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MICRONUTRIENT ENCAPSULATION USING NANOTECHNOLOGY : NANOFERTILIZERS

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Abstract

Globally, micronutrients are being encapsulated using various materials to enhance its release, so that plants can have maximum availability of nutrients but to some extent plants are not getting hundred percent benefit of it. Initiating novel technologies and getting familiar with them is the only way out to get highest and greatest benefit of it. Introducing Nanotechnology to AgroSciences and entering into nanoworld can break all yield barriers by its excellent mechanism of nutrient release to crops. This entry summarizes reviews related to the potential of nanoencapsulated micronutrients to hasten the nutrient use efficiency, their properties that make them remarkable, the interaction of nanoparticles with plants, the methods used for nanofertilizer delivery to plants and comparison being done between the prevalent or old technologies with the nanofertilizers to know the value of this novel technology. In the methods discussed for nanotechnology used nutrient delivery, each method is discussed with its specific importance and being compared with one another to know which amongst them is better. In addition, this entry also comprises of the ethics that normally arises with any new innovation or technology amongst the supporters and opponents. This entry suggests the role of nanotechnology is of paramount in agriculture to fasten our yields and development in AgroSciences. Now time is to tighten our belts and welcome these new technologies with utmost success.
***Keywords*:** Encapsulation, Micronutrient, Nanofertilizers, Nanomaterials, Nanotechnology.

Introduction

Importance of micronutrients to world agriculture and human health is well known. It is seen that over billions of individuals are suffering from the deficiencies of micronutrients worldwide. Zinc (Zn), iron (Fe), manganese (Mn) and copper (Cu) are some of the micronutrients that are included in limiting factors in terms of yield and are in some way involve in stumpy food nutrition. And it has been found that bioavailability of micronutrients is very less in about fifty percent of the world's cultivated soils. The reason is their slow and steady re loading of soil minerals caused by weathering, inadequate cultivation of soil and crop fertilization Micronutrient deficiencies are mostly prominent in soil conditions ranging from neutral to alkaline, especially the micronutrients become less available under anaerobic conditions in dry regions. The micronutrient use efficiency (MUE) a very significant term which is necessary to be defined here i.e. the yield of biomass per unit input of fertilizer or nutrient content (Meena *et al.*, 2014) In soil-plant systems, interaction of fertilizer-micronutrient with macronutrients can occur in a synergistic way, antagonist way or a neutral response which may affect yields and thus the quality of food.

From many years, traditional and novel fertilizer technologies as well as the products are not that up to the mark to harmonize the micronutrient delivery from fertilizer as per the crop requirement during the growing season that results in reduced MUE. Novel efforts nowadays are being made for improving the yield of crop, food nutrition and fertilizer-micronutrient use efficiency. This involves encapsulations (micro and nano), nanomaterials, nanodevices and nanoparticles. Nanocapsules, nanoparticles followed by microcapsules, chelates, soluble salts following the order in which there is an increment in micronutrient use efficiency by the fertilizer products (Monreal *et al.*, 2015). Nanobiotechnology, an exclusive term can transform the agricultural world globally in the upcoming years.

Advancement in the knowledge of technology terms has significantly added value in order to find the solution of many problems, be it agricultural sector, pharmaceutical sector, water conservation and many more. One such technology that emerged and recognized as novel is Nanotechnology (Feynman, 1960; Nikalje, 2015). Nanotech, a multidisciplinary approach that takes into account the knowledge from biology, physics, chemistry, mathematics etc is a science dealing with the things or materials that measured with dimensions 1-100 nm. Thus, nanotechnology is the manipulation in design, characterization, production, and application of individual atoms or molecules at the nano scale in such a way that resulting structures emerges out as a new, better and improved properties (Joseph and Morrison, 2006). The objective of this review is to put stress on the current knowledge basically for previously used micronutrient fertilizers and provides new insights on latest knowledge related to nanotechnology in micronutrient-fertilizers. The review identifies technological gaps that usually exist in the sphere of micronutrient release and efficiency of using crop; and propound an innovative foresight involving technical and scientific theories, with a greater focus on augmenting the micronutrient use efficiency of essential elements such as Zn, Fe, Mn and Cu by crops.

Nano Encapsulated Micronutrients

Nanoencapsulation is simply the coating of micronutrients within another material at sizes on the nanoscale. The fusion of mesoporous materials [ordered and functionalities] of only silica or in amalgamation with Al (aluminosilicates) is exemplified here for nanoencapsulation. Features and properties of mesoporous silica and aluminosilicates include porous well- arranged and ordered channels, ion-exchange and active sites for adsorption (Wu *et al.*, 2008; Xu *et al.*, 2009; Zhao *et al.*, 1996). Mesoporous aluminosilicates have been noted to use as CuO nanoparticles carriers and thus have the potential for macro and micronutrients delivery to the soil (Huo *et al.*, 2014) Over the last several years, nanostructures and hollow core shell of nano-size have embellished into a cardinal explored field as it has number of promising approaches and implementations in the realms of agronomics and biomedicine (Burda *et al.,* 2005) Different studies like regulation of Zn discharge in a solution by hollow-core shell of nano-sized Mn-carbonate loaded with ZnSO4 concluded that these nanostructures could act as a brilliant medium for the growth of plant by supplementing micronutrients to the roots of the plant. These nano-formulated structures also resulted in slow release or discharge of Zn as compared to its salt ZnSO4, gratifying root demands of plant via ion exchange reactions, thus explaining the concept of nanoencapsulation (Yuvaraj and Subramanian, 2015).

Properties of nanoencapsulted micronutrients facilitating the higher nutrient use efficiency include-

1. They possess ***large surface area*** because of very small size of particles thus, providing it more area to ease distinct metabolic process in the plant system resulting in production of more photosynthetic products.
2. They have ***high reactivity*** with other compounds because of wide surface area and very minute size of particles.
3. They are ***highly soluble*** in solvent such as water.
4. They ***penetrate more*** in to the plant due to nano-fertilizers' particle size less than 100 nm.
5. They improve ***uptake capacity and efficiency of nutrient utilization*** due to large surface area of nano-fertilizer.
6. Nano-particles encapsulating fertilizers within themselves will hasten the ***bioavailability and uptake capacity of nutrients*** to the plants (Tarafdar *et al.*, 2012).

Bioavailability of Micronutrient-Nanoparticles in Soils

Bioavailability of mineral nutrients is important for the easy uptake by the plants (Barber, 1995). Bioavailability can be elucidated as the assimilation of nutrients by the soil-plant system followed by their absorption in the plant (Comerford, 2005). Nutrients concentration, their essence and inter-relation of nutrients are some of the factors that govern the total nutrients available to the plants. Formulation of mineral micronutrients by nanosized structures may not only enhance solubility but also aid in distribution of nutrients insoluble in soil, drive down absorption and fixation rate of soil and thus increase the bioavailability while in conventional fertilizers there is comparatively reduced bio availability to plants owing to low solubility and great size of particle (Cui *et al.*, 2010). Thus, nano-structured formulation might boost the efficiency of fertilizer while saving the fertilizer resource. It also amplifies the uptake proportion of nutrients by the plant and hence enhances crop production. Coating of nutrients by resin-polymer, waxes and sulphur for water soluble fertilizers can meticulously managed the rate and pattern of nutrient release (Cui *et al.*, 2010). These nano-structured formulations also have dynamic feature of reducing fertilizer nutrients loss into soil cause by leaching and therefore increasing the bioavailability of nutrients. Physico-chemical properties of nanomaterials can be determined by the Differential Adsorption concept, also known as Corona formation and examination of such protein corona formation elucidated the presence of inner “hard corona” in plasma with steady and gently swapping of proteins (Cui *et al.,* 2010). To understand the effects and fate of nanomaterials, research of these phenomenon is a high priority, especially when dealing with nano encapsulation. Conduction of numeral studies to assess the effects of nanoparticles on plants is being augmented. To research however, majority of the studies have been done in pure nutrient solution or the plants growing in media that is devoid of soil. Take a case of intact Cu nanoparticles that were absorbed by the roots and then translocate to the above parts of the plant (Wang *et al.*, 2013; Dimkpa *et al.*, 2013). It was meticulously noticed that after fourteen days of sand-wheat system incubation, there was an increment in the average sizes of copper and zinc oxide nanoparticles from <50 nm to 317 nm in case of CuO and from <100 nm to 483 nm in case of ZnO (Dimkpa *et al.*, 2013). This increment in size or nanoparticle aggregates was ascribes to unknown factors linked to plant or dissolution of nanoparticles. Due to their high surface area and less particle size, nanoparticles are more liable to accumulation in solvent phase, that can affect their paramount characteristics like bioavailability and toxicological parameters (Lin and Xing, 2008).

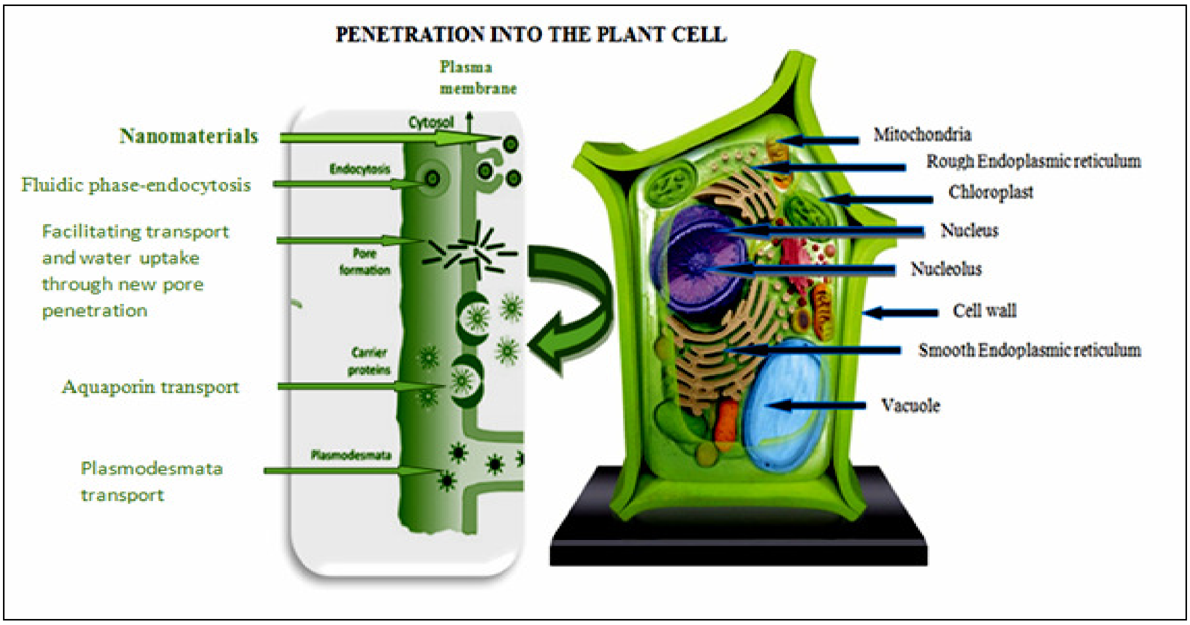

Fig. 1 : Nanomaterials penetration in the plant cell.

Nano-Fertilizer Formulations and Their Smart Delivery Systems

Nano fertilizer should be formulated in such a way that they hold all desired properties such as high solubility, stability, efficiency, controlled release with respect to time, enhanced targeted activity with effective concentration, and less eco-toxicity with safe, easy mode of delivery (Boehm *et al*., 2003; Green and Beestman, 2007; Torney *et al*., 2007; Tsuji, 2001).

Process of nutrients loading on these nanoparticles is as follows-

(a) Assimilation of nanoparticles,
(b) Ligand mediated adherence on nanoparticles,
(c) Encapsulation of nanoparticles in polymeric jacket,
(d) Nanoparticles entrapment, and
(e) Nanoparticles synthesis formed of the nutrient itself.

The mode of fertilizer application influences their efficiency as well as impact on plant systems. The following methods can be used for nano-fertilizer delivery to plants:

Soil less Methods

Aeroponics: Aeroponics involves growing of plants in air where spraying of nutrient solution occurs incessantly (Weathers and Zobel, 1992). The construction is simply followed by a square box of 1.2 m width and 5-10 m length in which the roots are allowed to mist constantly but no water layer formation takes place. However, one should take care that the upper plants should obtain sufficient water. Often at the bottom, a skeletal water layer formed; acting as a buffer system to the plants (Erik Van and Heinrich Lieth, 2008). Buffering is significant for plants here. Through this method, gaseous environment can be maintained around the roots. Due to the fact that it needs large extent of nutrients to support quick and speedy growth of plants, this soil less method is not prevalence.

Hydroponics: Hydroponics was pioneered by Gericke in the year 1937 for inorganic salts that are soluble in nature (Gericke, 1937). Hydroponics, also called as "solution culture" technique since growth and maturation of plants occur by the root's immersion in liquid nutrient solution i.e. deprived of soil. The factors that need to be looked gingerly are nutrient solution volumes, oxygen demands and pH maintenance, when the method of nutrient delivery is used. Here, entry of nutrient solution takes place from one end and exit of previous solution takes place from another end. Parameters like pH, electrical conductivity, temperature, and dissolved oxygen should be determined to maintain sufficient water and nutrients management in the hydroponic chamber. Since in the nutrient solutions, variations in ion concentrations is a time dependent process, it leads to the loss of proper nutrients balance in sealed hydroponic chambers and it necessitates to carry out the real-time measurements of all nutrients, but often there are some technical issues in performing such measurements. To that solution, there should be frequent evaluation of nutrient solutions; tuning of nutrient ratios, this can improve and restore the nutrient balance (Son and Ahn, 2016). Here, the studies envisage, that the use of hydroponic systems is most pertinent in situations where the nutrient media need to be well controlled and when intact roots need to be harvested (Nguyen *et al.,* 2016).

Field Methods

Soil Application: The method of supplementing nutrients in the form of chemical or organic fertilizers is known as soil application. Time duration of fertilizer in the soil, texture of soil and its salinity, soil content, pH alterations and plant sensitivity are some of the factors that must be carefully analysed while making the choice among different methods of fertilizer applications. Soil particles exhibiting negative nature influence nutrient adsorption. Most of the agricultural soil possesses less anion exchange capacity than cation exchange capacity. To exemplify this- in anions due to mobility of nitrate ions, it can be leached by water while going via soil. In comparison with cations, as phosphate ions binds (more strongly) to soil particles containing $Fe^{2+,3+}$ and Al^{3+} having hydroxyl group that interchanges with phosphate (Taiz and Zeiger, 2010).

Foliar Application: Foliar application involves delivery of micronutrients where leaves are directly sprayed with liquid fertilizers. The best part of this method is to trim down the time delay between fertilizer added and uptake of nutrients by plant in their exponential phase of growth. It also enhances the uptake of micronutrients such as Fe, Mn, Cu in contrast to the method of soil application in which they are more soaked on the particles of soil (Taiz and Zeiger, 2010). If this method is employed for nano-fertilizers, it can show agronomic boon, since the nutrient uptake involves stomata and leaf epidermal cells. Since stomata are involved so, the time of opening of stomatal pores has to be taken into concentration.

To get better understanding of these methods, a short summary is expressed in a tabular form (Table 1).

Prevalent and Frequent Fertilizers versus Nano-Fertilizers

Any material [natural or synthetic, chemical based] intended to provide nutrition required for the growth of plants upon its application to soils. These fertilizers act as a magical bullet for enhancing the productivity of agriculture. However, the use of fertilizers causes severe health hazards (Bhandari, 2014). Nutritional value for the traditional fertilizers only ranges from 30-35% for N, 18-20% for P and 35-40% for K, meaning very little concentration (much lower than minimum desired concentration) reaches to the targeted site due to the predicament of chemical leaching, hydrolysis by soil moisture, evaporation and degradation by photolytic and microbial method. Nano fertilizers are innovatively created carriers of nutrients developed using particle ranging from 1-100 nm dimensions. The surface areas of these nano particles are sufficiently high and thus have the potential of holding nutrients in large quantities. One of the main advantages of using nano fertilizers is that the nutrients it holds have a controlled and sustained release provided the nutrients uptake complement with the crop requirement (Preetha and Balakrishnan, 2017). In one study, it has been showed that NPK concentration in balanced amount along with micronutrients such as S, Zn and Mo results in higher productivity of pulses in red soils and the soil rich in iron and aluminium. There is about 13% increase in the yield of green grams and 38% in black grams upon the use of adequate amount of NPK formulations (Bhattacharya *et al.,* 2004). The regulation of nutrient release from the fertilizer is done by forming the polystyrene layer that is sandwiched between the carnitine layer (Liu *et al.,* 2006). Nanofertilizers offers benefits over prevalent fertilizers due to the reasons like they increase yield of soil fertility, enhances quality of the crop, non-toxic to both humans and environment, available at low cost, and raises more profit. Moreover, nano materials enhance nutrients use efficiency and minimize the threats of environmental pollution (Naderi and Abedi, 2012). Nano fertilizers are propitious over these prevalent fertilizers as they improve the nutritional content of crops and the quality of the taste, optimum use of iron and increase protein content in the grain of the wheat (Tabrizi *et al*., 2009).

Effect of foliar fertilization of nanofertilizer on growth

Nanofertilizers increase the nutrients' bioavailability and uptake, thus elevating the process of metabolism and supporting the meristematic activities resulting in the high-rise apical growth (Mahil and Kumar, 2019). It has been reported that NPK micronutrient formulation upon foliar spraying resulted in the increased height and branches count in black gram (Marimuthu and Surendran, 2015). Abdel-Aziz *et al*. (2018) observed the improved production of leaves in wheat, due to smooth infiltration of NPK formulation through openings of leaves. In one study, increased dry weight of peppermint leaf by 165% has been indicated upon foliar spray of nitrogen nanofertilizer. (Rostami *et al*., 2017; Alloway, 2008; El-Tohamy and El-Greadly, 2007; Cakmak,2000). Increased growth of *Ocimum basilicum* L. and dosage corn has been resulted upon foliar spray of iron nano-fertiizer due to more crude protein and soluble carbohydrates production. (Sharifi *et al*., 2016; Peyvendi *et al*., 2011). Dry weight of plants has also been increased by the foliar application of nano titanium dioxide due to enhanced assimilation of nitrogen, ROS scavengers and electron transport chain (Morteza *et al*., 2013; Raliya *et al*., 2015).

Ethical and Safety Issues in Using Nano-Fertilizers

As we know that the usual concomitant associated ethical issues always coexist with any new scientific or technological research, mainly targeting its containment and regulation. Novel advancements in nanotechnology can transform the agricultural world. The booming development of nanotechnology in the field of medicine in vitro has spawned interest in agriculture nanobiotechnology (Nair *et al*., 2010). Nano biotechnologies dwell a foremost position that can transform agricultural systems and crop production globally. Encapsulation of micronutrients in nanomaterials, nanoparticles and microcapsules, may render practical approaches to use fertilizer-micronutrients in a subjugated manner that is what nanoencapsulation means and these kinds of formulations for nano encapsulated fertilizers may capable of diminishing the potential ecological impact (as described in the whole review) with extreme site specificity, thus resulting in economic savings to farmers and trim down the burden on environment. Nanotechnology related ethical issues are manifested here as different people (the ones who see its great potential and the ones who express uncertainties) have distinguishing opinions. Nanotechnology proponents believe that it has the potential of transforming our lives dramatically, while opponents of nanotechnology fear that self-replicating "nanobots" could escape from laboratories consuming all biomass on earth (end-of-world situation) and reduce all life on earth and leads to a hypothetical scenario of "gray goo". One of the major challenges faced by the world before accepting nanotechnology is- Will the hidden environmental and health threats of nanoparticles exist over their potential benefits? Before fully implementing this technology, the threats related to nanoparticles' application must be assessed. Nanotoxicology," has been developed to accommodate the risks, that is accountable for examining various toxicological parameters or its potential as well as promoting safe design and use of nanoparticles (Oberdo¨rster *et al*., 2005).

Conclusion

In recent years there have been drastic fall in crop production and because of that we have faced great economic losses. The reason of this fall is- none other than but the nutrient deficiency in plants. Moreover, the prevalent methods of nutrient delivery are not that much efficient to make all the nutrients bioavailable to plants. The astounding entry of Nanotechnology has amazed the world in every field of science and technology so, why not to use it to solve our basic agony of increasing our yields in agriculture and meeting the high population demands to have sustainable future. The combination of nanotechnology and plants can result in a running progress in the field of fertilizer-micronutrient development for the smart delivery of nutrients giving an ample nutritious food. Now the priority is to more strengthen the field of nano-agronomy by exploring more research efforts so that we can have its replete benefits.

Table 1: Synopsis of the methods of nanofertilizer delivery in plants

Mode of the nano fertilizer delivery method	Name of the method	Problems faced during the process	Factors that need attention	Amount of nutrient solution required
***In vitro* method**	Aeroponics	Sometimes there is a lack of a buffer around the roots for water, nutrients and heat; lack of continuity in aeration	Relative humidity; oxygen availability (aeration); constant nutrient delivery to plant roots	High level of nutrients is required
	Hydroponics	Raised (high) moisture rates may cause wilting of plants; attacks by pathogen	Oxygen demands; pH requirements; nutrient solution	Depends on the type of plant growing in the system or their growth phase. Nutrient solution is well controlled
***In vivo* method**	Soil application	Chances of Leaching of anions (nitrate ions); availability of nutrients in soil	Soil texture; soil salinity; plant sensitivities to salts; salt content; changes in pH; longetivity of fertilizer in soil	Depends on accessibility of nutrients binding to soil particles
	Foliar application	A specific time of spraying the nutrient solution or fertilizer because the stomata open during these time periods only; possibility of plant damage if correct concentration of chemical (fertilizer) is not applied	Method of foliar application (as chances of plant damage is possible); time of application	Lower concentration as compared to other methods as liquid fertilizers are directly applied onto leaves

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