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A comprehensive overview of nanotechnology in sustainable agriculture

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ABSTRACT

Plant nutrition is crucial in crop productivity and providing food security to the ever-expanding population. Application of chemical/biological fertilizers and pesticides are the mainstays for any agricultural economy. However, there are unintended consequences of using chemical fertilizers and pesticides. The environment and ecological balance are adversely affected by their usage. Biofertilizers and biopesticides counter some undesired environmental effects of chemical fertilizers/pesticides; despite some drawbacks associated with their use. The recent developments in nanotechnology offer promise toward sustainable agriculture. Sustainable agriculture involves addressing the concerns about agriculture as well as the environment. This review briefs about important nanomaterials used in agriculture as nanofertilizers, nanopesticides, and a combination called nanobiofertilizers. Both nanofertilizers and nanopesticides enable slow and sustained release besides their eco-friendly nature. They can be tailored to the specific needs of to crop. Nanofertilizers also offer greater stress tolerance and, therefore, are of considerable value in the era of climate change. Furthermore, nanofertilizers/nanopesticides are applied in minute amounts, reducing transportation costs associated and thus positively affecting the economy. Their uses extend beyond such as if nanoparticles (NPs) are used at high concentrations; they affect plant pathogens adversely. Polymer-based biodegradable nanofertilizers and nanopesticides offer various benefits. There is also a dark side to the use of nanomaterials in agriculture. Nanotechnology often involves the use of metal/metal oxide nanoparticles, which might get access to human bodies leading to their accumulation through bio-magnification. Although their effects on human health are not known, NPs may reach toxic concentrations in soil and runoff into rivers, and other water bodies with their removal to become a huge economic burden. Nevertheless, a risk-benefit analysis of nanoformulations must be ensured before their application in sustainable agriculture.

1. Introduction

Nanoparticles (NPs) have revolutionized the field of medicine and have far-reaching applications in other fields, including agriculture. The economic times' 2019 reported that food grain production in an agricultural economy like India was likely to become 291.95 million tonnes (News, 2020). Eradicating hunger and poverty is one of the sustainable development goals of the United Nations (UN). NPs are particles of dimensions 1–100 nm (Feynman, 1959; Pokropivny and Skorokhod, 2007). Nanomaterials, also referred to as engineered nanomaterials (ENMs), have applications in fertilizers and pesticides (An et al., 2022). They can be classified based on their chemical nature, organic or inorganic. Inorganic nanoparticles CuNP, AlNP, AgNP, Zinc oxide (ZnO), Silica NP (SiNP), Cerium oxide (Ce_2O_3), titanium oxide (TiO_2). Each nanoparticle can be a nutrient source to plants and offers some advantages. For example, silica has a porous nature and improves soil aeration and moisture-holding capacity, encasing other macro/-micronutrient and iron particles that offer magnetic properties that allow their separation and re-use (An et al., 2022). The organic nanomaterials for agricultural use are polymers, lipids, and carbon nanotubes (Anandhi et al., 2020; Selyutina et al., 2017, 2020). Polymers of biodegradable nature may offer distinct advantages and promote sustainability. Plant nutrition involves the supply of macronutrients as well as micronutrients. The chemical fertilizers provide macronutrients and

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micronutrients; each of these is important to plant growth. They are increasingly being used in agriculture, such as in China, due to land fragmentation and the promotion of household agriculture (Zheng et al., 2020). The chemical fertilizers mainly provide Nitrogen (N), Phosphorous (P), and Potassium (K) to the plants. Micronutrient fertilizers supply mainly Zinc (Zn), Iron (Fe), Copper (Cu), and Molybdenum (Mo). Nanobiotechnology has solutions to both traditional fertilizers and traditional pesticides. Recent developments have also happened in the area of nanobiofertilizers (Kumari and Singh, 2020). Biofertilizers came to rescue the environmental hazards which chemical fertilizers posed. The chemical fertilizers have shown several disadvantages of leaching out into water bodies and ground water for they are applied as bulk, and plants cannot utilize them at once, leading to a vicious cycle of re-application, damage to soil fertility when applied in high amounts, and eventually, turn out to be expensive since they require application multiple times and so the transportation costs are high as well (Zulfiqar et al., 2019). Furthermore, nutrient use efficiency (NUE) for chemical fertilizers is quite low due to imbalanced nutrition. For example; NUE is reported as 20–50% for Nitrogen (Kumari and Singh, 2020) and 0–25% for Phosphorous (Shaviv, 2001). Strategies to increase NUE have been proposed, namely, precision fertilization, split or localized application, fertigation, and the use of nanofertilizers as well as nanobiofertilizers (Lü et al., 2016). To account for loss incurred upon application of chemical fertilizers, 40–70% Nitrogen, 80–90% Phosphorous and 50–90% Potassium are lost and or fixed in soil (Feregrino-Perez et al., 2018; Kumar et al., 2020; Mahmoudpour et al., 2021; Ombódi and Saigusa, 2000). The damage caused to the ecosystem due to eutrophication also deserves attention (Wilson et al., 2008). Statistics revealed that half of the applied nitrogen fertilizers are lost from agricultural fields into the water and air. The N-oxide released into the atmosphere are greenhouse gases that lead to global warming (Mastronardi et al., 2015). Fertility of soil and other physicochemical properties are also affected adversely by excessive use of chemical fertilizers (Congreves and Van Eerd, 2015). Biofertilizers came to the rescue of farmers several years ago and are one of the sustainable sources of fertilizers. They are bacteria and fungi which are classified based on nutrients that they supply, but biofertilizers also suffer some limitations. Biofertilizers improve the soil's moisture-holding capacity, increase soil nutrient (nitrogen and phosphorus) availability to plants, and keep the soil generally healthy by improving soil microbial condition, as well as improving soil aeration (Itelima et al., 2018). Biofertilizers are classified into different types depending on the nature and functions of the microorganisms such as nitrogen fixers, phosphorous solubilizers, phosphorous mobilizers, Zinc solubilizers, Potassium solubilizers, Silicon solubilizers, and Composites (Sharma et al., 2018).

Nanofertilizers can be classified as macronutrient nanofertilizer or micronutrient nanofertilizers, and examples of both are discussed in the review. Further, when a biofertilizer is combined with a nanofertilizer, the application is referred to as a nanobiofertilizer. Nanobiofertilizers also refer to microorganisms encased in NP which is a misnomer because microbial sizes are bigger than NPs. Therefore, multi-walled carbon nanotubes can be used to collect biofertilizers from ferment/broth, which can be applied to soils (Simarmata et al., 2016; Vandergheynst et al., 2007). There are certain properties of nanofertilizers that make them applicable to the agriculture industry. They are small in size and greater surface area, which leads to slow and sustained release of nutrients, leading to less wastage of nutrients (Guo et al., 2018), high surface tension also ensures better adsorption and sustained release (Brady and Weil, 1999), and formulations such as nanoencapsulation prevents deterioration due to heat, UV and oxidative damage (Anton et al., 2008). Nanofertilizers can be applied as a foliar application or seed application (Guru et al., 2015).

In the era of climate change, nanofertilizers improve plant nutrition and stress tolerance; therefore, valuable in promoting sustainability (Duhan et al., 2017). They reduce the investment on of fertilizers because the application in small amounts gives improved crop yields and concomitantly reduces transportation costs (Benzon et al., 2015). Nanofertilizers are used up by plants efficiently and leave very little residue in the soil, air, or ground water (El-Saadony et al., 2021). Nanofertilizers have benefited crop yield due to enhanced seedling growth, seed germination, nitrogen metabolism, protein and carbohydrate synthesis in crops (Rahman et al., 2021). Each nanoagricultural formulation has its own advantages. As every technology brings a positive change, there is a dark side to using nanotechnology in agriculture. The advantages of using nanofertilizers and some concerns associated with their use are highlighted in Fig. 1. In the pesticides sector, pesticides' active ingredients are lipid-soluble (Kaur et al., 2019). This limits their bio-availability. Nanopesticides offer a solution to this problem due to their smaller particle size and therefore increased bioavailability. Solid and liquid formulations are available for pesticides. Wettable powder (WP) and emulsifiable concentrate (EC) are two formulations of currently existing pesticides (Kole, 2021; Zheng et al., 2021b). In this review, we have discussed nanotechnology applications to agriculture in the form of nanofertilizers, nanopesticides, and nanobiofertilizers. We touched upon the merits of the use of nanoparticles in agriculture and some unaddressed concerns. The use of nanotechnology in agriculture requires the availability of skilled manpower in areas where agriculture is mainstay. Educating farmers to ensure appropriate use of new technology also requires certain reforms at policy making levels in all agricultural nations across the globe.

2. Plant nutrition

Plants require both macro- and micronutrients. The nutritional requirements of plants and how deficiencies of each element effect plant growth and nutrition are compiled in Table 1. Plant nutrition mainly comes from three main sources, which are macronutrients, micronutrients, and biofertilizers.

2.1. Macronutrients

Macronutrients are the nutrients that are commonly needed by plants in huge amounts. They play an important role in the growth and development of the plant. Macronutrients embrace Carbon, Hydrogen, Oxygen, Nitrogen, Phosphorous, Potassium, Calcium, Magnesium, and Sulphur. Carbon, Hydrogen, and Oxygen are essential to creating biological compounds like carbohydrates, proteins, and nucleic acids. Nitrogen plays a vital role in photosynthesis because it is a major structural part of the pigment known as chlorophyll (Grusak, 2001). Nitrogen is also a component of proteins, nucleic acids, and some carbohydrates. Phosphorous is crucial for energy storage because it results in converting food energy into chemical energy through a biological process. Potassium, a metallic element, maintains the regulation of water balance. Calcium plays a major role in controlling the transport of nutrients and protein activity. Magnesium is very important for the synthesis of pigment, and its inadequacy leads to the poor and scrubby growth of the

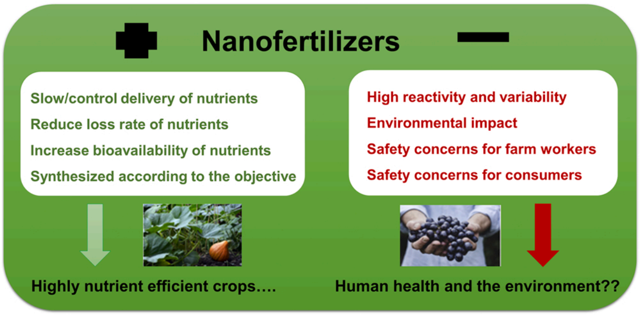

Fig. 1. Advantages of using nanofertilizers and some concerns associated with their use.

Table 1
Types of nutrients are required for plant growth and development (Grusak, 2001; Itelima JU, 2018; Nadeem et al., 2018).

Element	Function	Deficiency
Macronutrients		
Carbon	Photosynthesis, Metabolites	Stunted growth
Hydrogen	Photosynthesis	Chlorosis, foliage color changes, necrosis
Oxygen	Aerobic respiration	Root rot
Nitrogen	Protein production, Plant cell division	Chlorosis, short growth of the stalk
Phosphorous	Metabolites, Structural signaling, Improves the quality of fruits, grains, and vegetables	Lack of flowering, plant growth
Potassium	Osmotic, Electrochemical metabolism	Stunt growth, leaf necrosis, reduced gas exchange
Calcium	Structural signaling helps in the translocation process of photosynthesis from leaves towards the fruiting organs.	Lack of growth on meristems, blossom end rot disease.
Magnesium	Photosynthesis, Improves the consumption of iron in plants and influences maturity uniformity.	Necrosis of lower grown-up leaves
Sulfur	Stimulates the formation of nodes on the legumes, chlorophyll formation, helps in producing seeds.	Deplete growth in young leaves, thin, brittle stems
Micronutrients		
Boron	Necessary for growth of pollen tubes and pollen grains germination, involved in the formation of cell wall and seeds	Lack of growth; blackening of roots/shoots
Chlorine	Osmotic and stomatal regulation	Wilt stunt growth
Manganese	Carbohydrate metabolism	Necrotic spots on leaves, leaf shed
Iron	Chlorophyll synthesis	Necrosis of young leaves
Zinc	Enzyme activator facilitates the formation of starch and carbohydrate and of seed formation	Stunt growth
Copper	Cell wall metabolism, oxidative stress protection	Stunt growth, tip death, leaf twisting, the blue-green coloration of leaves, necrosis, loss of turgor
Molybdenum	Enzyme activator	Interveinal necrosis, mottling, marginal inward folding of older leaves

plants. Sulfur plays an important role in the electron transport chain necessary for plant growth and development.

2.2. Micronutrients

The essential nutrients that are needed in small amounts are referred to as micronutrients. They embrace minerals, trace minerals, vitamins, and organic acids (Warne, 2014). An increase in the concentration of micronutrients enhances the quality and yield of agricultural by-products. Micronutrients consist of seven main elements: Boron, Chlorine, Manganese, Iron, Zinc, Copper, and Molybdenum. Boron is crucial for cellular division and is concerned with the transport of carbohydrates to plants. Chlorine plays a vital role in maintaining the diffusion balance. Manganese acts a co-factor for activity of various proteins. Iron is found to be very important within the pathway of pigment biogenesis. The deficiency of Manganese and iron results in greensickness between the veins of the leaves. Zinc may be a metal part that acts as an associate degree protein substance and is assimilated by the plants in the form of a divalent cation. Copper increases the protein activity and is directly concerned with the synthesis of the semipermeable membrane used by most of the cells to absorb the required water and nutrients (Tripathi et al., 2015). Whereas Molybdenum plays the most important role in the nitrogen fixation process occurring in plants (Grusak, 2001). Hence, these nutrients are important for the appropriate plant's growth and development.

2.3. Biofertilizers

Biofertilizers are live formulations (very often) of microbes that improve plant growth and soil fertility by fixing nitrogen, solubilizing phosphate, having insecticidal properties, and/or synthesizing plant growth-promoting substances. The mechanism of improving plant growth may involve multiple factors together in action (Kole et al., 2013; Malusá and Vassilev, 2014; Singh et al., 2016). Rhizobacteria that promote plant development, such as Rhizobium, blue-green algae (BGA), fungal mycorrhizae, *Azotobacter, Azospirillum* (Raffi and Charyulu, 2021), and phosphate-solubilizing bacteria like *Pseudomonas* sp. and *Bacillus* sp., which augment the nutrient supply to crops by increasing biological nitrogen fixation and solubilization of insoluble complex (Itelima et al., 2018). Biofertilizers improve the microbial activity of the rhizosphere (Okur, 2018). Nanobiofertilizers define a new state of the art in sustainable agriculture where nanoparticles are combined with a biofertilizer (Simarmata et al., 2016). Following is a compilation of traditionally used biofertilizers that are eco-friendly but suffer few drawbacks.

2.3.1. Nitrogen fixing biofertilizers

Nitrogen is one of the principal nutrients for plant growth and development. Though 78% of the nitrogen is available in the atmosphere, it is not in usable form and thus remains unavailable to plants. The atmospheric nitrogen is converted into ammonia, and nitrate forms through a process known as biological nitrogen fixation (BNF). BNF utilizes microorganisms in the form of biofertilizers to make the usable forms of nitrogen for plants using an enzymatic complex called nitrogenase (Mącik et al., 2020). Microorganisms responsible for nitrogen fixation are divided into two types, known as symbiotic and non-symbiotic, based on their association with the host plant. Symbiotic microorganisms include *Rhizobium* and *Anabaena,* whereas *Azotobacter*, *Azospirillum*, and *Cyanobacteria* are the non-symbiotic or free-living microorganisms (Mahanty et al., 2017).

2.3.1.1. Rhizobium. *Rhizobium* is a gram-negative bacterium that is used as nitrogen fixers in leguminous plants. It also fixes nitrogen in certain non-leguminous plants such as *Parasponia* by forming nodules (Nath Bhowmik et al., 2018). *Rhizobium* performs its function by forming the root nodules after entering the plant through the root system. Inside the root nodules, the atmospheric nitrogen is converted into ammonia and nitrates, the usable form for the plants, and then later, they are utilized to synthesize amino acids and nucleotides. *Azorhizobium*, another *Rhizobium* strain which forms modules nodules in the stem and fixes the nitrogen over there (Lindström and Mousavi, 2020). They are responsible for producing Indole acetic acid and thus promote plant growth and development (Mahanty et al., 2017). Abiotic stresses such as drought affect *Rhizobium* function and the growth and development of leguminous plants (Igiehon and Babalola, 2017).

2.3.1.2. Azotobacter. *Azotobacter* is a group of gram-negative, free-living, aerobic bacteria that fixes the nitrogen in non-leguminous plants. They belong to the Azotobacteriaceae family and consist of different species such as *Azotobacter armeniacus, Azotobacter sinistral, Azotobacter beijerinckii, Azotobacter paspali, Azotobacter chroococcum, Azotobacter nigricans, and Azotobacter vinelandii* (Kumar et al., 2018). *Azotobacter* is also known for enhancing the production of hormones responsible for plant growth like Thiamine, Riboflavin, Nicotine, Gibberellin, and IAA. *A. vinelandii,* and *A. chroococcum* are responsible for the secretion of indole acetic acid (Das, 2019). *Azotobacter* can produce antifungal compounds against pathogens such as *Fusarium* sp., *Alternaria* sp., *Trichoderma* sp. (Sivasakthi et al., 2017). *A. nigricans* is well known for producing antifungal activity against *Fusarium* sp. apart from its plant growth-promoting activity (Nagaraja et al., 2016).

2.3.1.3. Azospirillum. *Azospirillum,* a gram-negative nitrogen-fixing aerobic bacteria, belongs to the Spirilaceae family. They play an important role in producing growth-promoting substances, especially indole acetic acid (IAA) (Tapia-Olivares et al., 2019). *Azospirillum* strains can also produce different polymers such as lignin, glycol polymers, etc. (Fendrihan et al., 2017). They form an associative symbiotic relationship mainly with plants having C4 dicarboxylic pathways such as sugarcane, maize, sorghum, etc., and enhance photosynthesis as they grow and fix the nitrogen on the organic salts of malic and aspartic acid (Mahanty et al., 2017). *Azospirillum* is used as the primary biofertilizer for rice cultivation (Suhameena et al., 2020).

2.3.2. Cyanobacteria

Cyanobacteria or blue-green algae are the most abundant form of nitrogen-fixing microorganisms. They are photosynthetic in nature and enhance plant growth by promoting the production of auxins and gibberellic acid production. Cyanobacteria serve as a beneficial biofertilizer mainly in rice fields as it mostly depends on fixed nitrogen for its growth (Sao and Samuel, 2015). They act as biological antagonists against various plant pathogens in wetland rice fields (Majeed et al., 2017). They can also develop and fix the nitrogen in snow, terrene, and hot spring environments. They are tolerant of extreme environmental conditions (Bhattacharjee and Dey, 2014).

2.3.3. Phosphorous solubilizing biofertilizers

Insoluble types of phosphorous like hydroxyapatite, tricalcium phosphate, dicalcium phosphate, etc., present in the soil remain unavailable to plants which are converted into a soluble form by certain bacteria and fungi known as phosphorous solubilizers. This includes *Pseudomonas putida* and *Bacillus megaterium* bacterial species and fungi like *Aspergillus* and *Penicillium.* The phosphorous solubilizing fungi secrete organic acids like succinic acid, citric acid, malic acid, fumaric acid, etc., that solubilize the insoluble form of phosphorous (Zhang et al., 2018). The phosphorous solubilizing microorganisms perform their function by lowering the pH of the soil, forming chelates, and mineralizing the organic phosphorous, thus leading to the release of inorganic phosphorous utilized by plants (Kalayu, 2019). Nanomaterials such as nanoclay and natural char nanoparticles are used as nano-carriers for phosphate solubilizing bacteria (Safari et al., 2020).

2.3.4. Phosphorous mobilizing biofertilizer

Phosphorous mobilizers are microorganisms that can enhance phosphorous absorption by mobilizing it from phosphorus-wealthy surrounding plants, such as Mycorrhizae. Mycorrhizae play a key function in mobilizing phosphorous to the flora. They shape a symbiotic relationship with roots and certain vascular flora like wheat, rice, maize, and potato (Mącik et al., 2020). Arbuscular mycorrhizal fungi (AMF) enhance uptake of plant nutrients and increase tolerance to root pathogens, salinity, and drought conditions (Battini et al., 2017). AMF secretes phosphatase enzyme, which is used for hydrolyzing phosphate from organic phosphorous compounds (Altuntaş and Kutsal, 2018). Other than this, they can also detoxify the toxic substances present in the soil and are therefore used in bioremediation.

2.3.5. Zinc solubilizing biofertilizer

Zinc is a crucial component that is required for proper growth and improvement of plants but in less amount. A high concentration of zinc metal is toxic and may reduce plant growth due to a decrease in enzyme activity, photosynthetic activity, and plant mineral nutrition (Kour et al., 2019). Zinc solubilizers perform their function by two methods depending on the pH of the soil. The first is based on the formation of organic acids by the zinc solubilizing microbes in soil and cation exchange. In contrast, the second method involves the synthesis of siderophores (Nitu et al., 2020). Zinc solubilizing microorganisms include strains of *Pseudomonas, Bacillus, Acinetobacter, Gluconacetobacter, Thiobacillus, and Rhizobium.* Plant Growth Promoting Rhizobacteria (Shahid et al., 2020) and *Agrobacterium tumefaciens* (Khanghahi et al., 2018) have also been studied as zinc biofertilizers to overcome the Zinc unavailability in soils.

2.3.6. Potassium solubilizing biofertilizer

Potassium is the most essential and ample nutrient in soil but remains unavailable for plant uptake due to its insolubility. Potassium is mainly present in the soil in four distinct forms: mineral, non-exchangeable, exchangeable, and solution potassium, among which mineral potassium is majorly present (Etesami et al., 2017). Potassium regulates plant cellular osmotic pressure, transportation of compounds in plants, activation of enzyme activity, and photosynthetic process (Bashir et al., 2017).

2.3.7. Silicon solubilizing biofertilizer and Composites

Silicon is usually present in the form of silicates of aluminum, magnesium, calcium, sodium, potassium, or iron, which remains unavailable to plants. Plants absorb silicon as soluble mono silicic acid that strengthens the cell wall (Bist et al., 2020). Microorganisms such as *Bacillus, Pseudomonas, Proteus, Rhizobia, Burkholderia*, and *Enterobacter* are used to release silicon from silicates and thus promote plant growth and improvement and increase abiotic and biotic stress tolerance (Bist et al., 2020). The novel strain of *Enterobacter* known as *Enterobacter ludwigii GAK2* is found to be a potential silicate solubilizer that promotes growth in rice plants (Lee et al., 2019).

Composites include microorganisms that can decompose organic matter faster and are used as biofertilizers to increase the release of nutrients. For example, cellulolytic fungi such as *Aspergillus*, *Penicillium*, *Trichoderma* lead to the breakdown of cellulose of plant material (Kyaw et al., 2018). Bio-composites prepared from biochar have positive social, environmental, and economic impacts (Zhang et al., 2020). Different types of biofertilizers, their mode of action and role in plant rhizosphere are mentioned in Table 2.

2.3.8. Limitations of biofertilizers

Despite having several benefits of biofertilizers, certain drawbacks limit their applications. The constraints of biofertilizers are as follows.

(i) Lack of popularization of biofertilizers and low level of farmers acceptance: Despite having different potential activities, biofertilizers have now no longer yet obtained popularity amongst the farmers for good enough acceptance (Bhattacharjee and Dey, 2014). Moreover, farmers are not much aware of biofertilizer applications in crop growth and development. Their lack of knowledge about the concentration, time, and technique of biofertilizer application and the efficiency of biofertilizer compared to chemical fertilizer limits their wide-scale applications.

(ii) Lack of raw materials in biofertilizer production: Generally, biofertilizers are produced as carrier-based inoculants with potential microorganisms. These carrier materials used in the applications of biofertilizers are not readily available and reachable in villages of remote areas (Debnath et al., 2019).

(iii) Technical and economic constraints: To meet the massive demand for biofertilizers, high-end instruments and technically trained laborers are missing. Without these facilities, contamination-free product development is very risky. No training center provides a degree in quality management and production techniques related to biofertilizers, which also aid in the limitation list. Again, all the rural areas of India do not have the suitable infrastructure to store long-time biofertilizers with high safety measures as they are live organisms. The fertilizer used as biofertilizer is much more than chemical fertilizer,

Table 2
Different types of biofertilizers, their mode of action and their role in the plant rhizosphere.

Sl. No.	Biofertilizers	Modes Of action	Role in plant rhizosphere	Ref.
1.	**Nitrogen Fixing Biofertilizers**			
	Rhizobium	Forms root nodules after entering the plant through root nodules.	• Inside the root nodules, the atmospheric nitrogen is converted into ammonia and nitrates which is utilized by plants to produce amino acid and nucleotide.	(Lindström et al., 2020; Mahanty et al., 2017; Nath Bhowmik et al., 2018)
	Azobacter	Colonize the plant roots and fixed the atmospheric nitrogen.	• Enhances the production of the hormone responsible for plant growth such as Thiamine, Riboflavin, Nicotine, Gibberellin, and Indole acetic acid. • Produces anti-fungal compounds against pathogen.	(Das, 2019; Sivasakthi et al., 2017)
	Azospirilum	Producing growth-producing substance	• Produces different polymers such as lignin, and glycol polymer. • Used as a biofertilizer for rice cultivation. • Forms symbiotic relationship with C4-dicarboxylic pathway and fix the on the organic salts of aspartic and malic acid.	(Fendrihan et al., 2017; Mahanty et al., 2017; Tapia-Olivares et al., 2019)
2.	**Cyanobacteria**	Enhances plant growth by promoting the production of auxins, and gibberellic acid.	• Beneficial for the rice field as it mostly depends on fixed nitrogen for the growth and production. • Biological antagonist against various plants pathogens in wetland rice field. • Fixes the nitrogen in snow, terrence and hot spring environment.	(Majeed et al., 2017;Sao et al., 2015)
3.	**Phosphorous Solubilizing biofertilizers**	Converts the insoluble phosphorous to the soluble forms	• The fungi secrete organic acid such as succinic acid, nitric acid, citric acid, malic acid and, fumaric acid that solubilize the insoluble forms of the phosphorous. • The microorganism performs their function by lowering the pH of the soil, chelating, and mineralizing the organic phosphorous.	(Kalayu, 2019; Zhang et al., 2018)
4.	**Phosphorous Mobilizing biofertilizers**	Enhance the phosphorous absorption by hydrolyzing the organic and inorganic phosphorous to soluble form that can be assimilated by the plants.	• Creates a symbiotic relationship with the roots and certain vascular flora like wheat, rice, maize and potato. • It supply nutrient to the plant and in return gets carbohydrate/sugar.	(Altuntaş et al., 2018;Mącik et al., 2020)
5.	**Zinc solubilizing biofertilizers**	Production of soluble zinc by the formation of organic acid in the soil and cation exchange. By formation of siderophores	• It is a crucial component required for proper growth and improvement of plants but required less in amount. • It improves the availability of zinc in soil and increases the crop yield.	(Kour et al., 2019; Nitu et al., 2020)
6.	**Potassium solubilizing biofertilizers**	Microorganism that are capable to solubilize potassium from the inorganic and insoluble compound for the plant uptake	• Most essential and ample nutrient in soil and remain unavailable due to its insolubility. • It regulates the plant cellular osmotic pressure, transportation of compound in plants activation of enzyme activity and photosynthesis process.	(Bashir et al., 2017; Etesami et al., 2017)
7.	**Silicon solubilising biofertilizers**	Release silicon from silicate and thus promote plant growth and improvement and increase abiotic and biotic stress tolerance.	• Plants absorbs silicon as soluble mono silicic acid that strengthen the cell wall.	(Bist et al., 2020)

increasing the implementation cost (Pathak and Christopher, 2019).

(iv) Insufficiency of microbial strains: Biofertilizer means 'Live fertilizer'; therefore, very specific strains are required for mass usage of biofertilizer in the land. Most strains used in biofertilizers depend not only on the specificity of crops but also on the specificity of soil and climate. Very adverse conditions of soils such as too hot or dryness can inhibit the growth of strains and eventually their effectiveness. It is also observed that in the presence of excess biological enemies (in soils), the growth of biofertilizers is hampered. Thus, the lack of specific strains and their adequate nutrient media can be considered one of the fundamental regulations in manufacturing biofertilizers (Bhattacharjee and Dey, 2014).

(v) Environmental constraints: Extensive and long-time utilization of biofertilizer results in the accumulation of salts, heavy metals, etc., that hinders plant growth, soil quality, development of rhizospheres, water quality, and human health (Chew et al., 2019). The presence of heavy metals such as lead, mercury, chromium, etc., poses a danger to nature because of their carcinogenic activity. As the crops accumulate the nutrients from such soils, those heavy metals will become part of the food chain (Kumar et al., 2018). Due to the leaching procedure, the same will contaminate the groundwater and endanger the aquatic animals.

3. Nanomaterials in agriculture

Agriculture is an important economic sector for producing various crops for different food and feed purposes (Malhotra, 2016). With the growing human population, it is to call out the need for the agri-sector towards developing efficient agriculture techniques to cater and nourish them (Zhang et al., 2015). Traditional fertilizers or chemical fertilizers provide an opportunity to the crops for optimal growth and productivity (Zhang et al., 2015); however, depending on such practices turned out to be a Hobson's choice. Furthermore, the intensive application of chemical fertilizers to mitigate the growing demand for food has caused severe environmental concerns (Congreves and Van Eerd, 2015). The low nutrient use efficiency of the plants associated with the use of chemical fertilizers causes hindrance in achieving sustainability in agriculture. The low nutrient use results from high release rates of chemical fertilizers considering the actual nutrient absorption by the plant and thus transforming fertilizers to a form that is not bioavailable to it (Chhipa, 2017). Hence there is a necessity for developing new innovative fertilizers to increase the fertilizer use efficiency (Van Eerd et al., 2017). The application of nanotechnology for the development of a new type of fertilizers in the form of nanofertilizers, nanobiofertilizers, and nanopesticides is regarded as a promising option for boosting the horticultural crop production to meet the growing demand of the expanding human population with the additional advantage of sustainability (Feregrino-Perez et al., 2018). Thus, the establishment of nanobiomaterials is recognized to increase crop yield, minimize leaching, and reduce environmental hazards (Solanki et al., 2015).

3.1. Nanofertilizers

Traditionally, chemical fertilizers supply three primary macronutrients, N, P, and K, and secondary macronutrients like Sulfur (S), Magnesium (Mg), and Calcium (Ca). Soil nitrogen requirements are high. The frequently used commercial fertilizers (Prasad et al., 2017) are triple superphosphate (TSP), monoammonium phosphate (MAP), urea, diammonium phosphate (DAP), nitrogen-phosphorous-potassium (NPK) (Tarafder et al., 2020). Statistics by the International fertilizer industry association (IFIA) revealed that the worlds' consumption of fertilizers has been on a sharp rise in 2016–17 (Shang et al., 2019). However, the NUE of traditional fertilizers was low; A lot of it ran off, leading to eutrophication. Nitrates leach into marine systems, and N-oxides are greenhouse gases with environmental consequences. Further, long-term application leads to damage to soil substructure, soil microflora, plants, and the ecosystem. Nitrates are potentially carcinogenic and adversely affect human health if they gain entry into the food chain via plants. The application of nanotechnology to improve plant productivity is known as 'Phytonanotechnology.' Nanoparticles for nanofertilizers can be prepared by physical, chemical, or biosynthetic processes. Broadly, nanofertilizers can be categorized into macronutrient nanofertilizer and micronutrient nanofertilizer. Various agricultural nanoformulations may be devised, such as (i) encapsulation of nutrients/fertilizer within nanomaterial, (ii) nanomaterial applied as a thin polymer coating over nutrient particles, and nutrients delivered as nanoemulsions. The nanoparticle-based nanofertilizers' applications and effects are mentioned in Table 3.

3.1.1. *Macronutrient nanofertilizers*

Slow-release urea-silica nanohybrid, high urea loaded (36% w/w/) slow-release nitrogen nanofertilizer with 83% loading efficiency was prepared. This prevented premature leaching into water bodies due to strong bonds between urea and nanomaterial (Tarafder et al., 2020). In another study, nanoparticles of Zinc, Copper, Iron were incorporated into urea-modified hydroxylapatite (HA) to enhance fertilizer efficiency. The formulation showed increased NUE, enhanced uptake of Fe^{2+}, Zn^{2+}, and Cu^{2+}, increased nutrient richness of fruits, improved soil physicochemical properties, high swelling ratio, and minimized leaching. This fertilizer, called hybrid nanofertilizer (HNF), had low cost and required low dosing (50 mg/week) (Iqbal, 2019). In another study by Kottegoda et al., urea's solubility was reduced by incorporating into hydroxyapatite nanoparticle (HA NP) matrix with urea: hydroxyapatite ratio of 6:1. HA-NP acted as a phosphorous (P) source and was highly biocompatible. HA-NP-urea combination led to the slow release and high NUE. This resulted in higher rice yields with 50% lower urea concentration (Kottegoda et al., 2017). Various experiments were done with HA-NP stabilized with carboxy methylcellulose (CMC) on seedling growth, metabolism, and seed germination of *Solanum lycoperscium* (Marchiol et al., 2019).

Phosphate (Pi) supplied as HA NP compared to bulk phosphate increased the growth and germination of sand-grown chickpeas (Bala et al., 2014). Similarly, spherical CMC coated HA-NP promoted the growth and yield of soybeans (Glycine max) compared to the same amounts of soluble phosphate fertilizer. This suggested higher solubility and dissolution of Pi in NP form (Liu and Lal, 2014, 2015). A needle-shaped nanoform HA Pi fertilizer was tested for its activity on soybean and impact on soil microbiome. This formulation did not impact the soil microbiome. However, the authors did not see a noticeable increase in plant growth/biomass, the whole plant phosphorous, and yields compared to controls (McKnight et al., 2020). One study to date has recorded higher yields of wheat (*Triticum aestivum)* with nanoHA formulation, yet not more effective than traditional TSP (Montalvo et al., 2015). Using Chitosan (CS) as a carrier for the slow release of nutrients is trending in agriculture (Michalik and Wandzik, 2020). CS-NP was obtained by polymerizing polymethacrylic acid (PMAA) to entrap N, P, K NPs each at a time. This resulted in CS-PMAA-NPK NPs complex. The effect was studied using garden peas (*Pisum sativum* var Master B) plants. Five-day seedlings were treated via roots at different concentrations for 1, 2, 4, and 7 days. The formulation led to reduced root elongation rate and also to starch accumulation at the root tip in a dose-dependent manner. However, the formulation was genotoxic as assessed by comet assay. This emphasizes vigorous testing of each formulation on plant growth. Also, much needed is the study of nanoformulations on soil microbiome (Khalifa and Hasaneen, 2018) which is a drawback of this study.

3.1.2. *Micronutrient nanofertilizers*

Minute quantities of trace elements essential to plant growth are called micronutrients. Various preparations of nanomicronutrient

Table 3
Nanofertilizers used in agriculture.

Sl. No	Nanoparticles	Size (nm)	Plants Used	Amount Used	Medium of Application	Effects	Ref.
Cerium-based Nanofertilizers							
1.	CeO_2 (Rod)	8 ± 1 231 (particle)	Wheat	125 mg/2 kg	Soil	Improved Plant height, biomass, grain yield, modified the amino acid ad fatty acid content	(Rico et al., 2014)
2.	CeO_2	10	Cucumber	400 mg/kg	Soil	Increased starch content, globulin, decreased non-reducing sugar content, glutelin, and phenolic content	(Zhao et al., 2014)
3.	CeO_2 (Rod)	8	Barley (*Hordeum vulgare L.)*	0–500 mg/kg	Soil	Improved plant height, biomass, and chlorophyll content reduced spike production	(Rico et al., 2015)
4.	CeO_2 (Rod)	8	Wheat	0–400 mg/kg	Soil	Increased the grain protein, no change in starch, sugar	(Du et al., 2015)
Copper-based Nanofertilizers							
5.	n-Cu	40	Cucumber (*Cucumis sativus*)	10–20 mg/L	Hydroponics	Up-regulation of phenolic content, amino acid, antioxidant enzymatic system, down-regulation of citric acid	(Zhao et al., 2016)
6.	CuNPs-Cs-PVA	25	Tomato (*Solanum lycopersicum*)	10 mg/g	Soil	Increased the stem diameter, numbers of leaves, fresh biomass of roots, dry biomass of stem leaves and roots of the plants, and yield	(Hernández et al., 2017)
7.	n-Cu	40	Cucumber (*Cucumis sativus*)	0–800 mg/kg	Soil	Increased in fruit metabolite, as well as the concentration of sugars, organic acids, amino acids, and fatty acids	(Zhao et al., 2017)
8.	CuNPs-Cs-PVA	25 (CuNPs)	Tomato (*Solanum lycopersicum)*	10 mg/g	Soil	improve plant growth, increase in chlorophyll concentration, phenolic compounds, and defensive enzymes	(Hernández-Hernández et al., 2018)
9.	CuO-NPs	18	Onion (*Allium cepa*)	0–2000 µg/ml		Reactive oxygen species enhanced in onion roots, enzymatic activities increased.	(Ahmed et al., 2018)
10.	n-Cu-Kinetin		Kidney Bean (Phaseolus vulgaris)	0–100 mg/kg	Soil	A negative impact on chlorophyll is observed, and nutrient element accumulation	(Apodaca et al., 2017)
11.	Nano-Cu	30–50	Maize (*Zea mays subsp.*)	4 mg/kg	Soil	Greatly improved the harvest, and productivity, Enhanced SOD, APX enzyme activity	(Huang et al., 2019)
Silicon-based Nanofertilizers							
12.	Nano-Si	40	Faba Bean (*Vicia faba L.*)	0–3 mM	Soil	Enhanced seed germination, GP, GR, and MGT, Salinity has a deleterious effect on seed germination	(Qados and Moftah 2015)
13.	N-Si (Nanopowder)	20	Tomato (*Solanum lycopersicum L.*)	0.5–3 mM	Petridish	Increased in GP, GR, root length, fresh weight of tomato seedlings. Upregulation of four stress genes and down regulation of six stress genes.	(Zainab, 2016)
14.	SiNP	10–95	Wheat (*Triticum aestivum*)	10 µM	Hydroponics	SiNP protects the wheat seedling from UV-B radiation through NO-medicated triggering of antioxidant defense system.	(Tripathi et al., 2017)
15.	SiO_2		Cucumber (*Cucumis sativa*)	0–120 mg/L	Foliar	Positive effect on plant growth and yield. Increase in nitrogen and phosphorus content and decrease in Na content	(Yassen et al., 2017)
16.	SiO_2 (Amrphous)	20–30	Barley (*Hordeum vulgare*)	125 &250 mg/L	Soil	Increased in chlorophyll and carotenoid, enhanced osmolytes, antioxidative enzyme	(Ghorbanpour et al., 2020)
17.	n-SiO_2	5–15	Sugarcane, (*Saccharum officinarum*)	300 ppm	Foliar	Enhancing photosynthesis and photoprotection, maintain and increase chlorophyll and carotenoid respectively content. Reduce the effect of chilling stress	(Elsheery et al., 2020)
18.	SiNPs	10	Marigold (*Tagetes erecta L.*)	200 & 600 mg/L	Soil and Foliar	High chlorophyll content, leaf area, number of flowers, shorter period of initiation of the first bud	(Attia and Elhawat 2021)
Zinc-based Nanofertilizers							
19.	ZnO-NPs	30	Tomato (*Solanum lycopersicum L.*)	15 and 30 mg/L	Tissue Culture	Upregulation of SOD and GPX, ZnO-NPs alleviate the effect of salt stress	(Alharby et al., 2017)
20.	ZnO-NPs	18	Sorghum (*Sorghum bicolor L.)*	6 mg/ kg	Soil and Foliar	Enhancing crop productivity, grain nutritional quality, modulate NPK accumulation	(Dimkpa et al., 2017)
21.	Parthenium-ZnO-NPs	28	Peanuts (*Arachis hypogaea L.*)	300 ppm	Soil	Enhanced growth of seed and ultimately increases crop yield	(Rajiv et al., 2018)
22.	Zn-NPs	< 50	Sweet basil (*Ocimum basilicum L.)*	0.5 mg/Kg	Soil and Foliar	Increase the pharmaceutical and nutritional property, Improves vegetative growth and essential oil yield	(Tavallali et al., 2018)
Titanium-based Nanofertilizers							
23.	n-TiO_2	19–20	Coriander (*Coriandrum sativum* L.),	2–6 ppm	Foliar application	Increase in plant height, fruit yield, and branches, increase in amino acid, sugar phenol, indole, and pigments	(Khater, 2015)
24.	n-TiO_2	25 ± 3	Tomato (*Solanum lycopersicum L.*)	0–1000 mg/kg	Soil	Enhanced plant height, root length and biomass, increased chlorophyll, and lycopene content	(Raliya et al., 2015)
25.	TiO_2NPs	20	Rice (*Oryza sativa* L.)	0–750 mg/Kg	Soil	Increased the shoot and root length, increased metabolites, no translocation of NPs from soil to rice grain	(Zahra et al., 2017)

(*continued on next page*)

Table 3 (*continued*)

Sl. No	Nanoparticles	Size (nm)	Plants Used	Amount Used	Medium of Application	Effects	Ref.
Cerium-based Nanofertilizers							
26.	TiO_2 NPs	30–50	Tomato (*Solanum lycopersicum*)	0.5–4 g/L	Hydroponics	Increased chlorophyll content hence photosynthesis, induced expression of PSI gene	(Tiwari et al., 2017)
27.	TiO_2 NPs	30–50	Wheat (*Triticum vulgare* L.)	0–40 mg/L	Hydroponics	Decreased chlorophyll content, plant growth not affected, increase in N, P, Zn, Cu concentration, and decrease in K, Mn conc.	(Dağhan et al., 2020)
Iron-based Nanofertilizers							
28.	Fe_2O_3 NPs	20	Peanut (*Arachis hypogaea*)	0–1000 mg/kg	Soil	Increased rot length, plant height, biomass, SPAD value, chlorophyll content, stimulate ROS	(Rui et al., 2016)
29.	Fe_2O_3 NPs	< 20	*S. lycopersicum* (tomato)	50–800 mg/L	Hydroponics	Enhanced seed germination, root and shoot length, ferric to ferrous reduction attributed to rich phytochemical in plants.	(Shankramma et al., 2016)
30.	Fe_2O_3 NPs	20–60	Squash Plant (*Cucurbita*)	20 ppm	Foliar Application	Higher content of organic matter, protein, lipids, and total energy (K cal/g) in fruits.	(Shebl et al., 2019)
31.	Fe NPs (Round)	52.4	Bell pepper (*Capsicum annuum)*	0.002–2 mM/L	Hydroponics	Low conc. Promote plant growth, increase in chloroplast number, and vascular bundle. At high conc. NPs aggregate and block the cell wall.	(Yuan et al., 2018)
32.	Fe_3O_4 NPs	< 36	Cucumber (*Cucumis sativus*)	0–2000 mg/L	Hydroponics	At higher concentration increase in biomass, and antioxidant enzymes SOD and POD	(Konate et al., 2018)
33.	Fe_3O_4 NPs	13	Barley (Hordeum vulgare L.)	125–1000 mg/L	Hydroponic culture	Increasing dose enhanced plant growth, hence fresh weights, No phytotoxic effect recorded at high conc. Increase in chlorophyll, soluble protein, and dry weight	(Tombuloglu et al., 2019)
Silver-based Nanofertilizers							
34.	Ag NPs	–	Tomato (*Solanum lycopersicum* L.)	0–40 ppm	Soil	It negatively affected the plant, reducing the fruit number, fruit diameter, average fruit weight, number, plant height.	(Younes and Nassef 2015)
35.	Ag NPs	20	Tomato (*Solanum lycopersicum* L.)	0.05–2.5 mg/L	Seed	Improved seed germination, root length, flesh, and seed dry weight. Alleviate adverse effects of salt stress. Four salt stress genes, *AREB*, *MAPK2*, *P5CS,* and *CRK1*, were up-regulated, and three genes, *TAS14*, *DDF2,* and *ZFHD1,* were down-regulated.	(Almutairi, 2016)
36.	Ag NPs	20	Soybean (*Glycine max L.*)	0–62.5 mg/kg	Soil	It affected plant growth negatively. The addition of GSH reduced the AgNP induced toxicity and promoted plant growth, Increase in the N content in tissue	(Ma et al., 2020)
37.	Ag NPs	50	Lavender (*Lavandula*)	20 mg/L	Tissue culture	Increase the number of shoots per explant and pigment content at low doses.	(Khattab et al., 2022)

Abbreviations: Cs: Chitosan; PVA: Poly vinyl alcohol; SOD: Superoxide dismutase; APX: Ascorbate peroxidase; GP: Germination percentage; GR: Germination rate; MGT: Mean germination time; GPX: Glutathione Peroxidase; SPAD: Soil Plant Analysis Development; ROS: Reactive Oxygen Species; POD: Peroxidase

fertilizers have shown promising results (Sharonova et al., 2015). Plants depend on Zinc (Zn) as a co-factor for enzymes, and proteins are also involved in synthesizing proteins, carbohydrates, production of auxin, and plant defense (Noreen et al., 2018). Boron (B) similarly is an essential micronutrient involved in synthesizing the cell wall and its lignification. It is also involved in various physiological processes and plant growth (Navarro-León et al., 2016). Foliar formulations of Zn and B were applied to pomegranate at multiple concentrations (*Punica granatum* cv. Ardestani). With multiple combinations tested; it was observed that low concentrations of B (34 mg tree^{-1}) and high of Zn nanofertilizer (635 mg tree^{-1}) increased the fruit yield by 30% (Khot et al., 2012). A study where cucumber seedlings were grown in a solution with rubbery nanosuspension supplying Zn; an increased shoot growth and fruit yield were observed compared to commercial Zn –sulfate fertilizer (Mattiello et al., 2015). Improved yields were also observed in a study with Zn supplied as nanofertilizer to maize, sugarcane, potato, wheat, rice, and sunflower (Monreal et al., 2016). Zn nanofertilizer applied to pearl millet (*Pennisetum americanum*) increased the crop yields by 38%, shoot length by 15%, increased root area by 24%, chlorophyll content by 24%, total soluble leaf protein by 39% and 12% plant biomass compared to control over a period 6 weeks (Moghaddasi et al., 2017). ZnO NPs were added during seed germination and root growth of *Cicer arietinum.* ZnO NP exerted phytostimulatory effects via increased indole acetic acid levels (IAA). ZnO NP increases IAA levels in roots and thus increases plant growth rate. The efficacy of this fertilizer was due to the high surface area: volume ratio (Pandey et al., 2010). Iron (Fe) is required in trace amounts for plant growth and development, wherein both its deficiency and excess lead to impaired plant growth and development via impeding key metabolic processes (Palmqvist et al., 2017), and stabilized maghemite NPs which supply Fe were applied to the soil via irrigation and significantly improved growth rate and chlorophyll content compared to control in *Brassica napus* (Palmqvist et al., 2017). Citrate-coated Fe_2O_3 NPs and Fe_2O_3 NPs (6 nm) showed improved root growth of *G. max*, relative to bulk Fe_2O_3 suspensions > 500 mg/ml. Foliar application of Fe_2O_3 NPs in the spray at the eight-trifoliate leaf stage resulted in significantly improved photosynthetic rates attributable to increases in stomatal opening and not CO_2 uptake at chloroplast levels (Alidoust and Isoda, 2013). Joseph et al. studied if mycorrhizal colonization improved upon the usage of artificially aged enriched biochar mineral complexes and tested their formulation on Wheat. The effects were improved growth and nutrient uptake attributable to increased mycorrhizal colonization (Joseph et al., 2015).

Traditionally, commercial fertilizers do not supply micronutrients, limiting plant growth and development. To address this, Rahman et al. prepared mixed nanofertilizer preparations where NPs supplied trace elements, and routine fertilizers supplied most macronutrients. Studies of this fertilizer on Tomato plants showed higher NUE, nutritive value, and productivity when both qualitative and quantitative parameters were included. The study was one of its kind that could replace the current commercial fertilizers (Rahman et al., 2021). Foliar application of Silicon (Si), Selenium (Se), and Copper nanofertilizer preparation improved bell peppers' saline tolerance and increased chlorophyll, lycopene, and β-carotene in leaves increased flavonoids and glutathione in fruits. Saline stress is known to cause a reduction in chlorophyll, lycopene, and β-carotene in leaves, while glutathione and flavonoids were reduced in fruits. These effects were reversed upon applying micronutrient nanofertilizer, improved bioactive contents in fruits, and promoted stress tolerance (González-García et al., 2021). Concluding this section with important considerations that NPs pay attention to plant demands in a more customized manner, and that is why the use of nanotechnology in sustainable agriculture is increasing. However, cytotoxicity is associated with some formulations that must be tested for, and more importantly, it is becoming overwhelming important to conserve the plant growth-promoting rhizosphere bacteria when these formulations are applied. These studies and cost-benefit analysis would turn agri-nanotechnology into a more sustainable and realistic dream.

The advantages of using nanofertilizers are: (i) slow and controlled release of nutrients leading to higher NUE, (ii) choice of foliar and root/seed applications, (iii) improved moisture retention and physicochemical properties of soil, (iv) less run-off of nutrients into water bodies, (v) Enhanced shelf-life of nutrients due to protection against volatilization, heat and UV damage, (vi) some formulations may be anti-microbial leading to disease control (e.g., AgNP), (vii) formulations may provide pest resistance, (viii) enhancement of biosynthesis of secondary metabolites (Ghorbanpour and Hadian, 2015; Syu et al., 2014), (ix) increased activity of antioxidant enzymes (Ghanati et al., 2005; Ghorbani et al., 2015), (x) more effective absorption of water and fertilizers (Li et al., 2015) and positive effect on photosynthesis (Lei et al., 2007). Fig. 2 depicts better NUE and less leaching of nutrients upon using nanofertilizers.

Disadvantages of nanofertilizers are accumulation at high concentrations in non-target cells leading to gene expression alterations, generation of reactive oxygen species (ROS), generation of reactive nitrogen species (RNS), resulting in damage to the plasma membrane, cell organelles, and intracellular proteins (Jampílek and Kráľová, 2017). The regulatory requirements for nanofertilizer use are not precise (Martín et al., 2020), they are expensive to synthesize (Hussain, 2018), and their effects on human health, in the long run, are not known (Rai et al., 2015). Further, the transformation of nanoparticles is observed in plants affecting their physicochemical properties, and some of them might become cytotoxic upon transformations (Lowry et al., 2012).

3.2. Nanobiofertilizers

Sustainable agriculture also depends on plant growth-promoting rhzobacteria (PGPR). They are the rhizosphere and the endophytic bacteria. These bacteria promote plant growth via nutrient uptake, plant stress resistance, and protection against phytopathogens by promoting induced systemic resistance (Batista et al., 2018; Castro et al., 2018; Glick, 2020; Redman et al., 2002; Ryan et al., 2008; Waller et al., 2005). Of these mechanisms, some are direct effects such as nitrogen fixation, production of exopolysaccharide, phytohormone, sideophore As mentioned already that precision agriculture involves the use of nanomaterials. Nanostructured materials also increase the potential of PGPRs. Zn, Titanium, Si and Au NP increase the number of bacterial cells and beneficial properties of PGPRs. Biofertilizers have certain undesirable features such as low shelf-life, and dessication sensitivity and the bacterial populations decline rapidly upon introduction to the field as Azospirillum brasiliense must be at a concentration of 10^6-10^7 cells/plant (Bashan and Biochemistry, 1986). Their application requires stabilization by peat-based or liquid carriers (Namasivayam et al., 2014). Biofertilizers increase soils' ability to hold moisture, enhance nitrogen (N) and phosphorous (P), improve the microbial activity of soil and provide natural aeration. However, their on-field effects, stability and mode of application for best efficacy are areas with scope for improvement. Nanobiofertilizers have shown promise due to the following advantages over traditional biofertilizers: (i) Biofertilizers have a limited life span. Nanoformulations increased the shelf-life of biofertilizers. (ii) Nanoformulations also increase biofertilizers' desiccation and UV and

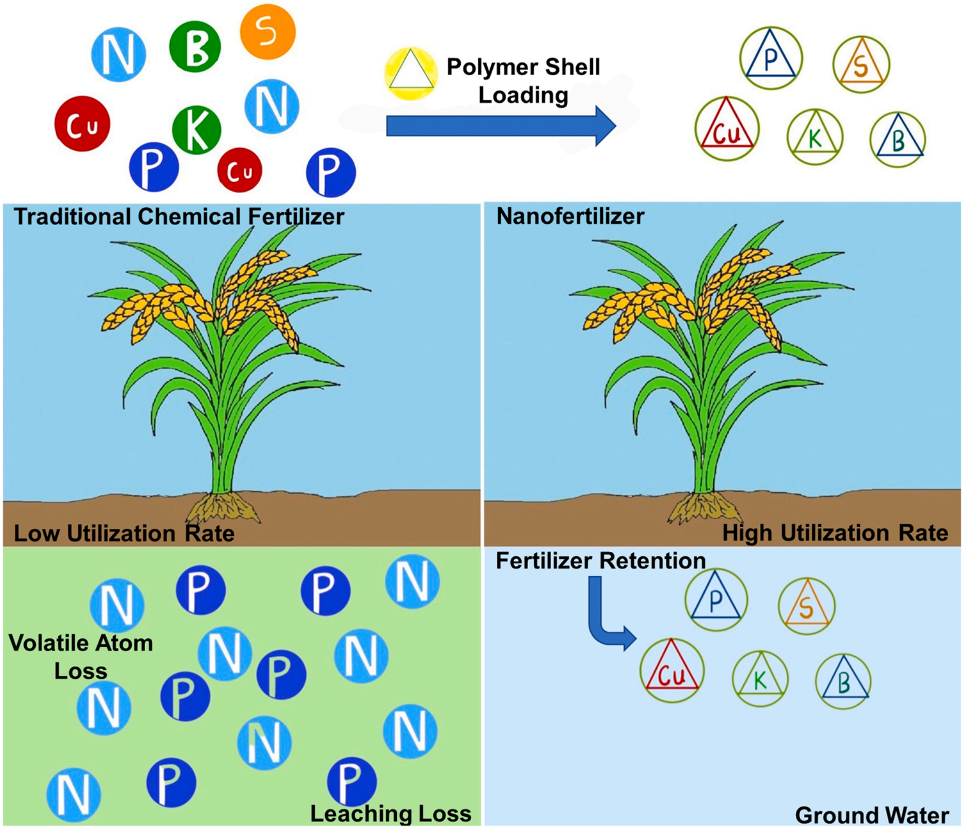

Fig. 2. Nanofertilizers overcome leaching issues caused by conventional fertilizers.

heat resistance. (iii) Controlled delivery and targeted release are another added advantage of nanobiofertilizers. (iv) Most importantly, some formulations positively impact the rhizosphere bacteria improving edaphic parameters (Malusá et al., 2012; Shukla et al., 2015) (v) Increase resistance of plants to biotic and abiotic stresses. (vi) conserving soil moisture. (vii) Increase production of siderophore (Shafiei-Masouleh and Nutrition, 2022; Sharma et al., 2021).

While most formulations have shown distinct advantages to plant growth Silver NPs (Ag NPs) cannot be used with biofertilizers due to their toxic effects on microbes (Duhan et al., 2017). An example of improved desiccation resistance is the use of polymeric nanoparticles (Jampílek and Kráľová, 2017). Straw compost and biofertilizer consortia. This complex induced systemic resistance in rice plants leading to improved yields. The preparation also promoted the diversity of beneficial microbes in the rhizosphere (Simarmata et al., 2016). Bioorganic components (plant growth-promoting microbes and urea) of nanobiofertilizers provide varied benefits such as stimulation of nitrogen-fixing ability, phosphate solubility, increased levels of plant hormones, and improved soil microbial activity (Dikshit et al., 2013; Shukla et al., 2015). Hydrophobic silica NPs as water in oil emulsion have been shown to improve biofertilizer delivery and enhance their shelf life by preventing desiccation (Kaushik and Djiwanti, 2017). However, nanobiofertilizers are hard to prepare because microbial sizes are bigger than nanoscale particles. Therefore, multiwall carbon nanotubes macroscopic filters may be used to adsorb and collect *E. coli* (Srivastava et al., 2004). The effect of nanobiofertilizers in tomato crops infected with bacterial wilt pathogen (*Ralstonia solanacearum*) was studied. It turned out that plants showed improved wilt resistance (Gatahi, 2017). A nanobiofertilizer with PGPR, Bacillus subtilis, Pseudomonas fluorescens, Paenibacillus elgi and Pesudomonas putida was studied against harmful fungal and bacterial infection pathogens present in the rhizosphere of leguminous crops. They emphasized nanoencapsulation and microencapsulation of biofertilizers to provide greater benefits to plants (Gouda et al., 2018). Mishra and Kumar studied the effects of various NPs on PGPRs and found several NPs were ecotoxic, and an alternative approach must be used (Mishra and Kumar, 2009). Nanoclay-coated biological agents containing *Trichoderma* sp. and *Pseudomonas* sp. have been protective in the control of fungal and nematode diseases in rabi crops. They also provided improved crop resistance against abiotic stress (Mukhopadhyay and De, 2014). NP and biofertilizer combinations although promising have varied effects and each formulation must be studied for its ecological and environmental effects before being called a sustainable solution to traditional biofertilizers.

The formulations of nanobiofertilizers are based on the fact that NPs have a total negative charge with some positively charged and hydrophobic sites (Breznak et al., 2012; Kurdish, 2019). Aggregation and binding patterns may be observed due to NPs leading to exposure of hydrophobic regions on the bacterial cell membrane or they attach to the hydrophobic region on the bacterial cell (Hayden et al., 2012). Bacteria and NP interact not only via electrostatic interactions but also by surface chemical reactions such as those associated with phospholipid membrane exposure (Palmqvist et al., 2015). Bacterial lipopolysaccharides (LPS) and lipoteichoic acid (LTA), proteins and phospholipids are interactors of NPs (Jiang et al., 2010). NPs may be transported into cells depending on their size but this requires more research (Shukla et al., 2015). Nanoencapsulation is enclosing the biofertilizers in a nanomaterial capsule. Capasules might be made up of alginate and starch wherein the latter provides energy (Du et al., 2018; Vafa et al., 2021). 'Smart seeds' are nanoencapsulation of specific bacterial strains inoculated into seeds. These seeds decrease seeding rates and improve crop performance. They may be dispersed over the field and allowed to germinate at an appropriate temperature, moisture and pH conditions (Chinnamuthu and Boopathi, 2009; El-Ramady et al., 2018). Application of nanomaterials to plants may be done in various ways such as seed application (via medium and spay) (Lahiani et al., 2013) or applied to the rhizosphere. When applied in the rhizosphere they enter roots via endocytosis through carrier proteins or by plasmodesmata. When nanoformulations are applied as foliar sprays; they enter plants via stomata and enter vascular bundles. The pathways of uptake and carriage depend on the plant and the type of nanoformulation (Anjum et al., 2019; Pérez-de-Luque, 2017).

3.3. Nanopesticides

In general, any toxic element that can kill other animals, insects, fungi, and plants that cause economic damage is known as a pesticide. To sustain crop productivity, countries are using different pesticides that are harmful to human health. With the population boom, there is an upcoming requirement for a large amount of food in the market as pesticide shows hazardous effects in the long run, so it is important to use nanopesticide that can enhance crop production and simultaneously shows adverse effects. The primary goal of designing nanopesticides is to improve pesticide efficiency, enhance its effect time and reduce general pesticide loads on the environment.

Depending on the nanoformulation (Kah et al., 2016), nanopesticides are classified into two major groups: organic molecules coated in polymers and inorganic molecules without a carrier (Zhang et al., 2019b). (Xiao et al., 2021) reported about the cellulose trapped pesticide release in a plant. The nanoformulation was temperature-dependent, which helped release the nano pesticides after a certain threshold in temperature. Among two types of nanopesticides, coated version is often used in the agriculture sector nowadays due to its sustainability in the plant body, targeted delivery, and extreme use (Zhang et al., 2019a). Different inorganic nanoparticles such as silica titanium dioxide formulated with polymer showed positive effects on plants (Kah and Hofmann, 2014). (Huang et al., 2018) formulated a light-responsive co-polymer (Poly(ethylene oxide-b-methacrylic acid) (PEO-PMAA)) that was encapsulated with pesticides. A control release mechanism can be developed with the help of these combinations of pesticide-carrier attached with some outer membrane groups. (Bhan et al., 2014) reported about PEG encapsulated nanopesticides that contain temephos and imidacloprid which shows more activity on larvae than in normal conditions. Similarly, (Campos et al., 2015) applied polymeric nanocapsules to fungicides and (de Oliveira et al., 2015) applied on herbicides to minimize the harmful effect and in both the cases the result shows more benefits than commercial products. It has been observed in other publications that PEG mixed with some essential oil with slow release can increase the toxicity level to insects (Solanki et al., 2015). Different properties of nanobiopesticides offer thermal stability and biodegradability and it is being observed that nanobiopesticides help in plant growth by inhibiting the pest (Manjunatha et al., 2016).

Nanopesticide offers a new avenue to agrieconomics due to its long durability, reducing the total application number of general pesticides and providing a potential solution to pest control. Till now few countries have only applied nanotechnology in agriculture, especially to pest control management systems. Europe is leading in adopting the usage of nanopesticide and share 30% of total revenue in 2020. The second-largest is Asia, due to the huge agricultural land India and China can apply nanopesticides during cultivation (Fig. 3A). The global revenue for nanopesticide is thought to be increased by 40% due to the high demand in the market but the environmental effects are still not known (Nanopesticide Market: Size, Trends, Growth and Industry Forecast to 2027 (credenceresearch.com)) (Fig. 3B) The four major sections of nanopesticide market falls are Harvesting, Production, Protection, and Packaging. Nowadays encapsulated nanopesticides are more common in the food preservation and packaging units. The nanoformulation, carrier, and size of different nanopesticides are mentioned in Table 4.

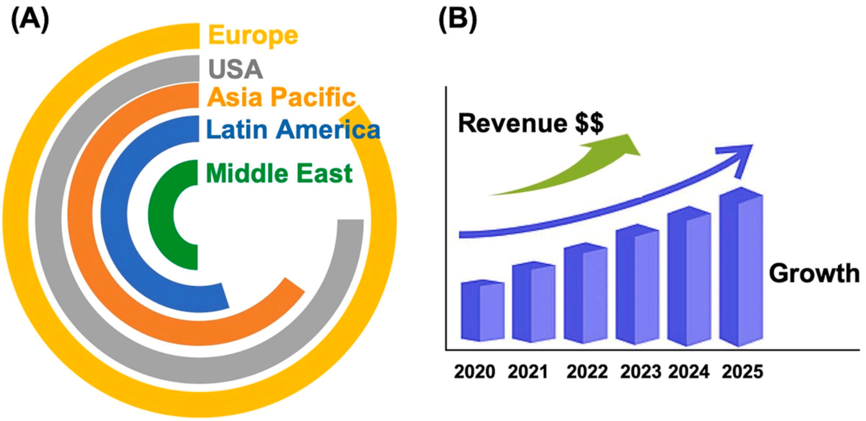

Fig. 3. Current scenario of nano pesticide (A) Global nano pesticide market share (B) Bar diagram representing global market of nano pesticide, with increasing revenue (2020–2025).

Table 4
The nanoformulation, carrier, size of different nanopesticides.

Sl. no.	Carrier	Nanoformulation	Size (nm)	Nanopesticides	Ref.
1.	Metallic NPs	Cu-NPs/ TM CuO-NPs	25 < 50	Thiophanate methyl (TM)	(Malandrakis et al., 2021)
2.	Calcium-alginate	CP@Ca-Alg	115–119	Cypermethrin (CP)	(Patel et al., 2018)
3.	Polymer-dsRNA IPC	pGPMA-dsRNA	318.1	dsRNA	(Parsons et al., 2018)
4.	Magnetic NPs	sAg-MNPs	64.5 ± 19.4	sAg-MNPs	(Starnes et al., 2015)
5.	MWCNT-g-PCA	CNT-g-PCA	20–40, Nanotube	Zineb, Mancozeb	(Sarlak et al., 2014)
6.	Mixed micelle	MMS-Pys-7	126.8	Pyrethrins (Pys)	(Zhang et al., 2019b)
7.	LCHP	p-BAGAP	0.5–1 mm	Glyphosate (Gly)	(Chen et al., 2018)
8.	MSN-CMCS	AZOX@MSN-CMCS	222	Azoxystrobin (AZOX)	(Xu et al., 2018)
9.	Pickering emulsion	LCH@Alg-SiO_2-x	–	λ-cyhalothrin (LCH)	(Chen et al., 2017)
10.	Nanoemulsion	NNE10 CNE10	11–17 8–12	NNE CNE	(Osman Mohamed Ali et al., 2017)
11.	poly-BMA-DAAM	Acetochlor@poly(BMA-DAAM)	100	Acetochlor	(Guo et al., 2014)
12.	Nanoliposome	NLP-chitosan	191–261	Etofenprox α-cypermethrin	(Bang et al., 2011)

Abbreviations: Cu-NPs/ TM: Copper nanoparticles / Thiophanate methyl; CuO-NPs: Copper oxide nanoparticle; CP@Ca-Alg: Cypermethrin@Calcium chloride-Alginate; dsRNA-IPC: double-stranded RNA-interpolyelectrolyte complexes; pGPMA-dsRNA: poly-[N-(3-guanidinopropyl)methacrylamide] -double-stranded RNA; sAg-MNPs: Sulfidized silver magnetic nanoparticles; MWCNT-g-PCA: Multiwall carbon nanotubes MWCNT-graft poly(citric acid); MMS-Pys-7: Mixed micelle-Pyrethrins; LCHP: Light-responsively controlled-release herbicide particle; p-BAGAP: poly- Biochar-ATP-Glyphosate-Azobenzene particles; MSN-CMCS: Mesoporous silica nanoparticles- Carboxymethyl chitosan; AZOX: Azoxystrobin; LCH@Alg-SiO2-x: Lambda-cyhalothrin Alginate-modified silica nanoparticle; NNE: Neem nano-emulsion; CNE: citronella nanoemulsion; poly-BMA-DAAM: Butyl methacrylate- diacetone acrylamide.

3.4. Environmental and health impacts of nanotechnology in agriculture

Ecotoxicology is a branch of science that evaluates the impact of pollutants in the biosphere on plants, animals and humans (Campana and Wlodkowic, 2018). Nanotoxicology is a much more recent area of development (since the beginning of 1990 s) because the use of nanoparticles is in vogue (Kahru and Dubourguier, 2010). NPs in agriculture are to be evaluated thoroughly through toxicology studies due to their increased penetration into cells owing to their smaller size, more lipophilicity and other features. NPs may be natural or synthetic (Buzea et al., 2007). NPs' toxicity varies based on their concentration, shape, specific surface, charge, structure, reactivity, or solubility (Doak and Dusinska, 2017). The mechanism of nanomaterials' toxicity is reliant on the material itself such as agro applications of Graphene oxide (GO) are thought to be safe and biocompatible as per few reports due to its hydrophilic and inert nature (Chandel et al., 2022; Gao, 2015; Kaur et al., 2021; Rosli et al., 2019). Lignin peroxidase from white-rot fungi could degrade GO making it environmental friendly (Kotchey et al., 2011) while there are reports suggesting GO causes intracellular reactive oxygen species (ROS) formation in plants (Zhang et al., 2012). Other carbon nanomaterials which are promising for sustainable agriculture like fullerene, and carbon nanotube (CNT) have similar effects (Zhang et al., 2012). Nanomaterials have anti-microbial properties and may impact soil microbial diversity and composition adversely (Khan et al., 2016). They are also emerging as major soil pollutants (Gottschalk et al., 2013). Nanomaterials are released into the environment during (a) production, (b) use, and (c) disposal. A significant contribution is made so far by-products other than agrochemicals with agrochemicals catching up (Fortunati et al., 2020; Karlsson et al., 2019). SiO_2, TiO_2, ZnO, Fe and Al_2O_3 are heavily abundant nanomaterials in the environment (Meramo et al., 2018; Nwidee et al., 2017). And therefore, the use of nanoagricultural chemicals must be limited to an extent that promotes food security but does not become a pollutant.

With regards to the impact of nanoagricultural materials on human health, the first risk that stands is biomagnification with their entry into the food chain and man being affected most being on a higher trophic level. The second concern is about nanomaterials being occupational hazards which warrants ecotoxicological research keeping in view (i) exposure evaluation, (ii) hazardous behaviors, (iii) dose-response relationships and as discussed above (iv) environmental fate. This would help to streamline occupational risk management strategies, safety practices and policies. National Institute for Occupational Safety and Health (NIOSH), CDC has clearly laid guidelines on hazard identification to the management of nanoparticles (SERVICES et al., 2012). They are evaluating the safety of nanoparticles based on the threat to health workers, the general public and the environment. The third concern is biotransformation. NPs might transform to toxic/recalcitrant form on the field. This may further disrupt the microbial ecology of the soil (Zheng et al., 2021a). This complex interplay between environmental conditions and the use of nanoagricultural particles is to be understood Toxic effects of nanoparticles are summarized in (Fontana et al., 2021). NPs may lead to the following effects on humans cells:

(i) Damage to plasma membrane: Cationic NPs induce the formation of holes within membranes leading to Ca^{2+} ion influx (Arvizo et al., 2010; Chen et al., 2009).

(ii) Alteration or disruption of cytoskeleton: uptake of NPs can alter cytoskeleton with reduced cell proliferation and motility (Holt et al., 2010; Tarantola et al., 2009). NPs like Iron oxide interact directly with the proteins of cytoskeleton (e.g. Actin) and disrupt their function (Mu et al., 2014).

(iii) Mitochondrial toxicity: Interaction of mitochondrial membrane alters mitochondrial membrane permeability via oxidative stress and indirect whole cell toxicity.

(iv) Nuclear damage: Rarely NPs may reach nucleus and the effects can be disruptive if they have affinity for chromatin leading to interference in cell division (Zakhidov et al., 2010).

(v) Reactive oxygen species (ROS): Interaction with NPs results in formation of ROS with a longer contact leading to cell death by necrosis (George et al., 2010; Pan et al., 2009).

(vi) Interferring with signalling pathways: NPs are known to interfere with signalling pathways such as MAP kinase, NF-κB, TGF-β leading to toxic effects (Mu et al., 2014).

4. Synthesis and formulations of agricultural nanomaterials

Nanomaterials are materials with any dimensions in the range of 1–100 nm. There are two main approaches used for the synthesis of nanomaterials. One of the main approaches involves top-down approaches, and another is a bottom-up approach. Recently, many studies were done which involve the biological synthesis approach for the production of nanomaterials. Further, these are formulated to carry the key or active ingredient to the site-specific area for controlled release of it. Three ways of synthesis of nanomaterials are depicted in Fig. 4.

4.1. Top-down and bottom-up approach

In general, nanoparticles are synthesized by physical methods and chemical methods. Physical methods involve excessive energy, making it non-economical (Wageh et al., 2015). Similarly, chemical methods involve the use of chemicals which indirectly or directly cause damage to the environment (Iravani et al., 2014). Chemical methods are categorized as follows: top-down and bottom-up approaches. The top-down approach involves breaking the intermolecular bond mainly the Van der Waals forces found between the stacked bulk components, which later forms thin layer crystals (Saravanan et al., 2021). This approach involves extensive energy use and includes the following techniques: mechanical milling, laser ablation, etching, sputtering, and electro-expulsion (Baig et al., 2021). In this method, though the process is relatively easier, attaining small-sized particles is a toilsome work.

Additionally, the problem associated with this approach is a change in the surface chemistry and the physiochemical properties, which is undesirable. The bottom-up approach involves the accumulation of atoms and molecules into nanoparticles. The smaller particles assemble like nanoscale blocks that congregate to produce nanomaterials. This approach includes chemical vapor deposition, solvothermal methods, hydrothermal methods, sol-gel methods, soft and hard templating methods, reverse micelle methods, and laser and sprays pyrolysis (Baig et al.). The use of chemicals, high temperature, and pressure of chemicals results in harm to the environment which is inadmissible (Iravani et al., 2014).

4.2. Biological synthesis

Biological synthesis is considered as the best alternative for the synthesis of nanomaterials. The method is cost-effective, eco-friendly, does not involve harmful chemicals. The method involves the use of microorganisms for the synthesis of nanomaterials. Commonly used microorganisms are bacteria (Saravanan et al., 2018), fungi (Anand et al., 2015), and algae (Sathishkumar et al., 2019), which involve the synthesis of the iron nanostructure, gold, and silver NPs (Saxena et al., 2012).

4.2.1. Synthesis by microorganisms

Silver nanoparticles (AgNPs) production by the bacteria was first obtained from AG259 strain of *Pseudomonas stutzeri* (Prabhu and Poulose, 2012). Bacteria usually produce many extra and intra-cellular inorganic materials which are used in AgNPs production (Rafique et al., 2017). Primarily, silver nitrate ($AgNO_3$) and bacterial biomass under ambient pressure and temperature are used to synthesize AgNPs. The bacteria use the bio-reduction process where the reductase enzyme reduces the silver ions to silver nanoparticles concomitantly gains an electron from NADH by reductase enzyme (Javaid et al., 2018). A recent study illustrates the synthesis of AgNP from the bacterial strain *Cupriavidus,* which was isolated from soil (Ameen et al., 2020). The protein present in the cell extract of *Bacillus brevis* (NCIM 2533) acts as a capping and stabilizing agent, resulting in the Ag^+ ion reduction that further agglomerates to form AgNP (Quinteros et al., 2019). The extracellular metabolite produced by the *Streptomyces sp.* could effectively synthesize AgNP, exhibiting enhanced porosity and surface area (Al-Dhabi et al., 2018). Using the strain of *Rhodococcus spp., a* silver nanoparticle was synthesized, which was spherical in nature with a size 10–12 nm. The antimicrobial activity of the nanoparticle was tested on Gram-positive and Gram-negative bacteria which showed excellent

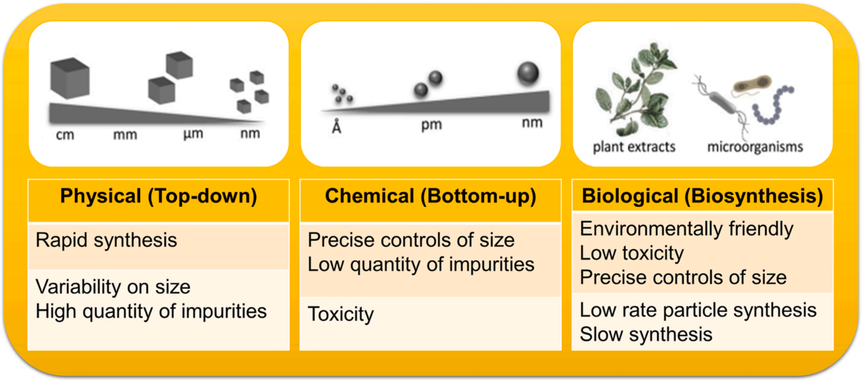

Fig. 4. Synthesis of nanomaterials: Physical method (Top-down), Chemical method (Bottom-up), and Biological method (plant extracts and microorganisms).

bactericidal activity (Otari et al., 2015). Similarly, the culture supernatant of Bacillus sp. was used to synthesize the AgNPs; the antimicrobial property was tested on Gram-negative bacteria such as *V. parahaemolyticus*, *S. enterica, E. coli,* and a better inhibition growth was achieved (Wang et al., 2016).

4.2.2. Synthesis by plants

The synthetic method for the synthesis of silver nanoparticles based on plants and its extraction procedures is simple, involving only a single step using non-pathogenic organisms, and possesses higher bioreduction potential (Ahmed et al., 2016). Plants extracts and the whole plant can synthesize the silver nanoparticle, but most of the work is focussed on plant extracts as the reducing agent is more concentrated on the extracts. Most of the syntheses are based on aqueous silver metal salt and plant extracts followed by ambient temperature and pressure conditions with timescale varying up to a couple of hours (Rajan et al., 2015). The mechanism taken into account for the synthesis of the silver nanoparticle is based on reduction, which is done phytochemically by terpenoids, flavones, organic acids, and quinones (Prabhu and Poulose, 2012). Some other reports for the synthesis of silver nanoparticles by plants are summarised in (Mittal et al., 2015, Chaudhuri et al., 2016, Bhakya et al., 2016) (Bhakya et al., 2016; Chaudhuri et al., 2016; Mittal et al., 2015).

4.3. Nanoformulations

Nanoformulations involve fertilizers, pesticides, nutrients supplement coated, encapsulated, adsorbed, entrapped into the spaces, pockets, pores of the nanomaterials (Bhardwaj et al., 2022). Studies show that overlaid or coated nanomaterials show better results in biosafety, stability, and nutrient release than non-coated nanomaterials (Cheng et al., 2011). Nanoformulation can be made in the following ways such as nanoemulsions, nanoencapsulation, and nanogels. By mixing surfactant, a biphasic system is formed that has some crucial ingredient such as organophosphate, chlorinated hydrocarbons, carbamates, which is dissolved in oil in the water phase (Solans et al., 2005). Nanoemulsion of fertilizers or pesticides prepared/dispersed in a biphasic medium which dissolves it and greatly enhances bioavailability and efficacy (Feng et al., 2018). This approach dramatically reduces the utilization of organic solvents and surfactants (Pavoni et al., 2019). Similarly, nanoencapsulation is a delivery method in which key ingredients are encapsulated into nanomaterials and released in a controlled way (Nuruzzaman et al., 2016). It protects the critical ingredients from unnecessary leaching and premature degradation, which is more effective than traditional pesticides formulation (Vurro et al., 2019).

Further, modification of nanomaterials has enabled the encapsulation and presented a sustained release behavior, or stimuli release behavior (Camara et al., 2019; Mattos et al., 2017). Polymer-based nanoencapsulation of fertilizers and pesticides has provided excellent biocompatibility and biodegradability due to their functional groups. The encapsulation occurs via incorporation, complexation interactions, covalent bonding, which improves the uptake, mobility, and dispersibility in a controlled manner, thus leading to increased bioavailability and sustained lifetime. Nanogels have gained substantial interest among researchers as nanoscopic guest carriers and are mainly used for delivering them in a target-specific and time-controlled manner (Bhardwaj et al., 2022). These are the nanoscale size, three-dimensional hydrogel material formed by a swellable polymer of a cross-linked network that can hold water without dissolving into the aqueous medium (Soni et al., 2016). Chitosan and cashew gum are used as nanogel to load *Lippia sidoides* essential oil that targets the *Aegypti larvae* (third instar) and attain mortality of 90% even at a low concentration of 48 ppm (Abreu et al., 2012). Similarly, poly-phenylenevinylene bis-aldoxime is used as nanogel to carry methyl eugenol pheromone that targets *Bacterocera dorsal* that could carry out a sustained release of the active ingredient for a period of 30 days (Bhagat et al., 2013). Various nanoformulations that are applied in agriculture are discussed in Table 5.

5. Effects of nano-/biofertilizers on plant growth and productivity

In India, most farmers are not aware of the utilization of biofertilizers. Due to the slow response of the biofertilizers as compared to the chemical fertilizers, farmers kept away from its application. As the biofertilizers consist of microorganisms, they get spoiled, or their efficiency is reduced when they reach the farmer in villages (Barman et al., 2017). For optimal NUE, they also need amenable growth and storage conditions such as optimum temperature, pH, etc. Since biofertilizers play a key role in sustainable agriculture, they can be used along with chemical fertilizers to increase the fertility of soil and crop production. Generally, biofertilizers are applied on seeds, seedlings, or straightaway to the soil (Fig. 5). To improve their efficiency, they are used along with carrier materials that help the consumers deal with them simply and increase their long-time storage. The applications of biofertilizers depend on the characteristics of inoculants, type of crops, and environmental conditions. The main applications of biofertilizers are described as follows (Debnath et al., 2019; Mącik et al., 2020; Wahane et al., 2020).

5.1. Seed germination and treatment

The most familiar and simple techniques of applying biofertilizers on seed are dusting, slurry, and seed coating (Mącik et al., 2020). The most commonly used is the slurry technique, wherein the inoculant is blended with water and later with seeds. *Rhizobium*, *Azotobacter*, *Azospirillum*, phosphorus solubilizers, etc., are mainly used in seed treatment. Around 200 g of inoculant is adequate to treat 10 kg of seeds (Wahane et al., 2020). Different metal/metal oxide nanoparticles have shown positive effects on different crops starting from seed germination to fruit ripening (Da Costa and Sharma, 2016; Shaw et al., 2014; Song et al., 2016; Vinković et al., 2017). Depending on their size and concentration of metal/metal oxide NPs, uptake and translocation occur in the plant body leading to positive or negative effects (if undesired NPs accumulate). The positive response was found in maize plants, canola, tomato, and capsicum after treating with a lower dose of engineered metal/metal oxide nanoparticles such as TiO_2, Fe, SiO_2 (Lau et al., 2020; Mittal et al., 2020). Other metal/metal oxide nanoparticles (Cu/Zn) are also reported to positively affect seed germination (Raja et al., 2019). The PVP-coated platinum NPs also display growth-promoting properties and help in seed germination (Rahman et al., 2020). Multiwalled carbon nanotubes show some promise in seed germination on various crops such as wheat, maize, corn, barley, tomato, etc. (Joshi et al., 2018).

5.2. Seedling root tip

This technique is mainly used for transplanted crops. Here, the roots of seedlings are soaked into the mixture of biofertilizer and water for about 5–10 min (Debnath et al., 2019). In many studies (Feizi et al., 2012; Zheng et al., 2005), nanofertilizers can increase nitrate reductase, catalase, and peroxidase enzymes amounts that are indirectly involved in natural fertilizer intake from soil and enhance the chlorophyll content for the seedling development. Application of engineered TiO_2 NPs in the soil promotes seed germination and seedling growth in spinach. Further, (Navarro et al., 2008) informed that engineered NPs with a high surface area used as biofertilizers act as a reservoir of nutrients in the root of plants.

5.3. Soil and set treatment

In soil treatment, two different approaches are taken for soil

Table 5
Application of nanoformulation in agriculture.

Sl. no.	Nanoformulation	Nano-carrier	Size (nm)	Plants	Medium	Effect	Ref.
1.	Zn/B nanofertilizer	Cs-TPP	700	Coffee (*Coffea arabica)*	Foliar application	Growth effect on seedlings. Increase chlorophyll content—promoted leaf area growth, plant height, and stem diameter.	(Wang et al., 2018)
2.	Selenium nanofertilizer	PEI-CPs	100	Barley (*Hordeum vulgare*), Leek (*Allium porrum*), Wheat (Triticum durum)	Soil amendment	Excellent anion-responsive release behavior. Enhances yield by simulation of anion and site-specific delivery.	(Zhang et al., 2018a)
3.	Zinc Cs nanoparticles	Cs-TPP	200–300	Maize (*Zea mays*)	Foliar application	Enhance seedling growth promotor activities, and strengthen innate immunity by elevating defensive enzymes.	(Choudhary et al., 2019)
4.	NPK-nanofertilizer	Cs-TPP	500	Coffee (*Coffea arabica*)	Foliar application	NFs enhance nutrient uptake and photosynthesis. Similarly, improvement in leaf number, leaf area, and plant height	(Ha et al., 2019)
5.	Nano-NPK	Cs-PMAA	9	Cucumber (*Cucumis sativus*)	Soil amendment	Improves crop yield of cucumber and plant growth.	(Merghany et al., 2019)
6.	Nano Zn fertilizer	Cs-TPP-Zein coating	709	Cotton (*Gossypium hirsutum*)	Foliar application	Significant improvement in plant height and root length.	(Kanjana, 2019)
7.	Cs-K fertilizers	Cs-MAA	39–79	Maize (*Zea mays*)	Soil amendment	Soil conditioning enhances porosity, friability, water conductivity, and favored root growth.	(Kubavat et al., 2020)
8.	Sulfate-supplemented NPK nanoformulated with Cs Nanofertilizer	Cs-TPP	145 & 450	Maize (*Zea mays*)	Soil amendment	A higher magnitude of nutrient uptake and higher plant growth followed by superior chlorophyll content is observed	(Dhlamini et al., 2020)
9.	Chitosan (Cu and SA) nano fertilizer	Cs-TPP	539	Maize (*Zea mays*)	Seed treatment followed by Foliar	Upregulated source activity, increased activity of antioxidant enzymes and chlorophyll content, induced sucrose translocation	(Sharma et al., 2020)
10.	Urea-doped calcium phosphate Nanoparticles	Ca-P	13.8	Durum wheat (*Triticum durum*)	Foliar and root application	Controlled release multinutrient nanosystem	(Ramírez-Rodríguez et al., 2020)

Abbreviations: PEI: Polyethylenimine; CPs: Cabon nanoparticle; Cs: Chitosan; TPP: Tri-polyphosphate; NFs: Nanofertilizers; PMAA: Polymethacrylic acid; Cs-K: Chitosan-Potassium; MAA: Methylacrylic acid; Ca-P: Calcium phosphate.

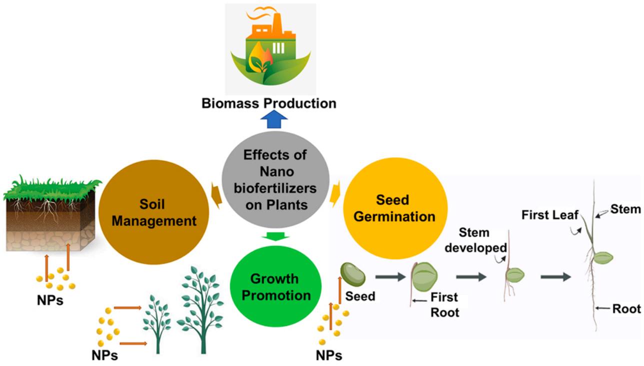

Fig. 5. Effects of nanobiofertilizers on plant growth and productivity.

treatment: either the biofertilizers are mixed uniformly directly with compost and stored overnight, and later, these composites are spread in the field during the time of plantation (Debnath et al., 2019). Another way is to apply indirectly through a foliar application on the plants. It is observed that nanofertilizers might help the nutrients to move in the soil, which further facilitates the uptake of nutrients by roots. (Teng et al., 2018) perform research on the effect of slow-release nanofertilizer in the pot for green pepper production. It was noticed that slow-release helped in nutrient (alkaline nitrogen) enhancement in the soil and also increased enzymatic activity. Due to the increment of soil nutrient and enzyme activity, the microbial diversity also increased considerably. The paper also reported that dehydrogenase and catalase activity increased by more than 30% compared to control (without nanofertilizer). (Sahar et al., 2020) used nanofertilizer and compost with/without normal NPK fertilizers by foliar technique on the soil to check the soil quality enhancement, and it was observed that Fe plays a significant role in seed weight than others. Set treatment is mainly used to treat the cut pieces of potato, the base of banana suckers, and sugarcane sets. In this technique, the culture suspension is prepared by blending 1 kg of biofertilizer with 40–50 liters of water (Wahane et al., 2020). (Marzouk et al., 2019) applied three types of nano micronutrient fertilizers (Fe, Mn, Zn) on sandy soil by the foliar mechanism to check the quality of the soil.

5.4. *Biomass and productivity*

Various types of NPs have shown a good impact on biomass and productivity increase, such as ZnNPs increased productivity in rice, tomato, wheat, chickpea, maize, and tomato seedlings (Verma et al., 2022). It was reported (Yuan et al., 2018) that FeNPs at lower doses show promising effects on capsicum photosynthesis. (Boykov et al., 2019) studied the effects of TiO_2 NPs on a molecular level that trigger the growth-promoting pathway in switchgrass. Foliar treatment provided on plants showed growth enhancement and also reported a high production yield. Improved crop yield in peanuts was noticed after the application of FeNPs, MnNPs, and ZnNPs (El-Metwally et al., 2018), whereas the nano-chelated molybdenum (Mo) also boosted geomorphological qualities and productivity in *Arachis hypogaea* (Mehrangiz et al., 2014). Farnia et al. (2015) reported the enhancement of maize yield production after applying nano-Zinc chelate and nanobiofertilizer by foliar application in the ground clay soil. Ibraheem et al. (2021) studied the four types of nanofertilizers and their application in the vegetable field to check the production enhancement of two varieties of broccoli. Nano fertilizers (K, Zn, Fe) showed promising results among the four types.

6. Biosafety and regulatory aspects of nanoparticle application for agricultural sustainability

In the agriculture sector nanotechnology is contributing to various parts like pest management, growth promotion, soil improvement, etc (Kah et al., 2013; Kah and Hofmann, 2014). It is therefore important to find any adverse effects of these nanoparticles in all living bodies that are associated with soil, water and plant food products. The main problem concerns the risk assessment of the permissible dose of agri-nanoproduct that are not practised by end-users. Lots of obstacles are encountered by nanotechnological products or nano-enabled products at the commercial level such as social acceptability, ethical concerns, economic viability and biosafety. As biosafety is concerned with the health of all human bodies so more cautiousness must be taken in the production process of the nano-enabled products otherwise serious environmental and health risks will be there (R.K, 2020). Till date, there is no standard protocol to evaluate the risk of agri-nanoproducts.

For any nano-enabled product commercialization, the applicant must confirm the safe usage of the product on consumers and the environment. Many nano-enabled products which are under lab-scale research and yet to come into the market must apply for market approval first. To regulate the production and safe-handling of the nano-enabled products, globally two approaches are taken care legislation and recommendation-guidance (Bernd Meulen et al., 2014). Several countries all over the world have been trying to find the relevant regulatory frameworks to deal nano-enabled products (Amenta et al., 2015). To ensure the possible risk and safe use of nano-enabled products various organizations are also established such as EU Scientific Committees and Agencies, the Organisation for Economic Cooperation and Development (OECD), the International Standard Organization (ISO), US Food and Drug Administration (FDA) which are accepting the application of applicants and verify the documents with a test. With reference to NAAS (National Academy of Agricultural Sciences), seven countries (China, Germany, France, Japan, Switzerland, South Korea and USA) all over the world are mainly involved with nanotechnology and its products. Some countries are taking regulatory steps in the process and some are checking the product value for consumers. The USA published several guidance documents for nanomaterial manufacturing industries which state about “a-case-by-case-approach”. Whereas European Union (EU) are following a legislative framework for the nano-enabled products that are going to be applied in the agriculture sector (zero-draft-policy.pdf (teriin.org).

7. Global scenario of biofertilizers

Due to the overuse of chemical fertilizers (urea, ammonium sulphate/phosphate etc.), the soil quality is deteriorating, and essential soil bacteria and fungi that help create carbon-based nutrients for plants are also killed. The mission of high yield crop production now shows many side effects through the rotation of fertile soils to infertile ones. Therefore, using bacteria, fungus, and algae-based biofertilizers is becoming a robust option. It is reported that the global market of biofertilizers will reach US$3.3 billion by 2025 (Global Biofertilizers Industry (globenewswire.com)). On one side, different types of nitrogen-fixing bacteria decrease the dependencies on chemical-based fertilizer, and on another side, they are eco-friendly and natural soil fertilizers (Fig. 6). Many countries’ governments have been funding sustainable agriculture due to the harmful effects of chemical fertilizers and pesticides on the environment. The US Department of Agriculture (USDA) has implemented the National Organic Program (NOP) to develop the quality of organically grown agricultural products and their growth in the future (Saritha and Prasad Tollamadugu, 2019). Taiwan’s national and central government agencies uplift biofertilizers’ widespread use, especially in soybean cultivation. Although countries with advanced R&D technologies such as Japan, Taiwan, and South Korea are moving towards producing biofertilizers and nanobiofertilizers, the unaware farmers need to be educated on the comparative use of chemical fertilizers and biofertilizers.

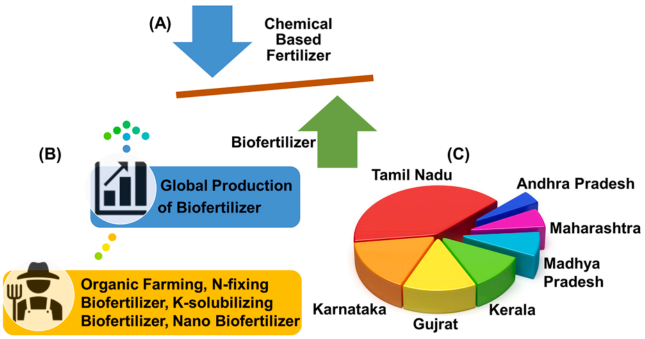

Fig. 6. Scenario of biofertilizers in global market: (A) rise of biofertilizer and downfall of chemical-based fertilizer in the market, (B) various forms of alternative farming and fertilizer supply in fields, the increasing rate in biofertilizer production, (C) different states of India involved in biofertilizer production.

The production of biofertilizers is always in demand, and thus to increase its demand to farmers, the governments are taking the initiative by making policies for the promotion of biofertilizers. The Indian government has been enacting the scheme to promote biofertilizers since the 7th Five Year Plan. One national and six regional centers in different states have been established (Fig. 6) under this scheme that promotes the application of biofertilizers through training, demonstration, and seminars (Majumdar, 2015). National Project on Development and Use of Biofertilizers (NPDB) is a central sector scheme implemented by the Government of India (GOI) during the ninth-year plan for the production, distribution, and promotion of biofertilizers (Ghosh, n.d.). The Indian Government has introduced many policies and plans to increase the market of biofertilizers for sustainable agriculture, which includes schemes like the National Mission of Sustainable Development (NMSA)/Paramparagat Krishi Vikas Yojana, Rashtriya Krishi Vikas Yojana (RKVY), National Mission on Oilseeds, and Oil Palm (NMOOP), and Indian Council of Agricultural Sciences (ICAR) (Saritha and Prasad Tollamadugu, 2019).

8. Conclusion

The article discussed the state of art in the field of sustainable agriculture and the role of nanotechnology in its sustainability. It provides the groundwork for formulating further studies concerning the effects of nanofertilizers/nanopesticide on humans if they reach through the food chain. Agricultural economies take the onus of providing food security to the world, but they are posed with challenges in this era of technological advancement, especially when technology is at its nascent state of evaluation. On the one hand, the application of nanotechnology can resolve the issue of food security; on the other hand, it raises some serious concerns which need to be addressed. For example, there is a lack of clinical data on the long-term effects of the use of nano-based agrichemicals on human health, microbial diversity of soils, and the whole ecosystem. This review also deliberated that although promising in agriculture, nanotechnology requires more evaluation on improving soil microbial diversity. The cost of production of nano-based agricultural solutions must be brought down. Moreover, the preparation and application should not harm the environment by causing air, soil, and water pollution. Furthermore, controlled use of nanotechnology can be recommended to provide increased food security.

9. Future perspectives

Nanoagricultural materials will certainly improve crop yield and food security in the coming decades. However, the environment might be posed with a newer pollutant; a xenobiotic which might disrupt the microbial ecology of soil and water. Nanobiofertilizers seem to be particularly promising in this regard. Iron is essential for plant growth and presents abundantly in soil. However, plants show iron deficiency very often. External application often goes in vain due to soil carbonate/bi-carbonate ion assisted conversion into unavailable oxy-hydroxyl forms. A chitosan-coated iron powder-loaded mesoporous silica formulation has been shown to improve iron availability to plants. The formulation was tested on tomato plants which revealed reduced iron deficiency (Bindra et al., 2019). Post nanotoxicological studies in-field such formulations might be used in real-time by farmers. Further carbon allotropes such as Graphene oxide, Fullerene, mesoporous carbon (MC), and nanodots have been employed in agriculture showing great promise toward food security (Goh et al., 2016; Mota et al., 2013). Carbon nanomaterials have a high surface area and hydrophobicity making strong interactions with leaves and drugs (Wang et al., 2019). However, much of the work based on guidelines laid by the government on the safety and toxicity of these formulations is warranted. Further, attention needs to be paid to microbial number and diversity changes in the soil upon application of NPs and also of earthworms and other beneficial life forms. Evaluation as per agencies such as Environment Protection Agency (EPA) must be done before any nanoagricultural formulation reaches fields to prevent long-term consequences.

CRediT authorship contribution statement

Smriti Arora: Conceptualization, Writing – original draft, Writing – review & editing. **Gajiram Murmu:** Writing – original draft, Writing – review & editing. **Koel Mukherjee:** Conceptualization, Writing – original draft, Writing – review & editing. **Sumit Saha:** Conceptualization, Writing – review & editing, Supervision. **Dipak Maity:** Conceptualization, Visualization, Writing – review & editing, Supervision.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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