

Review Article

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Nanotechnology in Agriculture- A Review

Anupama Rawat*, Rajew Kumar, Bandana Bhatt and Pradeep Ram

Department of Agronomy, College of Agriculture, G. B. Pant, University of Agriculture and Technology, Pantnagar, U. S. Nagar (263145), Uttarakhand, India

*Corresponding author

ABSTRACT

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To meet the food requirement of a huge population the food grain production need to be enhanced accordingly. However the goal of higher production must not come at the cost of heavy exploitation of natural resources. In order to attain higher yields, need of the hour is to develop and promote new technologies and reform agricultural research. Nanotechnology holds promise in improving the fertilizer use efficiency of fertilizers. The unique properties can be exploited beneficially for improving the nutrient use efficiency. Since the research work on nanotechnology in agriculture is at nascent stage there is a dearth of information on the response of nanomaterials application in crops. An effort has been made to review and extend the work done worldwide on these minerals which can efficiently deliver fertilizers, herbicides, pesticides, plant growth regulators etc.

Introduction

Fertilizer being the major determinant of yield has gained much attention in research since long time. Though the research has achieved high productivity still the nutrient use efficiency is surprisingly low. Subhramanian *et al.*, (2015) reported that the nutrient use efficiency of N, P and K stand still at 30-35%, 18-20% and 35-49 % respectively. Nanotechnology is a new emerging and fascinating field of science that permits advanced research and nanotechnological discoveries which could open up novel applications in the field of biotechnology and agriculture (Siddiqui *et al.*, 2015).

Chinnamuthu and Boopathi (2009) stated that nanotechnology is a powerful technology having the ability of creating massive changes in food and agriculture. Basic concept of nanotechnology is that a substance can be manipulated at an atomic level. It is like working with the smallest possible particles. Today, nanotechnology is a rapidly growing interdisciplinary field of science that combines engineering with physics, chemistry and biology and removes the traditional boundaries between them (Ray *et al.*, 2009). Development of various technologies are facilitated and accelerated by nanotechnology and enables a greater degree of integration and coverage across the various

disciplines, technologies and technical products (Shand and Wetter, 2006). Royal Society defines nanotechnology as “the designs, characterization, production and application of devices, system and structure by controlling their size and shape at nano scale” (RSRAE, 2004). Nanotechnology has presented its great prospects in the breakthrough of controlled release fertilizer, a technical bottleneck using nano-structured or nano-scale materials such as fertilizer carriers or controlled-release for constructing so-called smart fertilizer (Cui *et al.*, 2009). Nanotechnology is a smart and intelligent system that delivers precise amount of nutrient and other agrochemicals required by plants, minimising use of pesticides and antibiotics (Sharon *et al.*, 2010).

Nano particles

Nano-particles are atomic or molecular aggregates of size in nano-scale range of 1-100 nm (Rai and Ingle, 2012). Nano-particles possess unique and novel physicochemical properties like high specific surface area, highly reactive, tunable pore size and particles morphology. Nano-particles can serve as “magic bullets” that contain herbicides, fertilizers, nano-pesticides or genes which are target specific cellular organelles in plants to release their content. The effect of nano-particles varies from plant to plant and depends on their mode of application, concentrations and size (Siddiqui *et al.*, 2015). Nano particles generally have higher intercellular uptake than micro sized particles and due to their small size and mobility are available to wide range of biological target.

Nano-particles have enhanced reactivity because of increased solubility, greater proportion of surface atoms relative to the interior of a structure, unique magnetic properties, electronic states and catalytic reactivity that differ from equivalent bulk

materials (Agrawal and Rathore, 2014). The matter at nano-scale has altered properties that differ from those observed at macroscopic level. The change in the properties is because of the reduced molecular size and also because of the changed interactions between the molecules.

Shah and Belozerova (2009) reported that recently nano-particles are being used in plant growth and insect pest control. The unique physicochemical properties of nano-particles have the potential to boost the plant's metabolism (Giraldo *et al.*, 2014). Engineered nano-particles can enter into the plant cells and can also transport DNA and chemicals into plant cells (Torney *et al.*, 2007). Nano-particles of gold, silver, zinc, zinc oxide, copper, aluminium, silica cesium oxide, titanium dioxide and magnetized iron have found their application in agriculture (Zhang and Webster, 2009).

Nano-fertilizers

Nano-fertilizers or nano-encapsulated nutrients might have novel properties that are effective to crops, controlled release of chemical nutrients and release nutrients on demand that regulate plant growth and enhance target activity (De Rosa *et al.*, 2010). Nano-fertilizers can enhance growth and yields of the plant by supplying one or more nutrients whereas nanomaterial-enhanced fertilizers improve the performance of conventional fertilizers, but do not provide crops with nutrients directly. Nano-fertilizers compared with the conventional ones, are expected to significantly improve growth and yields of crops (Liu and Lal, 2015). These nanofertilizers are being developed for their slow release and efficient dosages for plants (Singh, 2012). It is reported that nano-composites and nano-fertilizers can control nutrient release from fertilizer granules to enhance nutrient use efficiency (Subramanian

et al., 2007). Combination of Nano-fertilizers and nanodevices synchronizing the release of fertilizers N and P with their uptake by crop, preventing undesirable nutrient losses to soil, air and water through direct internalization by crops, avoiding nutrient interaction with microorganisms, soil, water and air (DeRosa *et al.*, 2010). Some beneficial effects of nano-fertilizers include increase in NUE (Nutrient Use Efficiency), enhanced yield and reduced soil pollution (Naderi and Danesh-Sharaki, 2013). Chitosan nano particles can be used for controlled release of NPK fertilizer sources such as urea, potassium chloride and calcium phosphate (Corradini *et al.*, 2010).

Biobased nano particles synthesis and characterization

Biological approach uses plant extracts and microorganisms for the synthesis of metal nano particles have been suggested recently to substitute hazardous methods (Singh *et al.*, 2011). As the physical and chemical processes are costly there rose a need to search for a cheaper pathway for synthesis of nano particles. Scientists used microorganisms and then plant extracts. There are various processes in nature for the synthesis of nano- and micro-length scaled materials which have contributed to the development of new and largely unexplored area of research based on the biosynthesis of nanomaterials (Mohanpuria *et al.*, 2007). Plant extracts have combinations of molecules that perform both as reducing as well as capping agents in nano particles synthesis (Singh *et al.*, 2010). Using alfa alfa plants gold nano particles have been synthesized (Torresday *et al.*, 2002).

Cobalt nano particles were synthesized by Ahmed *et al.*, (2016) using leaf extracts of plant *Nerium indicum* or *Conocarpus erectus*. The nano particles so formed were characterized using SEM (scanning electron microscope) for their external appearance.

Vegetable waste can be used for nano particles synthesis. The extract of *Pisum sativum* peel has antioxidative potential (Dixit and Kar, 2009). Pure CaSO₄ nano particles were synthesized by dissolving calcium acetate in distilled water and stirring it for 5 minutes in magnetic stirrer followed by dissolving of ammonium sulfate in a mixture of ethanol and distilled water for 10 minutes on stirrer. Brij35 was dissolved in distilled water for 5 minutes on a stirrer and added to calcium acetate solution. pH of calcium acetate is maintained to 4 by adding sulphuric acid slowly to it. This solution is then mixed with ammonium sulphate solution and stirred for 15 minutes and the final solution was then centrifuged. The solid part was collected and washed with ethanol, dried in oven at 90 °C for 2 hours followed by heating at 350 °C for 1 minute to let the nanostructure anneal. The final product was confirmed by XRD and it was CaSO₄ nanostructure and its particles size was confirmed by SEM (Mehrabi *et al.*, 2014). Nano-gypsum prepared by flame spray synthesis had improved mechanical properties due to the presence of CaSO₄ nano-needles as confirmed by SEM (Osterwalder *et al.*, 2007).

Nano-particles of zinc, nickel, silver, cobalt and copper have known to be synthesized inside living plants of *Medicago sativa*, *Helianthus annuus*, and *Brassica juncea*. *Brassica juncea* had better metal accumulating power and later converting it as nano particles (Bali *et al.*, 2006). Copper nano particles were synthesized by reducing CuSO₄.5H₂O solution using onion extract by stirring it continuously at 100 °C. nano particles formed were analysed by Zeta potential Analyser (Hafeez *et al.*, 2015). Silver nano particles were synthesized using aqueous leaf extract of neem (*Aradirachta indica*) which acted both as reducing and stabilising agent. The size distribution of these synthesized nano particles was confirmed by DLS and found to 34nm (Ahmed *et al.*, 2015). Savithamma *et*

al., (2012) conducted an experiment to see the effect of nano particles on seed germination and seedling growth of *Boswellia ovalifoliolata*- an endemic and endangered medicinal tree taxon. Silver nano particles were synthesised using dried stem bark *Boswellia ovalifoliolata*. The bark extract reduced silver ions leading to formation of silver nano particles in solution. The formed nano particles characterization was carried out by SEM (Scanning electron microscopy) and UV-VIS spectrum. Seeds were treated with different concentrations of silver nano particles and were germinated on MS basal medium and they found that treated seeds showed higher germination percentage and plant height compared to control. Similarly, Manokari *et al.*, (2016) synthesized zinc oxide nano particles using extracts of roots, shoot, leaves, flowers and fruits of *Melia azadirach* L. and were characterized and confirmed by UV- Visual spectral studies.

Effect of nano-particles on plant growth

Seed germination

Engineered carbon nanotubes boost seed germination, growth and development of plants (Lahiana *et al.*, 2013). Application of nano-particles has been proved to be effective in enhancing seed germination and seedling growth (Pandey *et al.*, 2010). Nano-particles facilitate the absorption of water and nutrients by roots and enhance antioxidant enzyme activity such as catalase and superoxide dismutase. Thus, nano-particles can improve plant's tolerance against different stresses (Harrison, 1996).

Application of nanofertilizers promoted growth, development, antioxidant activity and TPC (Total Phenol Content) in rice thus demonstrating its potential to improve plant nutrition and crop production (Benzon *et al.*, 2015). Nano materials have porous and hydrated nature due to which they control

permeability, moisture retention, solute transport and availability of nutrients in soils. Nano materials also control exchange reaction of dissolved inorganic and organic species between the colloidal surfaces and soil solution. The physic-chemical properties of nano-composites provide much reactivity to biotic and abiotic processed (Navrotsky, 2004).

Lu *et al.*, (2002) conducted an experiment to study the effect of mixtures of nano-TiO₂ and nano-SiO₂ on soybean seeds. They found that, the nano particle mixtures increased enzymatic activity of nitrate reductase in soybean resulting in enhanced germination and growth. Yasmeeen *et al.*, (2015) conducted a laboratory experiment to see the effect of Ag, Cu and Fe nanoparticles on wheat germination. Seeds were soaked in distilled water and suspension of nano particles for 2 hours and then washed the seeds with distilled water three times followed by incubating seeds in petri-plates on filter papers in distilled water or nano particles suspension. Khodakovskaya *et al.*, (2009) observed that carbon nano-tubes (CNTs) penetrate tomato seeds and effect their germination and growth rates. The seeds that were germinated on medium containing CNTs had dramatically higher germination compared to control. Analysis indicated that CNTs were able to penetrate the thick seed coat of tomato and favoured water uptake, which improved seed germination and growth of tomato seedlings.

Prasad *et al.*, (2012) conducted an experiment to observe the effect of nanoscale zinc oxide particles on the germination, growth and yield of peanut seeds treatment and foliar spray was done. The results revealed that a higher amount of Zn was present in the seeds treated with nano ZnO. It improved the germination, root growth, shoot growth, dry weight and pod yield of the treated seeds. With foliar application of nano ZnO, zinc uptake by the leaf and kernel was significantly higher

compared to chelated zinc sulphate. Zhu *et al.*, (2008) reported that *Cucurbita maxima* growing in an aqueous medium containing magnetic nano particles can absorb, accumulate and move the nano particles in the plant tissues, whereas *Phaseolus limensis* is not able to absorb and move these particles. It indicates that different plants respond differently to the same nanoparticle

The effect of nano particles is different in different plant species and this can be justified by the work of Gruyer *et al.*, (2013). Hethey reported that silver nano particles have both positive and negative effect on root elongation depending upon the plant species. They found that root length was increased in barley but inhibited in lettuce Suriyaprabha *et al.*, (2012) reported that application of nano SiO₂ to maize seeds increased germination by providing better nutrient availability, pH and conductivity to the growing medium. Ramesh *et al.*, (2014) conducted an experiment in wheat and reported that ZnO nano particles at lower concentration exhibits beneficial effect on seed germination whereas, high doses of ZnO nano particles impaired seed germination. Same results were obtained by Prasad *et al.*, (2012) in groundnut. They conducted an experiment to study the effect of zinc oxide nano particles on seed germination and seedling growth of groundnut and reported that, seeds treated with nano sized zinc oxide @ 1000 ppm showed significant increase in germination, shoot and root length and vigour index over control. Rezvani *et al.*, (2012) reported that silver nano particles induce root growth by blocking ethylene signalling in *Crocus sativus*.

Seedling growth

Canas *et al.*, (2008) conducted an experiment in onion and cucumber to see the effect of nanofunctionalized carbon nanotubes (CNTs) and they found that CNTs enhanced root

elongation. Dhoke *et al.*, (2013) conducted an experiment to see the effect of suspension of nano particles on the growth of mung seedlings by foliar spray. They reported an increase in number of roots and root length, shoot length in the presence of nano particles compared to the control. Application of iron oxide nano particles in pumpkin enhanced root elongation and this was attributed to Fe-dissolution. Tarafdar *et al.*, (2014) reported that zinc nano fertilizer application on pearl millet improved root length, shoot length, root area, chlorophyll content, plant dry biomass and increased grain yield and nano titanium dioxide increased grain number/spike.

Taran *et al.*, (2017) conducted an experiment to see the effect of zinc and copper nano particles on drought resistance of wheat seedlings and concluded that nano particles of zinc and copper resulted in increase in catalase and SOD activity that characterize increase in antioxidative status of plant at the influence of nano particles under drought condition. Under the influence of Cu and Zn nano particles there was a change in the ratio of chlorophyll a to chlorophyll b, along with high carotenoids content in leaves.

Saedpanah *et al.*, (2016) conducted an experiment to study the effect of nano fertilizers, ascorbic acid and salicylic acid on agronomic traits of forage maize. It was observed that application of nano chelate iron increased leaf chlorophyll, plant height and leaf dry weight over other treatments.

Mohamed (2015) conducted an experiment to study the effect of titanium nano particles on growth, yield and chemical constituent of coriander plants. He found that titanium nano particles significantly increased plant height, no. of branches and fruit yield and also increase in amino acids, total sugars, total indols, total phenols and pigments.

Concentration of nano particles and plant species

It is important to identify and know the limit or concentration of different nano particles within which it is beneficial and beyond which it has negative effect on plants. Effect of nano particles on plants depends upon the type, size, shape and concentration of nano particles and plant species. Raskar and Laware (2014) studied the effect of zinc oxide nano particles on seed germination and seedling growth in onion and found that at lower zinc nano particles concentration seed germination increased but a higher concentration seed germination decreased.

Effect of nano particles on seed germination depends upon nano particles's concentration and varies plant-plant (de la Rosa *et al.*, 2013). Application of silver nano particles in wheat showed enhanced yield @ 25 ppm but further increase in concentration reduced the yield, number of grains/spike and 100 grain weight (Jhanzab *et al.*, 2015).

Zinc nano particles were foliar sprayed on 10 days old chickpea seedlings @ 1.5 or 10 ppm. The results revealed that applied nano particles promoted shoot dry weight at 1.5 ppm compared to ZnSO₄ and normal ZnO but at 10 ppm root growth was inhibited and concluded that response of plants to nano particles varies with concentration.

Jhanzab *et al.*, (2015) synthesized silver nano particles via chemical method and conducted pot experiment to see the effect of Ag nano particles on growth, yield and nutrient use efficiency of wheat.

The results revealed that application of Ag nano particles @ 25 ppm enhanced root growth, no. of grains/pot, yield/pot and N, P, K use efficiency significantly.

Mechanism of nano particles uptake

Pore diameter of cell wall is in the range of 5-20 nm (Fleischer *et al.*, 1999) and this determines sieving properties of plant cells and act as a barrier against easy entry of any external substance of large size. Nano-particles having less diameter than cell's pore diameter, can easily cross this barrier and make their entry into the plant cell (Navarro *et al.*, 2008). Nano-particles after entering the cells move cell to cell through plasmodesmata. Nano particles upon their interaction with wall proteins and polysaccharide enlarge the pore size of plants' cell wall and thus results in successful entry to plant system (Nair *et al.*, 2010). Use of ZnO nano-particles enhances permeability of cell and creates holes in bacterial cell wall (Brayner *et al.*, 2016).

Eichert *et al.*, (2008) reported that application of nano-particles on leaf surface enters the plant cell via stomatal openings or bases of trichomes and translocated to various plant tissues.

In conclusion, nanotechnology holds promise in enhancing crop yields by improving the fertilizer use efficiencies. Nanoparticles accrue their unique properties from their smaller size, high specific surface area, high surface energy and high solubility. Owing to these unique properties, their uptake by plants is increased. Hence, nanotechnology can be used in agriculture to deliver agrochemicals smartly to the site of action with minimal wastage.

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