for nanofertilizers is assuring their safety and eliminating any potential harmful environmental repercussions. This necessitates close monitoring of their production and usage, as well as extensive testing to verify that they have no unforeseen repercussions for ecosystems. Another issue is the cost of manufacture, which can be prohibitively expensive because of the specialized equipment and materials required (Verma et al., 2022). Despite these obstacles, the future of nanofertilizers is bright. According to research studies, they have the potential to increase agricultural yields while decreasing fertilizer consumption, which can benefit both the environment and food security. Furthermore, technological developments and greater investment in this sector are likely to result in more cost-effective and sustainable production methods in the future (Verma et al., 2022). Overall, the use of nanofertilizers in agriculture is a promising trend that has the potential to transform crop production

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while also contributing to a more sustainable future (Mikkelsen, 2018). However, it is critical to address the issues and concerns related to their use, as well as to ensure that they are designed and deployed in a safe and responsible manner (Zulfiqar et al., 2019; Tarafdar, 2021). While nanofertilizers show promise for increasing fertilizer efficiency and agricultural output, considerable technological, economic, and safety barriers must be overcome before they can be commercially feasible and responsibly applied on a broad scale (Gade et al., 2023). The current chapter intends to shed light on the challenges and opportunities related to nanofertilizers. To fully exploit the potential benefits while avoiding unforeseen consequences, more research and cautious testing are required. Nanofertilizer creation and application necessitate significant thought and research to ensure their safety, effectiveness, and long-term viability.

2 Challenges

Due to their potential to increase crop yields while reducing environmental damage, nanofertilizers, a novel type of fertilizer, have grown in popularity recently. These fertilizers have high-precision nutrient delivery nanoparticles that enable them to enter plant cells more effectively. While there is a lot of potential for nanofertilizers, there are a lot of obstacles that need to be removed before they can be fully utilized in agriculture (Fig. 19.1).

Fig. 19.1 Numerous issues confront the nanofertilizer business, posing significant and practical impediments to their development and use

The following is a list of the key challenges that nanofertilizers face.

2.1 Production Costs

Nanofertilizers are currently more expensive to manufacture than standard fertilizers. Researchers must figure out how to cut production costs while still scaling up synthesis procedures. Now, nanofertilizers are more expensive than regular fertilizers, making them less accessible to farmers, particularly in underdeveloped nations. The high production cost is attributable to the complicated manufacturing process and the usage of costly materials. Furthermore, the expensive expense of these fertilizers may dissuade some farmers from using them as their major source of fertilizer.

2.2 Release and Uptake

One of the most difficult difficulties is the possibility of nanoparticles accumulating in soil and streams, where they could have unforeseen environmental repercussions. Long-term effects of nanofertilizers on soil and water quality are mostly unknown, and additional research is required to examine the hazards and benefits of this technology. It is still challenging to tailor nanostructures to release nutrients just when and where plants require them. Researchers are currently working on improving controlled release and plant absorption efficiency.

2.3 Stability

To perform successfully, nanofertilizers must be stable during storage, transportation, and application. Researchers are striving to increase their stability in a variety of environments.

2.4 Sensing and Feedback

It remains a challenging task to enable nanofertilizers to effectively sense soil conditions and plant needs and then respond accordingly. More complex sensing and feedback mechanisms are required.

2.5 Large-Scale Production

Another issue to consider is the scalability of nanofertilizer production. Nanofertilizer manufacture is currently relatively expensive and time-consuming, making them less accessible to small-scale farmers who may lack the finances to invest in this technology. The manufacture of nanoparticles is an expensive process that necessitates specialized equipment and intricate chemical interactions. Furthermore, the scalability of these procedures is restricted, and it is difficult to ensure uniformity in product quality. Manufacturing costs can be decreased by optimizing processes, but this may not be enough to meet the demand for nanofertilizers. As the need for nanofertilizers increases, it will be critical to create more efficient and cost-effective production processes that can be scaled up to satisfy the needs of farmers all over the world. Furthermore, there is still a lot to learn about the best nanofertilizer formulation for crops and soil types. While some studies suggest that nanofertilizers can boost crop yields, the effectiveness of these fertilizers may vary depending on soil pH, moisture levels, and nutrient availability. More study is needed to determine the best effective nanofertilizer compositions for various crops and growth environments. Many nanofertilizers have only been tested in controlled circumstances on a small scale. More thorough field testing is required to demonstrate their commercial viability and performance.

2.6 Regulatory Approval

Regulations have not kept up with this new technology, and nanofertilizers will need to go through considerable safety testing before they can be used in agriculture. There are currently no regulatory frameworks in place for nanofertilizers. Before approving widespread use of nanofertilizers, regulatory agencies must ensure that they are safe for human health and the environment.

2.7 Adoption by Farmers

Farmers may be hesitant to use nanofertilizers due to a lack of information, expensive costs, and concerns about safety and soil health. Programs of education and demonstration will be required. Furthermore, strong marketing techniques are required to promote the benefits of nanofertilizers to farmers. Many farmers are wary of new technology, and they need substantial education and training on the efficacy and safety of nanofertilizers.

2.8 Safety and Toxicity

The toxicity and safety of nanofertilizers are still unknown. There are concerns that nanoparticles will harm human health and the environment. Furthermore, some nanoparticles have the potential to be hazardous to plants, soil microorganisms, and the environment. More biocompatible and biodegradable nanostructures are required. While studies have demonstrated that nanoparticles can be consumed by plants without causing harm to human health, additional research is needed to determine the long-term consequences of nanofertilizer consumption on human and animal health. Another key problem is guaranteeing nanofertilizer safety. Because of their lower toxicity, nanofertilizers are regarded safer than regular fertilizers, yet the dangers connected with their use are not fully understood. More comprehensive safety testing is required to assess the possible environmental and human health implications of nanofertilizers. Furthermore, the creation of nanofertilizer safety rules and laws may raise costs and limit its adoption. More research is needed to evaluate the potential dangers of using nanofertilizers.

2.9 Compatibility with Existing Infrastructure

Nanofertilizers may be incompatible with existing agricultural infrastructure, such as irrigation and fertilizer spreaders. A fundamental issue in the development of nanofertilizers is the lack of uniform testing methodologies. Advanced technologies are required to precisely assess the nutrient content of nanofertilizers and determine their efficiency. This is critical to ensuring that nutrients are delivered in a targeted and suitable manner by nanofertilizers.

2.10 Long-Term Effects on Soil Health

The long-term impacts of nanofertilizers on soil health remain unknown. It is critical to guarantee that nanofertilizers have no negative effects on soil health, such as decreasing microbial activity or changing soil pH levels.

3 Future Outlook

The creation of cutting-edge nanoparticles for improved seed germination and micronutrient delivery, as well as the reduction of biotic and abiotic stress, is an advantage of nanotechnology in this field. Although this technology is still in its infancy, we may anticipate the development of nanofertilizers that are even more successful in enhancing crop yields and soil health as time goes on. One of the most recent advancements in agronomy is the use of nanofertilizers, which is a technology that is predicted to take the world by storm in the next years. With the help of modern technologies, farmers may enhance crop yields while using less fertilizer. By using tiny particles that may reach the roots of the plants and enter the soil, nanofertilizers are made to supply nutrients more effectively to plants. These particles are far smaller than conventional pellets, and they can be made to release nutrients gradually, giving the plant a consistent supply of food.

There are several future trends that are expected to shape the development and adoption of nanofertilizers in agriculture.

3.1 Increased Variety of Nanostructures

The use of nanotechnology in the formulation of these fertilizers is one of the most important trends in the development of nanofertilizers. Currently, nanoparticles are used as the delivery method for the majority of nanofertilizers. Nevertheless, scientists are investigating more nanostructures like nanotubes, nanofibers, and nanocomposites that might be more useful. Because of this variability, nanofertilizers can be customized for certain crops and soil types.

3.2 Use of Multifunctional Nanostructures

One or more nutrients may be combined into a single nanostructure in future nanofertilizers. They could also be made to behave as insecticides, enhance water retention, or promote plant growth, among other things. Their versatility may greatly increase their effectiveness. For instance, utilizing potassium humate as the parent humic material and ^{57}Fe in the form of $^{57}Fe(NO_3)_3$ (product F) and $^{57}Fe_2(SO_4)_3$ (product M), three different forms of humic nanomaterials were created (products S and M) (Cieschi et al., 2019). To ascertain the iron speciation and phase composition of the nanoparticles, these nanomaterials underwent analysis. On a growth chamber, the bioavailability of these nanomaterials to iron-deficient soybean plants grown in calcareous soils was also assessed (Fig. 19.2).

3.3 Targeted Nutrient Delivery

The use of intelligent delivery systems is a further breakthrough in nanofertilizers. Smart delivery systems monitor the nutrient requirements of plants and administer the correct amount of fertilizer at the appropriate time using sensors and other

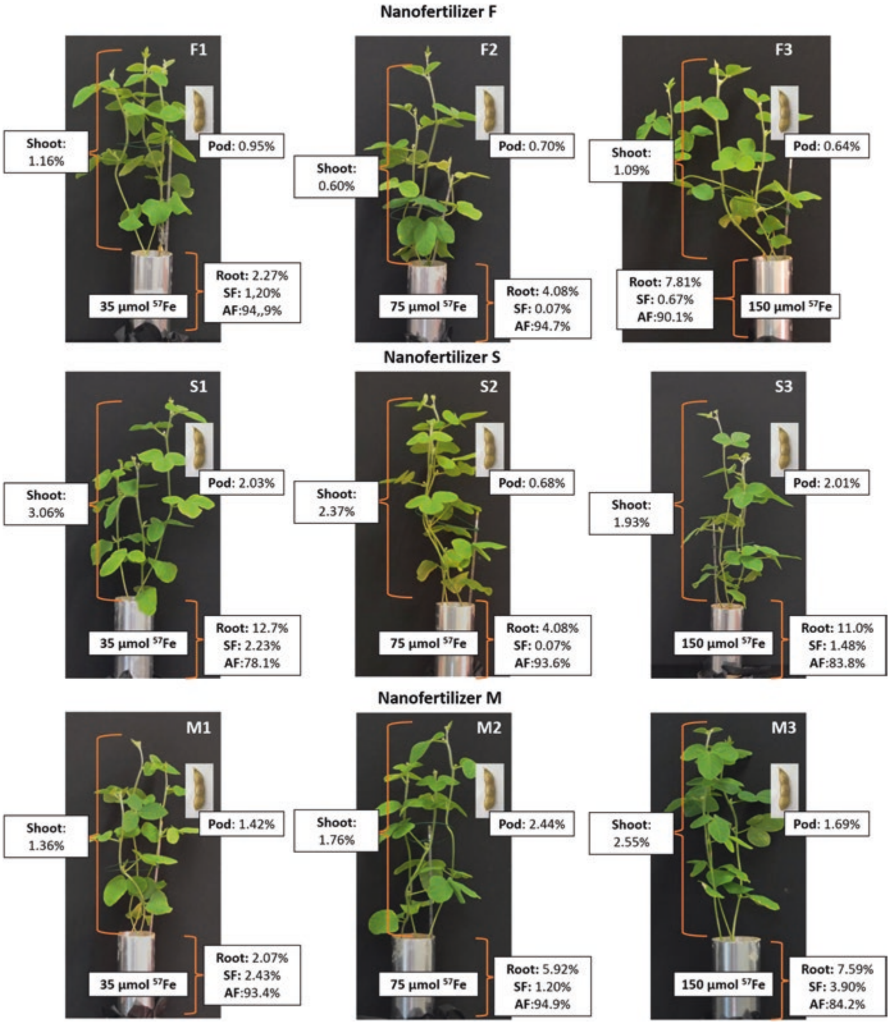

Fig. 19.2 Distribution of ^{57}Fe (percent) in soybean shoots, pods, and roots of plants fertilized with the ^{57}Fe products F, S, and M at doses of 35, 75, and 150 mol ^{57}Fe pot^{-1}, as well as in the soluble and accessible fraction soil. The Fe-NFs provide a natural, low-cost, and environmentally friendly alternative to standard iron fertilization in calcareous soils (Cieschi et al., 2019)

technology. Nutrient distribution will be more precisely based on the unique requirements of various plant parts and growth phases thanks to nanotechnology. This strategy might increase the effectiveness of fertilizer use, cut down on waste, and lessen the impact of fertilizers on the environment.

3.4 Sensing and Feedback Mechanisms

Another significant advancement will be the employment of sophisticated sensors to more precisely gauge the nutritional requirements of plants. Farmers will be able to precisely control their fertilizer use and prevent over-fertilizing their crops thanks to this technology. This will help farmers save money on fertilizer prices and lessen the impact of agriculture on the environment. Nanotechnology might make it possible for fertilizers to sense the needs of plants and the state of the soil and release nutrients only when necessary. This might increase the efficiency of nutrient intake and utilization.

3.5 Biodegradability

Future nanofertilizers will probably concentrate on creating biodegradable nanostructures that decompose harmlessly in soil and plants in order to promote sustainability. The use of nanofertilizers to solve environmental issues including climate change is gaining popularity. The use of synthetic fertilizers can be decreased by using nanofertilizers, which can significantly cut greenhouse gas emissions. The use of nanofertilizers to increase crops' resistance to drought and other adverse weather conditions is also being researched. Nanofertilizers have the potential to lessen the use of synthetic fertilizers while also boosting crop yields and reducing environmental impact. It has been established that synthetic fertilizers have detrimental impacts on soil health and can contaminate local water supplies. Farmers can lessen their dependency on synthetic fertilizers and advance sustainable farming practices by utilizing nanofertilizers.

3.6 Improvements in Cost and Scalability

Researchers must figure out ways to lower prices and scale up production if nanofertilizers are to be commercially successful. New production methods and the utilization of less expensive and more plentiful resources may be required for this.

3.7 Smart Agriculture

The rising importance of precision agriculture is another trend. Utilizing cutting-edge technology, precision agriculture aims to enhance yields and optimize crop growth. In order to give crops a consistent supply of nutrients and lower the chance of over-fertilization, nanofertilizers can be made to release nutrients gradually over an extended period of time. These intelligent agricultural nanofertilizers can also raise soil fertility, which promotes better plant development and higher food harvests. These nanoparticles' distinctive size and shape make them an efficient instrument for soil remediation, which lowers soil contamination.

3.8 Biotic Stress

Additionally, nanofertilizers can be employed to improve plants' resilience to pathogens and pests. Insecticides or fungicides that can be introduced right into the plant's system to protect it from pests and diseases can be carried by nanoparticles. This may lessen the need for traditional pesticides, some of which may be hazardous to both human health and the environment. It has been demonstrated that nanofertilizers improve plant defense mechanisms against pathogens and pests. For instance, by making plants less appealing to insects, nanofertilizers with zinc oxide nanoparticles can help plants battle against pests.

3.9 Soil Health

Finally, soil health can be improved by using nanofertilizers. An important environmental issue called soil degradation can lower crop production and cause food shortages. Nanoparticles can be created to promote plant nutrient uptake, improve soil structure, and increase water retention. Agricultural ecosystems' general health can be improved, and damaged soil can be restored. There is a debate concerning the impact of nanofertilizers on soil health, and much research has produced contradictory findings. Some experts contend that the soil microbiology, nitrogen cycling, and soil structure may all be negatively impacted by these fertilizers. On the other side, other research indicates that nanofertilizers might improve soil enzymatic activity, plant growth, and soil carbon sequestration.

4 Conclusion

The creation and application of nanofertilizers is a fascinating area of agricultural research. We may anticipate the development of ever more effective and efficient nanofertilizers as technology develops, which could enhance crop yields, soil health, and the caliber of our food. Nanofertilizers are projected to play an increasingly significant part in farming in the future due to the rising demand for sustainable agriculture and the need to solve environmental concerns. By lowering the quantity of fertilizer needed for crop growth, increasing yields, strengthening plant resilience to pests and diseases, and enhancing soil quality, nanofertilizers help allay these worries. However, their success and widespread adoption will depend on developments in fields like multifunctionality, sensing capacities, and sustainability.

Although nanofertilizers have the potential to alleviate several of the issues affecting the agriculture sector, there are still a number of significant issues that must be resolved before their mainstream use. Concerns about safety and toxicity, regulatory frameworks, compatibility with the existing infrastructure, high cost of production, the scalability of production, safety, and toxicity issues, and long-term consequences on soil health are a few of these. Before they can realize their full commercial potential, significant improvements in terms of cost, environmental effects, and fine-tuning their release and absorption qualities still need to be made. Finally, these difficulties include worries about possible health consequences, the potential environmental impact of nanoparticles, and the ideal composition of nanofertilizers for various crops and soil types. To overcome these obstacles, scientists, regulators, and politicians must work together to create novel solutions that support the commercialization and use of nanofertilizers.

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