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A review on potentiality of nano-fertilizer for sustainable crop production

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Abstract
In the upcoming years, pressure on the world's agricultural systems to ensure environmental and food security for a population that is expanding will increase. Chemical fertilisers contribute to environmental degradation and climate change by causing nutrient loss from agricultural fields through leaching and gaseous emissions. Advanced nanotechnology is employed to increase environmentally friendly agricultural yield while minimising the negative effects of chemical fertilisation. Due to the greater specific surface area nature of the nano fertilizers, it improves agricultural productivity by boosting the efficiency of inputs while minimising the related losses. The regulated distribution of nutrients by nano fertilizers increases crop protection by carrying agrochemicals. Field crops production and nutritional quality are increased by nano fertilisers due to their enhanced lowered nutrient losses and improved nutrient use efficiency (NUE). This paper provided an overview of recent efforts to develop intelligent fertilisers and the use of nanotechnologies in agriculture, which may help find answers to challenges with chemical fertilization in the recant years.

Keywords: Agriculture, nanotechnology, productivity and sustainability

Introduction

The growing population and a decreasing cultivable land base and water resources create the demand in agriculture for greater efficiency in food production. In soil-crop systems, natural or synthetic fertilisers are used to support the plants basic macronutrient and micronutrient needs while increasing crop output (Mastronardi *et al.*, 2015) [10]. In order to maintain a balanced distribution of the three primary macronutrients, such as nitrogen (N), phosphorous (P) and potassium (K) and three secondary macronutrients, such as sulphur (S), magnesium (Mg) and calcium, farmers have applied commercial fertilisers to crop plants for the past 50 years. However, the growth of plants requires only small amounts of micronutrients including selenium (Se), boron (B), molybdenum (Mo), manganese (Mn), chlorine (Cl), copper (Cu), iron (Fe), and zinc (Zn) micronutrient. Due to their inadequate nature in soil, the major macronutrients must be known to be effective (Kottegoda *et al*., 2014) [8]. The most popular commercial fertilisers are urea, triple superphosphate, di ammonium phosphate, single superphosphate, mono ammonium phosphate and nitrogen-phosphorous-potassium (NPK), which includes the nitrogen, potassium, and phosphorus, three vital plant nutrients (Tarafder *et al*., 2020) [13]. Nitrogen is the first and foremost required nutrient for crop plants among mineral nutrients that is the integrant of many enzymes and proteins and chlorophyll thus critical to vegetative growth of crops. Unfortunately, it has been observed that the nutrient use efficiency of nitrogenous fertilisers in current profit-oriented agricultural systems is only 45–50% and that of phosphorous fertilisers is just 10–25% (Iqbal *et al*., (2019) [6].

According to reports, in early 1970, one tonne of grain could be produced using just 27 kg of NPK per hectare, but by 2008, that number had increased to 109 kg per hectare. According to the International Fertilizer Industry Association (IFIA), fertiliser consumption worldwide has been sharply increasing. The overuse of chemical fertilisers in runoff causes eutrophication in aquatic environments, or the development of algae on the water's surface as a result of the water's enhanced nutrients, which creates a barrier to living species' access to oxygen. The NUE of applied chemicals or mineral fertilisers has frequently remained below 30% (Iqbal *et al.*, 2019 [6]), necessitating the external application of macronutrients. Environmental pollution, climate change and weak economic effects are caused by ineffective fertiliser management. For instance, about half of the nitrogen fertiliser applied to agricultural fields is lost to air, water and other processes that have an adverse effect on the environment, such as the release of N-oxides into the atmosphere which contribute to global warming and the leaching of nitrates into marine ecosystems (Mastronardi *et al*., 2015) [10]. Ammonium ions form the ammonia gas with alkaline rainwater that creates environmental pollution via escape to the atmosphere (Iqbal *et al.*, 2019) [6]. Furthermore, long-period usage of large-scale commercial fertilisers is also not a good way to increase crop productivity because that leads to soil structure, soil microbial flora plants and the ecosystem (Tarafder *et al.*, 2020) [13]. Many ammonium and nitrates ions accumulate into the leaves of plants, especially in leafy vegetables that become toxic to human health.

Therefore, to prevent pollution and save agro-ecosystems, consumers and environmentalists suggest limiting the use of synthetic fertiliser's (Iqbal *et al*., (2019) [6]. Nanotechnology is already utilised in a number of fields for sustainable production. Numerous studies have been done on using nanotechnology to increase agricultural output. Due to their tiny size, high surface area, catalytic reactivity and form, nano materials can improve the release profiles, interaction and effective absorption of plant nutrients for agricultural fertilisation, which also increases the environmental and economic advantages (Mastronardi *et al.*, 2015) [10]. "Phyto nanotechnology" is the use of nanotechnology to plant production systems. Nano fertilizer, is one use of phyto nanotechnology (Marchiol *et al.*, 2019) [9]. Fertilizers with nano-size can provide essential plant nutrition and improve agricultural production sustainability without reducing crop yield.

For food security, higher productivity, easier site-targeted controlled delivery of nutrients, and improved economic performance through sustainable farming practices, the ultimate goal of synthesising and evaluating nano-fertilizers is to improve the uptake and efficiency of nutrients while minimising the loss of nutrients via gaseous emissions and leaching and preventing the risk of nutrient toxicity. Nano scale ingredients are added to fertiliser to provide it antibacterial or insect resistant qualities. Some fertilisers are contained within host materials by nano scale films, or they remain in nano scale pores or gaps. They serve as a medium for the adsorption of nutrients and the protection of fertilisers against microbial, thermal, and solar breakdown while minimising fertiliser loss.

Nano fertilizers are slow-releasing fertilisers due to its low solubility in water or other solvent gradually breaks down and release nutrient over certain period of time and eventually effects the microbial population. The benefits of such fertilizers includes: higher plant NUE, decreased capital and labour costs, less frequent application, easier handling, reduced environmental contamination from nutrient leaching, storage features and flexibility in release durations (40-90 days).

Biological Mechanisms of Nano-fertilizers Action:

Many plant biology components, such as the nutrient gateway and plant roots, are on a nano scale size. Ionic and molecular transport activities have been seen in roots with pores ranging in size from a few tens of nano meters. However, nano-fertilizers might be absorbed by these nano-scale pores, or through complication with root exudates or molecular transporters via the formation of new pores, or through the use of ion channel endocytosis (Iqbal *et al.* (2019) [6]. Plant leaves also feature stomata holes and nano pores that allow nano material to readily enter and penetrate deep into the leaves, allowing for greater nutrient utilisation efficiency (NUE). The plasmodesmata are nano sized (50-60 nm) passageways between cells that promote cell-to-cell transfer inside a plant. Because of their tiny size, nano scale fertilisers carry and release nutrients to numerous transport routes and plant surfaces via plasmodesmata (Mastronardi *et al* 2015) [10]. As a result, nano fertilizers increase production (6-17%) and nutritional quality of field plants through increased NUE and lower nutrient losses (Iqbal *et al*. 2019) [6].

Conventional fertilizer v/s nano- fertilizers

When compared to conventional fertilizer, the rate of nutrient release in nano fertilizers may be regulated based on environmental characteristics such as temperature variations, the amount of soil moisture, and the degree of soil acidity. The introduction of nano-fertilizers aims to provide and release nutrients for over than 35 days on purpose and on a regular basis. This may help to decrease the negative improves the strength of applied fertilizers and has positive impacts on soil, plants, and the environment, as a result, minimizing nutrient leaching. Due to the delayed and regulated release of chemicals, nano fertilizers are recommended over conventional fertilizers because they are more efficient and can be readily absorbed by both roots and shoots. Even though they do not directly supply nutrients to crops, they can perform better than traditional fertilizers. A nano fertilizer, as opposed to conventional fertilizer, is any product created employing nanoparticles or nanotechnology by giving nutrients to the adsorbents in order to improve the performance of nutrients and plant nutrition. The high surface area of nanoparticles enabled them to retain nutrients in large quantities and release nutrients on purpose to satisfy the needs of crops without having any adverse effects. Lean protective polymer layer formed as an emulsion or nano scale-sized particles can be applied on nano porous materials or nano tubes to encapsulate nano fertilizers.

Table 1: Differentiations between conventional fertilizer and nano- fertilizers

Index	Conventional fertilizer	Nanofertilizer	Reference
Loss rate	High loss rate via drifting, leaching, run-off	Low loss of fertilizer nutrients	Thavaseelean and priyadarshana (2021)
Controlled release	Excess release of nutrients lead to high toxicity and soil imbalance	Rate of release and release pattern precisely controlled	
Solubility	Low	High	
Bioavailability	Low	High	
Dispersion of mineral micronutrient	Lower solubility due to large size particle	Improved dispersion of insoluble nutrients	
Effective duration of release	Used by the plant at the site and time of application; the rest is converted into an insoluble form	Effective and extended duration	
The efficiency of nutrients uptake	It is not available to roots and the efficiency of nutrients uptake is low	Enhanced uptake ratio and saves fertilizer resource	
Soil adsorption and fixation	High	Reduced	

Use of Nano-fertilizers for Sustainable Crop Production

Nano fertilizers is more effective as compared to conventional fertilizer in producing more the crop yield by reducing soil toxicity, fertilizer application frequency, minimizing excessive use of chemical fertilizer and enhancing the nutrient use efficiency. There are numbers of evidences on researches conducted on the effect of nano-fertilizers in crop production.

Helaly *et al.,* (2021) [3] examine the effect of nano NPK fertilizer at varying percentages from the prescribed amount of NPK chemical fertilisers on lettuce head growth, harvest and quality and found out that, nano nitrogen at 50 percent concentrations considerably boosted plant development as measured by the weight of newly formed plants and the size of their heads, as well as their overall yield and saleable harvest. The ascorbic acid, TSS and sugar level also increase.

A novel formulation of a hybrid nano-fertilizer (HNF) was proposed by Tarafder *et al*., (2020) [13] for the sustained and delayed release of plant nutrients into water and soil. To improve the efficacy of the fertilizer, nanoparticles such as zinc, copper and iron were included into urea-modified hydroxyapatite. HNF has been tested on the lady finger (*Abelmoschus esculentus*) plant and revealed that, a slow-release nature, increased nutrient uptake such as Zn^{2+}, Fe^{2+} and Cu^{2+}, eliminate leaching problem, reduced crop nutritional deficiencies, produce nutrient-rich fruits and increased physiochemical properties such as water retention and absorption capacities and swelling ratio, making the fertilizer more appealing and helpful than commercial fertilizer. Finally, HNF is proposed as a viable fertilizer with several benefits including gradual and sub stained nitrogen release, minimum pollution, cost effective and low dose (50 mg/week).

Hu *et al.,* (2020) [5] conducted an experiment on lettuce (*Lactuca sativa* L.) sprayed with a nutrient standard solution @ 0, 50, 100, 200 or 400 mg/l TiO_2 NPs. The exposure of crop to NP @50–200 mg L^{-1} TiO_2 was known to be significantly higher in Chlorophyll a, total chlorophyll and carotenoid concentrations, shoot and root dry matter content by 14.7–24.5%, 10.3–18.5%,12.6–20.5%, 0.69-1.3 fold and 32.0–75.6% respectively as compared to control. While 400 mg/L TiO_2 NPs seemed to have no effect on plant growth (dry biomass) as well as on nutrient content. Instead, nutritional content improved in relation to 50-200 mg/L NPs treatment, demonstrating that the changes were mediated by biomass dilution.

Juthery *et al.,* (2019) [1] studied the fertilizer use efficiency of foliar application of nano fertilizers on Jerusalem artichoke and found that single spray treatment was superior in terms of micronutrients (Zn + Cu + Fe + Mn) as well as uptake by arial parts and tubers, while achieving the sequential nutrient use efficiency of nano-zinc, nano copper, nano-iron and nano-manganese (93.10, 85.00, 99.00 and 85.50% respectively) as well as consecutive treatments (91.60, 81.30, 91.85 and 83.40%) as well as consecutive nano spray treatment using in the conventional Zn, Cu, Fe and Mn.

Khanm *et al.,* (2018) [4] studied the effect of nano scale zinc oxide particles on the germination, growth and yield of tomato (*Solanum lycopersicum*) and found that, the use of ZnO NPs fertilisers via any form of application shows a considerable beneficial effect on tomato as compared to zinc sulphate.

Yasse *et al.,* (2017) [15] examine the effects of foliar sprays of nano-fertilizer SiO_2 at 0,15,30,60 and 120mg/l on cucumber (*Cucumis sativa*) and reported that higher concentration i.e., 120m/l increase in plant height (cm), number of leaves/ plants, fresh and dried leaf weight/plant (g), number of fruits/plants, mean fruit weight, fruit lenght, yield per plant (kg) and total yield per hectare (t).

Kottegoda *et al*., (2014) [8] worked on the integration of low solubility urea into a matrix of hydroxyapatite nanoparticles at 6:1 weight ratio. The phosphorus-rich hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$) nanoparticles (HA NPs) have good biocompatibility. In urea-HA NP nano hybrids, the weak connections between urea and HA NPs cause a delayed release of urea nature for up to a week, improving nutrient use efficiency (NUE) in plants and slowing the rate of urea breakdown in soil. With a 50% lower urea content, this suggested nanofertilizer resulted in a superior rice yield. This fertilizer's slower nitrogen release than that of pure urea as caused by the interaction of urea with HA NPs through carbonyl and amine group (Kottegoda *et al.,* 2017) [7].

Limitations of Nano-fertilizers

Due to gaps in research, a lack of laws and inadequate monitoring, nano fertilizers have some drawbacks. The following is a list of several disadvantages and restrictions that nano fertilizers for sustainable crop production have. Before they are released, this unfavourable behaviour of nanoparticles has to be extensively researched.

1. Because of their greater cost, nano fertilizers can only be used in certain pedo-climatic conditions to produce crops.
2. The issue arises when nanoparticles of uniform size (1–100 nm) are present.
3. The lack of acknowledged standardisation and formulation causes the same nano materials to have diverse impacts under various pedo climatic situations.
4. The insufficient manufacturing and availability of nano fertilizers in the necessary amounts.
5. In promoting and supporting nano fertilizers for sustainable agricultural production, there are restrictions on nano fertilizers connected to risk management and regulation.
6. Plants and a number of soil microorganisms, such as bacteria, yeasts, and fungus, are poisonous to nano materials (Marchiol *et al*., 2019) [9].
7. Because of their tiny size, nanoparticles can now affect functioning bio molecular structures like DNA and ribosome by entering cells, tissues, and organelles.

The negative effects of nanoparticles on plant growth and development is that, when nano particle concentration is increased, agricultural plants physiological and morphological processes are altered. An increase in the concentration of nanoparticles in the root zone limits root growth, reduces biomass output and leaf development and prevents seed germination. Additionally, the toxicity of nano particles causes an oxidative outburst that damages cells, disrupts membranes, modifies gene expression, reduces photosynthesis and disorganizes chloroplasts.

Conclusions

By minimising nutrient loss and enhancing greater absorption rates, nano-fertilizers are used alone or in combination with organic materials to effectively boost nutrients to agricultural plants while lowering environmental contamination. To improve the root growth, plant height, germination rate, number of roots, antioxidant content of the fruits and chlorophyll content of the leaves, several types of study involving various nano materials have been documented. For sustainable agricultural production, intelligent nano fertilisers release nutrients in accordance with plant needs. Lastly, in order to fully utilise nano fertilisers for sustainable crop production under changing climates while lowering the danger of creating environmental contamination, researchers and regulators should be in charge of the risk and limits of nano fertiliser usage.

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