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Agronomic Bio-fortification of Iron and Zinc through Nano-fertilizers: A Review

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ABSTRACT

The task of feeding the global human population estimated at 9.6 billion by 2050 and more than 3 billion people around the world suffer from micronutrient deficiency specially Zn and Fe, due to the consumption of poor-quality food. Micronutrient malnutrition or the hidden hunger is most prevalent amid women and preschool children triggered chiefly by low dietary intake of micronutrients. Biofortification is the process of fostering the bioavailable concentrations of essential elements in edible portions of crop plants by way of agronomic intervention or genetic selection, may perhaps be the solution to malnutrition or hidden hunger mitigation. It provides a comparatively cost effective, sustainableand long-term means of delivering more micronutrients. Thus, the time is to apply nanoparticles or nanofertilizers in solving some of these problems. Nanofertilizers can easily get absorbed by plants due to their high surface area to volume ratio. The sizes and morphologies of nanoparticles are however strong factors that determine the level of bio-accessibility by the plants from the soil. Nanofertilizers will allow controlled release of nutrients, so that this exactly synchronized with the nutritional needs of the crops and helps in improving the accumulation of nutrients in the plant. The plants applied with nanofertilizers not only grow but also accumulate such nutrients, which bridges the gap of nutrient deficiency.

Key words: Biofortification, Malnutrition, Nano fertilizers.

On a global scale, over three billion people suffer from micro nutrient deficiencies of essential minerals and vitamins (Micha *et al*., 2020). Deficiencies in iron (Fe) and zinc (Zn) are two of the most common and widespread micro nutrient deficiencies (Shukla *et al*., 2021). Biofortification is the process of increasing the content and/or bioavailability of essential nutrients in crops during plant growth through genetic and agronomic pathways (Bouis *et al*., 2011). It may perhaps be the solution to malnutrition or hidden hunger mitigation. Genetic biofortification may involve both conventional breeding as well as biotechnological tools. In conventional breeding, crops such as legumes and cereals with high micronutrient content are selected, purified and multiplied (Lucca *et al*., 2002). Then, newly improved food crops of varying nutritional contents can be conventionally developed and isolated from the varieties of the same plant. Breeding of crops is principally committed to increasing micronutrients and vitamin A content in the common food crops (Pandya-Lorch, 2012). The overall objective of nutritional genet ic modification is to integrate high micronutrient traits in already proven highest-yielding varieties (Datta and Vitolins, 2016). Crops produced through conventional breeding have gained more acceptance than those from gene modification. (Bilski *et al*., 2012) reported that improving the Fe, Zn and Se content of crops by utilizing the plant genetic makeup and applying biotechnological process could solve nutritional inadequacies in human foods; unfortunately, it is an expensive approach and involves a lot of time (Bilski *et al*., 2012). In addition, available micro nutrient in the soil limits the effectiveness of new genotypes in increasing micronutrient content (Cakmak, 2008; Velu *et al*., 2014). Moreover, these genetically-modified micronutrient-rich crops may not be adopted by many. Consequent upon these limitations, agronomic biofortification is an alternative mechanism to increase micronutrients content in staples to overcome the limitations accruing from crop breeding biofortification technique. Agronomic strategies to increase the concentrations of mineral elements in edible tissues generally rely on the application of mineral fertilizers and/or improvement of the solubilization and mobilization of mineral elements in the soil (White and Broadley, 2009). This method uses fertilization as a strategy to increase micronutrient content of cultivated crops such as cereals and legumes (Velu *et al*., 2014). The progress of agronomic fortification is a function of the application methods, fertilizer type and the crop developmental stage during application (Cakmak, 2008; Jones and Brauw, 2015). Conventional fertilizers are readily available for plant uptake but also easily lost through leaching, which is a major challenge. NPK and other agrochemicals have been found to have low use efficiency by plants because of ûxation, leaching, microbial

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degradation, photolysis and volatilization (Dimpka and Bindraba n, 2016; Raj and Khan, 2016). As such, q uantities of the inputs are usually lower than minimum effective doses that reach the crops. Inorganic fertilizers usually with sizes more than 100 nm are easily lost due to leaching and volatilization, while organic matter utilization is hampered by its low mineral content and long-period of nutrient release. Numerous attempts to increase the efficiency of nutrient uptake of crops and thus biofortify them have not been so successful. To deal with the situation, it is pertinent to develop smart materials that can release nutrients to targeted areas. Thus, the time is to apply nanoparticles or nanofertilizers in solving some of these problems. The term "nanofertilizer" specifically refers to a structure in the dimension of 1-100 nm that delivers to crops macro/micronutrients in different ways. The effectiveness of nanofertilizers is expected to be better than conventional fertilizers, because they allow a controlled release of nutrients by minimizing product loss and leaching (Jakhar *et al*., 2022). In fact, it has been demonstrated that particles size reduction by physical or chemical methods increases the surface to mass ratio of fertilizers, which in turn allows a significant increase of nutrient root absorption (Subramanian *et al*., 2015). In that way slow, targeted and more efficient nutrient release becomes possible allowing: (i) reduction of dosages and application costs, (ii) reduction as much as possible of losses due to unused nutrients from plantsand (iii) significantly increase of NUE. Nanofertilizers can easily get absorbed by plants due to their high surface area to volume ratio. The sizes and morphologies of nanoparticles are however strong factors that determine the level of bio-accessibility by the plants from the soil. The key point of crop fertilization is to avoid nutrient losses and synchronize the release of nutrients with their uptake by crops. Currently the development of the potential of nanotechnologies in crop fertilization is a high priority in fertilizer research with the target to prevent or minimize nutrient losses (Liu and Lal, 2015). It is expected that properly designed nanostructures will allow controlled release of nutrients, so that this exactly synchronized with the nutritional needs of the crops (De Rosa *et al*., 2010). Since the nutrients are in nanoscale, the fortiûcation of the plant with such nano nutrients seems to be a viable option. The plants not only grow but also accumulate such nutrients, which bridges the gap of nutrient deûciency. Keeping this in view the review focused on exploring recent available literature on the use of nanoparticles in biofortification and the use of nanofertilizers in biofortification.

Agronomic biofortification of zinc through nanofertilizers

Zinc (Zn) is a micronutrient required for plant's growth and development. Zinc deficiency is ubiquitous in arable soils because availability of Zn for plant uptake is restricted in the root zone. Normally, Zn-use efficiency does not exceed 2 to 3 per cent and the major portion of added Zn gets fixed in the soil. This causes Zn deficiency in cereals and legumes growing on potentially Zn-deficient soils. The low human dietary bioavailability of Zn from plant-based diets causes its deficiency worldwideand may impair growth and immune functions. However, the zinc-based nanofertilizers have shown a great promise (Wang *et al.,* 2016). Due to ultra-small size and high surface area to volume size ratio, Zn nanoparticles, applied either as foliar spray or root placement, can be transported efficiently in the plant system.

Researchers at the Agharkar Research Institute, Pune, Maharashtra, studied the efficacy of zinc complexed chitosan nanoparticles (Zn-CNP) and conventionally applied $ZnSO_4$ (0.2%; 400 mg L^{-1} zinc) in two durum wheat genotypes (MACS 3125, an indigenous high yielding genotype and UC 1114, a genotype containing the Gpc-B1 gene). They observed that using nanofertilizers in right doses can enhance nutritional quality of wheat by increasing its zinc content. The observed grain zinc enrichment using Zn-CNP nanocarrier (~36%) and conventional $ZnSO_4$ (~50%) were comparable, despite 10 folds less zinc (40 mgL^{-1}) used in the former. Nanofertilizer application increased grain zinc content without affecting grain yield, protein content, spikelets per spike, thousand kernel weight, *etc*. Grain zinc enrichment observed in the four-year field trials on plots with varying soil zinc content was consistent, proving the utility of Zn-CNP as a novel nanofertilizer which enhanced fertilizer use efficiency (Dapkekar *et al*., 2018). Subbaiah *et al*. (2016) sprayed 25 nm ZnO nanoparticles on maize foliage and observed that the nanoparticles positively influenced plant growth, yield and Zn content in the maize grains. Notably, about 36 ppm Zn was recorded in the grains of plants sprayed with 100 ppm ZnO nanoparticles. The authors concluded that the accumulation of Zn in various plant parts depends on nanoparticle concentration, particle solubility, plant's ability to uptake the nutrientand size and delivery of the nanoparticles. Du *et al*. (2019) observed that, in wheat crop, all plant organs showed increased Zn content with the increase in ZnO NPs concentrations. The concentration of Zn in wheat grains increased by 3.3 times and 2.4 times for ZnO NPs and $ZnSO_4$ at 1000 mg kg^{-1} compared to control. Dimpka *et al*. (2017) reported that application Zno nanoparticles significantly (23%) increased grain Zn concentration in soybean. Bala *et al*., 2018 observed that foliar application of ZnO NPs treatments significantly affected the root, shootand grain Zn contents in rice. The lowest Zn concentration in shoot (33.32 mg kg^{-1}), root (35.58 mg kg^{-1}) and grain (13.61 mg kg^{-1}) was observed in control plants, while higher Zn contents were recorded in ZnO NPs spray treatments. The highest zinc content of shoot (120.39 mg kg^{-1}), root (89.58 mg kg^{-1}) and grain (20.28 mg kg^{-1}) was observed in 5.0 g L^{-1} foliar treatment. Prajapati *et al*., 2018 observed that the seed treatment of ZnO NPs @1000 ppm followed by three foliar sprays of ZnO NPs @1000 ppm at 21, 45 and 90 days after sowing in wheat crop proved to be significantly enhanced the grain (31.70 mg kg^{-1}) and straw (85.65 mg kg^{-1}) zinc content. Itroutwar *et al*., 2019 observed

that application of ZnO NPs @ 50 mg L^{-1} in the leaves increased zinc content to 35 mg kg^{-1} as compared to control (23.5 mg kg^{-1}). The results indicate that the movement of nutrients across the leaf surface has the potential to promote the efficiency of zinc foliar fertilizers. The squash plants, which were treated by iron+manganese nano oxide, recorded the highest value of zinc content in leaves. These results might be due to manganese interaction with other elements (Schmidt *et al*., 2016). Zinc content in the grain was higher in 500 ppm NFS (19.73 ppm) as compared to 1000 ppm BFS (18.68 ppm), whereas lowest is observed in control (16.6 ppm). The gain zinc content was 5.6 per cent higher in 500 ppm of NFS as compare to 1000 ppm of BFS. Zinc content in grain has improved in both nano and bulk treatments as compared to control, but interestingly the percent increase over control was high in nano ZnO (18%) than Bulk $ZnSO_4$ (11%) (Poornima and Koti, 2019). Parmar Snehalbhai 2016, Studied the effect of foliar application of ZnO nanoparticles on Zn content of groundnut kernel and observed that application of ZnO NPs @ 500 ppm increased the zinc content of kernels to 52.75 mg kg^{-1} as compared to control (39.29 mg kg^{-1}). Priester *et al*., 2012 observed that zinc concentrations increased in a dose-dependent fashion in the stem, leafand soybean pod tissues, with more than six times more Zn in the stem (126 mg kg^{-1}), four times more in the leaf (344 mg kg^{-1})and nearly three times more in the soybean pod (81 mg kg^{-1}), when comparing the high nano-ZnO treatment (0.5 g kg^{-1}) vs. control. Application of low concentrations (≤100 mg kg^{-1}) of ZnO NPs to the soil increased Zn uptake by cucumber plant in comparison to the application of their bulk counterparts, but higher concentrations (1000 mg kg^{-1}) inhibited plant growth (Moghaddasi *et al*. 2017). Davarpanah *et al*. (2016) tried foliar application of zinc (Zn) and boron (B) NFs on pomegranate (Punica granatum cv. Ardestani) before full bloom. It increased the leaf concentrations of both microelements and the pomegranate fruit yield. Seed priming of wheat with ZnO NPs at a concentration of 0, 25, 50, 75 and 100 ppm increased the growth characteristics, biomass and the content of Zn in roots, shoots and grains of wheat with ZnO NPs than control in a pot experiment. Zinc concentration linearly increased in shoot, root and grains than control plants. As compared to control, Zn concentration in shoots increased by 25, 43, 51, 65 per cent, in roots increased by 20, 21, 29, 43 per cent and in grains increased by 8, 35, 50 and 64 per cent, respectively. Hence, it was confirmed that nanoparticles could be a source of Zn aiming to reduce zinc deficiency in plants (Solanki and Laura, 2018).

Agronomic biofortification of iron through nanofertilizers

Iron (Fe) is an essential dietary nutrientand is important for crop growth and development. Iron is involved in chlorophyll biosynthesisand required for certain enzyme functions, notably, heme-proteins (*e.g*., cytochromes-found in chloroplast and mitochondria) and involved in electron transfer system. Therefore, the primary symptom of Fe deficiency is chlorosis in young plant leaves that affects normal physiological function and nutritional quality. The most abundant form of Fe in soils is ferric oxide (Fe_2O_3) or hematite, which is extremely insoluble; thus Fe uptake by the plant is often low. Conventionally, Fe uptake is dependent on the plant's ability to reduce Fe^{3+} (ferric) to the Fe^{2+} (ferrous) formand remove it from the complex or chelating compound (often phyto-siderophores). Considering the food chain, Fe deficiency not only affects plant growth and development, but also leads to Fe deficiency in animals and humans. Therefore, it is important to increase the use efficiency of Fe fertilizers (Rout and Sahoo, 2015).

Rui *et al*. (2016) observed that, the total Fe content in the shoots and roots of peanut plants significantly increased in the EDTA-Fe and Fe_2O_3 Nano Particle treatments. The highest Fe content in shoots was in the 10 and 250 mg kg^{-1} Fe_2O_3 NPs treatments followed by the 1000 mg kg^{-1} Fe_2O_3 NPs and EDTA-Fe treatments. The Fe content in roots was higher in the EDTA-Fe treatment and Fe_2O_3 NPs treatments than in the control. Due to their Nano-effects, Nano Particles able to penetrate plant cell, which is different from the bulk Nano particles (in micrometer)and accumulate in plant tissues. Siva and Benita (2016) reported that, application of iron oxide nanoparticles significantly increased iron content of rhizome of ginger (3.5 ppm) in comparison to the rhizomes of Fe-EDTA (2.7 ppm) and control (2.5 ppm). Ghafari and Razmjoo (2013) suggested that application of 2 g L^{-1} nano iron oxide was more effective than other Fe sources and rates that was because nano-iron oxide had more number of particles per unit of weight and specific surface area which increased contact of fertilizer with plant leading to increase in Fe (131.66 ppm) uptake up to the extent of 42 per cent as compared to control (92.33 ppm). Hu *et al*. (2017) reported an increase in the iron concentration of *Citrus maxima* shoots when the plants were exposed to both γ-Fe_2O_3 NPs and Fe^{3+} treatment compared to controls and Fe(II)-EDTA treated plants. Sundaria *et al*. (2019) reported that, priming of wheat seeds with different concentrations of iron oxide nanoparticles in the range of 25-600 ppm, observed a pronounced increase in germination percentage and shoot length at 400 and 200 ppm treatment concentrations in IITR26 and WL711 genotypes, respectively. Intriguingly, the treatment concentration of 25 ppm demonstrated higher accumulation with a significant increase in grain iron contents to 45.7 per cent in IITR26 and 26.8 per cent in WL711 genotypes, respectively.

Conclusion

Several attempts to increase the efûciency of nutrient uptake of crops and thus biofortify them have not been so successful. Thus, the time is to apply nanoparticles or nanofertilizers in solving some of these problems.

Nanofertilizers can easily get absorbed by plants due to their high surface area to volume ratio. The sizes and morphologies of nanoparticles are however strong factors that determine the level of bio-accessibility by the plants from the soil. Nanofertilizers will allow controlled release of nutrients, so that this exactly synchronized with the nutritional needs of the crops and helps in improving the accumulation of nutrients in the plant. The plants applied with nanofertilizers not only grow but also accumulate such nutrients, which bridges the gap of nutrient deficiency.

Conflict of interest

All authors decalre that they have no conflict of interest.

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