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Review Article



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Nanofertilizers: Perspective to Enhance Growth, Yield and NUE of Crops

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ABSTRACT

Since green revolution crop fertilization has become one of the major components for crop production. The major drawbacks with conventional fertilizers are that they were highly prone to losses, low nutrient use efficiency and causes environmental pollution. Efforts to increase NUE of conventional fertilizers have not shown any considerable outcome. So, there is a need to intervene with alternate technology, among them nanofertilizers have the potential to increase NUE. Synthesis and application of macroutrient nanofertilizers at reduced recommendation enhances nutrient release pattern and increases the growth, yield and NUE of crops. Similarly, Seed treatment and foliar application of micronutrient nanofertilizers enhances crop nutrient uptake that leads to increased yield and NUE of crops. It also enhances quality parameters of the crops. Nanomaterial enhanced fertilizers loaded with plant nutrients enhanced nutrient release pattern and increasing plant uptake efficiency and reduce the adverse impacts of fertilization application.

Keywords: Crop nutrition, Nanofertilizers, Nutrient use efficiency, Synthesis.

INTRODUCTION

Since Green Revolution, crop fertilization has been essential to feed world. Considering that long-term field studies demonstrated that 30–50 per cent of crop yield is attributable to fertilizer inputs in temperate regions and tropical climates (Stewart & Roberts, 2012 & Stewart et al., 2005), we might therefore say that optimal crop nutrition is a fundamental requirement to ensure food security over the current century. The major drawbacks with conventional fertilizers are that they were highly prone to losses, low nutrient use efficiency and causes environmental pollution. With the growing limitation in arable land and water resources, the development of agriculture sector is only possible by increasing resource use efficiency with the minimum damage to agro ecology through effective use of modern technologies. Among these, nanotechnology has the potential to revolutionize agricultural systems (Manjunath et al., 2016).

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Nanotechnology has provided the feasibility of exploring nanoscale or nanostructured materials as fertilizer carrier or controlledrelease vectors for building of the so-called "smart fertilizers" (Nano fertilizers) as new the fertilizers to enhance nutrient use efficiency reduce and the cost of environmental pollution (Chinnamuthu & Boopati, 2009). Nano-fertilizer refers to a product in nanometer regime that delivers nutrients to crops more precisely through mechanisms such as targeted delivery, controlled release and conditional release of ingredients active in response to environmental triggers and biological demands, so that is exactly synchronized with the nutritional needs of the crops (De Rosa et al., 2010). Nano fertilizer is an important tool in agriculture to improve crop growth, yield and quality parameters with increased nutrient use efficiency, reduction in wastage of fertilizers and cost of cultivation (Mahil & Kumar, 2019). Due to a higher surface area to effectiveness volume ratio, the of nanofertilizers is expected to be better than conventional fertilizers, because they allow a controlled release of nutrients by minimizing product loss and leaching (Naderi & Danesh Shahraki, 2013) and in turn allows a significant increase of nutrient root absorption (Subramanian et al., 2015). In this 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 plants, and (iii) significantly increase of NUE. Liu and Lal (2016), divided nanofertilizers into four classes, (i) macronutrient nanofertilizers, (ii) nanofertilizers, micronutrient (iii) nanomaterial-enhanced fertilizers and (iv) plant growth stimulating nanomaterials. This review is focused on to study the effect of nanofertilizers on the growth, yield and nutrient use efficiency of crops.

Effect of macronutrient nanofertilizers on crop growth, yield and NUE of crops

Kottegoda et al. (2017) synthesized urea HA NPs and studied the nutrient release behavior in water. The Synthesized urea-HA nanohybrids exhibit a slow release of N relative to pure urea. It might be due to urea interacts with HA NPs by amine and carbonyl groups. This allows a slow release of nitrogen, an important nutrient for plants. They also studied its effect on grain yield of rice and significantly higher grain yield was obtained in the treatment T_3 (Urea-HA nanohybrids at 50 % of the recommended amount: 50 kg of N ha ¹) followed by the treatment T_2 (Granular urea: 100 kg of N ha⁻¹) and lowest yield was recorded in the treatment T_1 (Control). The higher yield in treatment T_1 was due to continuous availability of nutrient to the crop and reduced nutrient losses. Madusanka et al. 2017 synthesized nanohybrid composites by two approaches; solution phase synthesis and liquid assisted grinding techniques and were tested for their slow release nitrogen in soil. The rate of release of N was significantly lower in the nanohybrid composite prepared using liquid assisted grinding techniques and composite (U-HA-Mt-LAG), in this а significant amount of nitrogen release was observed up to the 140th day. In comparison, commercial fertilizer composition containing pure urea as the N source had released almost 80 per cent of N within 10 days and release of nitrogen had stopped after the 30th day. At the 60th day, in the commercial fertilizer, about 90 per cent of N had been released out while the U-HA-Mt-LAG Mt based nanocomposite had released only about 65 percent. They conducted a pot experiment to study its effect on grain weight, number of tillers and filled grains per pot and significantly higher filled grains and grain weight per pot of rice was recorded in the treatment T_4 (U-HA-Mt-LAG nanohybrid composite 50 per cent of the standard dose described as a basal dressing only, all other nutrients were supplied as per standards). It was due to U-HA np encapsulated into Mt nanocomposite are expected to show unique slow release behavior which is distinctly different from that of free urea when it is broadcasted over the soil surface as a fertilizer. UHA np are located within Mt particles bonded to the active sites

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on the Mt layers while some of urea molecules are present in the interlayer space of Mt. Therefore, these urea molecules could be protected against decomposition by photochemical, thermal, enzymatic, and other catalytic activities of soils unlike free urea molecules on the surface of soil particles. When U-HA np encapsulated Mt composite is in contact with soil water, it adsorbs water and urea molecules are slowly transferred into the soil solution by difusion. Further, when urea are molecules hydrolyzed to ammonia/ammonium ions, Mt can quickly adsorb the resultant ammonium ions through physical and chemical interactions due its very high afnity towards intercalation of ammonium ions among all the cations. Therefore, Mt is expected to play an essential role in releasing nitrogen in a slow and sustained manner while suppressing emission of ammonia. Subbaiya et al. (2012) compared the effects of urea modified hydroxyapatite NPs and urea alone on seed germination and seedling growth of Vigna radiata. The nanohybrid gave better results by increasing its germination rate and biomass yield. FTIR analysis indicated that the structural integrity of the nanohybrid was maintained over time; for this reason, the N release was slower than that of urea. Liu and Lal, 2014 studied the effects of nano-sized hydroxyapatite (nHA) on aboveground biomass, below ground biomass and yield of soybean. The average dry aboveground biomass was 13 g per plant under nHA treatment compared with 11 g for the regular P fertilizer application. In comparison, less than 2 g per plant biomass were harvested in cases without P application (controls). Similarly, below-ground biomass was the highest under nHA treatment of 80.9 g per plant, compared with 57.2 g per plant for the regular P application and less than 2 g dry roots harvested from soybean without P additions. More importantly, nHA application produced 5.9 g soybean seeds per plant, compared with about 4.9 g per plant under regular P treatment, and merely 1.1 and 0.6 g soybean per plant respectively for the controls without P application. Application of the nanoparticles

increased the growth rate and seed yield by 32.6 % and 20.4 %, respectively, compared to those of soybeans treated with a regular P fertilizer ($Ca(H_2PO_4)_2$). Biomass productions were enhanced by 18.2 % (above-ground) and 41.2 (below-ground). % Using apatite nanoparticles as a new class of P fertilizer can potentially enhance agronomical yield and reduce risks of water eutrophication. Beeresha and Jayadeva (2020) carried out a field experiment and studied the effect of nano potassium fertilizer on kernel yield and stover yield of maize. The results showed that, Significantly higher kernel and stover yield (9051 and 11667 kg ha⁻¹, respectively) was noted with in soil application of K₂O at 15 kg ha⁻¹ + foliar application of 2500 ppm Nano-K @ 30 and 60 DAS as compared to rest treatments. The increase in kernel yield was due to increased yield parameters like cob length, girth of the cob, number of rows cob⁻¹, number of kernels row⁻¹, number of kernels cob⁻¹, kernels weight cob⁻¹ and 100 kernel weight. Babubhai et al. (2014) conducted a pot experiment to study effect of chemical and nano-potassic fertilizers on yield and yield attributes of maize crop and the results showed that, the grain yield was significantly increased from 27.74 to 44.00 g pot⁻¹ under different treatments of nano and chemical fertilizer. The application of 2.5 times reduction of RDK through nano fertilizer produced significantly highest grain yield (44.00 g pot⁻¹) but it was statistically at par with treatment of T₇ (RDK through nanofertilizer). The treatment of T_5 and T_6 was remain statistically at par with each other. While, the lowest grain yield was recorded under control $(27.74 \text{ g pot}^{-1})$ treatment, but it was statistically at par with T_2 treatment (28.80 g pot⁻¹). Deepa, 2014 studied the effect of nano CaO on groundnut seed germination, growth, yield and calcium content in Stem, leaf and kernels. The results showed that, significantly higher germination percentages (97.33 %), root length (6.30 cm), shoot length (3.33 cm) and seedling vigor index (933.15) was recorded in the treatment T_7 with application of nano CaO @ 500 ppm. The lowest value was recorded with CaO @

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0.1 %. Similarly, significantly higher plant height (45.33 cm), dry matter accumulation (26.08 g), leaf area index (5.29), pod yield $(179.44 \text{ g m}^{-2})$ and kernel yield $(116.87 \text{ g m}^{-2})$ was recorded with application of nano CaO @ 500 ppm. Application of nano CaO @ 500 ppm recorded significantly higher calcium content in stem, leaf and kernels. Shinde et al. (2018) conducted a laboratory experiment and studied the effect of Mg (OH)₂ NPs on germination percentage and mean germination time (MGT) in maize and observed that, higher germination percentage (100%) and reduced mean germination time (1.2) was recorded with seed treatment of nano magnesium @ 500 ppm. Tarafdar and Rathore (2015) conducted a pot experiment and reported that application of nano MgO @ 20 ppm recorded significantly higher grain yield $(0.93 \text{ g plant}^{-1})$ and dry matter production (4.27 g plant⁻¹) compared to mega MgO and Control. Salem et al. (2016) conducted a pot experiment to study the effect of soil applied sulfur nanoparticles (S-NPs) on growth parameters of tomato. The results showed that, significantly higher root length (18.6 cm), shoot lengths (68.9 cm), fresh and dry weights of root (7.7 and 0.98) g and shoot (29.7 and 6.2 g) of tomato was found at 300 ppm. Beyond this concentration > 400 ppm, the roots and shoots growth, fresh and dry weights of roots and shoots were declined. The effective growth at certain SNPs concentration may be attributed to the absorption of SNPs by roots and shoots and formed organosulfur compounds, which help in enhancing the growth as necessary gradient for plant growth. Further, higher concentrations of SNPs > 400ppm caused a drop in values of the growth of root and shoot lengths. Tomato plants planted in soil treated with 300 ppm SNPs were visibly compact, vigorous, and greener in color with stronger root system.

Effect of micronutrient nanofertilizers on crop growth, yield and NUE of crops

Li et al. (2016) conducted a lab experiment and studied the effect of Fe_2O_3 NPs on germination rate and vigor index. The results showed that, germination rate and germination energy were not significantly different among all treatments. However, germination index in the treatments with 20 and 50 mg/L g-Fe₂O₃ NPs was 27.2 % and 18.9 % higher than the control, respectively. Vigor index in 20 mg/L g-Fe₂O₃ NPs treatment was 39.6 % higher than the control, while that of 100 mg/L g-Fe₂O₃ NPs was significantly lower (12.5 %) than the control. Overall, g-Fe₂O₃ NPs at lower concentration (20 mg/L) might enhance plant growth at early stage of germination. They also observed that, after 2 days incubation, root length was measured every 3 h for successive 12 h. Exposure to 20 mg/L notably increased g-Fe₂O₃ NPs root elongation compared with the control group. At the last record, 20 mg/L of g-Fe₂O₃ NPs significantly promoted root elongation by 11.5 per cent compared with control. It might be due to cell elongation in the root system could lead to faster root growth. In addition, NPs inhibited root elongation as exposure doses increased, especially at 100 mg/L g-Fe₂O₃ NPs treatment. This might be attributed to the fact that NPs in high concentration could form clusters and tend to block the pathways of nutrition uptake. Bakhtiari et al., 2015 conducted a field experiment to study the effect of foliar applied nano iron-oxide at flowering stage on the yield and yield attributes of wheat and results showed that, mean comparison of iron nanoparticles concentrations showed that spike weight was the highest in 0.04 % concentration (666.96 g) and the lowest in the control (536.33 g). The highest value of 1000 grain weight was related to 0.04 % concentration (37.96 g) and the lowest value was related to the control (32.82 g). Results showed that both biologic yield and grain yield were the highest in 0.04 % concentration $(8895.0 \text{ and } 3776.5 \text{ kg ha}^{-1})$ and the lowest in the control (8320.0 and 3316.5 kg ha^{-1}). Pradhan et al. (2013) conducted a pot experiment to study the effect of seed soaking of MnNP and MnSO₄ on root and shoot length, fresh and dry weight of mung bean plants. The reults showed that, 0.05 mg/L concentration of

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MnNP was found to be the most effective among all the dosages of MnNP as well as MnSO₄ treatments. At 0.05 mg/L dose MnNP significantly increased root and shoot length of mung bean plants by 52.26 % and 38.29 %, respectively, with respect to control. Fresh and dry weight of MnNP-treated plant at 0.05 mg/L concentration was also increased by 38.97 % and 53.6 %, respectively, with respect to control. MnNP-treated plants did not exhibit any toxicity symptoms neither in leaf nor in root at higher concentration; even all the plants were healthy. Meanwhile plants dosed at 0.5 mg/L or above of MnSO₄ showed severe toxicity symptoms like necrotic leaves, brown roots, and gradual disappearance of the rootlet after 15 days of treatment. Hafeez et al. (2015) studied the impact of soil applied Cu-NPs to wheat plants in pots and reported that, progressive increase in chlorophyll content and leaf area was observed with application of 10, 20 and 30 ppm Cu-NPs. Increasing the level of Cu-NPs to 40 and 50ppm was accompanied by a significant reduction in chlorophyll and leaf area due to more absorption of nanoparticles leading to phytotoxic effects. In general, addition of 10 to 40 ppm Cu-NPs in pots produced significantly higher leaf area and chlorophyll than those of control plants. Similar trend was observed for number of grains/spike, 100 grain weight and grain yield per pot. Nonetheless, the best results were achieved with application of 30ppm Cu-NPs to wheat in pots. Therefore, 30ppm Cu-NPs applied in soil may be considered the best for inducing good growth and maximum yield. Nanoparticles induced increased activity of chloroplast, rubisco, antioxidant enzyme system and nitrate reductase might be the possible underlying mechanism responsible for enhanced growth and yield. Shende et al. (2017) conducted a pot experiment to study the effect of of CuNPs on shoot length and root length of pigeon pea plants and reported that, the rate of plant growth, as determined by their shoot and root length, was maximum for CuNPs treatment when compared with the control, which demonstrated the minimum growth. In

particular, CuNPs showed 22.79 % increase in shoot length and 64.86 % growth in root length over control. The wet and dry biomass was estimated with respect to the treatment of NPs for pigeon pea after 4 weeks. CuNPs (20 ppm) inoculated plants showed a 34.74 % increase in fresh biomass and 82.35 % increase in dry biomass over the control. The biomass yield was found to be in agreement with the root and shoot for the corresponding NPs treatment. Goudar et al. (2017) conducted a field experiment to observe yield and yield attributes of sunflower as influenced by different levels and methods of nano boron and borax application. The results showed that significantly higher seed yield and stalk yield was observed with application of nano boron nitride @ 0.2 % seed priming and it was on par with Nano boron nitride @ 0.2 % spray to capitulum at RFO stage and they concluded that, higher seed yield might be attributed to improvement in yield contributing characters viz., seed yield per plant, higher head diameter, higher number of seeds per capitulum, 100 seed weight and volume weight. This improvement in yield components was in turn due to improved growth parameters such as higher plant height, chlorophyll content, higher leaf area and total dry matter production and distribution in different parts. Higher seed yield might be associated with application of nano boron (both seed treatment and foliar spray) met the crop nutrient demand for boron during the pollen development, which may result in increased pollen germination and pollen viability and increasing the translocation of sugars and photosynthates from source to sink which in turn enhances the seed setting percentage in the capitulum. Patel et al. (2019) studied the effect of foliar application of nano Zn particles on yield and vield attributes of sunflower and the results showed that, foliar application of nano ZnS @400 ppm+boron @0.5 % increased the seed yield from 7.06 g to 10.24 g plant⁻¹ resulting into 45 % increase; and was on par with nano ZnO @ 1,000 ppm + boron @ 0.5 % (9.88 g plant⁻¹). This might be due to more availability of soluble forms of sulphur and zinc in ZnS nano-

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formulation. The average increase in seed yield owing to application of nano ZnS @ 400 ppm + boron @ 0.5 % and nano ZnO @ 1,000 ppm + boron @ 0.5 % over control were 45 % and 40 %, respectively. The per cent seed oil content in control increased from 37.06 to 41.15 with the foliar application of nano ZnS @ 400 ppm + @ 0.5 %. This treatment also boron significantly increased oil yield (4.21 g plant⁻¹) compared to rest of the treatments to an extent of 59 and 42 per cent over control and ZnSO₄ @ 5,000 ppm, respectively. Further, foliar application of ZnO @ 1,000 ppm alone and in combination with boron @ 5 % also increased the seed oil content and oil yield to an extent of 23 and 42 per cent, respectively. This increase in oil content is attributed to efficient fatty acid synthesis wherein, acetyl Co-A is converted into malonyl Co-A. This conversion is mediated by enzyme thiokinase, the activity of which depends on sulphur supply. Moreover, acetyl Co-A itself contains sulphur and sulphur hydroxyl group. Hence the sulphur containing nano ZnS formulation might have accelerated this process. Singh and Kumar (2017) studied the effects of different concentrations of nano ZnS on plant height, leaf area and seed yield of sunflower and reported that among the different concentration of nano zinc sulphide, 400 ppm sprayed at 35 DAS record significantly higher plant height (124.73 cm) which were on par with 500 ppm nano zinc sulphide sprayed at 55 DAS and 500 ppm nano zinc sulphide sprayed at 35 DAS. This might be due to more availability of nutrient to the crop during initial growth period, which enhance growth rate of these growth parameters by more photosynthesis. Similarly, 400 ppm nano zinc sulphide sprayed 35 DAS recorded significantly higher leaf area $(537.67 \text{ cm}^2 \text{ plant}^{-1})$ at harvest. Among the different concentration of nano zinc sulphide, 500 ppm nano-ZnS sprayed at 55 DAS recorded significantly higher vield (5.27g plant⁻¹) superior over rest of the treatments, which was on par with seed weight (4.87 g plant⁻¹) 400 ppm at 35 DAS. They also observed a marked increase in the zinc and sulphur (58.92 mg and 0.41 mg plant⁻¹) uptake with the application of 500 ppm nano ZnS sprayed at 55 DAS followed by 400 ppm nano-ZnS sprayed at 35 DAS. This might be due to higher biomass production lead to

higher uptake of nutrients from soil at higher sulphur levels. Thomas et al. (2017) studied the effect of different doses of nano molybdenum on grain yield and dry biomass of chickpea. results showed The that. significant improvement in dry matter biomass and grain yield with the application of 4 ppm concentration of nano-molybdenum. The maximum dry matter yield among the treatments was also observed at 4 ppm concentration that confirms the application of 4 ppm nano-molybdenum is the optimum dose for chickpea. The higher yield may be because of the more root development and photo catalytic activity at that concentration.

Effect of Nanomaterial enhanced fertilizers on crop growth, yield and NUE of crops

Manikandan and Subramanian (2015) studied the effect of zeolite based N fertilizers on maize yield, crude protien and N content and the results showed that application of urea in the form of nanozeourea recorded significantly higher grain yield (156 g), 100 seed weight (29.4 g) and crude protein (4.7%). It may be the effect of slow release and controlled release of nitrogen from the nanozeourea application and availability of nitrogen throughout crop growth period. The highest N content was registered in grain (0.32) and stover (0.76) of maize plants fertilized with nanozeourea while urea fertilized plants. The slow release pattern might be the responsible factor for enhanced nitrogen uptake. Malekian et al. (2010) studied the effect of different soil amendment types on grain yield, stover yield and nitrogen content of maize and the mean grain yield, grain nitrogen content, stover dry matter, and N were significantly greater uptake in clinoptilolite-amended treatments compared to those in surfactant-modified zeoliteamended treatments. Clinoptilolite has the capacity to adsorb the NH4⁺ present in fertilizer, which can then be released by clinoptilolite and taken up by plants before it is nitrified. This result implicitly suggests that plants may have a better response if clinoptilolite is used as a fertilizer carrier rather than surfactant-modified zeolite.

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Application rate had a significant effect on grain yield, grain N concentration, stover dry matter. However, stover nitrogen content was not affected by the soil amendment application. The ratio of N uptake to the applied N fertilizer (RUF) was 77.4 % for the control. The application of soil amendments increased the mean RUF to 81.83 % and 80.08 % for clinoptilolite and surfactant-modified zeolite, respectively. A significant difference between the RUF of the higher rate of soil amendment application and that of the lower rate of application was also observed. Application of surfactant-modified zeolite and clinoptilolite at a higher rate resulted in an increase in RUF of approximately 5 % and 10 %, respectively. Rajonee et al., 2016 studied the, available nitrogen of soil after nano fertilizer applications at different incubation days and the release of inorganic nitrogen was prominent in case of nano fertilizer throughout the entire experiment and all the experimental units exhibited the same trend, though at different degrees. The control soil contained less N than the rest. On Day 15 of incubation, the conventional fertilizer treated soil showed an increase followed by an eventual decrease. The nano fertilizer incorporated soils showed slight increase on Day 30 of incubation. The N content in soil remained high in the nitrogen incorporated zeolite and released higher percentage of available nitrogen as compared to the others. Rajonee et al. (2017) studied the available phosphorous of soil after nano fertilizer applications at different incubation days and the results showed that, the initial P was the highest in nano fertilizer treated soils while the control soil had the least. However, the release of P was apparently steeper in case of nano fertilizer than the rest. The release of higher amount of phosphorous by nano fertilizer treated soil may be because of well incorporation of KH₂PO₄ onto zeolite as revealed in XRD analysis. The P supply from nano fertilizer remains available even after a long time compared to conventional fertilizer. From, Percent release of phosphorous in conventional fertilizer and nano fertilizer shows that conventional fertilizer has an initial higher rate of release then a sharp decrease continued for the other days of incubation. Conventional (T.S.P) fertilizer gives an indication of exhaustion after 15 days to 30 days of incubation. This may be a sign of fixation at lower pH. But in case of nano fertilizer though the trend is similar to that of conventional fertilizer, the rate of release however, was higher even for the last day of incubation. The release did not level off like the conventional fertilizer. This could be an indication of continuous release of P or a fixation of the nano-P smaller than conventional one. Rajonee et al. (2017) studied the available potassium of soil after nano fertilizer applications at different incubation days and observed that percent release of potassium in conventional fertilizer and nano fertilizer shows a decreasing trend but the release is always higher for nano fertilizer throughout the whole incubation period even in the last day of observation. But nano fertilizer shows a quicker decrease from 15 days to 30 days than conventional. The same fertilizer is used as the source of potassium (KCl) but the release is higher for nano fertilizer. The trend of K release from the synthesized nano fertilizer could be an indication that the bond of K with the surface modified zeolite has not been strong. This however, needs further study using a different carrier. Yuvaraj and Subramanian (2018) studied the nano zeolite nutrient release pattern and reported that, at the start of the experiment nutrient release pattern, a maximum concentration of 22 ppm Zn was observed in the leachate from nano-zeolite. The data revealed that the entire available Zn from ZnSO₄ was exhausted after 120 h beyond which the concentration of Zn^{2+} reached below detectable limits. However, the release of Zn from nano-zeolite was continued even after 1,176 hr, with a concentration of 1.3 ppm. The mechanism for this effect may be that sparingly soluble minerals are dissolved by the sequestering effect of the exchanger, thereby releasing trace nutrients to zeolite exchange

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sites where they are more readily available for uptake by plants. Saharan et al. (2016) studied the effect of Cu-chitosan NPs on *Zea mays* germination and results showed the enhanced germination percentage as well as an increase in root and shoot biomass of seedlings. Influence of Cu-chitosan signals were studied also at biochemical levels and observed an increase in the activity of both α -amylase and protease, and total soluble protein. Dapkeker et al. (2018) investigated the use of Cu complexed chitosan NPs for biofortification of *Triticum durum* in a field experiment. Two genotypes of durum wheat were grown under conventional agronomic management during vegetative stages. Then, for the entire grain development stage Zn foliar application was scheduled once a week using zinc sulfate solutions and Znchitosan NPs. At harvest yield components (Spikelet's per spike, grains per spike, spike length, kernel weight and total grain weight) and grain quality (protein content) were measured. Comparing the treatments, consistent comparable grain enrichment was observed. However, Zn-chitosan treatment used 10-folds less than conventional one demonstrating a relevant enhancement in the Zn use efficiency.

Nutrient	Crop	Material	Treatment	Experiment type	Response	Reference
Ν	Oryza sativa	Urea-modified Hydroxyapatite nanohybrid composite (HAU)	Granular urea compared to HA- U	Field study	Slow N release relative to pure urea and increased	Kottegoda et al. (2017)
N	Vigna radiata	(i) nano Urea (nU) (ii) nano Hydroxyapatite (nHA) composite	(i) normal U; (ii)chemically synthesized nU + nHA; (ii)biologically synthesized U + nHA	Pot trial	Promoted seedgermination; increased seedling growth	Subbaiya et al. (2012)
Ν	Oryza sativa	Urea-Hydroxyapatite Montmorillonite nanohybrid composite (U-HA-MMT)	Conventional fertilizer: 120 kg ha ⁻¹ N; 40 kgha ⁻¹ P ₂ O ₅ , 40 kg ha ⁻¹ K ₂ O	Soilcolumns, pot trial; Ceylon tea soil	SlowerNrelease;significant yield enhancement compared to control	Madusanka et al. (2017)
Р	Glycine max	Apatite,Ca5(PO4)OH	(RF+NP) Synthetic fertilizer solution with nano hydroxy apatite (F + nHA)	Pot trial	Increased growth rate (+32.6 %), aerial biomass (+18.2 %) and seed yield (+20.4 %) than control	Liu and Lal, 2014
К	Zea mays	Nano-K	Soil application of K ₂ O at 15 kg ha ⁻¹ + foliar application of 2500 ppm Nano-K	Field study	Higher kernel and stover yield was noted with in as compared to rest treatments.	Beeresha and Jayadeva, 2020
К	Zea mays	Nano-K	2.5 time reduction of RDK through nano fertilizer	Pot trial	Higher Grain yield (g pot ⁻¹) and Fodder yield (g pot ⁻¹)	Babubhai et al., 2014
Ca	Arachis hypogea	Nano Ca	Nano CaO 500 ppm	Field study	Higher pod yield and kernel yield	Deepa, 2014
Mg	Zea mays	Nano Mg(OH) ₂	Seed treatment of nano Mg(OH) ₂ @ 500 ppm	Germination study	Higher germination percentage and mean germination time (MGT) were recorded	Shinde et al. (2018)
Mg	Triticum aestivum	Nano MgO	Foliar application of nano MgO @ 20ppm	Pot trial	higher grain yield and dry matter production	Tarafdar and Rathore, 2015
s	Lycopersicon esculentum	Nano S	Soil applied sulfur nanoparticles @ 300 ppm	Pot trial	significantly higher root length, shoot lengths, fresh and dry weights of root and shoot	Salem et al., 2016

Table 2: Effect of micronutrient nanofertilizers on crop growth, yield and NUE of crops

Nutrient	Crop	Material	Treatment	Experiment type	Response	Reference
Fe	Zea mays	Nano Fe ₂ O ₃	Seed treatment with 20 mg/L Fe ₂ O ₃ NPs	Germination study	Higher germination index and root elongation	Li et al., 2016
Fe	Triticum aestivum	Nano FeO	Foliar application of FeO @ 0.04 % concentration at flowering stage	Field study	Higher grain yield and biological yield	Bakhtiari et al., 2015
Mn	Vigna radiata	Nano Mn	Seed soaking of nano Mn @ 0.05 mg/L	Germination study	Increased root length, shoot length, fresh and dry weight	Pradhan et al. (2013)
Cu	Triticum aestivum	Nano CuO	Soil applied nano Cu @ 30ppm	Pot trial	Higher leaf area, chlorophyll, number of grains/spike, 100 grain weight and grain yield	Hafeez et al. (2015)
Cu	Cajanus cajan	Nano CuO	Foliar application of 20 ppm nano Copper at fifth and tenth DAS	Pot trial	Increase in shoot length by 22.79 % and root length by 64.86 % over control	Shende et al. (2017)
В	Helianthus anus	Nano B	Seed priming of Nano boron nitride @ 0.2 %	Field study	Higher seed yield and stalk yield	Goudar et al. (2017)
Zn	Helianthus anus	Nano ZnS	Foliar application of nano ZnS @ 400 ppm + boron @ 0.5 %	Pot trial	Increase in seed yield by 45 % compared to control and higher Oil content	Patel et al. (2019)
Zn	Helianthus anus	Nano ZnS	Foliar application of nano ZnS @ 35 DAS	Pot trial	Higher seed yield, stalk yield and nutrient uptake (Zn & S)	Singh and Kumar (2017)
Мо	Cicer aeriatinum	Nano Mo	Foliar application of nano Mo @ 4 ppm	Pot trial	Higher dry matter and yield	Thomas et al. (2017)

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Table 3: Effect of Nanomaterial enhanced fertilizers on crop growth, yield and NUE of crops								
Nutrient	Crop	Material	Treatment	Experiment type	Response	Reference		
N	Zea mays	Zeolite based N fertilizers	Nano zeolite urea intercalated @ RDF- 250:75:75 kg ha ⁻¹	Pot trial	Higher grain yield, 100 seed weight and crude protein	Manikandan and Subramanian (2015)		
N	Zea mays	Zeolite clinoptilolite	60 g zeolite kg ⁻¹ and 150kgN ha ⁻¹ fertilizer	Pot trial	Lower NO ₃ -N leaching than control and higher grain and stover yield	Malekian et al. (2010)		
Ν	Ipomea aquatica	N-Zeolite	Conventional fertilizers Vs. N- loaded zeolite	Soil incubation (30 days) and Pot experiment	Enhanced N accumulation in plant biomass	Rajonee et al., 2016		
P & K	Ipomea aquatica	P-Zeolite & K- Zeolite	Conventional fertilizers Vs. N- loaded zeolite	Soil incubation (30 days) and Pot experiment	Enhanced P and K accumulation in plant biomass	Rajonee et al., 2017		
Zn	-	Zeolite Zn	Conventional fertilizers Vs. Zn- loaded zeolite	Soil incubation	Enhanced Zn release by	Yuvaraj and Subramanian (2018)		
Cu	Zea mays	Chitosan Cu	0.16 % w/v	Germination study	enhanced germination,root and shoot biomass; increased α-amylase and protease, and total soluble protein	Saharan et al. (2016)		
Cu	Triticum durum	Chitosan Cu	Foliar application @ 40 mg L ⁻¹	Field experiment	Enhanced grain yield and protein content	Dapkeker et al. (2018)		

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CONCLUSION

Since green revolution crop fertilization has become one of the major components for production but the crop NUE of conventional fertilizers is too low. Efforts to increase NUE of conventional fertilizers have not shown any considerable outcome. So, there is a need to intervene with alternate technology, among them nanofertilizers have the potential to increase NUE. Synthesis and application of macroutrient nanofertilizers at reduced recommendation enhances nutrient release pattern and increases the growth, yield and NUE of crops. Similarly, Seed treatment and foliar application of micronutrient nanofertilizers enhances crop nutrient uptake that leads to increased yield and NUE of crops. It also enhances quality parameters of the crops. Nanomaterial enhanced fertilizers loaded with plant nutrients enhanced nutrient release pattern and increasing plant uptake efficiency and reduce the adverse impacts of fertilization application.

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