REVIEW ARTICLE

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Nano Fertilizers: New Vistas towards Sustainable Agriculture and Climate Change Mitigation: A Review

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ABSTRACT

To ensure the food and nutritional security of the burgeoning global population, food production needs to be doubled in developing countries by 2050. Currently, 30-40% of agriculture production predominantly relies on chemical fertilizers. Precise crop nutrition, low nutrient efficiency, maintaining soil fertility, less damage to soil flora and minimal environmental footprint are the major challenges in modern agriculture. Recent developments in the application of nanotechnology to produce agriculture inputs emerged as a sustainable solution for addressing the challenges in modern intensive agriculture by replacing synthetic bulk fertilizers with their nanoparticle size (<100 nm), superior properties and smart delivery system. Nano fertilizers had the potential to fulfill the requirements of plant nutrition along with imparting sustainability in crop production without compromising the yield of the crops. Some of the current research studies have been reviewed in this paper with citation and these results showed that nano fertilizers have a substantial effect on plant growth, development and physiological parameters including chlorophyll content and photosynthetic activity, it depends on their composition, method and time of application. Their enhanced nutrient use efficiency, correlated with mitigating greenhouse gas emissions. Hence evolving as a cutting-edge approach for sustainable agriculture in climate change is enlightened in this review.

Key words: Climate change, Crop production, Food security, Nano fertilizers, Sustainability.

The world population is expected to reach 2.3 billion by 2050 and almost all of this growth is predicted to take place in emerging countries. Agriculture plays a key role in the world economy and is one of the most important pillars of many developing countries. In the 21st century agriculture faces numerous challenges, it has to generate additional food, fibre to nourish the growing population with a smaller rural labour force, more feedstocks for a potentially huge bioenergy market and contribute to overall development in the many agriculture-dependent developing countries. Presently, food security faces a huge encounter, which is determinedly denoted by the quick rise in the worldwide population and the severe vagaries happening in the climate. The food and nutritional security are mainly reliant on the agriculture sector, particularly on crop production. Conventional chemical fertilizers are used to achieve higher crop production to feed the ever-increasing global population. According to estimates, feeding the world population of 9.1 billion people in 2050 would entail a 70% increase in overall food production between 2005-07 and 2050. There is a need to increase production twofold in developing countries (FAO, 2009). This would result in a considerable increase in the yields of some important commodities. For example, annual cereals production would have to increase by over one billion tonnes, feeding the global population sufficiently would also mean producing the types of foods that are lacking to ensure nutritional security. There is a need to produce 56% more crop calories than that produced in 2010 necessary to meet anticipated food demand in 2050. According to FAO (2009) report on how to feed the world in 2050, climate change is a major risk for abiding food security. Although countries situated in

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the Southern Hemisphere are not the core originators of climate change, they may grieve the maximum share of damage in the form of diminishing yields and greater frequency of extreme weather anomalies. Findings estimate that the cumulative negative effect of climate change on African agricultural output up to 2080-2100 could be around 15 and 30%. Approximately 15 gigatons of annual greenhouse gas (GHG) emissions are projected from the agriculture and land-use changes in 2050 but it is needed to maintain not more than 4 gigatons of annual greenhouse gas emission and free up hundreds of millions of hectares for reforestation to keep the global warming under 1.5°C.

Agriculture will have to acclimatize to climate change, but it can also help to alleviate the consequences of climate change and useful synergies exist between adaptation and mitigation.

Problems associated with conventional fertilizers in agriculture

Chemical fertilization to the crop has become essential to feed the ever-increasing global population with the introduction of high yielding, greater nutrient responsive varieties and hybrids so, chemical fertilizers are associated with higher crop production. Long-term field investigations demonstrated that 30 to 50% of crop yield is attributed to fertilizer inputs in temperate regions and their contribution is much superior in tropical climates (Stewart and Roberts, 2012). Overdose of chemical fertilizers has become evident through the phenomenon of eutrophication, accelerated soil degradation and volatilization of nitrogen resulting in the release of nitrous oxides and thus being the greenhouse gases causing global warming and ammonium ions in soil react with alkaline rainwater which results in the formation of ammonia gas that escapes into the atmosphere and thus becoming a basis of environmental pollution. Excess application of conventional nitrogen fertilizers, nitrates and ammonium ions accumulate in the crop's foliage, especially leafy vegetables and become harmful to human health resulting in nitrate toxicity. In addition, nitrate-rich diets have been reported to be associated with various human diseases such as methemoglobinemia as well as bladder and gastric cancer and also negative impact on soil biology. The results of ten-year field trials indicated that long-term nitrogen fertilizer application in the soil can significantly affect the dominant soil bacterial population by altering the soil pH (Ren et al., 2020). One of the potential factors related to the GHG emissions in wetlands is attributed to the use of nitrogenous fertilizers (Rajkishore et al., 2015). Global nitrogen fertilizer consumption increased by over 190 million tonnes, accounting for greater than 56 percent of the total global consumption, whereas phosphate and potassic fertilizers held shares of 24 and 19 percent, respectively (Lucia Fernandez, 2022). Global consumption of urea has risen 100 times in the last 4 decades and constitutes >50% of total nitrogenous fertilizers (Gilbert et al., 2006). Agriculture contributes 70 % of nitrous oxide emission out of urea alone contributes to 80 % emission of nitrous oxide, as it is 300 times more potent than CO2 in causing global warming (Canadell et al., 2020). Indiscriminate and imbalanced application of nitrogenous fertilizers is vulnerable to various losses such as leaching, volatilization and immobilization that collectively contribute up to 60% losses and also lower nitrogen use efficiency (30-40%) affecting the sustainability of our agriculture production systems. It has been reported that around 40-70% of nitrogen, 80-90% of phosphorus and 50-90 % of potassium content of applied fertilizers are lost in the environment in different forms and cannot reach the plant which causes considerable economic losses (Trenkel, 2010 and Solanki et al., 2015).

Besides, these problems directly or indirectly affecting the worldwide food and nutritional security, one of the major challenges of the present agriculture system is to satisfy present and future global food demands effectively. The current nutrient use efficiency needs to be improved significantly by increasing the productivity of agrarian systems by adopting environmentally sound agronomic practices and discovering restoring technologies. It is being stressed to deliver the required quantities of active agents only where they are directly needed Hence, an alternative mechanism is to be developed to improve agriculture production and environmental sustainability. Nano fertilizers are excellent alternatives to overcome the adverse effects of traditional chemical fertilizers without impairing global food security.

Nano fertilizers and their role in agriculture

Nano fertilizers are encapsulated plant nutrients completely or partially engineered of nanostructured formulations that can release active ingredients slowly and in a controlled manner into the soil. Thus, preventing nutrient loss, eutrophication and atmospheric pollution. Because of the greater surface area to volume ratio, performance, efficacy and long-lasting availability, utilization of nano fertilizers is greater than that of conventional fertilizers therefore, the former offer a platform for the development of sustainable and novel nutrient delivery systems (Elemike et al., 2019). Nano fertilizers having particle sizes less than 100 nm can be used as fertilizer sources for cost effective, eco-friendly nutrient management. Thus, nanoparticles developed with the help of nanotechnology are exploited in the value chain of the whole agriculture production system (Morales-Diaz et al., 2017; Al-Juthery et al., 2018). The nano fertilizers offer smart nutrient delivery mechanisms in plants to ensure optimal plant uptake and are more efficient than bulky chemical fertilizers in terms of agricultural productivity and environmental sustainability. Plants can absorb Nano fertilizers by foliage or roots depending upon the application methods and properties of the particles. Nano fertilizers improve the tolerance in plants towards biotic and abiotic stress. Multiple benefits of the nano fertilizers open new vistas toward sustainable agriculture and climate change mitigation. Liquid nano urea has been manufactured for the first time in the world at Indian Farmers Fertilizer Cooperative Limited (IFFCO)-Nano Biotechnology Research Centre, Kalol, Gujarat through indigenous proprietary patented technology. Nano urea contains 4.0% total nitrogen (w/v) and particle size varies from 20-50 nm. These particles are evenly dispersed in water and because of their small size (20-50 nm) and higher use efficiency (>80%) increase the availability of nitrogen to the plant (IFFCO, 2021), Apart from considerably increasing farmers' income by cutting down on input and storage costs, liquid nano urea also targets to surge the crop yield and many benefits against conventional urea as shown in Fig 1. It is proven to upsurge the average crop yield by 8% along with improving the quality of farm produce by providing better nutrition to crops (The print media, 2021). The application of nano-nitrogen resulted in a 9.76% greater yield in wheat with 50% less nitrogen with two sprays of nano-urea liquid in standing crops as compared to the farmers' practice (Yogendra *et al.*, 2020). To overcome the glitches in modern crop production nanofertilizers are an effective tool for sustainable nutrient management and mitigating climate change in agriculture.

Fate of nano fertilizers in soil

The use of nano fertilizers in soil results in increased nutrient efficiency, reduces soil toxicity, least negative effects caused by the consumption of excessive chemical fertilizers and reduces frequent fertilizer application (Naderi et al., 2013). Production of nano fertilizers, these nano compounds are rapidly and completely absorbed by plants meet their nutrient requirement and make a quick recovery from deficiencies. These nano fertilizers are completely compatible with the surrounding environment.

Nano fertilizers and their smart delivery system

In general nano fertilizers are delivered to the plant system mainly in three ways, seed treatment, soil application or amendment and direct foliar application. Soil application is one of the important nutrient applications for chemical fertilizers and organic manures. Supplying nutrients via plant root system by applying near the rhizosphere. These nanomaterials have some consequences when nano fertilizers are mixed with soil, the availability of nutrients to plant roots depends on various factors such as the lasting time of native nutrients in the soil, soil physical properties, soil salinity and exchange capacity of the soil. A higher dose of application of nanomaterials may have negative consequences on rhizosphere microbial communities. Many comparative investigations on foliar spraying and soil application have proved that foliar fertilization has significant advantages for the uptake of nutrients from nano fertilizers (Alidoust et al., 2013). The foliar fertilization reduces the time lag between the spraying and plant uptake during its growth phase and it is also a guick method to treat nutrient deficiencies. Soil amendment and seed treatment are done on nutrient deficiencies in the soil whereas foliar nutrition is done based on plant nutrient deficiencies (Fageria et al., 2009). Making foliar nutrition more efficient requires optimum leaf area index, multiple applications and time of application based on the weather to avoid nutrient loss (Fernandez et al., 2013). Fig 2 shows the application of nano-fertilizers in crops indicating that foliar application nano fertilizers have essential nutrients under a controlled release pattern as a function of time and environmental stimuli as recorded on the right side. Nanoparticles of essential nutrients that are applied directly to the soil, irrigation water or the surface of plants, fruits or seeds (Morales-Diaz et al., 2017).

Fate of nano fertilizers in plant system

Foliar application of traditional fertilizers faces some physical obstacles because many nutrients are salt-based and the size of particles is more than pore size which may cause difficulty in penetration into the plant tissue (Benzon et al., 2015). Hence, Nano fertilizer formulations possess all the desired properties such as greater solubility, effectiveness, stability, desired particle size, controlled release pattern, improved target active points, effective concentration and ecologically safe and easy mode of supply and retention. The nanoparticles have a greater potential to supply nutrients to precise target sites in plant systems. The size of the nanoparticle is less than the diameter of the stomatal opening which favors easy entry into plant cells and reaches up to the plasma membrane (Moore, 2006; Navarro et al., 2008). The foliar application of nanomaterials to crops is promising and efficient translocation of nutrients to the desired plant parts (Deepa et al., 2015). The foliar sprayed nano nutrients were translocated from the site of application to the heterotrophic cells via plasmodesmata of conductive phloem vessels (Knoblauch and Oparka, 2012; Etxeberria et al., 2016). Nanomaterials can enter from the outer leaf surface into the leaf stomata and then redistribute to the different parts of a plant as observed by Wang et al. (2013) in watermelon plant (Fig 3). The coating of essential nutrients to nanoparticles is generally done by (a) absorption on nanoparticles (b) attachment on nanomaterials mediated by ligands (c) encapsulation in polymeric shell (d) manufacturing of nano fertilizers composed of nutrients itself and (e) synthesis of nano urea comprises two steps urea quinhydrone mixed liquor is firstly prepared and then, the obtained mixed liquor is sprayed onto calcium cyanamide granules to form the nano urea as urease inhibitor quinhydrone delays the hydrolysis and calcium cyanamide suppress the microbially mediated nitrification and denitrification. The combination of urease and nitrification inhibitor regulates N-transformation resulting in an effective bio pathway of nano urea in soil and plant systems (Table 1).

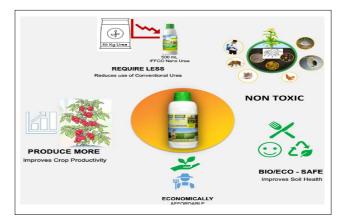


Fig 1: Liquid nano urea and its advantages.

Nano fertilizers on growth and yield

Nano fertilizers play a key role in improving plant biochemical and crop physiological processes by enhancing nutrient availability. Nano fertilizers are gaining importance in agriculture in increasing crop yields, nutrient use efficiency and reducing excessive usage of chemical fertilizers. Kumar *et al.* (2021) reported that the use of 50% N along with the foliar spraying of nano urea in rice at the tillering stage, nano zinc at 38 DAS and nano copper at 53

days after sowing significantly increased the grain and straw yield. Similarly, nano-Fe application at three different stages of crop growth (tillering, stem elongation and tillering + stem elongation) at 4% concentration resulted in a significant rise in the number of tillers per plant and seeds per spike in wheat (Armin et al., 2014). Reddy et al. (2022) concluded that the combined application of 50% conventional urea and 50% N through nano urea along with nano Zn improves the grain yield and straw yield in

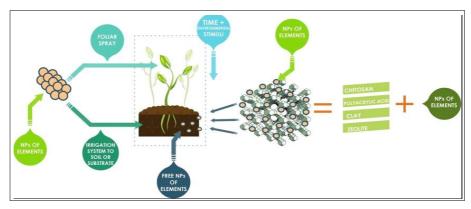


Fig 2: Smart delivery system of nano fertilizers.

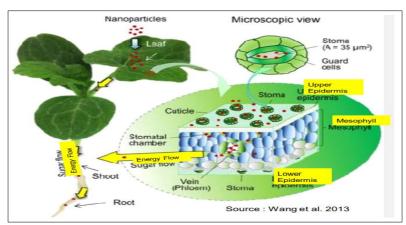


Fig 3: Schematic diagram of nano particle transport inside the plant system.

Table 1: Nano fertilizers vs conventional fertilizers.

Properties	Nano fertilizers	Conventional fertilizers
Solubility and bioavailability	Greater solubility and improved bioavailability by reducing the soil absorption and fixation	Lesser bioavailability due to macroparticle size
Nutrient uptake efficiency	Increased nutrient efficiency and uptake ratio of applied nutrients in crop production and saves fertilizer resources	Decreased nutrient efficiency due to non-available the roots
Nutrient release patterns	Nutrient release is precisely controlled according to the plant nutrient demand	Excess release of nutrients leads to soil toxicity and ecological imbalance
Duration of nutrient release	Extended period of nutrient release into the soil for plant uptake	Quick-release of nutrients results in mineral transformations
Soil absorption and fixation	Low	High

maize. Janmohammadi et al. (2017) results showed that the application of multi-nutrient nano fertilizer, conventional NPK fertilizer and nano-chelated Zn considerably improved both vegetative growth (plant height, canopy width and number of branches) and yield components. Vasuki et al. (2023) reported 50% Conventional N and K along with 50% nano N and K recorded higher yield attributed and grain yield of rice. Foliar spraying of nano nitrogen formulation in wheat (cv. HD 2967) and rice (Ranjit) gave numerically higher additional yield (245 kg ha-1) along with 50% nitrogen application than with 100% nitrogen (188 kg ha-1) (Kumar et al., 2021). Similarly, the results of Salama and Badry (2020) indicate that the application of 50 % nanoparticle urea + 50% bulk urea produced an increased amount of fresh yield with the maximum growth parameters, significantly higher crude protein (66.10 g kg⁻¹), non-fibre carbohydrates, low acid-detergent fibre (284.09 g kg⁻¹) and crude fat (36.97 g/kg) were recorded in teosinte. Soil application of nano Fe₂O₃ in peanut at 2-1000 ppm improved plant growth characteristics, root morphology and productivity (Rui et al., 2016). Foliar application of nano ZnO at 50-2000 ppm has significant improvement in germination percent, seedling vigor index, yield, biomass and nutrient accumulation in seeds when compared to control (Subbaiah et al., 2016).

Under arid climatic conditions like Rajasthan, foliar application of nano phosphorus @ 40 ppm gave an equivalent yield of cluster bean and bajra with 80 kg/ha phosphorous through RDF and it had come out that with the application of nanomaterial to reduce the usage of bulk fertilizer quantity (Raliya et al., 2018). A novel combination of N P and Zn nano fertilizers in wheat improves the growth and yield parameters (Sheoran et al., 2021). Metwally (2018) results indicated that the use of nano-fertilizers at 30 ppm in peanut improves the growth and yield traits and also appreciably influences the nutrient contents and chemical constituents in seeds. Payghan (2016) found an increased nutritive value of fodder millet (Panicum miliaceum) in terms of more CP and less Neutral detergent fibre (NDF) and Acid detergent fibre (ADF) contents with the combined application of nanoparticle and chemical fertilizers.

Nano fertilizers on physiological parameters of crops

Nano fertilizers enhance growth parameters, dry matter production, chlorophyll production and rate of photosynthesis which result in more synthesis and translocation of photosynthates to different parts of the plant (Singh et al., 2017). When nanoparticles are applied through the foliar application on leaf surfaces, they enter through the stomatal openings or the bases of trichomes and they are translocated to various tissues (Uzu et al., 2010). Application nano fertilizers (nano Fe, Mn and Zn) produce an appreciable increase in chlorophyll, carotenoids in peanut leaves, total carbohydrate and total soluble sugars in seeds (Metwally et al., 2018). Similar effects are observed in chickpea (Janmohammadi et al., 2017). Similarly, nano-KH₂PO₄ helped greater physiological efficiency for

phosphorous in both shoots and roots, thus increasing the phosphorous concentration and inducing higher biomass accumulation in plant organs in rice (Miranda et al., 2019). Foliar application of nano fertilizers of iron and zinc improves the leaf area and seed quality in terms of protein content and also enhances the activity of antioxidant enzymes, proline and soluble sugar content. (Fatollahpour et al., 2020). Using TiO₂ (0.25-4%) nanoparticles in lower concentrations has not exhibited any harmful effect on plants instead they are capable of activating specific physiological and molecular responses and enhancing the photosynthesis and nitrogen metabolism in spinach (Zheng et al., 2005; Klaine et al., 2008). Soil application of nano Fe₂O₃ in peanut at 2-1000 ppm improved photosynthetic pigments, Chlorophyll index, plant hormones, enzymatic activities and Fe uptake (Rui et al., 2016). Foliar application of nano ZnO at 150-300 ppm enhanced biochemical and physiological activities in maize (Raddy et al., 2018).

Nano fertilizers on nutrient use efficiency

Nutrient availability in the soil over time can be enhanced by the application of nano fertilizers, subsequently, it increases nutrient use efficiency (Suppan, 2013). Nano fertilizer releases nutrients in a controlled pattern, which curtails the leaching of the nutrients among other interesting properties. The use of nanofertilizers is the most important application of nanotechnology in agriculture so far (Agrawal and Rathore, 2014). Regarding nitrogen fertilizers, the application of nanotechnology can provide fertilizers that release N according to the crops' needs, ultimately leading to increases in N use efficiency through minimizing N leaching and emissions and long-term incorporation by soil microorganisms (Suman et al., 2010; Naderi and Danesh-Shahraki, 2013). The nano fertilizers release nutrients slowly into the crops and thus increase their availability over the entire growing cycle. This is an important mitigation measure as it prevents loss of nitrogen through the process of denitrification, volatilization, leaching and fixation in the soil particularly into nitrate (NO3-) and nitrate (NO3-) forms of nitrogen (Preetha et al., 2017).

Apart from considerably increasing farmers' income by cutting down on input and storage costs, nano urea liquid also aims to increase crop yield and productivity against conventional urea. The use of nano NPK fertilizers in potatoes at 50% of the recommended level showed higher values of NPK nutrient use efficiency (Azeim *et al.*, 2020). maximum Agronomic efficiency, apparent nutrient recovery and partial factor productivity were recorded with the application of nano NPK fertilizer alone when compared to other treatments in maize (Sankar, 2020).

Effect of nano fertilizers on economics

Nano fertilizers facilitate the slow and steady release of nutrients, thereby reducing the loss of nutrients and increasing nutrient use efficiency and also deducting the cost of production. Results of Ajithkumar *et al.* (2021)

indicated that the highest economic returns and costbenefit ratio were obtained with the 50% RDN, two sprays of nano urea with IFFCO Sagarika in maize. The same results are observed in wheat and rice (Kumar *et al.*, 2020).

Nano fertilizers on environmental footprint

Perhaps no case is more convincing than transforming and reducing the use of concoction compost inputs using nanotechnology among the improvements whose fairly clear to increase farming harvest yields while reducing the environmental harm of agriculture endeavours. Only two of the severe ecological consequences of the widespread use of traditional synthetic fertilizers for major commercial crops are greenhouse gas emissions and hypoxia (Park et al., 2012; PHYS.ORG, 2015). Mohanraj et al. (2019) investigated the role of nano fertilizers in GHG emission in rice soils and nitrous oxide and methane emission was measured at 30 and 60 DAT in rice soils exposed to various fertilization treatments and the results indicated that nano-fertilizer has the potential to regulate the release of N for an extended period (20 days) in comparison to the conventional urea fertilizer (9 days). The slow and steady release of N assisted in the reduction of nitrous oxide emission by 50% in nanozeolite fertilizer (0.88 mg m⁻² per day) fertilized soils in comparison to conventional fertilizer (1.67 mg m⁻² per day) applied soils. There was a slight reduction in methane emission from the nanofertilizer applied soils. A similar trend of response was seen at 60 DAT. The application of nano fertilizers in agriculture allows nutrient release into the soil gradually in a controlled pattern which maintains the soil fertility and thus, prevents eutrophication and water pollution (Sekhon, 2014; Naderi and Abedi, 2012). The fact that use of nano fertilizers may enhance crop production by about 20 to 30% more compared with traditional fertilizers. Achieving similar levels of crop protection and nutrition with use of agrochemicals by 20-30% less could substantially mitigate environmental pollution.

CONCLUSION

The application of nanotechnology in developing nano fertilizers made a revolution in overall agriculture to feed the future food demand with minimum environmental hazards. The use of nano fertilizers in Indian agriculture is still in the budding stage. Research studies showed both soil application as well as foliar application of macro and micro nutrient-based nano-fertilizers to have remarkable advantageous effects on plant growth, yield and physiological parameters as compared to conventional fertilizers. Smart release pattern results in high nutrient use efficiency drives towards lower application of conventional fertilizers thus reducing the cost incurred on traditional chemical fertilizers in crop production. Besides, reduced consumption and production of conventional fertilizers mitigates the GHG emissions. Thus, nano fertilizers become a new window for agricultural and environmental sustainability.

Future line of work

This review paper mainly addresses on effect of nano fertilizers on crop growth, development, physiology, crop nutrition and nutrient use efficiency. There is a need to research the impact of nano fertilizers on soil and soil biology, the fate of nano nutrients on soil and plant systems and intensified research on environmental footprint.

Conflict of interest

All the authors declare that there is no conflict of interest regarding the publication of this article.

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