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Recent Advances in Plant Fertilizers Technology

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ABSTRACT

Fertilizer is a crucial subject as it affects plant growth besides the surrounding soil environment and the environment at large. Deep water percolation usually drains excess soluble fertilizers to the underground water reservoirs. Finding the most proper fertilizer that can gradually and efficiently feed plants' requirement from nutrients and keep good interaction with soil, microorganisms and the surrounding environment can be promising. Conventional fertilizers have been in use for decades. The development of nanoparticulate fertilizers is becoming a trend in the industry. Plants and soil interact positively or negatively with nanoparticles depending on nanoparticle type, concentration, and level. Nano-size particles are premium fertilizers when taken in precise levels, sizes, and types, and given to the most proper plants; they can provide great advantages to the plants and surrounding environment. Microsize particle fertilizer can be promising, but the topic needs further studies.

Keywords: Fertilizers, Nanoparticle, Concentration, Types, Microparticles, Soil factor, Environment.

INTRODUCTION

Plants as sessile organisms feed on dissolved nutrients. Most references agreed on sixteen essential nutrient elements divided into three groups of universal available (C, H, O), six macronutrients (N, P, K, Ca, Mg, and S), and seven micronutrients (Fe, Mn, Zn, Cu, B, Cl, Mo). Either excess or deficiency in one or more of these elements will cause malnutrition of plants and symptoms will appear. Plants absorb nutrients only when found in the available form of absorption in the root zones. For example, nitrogen is available for plants in either NO_{3-} or NH_{4+} ions. Moreover, excess levels of NO_3^- lead to the transport of anions from plants' cells while a high level of NH4+ leads to reduced uptake of Ca, Mg, and K (Havlin *et al.*, 2017).

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The history of plant fertilizers started in an early stage of human farming by adding manure, compost, ashes, etc (UNIDO and IFDC, 1998). The experimental research on plant fertilizers was conducted by Van Helmont in the period from 1577 into 1677 while Von Liebige was the first who created the first step in the fertilizer industry in the period from 1803 to 1873. The global fertilizer production reached 258.7 million tonnes as of the year 2020 (Fertilizer Europe 2022).

Fertilizers are the backbone of plant growth and development. Both excess and deficiency can be major problems. Leaching and volatilization are some of the great problems found in traditional methods of soil fertilization, especially because of the increasing demand for application (FAO, 2002). Nitrogen fertilizer had a pollutant effect on water and air, the farmers cannot substitute for nutrient loss. According to Tan et al. (2005), the estimated losses of N, P, and K reached 18.7, 5.1, and 38.8 Kg/ha/year, respectively. Table 1 shows a summary for the amount of NPK application and loss in different crop plants. Adding fertilizers within coating materials helps reduce the speed of nutrient release (Volova *et al.*, 2020) and creates a very balanced system between plants and soil, and the surrounding environment. The slow release of nanoparticles increases the level and opportunity to uptake nutrients in plants (Tarafder et al., 2020). According to Lewu *et al.* (2021), the materials that can be used in the coating of slow-released fertilizers are nonorganic as sulfur coating urea, organic polymers, hydrophobic resin, thermoplastic, and combined materials between thermoplastic and gel coating substances. The organic polymer can be synthesized either from natural polymers such as starch, cellulose, lignin, and humic acid or semi-natural ones such as methylcellulose, sulfonated lignin, polyacrylamide, and polyethylene (Fu et al., 2018). However, the release speed could vary among coated fertilizers in both organic and inorganic ones (Sales et al., 2024). Different fertilizer forms can be coated and held within a fertilizer structure, including macronutrients such as NPK, Ca, Mg, and micronutrients such as B, Cu, Fe, Mo, and Zn. Control-release fertilizers and slow-release ones; this terminology first appeared in 1920 (Fu *et al.*, 2018). Fu et al. (2018) also explained the three distinct historical periods where the slow-releasing fertilizers were developed, passed through theoretically thoughtful scholarly research, and then classified and spread. Coating fertilizers can be divided according to their size into nano, micro, or macro-size particle fertilizers.

This review will comprehensively focus on nano- and micro-size particle fertilizers in reaction with growing media and plants to find the best aspects that could provide the optimum plant condition. Nanofertilizers are debatable subjects Some articles argue the positive influence on the surrounding environment and plants; others argue the opposite. This article will exhibit the two opposite arguments and will provide an approach to finding the problems and give recommendations. Although micro-size particle fertilizer is not a new discipline but a few articles have been found to cover it, but it could have a better influence on plant growth than nano for reasons that will be discussed in this review.

Table 1: Amount of Nitrogen, phosphorus, and potassium application rate and the amount of losses in each crop plant (compiled by the authors)

Fertilizer	Amount of application	Amount of losses	Plant	References
Nitrogen	56- 135 Kg/ha	35-52%	Corn + Soybean	Jaynes et al .(2001)
Nitrogen	0-300 Kg/ha	65-76%	Wheat	Wang et al. (2010)
Nitrogen	180-225 Kg/ha	70-94%	Wheat+ rice	Wang et al. (2019)
Potassium	113-225 Kg/ha	9-20%	Maize	Qiu et al.(2014)
Potassium	120-133 Kg/ha	66-74%	Rye, Potato, Maize, Sugar beet	Wulf et al (1998)
Phosphorus	20-35 Kg/ha	51-85%	Wheat+ rice	Wang et al. (2019)

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Fertilizer Formulation

The available formulations of traditional fertilizers can be crystalline as in urea ($CO(NH_2)_2$) and nitrophosphate (NO_6P^{-2}), powder as in mono ammonium phosphate ($NH_4H_2PO_4$) and potassium nitrate (KNO_3), and granules as in ammonium polyphosphate ($(NH_4PO_3)_n(OH)_2$) and single superphosphate $Ca(H_2PO_4)_2$ (Hakeem *et al.*, 2021). According to Gowariker *et al.* (2009), granule fertilizer is a fertilizer in a size range from 1 to 5mm and has greater advantages over other formulation types through having low dust, less storage space, controlled release of fertilizer, and lower leaching capacity. On the other hand, the formulation of controlled-release fertilizer depends on the coating materials, where some coating materials are water soluble with a physical barrier and others are inorganic with low soluble compounds (Lewu *et al.*, 2021). Moreover, the water-soluble with a physical barrier can be organic or inorganic in its origin, and can be a hydrophobic or hydrophilic matrix or gel.

A. Conventional Fertilizer

Conventional fertilizer is a single or compound synthetic fertilizer consisting mainly of N, P, K, and trace elements (Colipano and Cagasan 2022). According to Kumar Bhatt *et al.* (2019) conventional fertilizers have a positive influence on plant yield and soil fertility, but at the same time could lead to soil degradation by enhancing decomposition and overdosage, leading to soil salinization. According to Statista (2022), the world consumption of N, P, and K in 2021 reached 109.17, 47.81, and 38.4 million tonnes, respectively. Mixing organic and inorganic fertilizers led to enhanced soil properties and plant yield (Kaur and Singh, 2014; Sharma *et al.*, 2014; Brar *et al.*, 2015; Sharma *et al.*, 2018; Fu *et al.*, 2022) .

Nitrogen, phosphorus, and potassium levels in the dry weight of plants ranged from 1.50 to 6.00%, 0.15% to 1.00%, and 1.00% to 5.00%, respectively, where it is species-dependent (Nielsson, 1987). Knowing the proper quantity of nitrogen-adding levels in the fields depends on two key factors, including the amount of absorption and use in the plants in grain formation (Fageria and Baligar, 2005). Maize nitrogen fertilizer recovery, which reflects the amount of nitrogen application in the grain over the recommended rate, depends on the year of application and the climate conditions (Liangl and MacKenzie, 1994). Moreover, in coarse-textured soil, split nitrogen application and applying it close to the plant led to enhanced maize grain yield (Davies *et al.* 2020). In wheat, applying compound fertilizers including nitrogen and sulfur in its components led to increased plant agronomic and physiological efficiency (Tabak *et al.*, 2020). Agronomic efficiency measures the differences in grain yield between fertile and unfertile plants over the amount of nutrients applied, while physiological efficiency measures it with yield (Fageria and Baligar 2005) .

Phosphorus level and depth of application are the most affected points that influence plant yield. Adding phosphorus at 15cm soil depth led to an increase in the root length and plant photosynthetic performance of maize (Chen et al. 2024) and plant yield in cotton (He et al. 2024). In addition, the proper level of application of phosphorus led to an increase in the yield of wheat and maize by up to 90% and phosphorus use efficiency by up to 94% (Xu et al. 2023) .

Potassium had a significant influence on plant yield and net quality. Increased levels of potassium application led to increased tea yield and quality (Xi et al. 2023). According to Liu et al. 2021 adding a great quantity of potassium under deficit irrigation conditions leads to an increase in the quality and yield of tomato plants (Liu et al. 2021). On the other hand, adding a low quantity of potassium in durum wheat increased plant quantitative and qualitative related traits (Messaoudi *et al.* 2023).

B. Nanoparticle Fertilizers

Nanoparticles are particles or structures ranging from 1 to 100nm in size (Fond and Meyer, 2006; Auffan *et al.*, 2009). Nanoparticles have a wide range of uses in a great number of sectors including medicine (Feron, and Préat, 2010; Danhier *et. al.*, 2010; Bhandari *et al.*, 2018; Vega-

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Vásquez *et.al.,* 2020; Abdel-Moneim *et al.*, 2022; Yusuf *et al.*, 2023), genetic (Nair and Chung, 2014), food science (He and Hwang, 2016; Hu *et al.*, 2020; Chawla *et al.,* 2021), bioremediation (Bala *et al.*, 2022) and agricultural sectors. In agriculture nano particles are used in pest management formulations (Gamal, 2018; Kaur *et al.,* 2018; He *et al.,* 2023), plant growth hormone (Santo Pereira *et al.,* 2017), and soil fertility (nanofertilizer). Nanofertilizer is a fertilizer encapsulated within a structure (Al-Juthery *et al.,* 2019). The important role of nanofertilizers is that they can protect nutrients from leaching and volatilization (Dhlamin *et al.,* 2022). According to Giroto *et al*. (2017), nanofertilizers are gradually released fertilizers that help to protect them from volatilization and adsorption.

The nanofertilizers' performance and interaction are affected by knowing the methods of synthesis and the external factors that could lead to changes in their properties. Nanofertilizers can be synthesized using biological, chemical, and physical methods (Kolahalam *et al.,* 2019). In the biological methods, bacteria, fungi, and algae can be used, and the resulting products are less toxic to the surrounding environment (El-Saadony *et al.,* 2020). According to Dikshit *et al.* (2021), there are three main biological synthesis methods. These methods include extracellular, intracellular, and phytochemical where the size of nanoparticles that resulted from this method was equal to or above 40 nm and it is a very good particle size for preventing direct penetration or genetic variability (Kalishwaralal *et al.*, 2008; Kalimuthu *et al.*, 2008; Pugazhendhi *et al.*, 2018). The physical methods fall into two main categories: top-down or bottom-up (Kolahalam et al., 2019). According to Nisar et al. (2019), the top-down method yields a wide range of nanoparticle sizes that range from 10 to 100nm, while another physical method as the expansion cooling method, can produce a consistent 100nm level. The chemical method can be formed by col -col-precipitation, sol-gel, hydrothermal, sonochemical, and microwave-assisted methods (Kolahalam et al., 2019). One of the problems of using the chemical method is the high processing temperature as in the chemical vapor deposition method, and a wide range of resulting nanoparticle sizes, as in electrodeposition and chemical precipitation methods (Nisar et al., 2019).

B1. Factors Influencing Nanoparticles' Negative Consequences

From previous studies, the toxicity of nanoparticles in the surrounding environment depends on internal factors, including their type, size, shape, and methods of synthesis and application; and external factors, including soil type, and the surrounding organism types and species. According to Aslani et al. (2014), the intrinsic physical and chemical properties of nanoparticles play a vital role in the prospect toxicity in plants. From the nanofertilizer definition, the size comes in a wide range from 1 to 100nm. As the size of nanoparticles decreases the toxicity increases (Nel et al., 2006; Dimkpa *et al.,* 2013a). The negative influence of nanofertilizer size comes from its ability to penetrate inside the plant and cause changes in gene expression (Yan et al., 2013), and oxidative stress on leaf cells (Rãcuciu and Creangã, 2007). According to Choi and Hu (2008), Silver (Ag) nanoparticles present in a size range from 9-21nm play an important role in increasing the level of Reactive Oxygen Species (ROS). Moreover, Yin *et al.* (2011) found that the smaller size (6nm) Ag nanoparticles had a greater toxic effect than the 25nm particle size on the *Lolium multiflorum* plant using the same concentration. While Ag nanoparticles in 25nm size can bind to the inhibitory ligand for photosynthesis and create adverse negative effects on growth (Navarro *et al.* 2008). According to Zhu *et al*. (2008), Fe_3O_4 in 20nm nanoparticles can translocate inside pumpkin tissues. Yusefi-Tanha *et al*. (2020) used levels above the previous ones on soybean, and they documented the same behavior trend when three level sizes of CuO nanoparticles were used at 25, 50, and 250nm; the greatest negative influence of nanoparticles on the seed yield was negatively adversely affected by 25nm (the smallest ones). According to Su *et al*. (2019), leaf cuticles in plants have the lowest penetration capability, which can penetrate at a level of less than 5nm, while the root can allow particles that are less than 50nm to pass through. Moreover, the plant's stomata and xylem possess the largest pore sizes which are measured at the micro level, giving it a large opportunity to permeate all particle levels included in nano levels. According to Schwab *et al.* (2015), the cell wall, which is the most important barrier in plants against nanoparticles, cannot pass through when the level of nanoparticles exceeds, 5-20nm. Wang *et al.* (2012) gave clear evidence for the penetration of huge-size nanoparticles through the cell wall but that may be because it is in a carbon form. According to El-Saadony *et al.* (2021a), nanoparticles can penetrate the epidermis of plants. A comparison study in *Vicia faba* studied the penetration level throughout plant stomata; between two levels, sizes 43nm and 1.1µm; the penetrations happened only in the case of 43nm (Eichert *et al.*, 2008). On the other hand, the level of toxicity of nanoparticles is species-dependent (Song *et al.*, 2015). According to Schwab *et al.* (2015), plants that can tolerate adverse stress conditions show a lower ability in nanoparticle translocation than others. On the other hand, some plants as wheat could secrete organic acid that leads to the transfer of nanofertizers into ionic form before translocation in the plants (Dimkpa et al., 2013a).

The nanoparticle type is one of the important factors that must be taken into consideration; in a comparison study for CuO and ZnO, the toxicity of CuO nanoparticles on wheat was much greater than ZnO (Dimkpa *et al.*, 2013a). According to Mathur *et al.* (2022), plant shoots and roots showed better growth when the nanoform of ZnO or Fe_2O_3 was used rather than the nanoform of TiO_2 and Ag. Moreover, among the three nanoparticle types, Al_2O_3, ZnO, and Ag in soybean; the ZnO and Ag had the most toxicity effect (Hossain *et al.*, 2016). On the other hand, the sizes of Al_2O_3, ZnO, and Ag that were used in the Hossain *et al.* (2016) study are not equal in size (30-60, <50, and 15nm for Al_2O_3, ZnO, and Ag, respectively). Thus, the particle size may have a greater influence in an equal manner to particle types in this case.

The concentration of nanoparticles is a second factor. It must be taken at a precise level, which at a high level could be toxic, while the optimum level leads to optimum growth (Yang *et al.*, 2006). According to Yusefi-Tanha *et al.* (2020), both concentration and particle size cause toxic effects on soybeans. Hussain *et al*. (2006) also agreed with Yusefi-Tanha et al. (2020) in their results, where the toxicity of nanoparticles could be caused by type and concentration. In contrast with Unrine *et al.* (2010); where the toxicity is influenced by particle size rather than concentration.

Both nanoparticles' form and size have influenced action toward arabidopsis where triangular 47nm promotes root growth; the spherical 8nm reduces it (Syu *et al*., 2014). The shape of nanoparticles was mainly influenced by the synthesis's temperature (Wu *et al.*, 2006). According to Wang *et al.* (2019) temperature, pH and reaction time have a great influence on the shape and size of the resulting nanoparticles. Synthesizing nanoparticle hydroxyapatite needs 8 pH and 37ºC to form particles in 25 to 30nm size (Mostaghaci *et al.*, 2009).

Another factor that may have an influence is the nanoparticles' charges; the most negative value of hydroxyapatite nanoparticles (- -13.8 mV) had the most positive influence on plant growth (Xiong *et al.*, 2018). The time of exposure can be considered as another affected factor on toxicity, where even at low concentrations of nanoparticles, the toxicity will be increased by increasing the time of exposure (Gubbins *et al.*, 2011).

According to Suresh *et al.* (2013), knowing the factors that affect the stability of nanoparticle coating material could lead to much more stable nano molecules, helping to protect the surrounding environment and organisms. Soil factor has a great influence on nanofertilizers' availability, transformation, solubility, and toxicity. According to Lv *et al.* (2022), both the soil's physical and chemical characteristics and existing plants influence the availability of nanofertilizers. The soil texture has an influence on nanoparticle mobility; the finer the texture, the less mobility of particles, while high pH levels increase the mobility of nanoparticles (Cornelis *et al.*, 2014). Soil pH influences nanoparticle availability (Kottegoda *et al.*, 2011; Wu *et al.*, 2021), where the neutral pH increased the level of nanofertilizer much more than the acidic one. According to Gao *et al.* (2019), low soil pH levels decrease dissolution but not the solubility of nanoparticles.

Soil organic matter increases the availability (Lei et al., 2018; Xu *et al.*, 2019), mobility (Al-Sid-Cheikh *et al.*, 2019), and stability (Grillo *et al.*, 2015) of nanofertilizers. On the other hand, the influence of organic matter has a greater influence on the mobility of nanoparticles than soil pH (Ben-Moshe *et al.*, 2010). Soil components are also important, such as phosphorus, which leads to the dissolution of ZnO nanoparticles and transformation into ionic form (Lv *et al.*, 2012; Dimkpa *et al.*, 2013a). Nevertheless, the effect of phosphorus can be reduced when the soil pH is high because of the tendency of the soil in this situation to adsorb phosphorus (Ajmal *et al.*, 2018). Using or presenting some substances like citric acid causes changes in the coating of CeO_2 nanoparticles, leading to reduced toxic influence against radish seeds (Trujillo-Reyes *et al.*, 2013).

Nanoparticle has its influences on soil, where the soil microbes were mostly affected negatively when metallic or metallic oxide nanoparticles are used, while organic form particles gave a positive response (Simonin and Richaume, 2015). Using Ag nanoparticles led to weakened soil nitrification bacteria, while the FeO increased it (He *et al.*, 2016). Moreover, the concentration of nanoparticles is also important, where at high levels of CuO and Fe_3O_4, the soil bacterial community and soil macroscopic properties have been affected negatively (Ben-Moshe *et al.*, 2013). Another important factor that should be taken into account is the long run of exposure; the hazardous effects are cumulative processes where some results cannot appear immediately but need time (Diez-Ortiz *et al.*, 2015).

B2. Safety of Nanofertilizer Application

The nanopfertilizer can be considered a complex topic because of its crop specificity (Dimkpa *et al.*, 2013a), and its ability to transition from one trophic level to another in the food chain (Ghosh *et al.*, 2010; Unrine *et al.*, 2012). The safe application of nanofertilizer can be acheived by many techniques: Increasing the nanoparticles size(Nel *et al.*, 2006; Yin *et al.*, 2011; Dimkpa *et al.*, 2013a), using biologically synthesized nanoparticles ((Kalishwaralal *et al.*, 2008; Kalimuthu *et al.*, 2008; Pugazhendhi *et al.*, 2018; El-Saadony *et al.*, 2020), Using stress tolerant plants (Schwab *et al.*, 2015), Using ZnO and Fe_2O_3 nanoparticles, avoid or minimize the use of CuO, TiO_2 and Ag (Dimkpa *et al.*, 2013a; Hossain *et al.*, 2016; Mathur *et al.* 2022), finally decreasing the time of exposure (Diez-Ortiz *et al.*, 2015).

B3. Nanoparticle Fertilizer and Plants

Nanofertilizer has a vital role in improving plant growth by increasing their resistance and enhancing soil water retention. Nanofertilizers were found to enhance the fresh weight and protein content of cucumber, wheat, maize, hot pepper, and groundnut (Abu-Elsaad and Abdel Hameed, 2019; Abdesalam *et al.*, 2019; El-Naggar *et al.*, 2020; Abdel-Aziz *et al.*, 2021; Chehrehnoorani *et al.*, 2023). Furthermore, biologically synthesized Se nanoparticles increase the level of wheat tolerance against drought stress and help in the biocontrol of plant Fusarium disease (El-Saadony *et al.*, 2021c). ZnO nanoparticles have an antifungal outcome against fungal plant diseases (Dimkpa *et al.*, 2013b).

Various types of nanofertilizers were studied, including NPK(macro) and micro-nutrient nanofertilizer, and silicon nanofertilizer; NPK nanofertilizer has a significant effect on growth and yield components (Abdesalam *et al.*, 2019; Abdel-Aziz *et al.*, 2021). Different explanations were proposed for the effects of nanofertilizers. According to Yang *et al.* (2006), TiO_2 increases the spinach protein content by accelerating the rate of nitrogen absorption by plants. Moreover, biologically synthesized ZnO nanoparticles help increase the activation of mung bean enzymes that help in phosphorus absorption from soil (Raliya *et al.*, 2016). Macro and micro-nutrient nanofertilizer can be enhanced by silicon application; yield quality and quantity (Al-Juthery *et al.*, 2019). Nanofertilizer can be applied as a foliar fertilizer. Table 2 summarizes different references documenting its use as a foliar spray.

Table 2. Foliar application of nanofertilizer on different crops (compiled by the authors)

Plant	Plant stage	Treatments	Nano particle	Method of synthesis	Size	Reference
Wheat	21 days after planting	10+25+100% 500:60:400 ppm N: P: K chemical+ nano on sandy soil	nano Chitosan poly-methacrylic acid nanoparticles	Chemical method	20 nm	**Abdel-Aziz, Hassaneen, and Omer (2016)**
Wheat	21 days after planting	10%+ 25%+ 100% 500:60:400 ppm N: P: K chemical+ nano.+ clay and clay-sandy soil	nano Chitosan poly-methacrylic acid nanoparticles	Chemical method	20 nm	**Abdel-Aziz, Hasaneen, and Aya (2018)**
Wheat	Two weeks after seed germination + at the five & eight weeks after germination	nano-K (0+ 20 ppm, 40 ppm, 60 ppm+ chemical KSO_4	nano-potassium	Biological method	21–30 nm	**Sheoran et al. (2021)**
Rice + Maize	Seeds germination nanofertilzer soaked for 12 hours in rice and 3 hours in maize + before and after flowering	0, 100, 250, 500, 50, 1000 and 2000 ppm Fe_2O_3 and zinc (ZnO) nanoparticle	Bio-synthesis of nano iron (γ-Fe_2O_3) and zinc (ZnO)	Biological method	nanoscale γ-Fe_2O_3 and ZnO (500 and 750 ppm)	**Kasivelu et al. (2020)**
Spinach plants	On day 20 after plants were sown	Nualgi + NovaLand recommended dosage 0, (1x), 10x, 100x, and 500x	Nualgi =nano-combining 12 essential nutrients on nano-silica + NovaLand= nano macro- and micro-elements	-----------	Nualgi= 4–20 nm NovaLand= 4–50 nm	**Gil-Díaz et al. (2022)**
Black-Eyed Pea	Applied 56 and 72 days after sowing	Fe nano + ionic 0, 0.25, and 0.5 g L^{-1}	Fe nano + Mg nano	-----------	-----------	**Delfani et al. (2014)**

		Mg nano+ ionic 0, 0.5 g L^{-1} nano, and 0.5 g L^{-1}				
Squash	After 20 days from the sowing of the seeds	ZnO, Fe_2O_3, Mn3O4, ZnO = 20ppm	Nano of: ZnO, Fe_2O_3, Mn_3O_4, and combinations	Biological method	Fe_2O_3= 5nm Mn_3O_4=7nm ZnO=8nm	**Shebl et al. (2019)**

B4. Nanoparticle Fertilizer and the Surrounding Environment

At the soil level, some types of nano material as zero-valent iron, can aid in washing soil from toxic heavy metals (Boente *et al.*, 2018). According to Gong *et al.* (2017), nanoparticles can help plants and microorganisms in bioremediation by translocation and degrading contaminants. Moreover, using smart synthesized non-fertilizer thermoplastic starch urea can help release phosphorus from the soil profile while the urea gradually releases (Giroto *et al.*, 2015).

B5. Plants and Nanoparticle Fertilizers' Interaction

Wheat seed germination was enhanced by 2- 100 ppm TiO_2 Nano particles in a petri dish experiment (Feizi *et al.*, 2012). This was further supported by Noor *et al.* (2022) using Cumin biologically synthesized 1.6mM Fe_3O_2 nanoparticles. Early wheat seedling stage growth was enhanced by using 10% nano Chitosan of 20 nm in both soil and clay and sandy clay pot experiments (AbdelAziz *et al.*, 2016; AbdelAziz *et al.*, 2018). Furthermore, Sheoran *et al.* (2021) showed that K nanoparticles had the same positive influence even at a later stage of plant growth (i.e., 8 weeks after germination).

In Maize, adding 1.1 mg/L magnetite aspartic acid at the seed germination stage led to an enhancement of the process (Răcuciu *et al.*, 2022). As well, adding 0.01-0.16% chitosan nanofertilizer at seed germination and after 55 days of seed sowing had positive consequences on seed germination and plant growth (Kumaraswamy *et al.*, 2021). Chitosan is a polysaccharide molecule formed from the deacetylation of chitin (Li *et al.*, 2020). The same positive influence was recorded by adding 18-27nm γ-Fe_2O_3 and 19-27 nm at the seeds' germination stage and before and after flowering (Kasivelu *et al.*, 2020). The positive influence of nanofertilizers when added at a proper level on seed germination was also recorded on onion (Raskar and Laware, 2014), Broccoli (Awan *et al.*, 2021), Sage (Feizi *et al.*, 2013), and Common bean (Prażak *et al.*, 2020). In common beans, Ag nanofertilizer not only enhances germination but also reduces fungal infection and produces plants able to tolerate adverse conditions in the field.

Citrus maxima was studied in two different experiments grown under a hydroponic agricultural system at the seedling stage (Hu *et al.*, 2017; Li *et al.*, 2018); in both experiments, the nano Fe_2O_3 was added but one at a different concentration(0, 20, 50, and 100 mg/L) and another one at different types (α Fe_2O_3 and γ Fe_2O_3). The best growth response was recorded when γ Fe_2O_3 had been used and when the concentration was at 20 and 50 mg/L.

Lettuce seed germination had the best response when nano-Mn and Fe were used (Liu *et al.*, 2016). On the other hand, treating lettuce seed with nanofertilizers could have toxic effects in certain cases because of the tiny seed size, which could lead to being adsorbed by nanoparticles and cause toxicity (Wu *et al.*, 2012). Adding nano Fe_3O_4 at the seedling stage (Trujillo-Reyes *et al.*, 2014) and at the four-leaf stage (Roosta *et al.*, 2015) under hydroponic systems gave a good response on plant growth.

Tomato seed germination was enhanced by adding 8gm/L nano silicon (Siddiqui and Al-Whaibi, 2014), while adding nano-Ag at the seedling stage responded negatively (Noori et al., 2020). López-Moreno et al.

(2010) studied the effect of using CeO_2 nano fertilizer on tomatoes and other plants, including alfalfa, corn, and cucumber. The plant rooting system recorded different responses depending on the plants, while the shoot system of all plants was influenced positively by the application level of nanofertilizer.

The spinach plant was influenced by the concentration of nanofertilizer and was not affected by the type, either in seed germination (Zheng *et al.*, 2005) or at the seedling stage (Gil-Díaz *et al.*, 2022).

Barley and saffron were grown under a hydroponic system, and both plants show positive responses to wide nano levels (Tombuloglu *et al.*, 2019; Nazari, Feizi, 2021). Moreover, when growing plants in tissue culture conditions as in Mung (*Vigna radiate*) and Gram (*Cicer arietinum*), the applications of nanofertilizer enhanced the plants' growth, but the positive response occurred at very specific applications (Mahajan *et al.*, 2011).

B6. Nanoparticles for Mitigation of Plant Stresses

Plants are grown in fields where the conditions are not optimal for their growth, thus, the plants will face one or more stresses, which could threaten their performance, yield, or even their existence. The stresses could be of Biotic and Abiotic sources; high temperature, chilling, salinity, high light intensity, drought, and heavy metals as the Abiotic stresses (Table 3). Fungi, insects, and bacteria are the major biological stressors. All stresses lead to the increased formation of ROS species that have the main response to plant cell death through damaging plant components, including carbohydrates, proteins, lipids, and even DNA (Das and Roychoudhury, 2014). According to Hashemi *et al.* (2010), silicon application mitigated the effect of salinity stress due to the accumulation of lignin and a decrease in Na in the plant shoot. The same positive effect for nanosilicon against drought stress and heavy metal stress was recorded on *Phaseolus vulgaris* L. (El-Saadony *et al.*, 2021b). According to Elsheery *et al.* (2020), silicon dioxide, zinc oxide, selenium, and graphene nanoparticles can reduce the adverse effects of chilling stress by enhancing photosystems I and II. In addition, CeO nanoparticles can reduce drought stress by increasing antioxidant levels in sorghum (Djanaguiraman *et al.*, 2018) and by enhancing the defense action against ROS (Alabdallah and Hasan, 2021; El-Saadony *et al.*, 2022). Hong *et al.* (2005) found that TiO_2 nanoparticles also help protect spinach against illumination stresses by protecting chlorophyll. Moreover, according to Liang *et al.* (2003), silicon plays an important role in protecting membranes that become more integral and stable. Silicon fertilizer enhances plant yield and growth under salinity stress by keeping the uptake of nutrients (Alsaeedi *et al.*, 2019) and reducing Na uptake (Tahir *et al.*, 2006). According to Abdelaal *et al.* (2020), silicon nanofertilizers can reduce lipid peroxidation, superoxide, and hydrogen peroxide. Under salinity conditions, silicon fertilizer can help the seeds to germinate (Alsaeedi *et al.*, 2017), increase the resistance of the seeds' coat, and increase the availability of nutrients (Suriyaprabha *et al.*, 2012).

Table 3. Nanoparticles source for mitigating plant stresses on different crops

Nanoparticle type	**Stress type**	**Plant**	**References**
Si	Drought	*Hordeum vulgare*	Ghorbanpour et al. (2020)
Si	Salinty+ heavy metals	*Phaseolus vulgaris L.*	El-Saadony et al. (2021)
Si	Drought + Salinity	Cucumber	Alsaeedi et al. (2019)
Si	Salinity	Cherry Tomato	Haghighi and Pessarakli (2013)
Si	Salinity	Tomato	Sayed et al. (2022)
Si	Heavy metal (Cr)	*Pisum sativum* (L.)	Tripathi et al. (2015)
Si+ Zn+ Se+ graphene	Chilling	Sugarcane	Elsheery et al. (2021)
ZnO	Salinity	*Abelmoschus esculentus* L. Moench	Alabdallah and Alzahran (2020)
Zn+B+ Cu	Salinty + drought	Soybean	Dimkpa et al. (2017)

CeO_2	Drought	*Sorghum bicolor* (L.) *Moench*	Djanaguiraman *et al.* (2018)
TiO_2	Light	Spinash	Hong *et al.* (2005)
Cu	Salinity	Tomato	Pérez-Labrada *et al.* (2019)
Cu	Pests	Wheat	El-Saadony (2020)
Ag	Salinity	Pearl millet	Khan *et al*. (2020)
Ag	Salinity	*Maerua oblongifolia*	Shaikhaldein *et al*. (2022)
Ca+ P	Salinity	Broad Bean	Nasrallah *et al.* (2022)
Ca	Salinity	Tomato	Abeed *et al*. (2023)
K	Salinity	Common Bean	El-Beltagi *et al.* (2023)

B7. Global Production and Distribution of Nano Fertilizers

According to Region and Segment Forecasts (2022), the global production of nanofertilizer reached 2705.5 million dollars, and it is expected for a yearly increasing level around 14.8% by 2030. In Jordan, there are no statistical records for the nanofertilizer industry (Ministry of Environment project) and that was traced back to the recent development of nanomaterials is not well understood or recognized in statistical terms. The industry uses imported nano raw materials, and insufficient awareness of the production and use of nanofertilizers.

C. Microparticle Size Fertilizer

Microparticles are particles with a size of 1000nm. Microparticles can be synthesized by emulsifying and evaporation (Chagas *et al.,* 2020), and gelation methods on chitosan polymers (Colman *et al.,* 2024) and starch (Chiaregato and Faez, 2021). Moreover, microparticles have a greater ability to keep nutrients in the soil for a long period (Messa *et al.,* 2020), reduce swelling degree (Chiaregato and Faez, 2021), and have larger sorption characteristics (Usman *et al.,* 2014). Microparticle has the beneficial effect of nano by being gradually released into the environment but do not have the negative influence of very small behavior as Nanos. The dangerous problem of nanofertilizer is their size and what could be transferred from one trophic to another where it will ultimately reach the human. According to Ghosh *et al.* (2010), nanofertilizers that transfer from plants to humans lead to DNA damage. According to Unrine *et al.* (2012) nanoparticles have a much more negative influence when they transfer from one trophic level to another rather than direct eating for it.

According to Colman *et al.* (2024) and Chagas *et al.* (2020), using microparticles as a source of fertilizer leads to an efficient increase in nutrient supply and continuous supply of it. Moreover, using microparticles in tissue culture in *Arabidopsis thaliana* (Lee *et al.,* 2010) and *Nicotiana tabacum* (Mazaheri-Tirani and Dayani, 2020) showed a significant increase in the growth even at high concentrations compared with nano size (Prażak *et al.,* 2020). Table 4 pinpointed the main differences among conventional, nanoparticle, and microparticle fertilizers.

Table 4 The main differences among different fertilizer types

Parameter	**Conventional fertilizer**	**Microparticles fertilizer**	**Nanoparticles fertilizer**
Particles size	0.15-4mm	1000 nm	1-100 nm
Impact on the environment	The most negative impact (Leaching +volatilization)	The lowest negative impact on the environment, but it needs further improvement	Lower impact on the environment, but the size of it can have a negative risk

Amount of application	It should be applied in large quantities	Lower application level	Lower application level
Control of the particle release level	The lowest one	High controlling level	High controlling level
Cost	The lowest	High cost	High cost
Commercially acceptance	The accepted and recommended fertilizers for farmers	Lower acceptance	Lower acceptance

D. Mechanism of Action of Nano- and Micro-Sized Particles

The mechanism of action in both nano- and micro-size particle fertilizers starts from the release process and continues in the plant's tissues. Releasing is gradual and starts when water penetrates the fertilizer capsule (Priya *et al.*, 2024) or the encapsulated fertilizer is exposed to plant root exudates, leading to the loosening of the fertilizer-capsule structure and causing the release of nutrients. Nanoparticles can enter the rooting system and the leaf (foliar application). They can cause an accumulation, increase the ROS level, and cause genetic problems. On the other hand, the microparticles most likely are not expected to go further in the plant structure, thus are not expected to have the same negative influence, but that needs to be proved by further studies (Fig.1).

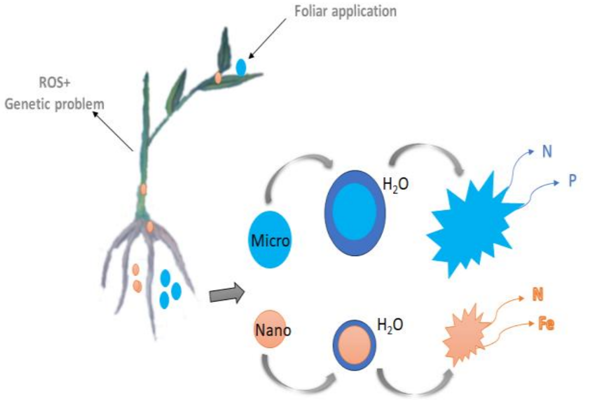

Fig. 1 A depicts a scheme for both foliar and soil-applied fertilizers.(by the authors)

Conclusion

Nanoparticles as a source of fertilizer are the best type when used at specific sizes, types, concentrations, methods of synthesis, plant types, and even the media or soil where that plant is grown. Thus, the positive or negative impact on plants and the surrounding environment will depend on properly taking those factors. The biosynthesis method had good advantages over other methods; the resulting larger particle size can be exhibited. The smaller sizes of nanoparticles can be penetrated through plants, but the larger ones are much more difficult to get in. Stress-tolerant plants have a greater ability to do well with nanoparticles. Moreover, some groups of plants could secrete compounds leading to the transfer of nanoparticles to an ionic form before absorption.

Microparticle fertilizer can be a promising fertilizer. Few studies have focused on microparticle fertilizers thus, it needs deeper studies using various plant and soil types or growing media.

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التطورات الحديثة في تكنولوجيا اسمدة النباتات

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ملخص

يعد موضـــوع الاســـمدة من اهم المواضـــيع لدوره المؤثر على نمو النباتات بالاضـــافه لدوره المؤثر على التربة و البيئة المحيطه. يؤدي الترشـيح العميق للماء الى وصـول الاسـمدة الزائدة الى الخزانات الطبيعية للمياه. و بالتالي ايجاد اسـمدة قادرة على تزويد النباتات بما تحتاجه من عناصـر و تبقي على وضـع ممتاز مع التربة والاحياء الدقيقه الموجودة فيها امر واعد في مجال الزراعة. النوع التقليدي من الاسـمدة كان يسـتخدم لعدة عقود. و اصـبح التطور في اسـتخدام اسـمدة النانو كنزعة هو الاتجاه في مجال الصناعة. يعتمد تفاعل النبات او التربة مع اسمدة النانو بشكل ايجابي او سلبي بشكل اساسي على نوع, و تركيز و مستوى النانو المستخدم بحيث يجب اضافته بمستوى دقيق حتى يكون له فائدة كبيرة على النبات و البيئه المحيطه به. تعد جزيئات الاسـمدة التي بحجم المايكرو من الموضـوعات الواعده لكنها تحتاج الى دراسـات حديثه اكثر.

الكلمات الدالة: الأسمدة، جزيئات النانو، التركيز، النوع، جزيئات الميكرو، عامل التربة، البيئة.

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