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

**Dibakar Ghosh, Mahima Misti Sarkar, and Swarnendu Roy**

## 1 Introduction

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

D. Ghosh · M. M. Sarkar · S. Roy (✉)
Plant Biochemistry Laboratory, Department of Botany, University of North Bengal, Raja Rammohunpur, Siliguri, West Bengal, India
e-mail: swarnendubotany@nbu.ac.in



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

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

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

## 2 Nanofertilizer Application—Present Status

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

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

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

## 2.1 Macronutrient Nanofertilizers

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

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

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

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

## 2.2 *Micronutrient Nanofertilizers*

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

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

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

### *2.3 Nano-Biofertilizers*

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

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

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

(continued)

**Table 13.1** (continued)

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

(continued)

**Table 13.1** (continued)

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

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

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

## 4 Slow-Release Nanofertilizers

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

### *4.1 Synthesis of Slow-Release Fertilizers*

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

#### 4.1.1 Nanoprecipitation

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

#### 4.1.2 Emulsion Evaporation

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

#### 4.1.3 Ionotropic Gelation

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

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

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

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

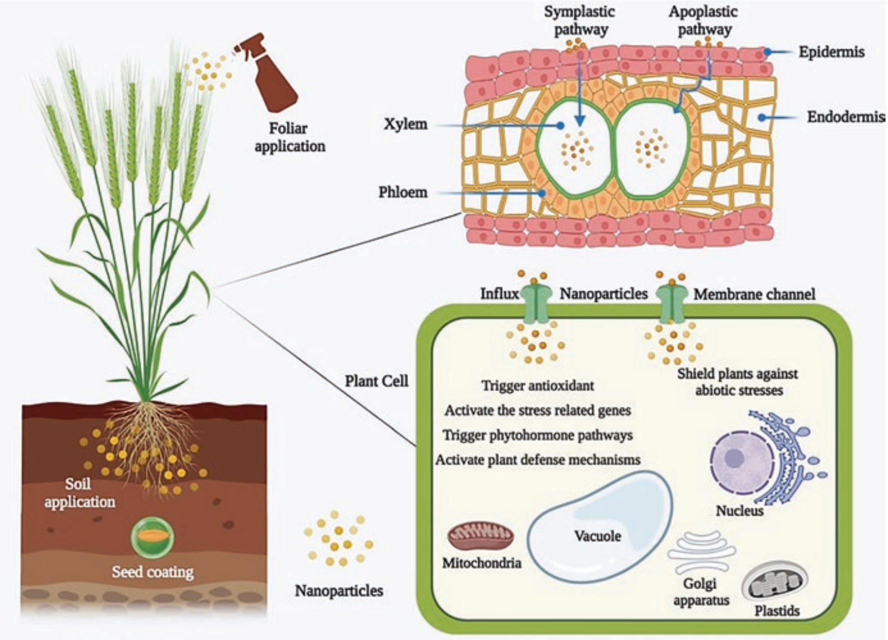


**Fig. 13.1** Schematic portrayal of nanofertilizers application, uptake, and translocation of nutrients in plants. NPs delivered to plants by soil application, seed coating, and foliar spray to improve overall plant growth and development (Source: Manzoor et al., 2022)

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

## 5 Recent Status of Different Slow-Release Nanofertilizers

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

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

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

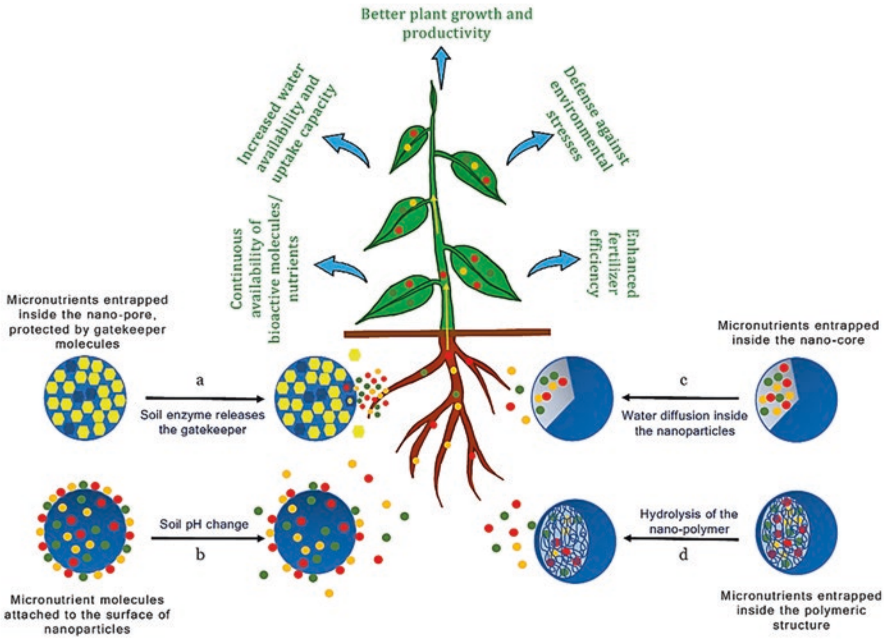


**Fig. 13.2** Mechanism of controlled release of micronutrients by slow-release fertilizer. (**a**) Micronutrients entrapped inside the nanoparticle's pore and secured by some gatekeeper materials (biomacromolecules and biopolymers); (**b**) micronutrients get attached to the surface of the nanoparticles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

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

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

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

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

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

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

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

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

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

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

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

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

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

## 7 Future Perspectives

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

## 8 Conclusion

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

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