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Nanomaterials for efficient plant nutrition

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Abstract
Population of the country is increasing at an alarming rate and agricultural land is shrinking on the other hand. To feed this burgeoning population crop productivity and production need to be enhanced at increasing rate. Since green revolution, fertilizers have played a major role to increase crop production. But in recent years the crop productivity has reached to the plateau whereas rate of fertilizer application is still increasing. This is owing to low fertilizer use efficiency, low productivity, higher application doses of fertilizers, environmental pollution and residual toxicity problem in produced food. To cater these problems a new technology namely; nanotechnology needs to be introduced in agriculture for more efficient plant nutrition. Nanomaterial is needed in minute quantity to enhance crop growth and yield significantly. Thereby, nanomaterials hold promise in increasing fertilizer use efficiency along with increase in agricultural production in terms of quantity and quality. This review is presented to find out the future scopes of nanomaterials to revolutionise agricultural sector by ensuring food security for next generations.

Keywords: Nanotechnology, nanomaterial, productivity, fertilizer use efficiency, nutrition

Introduction
Fertilizers have been proved its important role in improving the food production in country especially during the green revolution era after the introduction of the high yielding and input responsive crop varieties. In spite of this, in recent times yields of many crops have begun to depress as a result of imbalanced fertilization and decreased soil organic matter. Moreover, excessive fertilizer application negatively affects the groundwater and leads to eutrophication in aquatic ecosystems. Water soluble fertilizers applied to soil go through various losses and fixation, thereby reducing nutrient use efficiency to extremely low level. To cater this problem encapsulation of fertilizers with nanomaterials has been explored, *viz*; carbon nanotubes/CNTs [1], clay montmorillonite-urea nano compounds [2], nano SiO_2, nanoporous or mesoporous silica, and synthetic zeolites [3-5]. Nanotechnology can be defined as the research and technological development on a scale of 1 to 100 nm using atoms, molecules, or macromolecules [6]. However, the phenomena associated with nano scales occur with larger nanomaterials [7] and thus the particles having size upto 1000 nm are considered as nanoparticles/ nanomaterials/nano-sized material [8]. Nanomaterials having unique properties have promised applications in various fields including agriculture. It has provided various solutions in the field of plants and food science and it offers new technology for disease control, slow release pesticides and diagnostic tools [9].

Nanomaterials because of their tiny size show unique characteristics. They can change physic–chemical properties compared to their bulk materials, they have a great surface area than bulk materials. Because of these larger surface areas, their solubility and surface reactivity is higher [10]. There is some group of nanomaterials that are used commonly are carbon nanotubes and metal based nanomaterials like metal oxides. Smaller particle size increases specific surface area and number of particles per unit area that provide more opportunity for contact of nanomaterial which leads to more penetration and uptake of the nutrient [11]. The effects of nanoparticles on different plant species can vary greatly with plant growth stages and method and duration of exposure and also depend on nanoparticle size, concentration, chemical composition, surface structure, solubility, shape, and aggregation [12].

The use of nanoparticles in the growth of plants and for the control of plant diseases is a recent practice. Various studies had been carried out to understand the effect of nanomaterials on the growth of plants. Single walled carbon nanotubes penetrate cell wall and act as transporter [1];

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nano TiO_2 increases water and fertilizers uptake due to increased nitrate reductase activity and also it protects aging of the chloroplast [13]. Nanopatcles mixture including TiO_2 and SiO_2 increased nitrate reductase which increased germination and growth of soybean plant [13]. Since, nanomaterial is needed in very small quantity, its precise application technique is necessary to realise better results in term of crop productivity, plant protection and economic viability. Plants can uptake nanomaterial through roots, leaves or seed priming. Therefore nanoparticles can be supplied to plant by means of seed treatment, soil application and foliar application.

Seed priming with nanomaterials

The tiny sized nanomaterial can pierce seed coat to enter inside seed to affect germination and seedling growth parameters. There are various studies proving the effect of nanomaterial primed seeds on better germination and seedling growth. Seed treatment with nano ZnO at 1000 ppm promoted seed germination and seedling vigor of groundnut and in turn promoted early establishment of seedlings manifested by early flowering and higher leaf chlorophyll content [14]. They also recoded increases stem, root growth and pod yield per plant (34% higher than chelated bulk $ZnSO_4$) due to nanoparticles of ZnO. The presence of ZnO nanoparticles affected the growth of mung and gram seedlings and accumulation and uptake of nanoparticles was dependent on the exposure concentration [15]. These results might be due to the increases production of chlorophyll, pollen functioning, fertilization and germination and biomass production mediated by zinc [16-19].

Nanosized TiO_2 at 10 ppm significantly reduced mean germination time and increased shoot and seedling lengths of wheat [20]. Canola seeds treated with 2000 ppm nano TiO_2 recorded significantly higher germination percentage, germination rate and seedling vigor [21]. Similar promotry effect of nano TiO_2 and SiO_2 was reported in germination of soybean [13], in which nitrate reductase enzyme activity and antioxidant were enhanced. Tomato seeds treated with TiO_2 nano particles increased plant dry weight by 73%, photosynthetic rate by thrice, and chlorophyll-a formation by 45% as compared to the control [22]. The significant effect of nanosized TiO_2 on spinach germination might be attributed to the small particle size which allows its penetration into the seed which exerted enhancing functions during growth [23].

An increase of the shoot/root ratio compared to that of the control was reported while analyzing the influence of metal nanoparticles on germination of *Lactuca* seeds [24]. Due to its promotory effects, nano ZnO significantly increased plant growth, root growth and pod yields of groundnut over control and $ZnSO_4$ [14]. While, nanocsale ZnO at higher concentration (2000ppm) decreased both plant growth and pod yield and similar results were reported on radish, rape, lettuce, cucumber and corn [11]. Seed priming with Zn improved seed germination and seedling development of barley very effective [25]. These results may indicate that there are very important physiological roles of high Zn concentration in seeds during seed germination and during early seedling growth. Rice seed treated with Zn greatly increased grain yield [26] and it can be concluded that application of Zn through this method is economically more viable as compared to the expensive broadcast application of Zn fertilizer.

Carbon nanotubes (CNTs) reported to have the ability to penetrate plant cells [1] and induce phytotoxicity at high doses [27]. Carbon nanotubes are able to penetrate the thick seed coat of tomato and support water uptake in seeds, which can affect germination and growth of seedlings [28]. Some of carbon nanostructures, particularly CNTs significantly increased germination rate of rice seeds [29]. Carbon nanomaterial also increased water content in seed during germination as compared to the control.

Tomato seed treated with 8 g/L of nano SiO_2 improved seed germination percentage, seedling fresh weight, seedling dry weight, seed germination index, mean germination time and seed vigour index [30]. Wheat seeds soaked for 4 hours with TiO_2, ZnO, and chitosan nanoparticles enhanced germination and seedling growth [31]. Nanoparticles seed treatment cause faster and steadier seed germination along with increase in water absorption and their resistance to environmental stress [32]. Seeds treated with nanoparticles indicated a 90% increase in drought resistance [33] and 16.5% increase in seed longevity during storage [34]. Wheat seed treated with Cu and Zn nanoparticles decreased the negative effect of drought [35] by means of increased activity of antioxidative enzymes which in turn reduced the thiobarbituric acid reactive substances accumulation and stabilized the contents of photosynthetic pigments and increased relative water content.

Soil application of nanomaterials

Nanomaterials applied to the soil is absorbed by the roots, move through the apoplastic and symplastic pathways to the xylem, cross the endodermis and then move to the rest of the plant through the vascular bundles [4, 36]. Nanoparticles are transported inside the cells either through endocytosis [37, 38] or through pores or channels [39]. Plants are an important component of the soil ecosystem and may serve as a potential pathway for nanoparticle transport and bioaccumulation into the food chain [40]. In plants transported compounds need to penetrate through the cell wall prior to membrane invagination. Plants are able to take up nanoparticles from the environment and transport them through the vascular system to various shoot organs [40, 41].

Soil application of Udaipur nano-sized rock phosphate (34% P_2O_5) at 60 kg P_2O_5/ha recorded significantly higher shelling percentage, 1,000 grain weight, grain and stover yield of maize plant as compared to the control, which was at par with single super phosphate at 60 kg P_2O_5/ha [42]. Results also showed that crop utilization of phosphorus from nano-sized rock phosphate was at par with that of phosphorus from SSP while yield response to nano-sized rock phosphate was marginally lower than SSP but it served as a cheaper source. Apatite nanoparticles increased above-ground biomass, below-ground biomass and yield of soybean by 18.2, 41.2 and 20.4%, respectively as compared to the regular P fertilizer, TSP [43]. Compared to NPK chemical fertilizer, the application of slow/controlled release fertilizer coated and felted by nanomaterials were reported to improve grain yield with an in significant increase in protein content and a decrease in soluble sugar content in wheat [44]. Application of K nanofertilizer at 400 kg/ha had the highest plant height and stem diameter among K nanofertilizer at 0, 100, 200, 300 and 400 kg/ha [45]. While, application of K nanofertilizer at 300 kg/ ha had the highest fruit diameter, number of fruit per plant, fruit weight and fruit yield. The K nanofertilizer also increased the absorption of nitrogen, phosphorus, potassium, calcium and magnesium.

Nanoscale titanium dioxide (TiO_2) was reported to promote photosynthesis and growth of spinach [46, 47]. Similarly, mixture of nanoscale SiO_2 and TiO_2 hasten germination and growth of soybean [13]. Under hydroponic culture an increased in germination percentage (95.5%), dry weight (6.52±0.2), silica accumulation (18.2%) and alleviated nutrients in seed of maize was recorded with nano-SiO_2 [48]. Under hydroponics study improvement in length of aerial part and root of wheat was observed by magnetite iron nanoparticle over control either applied at germination or after germination [49].

Foliar application of nanomaterials

Plants mostly take up nutrients from soil through their roots although nutrients can also be supplied to plants as foliar spray is a relatively new and controversial technique of feeding plants by applying fertilizer solution directly to their leaves [50, 51]. Nanoparticles are capable to penetrate living plant tissues and to transport to different plant parts when applied as foliar spray. Since, application of nanoparticles to the soil is not economical as nanoparticles form agglomerates in soil and lost in one and other way. Therefore foliar feeding of nanomaterials is more effective and economical. Nano urea applied as foliar spray significantly increased essential oil yield in borage (*Borago officinalis* L.) [52]. Spraying nano-P at 1.0 g/l recorded the highest N, P, K, Ca, Mg, Na, Fe, Mn, Cu and Zn nutrients uptake in the leaves and N, K, P, Ca, Mg and Na nutrients in branches of cotton plants [53]. However, the uptake of micronutrients (Fe, Mn, Cu and Zn) was higher with nano-P at 0.5 g/l in branches of cotton. They also reported the encouragement of drought tolerance in cotton due to nano-P by the enhancement of nutrients uptake.

Nano-ferric oxide applied as foliar application significantly promoted the growth and photosynthesis of groundnut along with the increased absorption and utilization nitrogen, phosphorus and potassium [54]. Silver nanoparticles are used in agriculture to extend the maintenance of asparagus leaves (from 2 to 21 days) and to increase the ascorbate, chlorophyll, and fiber contents of leaves [55] and decrease seed abscission in borage (*Borago officinalis* L.) [56]. Silver applied as foliar spray prevents fungi, moulds, rot and other plant diseases and also acts as a great plant growth stimulator [57]. Nano iron increased pod weight, leaf and pod dry weight and yield of soybean [58]. Nano ZnO application had a positive effect on the plant growth and yield of sunflower. Because too low concentration of ZnO was used in the nano treatments, this is very important as a view of environmental pollution [59]. In another study, application of nano zinc oxide at 60 g/ha was found superior among five levels of nano-sized zinc oxide (0, 24, 36, 48 and 60 g/ha) and five levels of zinc oxide (0, 24, 36, 48, 60 g/ha) for growth and yield traits of wheat [60]. Foliar application of nano silver (50 or 100 ppm) under waterlogged conditions increased in plant height and corm numbers of saffron [61]. Therefore effects of flooding stress might be modulated by nano-silver. Since, deprivation of oxygen supply to the plant roots is the main consequence of flooding which increases ethylene production in most of the plants [62]. It is known that silver ions inhibit the action of ethylene by preventing its connection to ethylene in plant cells [63]. Application of nanobiofertilizer at 4 litre/ha (containing *Azotobacter* and *Pseudomonas* bacteria and nano-fertilizers such as Fe, Zn and Mn) increased spike length, spikes number in m^2, seed number in m^2, seed number in spike, seed weight and number of days to physiological maturity and grain yield of wheat (Mardalipour *et al*., 2014) [64].

Conclusion

Nanotechnology is an emerging branch of science which promises to revolutionize agriculture. Owing to its unique properties, nanomaterials have smart delivery system, which make their uptake efficient. Nanoparticles can be applied to seed, soil and foliage. Nanomaterials say nanofertilizers enhances the fertilizer use efficiency. Applications of nanomaterials can help faster seed germination, uniform plant stand, enhances production, effective in plant protection with reduced environmental impact as opposed to traditional approaches. Thus, the problems of today's agriculture can be tackled by utilising the novel properties of nanomaterials. And it can be said that future needs of agricultural production can be meet out by application of nanomaterials.

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