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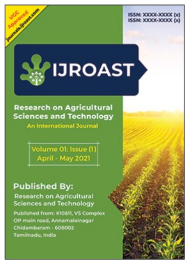

Consequences of Nano fertilizers usage in agriculture- A Little Review

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Agricultural fertilization has been one of the most important components of crop production since the start of the green revolution. The main disadvantages of conventional fertilizers are that they are very susceptible to losses, have a low nutrient usage efficiency, and pollute the environment. Efforts have been undertaken to raise the NUE of conventional fertilizers, but they have had little success. As a result, there is a need to intervene with alternative technology, one of which is nano fertilizers, which have the ability to boost NUE. The use of macronutrient nano fertilizer reduces fertilizer rates while increasing nutrient release patterns, resulting in increased crop growth, yield, and NUE. Similar to foliar application of micronutrient nano fertilizers, foliar application of micronutrient nano fertilizers improves crop nutrient uptake, resulting in enhanced crop output. It also improves crop quality parameters. Nanomaterial enriched fertilizers containing plant nutrients improved nutrient release patterns, increased plant absorption efficiency, and reduced fertilization application's negative impact.

Introduction

According to a UN DESA assessment, the present global population of 7.7 billion people will grow to 8.5 billion by 2030, 9.7 billion by 2050, and 11.2 billion by 2100 [1]. Producing enough food to feed the world's growing population would be tough. Agriculture is currently confronting a number of issues around the world, the most significant of which is nutrient management. Farmers are using inorganic fertilizers indiscriminately to replenish the nutrients shed by crops in order to meet crop nutritional needs. Inorganic fertilizer use has a negative impact on soil health, human wellbeing, and production. Due to leaching losses, as well as volatilization and denitrification losses, high analysis fertilizers like urea, diammonium phosphate, and more of potash have been found to have lower fertilizer efficiency ranging from 20 to 50 per cent for nitrogen, 10-25 per cent for phosphorus, and 70-80 per cent for potassium. The idea of nutrient usage efficiency (NUE) is significant in agricultural production systems [2]. Traditional fertilizers, often known as conventional fertilizers, are both costly to the producer and detrimental to persons and the environment. As a result, we must look for ecologically friendly or smart fertilizers that also have excellent nutrient utilization efficiency, and nanotechnology is emerging as a possible solution. Because of the increasing issues in agriculture, interest in nanotechnology has grown with the goal of increasing agricultural yield and resource efficiency. Although nano fertilizers and nanomaterials are clearly paving the way for new approaches to precision and sustainable agriculture, their limitations must be carefully considered before they are put on the market. We can employ nano-fertilizers, which are nutrient carriers with nano diameters of 30 to 40 nm. They can retain a lot of nutrients ions and release them slowly and steadily to suit crop requirements since they have a lot of surface area. Because of their ease of solubility, stability regulated release, nutrient supply at the right moment, and simple manner of delivery and disposal, nano-fertilizers are easily absorbed and blended in by plants. Although nano-fertilizers can help farmers perform better, they have a negative impact on soil microbiology, fauna, animals, and humans. It's linked to a number of disorders and risks, including high blood pressure, blood clots, stroke, arrhythmia, and heart disease [3]. Nano fertilizers also have the potential to solve problems that arise in modern agriculture as a result of the use of conventional fertilizers. It has the potential to boost yields in a variety of agricultural crops. They release active substances precisely to protect soil health and environmental purity. Nano fertilizers boost agricultural yield by increasing seed germination, seedling growth, photosynthetic activity, nitrogen metabolism, and carbohydrate and protein synthesis rates.

Need for nano fertilizers

Agriculture has a wide range of issues in the production system, including decreased crop yields, decreasing

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soil organic matter content, increased levels of multi-nutrient deficiencies, and harsh weather. Agricultural scientists are dealing with a variety of issues in the crop production system, including decreased crop yield, declining organic matter content, multi-nutrient deficiencies, climate change, dwindling primary agricultural resources such as arable land and water, resistance to genetically modified organisms, and labour efficiency. The majority of agricultural output is stalled as a result of unbalanced fertilizer and decreased soil organic matter concentration. The total nutrient consumption ($N+P_2O_5+K_2O$) increased by 2.9 per cent. According to studies in India, the present NPK fertilizer use ratio is 10: 2.7: 1, which is lower than the optimal NPK fertilizer ratio of 4: 2: 1 for crop productivity.

Nitrogen fertilizers are widely recognized for fast evaporating through multiple paths, but leaching loss causes groundwater pollution, which leads to eutrophication. The fertilizer response ratio has dropped dramatically from 13.4 kg grain per kilogramme of nitrogen applied in the 1970s to 3.7 kg grain in 2005. Crop loss is increasing every year, approaching 25 to 30 per cent, due to widespread multi-nutrient deficits, which have a direct impact on crop yield."For N, P, K, S, Zn, and B, respectively, the degree of nutrient shortages in the country is on the order of 89, 80, 50, 41, 49, and 33 per cent." Nano fertilizer is the final solution. Nano fertilizers are nano-formulated particles that can deliver vital plant nutrients to the rhizosphere at the precise time and dose required by crops.

Why are Nano-fertilizers better than Conventional fertilizers

Nanoparticles have unique qualities that make them a potential plant growth enhancer, such as enhanced sorption capacity, the increased surface to volume ratio, and controlled-release kinetics to targeted areas.

Nano-structured fertilizers can be employed as a smart delivery system of nutrients to plants because of these qualities. In comparison to conventional fertilizers, nano-fertilizers release nutrients very slowly. This method improves fertilizer nutrient effectiveness and reduces nutrient loss into groundwater.

Nano-fertilizers are carefully engineered to release active components in response to biological and environmental demands. Nano-fertilizers also boost agricultural output by improving photosynthetic activity, seedling growth, seed germination rate, nitrogen metabolism, and carbohydrate and protein synthesis, according to scientists.

How do Nano-fertilizers enter the plant system?

According to researchers, the plant root system, which serves as a nutrient gateway, is more permeable to nanomaterials (nano-fertilizers) than conventional fertilizers. Leaf stomatal apertures have also been found to facilitate the uptake of nanomaterials and their entrance into leaves. Scientists used the faba bean (*Vicia faba*) in trials to determine the nanoparticles' ability to permeate the plant system. In comparison to nanoparticles larger than 1.0 nm in size, they discovered that nanoparticles (43nm in size) could penetrate leaf in significant numbers. Nano-fertilizers also use plasmodesmata to deliver nutrients. Plasmodesmata are nano-sized channels that carry ions between cells and have a diameter of 50-60 nm. Carbon nanotubes and silica nanoparticles are effective tools for carrying and delivering cargo to plant target sites (nutrients and other essential biochemicals).

Nano fertilizers in improving NUE

Different crops have different nutrient requirements, so nano-fertilizers are synthesized to release nutrients which match the crop nutrient requirement. This can be achieved by nano fertilizers coated with nanomembranes particles that help in the slow and sturdy release of nutrients. After the application of nanoparticles, an incredible improvement in NUE was observed in plants. In general, 3-4 times improvements in use efficiency were noticed for many nutrients, including P, Zn, Fe and Mg nanoparticles (Meghana *et al.*, 2021).

The reasons are particles of nano-fertilizers are very less in size, so they have a higher surface area, which provides more sites to facilitate a different metabolic process in the plant system, resulting in the production of more photosynthates. Due to this, they have high reactivity with other compounds. Fertilizers encapsulated with nanoparticles will increase the availability and uptake of nutrients to the crop plants. Zeolite based fertilizers are capable of releasing nutrients slowly to the crop plant, which increases the availability of nutrients to the crop throughout the growth period and prevents loss of nutrients from denitrification, volatilization, leaching and fixation in soil. Why the interest in adopting nano fertilizers is increasing now is their penetration capacity, size and very higher surface area, these characteristics differ from the same material found in usual bulk form.

Types of nanomaterials

- **Carbon-based nanomaterials:** These nanomaterials are composed of carbon; commonly, the carbon forms are hollow spheres, ellipsoids, or tubes. Spherical shaped carbon-based nanomaterials are called fullerenes, and those with a cylindrical shape are called nanotubes.
- **Metal-based nanomaterials:** These nanomaterials include quantum dots, Nanogold, Nano silver and metal oxides, such as titanium dioxide, zinc oxide, magnesium oxide, iron oxide etc.
- **Dendrimers:** Dendrimers are Nano-sized polymers of branched units with a large number of chains ends on their surface. Dendrimers are planned to design in a way that they can be altered in different ways and then only perform specific chemical functions. Because of this property, dendrimers can be used as a catalyst, and it has a three-dimensional structure with inner cavities; placing the drug molecules inside the cavities allows for to use of dendrimers for drug delivery.

Nanocomposites: A formulation obtained by combining nanoparticles with other nanoparticles or with larger bulk type materials is called nanocomposite. These are generally used to enhance the mechanical, thermal barrier, and flame-retardant properties of other materials ((Meghana *et al.*, 2021).

Unique properties of nanoparticles

- Smaller size, larger surface area

• Increased surface area to volume ratio
• Nanoparticles are very small in size, so they even pass through the plant and animal cells, which is the main clue through which nanotechnologists are able to achieve the phenomena of delivering the required product at a cellular level. This thing makes nanotechnology advantageous over conventional methods.
• Slow release
• Specific release

The nanoparticles have a high specific surface area (SA) for their volume, and atoms of NP occur at surfaces which leads to the higher reactivity of nanoparticles. This higher SA to volume ratio provides higher reactivity and better penetration into soil and plant.

Effect of Nano fertilizers on growth and development of agricultural crops

Depending on the qualities of nanoparticles, they interact with plants and cause a variety of morphological and physiological changes. The chemical composition, size, surface coverage, reactivity, and, most crucially, the dose at which nanoparticles are effective to define their efficacy. The efficacy of plants is determined by their concentration, according to [4]. Higher seed germination, shoot length, and root length was recorded under seeds treated with nano fertilizers. It increases the availability of nutrients to the growing plant, which increases chlorophyll formation, photosynthetic rate, dry matter production, and results improve overall growth of the plant [5]. [6] opined that application of nano CaO @ 500 ppm increase the seed germination, growth, calcium content in the stem, leaf and kernels, root length, and shoot length in groundnut. [7] reported that applying NPK Nano fertilizer as foliar application increased different plant growth traits, which include root length, shoot length, and leaf area. The application of nano NPK fertilizer increases plant growth. It leads to more vegetative biomass yield compared to normal or unfertilized treatments. [8] suggested that the application of Cu-chitosan NPs on *Zea mays* increases the germination percentage as well as an increase in root and shoot biomass of seedlings.

[9] rice plant height was enhanced by the application of the full recommended rate of nano fertilizer at 15 an AT compared to other treatments due to nano fertilizer an either provide nutrients for the plant or aid in the transport or absorption of available nutrients resulting in better crop growth. In soybean, the synthesized new type of hydroxyapatite phosphorus nanoparticles (NPs) of ~16 nm in size and assessed fertilizing effect of the NPs on soybean in inert growing medium in a greenhouse experiment. The data revealed that the growth rate was increased by 33% using phosphors Nps. Chlorophyll content of wheat plants significantly differed by application of SNPs. Maximum chlorophyll content (51.2) was recorded at 75 ppm, followed by 100 ppm of (46.1) SNPs. SNPs induced enhancement of chlorophyll content may enhance photosynthesis leading to more production of bio-mass and yield [10]. Several researchers reported that nano fertilizers influenced seed germination and seedling growth, which discovered the effect of nano fertilizers on seed and seed vigour. Nano fertilizers can easily penetrate into the seed, so it increases the availability of nutrients to the growing seedling, which leads to increased shoot length and root length but if the concentration is more, it may show inhibitory effects on the seed germination and seedling growth of the plant. Nano fertilizers increase nutrient availability to the growing plant, which increase chlorophyll formation, photosynthesis rate, dry matter production and also improves overall growth of the plant [11].

Moreover, the highest plant height (57.9cm), a number of tillers per plant (6), plant dry weight during the ripening stage (9.9g) recorded in plants treated with 100% Nano-N fertilizer [12]. Application of phosphorus nanoparticles has positive relationship between the number of rice tillers and the initial P concentration in the nutrient solutions [13]. Rate of plant growth, shoot length, and root length was maximum for Cu NPs treatment when compared to the control, which demonstrated the minimum growth. In particular, Cu NPs showed a 22.79% increase in shoot length and 64.86% growth in root length over control.

Effect of Nano fertilizers yield on yield attributes of agricultural crops

The soil application of NPK + Zn+ S recorded higher grain yield and yield attributes of rice. [14] reported that the application of zinc fertilizer increases the higher grain and straw yield, with might be due to the fact that zinc plays an important role in the biosynthesis of IAA.. The yield of rice increased significantly with the application of zinc @ 2.5, 3.0, 10 kg Zn ha^{-1} by 17.5, 26.3, and 29.9 per cent in grain and 21.0, 31.9 and 42.7 per cent in straw yield respectively over control. Maize grain yield was increasing significantly from 27.74 to 44.00 g pot-1 under nano fertilizer. The application of the Recommended Dose of Potassium (RDK) was lowered by 2.5 times using nano fertilizer, and the grain production was much higher [15].

Foliar application of nano-oxide at the flowering stage increases the yield and yield attributes of wheat. The spike weight was highest in 0.04% concentration and the lowest in control. Both biological yield and grain yield were highest in 0.04% concentration [16]. Urea applied in the form of nanozeourea resulted in significantly better grain production, 100 seed weight, and crude protein, according to the study. It may be the effect of slow-release and controlled release of nitrogen from the nanozeourea application and availability of nitrogen throughout the crop growth period. The highest N content was shown in grain and stover of maize plants fertilized with nanozeourea. Improved nitrogen uptake due to the slow-release pattern of nano fertilizer [17]. [18] revealed varied quantities and methods of nano boron and borax administration affect sunflower production and yield characteristics. The results showed that application of nano boron nitride @ 0.2 per cent see priming resulted in significantly higher seed yield and stalk yield, which was comparable to Nano boron nitride @ 0.2 per cent spray to capitulum at RFO stag, and they concluded that higher seed yield could be attributed to improvements in yield contributing characters. Improved growth characteristics such as plant height, chlorophyll content, leaf area, and total dry matter production and distribution in different areas contributed to the increase in yield components. Higher seed yield could be linked to the use of nano boron to meet the crop's boron demand during pollen development, which could lead to increased pollen germination and viability, as well as increased sugar and photosynthesis translocation from source to sink, boosting seed setting percentage in the capitulum.

In comparison to bulk nutrient sources, increased grain production with the application of nano-K fertilizer is highly connected with an increase in seeds/panicles. Nano fertilizer treated plants also reported higher values of yield metrics. The amount of iron in the plant was higher in the nano iron treated plants than in the control plants. The use of 25% Nano-fertilizers can be enhanced and improve cotton yield by increasing the number of sympodial branches per plant [19]. The application of soil Nano Fertilizer 184 N, 39.56 P, 41.50 K kg ha^{-1} increases the grains yield, protein percentage, and flag leaf area, its dry weight, total chlorophyll content, nitrogen, phosphorus and potassium compared with the control treatment [20].

[21] studied the effect of foliar application of nano Zn particles on sunflower yield, and yield attributes were investigated, and the findings revealed that foliar application of nano ZnS @ 400 ppm + boron @ 0.5 per cent increased seed yield from 7.06g to 10.24g plant-1, a 45 per cent increase, and was comparable to nano ZnO @ 1000 ppm + boron @ 0.5 per cent. This could be owing to the fact that the ZnS nano-formulation contains more soluble forms of sulphur and zinc. ZnO at 1000 ppm alone and in conjunction with boron at 0.5 per cent improved seed oil and oil content and oil production by 23 and 42 per cent, respectively, when applied to foliar. The increase in oil content is due to efficient fatty acid synthesis, in which acetyl Co-A is transformed to malonyl Co-A. This conversion is aided by the thiokinase enzyme, whose activity is dependent on the availability of sulphur. Sulphur and a sulphur hydroxyl group are also present in acetyl Co-A. As a result, the sulphur-containing micro ZnS formulation may have sped up the process. The application of Nano-N, K, and Zn resulted in a statistically significant increase in wheat seeds per spike, root length, 100 seed weight, yield per pot of 23.87 g and biomass accumulation compared to the control and bulk/chemical N, K, Zn [22].

Effect of Nano fertilizers on nutrient uptake and nutrient availability of agricultural crops

Nanoparticle uptake, translocation, and gathering are influenced by crop species and age, growing environment, physicochemical properties, functionalization, stability, and route of delivery. Nanoparticle penetration through the cell wall is determined by the cell wall's pore diameter (5-20 nm). Nanotechnology can be used to make the availability of micronutrients to plants. Nano formulations of micronutrients either can be sprayed on plants or can be applied to soil for uptake by roots to enhance soil health and vigour [23]. Fertilizers encapsulated in Nano-particles would increase the availability and uptake of nutrients to the crop plants [24]. Nano fertilizers have a significant surface area and particle size but are smaller than the pore size of plant leaves, allowing them to penetrate deeper into plant tissues and improve uptake, nutrient utilization efficiency, and nutrient uptake [25]. The positive interaction that occurs between phosphorus and nitrogen indicates that the nitrogen uptake was increased with increasing uptake of phosphorus [24]. [27] studied the accessible phosphorus of soil following nano fertilizer applications was tested at various incubation days, and the results revealed that the initial P in nano fertilizer treated soils was the highest. Because of the well-integration of KH_2PO_4 onto zeolite, as demonstrated by XRD analysis, nano fertilizer treated soil releases a higher amount of phosphorus. When compared to traditional fertilizers, the P supply from nano fertilizers lasts for a long time.

The leachate from nano zeolite, a maximum concentration of 22 ppm Zn was recorded, suggesting the nutrient release pattern of nano zeolite. The findings showed that after 120 hours, all of the available Zn from $ZnSO_4$ had been used up, and the concentration of Zn^{2+} had dropped below measurable levels. However, even after a long period of time, the release of Zn from nano-zeolite remained, with a concentration of 1.3 ppm. The reason for this impact could be that the exchanger's sequestering function dissolves sparingly soluble minerals, releasing trace nutrients to zeolite exchange sites where they are more readily available for plant uptake [28]. [29] observed that Recommended Dose of Phosphorus (RDP) is reduced to 2.5 time through nano fertilizers and also it can increase protein content and protein yield in pearl millet as compared to remaining treatments and phosphorus nanoparticles showed a positive relationship between nitrogen and phosphorus uptake by pearl millet.

Release of inorganic nitrogen and the available nitrogen of soil following nano fertilizer applications at different incubation days were significant in the case of nano fertilizer throughout the entire experiment, and all of the experimental units demonstrated the same pattern, though to varying degrees. On Day 30 of incubation, the nano fertilizer incorporated soils exhibited a small rise. In the nitrogen integrated through zeolite application, the N concentration in the soil remained high, and it released a higher proportion of accessible nitrogen than the others. The application of 41 kg. ha^{-1} Nano chelated nitrogen fertilizer in comparison with urea led to an increase of 4% in RWC, 3% Ion leakage, 52% protein, 26% phosphorus, 6% potassium, 6% Remobilization and 21% photosynthesis rate in wheat crops compared to control [30].

Limitations of Nano fertilizers

- Lack of production and availability of nano fertilizers in required quantities.
- Lack of standardization in the formulation process.
- Nanoparticles produce toxic waste materials, which, if contacted with soil and aquatic environment, can cause contamination or pollution.
- It needs safety measures during its handling because it has a lot of potential to cause respiratory disorders and carcinogenic effects on

human health. So, it needs expertise persons during its application.

- ➢ It also has an ill-effect on the lant system viz., it may plug the stomatal pore, forming a toxic layer upon the stigmatic surface, which further prevent pollen tube penetration, it may enter into vascular tissue and impair translocation of water, minerals and photosynthesis.

Conclusion

Different nano-fertilizers play a bigger part in crop production, which lowers fertilizer costs and reduces environmental risks. Society should be more concerned about the use of nano-fertilizers in agriculture. Effective use of nano-fertilizers enhances the nutrient use efficiency of fertilizer in crop production. Optimal application dose and concentration of nano-fertilizers improve crop growth and yield; at the same time, if the concentration is more than the optimum, they also have an inhibitory effect on crop plants, reducing the growth and yield of the crop. Consequently, thorough knowledge about nano fertilizer application especially right quantity, time and mode of application will enhance the growth, development and yield betterment of crops.

Future aspects

Nanotechnology has huge prospective and profits in the field of agronomy and biotechnology. As discussed in the present review the possibility of negative impact of nanoparticles on plants along with positive implications, it is necessary to carefully examine the concentration of nanoparticles and its interaction with plants. Such knowledge is important before the use of nanoparticles in future research work in plant sciences. The size of NP's also plays an important role in the interaction and accumulation inside the plants. Although there are new approaches for plants improvement using NP's has shown the successful effect even though NP's has shown many lethal effects on plant growth and survivability rate. Therefore, the research on NP's especially related to interaction with plants and their impacts on physiological, biochemical and molecular impacts need to be carried out [31].

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