Nano-fertilizers: Bio-fabrication, application and biosafety

Rabaa Yaseen1; Ahmed I. S. Ahmed2; Amal M. Omer1*; Mohamed K. M. Agha2; Tamer M. Emam1

1Soil Fertility and Microbiology Department, Desert Research Center, Cairo, Egypt; 2Nano-Phytopathology Laboratory, Plant Protection Department, Desert Research Center, Cairo, Egypt

*Corresponding author E-mail: amal omaram@yahoo.com

Received: 15 June, 2020; Accepted: 8 August, 2020; Published online: 13 August, 2020

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, micronanofertilizers, 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 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.](image_url)

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 nanotechnology 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 Ombodi 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 pants 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 nanomaterials, 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 obsession, 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, nanocapsulation 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.
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 (TiO$_2$) NPs

TiO$_2$ NPs comprises the most commonly used and highly processed NPs, and became an essential component of drug delivery in many regions. Its specific properties make TiO$_2$ NPs 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 TiO$_2$ 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 TiO$_2$ 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 nanoslica 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 un-capsulated 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-alumni 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-% of TiO2 NPs. 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-TiO$_2$ could significantly promote photosynthesis and improve the spinach growth; however, the remarkable increase in spinach growth as a result of treatment with nano-anatase TiO$_2$ could be attributed to changes in the nitrogen metabolism. Moreover, they demonstrated that nano-anatase TiO$_2$ 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 nanomaterials 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.

Acknowledgment

This work was supported by the Nano-Phytopathology Lab., which was established with the full financial support of the Desert Research Center, Cairo, Egypt, through the collaborative work in the research project entitled “Isolation and identification of fungi and bacteria from desert Egyptian ecological habitats for bio-pesticides production”.

Conflict of interest

There is no any conflict of interests between the authors.

Funding source

This work was supported by the Nano-Phytopathology Lab., which was established through the full financial support of the Desert Research Center, Cairo, Egypt, with collaborative work in the research project entitled “Isolation and identification of fungi and bacteria from desert Egyptian ecological habitats for bio-pesticides production”.

Ethical Approval

Non-applicable.

7. References

Abd-Elsalam, K.A. (2020). Multifunctional Hybrid Nanomaterials for Sustainable Agri-food and Ecosystems. Chapter 16, 1st Edition, Elsevier. 16: 355-391.

Adhikari, T.; Biswas, A.K. and Kundu, S. (2010). Nano-fertilizer- A new dimension in agriculture. Indian Journal of Fertility. 6: 22-24.

Ahmed, S.; Niger, F.; Kabir, M.H.; Chakrabarti, G.; Nur, H.P. and Imamul Huq, S.M. (2012). Development of Slow Release Nano Fertilizer. Proceedings of the International Workshop on Nanotechnology, Dhaka, Bangladesh. 1(45): 21-23.

Ammar, A.S. (2018). Nanotechnologies associated to floral resources in agri-food sector. Acta Agronómica. 67(1): 146-159.

Antar, B. and Igor, S. (2018). Effect of Nano-Fertilizer on Seed Germination and First Stages of Bitter Almond Seedlings’ Growth Under Saline Conditions. BioNanoScience. 8: 742-751.
Anton, N.; Benoit, J.P. and Saulnier, P. (2008). Design and production of nanoparticles formulated from nano-emulsion templates: a review. Journal of Controlled Release. 128:185-199.

Arole, V.M. and Munde S.V. (2014). Fabrication of Nanomaterials by Top-Down and Bottom-Up Approaches – An Overview. Jaast: Material Science. 1(2): 89-93.

Ayman, M.E.; Ahmed, A.M.; Tarek, A.A. and Hassan R.E. (2018). Nanofertilizers vs. Biofertilizers: New Insights. Environmental Biodiversity Soil Security. 2: 51-72.

Babaei, K.; Sharifi, R.S.; Pirzad, A. and Khalilzadeh, R. (2017). Effects of bio fertilizer and nano Zn-Fe oxide on physiological traits, antioxidant enzymes activity and yield of wheat (Triticum aestivum L.) under salinity stress. Journal of Plant Interactions 12(1): 381-389.

Barik, T.; Sahu B. and Swain, V. (2008). Nanosilica— from medicine to pest control. Parasitology Research. 103: 253-258.

Baruah, S. and Dutta, J. (2009). Nanotechnology applications in sensing and pollution degradation in agriculture. Environmental Chemistry Letters. 7: 191-204.

Bhattacharya, R. and Mukherjee, P. (2008). Biological properties of ‘naked’ metal nanoparticles. Advanced Drug Delivery Reviews. 60(11): 1289-1306.

Brady, N.C. and Weil, R.R. (1999). The Nature and Properties of Soils. 12th Edition, Prentice Hall Publishers, London. 1-9: 453-536.

Chandini, K.R.; Kumar, R. and Prakash, O. (2019). The Impact of chemical fertilizers on our environment and ecosystem. Research Trends in Environmental Sciences. 69-86.

Chen, H. and Yada, R. (2011). Nanotechnologies in agriculture: New tools for sustainable development. Trends in Food Science and Technology. 22(11): 585-594.

Chhipa, H. and Joshi, P. (2016). Nano-fertilizers, nanopesticides and nanosensors in agriculture. In: Ranjan, S.; Dasgupta, N. and Lichtfouse, E. (eds). Nanoscience in food and agriculture. Sustainable Agriculture Reviews. 20: 247-282.

Chinnamuthu, C.R. and Boopathi, P.M. (2009). Nanotechnology and Agroecosystem. Madras Agricultural Journal. 96: 17-31.

Cui, H.X.; Sun, C.J.; Liu, Q.; Jiang, J. and Gu, W. (2010). Applications of nanotechnology in agrochemical formulation, perspectives, challenges and strategies. In: International conference on Nanoagri, Sao Pedro, Brazil. 28-33.

De Rosa, M.C.; Monreal, C.; Schnitzer, M.; Walsh, R. and Sultan, Y. (2010). Nanotechnology in fertilizers. Nature Nanotechnology. 5: 91.

Devnitaa, R.; Joy, B.; Arifin, M.; Hudaya, R. and Oktaviani, N. (2018). Application of Nanoparticle of Rock Phosphate and Biofertilizer in Increasing Some Soil Chemical Characteristics of Variable Charge Soil. AIP Conference Proceedings. 1927: 030027.

Dimkpa, C.O. and Bindraban, P.S. (2016). Fortification of micronutrients for efficient agronomic production: a review. Agronomy for Sustainable Development. 36(1): 7.

Dinali, R.; Ebrahiminezhad, A.; Manley-Harris, M.; Ghasemi, Y. and Berenjian, A. (2017). Iron oxide nanoparticles in modern microbiology and biotechnology. Critical Reviews in Microbiology. 43(4): 493-507.

Djaya, L.; Istifadah, N.; Hartati, S. and Joni, I.M. (2019). In vitro study of plant growth promoting rhizobacteria (PGPR) and endophytic bacteria antagonistic to Ralstonia solanacearum formulated with graphite and silica nano particles as a biocontrol delivery system (BDS). Biocatalysis and Agricultural Biotechnology. 19: 101153.
Dubey, A. and Mailapalli, D.R. (2016). Nanofertilisers, Nanopesticides, Nanosensors of Pest and Nanotoxicity in Agriculture. In: E. Lichtfouse (ed.). Sustainable Agriculture Reviews. 19: 307-330.

El-Ramady, H.; Alshaal, T.; Elhawat, N.; El-Nahrawy, E.; Omara, A.E.D.; El-Nahrawy, S.; Elsakhawy, T.; Ghazi, A.; Abdalla N. and Fári, M. (2018). Biological aspects of selenium and silicon nanoparticles in the terrestrial environments. Phytoremediation. 6: 235-264.

Farnia, A. and Ghorbani, A. (2014). Effect of K nano-fertilizer and N bio-fertilizer on yield and yield components of red bean (Phaseolus vulgaris L.) International Journal of Biosciences. 5(12): 296-303.

Fleischer, A.; O’Neill, M.A. and Ehwald, R. (1999). The pore size of non-graminaceous plant cell walls is rapidly decreased by borate ester cross-linking of the pectic polysaccharide rhamnogalacturonan II. Plant Physiology. 121: 829-838.

Gamliel, A. and Katan, J. (1993). Suppression of Major and Minor Pathogens by Fluorescent Pseudomonads. Phytopathology. 83: 68-75.

Gatahi, D.M.; Wanyika, H.N.; Kavoo, A.; Kihurani, A. and Ateka, E.M. (2016). Enhancement of bacterial wilt resistance and rhizosphere health in tomato using bionanocomposites. International Journal of Horticultural Science and Technology. 3(2): 129-144.

Guru, T.; Veronica, N.; Thatikunta, R. and Reddy, S.N. (2015). Crop Nutrition Management with Nano fertilizers. International Journal of Environmental Science and Technology. 1(1): 4-6.

Hack, B.; Egger, H.; Uhlemann, J.; Henriet, M.; Wirth, W.; Vermeer, A.W.P. and Duff, D. (2012). Advanced agrochemical formulations through encapsulation strategies? Chemie-IngenieurTechnik. 84(3): 223-234.

Haji, B.; Faheem, M.; Kamal, N. and Abdollahi, M. (2016). Toxicity of Nanoparticles and an Overview of Current Experimental Models. Iran Biomedical Journal. 20(1): 1-11.

Heidari, M.; Salmanpour, I.; Ghorbani, H. and Asghari, H.R. (2018). Iron Chelate and Rhizobacteria Changed Growth, Grain Yield, and Physiological Characteristics in Maize. Scientia Agriculturae Biohemica. 49(4): 245-254.

Hong, F.H.; Yang, F.; Liu, C.; Gao, Q.; Wan, Z.G.; Gu, F.G.; Wu, C.; Ma, Z.N.; Zhou, J. and Yang, P. (2005). Influences of nano-TiO2 on the chloroplast aging of spinach under light. Biological Trace Element Research. 104: 249-260.

Huiyuan, G.; Jason, C.W.; Zhenyu, W. and Baoshan, X. (2018). Nano-enabled fertilizers to control the release and use efficiency of nutrients. Current Opinion in Environmental Science and Health. 6: 77-83.

Jaison, J.; Yen, S.C; Alain, D. and Michael, K.D. (2018). Review on nanoparticles and nanostructured materials: history, sources, toxicity and regulations. Journal of Nanotechnology. 9: 1050-1074.

Jaiswal, J.; Gupta, S.K. and Kreuter, J. (2004). Preparation of biodegradable cyclosporine nanoparticles by high-pressure emulsification solvent evaporation process. Journal of Controlled Release. 96: 169-178.

Jitao, L.; Peter, C. and Shuzhen, Z. (2018). Uptake, translocation, and transformation of metal-based nanoparticles in plants: recent advances and methodological challenges. Environmental Science: Nano. 6: 41-59.

Josef, J. and Katarína, K. (2015). Application of nanotechnology in agriculture and food industry, its prospects and risks. Ecological Chemical Engineers. 22(3): 321-361.

Juárez-Maldonado, A.; Hortensia, O.; América, B.M.; Susana, G.; Álvaro, M.M.; Cabrera-De la Fuente; M. Sandoval-Rangel, A.; Cadenas-P, G. and Benavides-Mendoza, A. (2019). Nanoparticles
and Nanomaterials as Plant Biostimulants. International Journal of Molecular Sciences. 20(1): 162.

Kadri, T.; Cuprys, A.; Rouissi, T.; Brar, S.K.; Daghrrir, R. and Lauzon, J.M. (2018). Nanoencapsulation and release study of enzymes from Alkanivorax borkumensis in chitosan-tripolyphosphate formulation. Biochemical Engineering Journal. 137: 1-10.

Kalimuthu, K.; Babu, R.S.; Venkataraman, D.; Mohd, B. and Gurunathan, S. (2008). Biosynthesis of silver nanocrystals by Bacillus licheniformis. Colloids and Surfaces B: Biointerfaces 65: 150-153.

Kalishwaralal, K.; Deepak, V.; Ramkumarpandian, S.; Nellaiah, H. and Sangiliyandi, G. (2008). Extracellular Biosynthesis of Silver Nanoparticles by the Culture Supernatant of Bacillus licheniformis. Materials Letters. 62: 4411-4413.

Kashyap, P.L.; Xiang, X. and Heiden, P. (2015). Chitosan nanoparticle based delivery systems for sustainable agriculture. International Journal of Biological Macromolecules. 77: 36-51.

Kessler, V.G.; Seisenbaeva, G.A.; Unell, M. and Hakansson, S. (2008). Chemically triggered biodelivery using metal-organic sol-gel synthesis. Angewandte Chemie. 47: 8506-8509.

Khodakovskaya, M.; Dervishi, E.; Mahmood, M; Xu, Y.; Li, Z.; Watanabe, F. and Biris, A.S. (2009). Carbon nanotubes are able to penetrate plant seed coat and dramatically affect seed germination and plant growth. American Chemical Society Nano. 3(10): 3221-3227.

Kottegoda, N.; Munaweera, I.; Nadeesh, M.A. and Karunaratne, V. (2011). A green slow-release fertilizer composition based on urea-modified hydroxyapatite nanoparticles encapsulated wood. Current Science. 101(1): 73-78.

Leggo, P.J. (2000). An investigation of plant growth in an organo-zeolitic substrate and its ecological significance. Plant and Soil. 219: 135-146.

León, A.; Reuquen, P.; Garín, C.; Segura, R.; Vargas, P.; Zapata, P. and Orihuela, P. (2017). FTIR and Raman characterization of TiO₂ nanoparticles coated with polyethylene glycol as carrier for 2-methoxyestradiol. Applied Sciences. 7(1): 49.

Lin, D. and Xing, B. (2007). Phytotoxicity of Nanoparticles: Inhibition of Seed Germination and Root Growth. Environmental Pollution. 50: 243-250.

Liscano, J.F.; Wilson, C.E.; Norman, R.J. and Slaton, N.A. (2000). Zinc availability to rice from seven granular fertilizers. AAES Research Bulletin. 963: 1-31.

Lyon, D.Y.; Fortner, J.D.; Sayes, C.M.; Colvin, V.L. and Hughe, J.B. (2005). Bacterial cell association and antimicrobial activity of a C₆₀ water suspension. Environmental Toxicology and Chemistry. 24: 2757-2762.

Mahawar, H. and Prasanna, R. (2018). Prospecting the interactions of nanoparticles with beneficial microorganisms for developing green technologies for agriculture. Environmental Nanotechnology Monitoring and Management. 10: 477-485.

Malerba, M. and Cerana, R. (2016). Chitosan effects on plant systems. International Journal of Molecular Sciences. 17(7): 996.

Manjunatha, S.B.; Biradar, D.P. and Aladakatti, Y.R. (2016). Nanotechnology and its applications in agriculture: A review. Journal of Farm Sciences. 29: 1-3.

Milani, N.; McLaughlin, M.J.; Stacey, S.P.; Kirby, J.K.; Hettiarachchi, G.M.; Beak, D.G and Cornelis, G. (2012). Dissolution kinetics of macronutrient fertilizers coated with manufactured zinc oxide nanoparticles. Journal of Agricultural and Food Chemistry. 60(16): 3991-3998.
Millán, G.; Agosto, F. and Vázquez, M. (2008). Use of clinoptilolite as a carrier for nitrogen fertilizers in soils of the Pampean regions of Argentina. International Journal of Agriculture and Scientific Research. 35(3): 293-302.

Mody, V.V.; Cox, A.; Shah, S.; Singh, A. and Bevins, W. and Parihar, H. (2014). Magnetic nanoparticle drug delivery systems for targeting tumor. Applied Nano science. 4: 385-392.

Mokarram-Kashiiban, S.; Hosseini, S.M.; Kouchaksaraei, M.T. and Younesi, H. (2019). The impact of nanoparticles zero-valent iron (nZVI) and rhizosphere microorganisms on the phytoremediation ability of white willow and its response. Environmental Science and Pollution Research. 26(11): 10776-10789.

Moore, M. (2006). Do nanoparticles present ecotoxicological risks for the health of the aquatic environment?. Environment International. 32: 967-976.

Nair, P.M.G. and Chung, I.M. (2017). Regulation of morphological, molecular and nutrient status in Arabidopsis thaliana seedlings in response to ZnO nanoparticles and Zn ion exposure. Science of the Total Environment. 575: 187-198.

Nair, R.; Varghese, S.H.; Nair, B.G.; Maekawa, T.; Yoshida, Y. and Kumar, D.S. (2010). Nanoparticulate material delivery to plants. Plant Science. 179: 154-168.

Naraghi, L.; Negahban, M.; Heydari, A.; Razavi, M. and Afshari-Azad, H. (2018). Growth inhibition of Fusarium oxysporum f. sp. lycopersici, the causal agent of Tomato Fusarium Wilt Disease by nanoformulations containing Talaromyces flavus. Ekoloji. 27(106): 103-112.

Nasr, M. (2019). Nanotechnology application in agricultural sector. In nanobiotechnology in bioformulations. Springer Cham. 317-329.

Navarro, E.; Baun, A.; Behra, R.; Hartmann, N.B.; Filser, J.; Miao, A.J.; Quigg, A.; Santschi, P.H. and Sigg, L. (2008). Environmental behavior and ecotoxicity of engineered nanoparticles to algae, plants, and fungi. Ecotoxicology. 17: 372-386.

Nel, A.; Xia, T.; Mädler, L. and Li, N. (2006). Toxic potential of materials at the nanolevel. Science. 311(5761): 622-627.

Oberdörster, Günter; Eva, O. and Oberdörster, J. (2005). An emerging discipline evolving from studies of ultrafine particles. Environmental Health Perspectives Journal. 113(7): 823-839.

Ombódi, A. and Saigusa, M. (2000). Broadcast application versus band application of polyolefin-coated fertilizer on green peppers grown on andisol. Journal of Plant Nutrition. 23: 1485-1493.

Palmqvist, N.G.M.; Bejai, S.; Meijer, J.; Seisenbaeva, G.A. and Kessler, V.G. (2015). Nano titania aided clustering and adhesion of beneficial bacteria to plant roots to enhance crop growth and stress management. Scientific Reports. 5: 10146.

Pandian, S.R.; Deepak, V.; Kalishwaralal, K. and Gurunathan,S. (2010). Mechanism of Bactericidal Activity of Silver Nitrate – a Concentration Dependent Bi-Functional Molecule. Brazilian Journal of Microbiology. 41(3): 805-9.

Park, M.R.; Banks, M.K.; Applegate, B. and Webster, T.J. (2008). Influence of nanophase titania topography on bacterial attachment and metabolism. International Journal of Nanomedicine. 3: 497-504.

Patel, H. and Krishnamurthy, R. (2015). Antimicrobial efficiency of biologically synthesized nanoparticles using root extract of Plumbago zeylanica as biofertilizer application. International Journal of Bioassays. 4(11): 4473-4475.

Prasad, R.; Kumar, V.; Kumar, M. and Shanquan, W. (2018). Fungal Nanobionics: principles and applications. Chapter 1, Springer, Singapore. 1-19.
Prasad, R.; Bhattacharyya, A. and Nguyen, Q.D. (2017). Nanotechnology in sustainable agriculture: recent developments, challenges, and perspectives. Frontiers in Microbiology. 8: 1-13.

Preetha, S. and Balakrishnan, N. (2017). A review of nano fertilizers and their use and functions in soil. International Journal of Current Microbiology and Applied Science. 6(12): 3117-3133.

Pullagurala, V.L.R.; Adisa, I.O.; Rawat, S.; Kim, B.; Barrios, A.C.; Medina, I.A. and Gardea-Torresdey, J.L. (2018). Finding the conditions for the beneficial use of ZnO nanoparticles towards plants. Environmental Pollution. 241: 1175-1181.

Qureshi, A.; Singh, D.K. and Dwivedi, S. (2018). Nano-fertilizers: A novel way for enhancing nutrient use efficiency and crop productivity. International Journal of Current Microbiology and Applied Sciences. 7(2): 3325-3335.

Rangaraj, S.; Gopalu, K.; Muthusamy, P.; Rathinam, Y.; Venkatachalam, R.; and Narayanasamy, K. (2014). Augmented biocontrol action of silica nanoparticles and *Pseudomonas fluorescens* bioformulant in maize (*Zea mays* L.). Royal Society of chemicals Advances. 4(17): 8461-8465.

Reddy, P.V.L.; Hernandez-Viezcas, J.A.; Peralta-Videa, J.R. and Gardea-Torresdey, J.L. (2016). Lessons learned: are engineered nanomaterials toxic to terrestrial plants?. Science of the Total Environment. 568: 470-479.

Riediker, M.; Devlin, R.B.; Griggs, T.R.; Herbst, M.C.; Bromberg, P.A.; Williams, R.W. and Cascio, W.E. (2004). Cardiovascular effects in patrol officers are associated with fine particulate matter from brake wear and engine emissions. Particle and Fibre Toxicology. 1(2): 1743-8977.

Saifullah, M.; Shishir, M.R.I.; Ferdowsi, R.; Rahman, M.R.T. and Van-Vuong, Q. (2019). Micro and nano encapsulation, retention and controlled release of flavor and aroma compounds: A critical review. Trends in Food Science and Technology. 86: 230-251.

Sasson, Y.; Levy-Ruso, G.; Toledano, O. and Ishaya, I. (2007). Nanosuspensions: emerging novel agrochemical formulations. In: Ishaya, I.; Horowitz, A.R. and Nauen, R. (eds). Insecticides design using advanced technologies. Springer, Berlin. 1-39.

Satyanarayana, T. and Reddy, S.S. (2018). A review on chemical and physical synthesis methods of nanomaterials. International Journal for Research in Applied Science & Engineering Technology. 6(1): 2885-2889.

Shah, M.; Fawcett, D.; Sharma, S.; Tripathy, S.K. and Poinern, G.E. (2015). Green synthesis of metallic nanoparticles via biological entities. Materials. 8: 7278-7308.

Sharifi, R.S. (2016). Application of biofertilizers and zinc increases yield, nodulation and unsaturated fatty acids of soybean. *Zemdirbyste-Agriculture*. 103(3): 251-258.

Shaviv, A. (2000). Advanced in controlled release of fertilizers. Advanced Agronomy Journal. 71: 1-49.

Singh, A. and Prasad, S.M. (2017). Nanotechnology and its role in agro-ecosystem: a strategic perspective. International Journal of Environmental Science and Technology. 14(10): 2277-2300.

Spadaro, D. and Gullino, M.L. (2004). State of the art and future prospects of the biological control of postharvest fruit diseases. International Journal of Food Microbiology. 91: 184-194.

Subramanian, K.S. and Rahale, S. (2009). Synthesis of nano-fertiliser formulations for balanced nutrition. Proceedings of the Indian society of soil science-platinum Jubilee celebration. IARI Campus, New Delhi. 85.

Tandy, S.; Schulin, R. and Nowack, B. (2006). Uptake of metals during chelant assisted...
phytoextraction with EDDS related to the solubilized metal concentration. Environmental Science of Technology. 40: 2753-2758.

Tarafdar, J.C.; Raliya, R.; Mahawar, H. and Rathore, I. (2014). Development of zinc nano-fertilizer to enhance crop production in pearl millet (Pennisetum americanum). Agricultural Research. 3: 257-262.

Tarafdar, J.C.; Sharma, S. and Raliya, R. (2013). Review nanotechnology: interdisciplinary science of applications. African Journal of Biotechnology. 12(3): 219-226.

Tarafdar, J.C.; Raliya, R. and Rathore, I. (2012). Microbial synthesis of phosphorous nanoparticle from tri-calcium phosphate using Aspergillus tubingensis TFR-5. Journal of Bionanoscience. 6: 84-89.

Tilman, D.; Knops, J.; Wedin, D. and Reich, P. (2002). Plant diversity and composition: effects on productivity and nutrient dynamics of experimental grasslands. In: Loreau, M.; Naeem Inchausti, P.S. (eds). Biodiversity and ecosystem functioning, Oxford University Press, Oxford. 21-35.

Timmusk, S.; Seisenbaeva, G. and Behers, L. (2018). Titania (TiO$_2$) nanoparticles enhance the performance of growth-promoting rhizobacteria. Scientific Reports. 8: 1-13.

Tiwari, J.N.; Tiwari, R.N. and Kim, K.S. (2012). Zero-dimensional, one-dimensional, two-dimensional and three-dimensional nanostructured materials for advanced electrochemical energy devices. Progress in Materials Science. 57: 724-803.

Yang, F.; Hong, F.S.; You, W.J.; Liu, C.; Gao, F.Q.; Wu, C. and Yang, P. (2006). Influences of nano-anatase TiO$_2$ on the nitrogen metabolism of growing spinach. Biological Trace Element Research. 110: 179-190.

Yang, L. and Watts, D.J. (2005). Particle surface characteristics may play an important role in phytotoxicity of alumina nanoparticles. Toxicology Letters. 158: 122-132.

Zargar, V.; Asghari, M. and Dashti, A. (2015). A review on chitin and chitosan polymers: Structure, chemistry, solubility, derivatives, and applications. Chemical and Biomolecular Engineers Reviews. 2(3): 204-226.

Zheng, L.; Hong, F.S.; Lu, S.P. and Liu, C. (2005). Effect of nano-TiO$_2$ on strength of naturally and growth aged seeds of spinach. Biological Trace Element Research. 104: 83-91.