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Employing engineered nanoparticles to improve nutrient use efficiency

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Abstract
With the increase in the global population, which is projected to be around 10 billion by 2050, fulfilling the rising food demand seems to be a major concern. This increase has prompted a soaring and heedless use of low-efficiency chemical fertilizers to obtain a higher yield. Nanofertilizers show a great deal of potential in eliminating the issues related to chemical fertilizers. The application of nanofertilizers has a crucial role in but is not limited to enhancing nutrient use efficiency and crop nutrition. The efficient use of nanofertilizers relieves the dramatic increase in cost to the farmer, minimizes the pollution hazard, and boosts the plant productivity. So, the application of nanofertilizers for smart, sustainable, and precision agriculture using a controlled and targeted delivery system becomes the need of the hour. All these aspects of nanofertilizers are discussed in this paper. The delivery system and its effect on plants are also addressed.

Keywords: Nanofertilizers, chemical fertilizers, efficiency

Introduction
Due to the shortage of agricultural land, nutrient resources, and water the expansion in the agriculture sector is possible only by increasing the resource use efficiency with the minimum losses through the use of effective modern technologies (Naderi and Shahraki, 2013) [13]. Nanotechnology holds promise and nanofertilizers can go a long way in ensuring sustainable crop production and uphold soil health (Lal, 2008) [8].

Mineral fertilizers, nutrients encapsulated inside nanoporous materials, coated with a thin polymer film, or delivered as particles or emulsions of nano-scale dimensions are known as Nano-fertilizers (Rai *et al*., 2012) [16]. Nano-particles under 100 nm can be used as fertilizer for efficient nutrient management with an added benefit of stress tolerating capability. Nanofertilizers deliver the nutrients to the crop as per the requirement in a controlled and phased manner because it contains nutrients and growth promoters encapsulated in nano-sized polymers. These nano-sized particles ensure slow and target efficient release of the nutrients to the crop during its lifespan consequently ensuring increased nutrient use efficacy. Nanofertilizers can also release their active ingredients in reaction to environmental triggers and biological demands of crops more accurately. They play a valuable role in improving soil health by improving soil aggregation, building up carbon uptake, and improving water holding capacity. Nanofertilizers being encapsulated in nano-particles increase the nutrient use efficiency and uptake of nutrients (Tarafdar *et al*., 2014) [22]. These nanofertilizers made through biological processes are eco-friendly and have been designed to match inorganic fertilizers in terms of nutrient composition and application rates. Nanofertilizers are more efficient than conventional chemical fertilizers and are synthesized to regulate the release of nutrients depending on the requirements of the crops (Liu and Lal, 2015) [10].

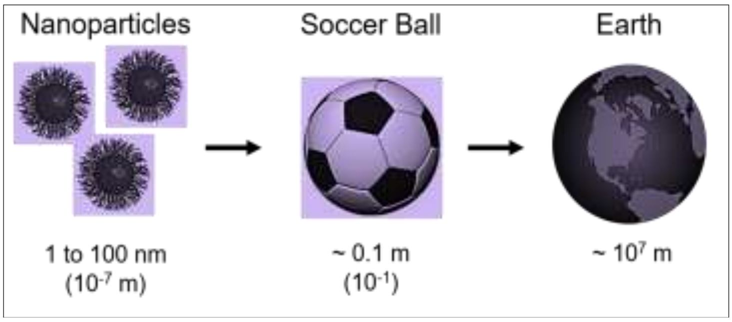

Fig 1: Scale of Nanoparticles

Objectives of Review

Nanotechnology can be credited as the forerunner amongst the recent technological innovations that have the potential of transforming agriculture and food production. This paper summarizes our venture in understanding the working of nanofertilizers, their corresponding role in enhancing nutrient utilization efficiency, the various ways in which they can be exploited in agriculture and the advantages they offer over conventional fertilizers. This review presents our attempt to explore the nuances of the existing employment of nanotechnology in agriculture and the prospects it may offer. The purpose of this review paper is to compendiously review recent progress made in the field of nanofertilizers. Overall the above-proposed review will be focused on two major objectives:

i. To identify the advantages of employing nanofertilizers to improve fertilizer use efficiency.
ii. To review the benefits of nanofertilizers over conventional mineral fertilizers.
iii. To identify the specific applications of the new advancements and to have a better understanding of the technologies currently being used in the field of nanotechnology.

Nutrient Use Efficiency with Nano-Fertilizers

One of the key factors that play an important role in deciding the good yield of crops is nutrient use efficiency. The factors like fertilizer management, soil, and plant water relationship have a great impact on it. Nowadays, replenishing and improving soil's nutrient use efficiency has become a need of today's scenario. Today soil fertility is degrading day by day. So, the nutrients are added with an aim of increasing crop yield, the overall productivity of the field with different cropping systems, rendering proper nutrition to the soil so that its characteristics like cation exchange capacity, water holding capacity, mobility of nutrients would increase to a sufficient level. If we talk about the mobility of nutrients, then micro or nanoparticles have great mobility. In agriculture, nanofertilizers play an important role to fulfil this criterion and have become an important pillar of modern agriculture. Due to their high rate of mobility, they lead to the transport of nano-formulated nutrients to all parts of the plant.

They possess certain properties that make them specific for the crops are:

1. They have large surface areas that provide sufficient surface for assimilation and metabolization of nutrients. This results in the production of more photosynthates and less consumption of nutrient elements.
2. They are highly soluble in various solvents such as water.
3. Due to their small particle size (less than 100 nm), they penetrate easily into the plant system.
4. Their particle size is less than that of the roots and leaves of the plant. This leads to easy penetration into the plant system and thus improves the nutrient use efficiency of the nanofertilizes.
5. The reduced nature of particle size results in increased specific surface area and a number of particles per unit area of fertilizers, which provides more chances for the contact of nanofertilizers that leads to more penetration.
6. The incorporated fertilizer elements in nano-particles increase the availability and hence uptake of the nutrients to the crops.

Nanofertilizers based on zeolite release nutrients slowly to the crop which increases the availability of nutrients to the crops throughout their growth period and processes like leaching, denitrification, volatilization, fixation, can be reduced through nano-technology. It is highly beneficial to prevent the fixation of NO_3 and NH_4 forms of nitrogen.

Smart Delivery of Nanofertilizers

Using chemical fertilizers indiscriminately may lead to various unfavorable results like reducing the soil fertility, turning the soil toxic, soil and water pollution, etc. To overcome these problems and, at the same time, enhance the nutrient use efficiency, nanofertilizers might be the best alternative to the traditional soluble fertilizers. They are being developed for slow release and efficient dosages of fertilizers to plants (Tarafdar *et al*., 2012a) [21].

These Nanofertilizers shall be designed in such a manner that they have a time-controlled and slow-release, enhanced targeted activity, and a relatively sustainable impact on the environment avoiding any eco-toxicity, an effortless mode of delivery, and an effectual concentration (Tarafdar *et al*., 2012b) [20]. The slow-release fertilizers provide nutrients to the crops throughout their growth and are used up by the crops efficiently, thus avoiding wastage of nutrients by leaching.

This controlled and slow release of nanofertilizers can be achieved in several ways:

1. Slow-release of nutrients in the environments could be achieved by using zeolites. They have a honeycomb-like structure and can be laden with Nitrogen and Potassium as well as various other minor and trace nutrients. Fertilizer particles are then coated with these nanomembranes for the slow and steady release of the nutrients and therefore enhance the nutrient uptake and utilization (Qureshi *et al*., 2018) [14].
2. For controlled release in the soil environment, nanofertilizers can be mixed with various materials like hydrogels, special films, and biopolymers like chitosan (Kashyap *et al*., 2015) [6].

3. For the elements like Fe, Cu, Ni having a limited bioavailability in the soil foliar spray is a good alternative for releasing the nanofertilizers into the soil. This can be done using emulsions or encapsulated nanoparticles (Mahanta *et al*., 2019) [11].

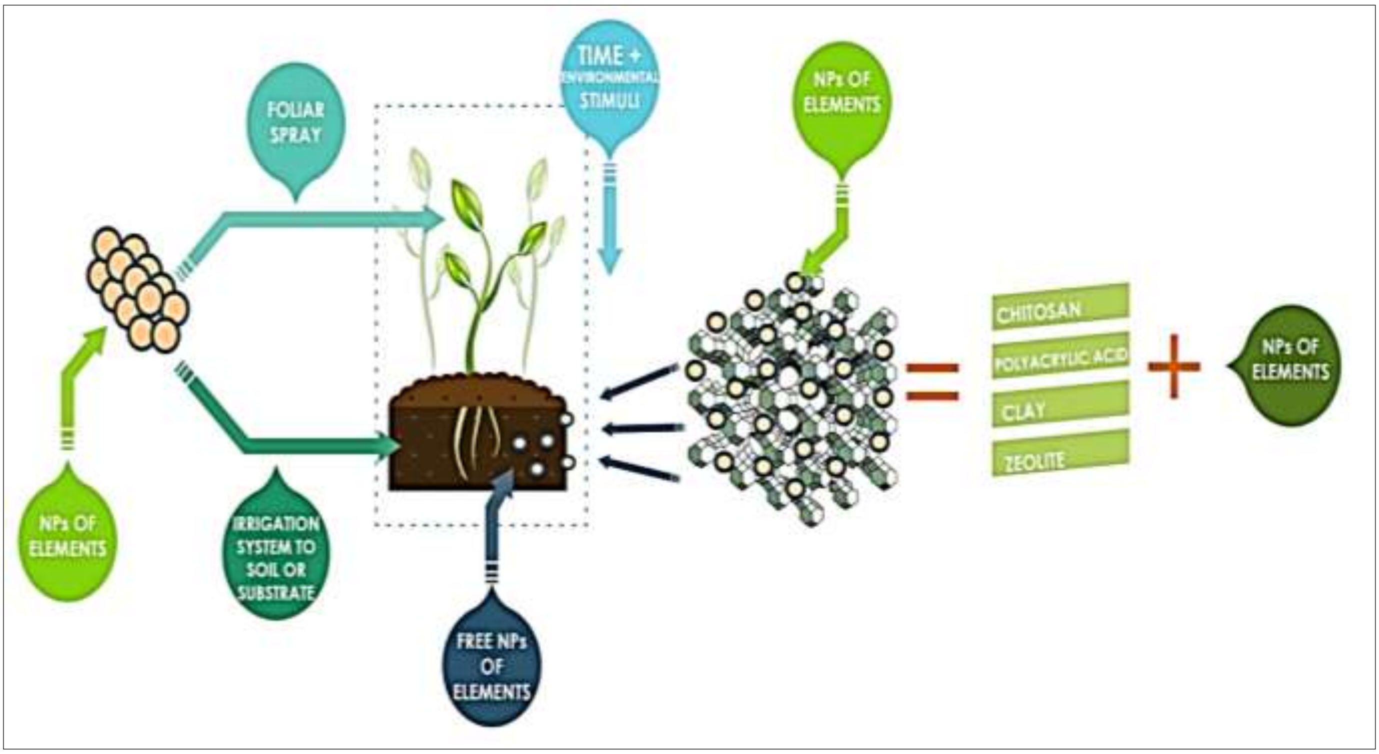

Fig 2: Smart Delivery System of Nanofertilizers

Nano Fertilizers and Their Roles

Fertilizers have a pivotal role in increasing food production many folds in developing countries after the introduction of high yielding and fertilizer responsive crop varieties. That being said, it's known that yields of various crops have begun to decrease as a consequence of imbalanced fertilization and reduction in soil organic matter. Furthermore, indiscriminate applications of nitrogen and Phosphorus fertilizers affect the groundwater negatively and also cause eutrophication in aquatic ecosystems. Such reported instances alongside the very fact that the fertilizer use efficiency for nitrogen is merely about 20-50 per cent and merely 10-25 per cent for phosphorus fertilizers which means that food production must be amplified and also must be far more efficient than ever before (Tarafdar *et al*., 2013; Shaviv, 2000) [23, 18].

In recent times nanotechnology is progressively shifting from the experimental into its practical application in the fields. We are aware that the fast depleting ecological system is foreseeing an alarming scenario for the survival of future generations. Wastage of natural resources and indiscriminate use of pesticides and fertilizers are among the principal reasons for this decline. Undoubtedly, nanotechnology has provided us the feasibility of exploiting nanoscale substances as fertilizer carriers or controlled-release vectors as a novice way to enhance nutrient use efficiency and keep a check on the environmental harm caused otherwise (Baruah and Dutta, 2009; Cui *et al*., 2010) [1, 2].

1. Increasing Productivity

Nanostructured formulations might increase fertilizer efficiency and uptake ratio of the soil nutrients in crop production, and save fertilizer resource. Controlled release methods have properties of both release rate and release pattern of nutrients for water-soluble fertilizers could be precisely controlled through encapsulation in an envelope like semi-permeable membranes coated by resin-polymer, waxes, and sulphur. Modern intensive farming systems use organic and mineral manures to supply essential nutrients to the plant; however, this approach has caused serious damage to ecosystems and the environment (Lin *et al*., 2009) [9]. Loss of nitrogen as nitrous oxide and nitrates leaching leads to eutrophication of water bodies and has an apparent role within the heating and global climate change (Davidson *et al*., 2012) [3]. Nanofertilizers have the potential to increase NUE owing to higher nutrients uptake caused by a smaller area of nanomaterials which increases nutrient-surface interaction. Alongside boosting crop yield on a sustainable basis, nanofertilizers hold the potential to put a halt to environmental pollution caused by fertilizers. Slow-release fertilizers (chemical compounds have slight solubility in water or other solvents, and are broken down gradually and slowly by soil microbial population) coated with nanoparticles significantly reduced nitrate leaching and denitrification (Kottegoda *et al*., 2011) [7]. Moreover, controlled releasing fertilizers (have better solubility in contrast to slow-release fertilizers but are coated with materials which evidently reduce the exposure of active ingredient with the solvent resulting in controlled liberation of nutrients through diffusion) coated with nanomaterials for reducing area may prove an excellent source of supplying plant nutrients in the coming years.

2. Protecting the Ecological Environment

The inception of the revolution paved way for a huge upsurge in the use of fertilizers for feeding the growing population however, it came with a price; the unsustainable agricultural practices have caused significant ecological disruption and also the utilization efficacy of applied chemicals including mineral fertilizers has remained far below the specified level (Eliazer Nelson *et al*., 2011). Fertilizers have played an axial role with regard to boosting crop yield and nutritional quality especially after the introduction of fertilizer responsive crop varieties. Among mineral nutrients, nitrogen is one of the foremost important nutrients required for crop plants since it's the constituent of chlorophyll and much of proteins and enzymes and thus plays an enormous role during the vegetative growth of crops. Nitrogen is absorbed by the plants in the form of nitrate (NO_3^-) and ammonium (NH_4^+). Nitrogen becomes all the more important because a majority of the applied amount is lost through various wasteful processes. Nitrogen is lost through the processes of nitrate leaching, denitrification, and ammonia volatilization. Loss of mineral nutrients through leaching and runoff to the surface and groundwater alongside abundant volatilization constitute growing concerns due to economic losses and environmental pollution. Conventional application techniques have resulted in serious overdosing of chemical fertilizers which has become evident through the phenomenon of eutrophication (the gradual increase in the concentration of phosphorus, nitrogen, and other plant nutrients in an aging aquatic ecosystem like a lake, the productivity or fertility of such an ecosystem naturally increases because the quantity of organic material which can be weakened into nutrients increases) in many European and North American countries. Despite the beneficial role synthetic N fertilizers have played in fostering the increase of agricultural crop and livestock production, findings are suggesting the destructive effect of excessive usage of N in the environment, all over the globe. Excessive rainfall and irrigation are the 2 friendly factors furthering fertilizer farther into the soil beyond the reach of the root zone. Luo *et al*. (2010) also concedes the very fact that natural efforts such as heavy watering and rainfall of good magnitude also wash away excess surface nitrate fertilizer, polluting waterways Hypoxia (low levels of dissolved oxygen), relative to an algal bloom, is noted to be caused by excessive levels of nitrates in waterways, can even become toxic to warm-blooded animals at higher concentrations (10 mg/L) or higher) if unchecked (WHO, 2017) [25]. Additionally, nitrate-rich diets are reported to be related to numerous human diseases like bladder and gastric cancer as well as methemoglobinemia (Sandor *et al*., 2011). One of the prime causes for nitrogen pollution is the poor nitrogenous fertilizers use efficiency of <40%, while the corresponding figure for phosphorous fertilizers has been reported to be only 10–25% (Vinod and Heuer, 2012) [24]. It is to deliver the required quantities of active agents only where they are direly needed. Environmentalists and consumers have been demanding a reduction in the use of synthetic fertilizers to control pollution and residue effect on the farm produces along with protecting the agro-ecosystem.

Table 1: Advantage of Nanofertilizers

Sr. No.	Properties	Advantages
1	Nutrient use efficiency	• The small size of nanoparticles improves the uptake of nutrients and nutrient use efficacy.
2	Nutritional value	• More nutrient availability increases crop quality parameters like protein, sugar, oil content, etc.
3	Controlled release of nutrients	• Encapsulated fertilizers control the speed of release of nutrients and increase the actual duration of nutrient supply.
4	Reduced loss	• Due to slower nutrient release wastage by leaching and other ways reduces significantly.
5	Improve soil quality	• Increase the water holding capacity of the soil. • Increase microbial activity due to controlled release.

Advantages of nanofertilizers over conventional mineral fertilizers

Nanofertilizers have the potential to enhance nutrient use efficiency because of higher nutrients uptake caused by the smaller surface area of nanomaterials which increases nutrient-surface interaction. Along with boosting crop yield on a sustainable basis, nanofertilizers hold the potential to put a halt to environmental pollution caused by fertilizers. Slow-release fertilizers (chemical compounds have low solubility in water or other solvents and get broken down gradually by the soil microbial population) coated with nanoparticles significantly reduced nitrate leaching and denitrification (Milani *et al*., 2012) [12]. Moreover, controlled releasing fertilizers (have a 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 release of nutrients through diffusion) coated with nanomaterials for reducing surface area my provide excellent of the source of supplying plant nutrients timely.

Mineral nutrients if applied to crops in the form of nanofertilizers hold the potential to offer numerous benefits for making crop production more sustainable and eco-friendly (Subramanian *et al*., 2015) [19]. Some of the big advantages they offer are:

1. Nanofertilizers feed the crop plants gradually in a controlled manner in contradiction to the rapid and spontaneous release of nutrients from chemical fertilizers.
2. Nanofertilizers are more effective when it comes to nutrients absorption and utilization due to considerably lesser losses in the form of leaching and volatilization.
3. Nanoparticles record significantly higher uptake because it can pass easily through nano-sized pores and by molecular transporters as well as root exudates. Nanoparticles also utilize various ion channels which results in higher nutrient uptake by crop plants. Within the plant, nanoparticles may pass through plasmodesmata that result in the effective delivery of nutrients to sink sites (Iqbal, 2019) [5].
4. Due to considerably small losses of nanofertilizers, these are required in smaller amounts in contrast to synthetic fertilizers which have to be applied in greater quantities keeping in mind the fact that their major portion gets lost owing to leaching and emission.
5. Because nanofertilizers are required in lesser amounts they pose a lower threat of causing environmental pollution.
6. Nanofertilizers are comparatively more soluble thus providing it an edge over conventional synthetic fertilizers.
7. The surface coatings of such as, encapsulation within nanomaterials coated with a thin protective polymer film or in the form of emulsions of nanoscale dimensions, allow the nanomaterials on fertilizer particles to hold the material more strongly owing to its higher surface tension as compared to the conventional surfaces which help in controlled and timely release (Eliazer *et al*., 2011).

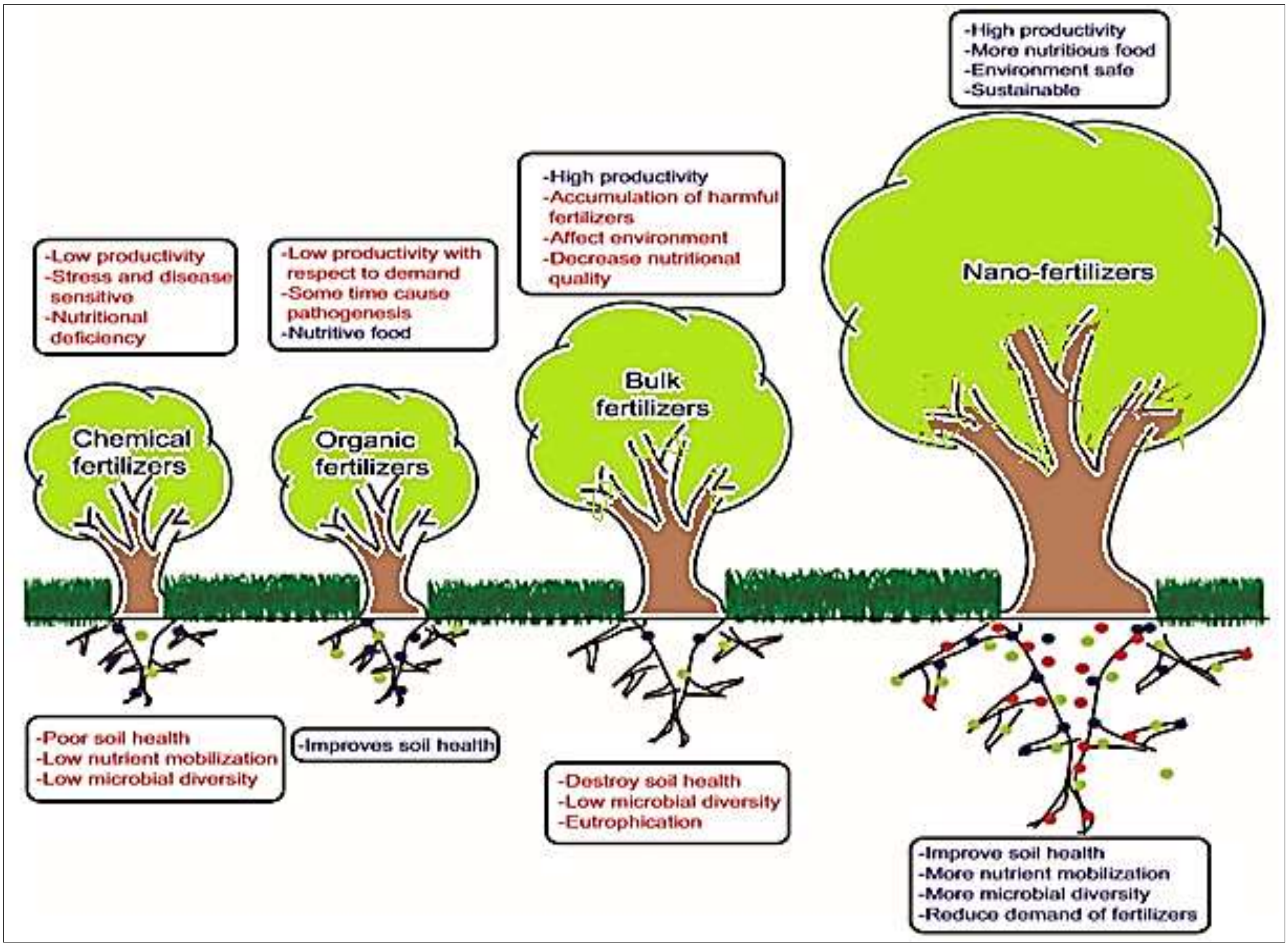

Fig 3: Comparative Evaluation of Fertilizers, Organic Fertilizers, Bulk Fertilizers and Nanofertilizers

Future Prospects

Even with stout theoretical validation and lucidity, the practical application of nanofertilizers still has a long way to go. There are some important reasons and explanations for this unscrupulous underestimated expectant scenario. To begin with, developing countries such as India and some others follow extensive agriculture practices, which are being allayed due to the rural background. Supporting and assisting the farmers in such intriguing circumstances is a huge challenge that has perhaps alluded to most of the scientific discrepancies. So there is a need to make grass-root efforts for awakening the farming community about the positives of nano-carrier mediated fertilizer delivery. In many regions, there is a continuous setback because of variable climate patterns about how, when, and what kinds of fertilizers are suitable for which kind of soil. Although efforts have convinced farmers that fertilizers are distinct from manures in chemical composition and mode of action still which kind of fertilizer, time of application, and method of application emerges a daunting challenge. Therefore, scientists and the communication workforce must initiate symphonic and dedicated cooperative efforts along with governmental support to understand the exact scientific validation for nanofertilizer usage. The predictions regarding how nanocarriers can allow homogeneous delivery of nutrients and reduce the net quantity of fertilizers used are highly crucial. Policies of government should emphasize less on compensation but more on a scientific resolution of this technology. This would inculcate a big boost in farmer's minds regarding the willingness to accept nanotechnology. For instance, what are the potential gradual consequences of unaided (nano-carrier is absent) fertilizer to the concerned crop variety and soil can be highly important contributions for readiness to accept the nanotechnology. Similarly, the benefits of getting significantly better yield by nanofertilizers can be a significant game-changing strategy. Many other methods could be hypothesized, but the success of all of them depends on dedicated efforts keeping the nation's development at the uppermost and not particular individual interests.

Conclusion

The widespread presence of multi-nutrient deficiency in cultivated soils has resulted in significant decreases in agriculture productivity and pronounced economic losses in agriculture. Even though the application of fertilizers can increase crop production, their extensive use is not recommended for the long run. Furthermore, the available macro and micronutrients present in the bulk chemical formulation as supplied by conventional chemical fertilizers are not completely available to plants. Moreover, the consumption of most of the macro and micronutrients is very low due to their precipitation to insoluble form in the soil. Delivery of agrochemicals such as chemical fertilizer supplying nutrients to the plants is a central aspect of the nanotechnology application in the agriculture sector. Nanostructured or nanoscale materials can be used as controlled-release vectors or fertilizer carrier for the building of smart nanofertilizers effectively. These nanofertilizers can significantly increase nutrient use efficiency and reduce environmental pollution. They can precisely release their active ingredients through their smart delivery system in response to the biological demands of plants. Nanofertilizers can be delivered to plants by using both in vitro and in vivo methods. However, the uptake, translocation, and fate of nanoparticles in the plant system are mostly unknown and undiscovered. This has resulted in the rise of various safety and ethical issues regarding the use of nanofertilizers in agriculture ecosystems. A systematic and methodical qualitative and quantitative analysis regarding the potential health impacts, environmental safety, and safe disposal of nanomaterials can lead to improvements in designing further technology for applications of nanofertilizers.

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