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REVIEW PAPER

Application of Nanotechnology in Soil and Plant System with Special Reference to Nanofertilizers

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ABSTRACT

Agriculture is the backbone of developing countries, with more than 60% of the population depending on it for their livelihood. Presently, the agricultural sector is facing various global challenges; climate change, urbanization, sustainable use of resources, and environmental issues such as run-off and accumulation of pesticides and fertilizers. These situations are further exacerbated by stagnation in crop yields, low nutrient use efficiency, declining soil organic matter, multi-nutrient deficiencies, climate change and shortage of labour besides exodus of people from farming. 35-40% of the crop productivity defends upon fertilizers but some of the fertilizers effect the plant growth directly. To overcome all these drawbacks a smarter way i.e., nanotechnology can be one of the source. Since fertilizers are the main concern, developing nano based fertilizer would be a new technology in this field. This review is focused on fate of nano fertilizers in soil, uptake, translocation of nano fertilizers in plants and, nano fertilizers on plant growth and development.

Key words *Agriculture, nanotechnology, nanoencapsulation, nanofertilizers, plant growth*

The term "Nanotechnology" was first defined in 1974 by Norio Taniguchi of the Tokyo Science University. Nanotechnology, abbreviated to "Nanotech", is the study of manipulating matter on an atomic and molecular scale. By and large nanotechnology deals with structures in the size range between 1 to 100 nm and involves developing materials or devices within that size. At the nanoscale the matter presents altered properties which are novel and very different from those observed at macroscopic level. The change in properties is due to the reduced molecular size and also because of changed interactions between molecules. The properties and possibilities of nanotechnology, which have great interest in agricultural revolution, are high reactivity, enhanced bioavailability and bioactivity, adherence effects and surface effects of nanoparticles (Gutierrez *et al.*, 2011). Customized manufactured products are made from atoms; their properties depend on how those atoms are arranged.

Smaller particles allow better coverage of surface area. Nano sized particles can even pass through the cell wall in plants and animals. Nanotechnologists use this process to deliver at cellular level which is more effective than the conventional method. The key focus areas for nanotechnology agricultural research are nanogenetic manipulation of agricultural crops, agricultural diagnostics, drug delivery and nanotechnology, nano biosensors, nano pesticides, nano herbicides and nano fertilizers.

Nanofertilizers

Nano fertilizers are synthesized by fortifying nutrients singly or combination on to the adsorbents with nano-dimension. Nano fertilizer refers to a product that delivers nutrients to crops in one of three ways the nutrient can be encapsulated inside nano-materials such as nanotubes or nanoporous materials, coated with a thin protective polymer film and delivered as particles or emulsions of nanoscale dimensions.

According to the report of Iranian Nanotechnology Initiative Council (2009), Iranian researchers have produced the first nano organic iron chelated fertilizers in the world. Fertilizer particle can coated with nano membranes that facilitate in slow and steady release of nutrients this process helps to reduce loss of nutrients while improving fertilizer use efficiency of crops (Subramanian and Tarafdar, 2009).

Preparation of Nano Fertilizers

The loading of nutrients on the nanoparticles is usually done by absorption on nanoparticles, attachment on nanoparticles mediated by ligands, encapsulation in nanoparticulate polymeric shell, entrapment of polymeric nanoparticles and synthesis of nanoparticles composed of the nutrient itself. Basically there are two approaches for nanoparticle synthesis namely top down approach and bottom up approach. In top down approach nano objects and materials are created by larger entities without bouncing its atomic reactions usually top down approach is practiced less as compared to the bottom up approach. Top down approach methods includes, milling or attrition, chemical methods and volatilization of a solid followed by condensation of the volatized

Table 1. Comparison of nano fertilizers and conventional fertilizers applications (Cui *et al*., 2010)

Properties	Nano fertilizers	Conventional fertilizers
Solubility and dispersion of mineral micronutrients	Improve solubility and dispersion of insoluble nutrients in soil, reduce soil absorption and fixation and increase the bioavailability	Less bioavailability to plants due to large particle size and less solubility
Nutrient uptake efficiency	Might increase fertilizer efficiency and uptake ratio of the soil nutrients in crop production and save fertilizer resource	Bulk composite is not available for roots and decrease efficiency
Controlled-release modes	Release rate and release pattern of nutrients for water-soluble fertilizers might be precisely controlled through encapsulation in envelope forms	Excess release of fertilizers may produce toxicity and destroy ecological balance of soil
Effective duration of nutrient release	Nanofertilizers can extend effective duration of nutrient supply of fertilizers into soil	Used by the plants at the time of delivery, the rest is converted into insoluble salts in the soil
Loss rate of fertilizer nutrients	Reduce loss rate of fertilizer nutrients into soil by leaching and/or leaking.	High loss rate by leaching, rain off and drift.

components (Ghorbani, 2014). In the bottom up approach different materials and devices are constructed from molecular components of their own. The methods include sol gel processing, chemical vapour deposition, plasma or flame spraying synthesis, laser pyrolysis and atomic or molecular condensation.

An Indian agro-scientist has innovated nano fertilizers using biosynthesis, for the first time in the world. The new variant of fertilizer was developed by Dr. Jagdish Chandra Tarafdar of the Central Arid Zone Research Institute under the ICAR. The fertilizer was prepared by developing a methodology to use microbial enzymes for breakdown of the respective salts into nano-form. "Since it is complete bio-source, nano fertilizer is eco-friendly and improves soil aggregation, moisture retention and carbon build-up. There is no health hazard and is suitable for all crop varieties including food grains, vegetables and horticulture," said Dr. Tarafdar. IARI has signed a Memorandum of Understanding with Secunderabad-based Prathista Industries Limited, for commercially exploitation of the process.

Fate Nano Fertilizers in Soil

The use of nano fertilizer in soil leads to increased efficiency of the elements, reduce the toxicity of the soil, to at least reach the negative effects caused by the consumption of excessive consumption of fertilizers and reduce the frequency of application of fertilizers (Naderi *et al*., 2011). Production of nano fertilizers, this nano compounds rapidly and completely absorbed by plants and fix it's nutrients shortages and needs. Base of iron nano fertilizer is natural quality and it made of organic and mineral material. This fertilizer is fully compatible with the environment and agricultural farms and organic materials with added to the soil to make it more organic material is to be.

Clays are sub-micrometric soil particles. Common clays are layered phyllosilicate materials, with a polymeric silicate base, which are nano dimensional in one plane. Transmission electron (TEM) and high resolution transmission electron (HRTEM) microscopy showed that clays are composed of stacked tetrahedral and octahedral sheets (Wilson *et al.,* 2008). Nanoparticles such as iron and silica originate from natural weathering of bedrocks. Other naturally occurring nanoparticles are iron oxides (2-5 nm length), as colloidal phases of ferrihydrite, associated with organic matter in river-borne material (Allard *et al*., 2004). These nano compounds are rapidly and completely absorbedby plants.

Nano porous Zeolite is slow release of the fertilizer to the plant, this way of doing makes the plant to grab entire amount of nutrients from the fertilizer supplied rather than the minimal uptake. Since it has larger surface area many molecules can fit into it and get released whenever the plant requires (Naderi and Shahraki, 2013). Its network of interconnected tunnels and cages can be loaded with nitrogen and potassium, combined with other slowly dissolving integrated containing phosphorus, calcium and a complete suite of minor and trace nutrients.

Dwairi (1998) suggested that zeolite impregnated with urea can be used as slow release fertilizer carrying the slow and steady release of N from nano-zeolite. Dwairi(1998) demonstrated that amending sandy soil with ammonium-loaded zeolite can reduce N leaching while sustaining growth of sweet corn and increasing N-use efficiency compared to ammonium sulphate. Zhou and Huang (2007) reported the slow and steady release of K from nano-zeolite. This may be due to the ion exchangeability of the zeolites with selected nutrient cations, zeolites can become an excellent plant growth medium for supplying plant roots with additional vital nutrient cations and anions. The nutrients are provided in a slow-release, plant root demand-driven fashion through the process of dissolution and ion exchange reactions. The adsorption of nutrients by plant roots drives the dissolution and ion exchange reaction, pulling away nutrients as needed. Sheta *et al*. (2003) suggested that natural zeolites, particularly clintopillonite have a high potential for Zn and Fe sorption with a high capacity foe slow release fertilizers. Slow release of Zn is attributed to the sparingly solubility of minerals and sequestration effect of exchanger, there by releasing trace nutrients to zeolite exchange sites where they are more readily available for uptakes by plants. Subramanian and Rahale (2012) reported that different concentration of zinc blended with zeolite, zinc sorption highest recorded with zeolite compared to montomorillonite and bentonite. In the same experiment slow release pattern of zinc less with the zeolite loaded with zinc, desorption upto 45 days compared to other clay minerals. Thirunavakkarasu and Subramanian (2014) have found that the SO_4^{2-} supply from fertilizer-loaded SMNZ (Surface Modified Nano-Zeolite) was available even after 912 hrs of continuous percolation, whereas SO_4^{2-} from $(NH4)_2SO_4$ was exhausted within 384 hrs. These properties suggest that SMNZ has a great potential as the fertilizer carrier for slow release of SO_4^{2-}.

The use of Zero-valent iron nanoparticles (nZVI) has been gaining increasing interest in the area of environmental remediation (Li *et al*., 2009). Transformation of a wide variety of environmental contaminants such as heavy metals, chlorinated hydrocarbons, pesticides, nitrate etc has been extensively documented (Li *et al*., 2009). nZVI is an excellent electron donor and has high capacity to reduce an array of toxicants, however its tendency for rapid oxidation and aggregation, reduces its reactivity.

Uptake, Translocation and Fate of Nano Fertilizers in Plants

The uptake, translocation and accumulation of nanoparticles depend on the plant species, age, growth environment, and the physicochemical property, functionalization, stability, and the mode of delivery of nanoparticles. The entry of nanoparticles through the cell wall depends on the pore diameter of the cell wall (5-20 nm) (Fleischer *et al*. 1999). Hence, nanoparticles or nanoparticle aggregates with diameter less than the pore size of plant cell wall could easily enter through the cell wall and reach up to the plasma membrane (Navarro *et al.* 2008). Functionalized nanoparticles facilitate the enlargement of pore size or induction of new cell wall pore to enhance the uptake of nanoparticles. Several reports have discussed the uptake of nanoparticles into plant cell via binding to carrier proteins through aquaporin, ion channels, or endocytosis (Nair *et al.* 2010). Further, nanoparticles can also be transported into the plant by forming complexes with membrane transporters or root exudates (Kurepa *et al.* 2010). Various other studies reported that nanoparticles could enter through stomata or the base of trichome in leaf (Uzu *et al.* 2010).

Zn in shoot and root was higher in plants sprayed with nano-Zn compared to control in pearl millet and cluster bean. Application of nano ZnO significantly decreased the C exuded from roots in both pearl millet and clusterbean. C exuded through roots was 2.19% of total C accumulated in plants for pearl millet and 0.81% for clusterbean studied by Burman *et al*. (2013). Raliya and Tarafdar (2013) reported that total soluble leaf protein, and plant P concentration were increased by 27.1 and 10.8%, respectively, by application of ZnO nanoparticle at 10 mg L^{-1} concentration, due slow release of nutrients. Prasad *et al*. (2012) revealed a significant increment in zinc content in leaves (42%, 29%) and kernels (42%, 36.6%) when supplied with nanoscale ZnO compared to chelated ZnSO4 (in *Rabi* seasons 2009 and 2010 respectively).

Effect of Nano Fertilizers on Plant Growth and Development

Nanoparticles interact with plants causing many morphological and physiological changes, depending on the properties of NPs. Efficacy of NPs is determined by their chemical composition, size, surface covering, reactivity, and most importantly the dose at which they are effective. Efficacy of NPs depends on their concentration and varies from plants to plants. Carbon nanotubes (CNT) are allotropes of carbon with cylindrical shape and can be utilized to use CNT as vehicle to deliver desired molecules either nutrient or biocides into the seeds during germination. Similarly, triazophos can also be effectively protected from hydrolysis in acidic and neutral media by including it in a nano-emulsion (Gutiérrez *et al*., 2011).

Prasad *et al.* (2012) reported that peanut seeds responded variably towards the treatment at various concentrations of both bulk ZnSO4 and nanoscale ZnO particles. The results from the bulk ZnSO4 treated seeds were not promising. Among the different nanoscale ZnO concentrations, 1000ppm showed the maximum and increased concentration (2000 ppm) showed decreased seedling vigor index. Nanoscale ZnO showed large root growth of seedling compared to bulk ZnSO4 and control. Prasad *et al*. (2012) observed that plant growth, in terms of plant height was significantly increased with 400 and 1000 ppm nanoscale ZnO compared to control and the respective bulk ZnSO4 concentrations. Seeds treated with 1000 ppm concentration of nanoscale ZnO recorded highest plant growth (15.4 cm) due to extended

Table 2. Beneficiary concentration(s) of nanoparticles for plants

Nanoparticle(s)	Beneficiary concentration(s)	Plant	Part of plant/process	Reference(s)
CNTs	40 µg/mL	*Lycopersicum esculantum*	Germination and seedling	Morla *et al*. (2011)
ZnO NPs	1.5 ppm (foliar spray)	*Cicer arietinum* L	Shoot dry weight	Burman *et al*. (2013)
Sulfur NPs	500,1,000,2,000 and 4,000 ppm	*Vigna radiata*	Dry weight	Patra *et al*. (2013)
SiO2NPs	15 kg/ha	*Zea mays L.*	Growth parameters	Suriyaprabha *et al*. (2012)
Iron oxide NPs	50 ppm (foliar spray)	*Vigna radiata*	Biomass	Dhoke et al. (2013)
CuO NPs	500 mg/kg (sand culture)	*Triticum aestivum*	Biomass	Dimkpa *et al*. (2012)

inter-nodal length. Such increase can be ascribed to higher precursor activity of nanoscale zinc in auxin production. Similarly 1000 ppm nanoscale ZnO produced early flowers compared to control and bulk ZnSO4.

The highest number of root nodule was found with sulphur application as SMNZ-NF @ 30 kg S ha^{-1} of 14.0, 42.3 and 63.0 (number) at 30, 60 DAS and harvest stage of groundnut respectively. The increases of root nodule might due to incremental levels of sulphur application which promotes nodule formation in legume crops. It is due to the fact that the nodulation in legumes is stimulated due to S application in soil and it helps in the production of large, branched and pinkish nodules leading to increased number and dry weight of nodules (Thirunavukkarasu and Subramanian, 2014).

Liang *et al*., 2013 reported that compared with conventional fertilizer, the carbon nano particles treatments 25, 75 and 125 mg pot^{-1} increased leaf area by 6.64%, 19.51% and 21.58% respectively, at the maturity stage. Raliya *et al*. (2014) studied that root length, root area and chlorophyll content significantly highest recorded with nano MgO (15ppm) application in clusterbean over control in 6-week-old plants. Rhizospheric microbial population increased between 11.8 and 13.8 % by application of ZnO nanoparticles during critical growth stage (6-weeks) of cluster bean (Raliya and Tarafdar, 2013).

Prasad *et al.* (2012) recorded 30.5% and 38.8% higher pod yield with the application of nanoscale ZnO at 2 g 15 L^{-1}+ NPK compared to NPK alone and 29.5% and 26.3% higher pod yield compared to chelated zinc at 30 g 15 L^{-1}+ NPK during 2008-09 and 2009-10 *rabi* season respectively. Application of 100% conventional fertilizers and nano carbon (N 215 kg hm^{-2} and NC 1.194 kg hm^{-2}) recorded highest number of spike m^{-2}, number of spiklets $panicle^{-1}$, 1000 grain weight and yield of rice in saline alkali soils (Fan *et al*., 2012).

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