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Nano-Fertilizers for Sustainable Crop Production under Changing Climate: A Global Perspective

Muhammad Aamir Iqbal

Abstract

Since green revolution, chemical fertilizers are deemed an indispensable input of modern crop production systems, but these have associated environmental and ecological consequences. Loss of nutrients from agricultural fields in the form of leaching and gaseous emissions has been the leading cause of environmental pollution and climate change. Ensuring the sustainability of crop production necessitates exploring other sources of nutrients and modifying prevalent nutrient sources. Nanotechnology, which utilizes nanomaterials of less than 100 nm size, may offer an unprecedented opportunity to develop concentrated sources of plant nutrients having higher-absorption rate, utilization efficacy, and minimum losses. Nanofertilizers are being prepared by encapsulating plant nutrients into nanomaterials, employing thin coating of nanomaterials on plant nutrients, and delivering in the form of nano-sized emulsions. Nanopores and stomatal openings in plant leaves facilitate nanomaterial uptake and their penetration deep inside leaves leading to higher nutrient use efficiency (NUE). Nanofertilizers have higher transport and delivery of nutrients through plasmodesmata, which are nanosized (50–60 nm) channels between cells. The higher NUE and significantly lesser nutrient losses of nanofertilizers lead to higher productivity (6–17%) and nutritional quality of field crops. However, production and availability, their sufficient effective legislation, and associated risk management are the prime limiting factors in their general adoption as plant nutrient sources.

Keywords: controlled release fertilizers, eutrophication, nanogels, encapsulated nutrients, slow released fertilizers

1. Introduction

Intensive farming practices introduced and evolved since the inception of green revolution have been deemed unsustainable as the utilization efficacy of applied chemicals including mineral fertilizers has remained below 30% [1]. Fertilizers have taken axial role with respect to boosting crops yield and nutritional quality especially after the development of fertilizer responsive crop varieties. Among mineral nutrients, nitrogen is the first and foremost nutrient

required for crop plants as it is the constituent of chlorophyll and many proteins and enzymes and thus plays a significant role during the vegetative growth of crops. Nitrogen is absorbed by the plants in the form of nitrate (NO_3^-) and ammonium (NH_4^+) [2]. Nitrogen is lost through the processes of nitrate leaching, de-nitrification and ammonia volatilization. Loss of mineral nutrients through leaching and runoff to surface and ground water along with abundant volatilization constitute growing concerns owing to economic losses and environmental pollution. Conventional application techniques are resulting in seriously overdosing of chemical fertilizers which has become evident through the phenomenon of eutrophication (algal growth on the surface of water bodies due to nutrients enriched water, which hampers oxygen supply to fish) in many European and North American countries. Moreover, nitrogen volatilization results in the release of nitrous oxides and thus being the greenhouse gases, contribute to the global warming. It is really unfortunate that modern profit-oriented farming systems encompass nitrogenous fertilizers use efficiency of only 45–50%, while the corresponding figure for phosphorous fertilizers has been reported to be only 10–25% [3].

It is also pertinent to mention that ammonium ions react with alkaline rain water which leads to the formation of ammonia gas that escapes into the atmosphere and thus becoming a source of environmental pollution. Whenever, there is excess of nitrogen, more and more nitrates and ammonium ions get accumulated in the leaves of crops especially leafy vegetables and become detrimental to human health. In addition, nitrate rich diets have been reported to be associated with numerous human diseases such as bladder and gastric cancer as well as methemoglobinemia [4]. It is being stressed to deliver the required quantities of active agents only where they are direly needed. Environmentalists and consumers call for reducing the use of synthetic fertilizers to decrease pollution and residue effect on farm produces along with conserving agro-ecosystems.

Nanotechnology is a promising field of research which has the potential to offer sustainable remedies to pressing challenges confronted to modern intensive agriculture. Nanotechnology employs nanomaterials which typically have the size of 1–100 nm and this small size imparts unique characteristics and benefits to nanomaterials. In addition to numerous other benefits, large surface area offers opportunity for better and effective interaction of nanoparticles to target sites. Nanofertilizers hold potential to fulfill plant nutrition requirements along with imparting sustainability to crop production systems and that too without compromising the crops yield [5].

This chapter entails and attempts to fulfill the need to periodically compile and review the present state and advances on nanofertilizers and to spur interest for conducting further in-depth research. The ultimate goal is to synthesize and assess the role of nanofertilizers in boosting nutrients uptake and nutrients use efficiency, reducing losses through leaching and gaseous emissions along with reducing the risk of nutrient toxicity for ensuring food security achieved through higher productivity and economic turn outs by practicing the sustainable farming practices. This chapter briefly sheds light on the critical role of nanotechnology pertaining to modern farming practices, its potential in developing smart fertilizers, nanofertilizers and their different types of formulations, biological mechanism of nanofertilizers in plants, numerous advantages offered by nanofertilizers and field evidences of superior performances of nanoparticles in imparting critical characteristics to crop plants leading to higher productivity. Lastly, few limitations pertaining to the development and use of nanoparticles as plant nutrient source have also been described.

2. Critical applications of nanomaterials in agriculture

Nanotechnology encompasses controlling matter at 1–100 nm dimensions for utilization in taking images, measurements and preparing models for making virtual predictions along with manipulation of matter at nanoscale. Like all other fields, the solid impact of nanomaterials is also being felt in agriculture sector. Previously, nanoencapsulation entailing encapsulation of active agents by microspheres of starch on a matrix having nanopores proved its resilience in accurately delivering the active agents to target sites [6]. These nanocapsules or micro-beads become attached to heir of bees in the similar fashion to pollens and keep parasites at bay owing to slow release of active agents gradually and slowly. Thus, nanoencapsulation resulted in minimum use of active agents and offered the maximum protection to bees against parasites. On the similar fashion, nanogels were developed which assist in controlled release of pheromones from insects to offer them protection against diversified pests. Nanoencapsulation has also yielded encouraging results for improving the fertilizer use efficacy with significant reduction of active ingredients use [7].

In order to detect pathogen and to prolong the shelf life of packaged foods, nanosensors and nanobiosensors have given encouraging results. However, development of nanomaterials using nanotechnology is an evolving field of research and future is destined to witness extensive and multidimensional benefits in food production and preservation. In future, it will be impossible to ensure food and nutritional security without developing nanomaterials based technologies for food production and agriculture.

3. Nanotechnology's strategic potential in developing fertilizers of future

Modern intensive farming systems utilize organic and mineral manures in order to supply essential plant nutrients, but this approach has resulted in serious deterioration of ecosystems and environment [8]. Loss of nitrogen as nitrous oxide and nitrates leaching has resulted in eutrophication and manifesting the impacts of global warming and climate change. Phosphate fertilizers have even lesser nutrient use efficacy (NUE) that has been reported to be below 20% [9]. Nanofertilizers have the potential to enhance NUE owing to higher nutrients uptake caused by smaller surface area of nanomaterials which increases nutrient-surface interaction. Along with boosting crops yield on sustainable basis, nanofertilizers hold potential to put a halt to environmental pollution caused by fertilizers. Slow release fertilizers (chemical compounds having slight solubility in water or other solvents and get broken down gradually and slowly by soil microbial population) coated with nanoparticles significantly reduced nitrate leaching and de-nitrification [10]. Moreover, controlled releasing fertilizers (have higher solubility in contrast to slow release fertilizers but are coated with materials which significantly reduce the exposure of active ingredient with the solvent resulting in controlled liberation of nutrients through diffusion) coated with nanomaterials for reducing surface area my provide excellent of source of supplying plant nutrients in times to come.

4. Nanoscale fertilizers and their formulations

Different fertilizers inputs have been reported to be resized into smaller fractions through mechanical means or by employing specific chemical methods,

which may increase nutrients uptake and reduce losses as well as nutrient toxicity. Nano-sized particles have been prepared from urea, ammonia, peat and other synthetic fertilizers as well as plant wastes. A formulation process involving urea deposition on calcium cyanamide resulted in nano-sized N fertilizer [11]. In another formulation, grinded urea was mixed with different biofertilizers to prepare an effective nanofertilizer to supply nutrients slowly and gradually for a longer period of time [12]. In similar way, ammonium humate, peat and other synthetic materials were mixed to prepare nanosized fertilizers. Mechanical cum biochemical approach is being employed to prepare such nanofertilizers where materials are grinded to nanosized particles through mechanical means and then biochemical techniques are put in action to prepare effective nanoscale formulations. In addition, nano-emulsions are also being prepared by adding nanosized colloids to emulsions [13]. In short, fertilizers encapsulation with nanoparticles offers wide perspective for developing plant nutrient sources with greater absorption and nutrient use efficiency. The encapsulation of nutrients with nanomaterials can be performed in three distinct ways;

1. Plant nutrients can be encapsulated within the nanomaterials of varying nature and chemical composition.
2. Nutrient particles may be coated with a thin layer of nanomaterials such as polymer film.
3. Nutrients may also be delivered in the form of emulsions and particles having dimension in the range of nanoparticles.

5. Biological mechanisms of nanofertilizers action

Nanofertilizers have been advocated owing to higher NUE as plants cell walls have small pore sizes (up to 20 nm) which result in higher nutrient uptake [14]. Plant roots which act as the gateways for nutrients, have been reported to be significantly porous to nanomaterials compared to conventional manuring materials. The uptake of nanofertilizers can be improved by utilizing root exudates and molecular transporters through the ionic channels and creation of new micro-pores [15]. Nano-pores and stomatal openings in leaves have also been reported to facilitate nanomaterials uptake and their penetration deep inside leaves. It was concluded that in broad/faba bean (*Vicia faba*), nano-sized particles (43 nm) were instrumental in penetrating deep to leaf interior in large number compared to larger particles of more than 1.0 micrometer size [16]. Similarly, the leaf stomatal radii of Arabian coffee (*C. arabica*) was below 2.5 nm, while that of sour cherry (*P. cerasus*) were also below 100 nm [17] and thus effectiveness of nanofertilizers in enhancing nutrient uptake was suggested.

Nanofertilizers have also been supported to have higher NUE owing to higher transport and delivery of nutrients through plasmodesmata which are nanosized (50–60 nm) channels for transportation of ions between cells [18]. Carbon nano-tubes transported fluorescent dyes to tobacco cells through enhanced penetration of cell membranes and effectively played the role of molecular transporters [19]. The nanoparticles of silica were also instrumental in transporting and delivering different cargoes to target sites in different plants [20].

6. Nanofertilizers advantages over conventional mineral fertilizers

Mineral nutrients if applied to crops in the form of nanofertilizers hold potential to offer numerous benefits for making the crop production more sustainable and eco-friendly [21]. Some of salient advantages are;

1. Nanofertilizers feed the crop plants gradually in a controlled manner in contradiction to rapid and spontaneous release of nutrients from chemical fertilizers.
2. Nanofertilizers are more efficacious in terms of nutrients absorption and utilization owing to considerably lesser losses in the form of leaching and volatilization.
3. Nanoparticles record significantly higher uptake owing to free passage from nano sized pores and by molecular transporters as well as root exudates. Nanoparticles also utilize various ion channels which lead to higher nutrient uptake by crop plants. Within the plant, nanoparticles may pass through plasmodesmata that results in effective delivery on nutrient to sink sites.
4. Due to considerably small losses of nanofertilizers, these can be applied in smaller amounts in comparison to synthetic fertilizers which are being applied in greater quantities keeping in view their major chunk that gets lost owing to leaching and emission.
5. Nanofertilizers offer the biggest benefit in terms of small losses which lead to lower risk of environmental pollution.
6. Comparatively higher solubility and diffusion impart superiority to nanofertilizers over conventional synthetic fertilizers.
7. Smart nanofertilizers such as polymer coated fertilizers avoid premature contact with soil and water owing to thin coating encapsulation of nanoparticles such as leading to negligible loss of nutrients. On the other hand, these become available as soon as plants are in position to internalize the released nutrients.

7. Field evidences of nanofertilizers use for sustainable crops production

The research findings of a field investigation proved in line with the postulated hypothesis where nano nitrogen fertilizers proved instrumental in boosting the productivity of rice. It was inferred that nano nitrogen fertilizer hold potential to be used in place of mineral urea and it can also reduce environmental pollution caused by leaching, de-nitrification and volatilization of chemical fertilizers [22]. Similarly, exogenously applied nutrients as nanomaterials increased the vegetative growth of cereals including barley [23] (man), while in contrast, nanofertilizers applied in conjunction with reduced doses of mineral fertilizers were found to be instrumental in boosting yield attributes and grain yield of cereals [24]. Nanofertilizer of zinc applied as ZnO was found to be instrumental in boosting peanut yield due to robust plant growth, increased chlorophyll content of leaves and significantly better root growth [25]. The growth and yield boosting impact of different nanomaterials is depicted in **Table 1**.

Nanofertilizers	Crops	Yield increment (%)
Nanofertilizer + urea	Rice	10.2
Nanofertilizer + urea	Rice	8.5
Nanofertilizer + urea	Wheat	6.5
Nanofertilizer + urea	Wheat	7.3
Nano-encapsulated phosphorous	Maize	10.9
Nano-encapsulated phosphorous	Soybean	16.7
Nano-encapsulated phosphorous	Wheat	28.8
Nano-encapsulated phosphorous	Vegetables	12.0–19.7
Nano chitosan-NPK fertilizers	Wheat	14.6
Nano chitosan	Tomato	20.0
Nano chitosan	Cucumber	9.3
Nano chitosan	Capsicum	11.5
Nano chitosan	Beet-root	8.4
Nano chitosan	Pea	20
Nanopowder of cotton seed and ammonium fertilizer	Sweet potato	16
Aqueous solution on nanoiron	Cereals	8–17
Nanoparticles of ZnO	Cucumber	6.3
Nanoparticles of ZnO	Peanut	4.8
Nanoparticles of ZnO	Cabbage	9.1
Nanoparticles of ZnO	Cauliflower	8.3
Nanoparticles of ZnO	Chickpea	14.9
Rare earth oxides nanoparticles	Vegetables	7–45
Nanosilver + allicin	Cereals	4–8.5
Iron oxide nanoparticles + calcium carbonate nanoparticles + peat	Cereals	14.8–23.1
Sulfur nanoparticles + silicon dioxide nanoparticles + synthetic fertilizer	Cereals	3.4–45%

Table 1.
Impact of nanofertilizers on productivity of different crops under varying pedo-climatic conditions [32–40].

In agreement to these findings, it was also reported that nanofertilizers of zinc improved the seed production of vegetables [26]. Similarly, nano carbon incorporated fertilizers effectively reduced the days to germination and promoted root development of rice seedling. It was inferred that nano-composites have the potential to promote vital processes such as germination, radicle and plumule growth and development [27]. Another aspect of nanofertilizers was explored regarding crop cycle as nanoparticles which were loaded with NPK, reduced the crop cycle of wheat up to 40 days, while grain yield was also increased in comparison to mineral fertilizers applied at recommended rates [28]. Slow release fertilizer coated with nanoparticles boosted the productivity of wheat-maize cropping system [29]. In addition to soil applied nanofertilizers, foliar application of chitosan was reported to be instrumental in boosting tomato yield by 20%, while it remained non-significant as far as carrot yield was concerned [30]. However, growth promoting effect of foliar applied chitosan was

Nanofertilizers	Crops	Imparted characteristics
Nanoparticles of ZnO	Chickpea	Increased germination, better root development, higher indoleacetic acid synthesis.
Nano silicon dioxide	Maize	Drought resistance, increment in lateral root roots number along with and shoot length.
Nano silicon dioxide	Maize	Increased leaf chlorophyll.
Nano silicon dioxide	Tomato	Taller plants and increased tuber diameter.
Colloidal silica + NPK fertilizers	Tomato	Increased resistance to pathogens.
Nano-TiO ₂	Spinach	Improved vigor indices and 28% increased chlorophyll.
Polyethylene + indium oxide	Vegetables	Increased sunlight absorption
Polypropylene + indium–tin oxide	Vegetables	Increased sunlight utilization
Gold nanoparticles + sulfur	Grapes	Antioxidants and other human health benefits.
Kaolin + SiO ₂	Vegetables	Improved water retention.
Bentonite + N-fixing bacteria inoculation	Legumes	Improved soil fertility and resistance to insect-pest.
Nanocarbon + rare earth metals + N fertilizers	Cereals	Improved nitrogen use efficiency
Stevia extract + nanoparticles of Se + organo-Ca + rare-earth elements + chitosan	Vegetables	Enhanced root networking and root diameter.
Nano-iron slag powder	Maize	Reduced incidence of insect-pest
Nano-iron + organic manures	Cotton	Controlled release of nutrients acts as an effective insecticide and improves soil fertility status.

Table 2.
Impact of nanofertilizers on different crops under varying pedo-climatic conditions [34–46].

also recorded for horticultural crops such as cucumber, beet-root etc. The significantly higher selenium uptake by many crops including green tea was observed when it was applied as nanosized particles [31]. There are various other impacts that can be imparted by nanomaterials in different crops and some of these have been described in **Table 2**.

8. Limitations of nano fertilizers

Despite offering numerous benefits pertaining to sustainable crop production, nanofertilizers have some limitations regarding research gaps, absence of rigorous monitoring and lack of legislation which are currently hampering the rapid development and adoption of nanoparticles as a source of plant nutrients [47]. A few of the limitations and drawbacks associated to nanofertilizers use for sustainable crop production are enlisted below.

1. Nano fertilizers related legislation and associated risk management continue to remain the prime limitation in advocating and promoting nano fertilizers for sustainable crop production.

2. Another limiting factor is the production and availability of nano fertilizers in required quantities and this is the foremost limitation in wider scale adoption of nano fertilizers as a source of plant nutrients.
3. The higher cost of nano fertilizers constitutes another hurdle in the way of promulgating them for crop production under varying pedo-climatic conditions across the globe.
4. Another major limitation pertaining to nanofertilizers is the lack of recognized formulation and standardization which may lead to contrasting effects of the same nanomaterials under various pedoclimatic conditions.
5. There are many products being claimed to be nano but in fact are submicron and micron in size. This dilemma is feared to remain persistent until and unless uniform size of nanoparticles (1–100 nm) gets implemented.

9. Conclusions

Nanofertilizers applied alone and in conjunction with organic materials have the potential to reduce environmental pollution owing to significant less losses and higher absorption rate. In addition, nanomaterials were recorded to improve germination rate, plant height, root development and number of roots, leaf chlorophyll and fruits antioxidant contents. Moreover, controlled and slow released fertilizers having coating of nanoparticles, boost nutrient use efficiency and absorption of photosynthetically active radiation along with considerably lower wastage of nutrients. The future of nanofertilizers for sustainable crop production and time period needed for their general adaptation as a source of plant nutrients depend on varied factors such as effective legislation, production of novel nanofertilizers products as per requirement and associated risk management. There is a dire need for standardization of nanomaterials formulations and subsequently conducting rigorous field and greenhouse studies for performance evaluation. For sustainable crop production, smart nanofertilizers having the potential to release nutrients as per plants requirement in temporal and spatial dimensions must be formulated. Lastly, researchers and regulators need to shoulder the responsibility by providing further insights in order to take full advantage of the nanofertilizers for sustainable crop production under changing climate with the risk of causing environmental pollution.

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