



Nano-fertilizers: Bio-fabrication, application and biosafety

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Abstract

At the global level, sustainable horticulture faces many challenges due to climate changes in addition to limitations in water and land resources. Nanotechnology is an innovative strategy for sustainable agricultural development. This eco-friendly technology is becoming vital in modern agricultural practices, due to its role in improving plants production, protection with environmental security, biological supportability and financial steadiness. Production of nano-fertilizers is considered as the most important alternative to the conventional fertilizers and pesticides, due to their potential roles in crop production, reducing the use of chemical fertilizers and mitigating the adverse impacts in soil. The aims of the current study were to highlight nanotechnology in terms of several important definitions including; nano-fertilization, biosynthesis of nano-fertilizers and the use of nanomaterial as an alternative to the traditional mineral fertilizers. This is in addition to the control of nutrient release in the soil, nanoparticles (NPs) role in enhancing the bio-agent activity, and the fate of nanomaterials in plants with respect to the toxicological data of any nano-product.

Keywords: Nano-fertilizers, Nano-pesticides, Biosynthesis, Nano-carrier, Nano-encapsulation

1. Introduction

Nanoparticles (NPs) is a molecular aggregates with a minute dimension ranging from 1-100 nm, which modifies their physico-chemical properties compared to the bulk materials ([Tarafdar et al., 2014](#)). A previous study of [Adhikari et al., \(2010\)](#) highlighted that due to the large surface area to volume ratio of NPs, they exhibit an ameliorated physical, chemical and biological properties, phenomena and functions. Focusing on nano-fertilizers, a previous study of [Dimkpa and Bindraban, \(2016\)](#) reported that some

beneficial nutrients are delivered to the plants at the nano-scale level, for supporting the plant growth and improving its productivity. Recent work of [Chhipa and Joshi, \(2016\)](#) reported that nano-fertilizers are divided into three categories i.e. macro-nanofertilizers, micro-nanofertilizers, and nano-particulate fertilizers, depending on nutrient requirements of the plants. According to [Josef and Katarína, \(2015\)](#), nano-fertilizers could be applied as powder or liquid of less than 100 nm. They afford minerals to the plant and/or

increase the efficiency of conventional mineral fertilizers that are absorbed completely by the plants. [Guru *et al.*, \(2015\)](#) revealed the common features of nano-fertilizers including; (1) delivering the appropriate nutrients for enhancing the plant growth through foliar and soil applications, (2) eco-friendly sources of plant nutrients and of low cost, (3) have high efficiency of fertilization process, (4) have a supplementary role with mineral fertilizers, and (5) protect the environment from pollution hazards. Accordingly, these nano-fertilizers help us to eliminate the contamination of drinking water and could be considered as emerging alternatives of the conventional fertilizers. In this context, the objectives of this article were to provide a brief overview and discussion of the developments and applications of agricultural nanotechnology, biosynthesis of NPs, use of NPs as nano-fertilizers and nano-pesticides, and its role in enhancing the activity of the bio-agents. Moreover, an emphasis is given on the recent researches that discussed NPs-plant interactions, fate and biosafety of nanomaterials in plants.

2. Synthesis of nano- fertilizers

2.1. Chemical and physical synthesis of nano-fertilizers

A recent work of [Qureshi *et al.*, \(2018\)](#) revealed that nano-fertilizers is synthesized from conventional fertilizers bulk materials, or extracted from various vegetative or reproductive parts of the plant using different chemical, physical, mechanical, and biological methods. [De Rosa *et al.*, \(2010\)](#) revealed that nano-fertilizers is used to enhance the soil fertility, quality of agricultural products and plant productivity. [Arole and Munde, \(2014\)](#) reported that two approaches were established for the synthesis of nano-materials; they are synthesized either by the Top-down approach (i.e. breaking down of bulk materials into small pieces by applying an external force), or by the Bottom-up approach (combining and gathering of gas and\ or liquid atoms or molecules). A study conducted by [Jaiswal *et al.*, \(2004\)](#) reported that nano-fertilizers can be stabilized or encapsulated using synthetic polymers.

Moreover, nutrients can be coated with a slight film of NPs or encapsulated with nano-fertilizers.

Pertaining to the fabrication methods of NPs, [Satyanarayana and Reddy, \(2018\)](#) highlighted that physical methods such as irradiations, mechanical pressure, ultra-sonication, thermal energy or electrical energy are applied to cause materials melting, abrasion, condensation or evaporation to fabricate NPs. These physical methods depend on top-down strategy and are advantageous for being time and energy consuming, free of solvent contamination and produce uniform monodisperse NPs; however, the abundant wastes produced during this synthesis makes physical processes less economical. On the other hand, chemical methods including sol-gel method, hydrothermal synthesis, micro-emulsion technique, polymer synthesis, chemical vapor synthesis or plasma enhanced chemical vapor deposition technique are some of the most commonly used methods in the NPs synthesis. Although these methods are simple and inexpensive; however, the use of toxic reducing and stabilizing agents make them harmful ([Satyanarayana and Reddy, 2018](#)). Bio-assisted methods including biosynthesis and green synthesis are presented as alternatives of the chemical and physical methods, as they are cost effective, low-toxic, environmentally benign and efficient protocols to synthesize and fabricate NPs. [Kalishwaralal *et al.*, \(2008\)](#) documented that these methods use biological systems like bacteria, fungi, yeast, actinobacteria, plant extracts, etc. for synthesizing the metal and metal oxide NPs. According to [Patel and Krishnamurthy, \(2015\)](#), these bio-assisted methods can be classified into three categories: (1) biological synthesis using microorganisms (2) biological synthesis using biomolecules as templates (3) biological synthesis using plant extracts. They are characterized by being rapid, easy, efficient, economic and eco-friendly methods, which consume less energy, eliminate the use of toxic chemicals, controlled sizes of NPs by altering the synthesis conditions, lesser toxicity, produce safer products, and synthesize of highly stable and well- characterized NPs.

2.2. Biosynthesis of nano-fertilizers

Biosynthesis of NPs using biological methods has received increasing attention, due to the growing need and demand to develop environmentally safe, reliable and non-toxic technologies in nano-material synthesis ([Kalishwaralal *et al.*, 2008](#)). Several molecules in plants and microorganisms such as; proteins, enzymes, alkaloids, phenolic compounds, pigments and amines are responsible for NPs synthesis through reduction reaction ([Shah *et al.*, 2015](#)). A recent study conducted by [Prasad *et al.*, \(2017\)](#) demonstrated that the origin of the idea of biological synthesis of NPs using microorganisms germinated from the experiments on biosorption of metals with Gram-negative and Gram-positive bacteria. According to [Bhattacharya and Mukherjee, \(2008\)](#), the 'green route' of synthesis of NPs is supported by the fact that most of the bacterial species inhabit ambient conditions of varying pH, temperature and pressure, through

enzymatic processes. The NPs generated by these bioprocesses have greater specific surface area, higher catalytic reactivity, and better contact between the enzyme and metal salt in the bacterial carrier matrix. In this field, biosynthesis of NPs by the various microbes requires resistance of the microorganism to these NPs ([Prasad *et al.*, 2018](#)). Several studies conducted by [Kalimuthu *et al.*, \(2008\)](#); [Pandian *et al.*, \(2010\)](#) reported that where the lower concentration of silver nitrate triggers synthesis of AgNPs, however higher concentrations can kill the microorganism within few minutes. [Ayman *et al.*, \(2018\)](#) revealed that for the biosynthesis of nano-nutrients, the microorganism is grown on the selected nutrient source at optimum growth conditions, and then after complete growth, the microbial biomass is separated. The filtrate is used for isolation of the specific extracellular proteins (enzymes) that are used for NPs synthesis, as shown in Fig. (1).

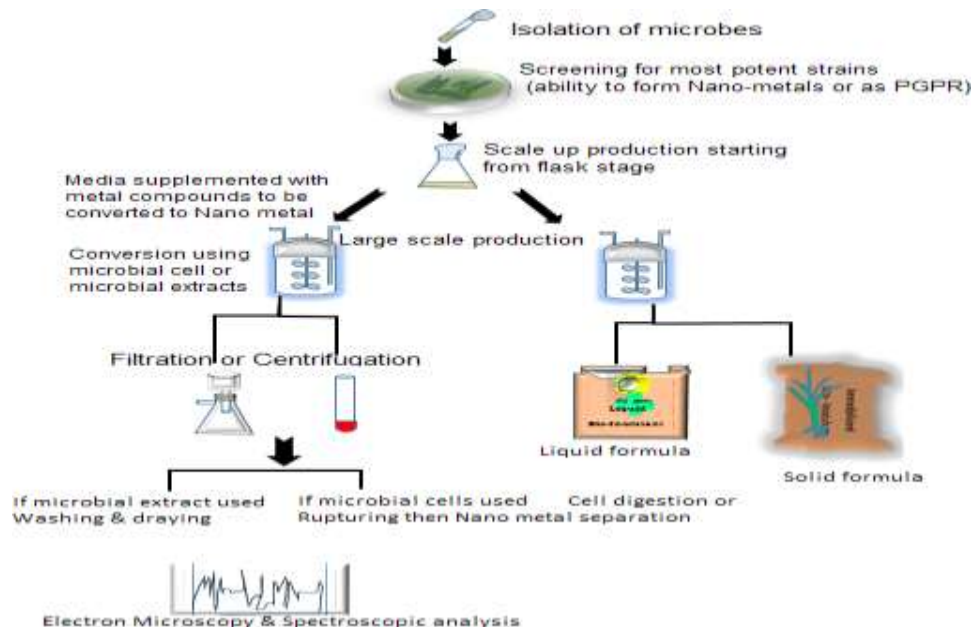


Fig. 1. General steps that could be used in the biosynthesis of nano-fertilizers. The first and second steps involve the isolation of microbes and screening for the most potent strains. After that, scale up production starting from flask stage to produce microbial inoculants through liquid or solid form and\ or to produce nano-fertilizer through media supplemented with metal compounds ([Ayman *et al.*, 2018](#))

Several substances could be used as reducing and stabilizing agents during this biosynthesis process including; enzymes, proteins, sugars and phytochemicals such as; phenolics, cofactors, terpenoids, flavonoids, etc. Moreover, [Dubey and Mailapalli, \(2016\)](#) added that biosynthesis of a nano-fertilizer could be achieved using several microorganisms and plant extracts. Day by day, a great attention will be boosted for searching about novel methods for the biosynthesis of nano-fertilizers. Previous study of [Patel and Krishnamurthy, \(2015\)](#) reported that certain NPs is used in nano-fertilization, that was generated through the biosynthetic route.

3. Nano-fertilizers as an alternative to the traditional mineral fertilizers

Recently, [Chandini *et al.*, \(2019\)](#) revealed that application of mineral fertilizers as nitrogen or phosphorus sources in excess amounts have great effects on both the soil and the ground water, due to leaching down of the remaining minerals into the soil and/or their contribution to air, thus have negative effects on both the sustainability and productivity of crops. So, [Ahmed *et al.*, \(2012\)](#) revealed that nano fertilization is one of the alternatives to these mineral fertilizers, as being an eco-friendly, able to increase soil fertility, improve yield, reduce pollution and increase microbial activities. A previous research work of [Baruah and Dutta, \(2009\)](#) also confirmed that nano-technology could be considered as a powerful solution in the different agriculture sectors, as it prevents pollution, causes soil and/or water remediation, and is used also in the food processing industry.

[Cui *et al.*, \(2010\)](#) highlighted that nano-fertilizers have a great roles in controlling the release of agrochemicals, reducing soil and plant toxicity, site targeted delivery, in addition to maximizing nutrient efficiencies of the utilized fertilizers. [Sasson *et al.*, \(2007\)](#) attributed these advantages of the nano-fertilizers to its innovated characters such as high surface area to volume ratio, specific targeting, its high

solubility due to its small size, high mobility and low toxicity. [Baruah and Dutta, \(2009\)](#) added that for these reasons nanotechnology is progressively shifted from the experimental areas to the practical application.

3.1. Maximization of nano-fertilizers efficiency

According to previous works of [Shaviv, \(2000\)](#); [Tarafdar *et al.*, \(2013\)](#), there is a fact that nutrients use efficiencies is hardly exceed 20-50% for N, 10-25% for P and 35-40 % for K fertilizers, which implies that food production will have to be much more efficient than ever before. [Liscano *et al.*, \(2000\)](#) added that fertilizers typified in nano-particles will have increased accessibility in addition to uptake of supplements to edit the plants. It is apparent that utilization of nano-fertilizers has a positive impact on both of the fertilizers effectiveness and take-up of crops of the soil supplements.

[Navarro *et al.*, \(2008\)](#) attributed the high proficiency of the nano-fertilizers to; 1) Reactivity of nano-materials with the other compounds is higher than those of ordinary ones, due to their higher surface area and very less particles size, which provides more sites for plant metabolism. 2) Enhancement of nutrients penetration and plant uptake, due to the reduced size of the NPs, that increased its specific surface area and particle numbers per unit, which led to increasing the contact surface between the nano-fertilizers and the plants, as reported by [Lin and Xing, \(2007\)](#). The diameter of the plant cell wall pores ranges between 5-20 nm, which is a critical factor determining the entry of NPs through the cell wall ([Fleischer *et al.*, 1999](#)). As the particle size of the nano-fertilizers is less than 100 nm, its penetration into the plant roots or leaves is easier. [Moore, \(2006\)](#) added that nano-fertilizers aggregates have diameters less than that of the plant cell wall pores, thus can easily enter through the cell wall and reach the plant cell plasma membrane. 3) According to [Juárez-Maldonado *et al.*, \(2019\)](#), active NPs can cause enlargement of the pore size and induce new pores in the plant cell wall, to enhance its uptake. A study conducted by [Nair *et*](#)

[al.](#), (2010) emphasized that the uptake of NPs by the plant cell takes place through binding to the carrier proteins, through aquaporin, endocytosis, or ion channels.

[Chinnamuthu and Boopathi](#), (2009) study highlighted that nano zeolites and clays, that is the normally available minerals, is one of the new strategies for increasing the efficiency of fertilizers use. The network of these NPs is filled with macro nutrients such as; nitrogen, phosphorous, potassium, calcium, or minor and trace nutrients, thus they act as a slow source of released nutrients supply. [Leggo](#), (2000) attributed the importance of nano -zeolites in agriculture to its ability to capture, store and cause slow release of nitrogen. According to [Millan *et al.*](#), (2008), urea- fertilized NaO-zeolite is classified as a slow releaser of nitrogen fertilizers, because the dynamics of releasing nitrogen from zeolites is slower than that from their ionic form.

3.2. Control of nutrients release

A recent study conducted by [Preetha and Balakrishnan](#), (2017) highlighted that not all the used doses of the traditional fertilizers can reach the targeted plant parts but only few concentrations, this is mainly attributed to the leaching of chemicals, runoff, evaporation, hydrolysis by soil moisture, and degradation by soil flora. In reference to [Ombódi and Saigusa](#), (2000), essentially about 40-70% of nitrogen, 80-90% of phosphorus, and 50-90% of potassium fertilizers are lost within the soil, thus do not reach the target plants leading to economic misfortunes. Accordingly, more fertilizers and pesticides will be applied to the soil to compensate the lost fertilizers, which adversely affects the balance of nutrients, as reported by [Baruah and Dutta](#), (2009). Many approaches are implemented to overcome the problem of excessive use of fertilizers, however nano-fertilizers is one of these approaches. These slowly-released nano-fertilizers could be utilized as a great alternative to the dissolvable mineral fertilizers, due to its moderate rate of discharging supplements during crop development; as plants will be able to absorb most of

their nutrient requirements without leaching ([Huiyuan *et al.*](#), 2018). Coating the surface of nanomaterials with fertilizer particles cause them to be stronger, as their surface tension is higher than that of the conventional ones, thus increase their efficiency to control the release of these fertilizers ([Brady and Weil](#), 1999).

A previous study of [Leggo](#), (2000) documented that although nitrogen fertilizers are very important; however, they cause severe damage to the plants and the surroundings due to their high solubility nature. Therefore, a nano porous zeolite was used with urea, resulting in considerable increase in the uptake of nitrogen efficient urea with controlled release. Similarly, [Kottegoda *et al.*](#), (2011) reported that urea-modified hydroxyapatite (HA) NPs was synthesized for gradual release of nitrogen during the crop growth. These nano-fertilizers have slower rate of nitrogen release reaching 60 days of plant growth, compared to that of the commercial mineral fertilizers which reach only up to 30 days.

On the other hand, [Huiyuan *et al.*](#), (2018) reported that the controlled- released nano-fertilizers are composed of soluble fertilizers enveloped inside nano-materials, to limit their exposure to the water soluble materials in the surroundings. These coated soluble fertilizers are released to the soil either by diffusion and/or osmosis. [Subramanian and Rahale](#), (2009) previously highlighted that nano-fertilizers is capable of releasing nitrate from urea fertilizer 50 days slower, compared to the conventional nitrogen fertilizers. A previous work of [Tarafdar *et al.*](#), (2012) highlighted that nano membranes can be utilized for coating the fertilizer particles, to encourage the slow discharge of supplements. Nano composite containing macronutrients such as N, P, K; mannose and amino acids is widely used, as they increase the uptake and utilization of nutrients by the grain crops.

3.3. Minimization of the environmental toxicity and pollution

The continuous and large-scale application of the fertilizers and pesticides negatively affect the balance

of soil nutrients that result in an environmental pollution which affect the normal flora and fauna. [Tilman *et al.*, \(2002\)](#) revealed that excessive use of fertilizers reduces the fixation of nitrogen, increases the resistance of pests and pathogens, contributes to the bioaccumulation of pesticides, and destroys the habitats suitable for birds, which lead to sustainable and economic losses.

Application of nano-fertilizers diminishes the rate of losing fertilizer supplements; this will decrease the use of the chemical fertilizers, and so minimize the soil contamination. A recent study of [Manjunatha *et al.*, \(2016\)](#) reported that nano-clays or zeolites are examples of encapsulated NPs that increase the efficiency of the used fertilizer, improve the plant health and soil fertility, which have a positive impact on the environmental pollution and agro-ecological degradation. Accordingly, it is vital to adjust the application of mineral fertilizers, to attain the necessities of editing supplementation, and to decrease the dangers of the environmental contamination, this will be accomplished by using the nano-fertilizers.

3.4. High solubility and dispersion of minerals in the soil

As reported by [Guru *et al.*, \(2015\)](#), as nano-mineral micronutrient formulations maximize the solubility of insoluble nutrients and their dispersion in the soil, cause reduction in their absorption and fixation in the soil, all these conditions lead to increase their bioavailability and also increase the efficiency of nutrients uptake. A recent work of [Qureshi *et al.*, \(2018\)](#) revealed that using nano-sized rock phosphate enhance the availability of phosphorus to the plants, because application of nano-rock phosphate NPs on the crop directly may prevent their process of fixation in the soil. Moreover, no iron, silicic acid or calcium are required for phosphorus absorption, thus leading to the increased phosphorus accessibility within the soil.

Similarly, as documented by [Milani *et al.*, \(2012\)](#), the solubility and dissolution kinetics of ZnO in the form of NPs showed faster dissolution rate than the

bulk ones. This new character of high ZnO NPs solubility may improve its efficiency as novel fertilizers.

4. Enhance the activity of bio-agents

Recently, a study conducted by [Mahawar and Prasanna, \(2018\)](#) highlighted that agriculturally important microorganisms are eco-friendly choices which regulate the efficiency and availability of nutrients to the crop plants, thereby enhancing soil fertility by enriching the biodiversity and nutrients in soil. Some of the limitations in extensive use of bio-agents as bio-fertilizers or biocontrol agents are their short shelf life, transportation and storage. In addition, artificially introduced bio-agents can initially colonize roots at 10^7 - 10^8 cfu; however, their populations decrease after a short time ([Gamliel and Katan, 1993](#)). Moreover, [Spadaro and Gullino, \(2004\)](#) revealed that the potent bio-agents often show some considerable limitations such as; their sensitivity to the adverse environmental conditions and climatic change, and their narrow range of activity. Applications of nanotechnology in the form of nano-carriers, nano-encapsulation and nano-nutrients have been reported by [Singh and Prasad, \(2017\)](#) as potential alternative formulations and delivery systems, which could enhance the performance of the bio-agents (Fig. 2). Understanding the pathways will increase the nano-carrier's efficiency and boost its controlled distribution and release. [Kessler *et al.*, \(2008\)](#) reported that the positive effects of nano-carriers may be attributed to their ability to modulate the formation of surface complexes with important types of bio-molecules such as the proteins and phospholipids.

Regarding the interactions between the bacteria and NPs, more studies have to be carried out in these perspectives including; (1) treatment efficacy, (2) adhesion stability of bacteria on the NPs, (3) residual concentration of NPs and its side effect on the environmental system. [Rangaraj *et al.*, \(2014\)](#) demonstrated that NPs can enter the cell wall of a specific bacterium, concentrate in this cell and then connect with the cell bodies.

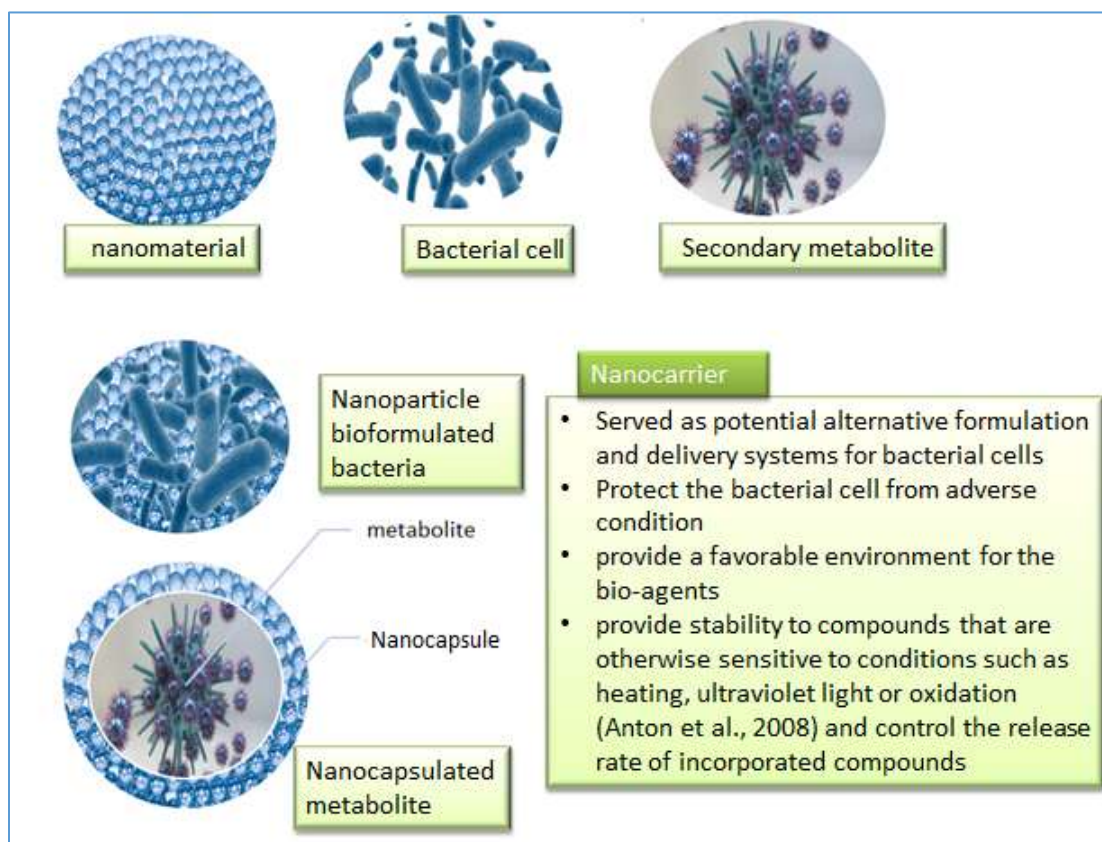


Fig. 2: Nano-carriers and nano-capsules as protecting agents for the bio-agent and its products

4.1. Types of nano-carriers

The small size of NPs makes them a significant carrier for bio-agents, and enhances its attachment and penetration into the plant surfaces (Chen and Yada, 2011). Nano-carrier could provide a favorable environment for the bio-agents to remain viable and active for a longer time (Nasr, 2019). In this part, the popular NPs used as carriers for bio-agents are outlined.

4.1.1. Titanium oxide (TiO₂) NPs

TiO₂NPs comprises the most commonly used and highly processed NPs, and became an essential component of drug delivery in many regions. Its specific properties make TiO₂NPs a promising

transporter in agricultural production due to its antioxidant activity, low environmental toxicity, cost efficiency, and its chemical stability. In addition, it has a bacterial attachment effect (Park *et al.*, 2008; León *et al.*, 2017). The bacterial formulas containing TiO₂ nanostructures improved the viability, competitive potency of *Bacillus amyloliquefaciens* for space and resources in the plant rhizosphere, in addition to its antifungal efficiency (Palmqvist *et al.*, 2015). Likewise, the Sol-Gel synthesized TiO₂ NPs improved the performance and adhesion of the plant growth promoting rhizobacteria (PGPR) to the plant roots. As reported by Timmusk *et al.*, (2018), this improved potential of PGPR will promote the reproducible field usage and sustainable agriculture productivity under stressful conditions.

4.1.2. Silica NPs

A previous work conducted by [Mody *et al.*, \(2014\)](#) highlighted that nano-silica is highly advantageous delivery transporter due to its ease of synthesis with a controlled size, shape, and structure. Its shape is commonly spherical with pore-like holes. [Barik *et al.*, \(2008\)](#) reported that the bio-agent is commonly loaded into the inner core of this silica NPs that provides protection and a sustained release. According to [El-Ramady *et al.*, \(2018\)](#), silicon has already been used to enhance the plant tolerance against various abiotic and biotic stresses and, therefore, silica NPs seems to be the natural choice for the microbial delivery system. [Rangaraj *et al.*, \(2014\)](#) demonstrated that application of the bioformulation of *Pseudomonas fluorescens* and nanosilica enhanced the biocontrol activity of this bacterium against several pathogens of maize. Recently, [Djaya *et al.*, \(2019\)](#) reported that a formulation containing PGPR and endophytic bacteria with the delivery system consisted of graphite and silica NPs, and its effect on pathogenic fungi was determined. Moreover, they observed that the widest *in vitro* inhibition zones resulted from biocontrol with graphite and silica NPs, indicating that the type of delivery system significantly affects the biocontrol mechanism.

4.1.3. Chitosan nanoparticles (CsNPs)

[Kashyap *et al.*, \(2015\)](#) demonstrated that chitosan is a chitin-derived polysaccharide, which has reactive hydroxyl and amine groups that are required for its modification, grafting reactions and ionic interactions, to improve the chitosan structure. CsNPs is easily biodegradable and shows low solubility in aqueous media, due to its hydrophobic properties. [Zargar *et al.*, \(2015\)](#); [Malerba and Cerana, \(2016\)](#) added that it also has fungicidal potential, and is widely used as a stimulator for plant development and production. As reported by [Malerba and Cerana, \(2016\)](#), chitosan adheres well to the epidermis of the plant leaves and stems, this property may aid also in the attachment process of the bio-agent carried on the CsNPs to the plant root. Recently, [Abd-Elsalam, \(2020\)](#) reported

that the biocontrol agent adsorbed on the chitosan-silica nano-composite showed considerable pathogen inhibitory potency, enhanced wilt resistance and rhizosphere health of the tomato plants. [Gatahi *et al.*, \(2016\)](#) added that due to the diverse materials used in synthesizing the nano-composite, it serves both as a biopesticide and a biofertilizer.

4.2. Nano-encapsulation of bioactive compounds

As revealed by [Anton *et al.*, \(2008\)](#), nano-encapsulation systems provide stability to the bioactive compounds that are otherwise sensitive to adverse conditions such as heating, ultraviolet light or oxidation, and control the release rate of the incorporated compounds. Nano-encapsulation is an advanced and promising nanotechnology in which the active substances are effectively released from the capsules or particles in a guided and gradual manner ([Saifullah *et al.*, 2019](#)). It resembles the microencapsulation, except that the size of used particles is on the nanoscale. Previous research works of [Hack *et al.*, \(2012\)](#); [Ammar, \(2018\)](#) demonstrated that different release mechanisms could be used for delivery of the bioactive compound in the nano-encapsulated materials including; dissolution, diffusion, or biodegradation. [Kadri *et al.*, \(2018\)](#) revealed that the crude lipase and alkane hydroxylase enzymes produced by the bacterium *Alcanivorax borkumensis* are trapped by a gelation process in the chitosan NPs. The nano-capsulated lipase and alkane hydroxylase enzymes showed increased *in vitro* half-life by more than two folds, compared to the uncapsulated enzymes that preserved only about 70 % of its initial activity after few days. [Naraghi *et al.*, \(2018\)](#) added that nano-formulations containing the active ingredients of *Talaromyces flavus* fungus in the form of nano-capsules, nano-emulsion and nano-powder had a great efficiency in inhibiting the colony growth of some important mycopathogens including *Verticillium dahliae* and *Fusarium oxysporum*.

4.3. Nano- nutrients

Recently, the scientists documented the effects of NPs interactions with PGPR on the plant growth, with the goal of encouraging its use in agricultural purposes. According to [Khodakovskaya *et al.*, \(2009\)](#), the efficacy of NPs differs from plant to plant depending on its composition, scale, surface area, reactivity and concentration. NPs may have either a good or bad effects on the soil microflora. Combination of the bio-fertilizers or biocontrol agents with nanomaterials may increase the efficacy and vitality of the bio-agents. [Devnitaa *et al.*, \(2018\)](#) reported that the combinations of rock phosphate NPs and bio-fertilizers decrease the P-retention, and increase the available phosphorus after being incubated for one month in the soil. Similarly, [Farnia and Ghorbani, \(2014\)](#) demonstrated that combined use of diazotrophs and K nano-fertilizer had a greater impact on the red bean yield components, rather than on single application.

Many micronutrients such as; silica, zinc, copper and iron have been synthesized in a nanoscale manner and used in the management of plant growth. A study conducted by [Dinali *et al.*, \(2017\)](#) demonstrated that iron oxide NPs are widely used in sustainable agricultural system, because of their ease of synthesis, modification, and/or coating. [Heidari *et al.*, \(2018\)](#) investigated the effects of PGPR and iron nano chelate on the growth, grain yield and physiological responses of maize. They noticed that foliar application of nano Fe and a nitrogen fixer bacterium *Azospirillum brasilens*, improved the maize plant growth and productivity. Another recent research of [Mokarram-Kashtiban *et al.*, \(2019\)](#) reported that inoculation of the plant with PGPR and an arbuscular mycorrhizal fungus with minimal-dose of Fe-NPS substantially increased the phytoremediation of heavy metals; additionally, the root zone and leaf space of the young plants have been improved. Furthermore, the addition of bioagents and nano Zn-Fe oxide also enhanced seed production, photosynthesis and osmolyte contents (i.e. proline, soluble sugars and antioxidant enzyme) of the wheat plant affected by salt stress ([Babaei *et al.*, \(2017\)](#)). Moreover, a work conducted by [Sharifi, \(2016\)](#)

observed that foliar application of Zn NPs and co-inoculation with PGPR *Bradyrhizobium japonicum*; enhanced the yield, oil content and quality of the soybean plant.

5. Nanoparticles-plant interaction and fate of nano-materials in plants

Few research studies were conducted on the interaction of NPs with plants. [Yang and Watts, \(2005\)](#) studied the phytotoxicity of Aluminum oxide NP on root elongation in five hydroponic plant species mainly; *Zea mays* (corn), *Cucumis sativus* (cucumber), *Glycine max* (soybean), *Brassica oleracea* (cabbage), and *Daucus carota* (carrot). This investigation revealed that while NP of aluminum oxide inhibited the root elongation; however, loading these nano-alumini with different percentages of monomolecular layer of phenanthrene (10.0%, 100.0%, or 432.4%) minimized this inhibitory effect. This means that a slight reduction in root elongation was recorded in presence of NP coated with phenanthrene. Thus, the surface characteristics of Alumina NPs are considered as vital factors affecting its phytotoxicity. [Hong *et al.*, \(2005\)](#) highlighted that the solubility of aluminum oxide increased with decreasing the particle size or with modification of its surface by adsorbing compounds, which will affect the dissolution rate.

[Antar and Igor, \(2018\)](#) recently demonstrated that nano-fertilizers can make strides both on germination of seeds and on development of seedlings. This is attributed to its capacity to enter the seeds effectively and to increment accessibility of diverse supplements into the developing seedlings. During the study of [Zheng *et al.*, \(2005\)](#), remarkable increase in both germination rate and vigor indexes of aged spinach seeds were observed as a result of seed treatment with 0.25-4% of TiO₂NPs. Moreover, the developing chlorophyll, dry weight of plant, rate of photosynthesis and the action of ribulose-bisphosphate carboxylase/oxygenase were essentially expanded. These results indicate the role of NPs on the physiology of the plant.

Although previous studies of [Yang *et al.*, \(2006\)](#) reported that nano-TiO₂ could significantly promote photosynthesis and improve the spinach growth; however, the remarkable increase in spinach growth as a result of treatment with nano-anatase TiO₂ could be attributed to changes in the nitrogen metabolism. Moreover, they demonstrated that nano-anatase TiO₂ treatment could improve the activities of numerous imperative enzymes including; nitrate reductase, glutamine synthase, glutamate dehydrogenase and glutamic-pyruvic transaminase. According to [Jitao *et al.*, \(2018\)](#), whatever is the potential interaction way of NPs with the plant roots, it could be through adsorption onto the root surface, uptake into the cell, incorporation into the cell wall, or through diffusion into the intercellular spaces.

The dominant process for the uptake of metal complexes into the plant cell is attributed to the negative charge on its surface, which permits transporting of the adversely charged compounds into the cells through their membranes. Although only the symplastic transport is possible into the xylem; however, the compounds can also enter the xylem through holes or damaged cells without crossing through the cell membrane ([Tandy *et al.*, 2006](#)).

6. Biosafety of nano-materials used in the agricultural applications

Although the nano materials is demonstrated to have awesome potential to be utilized in completely different imperative areas such as; pharmaceutical, horticultures and others; however, the dangers of these materials on human being and the environment are unidentified.

[Oberdörster *et al.*, \(2005\)](#) revealed that the term nanotoxicology is not used to assess and distinguishes the poisonous impact of these materials as it is, but also to advance the secure plan of utilizing them. Previous study of [Riediker *et al.*, \(2004\)](#) demonstrated that the troubles in comparing the security or poisonous quality of these nano materials are attributed to several factors including: size and

structure, used substances or salts, synthesis method, biological substrates, and reactions in the media of applications. In this way, [Oberdörster *et al.*, \(2005\)](#) added that the evaluation of NPs hazards has got to be assessed on the premise of a case-by case; in addition, the toxicological properties is restricted to a specified item at a given time.

To define the toxicological data about any nano-product, it is important to determine the expected concentrations of NPs that will remain in the ecosystem, and/or exposed to the biological system. Although there is no obvious evidence that use of NPs can initiate human diseases; however, some studies indicated that they can promote some biological responses that lead to toxicological outcomes including; cell inflammatory response and genotoxic effects in the form of DNA damage, as reported by [Haji *et al.*, \(2016\)](#). Conversely, nano-products have more noteworthy effects within the promotion of plant crops including; environmental safety, financial soundness and biological sustainability. An early work of [Tiwari *et al.*, \(2012\)](#) highlighted that nano-products improve the plant resistance against biotic and abiotic stress, nano-fertilizers enhances the overall health of the plant, and ZnO NPs recorded to improve the plant health under stress conditions.

Risks associated with nanotechnology must be evaluated before implementation of this technology. [Nel *et al.*, \(2006\)](#) demonstrated that the environmental and public health impacts of any new nano-fertilizer must be determined, validated, and diminished through regulation and re-design of the product before marketing. Different factors affect its behavior and toxicity such as: particle size, the used dose, the materials of fabrication, etc. A recent study conducted by [Pullagurala *et al.*, \(2018\)](#) highlighted that nano-materials have negative effects on plant after exposure to higher concentrations of these NPs, whereas applications of lower dose under specific conditions causes beneficial effects. A previous study of [Reddy *et al.*, \(2016\)](#) confirmed that a few designed nano fabric is clearly phytotoxic at high concentrations (>500

mg/l), but at lower concentrations (<50 mg/l), applications cause an advantageous impact.

According to [Nair and Chung, \(2017\)](#), when plants were exposed to high concentrations of ZnO NPs, diminishment of macro- or micronutrients occurred due to blockage of the roots, and this led to minimizing the take-up of other supplements. [Jaison *et al.*, \(2018\)](#) added that NPs of chemical origin may cause some toxicity upon contact with other media, and may produce unsafe byproducts as well. To overcome this problem, there is a recent shift from utilizing chemical strategies for nanomaterial synthesis to the bio-strategies.

Moreover, the environment influences the behaviors and security of the nano materials as NPs is recorded to be non-toxic to soil microorganisms, but poisonous to marine microflora, as reported by [Lyon *et al.*, \(2005\)](#). Recently, [Haji *et al.*, \(2016\)](#) reported that the US Food and Drug Administration (FDA); as an open human being organization has taken into consideration this critical issue of the harmful impacts of NPs products, and did not consider it either as completely secure or harmful for human utilization.

Conclusion

Nanostructured fertilizers in the form of nano-carriers, nano-capsules and nano-nutrients could be considered as smart fertilizers, which can enhance the efficiency of plant nutrients use, control the nutrients release and reduce the environmental pollution. However, there is an urgent need to standardize and assess the toxicity of nano-materials used in agriculture; accordingly, conducting rigorous field and greenhouse studies for execution assessment are highly recommended.

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Conflict of interest

There is no any conflict of interests between the authors.

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Ethical Approval

Non-applicable.

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