Application of Nanoparticles in Agriculture as Fertilizers and Pesticides: Challenges and Opportunities

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Abstract

Sustainable management of ecosystem implies the exploitation of ecofriendly approaches in agriculture for production of crops. Since crop production is linearly determined by exhaustive application of fertilizers to increase soil fertility and pesticides to suppress yield limiting diseases, these processes at the same time result in ecosystem destabilization besides economic costs. Nanomaterials which are prepared by employing different techniques and which range in size between 1 and 100 nm, are comparatively safer and effective than conventional fertilizers. Their utilization as fertilizers and pesticides in agriculture for maximizing production of field crops is gaining popularity across the scientific community and further research in this area can enhance our knowledge about the emerging technology and its wide scale adoption. Different nanoparticles may exhibit potential divergent properties than traditional fertilizers and pesticides in terms of efficiency, costs, and environmental safety. In this chapter, nanoparticles and their possible utilization in agriculture for enhancing the production of crops are discussed with latest literature review.

Keywords

Crop production · Agricultural sustainability · Environmental safety · Nanotechnology · Nanofertilizers

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17.1 Introduction

Global population of human being is increasing exponentially and an estimated rise to 9.7 billion is expected by the year 2050 which is linked with over 70% increase in demand for food than the current food requirements (Cole et al. 2018). Thus to meet the challenges concerned with producing more food for more than nine billion people, elevated production of principal crops is necessary, which depends on bringing more and more fertile land under cultivation. Sufficient production of crop plants and protection from diseases require sufficient fertile level of soil and suppression of plant pathogens. Most of the agricultural land is losing its fertility due to exhaustive agricultural practices which impart negative effects on the production of cultivated crops (Lal 2015). Likewise, different pathogens and pests increasingly curtail the attainable productivity of host plants, which pose economic and production challenges in addition to abiotic constraints (Majeed et al. 2018). To reduce the production gap created by nutrient depleted soils and pathogenic pressures, extensive application of fertilizers and pesticides is carried out in agriculture which seem effective approaches as they significantly increase crop production and protection. The food and agriculture organization (FAO) estimates that currently global fertilizer application in agriculture exceeds 186 million tonnes with projected increase between 1.5 and 2.4% in 2020 (http://www.fao.org/3/a-i6895e.pdf). Due to fertilizers and pesticides application, production of major crops has significantly increased during the last few decades (Tilman et al. 2002). However, the massive application of such chemicals in agriculture has staked at risk our ecosystem by generating diverse pollutions besides to their economic costs which in poorly developed nations remain a leading hurdle for farmers (Shuqin and Fang 2018; Almaraz et al. 2018; Benson and Mogues 2018). Thus to address the issues of environmental and ecosystem sustainability, and costs attached with fertilizers, exploitation of novel approaches in agriculture is required on emergent basis.

Nanotechnology, which employs the use of nanomaterials (particles of sizes which range between 1 and 100 nm), is an emerging field of research which has huge space in agriculture (Saxena et al. 2018). The technology offers a novel tool for creating particles of lesser size than bulk materials which possess several advantages such as high surface area, high reactivity, small size, optical characteristics, etc. (Khan et al. 2019; Prasad et al. 2017). There is a room of opportunities of nanotechnology for the development of nanofertilizers which may possess advantages of high affectivity, low ecological risks, and low economic costs over their inorganic counterparts. Nanofertilizers of different origins can make difference from conventional fertilizers because of reduced nutrient losses from plants, high absorption by plants, and relatively degradable nature (Solanki et al. 2015; León-Silva et al. 2018). A leading issue concerned with the application of traditionally used fertilizers is massive nutrient losses by leaching and volatilization (Pan et al. 2016; Huang et al. 2017), which can be minimized by exploiting nanofertilizers. Nanofertilizers may be prepared on the bases of plants' specific nutrient requirements. A diverse spectrum of elements and/or compounds may be utilized in the formation of nanoparticles and for subsequent formulation of nanofertilizers. In previous findings, silver nanoparticles improved germination of an important medicinal plant, *Boswellia ovalifoliolata* (Savithramma et al. 2012). A significant increase in the growth attributes and biochemistry of cotton was observed when plants were treated with ZnO nanoparticles (Venkatachalam et al. 2017). Stimulatory role of Cu nanoparticles on wheat (Hafeez et al. 2015), CuO nanoparticles on rice (Da Costa and Sharma 2016), ZnO nanoparticles on corn (Taheri et al. 2016), Cu and Zn nanoparticles on wheat (Taran et al. 2017), and silica nanoparticles on basil (Kalteh et al. 2018) has been successfully demonstrated in earlier works. Keeping in view the emergent rise of nanotechnology, this chapter is aimed at reviewing updates about the use of nanoparticles as "nanofertilizers and nanopesticides" in agriculture.

17.2 Nanoparticles: Synthesis and Characters

Preparation of engineered nanoparticles involves different techniques. The most widely used methods are physical, chemical, and biological strategies. Each method has specific advantages and disadvantages. The methods are based on construction of different phases which depends on the bulk materials and desired nanostructured particles (Fig. 17.1). The physical method is based on evaporation, condensation, laser ablation, ball milling, melt mixing, and several other steps while in chemical methods, sol gel, hydrothermal, polyol, and chemical vapor synthesis are carried out

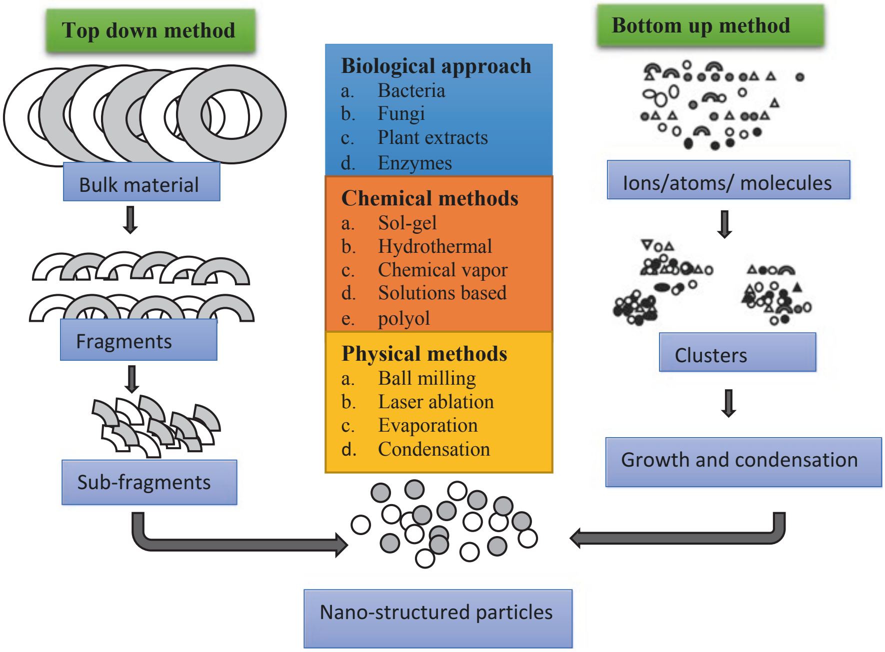

Fig. 17.1 An illustration of different methods used for synthesis of nanoparticles

(Iravani et al. 2014; Dhand et al. 2015). The two most widely employed approaches in nanoparticle synthesis are "bottom-up" and "top-down" methods (Dhand et al. 2015). In a "bottom-up technique," smaller molecules are allowed to grow into large-sized particles (within the range of nanoscale), by first subjecting the molecules to evaporation and then to controlled condensation (https://www.nanoshel.com/physical-methods). The materials to be converted to nanoparticles in bottom-up methods are either gases or liquids that are processed by a variety of physical (laser ablation, plasma arcing, thermal and electron beam evaporation, and sputtering) and chemical strategies such as pyrolysis, deposition of vapor phase of chemicals, microemulsion, sol and gel processing, self-assembly, etc. (De et al. 2014; Roy and Bhattacharya 2015). In a top-down approach, bulk materials are broken down to smaller and finally to desired nanoscale materials by applying attrition and milling to the subjected materials (Qin and Riggs 2013). Usually the materials to be nanofabricated in bottom-up techniques are solid in nature which are proceeded by mechanical methods (high energy ball milling, cutting, etching, grinding, machining, polishing, etc.) or by lithographic approaches such as electron beam and photolithography (Hornyak et al. 2008; Madou 2011).

Physical and chemical characteristics of nanoparticles are important determinants in their functionality and efficiency when they are used in agriculture. At nan oscale level, divergence in characters occurs in nanomaterials from their parent bulk materials due to changes in size, shape, and internal structure. Although it is very difficult to predict the exact characteristics of nanomaterial because of nano-size, different techniques such as x-ray diffraction, x-ray photoelectric spectroscopy, and electron microscopy, however, have been helpful in identifying some basic properties of the studied nanomaterial which can direct their appropriate application (Khan et al. 2019). The physical and chemical properties of nanoparticles greatly vary with the nature of nanoparticles and mode of synthesis. Organic and inorganic nanoparticles definitely exhibit different properties. It has been observed that nanoparticles below the range 20–30 nm are less stable due to interfacial tensions (Subbenaik 2016). The smaller sizes of nanoparticle may contribute to enhanced chemical reactivity due to instability and increased surface area comparative to volume (Gatoo et al. 2014). Depending on the potential application and with specific context in agriculture, size, surface area, surface charge, and surface reactivity of nanoparticles play central roles in highlighting the use of such materials (Bhatia 2016; Subbenaik 2016). Kanwar et al. (2019) argued that surface area, pore size, and chemical reactivity of nanoparticles are ideally important components in their wide applicability. In a recent study, it was observed that gold (Au) nanoparticles exhibited high reactivity to less-active molecules by transferring electron density (Oliver-Meseguer et al. 2018). Reches et al. (2018) demonstrated that smaller size of nanoparticles (Al_2O_3, Fe_2O_3, SiO_2, TiO_2) resulted in their high reactivity although pH and other factors influenced the rate of reactivity. Xu et al. (2018) discussed that nanoparticles possess high surface energy and less tendency towards equilibrium, thus ascribing them more reactive than their bulk counterparts. High reactivity and ability of oxidative breakdown of Rhodamine B by manganese oxide nanoparticles have been demonstrated (Soejima et al. 2018).

17.3 Application of Nanoparticles as Nanofertilizers and Nanopesticides

In general, nanofertilizers refer to small-sized particles obtained from large-sized materials (mineral fertilizers, plant parts, fungi, etc.) through a variety of physical and chemical techniques employing the science of nanotechnology (Singh et al. 2017). Nano forms of macro- and micronutrients such as nitrogen, phosphorus, potassium, zinc, magnesium, manganese, iron, etc. which are essentially required for better growth performance of plants when used in the capacity of fertilizers are termed as nanofertilizers (Dimkpa and Bindraban 2017). Kah et al. (2018) in a comprehensive review categorized nanoparticles into three groups: (a) nanoparticles which are prepared from macronutrients, (b) nanoparticles prepared from micronutrients, and (c) nanoparticles which are used as fertilizer enhancers. Guo et al. (2018) discussed the potential uses of nanoclays, hydroxyapatite nanoparticles, mesoporous silica, polymeric nanoparticles, carbon-based nanomaterials, and other particles as nanofertilizers. Raliya et al. (2017) described nanofertilizers as compounds which are based on nano-formulations and which fulfill nutrient requirements of plants. These nanoscale fertilizers bear several advantages over mineral fertilizers. They increase soil fertility, reduce the risk of toxicity and minimize the application rate (Naderi and Danesh-Shahraki 2013). Alipour (2016) stated that nanofertilizers are effective than conventional fertilizers due to low toxicity and efficient nutrient supply.

In several studies, efficient properties of nanofertilizers on different plants have been reported (Table 17.1). Panwar (2012) demonstrated that zinc oxide nanofertilizers had stimulatory effects on nutrient uptake, growth, and biomass production in tomato. Similar results were also reported by Tarafdar et al. (2014) who applied ZnO nanofertilizers to pearl millet which exhibited an improved growth, physicochemical and yield response when compared to control plants. Application of foliar spray with ZnO and iron nanofertilizers has been shown to reduce the adverse effects of salinity on growth, photosynthetic pigments, and biomass of moringa (*Moringa peregrina*) (Soliman et al. 2015). Kalteh et al. (2018) obtained promising results for chlorophyll, proline, biomass, and growth in basil (*Ocimum basilicum*) under salinity stress when silica nanofertilizers were applied. More recently, Rossi et al. (2019) evaluated the effects of ZnO nanoparticles on physiological and growth responses of coffee. They recorded a significant increase in photosynthetic rate, nutrient uptake, and growth of the treated plants.

Formulations or products which encompass nanoscale materials that are used for plant protections and disease control are termed as nanopesticides (Kah et al. 2013). In a comprehensive review dealing with nanopesticides and nanofertilizers, Kah (2015) outlined that nanopesticides may not explicitly mean “nano-sized particles” but may also include products which possess diverse properties, nature, novel and efficient actions than traditionally used agrochemicals. Nanoemulsions, nanocapsules, or metal nanoparticles have been widely ascribed to show superior activities in controlling plants’ diseases than pesticides (Kookana et al. 2014; Chhipa 2017). Conventional pesticides have several disadvantages among which poor solubility is

Table 17.1 Different nanoparticles used as "nanofertilizers" for enhancing performance of different crops

Nanofertilizers	Crop plants	Effects	References
Si NPs	Basil (*Ocimum basilicum*)	Improved photosynthetic pigments and growth and biomass under salinity stress	Kalteh et al. (2018)
Zn and Fe NPs	Moringa (*Moringa peregrina*)	Improved growth and biomass	Soliman et al. (2015)
Zn and B NPs	Pomegranate (*Punica granatum*)	Increased nutrient status, fruit quality and yields	Davarpanah et al. (2016)
Chitosan nanoparticles	Wheat (*Triticum aestivum*)	Enhanced growth and yields	Abdel-Aziz et al. (2016)
Carbon nanotubes and chitosan NPs	French bean (*Phaseolus vulgaris*)	Improved nutrient and water uptake, and growth	Hasaneen et al. (2016)
Fe and Mn NPs	Lettuce (*Lactuca sativa*)	Growth improvement	Liu et al. (2016)
FeO NPs	Pea (*Pisum sativum*)	Root growth improved	Palchoudhury et al. (2018)
Chitosan and Mg NPs	Sesame (*Sesamum indicum*)	Conferred drought resistance	Varamin et al. (2018)
Zn and B NPs	Coffee (*Coffea arabica*)	Enhanced growth	Wang and Nguyen (2018)
Zn NPs	Cotton (*Gossypium* sp.)	Improved growth under salinity stress	Hussein and Abou-Baker (2018)
Fe, Mg, and Zn NPs	Black cumin (*Nigella sativa*)	Increased yield and essential oil	Rezaei-Chiyaneh et al. (2018)
Fe chelate and Fe oxides NPs	Alfalfa (*Medicago sativa* L.)	Enhanced biochemical and growth parameters	Askary et al. (2018)
Bioorganic nanofertilizers	Barley (*Hordeum vulgare*)	Yield increments	Spruogis et al. (2018)
Fe, Ti and Zn NPs	Common bean (*Phaseolus vulgaris*)	Greater N uptake, growth and biochemical traits	Medina-Pérez et al. (2018)
Chitosan nanoparticles	Wheat (*Triticum aestivum*)	Improved biochemical attributes	Abdel-Aziz et al. (2018)
Chitosan nanoparticles	Coffee (*C. arabica*)	Growth improvement	Ha et al. (2019)

a significant issue and for improving their solubility potentials, surfactants and diverse organic solvents are generally added to them but they incur costs and environmental problems (Hayles et al. 2017). Nanoparticles when used as nanopesticides on the other hand may contribute to increased solubility of the formulations, increased specificity, reduced risk of toxicity, and efficient target delivery (Hayles et al. 2017; Mishra et al. 2018). Depending on nature, type, method of formulations, and purpose, nanopesticides may be categorized as nanoemulsions, polymer-based nanopesticides, clay-based nanopesticides, nanoherbicides, nanohybrids and nanogels, nanofibers, nanosuspensions, nanoliposomes, silica, metals, and oxides (Balaure et al. 2017; Pandey et al. 2018).

Table 17.2 illustrates role of nanopesticides in controlling different plant diseases. In a greenhouse trial, Elmer and White (2016) sprayed tomato plants with nanoparticles of different metal oxides (AlO, CuO, ZnO, MnO, FeO) and assessed their effect on disease severity caused by *Fusarium* sp. and they observed a significant reduction in disease severity and consequent improvements in growth of challenged plants. CuO nanopesticides were shown to exhibit strong antifungal potentials against *Fusarium oxysporum* causing wilt disease in water melon (Elmer et al. 2018). Hao et al. (2018) evaluated carbon- and metal-based nanoparticles for their efficacy against viral infection in tobacco. They found that turnip mosaic viral infection reduced considerably and biomass was improved in response to

Table 17.2 Role of different nanopesticides in plant protection

Nanopesticides	Disease/pathogen	Host plant	Effects	References
Silver nanoparticles (AgNPs)	Early blight/*Alternaria solani*	Tomato	Reduction in fungal growth	Abdel-Hafez et al. (2016)
Silver nanoparticles (AgNPs)	Wilt/*Fusarium oxysporum*	Tomato (*Solanum lycopersicum*)	Antifungal effects	Madbouly et al. (2017)
CeO_2	Wilt/*Fusarium oxysporum*	Tomato (*S. lycopersicum*)	Disease suppression by 35–57%	Adisa et al. (2018)
Zn NPs	Cercospora leaf spot/*Cercospora beticola*	Sugar beet (*Beta vulgaris*)	Reduced disease incidence and severity	Farahat (2018)
Si and Ti NPs	Powdery mildew/*Blumeria graminis*	Wheat (*Triticum aestivum*)	84–93% reduction in disease severity	Farhat et al. (2018)
Chitosan nanoparticles NPs	Downy mildew/*Sclerospora graminicola*	Pearl millet (*Pennisetum glaucum*)	Induced resistance to disease	Siddaiah et al. (2018)
Chitosan nanoparticles NPs	Early blight/*Rhizoctonia solani*	Tomato (*S. lycopersicum*)	Reduced pathogenic infection	Nadendla et al. (2018)
AgNPs	Different fungal diseases	Tomato (*S. lycopersicum*)	Inhibition in fungal growth and reduced disease symptoms	Elshahawy et al. (2018)
CuO	Bacterial wilt/*Ralstonia solanacearum*	Tobacco (*Nicotiana tabacum*)	Antibacterial potentials	Chen et al. (2019)
Chitosan nanoparticles NPs	Fusarium wilt/*Fusarium andiyazi*	–	Inhibition in mycelia growth	Chun and Chandrasekaran (2019)

nanopesticides application. A concentration of 1000 mg/L of CuO nanopesticides caused significant suppression of *Fusarium* wilt disease in water melon (Borgatta et al. 2018). Sathiyabama and Manikandan (2018) also reported that application of copper-chitosan nanoparticles elevated growth and yield in finger millet by 89% while suppressing the adverse effects of blast disease up to 75%. Hao et al. (2019) in a recent study recorded that treatment of roses with different nanopesticides (rGO, CuO, TiO_2) reduced powdery mildew caused by *Podosphaera pannosa*.

17.4 Prospects and Challenges

Human population increase and agricultural intensification have linked field crops and their production output with extensive use of agrochemicals. These chemicals though effective in achieving the targets, their poor solubility, nutrient losses, and inefficient uptake by plants, and contribution towards polluting water, soil and air make them less attractive for those who foresee challenges to ecological and environmental sustainability. Thus smart use of agrochemicals is the only way to safeguard the fate of ecosystem and environment. Many experts believe that nanoparticles in the form of nanopesticides and nanofertilizers can increase the efficiency of purposes for which they are applied by reducing nutrient losses from their counterpart agrochemicals (Kah et al. 2018). Reports have demonstrated their solubility as superior, less toxic, and efficient in delivery than traditional agrochemicals (Hayles et al. 2017; Mishra et al. 2018). They are regarded as smart nanotools to enhance the nutrient uptake and reduce their losses, and to precisely manage the inputs of chemicals (Kah 2015). Chhipa (2017) asserted that nanofertilizers developed with carbon nanotubes, P, K, Fe, Mn, Zn, Cu, and Mo while nanopesticides with copper, zinc, silver, and iron are more effective than widely used fertilizers and pesticides by providing higher performance.

Besides their excellent role in enhancing soil fertility, nutrient management of plants, smart delivery, and protective capacities, wide adoption of nanofertilizers and nanopesticides as analogue to their counterparts in agriculture has not been encouraging because of many challenges. First, since nanotechnology is still an emerging and naïve discipline, formulation of nano-agrochemicals directing sustainability of the environment is a challenging task. Secondly, costs, legislation, and marketing of nano-agrochemicals seem to offer hurdles in their prospective uses. Thirdly, gap of knowledge about their eco-toxicity, environmental implications, and adverse effects in the long term make score of concerns about their use in agriculture (Dubey and Mailapalli 2016).

17.5 Conclusions

Nanoparticles which generally mean nano-sized material have been extensively employed in agriculture for nutrient supply and protection of crop plants. They have been used as nanofertilizers and nanopesticides which in several cases have revealed efficiency over their counterparts. Nanofertilizers and nanopesticides are engineered through a variety of techniques among which physical and chemical methods employing "top-down" or "bottom-up" approaches are significant. Nanofertilizers and nanopesticides are generally conceived more efficient than commonly used agrochemicals because of their ability to reduce nutrient losses, improve solubility, enhance nutrient uptake, and reduce the rate of application of traditional fertilizers and pesticides. Development of nanoparticles particularly from carbon nanotubes, P, K, Fe, Mn, Zn, Cu, Mo, copper, zinc, silver, and iron has greater potentials of utilization as nanofertilizers and nanopesticides. Extensive studies on devising sustainable nanoparticles for agricultural input are necessary to enhance crop production and protection against pathogens.

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