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## Emergence of nanoscale fertilizers in agriculture: A review

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**Abstract**

There is an immense pressure on the agriculture sector to fulfil the increasing demands of the consistently growing global population. Chemical fertilizers are thought to be requisite for improving crop productivity and are indiscriminately applied through different methods. However, excessive use of fertilizers causes irreversible damage to soils and waters leading to the significant environmental hazards besides depletion in the agricultural productivity levels. Recent studies have shown that usage of nanoscale materials as crop nutrients (Nano fertilizers) was giving encouraging results in terms of growth, productivity and nutrient bio-fortification. Application of nanoscale fertilizers will reduce the cost of fertilizers per crop and also considerably minimizes losses and thereby the pollution hazard. In this review, we summarized the application of different nanoscale fertilizers on an array of crops and their effects on different parameters like, germination, growth, productivity, quality, nutrient uptake, nutrient bio-fortification and cost economics.

**Keywords:** Nano fertilizers, agriculture, yield, economics

**Introduction**

Agriculture is a major economic sector related to the production and provision of a wide range of specialty crops for food and feed purposes and it currently represents a worldwide multitrillion dollar industry (Malhotra, 2016) [31]. Crop production and global food security are greatly dependent on fertilizer input, as it supplements soil nutrients, promotes plant growth and increases crop productivity. In order to achieve desired higher yields intensive application of conventional fertilizers over extended period of time contrarily can lead to a decrease in soil fertility and increase salt concentrations thereby causing future crop losses. Furthermore, it caused serious environmental constraints worldwide including ground water pollution, water eutrophication, soil quality degradation and air pollution (Congreves and Van Eerd, 2015) [9]. Nutrient use efficiencies of conventional fertilizers hardly exceed 30-35%, 18-20% and 35-40% for N, P and K respectively. Application of conventional fertilizers to the soil or to foliage as exogenous source, most of the time the bulk forms are going to be fixed in the soil and making it non-available to the rhizosphere and becomes toxic to the soil microorganisms and plants. As such, there is a great interest towards the development of new innovative fertilizer sources in order to increase the fertilizer use efficiency (Van Eerd *et al.*, 2018) [58]. Several strategies have been proposed to increase fertilizer use efficiency, such as the use of precision fertilization, split or localized application, fertigation and the use of nano fertilizers (Lu *et al.*, 2016) [30]. The applications of nano fertilizers in agriculture have become a buzz word among the scientific community in recent years. Nano fertilizers (within the size range of 1-100 nm) are synthesized or modified form of traditional fertilizers, fertilizers bulk materials or extracted from different vegetative or reproductive parts of the plant by different physical, chemical or biological methods with the help of nanotechnology. Nano fertilizers are very effective for precise nutrient management in precision agriculture with matching the crop growth stage for nutrient and may provide nutrient throughout the crop growth period. Nano fertilizers are advantageous over conventional fertilizers as they are having large surface area and particle size less than the pore size of root and leaves of the plant which can increase penetration into the plant from applied surface and improve uptake and nutrient use efficiency (Liu and Lal, 2015) [29].

The usage of nano fertilizers in small quantities makes that the soil does not get loaded with salts that usually are prone to over-application using conventional fertilizers on a short- or long-term basis (Leon Silva, 2018) [28].

Nano fertilizers providing greater role in crop production and several research studies revealed that nano fertilizers enhanced crop growth, yield and quality parameters with increased nutrient use efficiency, reduced wastage of fertilizers and cost of cultivation. Rameshaiah *et al.* (2015) [44] reported that nano-fertilizers increase the Nutrient Use Efficiency (NUE) by 3 times.

### Effect of nano fertilizers on growth and physiological parameters of the crops

Nano fertilizers increase availability of nutrient to the growing plant which increase chlorophyll formation, photosynthesis rate, dry matter production and also overall growth of the plant (Hediat and Salama, 2012) [20]. It was documented by some research studies, where foliar application of nano fertilizers at 30 ppm increased the plant height and number of branches per plant, chlorophyll content and carotenoids in peanut as observed by El-Metwally *et al.* (2018) [15]. Burhan and AL-Hassan (2019) [7] found that liquid nano NPK fertilizer @ 750:90:600 mg L<sup>-1</sup> increased the flag leaf area, dry weight and total chlorophyll content in wheat compared to control treatment (soil fertilizer @ 184 N, 39.56 P, 41.50 K kg ha<sup>-1</sup>), which was due to enhanced availability of nutrients and easy penetration of nano NPK through stomata of leaves via gaseous exchange.

Prasad *et al.* (2012) [41] observed that nanoscale ZnO (25 nm mean particle size) at 1000 ppm concentration promoted seed germination, seedling vigour, stem and root growth and higher leaf chlorophyll content of groundnut compared to chelated ZnSO<sub>4</sub>. Seed coated with nano ZnO @ 50 mg Zn g<sup>-1</sup> of seed recorded highest dry matter weight and SPAD chlorophyll readings in maize, soybean and pigeon pea compared to seed coated with normal ZnO @ 25 and 50 mg Zn g<sup>-1</sup> of seed and control (Adhikari *et al.*, 2016) [3]. Significant increase in the plant height and dry matter production was observed with the foliar application of nano ZnO in sorghum at 500 ppm (Poornima and Koti, 2019) [40], in maize crop @ 750 ppm at 30 DAS (Chaitra and Hebsur, 2017) [8] and in pearl millet (Tarafdar *et al.*, 2014) [54]. Similar results were reported by Singh *et al.* (2017) and Meena and Aravinda Kumar (2015) [34] with the foliar spray of nano ZnS @ 400 ppm at 35 DAS of sunflower. Foliar application of nano-iron fertilizer increased the growth of forage corn (Sharifi *et al.*, 2016) [50] and also increase in the plant height, aerial organ dry biomass of sunflower was observed by the foliar spray of nano Fe-EDTA (Shahrekizad *et al.*, 2015) [49]. Hanumanthappa *et al.* (2019) [19] found that seed priming with borax @ 0.2% *fb* spraying of nano boron @ 300 ppm at 30 DAS increased plant height, number of branches, leaf area and dry matter production of groundnut. Kavitha *et al.* (2018) [26] reported similar results in sunflower crop with seed priming of nano boron @ 0.2%.

Nano-chelate zinc fertilizer application proved to enhance the activity of peroxidase, catalase and polyphenol oxidase enzymes in cotton (Rezaei and Abbasi, 2014) [46]. Zinc nanoparticles may significantly alters the antioxidant metabolism and protected rice plants from ROS damage by improving the levels of antioxidant enzyme activities during germination (Upadhyaya *et al.*, 2017) [56]. Abdel-Aziz *et al.* (2019) [1] also reported that seed priming of chitosan

nanoparticles (10%) increased SOD, peroxidase and catalase activities of french beans plant leaves.

### Yield attributes and yield

Nano fertilizers have potential to boost the yield and growth of many crops. Foliar spray of nanofertilizer significantly increased the yield and yield components of maize (El-Habbak *et al.*, 2019) [14] and peanut (El-Metwally *et al.*, 2018) [15]. Nano chitosan-NPK fertilizer @ 10% induced significant increase in no. of spikelets per main spike, no. of grains per main spike, 100 kernel weight, grain yield plant<sup>-1</sup> and straw yield plant<sup>-1</sup> of wheat (Abdel-Aziz *et al.*, 2016) [2]. Al-Juthery *et al.* (2018) [4] obtained significant response with the spraying of super micro plus (SMP) nano-fertilizer for grain yield, biological yield, 1000 grain weight and harvest index of wheat followed by the spraying of tri nano-fertilizer (N+P+K) compared to control and traditional fertilizer (NPK+TE) treatments. Highest seed yield of *Vigna radiata* was recorded with the application of nano slow release fertilizer (Rajendran *et al.*, 2017) [42]. Application of nano-zeolite phosphorus resulted in the highest values of yield and yield components of peanut (Hagab *et al.*, 2018) [18], which indicates that using these materials as a source of phosphorus gives a potential to reduce the application rate and consequently improve the overall efficiency.

Significant increase in yield was recorded with the foliar application of nano ZnO @ 400 ppm in maize (Subbaiah *et al.*, 2016) [51], at 500 ppm ha<sup>-1</sup> in finger millet (Saraswathi *et al.*, 2019) [48], at 1000 ppm in groundnut (Prasad *et al.*, 2012) [41] and RDF + two foliar sprays of nano ZnO @ 1000 ppm in rice (Jangid *et al.*, 2019) [24]. Similarly foliar spray of nano ZnS @ 500 ppm in sunflower (Meena and Aravinda Kumar, 2015) [34], Singh and Kumar, 2017), nano-chelate Zn application in maize (Mosanna and Behrozyar, 2015) [35] also recorded higher yield and yield attributes. These results indicates that nano ZnO has proved to be more effective in enhancing productivity and absorption of Zn because of high surface area to volume ratio and the required dosage of nano based Zn fertilizer had 10 folds less than the conventional ZnSO<sub>4</sub> (Dapkekar *et al.*, 2018) [10].

Naseeruddin *et al.* (2018) [37] reported that foliar application of nanoscale ZnO, CaO and MgO @ 100 ppm recorded significantly higher grain yield, cane yield and juice yield of sweet sorghum. Increased seed number per pod, pod number per plant, 100 seed weight and grain yield of chickpea with the foliar spraying of nano-iron chelate @ 2 g L<sup>-1</sup> over control was the outcome of the experiment conducted by Valadkhan *et al.* (2015) [57]. Manjili *et al.* (2014) [33] found that application of nano chelate molybdenum @ 3 g per litre had a significant effect on the yield attributes, pod yield and seed yield of groundnut. Yield attributes, seed yield and stalk yield of sunflower increased with seed priming of nano boron @ 0.2% (Kavitha *et al.*, 2018) [26] and also pod yield, kernel yield of groundnut was significantly higher with the seed priming of nano boron @ 300 ppm *fb* foliar application of nano boron @ 600 ppm at 30 DAS (Sushmitha *et al.*, 2018) [53]. Patel and Kumar (2017) [39] reported significant increase in head diameter, head weight, seed weight and stalk yield of sunflower with the foliar application of 400 ppm nano-ZnS and boron @ 0.5% compared to soil application of bulk zinc sulphate. Foliar application of titanium dioxide nanoparticles @ 0.02% significantly increased yield of wheat compared to control and bulk titanium oxide due to improved fertilizer use efficiency (Jaberzadeh *et al.*, 2013) [22].

### Quality parameters

Nutrients are required for improving the quality parameters of crops. Some research studies revealed that application of nano fertilizers gave better quality of crop products than the conventional fertilizers. El-Metwally *et al.* (2018) [15] reported that nano-fertilizers application at 30 ppm increased total carbohydrate (322.63 mg g<sup>-1</sup>), soluble sugars (30.68 mg g<sup>-1</sup>), protein (19.51%) and oil content (42.33%) in seeds of groundnut. Manikandan and Subramanian (2016) [32] observed significantly higher crude protein content of maize with nano-zeolite urea treatment in comparison to conventional urea. Significant increase in the total carbohydrate and protein content of French bean seeds was noticed by Abdel-Aziz *et al.* (2019) [11] with the foliar application of chitosan nanoparticles (10% ) followed by carbon nanotubes (20 µg l<sup>-1</sup>) when compared to control. Burhan and AL-Hassan (2019) [7] observed increase in the protein percentage of wheat when fertilized with liquid nano NPK fertilizer @ 750:90:600 mg L<sup>-1</sup>. The maximum protein content (10.67% ) and protein yield (6.57 g pot<sup>-1</sup>) of pearl millet crop were observed with the application of 2.5 times reduction of RDP through nano phosphatic fertilizer than RDP through chemical fertilizer and absolute control (Dhansil *et al.*, 2018) [12]. Soaking of seeds in 0.5 g litre<sup>-1</sup> concentration of *Lantana aculeate* mediated synthesized ZnO nanoparticles significantly increased protein (1.73 mg g<sup>-1</sup>), carbohydrate (5.59 mg g<sup>-1</sup>) and reducing sugar content (4.83 mg g<sup>-1</sup>) of the *Sesamum indicum* compared to chemically synthesized ZnO nanoparticles (Narendhran *et al.*, 2016) [36]. Ramesh *et al.* (2014) [43] reported significant increase of protein content with low concentration nano-ZnO in wheat crop whereas no changes was recorded with bulk ZnO and bulk-TiO<sub>2</sub> treated samples. Zinc plays a positive role in root development, which helps plants to absorb important nutrients, especially nitrogen responsible for protein synthesis. Additionally, zinc is involved in the metabolism of carbohydrate, protein and plant hormones especially IAA and helps in the formation of starch and seed maturity (Fageria *et al.*, 2002) [16]. Yazdpour *et al.* (2014) [59] recorded maximum protein content in grain of Iranian rice cultivar with the foliar application of nano silica @ 200 ppm over other silicon sources *i.e.*, calcium silicate, potassium silicate and control. Oil yield and oil content of groundnut increased with spraying of nano boron @ 300 ppm at 30 DAS (Hanumanthappa *et al.*, 2019) [19], seed priming with borax @ 0.2% fb foliar application of nano boron @ 300 ppm at 30 DAS (Sushmitha *et al.*, 2018) [53] and seed priming of nano boron @ 0.2% in sunflower (Kavitha *et al.*, 2018) [26]. Similar results of increased oil content of the sunflower crop were reported by Janmohammadi *et al.* (2016) [25] with nano-chelated Zn application @ 1 kg ha<sup>-1</sup>. Nano-Fe appreciably influenced the seed protein content by 2 per cent compared to common Fe in black-eyed pea (Delfani *et al.*, 2014) [11] and this indicates a positive close relationship between protein content and the concentration of iron.

### Nutrient uptake

Subhash (2019) [52] reported that the spray of nano phosphorus (P) and nano potassium (K) showed significantly higher nitrogen, phosphorus and potassium uptake in rice grain and straw. Dhansil *et al.* (2018) [12] observed that the application of 2.5 time reduction of RDP through nano phosphatic fertilizer significantly increased the nitrogen, phosphorus and potassium uptake by pearl millet crop grown in *Vertic Ustocrepts* medium black calcareous soil than RDP through chemical fertilizer and absolute control. Hussien *et al.* (2015)

[21] found that application of nano-P at 1.0 g l<sup>-1</sup> improved the N, P, K, Fe, Mn, Cu and Zn uptake in cotton plants. Application of nano-zeolite phosphorus @ 100% recorded the highest N, P, K uptake in seed and straw compared to zeolite phosphorus, super phosphate and control (Hagab *et al.*, 2018) [18]. Seed priming of nano boron @ 0.2% resulted in significantly higher N (114.58 kg ha<sup>-1</sup>), P (33.67 kg ha<sup>-1</sup>) and K (72.67 kg ha<sup>-1</sup>) uptake in sunflower than application of recommended dose of fertilizer (RDF-90:90:60 kg NPK ha<sup>-1</sup> and 7.5 t FYM) alone (Kavitha *et al.*, 2018) [26]. Foliar application of nano ZnS @ 400 ppm recorded higher N, P, K and Zn uptake of sunflower (Meena and Aravinda Kumar, 2015 [34]; Singh *et al.*, 2017). Dubey and Chattopadhyaya (2016) [13] observed maximum Zn uptake (303.42 mg kg<sup>-1</sup>) of rice with the application of nanoclay polymer composite (NCPC) based Zinc. Highest uptake of N, K and Zn in grain and straw of rice was observed with the RDF + Soil application of bio zinc @ 30 kg ha<sup>-1</sup> (Apoorva *et al.*, 2017) [5]. Jamadar (2016) [23] reported the positive effect of foliar applied nanoparticles which enhanced the zinc uptake in upland paddy by 48 per cent over control. Significant increase in total zinc uptake of rice was observed with application of RDF + two foliar sprays of nano ZnO @ 1000 ppm (Jangid *et al.*, 2019) [24].

### Economics

Application of nano fertilizers reduced cost of cultivation and also enhanced crop growth and yield. The gross, net returns and benefit cost (B:C) ratio of sweet sorghum were higher with nanoscale nutrients application individually or in combination compared to that of foliar application of bulk nutrients either alone or in combination (Naseeruddin, 2016) [38]. The spray of nano P and nano K recorded higher value of gross returns, net returns and B: C ratio of rice (Subhash, 2019) [52]. Sushmitha *et al.* (2018) [53] reported higher net returns of groundnut with seed priming with borax @ 0.2% fb foliar application of nano boron @ 300 ppm at 30 DAS on red sandy loam soil. Rawat (2017) [45] observed that the highest gross returns (80587 Rs per ha), net returns (56853 Rs per ha) and B: C ratio (2.39) of wheat with the application of 100% RDF and it seems comparable with 75% RDF plus nano-sized gypsum and 75% RDF plus clay based nano-sized gypsum. Experiments conducted by Kumar *et al.* (2014) [27] at Pant Nagar to study the effect of nano-fertilizers of gypsum and rock phosphate at the rate of 3 kg ha<sup>-1</sup> on the wheat revealed that B:C ratio obtained at 50% RDF with nano-materials was almost statistically similar with 100% RDF without nano-materials.

In addition to the above, nano materials plays an important role in alleviation of harmful effects of abiotic stress caused by salinity and drought (Upadhyaya *et al.*, 2017; [56] Jaberzadeh *et al.*, 2013) [22]. Roohizadeh *et al.* (2015) [47] reported that application of 1.5 mM nano silica significantly increased the activity of superoxide dismutase and peroxidase in *Vicia faba* L. which in turn, reduces damage caused by reactive oxygen species and protects the plant's physiological processes against stresses. Foliar application of nano-sized ZnO has greater effect on biomass production of sunflower under salt stress conditions (Torabian *et al.*, 2016) [55], on grain yield of wheat under salinity stress (Babaei *et al.*, 2017) [6] and on yield of maize under water stress condition (Farnia *et al.*, 2015) [17].

### Conclusion

Green revolution had led to increased consumption of chemical fertilizers by growers which resulted in the higher

productivity. But on the other hand it turned into environmental hazard and, also increased cost of cultivation. Further, it has been proved that nutrient use efficiency of conventional fertilizers is very low. To overcome all these exertion caused by chemical fertilizers, nanoscale fertilizers can be a ray of hope with the enhanced productivity and resistance to abiotic stresses. It has been well demonstrated by the different studies that nanoscale fertilizers can improve crop growth, yield, quality, nutrient uptake and thereby increase growers' profit margin from crops. Before introducing nano fertilizers at a commercial scale, uncertainty related to the interaction of nanomaterials with the environment and their potential affects on human and animal health must be explored in detail.

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