AGRICULTURE & ENVIRONMENT
E-NEWSLETTER
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Article ID: AEN-2021-02-06-008

Nanofertlizers- A Potential Alternative to Chemical Fertilizers

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In recent past, extensive use of agro-chemicals in agriculture systems not only put massive barrier in achieving the optimal yield of crops but also imposes malevolent effect on the environment. Farmers even could not get respite from such downfall of production scenarios which adversely affect their livelihoods. Under these circumstances, nano-scale technologies are envisaged as a potential tool to mitigate the environmental crisis as well as increasing the farmers income with minimizing the input wastage. Nanotechnology is an emerging new science and enabling technology that involves the use of materials and equipment capable of manipulating physical as well as chemical properties of a substance at molecular levels. Nanotechnology deals with structures in the size range between 1 to 100 nm and involves developing materials or devices within that size. This stream has gradually paved his way out from the experimental into the practical areas, like the development of slow/controlled release fertilizers, conditional release of fertilizers and pesticides etc. It has provided the feasibility of exploiting nanostructured materials as fertilizer carriers or controlled release vectors for building of so-called "smart fertilizer" as new facilities to enhance nutrient use efficiency and reduce costs of environmental protection. Nano-fertilizers are very effective for precise nutrient management in precision agriculture with matching the crop growth stage for nutrient. Realizing the importance of nano-scale technologies, Govt. of India has already sanctioned a good amount of money (Rs. 2000 crores almost) in their 12th Five year plan for research in different nano-products like nano-fertilizers, other nano-agrochemicals and nano-biotechnologies to make them more available for the use of farming community.

Nano fertilizers vs Chemical fertilizers

- Nano-technology provides the smart delivery system of nutrients through Nano-structured to the plants. Thus, Nanostructured formulation might increase fertilizer efficiency and uptake ratio of the soil nutrients in crop production, and save fertilizer resource.
- Nanofertilizers will combine nanodevices in order to synchronize the release of fertilizer-N and -P with their uptake by crops, so preventing undesirable nutrient losses to soil, water and air via direct internalization by crops, and avoiding the interaction of nutrients with soil, microorganisms, water, and air.
- Microbial degradation in soil has been slowed down due to slow release of fertilizers as well as it reduces water solubility and chemical hydrolysis in agricultural fields.
- Few unique properties like high sorption capacity, increased surface to volume ratio and regulated release of fertilizer materials to the targeted sites or main plants, eco-friendly sustainable crop development make a way for nano-fertilizers in the list of potential plant growth enhancer.

Absorption of Nano-Fertilizers in Plant System

Controlled release of nano-fertilizers make them more effective in reaching plant system as compared to traditional fertilizers. These feature of nano-scaled fertilizers can be considered as smart fertilizers in terms of providing adequate nutrients to the plant. As a result, nutrient management in plants in the form of enhancing nutrient use efficiency and minimizing leaching of nutrients contaminating underground water could be achieved. Few bio-sensors are sometimes incorporated with nano-fertilizers which release active nutrient ingredient in response to critical need of crops or in case of any stress biotic or abiotic etc. These indirectly help in curtailing the waste of fertilizer in agricultural crop production. Many scientists are of the opinion that root systems of plants particularly root hairs are highly porous to nano-structured materials as compared to traditional chemical fertilizers (Fig. 1). Therefore, application of even less amount of nano-fertilizers will be highly crucial in determining the final yield of crop plants.

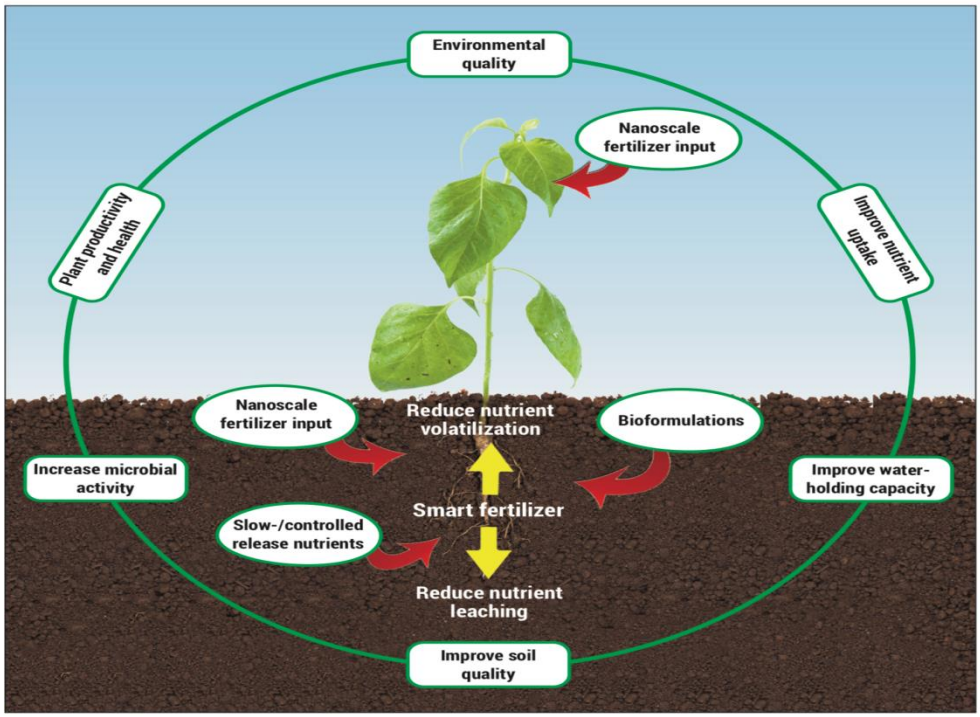

Fig 1. Schematic diagram of entry of nanofertilizers in the plant system (Adapted from Calaby-floody et al 2017)

Few specifically designed nano materials like silica nanoparticles and Carbon nanotubes etc. are also very user-friendly tools for transporting and delivering nutrient materials through target based approach. Experiments carried out in Faba bean reported that nano-scaled fertilisers could easily penetrate the foliage or canopy system in plants in large quantity than that of foliar application of conventional fertilizers. In contact with nano-fertilizers stomatal openings might favour the uptake of more amount of nano particles in the leaves thereby reducing fertilizer loss as well as environmental pollution to a great extent.

Synthesis of Nano-fertilizers

Generally two approaches are followed during nano-particle synthesis- Top-down approach and Bottom Up approach. Top-down approach mainly includes the mechanical or physical grinding, milling, crushing of large, bulky conventional materials into powdery product at first and then to nano-sized elements. On the other hand, entirely reverse procedure is utilized in case of bottom up approach to form nano-structured materials. For bottom up approach, atom level elements are subjected to different chemical and biological processes like precipitation, sol-gel, hydrothermal (for

liquid phased molecules) and aerosol processes, hydrolysis (for gaseous phase molecules) to form clusters which gradually converted into the shape of nano-structured materials by time (Fig. 2). Likewise, nano-fertilizers are prepared through both physical and bio-chemical methods whereas large traditional available materials are grounded and crushed to attain nano-scaled fertilizers and biochemical approaches are implemented to develop effective nano-formulations.

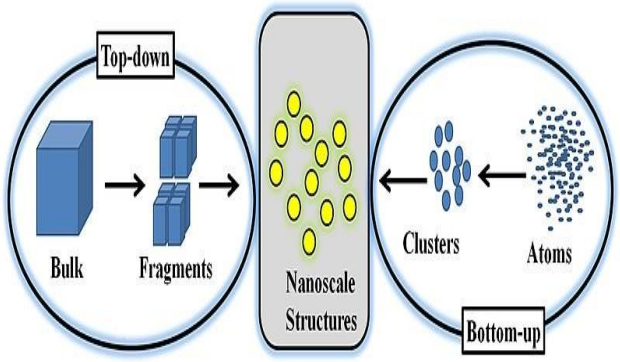

Fig 2. Formation of NPs from bulky and molecular materials using Top Down and Bottom up appraoch

Nanotechnology has crucial role to play in developing effective nano-formulations of fertilizers. These nano-fertilizers can even be successfully utilized in lieu of traditional chemical fertilizers. For example, grinding of urea physically and then mix the grounded product with most common biofertilizers may act as an effective nano-fertilizers. Additional advantage of these mixing is associated with the slow release nature of nutrients taking a long period of time in agricultural field. Soil borne humic acid or by-products like ammonium humate, waste products, peat, tar, ammonia, urea and other synthetic fertilizers may deliver nano-scaled fertilizers through proper recycling and processing. Nano-nitrogen or phospate can be derived from urea or calcium phosphate deposition on calcium cynamide though natural year-long processes.

Encapsulation of fertilizer in nanoparticles

Fertilizers are often encapsulated within nanoparticles. Nano encapsulated agrochemicals should be designed in such a way that they possess all indispensable properties such as effective concentration (with high solubility, stability and effectiveness), timely controlled release in response to certain stimuli, enhanced targeted activity and less Eco toxicity with harmless and effortless mode of delivery thus avoiding repetitive application (Nair et al 2010). Slow release of nano-fertilizers mainly depends on the water solubility, microbial degradation and chemical hydrolysis processes, whereas, in case of controlled release fertilizers, soluble nutrient materials are coated with nanoparticles that limit the exposure of active nutrient material to water or release the resultant nutrient to solution by diffusion. Coating and binding of nano and sub-nano composites are able to regulate the release of nutrients from the fertilizer capsule (Liu et al, 2006). Such nano-fertilizers offer a greater absorption capacity and nutrient use efficiency to the plant.

The process of encapsulation of nutrients with nanomaterials can be performed in three ways (Fig. 3). These are stated below—

- Nutrients encapsulated in nano-porous material
- Nutrient particles coated with a thin polymer film
- Nutrients encapsulated within the nanomaterials of varying nature and chemical composition
- Nutrients delivered in the form of nano-emulsion or in nano-scale dimension

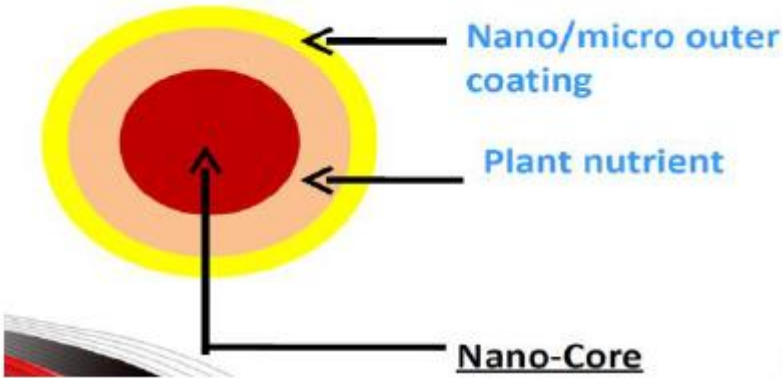

Fig. 3: Encapsulation process of fertilizers in nano-materials

Encapsulation of chemical fertilizers with nano-particles has several advantages as it provide precautionary protection, decreases the solubility of nutrients, reduce the direct contact of active ingredients with agricultural workers and finally reduces the run off rate of nutrients in environment. A Nano-sized nutrient eventually improve the nutrient solubility, helps in dispersion of insoluble nutrients in soil and finally increases the nutrient efficiency from crop production perspective.

Worldwide recently adopted Nano-fertilizers

Some of the approved nano-fertilizers accepted globally till today and their manufacturers are provided in Table 1.

Table 1: Approved nano-fertilzers and their manufacturing communities in different countries

Approved nano-fertilizers in the world	Manufacturing Companies	Country
Nano-Micronutrient	Shan Maw Myae Trading Co. Ltd.	India
Biozar Nano-Fertilizer	Fanavar Nano-PazhooheshMarkazi Company	Iran
Nano Calcium	AC International Network Co. Ltd.	Germany
Nano Green	Nano Green Sciences, Inc.,	India

Role of Nano-Fertilizers in agricultural production systems

Scientists believe that zinc nano-fertilizers are responsible for robust plant growth (shoot and root system) and increase the leaves' chlorophyll content. These nano products help in reduction in the requirement of conventional chemical fertilizer by 50 per cent, raise crop production by 15-30 per cent, improves soil health and cuts emission of greenhouse gases. The amendment of zinc nano-fertilizers in place of chemical fertilizers significantly increased the yield of peanuts. Lin and Xing (2008) reported that zinc oxide nanoparticles were shown to enter the root tissue of ryegrass and improved the germination.

In another instance, Nano-fertilizers also reduce the crop cycle period and increase crop yield, thus helping in contingent crop planning under changing climate conditions. Incorporation of nanoparticles carrying NPK (nitrogen, phosphorus, and potassium) in the maize cropping system showed an increase in grain yield and reduced the crop cycle of maize by 31 days. Similar results were obtained in the wheat based cropping systems also. SharmilaRahale (2011) studied the PO4-release pattern of surface modified using various nanoclays and zeolite in a percolation reactor. Nano- formulations have been shown to release phosphate for an extended period of 40- 50 days and the conventional fertilizer let out nutrients only upto 10- 12 days.

These nano-fertilizers were also found to promote the development of plant root systems in rice seedlings. These nano-fertilizers also improve seed production of vegetables. Similarly, carbon nanotubes containing fertilizers were reported to decrease the days to germination. Khodakovskaya *et al.*, (2009) demonstrated that carbon nano tubes (CNTs) exposed seeds germinated up to two times faster than control seeds and the seedlings weighed more than twice as much as the untreated plants. Further, they also reported that CNTs could effectively penetrate seed coat, thereby influencing the seed germination and plant growth

Apart from enhancing growth attributes, nano-fertilizers significantly influences the pest-disease incidence in crop plants also. Experiment conducted by Mahmoodzadeh et al (2006) recorded significant reduction in the incidence of rice blast and tomato spray mold with a correspondent 20% increase in grain weight was observed using TiO2 nano-particles due to its growth promoting effect.

Barriers in using Nano-Fertilizers

Although implications of nano-fertilizers in crop production scenarios are extremely high, yet, it has some limitations worth mentioning before adopting in farmer's field. Lack of sound knowledge, absence of adequate authentic literature, research gaps and less practical implementation causes great setbacks for nano-fertilizer development in the world. Some of the negatives associated with the use of nano-fertilizers for agricultural production are given below.

- The high cost of nano fertilizers
- Lack of production and supply of nano fertilizers in required quantities. This limits the wider scale adoption of nano-fertilizers as a source of plant nutrients.
- Absence of proper nano-fertilizer risk management systems
- Standardization missing mostly in nano-fertilizer formulation process.
- Various research studies suggested that free radical formation can be triggered by different nanoparticles (Quantum dots, CNTs etc.). Nano-fertilizers can be easily taken up by the plants in large quantity which may initiate the formation of reactive oxygen species (ROS) in plant cell. Sometimes ROS can develop directly on the larger surface area to mass ratio of smaller nano-fertilizer materials. These ROS gradually accumulate in the plant cells which can cause inflammatory reactions, tissue changes and lipid-protien-DNA damage through release of free radicles in different cells. In this way, it can cause mechanical damage within the cells and finally trigger the oxidative stress in plants.

Conclusion and Future Prospect

The emerging new science and enabling technology, equipped with nanodevices raises hope for new innovations in diversified field of science with special influence on agriculture. Nano-fertilizers could enhance crop yields to several extent by minimizing the nutrient loss which may contribute in environmental pollution. However, the full potential of nano-fertilizers in the agricultural and food industry is yet to be realized and is gradually moving from laboratory towards the application regime. Concentrated research is required in the area of environment, crop improvement, disease management and efficient resource utilization for increasing the crop productivity and maintaining the sustainability of agriculture. The future of nano-fertilizers may follow one of two scenarios. In the first, nano-agrochemicals are considered as emerging contaminants and the development of the technology will remain limited. The second scenario will require the establishment of highly collaborative and interdisciplinary research to provide fair assessment of both risk and benefits so that the full potential of nano-fertilizers can be explored. Uniform norms and monitoring before commercialization of nano-fertilizers should be imposed globally before its use in agricultural crop production.

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