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Nano fertilizers in plant soil interaction

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Abstract

Nanotechnology research has the potential to bring long-term solutions to serious issues confronting modern intensive agriculture. Nano fertilizers have a three-fold increase in nutrient utilisation efficiency (NUE) 80-100 as compared to chemical fertilizers. Chemical fertilizers make crops 10 times more resistant to stress. Nanomaterials with a size of 1–100 nm are used in nanotechnology, and their small size gives them unique properties and benefits. A big area provides the ability for better and more effective interaction of nanoparticles to focus on specific places having an advantage of completely biodegradable, making it eco-friendly [1]. The review majorly focuses on the synthesis and evaluates the role of nano fertilizers in increasing nutrient uptake and efficiency, reducing losses through leaching and gaseous emissions, and lowering the risk of nutrient toxicity in order to ensure food security through increased productivity and economic returns through sustainable farming practices [2, 5, 18, 30].

Keywords: biodegradable, eco-friendly, nano fertilizers, nutrient efficiency, toxicity

Introduction

The field of nanotechnology is an interdisciplinary field that is derived from engineering, physics, chemistry, and biology. Nanotechnology has rapid advances in science and technology by creating new prospects in the fields of medicine, foods, electronics, and environment. Nanomaterials are generally 1 to 100 nano-meters in size, can be found in nature or created artificially. Depending on their minute size, they exhibit novel properties that are now being explored for brand spanking new opportunities in agriculture. Previously, nanoparticles found in nature, such as zeolite minerals, were recommended for agricultural application. However, engineered nanomaterials exhibit different unique physical and chemical properties in the development of various applications. Nano fertilizers when compared to regular fertilizers, shows greater nutrient efficiency in plant and agricultural production [38]. Phyto nanotechnology for the synthesis of green nano fertilizers prefers to be the better choice, overcoming almost all the problems.

Coated nanomaterials show the discharge of nutrients or a porous nano fertilizer consists of a network of channels that retard nutrient solubility. Nanotechnology for fertilizers is still in the early stages of development, however it has already been used in medicinal and engineering applications [29]. Another challenging application of nanotechnology is encapsulation of helpful microorganisms that improves plant root health. It includes different bacteria or fungi that increases the nutrient availability in the root zone. The development of nano biosensors to react with specific root exudates is being explored.

Though farming practices were introduced and are evolved since inception of revolution, deemed unsustainable efficiency of applied chemicals, mineral fertilizers has persisted below 30%. Fertilizers take axial role in enhancing crops yield and nutritional quality specifically after development of fertilizer reactive crop varieties. Among minerals and nutrients, nitrogen is the first and is the most significant nutrient since it is a key component of chlorophyll, which is a major component of numerous proteins and enzymes, and therefore plays an important role in plant vegetative development. Nitrogen is absorbed by plants in the form of nitrate and ammonium. Ammonia gas is formed by reaction in between ammonium ions and alkaline rain water and that released into atmosphere and thus becoming the source of pollution. Whenever, there's excess nitrogen, conversion of nitrates and ammonium ions are high and get accumulated in crops especially leafy vegetables and become detrimental to human health.

Mineral efficiency Nano fertilizers

Fertilizers play foremost role to boost the production across the spectrum of crops. The nitrogen (N), phosphorus (P), and potassium (K) nutrient usage efficiencies (NUE) have stayed relatively consistent over the last several decades, barely exceeding 30–35, 18–20, and 35–40 percent, respectively. The use of conventional fertilizer has environmental risks in accordance with the contamination of the soil grassland leading to eutrophication [35].

The N loss in agricultural grassland are gaseous emissions (NH_3 and N_2O) and nitrate leaching and runoff (NO_3^- and organic N) [34] Due to its extensive use, there is an abundant atmospheric N_2O gaseous release in the air causing global warming. Denitrification as N_2O, a potent greenhouse gas (GHG) is another prevalent atmospheric gas that depletes the ozone layer. Worldwide, 12% of N_2O losses are due to synthetic fertilizers provided to grassland [39]. To avoid the environmental impact and to improve NUE, subsiding N leaching, NH_3 volatilization, the use of nanoparticles imparts a slow, substantial and time dependent release of essential nutrients to the grasslands.

To increase crop yield in marginal lands that have inadequate nutrient availability, NUE must be improved. But only small concentrations are increased in the NUE in conventional fertilizer formulations used so far. Fortunately, due to their high surface area to volume ratio, future nano fertilizer-based techniques are expected to outperform even polymer-coated conventional slow-release fertilisers. Nano fertilizers are predicted to enhance NUE by preventing nutrient ions from becoming fixed or escaping into the environment. When it comes to the amount of energy required for their synthesis, the amount of nitrogen fertilizer utilised, monetary worth, is comparatively less and is one of the most essential crop boosters. However, as compared with amounts of N applied to soil, the efficiency of nitrogen used by crops is very low. Urea is one of the commercially available, fast-release N fertilizers, which is easy to use in agricultural fields. Efforts to reduce the release rate of urea can increase its efficiency of use that further prevents ground water contamination.

In a follow up study using two different soil types (inceptisols and alfisols) and maize as a model crop, the grain N content of nano-zeolite urea on both the soils were found to be consistently higher than conventional urea but the response was more pronounced in alfisol than inceptisols [11, 15]. An early burst followed by a slow-release even on the 60th day was observed in an urea-modified hydroxyapatite nano encapsulated formulation under pressure into cavities of the soft wood of Gliricidia sepium [6], while commercial fertilizer showed a heavily early burst and subsequent release of low and non-uniform quantities until around day 30. When compared to conventional water-soluble fertilisers, the key benefits of employing slow-release nano formulation fertilisers include improved NUE efficiency, higher crop output, and reduced environmental impacts from nitrogen leaching [32]. Surface water eutrophication is the major problem also cited with phosphate salts that are heavily used in agriculture. Synthetic apatite nanoparticles (15.8 ± 7.4) were developed using a one-step wet chemical method, demonstrated to increase the growth rate and seed yield of soybean by 32.6 and 20.4 %, respectively [12, 31], as compared to $(Ca\ (H_{2-}\ PO_4)_2)$, a regular P fertilizer. In addition, above ground and below ground biomass production was enhanced by 18.2 and 41.2 %, respectively. Apatite nanoparticles may act as a novel class of P fertilizer that can potentially enhance crops yield and biomass production, while minimizing risks of water eutrophication. Recent research also highlighted the importance of the nano fertilizers in improving yield and biomass production. Cucumber leaves with sprayed nano fertilizers have shown the significant improvement in the yield when compared to control. Similarly, a significant increase in rice grain yield and nitrogen use efficiency was observed after applying slow-released fertilizer added to nanosized carbon. Nanocarbon, the average total N ion centration was decreased by 29.8 % and the time of N runoff loss was shortened by 1.8 day [14]. Recently, nanocomposites based on polyacrylamide (PAAm), methyl cellulose (MC), and calcic montmorillonite (MMt) hydrogels showed excellent controlled desorption of urea and indicated the release of higher amounts of nutrient that is almost 200 times slower than pure urea. Comparatively the release profiles of a urea based controlled release fertilizer indicated that 100 % release of urea takes place in the first 5 h, 100 % of urea was released in 97 h, and 87 % was released in 150 h from pure urea, urea intercalated kaolinite nanocomposite, and encapsulated nanocomposite respectively. Furthermore, the kind and concentration of salt solution supplied to the medium, pH levels of the solutions, and temperature all influenced urea swelling and release, with a Case II release mechanism with skeleton erosion predominating. Similarly, iron (Fe), P and K applied nano fertilizers were demonstrated that had a significant increase in yield, flower number, fresh stigma weight, dry stigma weight, stigma length, fresh flower weight and dry flower weight of saffron [16]. A new controlled release approach for N fertilizers based on urea–formaldehyde in the presence of MMt might be developed, with nanocomposites exhibiting greater mechanical resistance and urea release, clearly regulated by polymerization extent. These results observations are of stronger practical significance showing the efficacy of novel nanocomposites for slow-release of fertilizers that increases the nutrient use efficiency and yield, and also reduces pollution [35].

Broad range of Metal oxide nanoparticles have been used for the bioactivity, conductivity and chemical activity of the plants. The advantage of utilizing MNPs and MONPs have altered lattice symmetry and cell parameters, change in electrochemical effect and change in surface properties. These are some of the oftenly used metal and metal oxide nanoparticles.

Advantages of Nano Fertilizers over Traditional Fertilizers

Nano fertilizers are advantageous than conventional fertilizers as they increase soil fertility yield and quality of the crop, they're nontoxic except few that are harmful to the environment and humans, minimize the cost and increases profits. Nanoparticles improve nutrient efficiency while lowering environmental protection costs. The nutritious value of crops has increased, as has the flavour quality. There was increase in the protein content of wheat grains by availing optimal use of iron [17]. Several studies observed that nano fertilizers have a considerable impact on seed germination, seedling growth and plant growth metrics that determined the effect of nano fertilizers on seeds [23]. Nano fertilizers are easy to assimilate into seeds and boost nutrient availability to seedlings, resulting in healthier plants with longer shoots and roots. However, if the concentration is higher than the optimal, it may hinder plant germination and seedling growth. When compared to bulk zinc sulphate, nano ZnO resulted in higher peanut seed germination and root growth [8]. In soyabean, nanoscale SiO_2 and TiO_2 were found to have a similar favourable effect on germination [7, 12]. Seed germination, shoot length, and root length were all reported to have increased with nano fertilizer treatment compared to control or non-nano fertilizer treated seeds. Nano fertilizers boost nutrient availability to growing plants, resulting in increased chlorophyll formation, photosynthetic rate, and dry matter production, as well as improved overall plant growth. In comparison to the control, plants grown from nano-TiO_2 treated seed had higher dry weight, photosynthetic rate, and chlorophyll-a production [7]. This shows that nano fertilizers have a significant impact on seed germination and plant growth.

Effects on Beneficial Soil Microorganisms

Microbial population in the rhizosphere may play a key role in plant reaction to nanoparticles, thus objectives must be taken into consideration in effect assessment. For instance, a significant increase in the biomass of maize plants was observed with the application of 100 mg/kg of AgNPs (20 nm), this could be linked to a large change in the bacterial population associated with the rhizosphere, which influenced carbon utilisation and community composition profiles [14]. By comparision, application of 350 and 790 mg/kg AgNPs (20 nm) in soil significantly reduced lateral and fine root development and shoot biomass of pine after 4 months. Furthermore, no ectomycorrhizal fungi (EMF) were identified to be linked with AgNPs contaminated roots at the highest concentration, whereas five EMF taxa were found in the control. Similarly, 10 nm AgNPs (1 and 3 mg Ag/L) were shown to be toxic to the beneficial soil bacterium Pseudomonas in sand, as evidenced by a decrease in bacterial culturability, while no cell death was detected in loamy soil. Surprisingly, adding humic acid to AgNPs improved the culturability of the sand. The toxicity of nanoparticles depends on the morphology and surface properties of nanoparticles [21].

The comparative study on AgNPs bactericidal properties on E. Coli with lattice plane shaped nanoparticles shows greater action compared to rod and spherical shaped particles, which indicates that change in surface of the nanoparticle also affect the properties of product [21]. The susceptibility of symbiotic nitrogen-fixing bacteria under the order Rhizobiales, the family Bradyrhizobiaceae, and the genus Bradyrhizobium was discovered using bar-coded pyrosequencing to investigate the responses of diverse bacterial taxa to TIO_2NPs (15–20 nm) and ZnONPs (20–30 nm) in incubated soil microcosms [8]. The members of Methylobacteriaceae family contain methanotrophs, which metabolise the methane that use it as their only energy and carbon source is denied by both the nanoparticles [9]. Therefore, nanoparticles as agrochemicals have some serious consequences that hampers the fixation of nitrogen in legume crops and prevents the elimination of methane gas from the soil. In addition, maximum toxicity of ZnONPs on soil microorganisms was observed in acidic soil, followed by the neutral soil. Relatively, the toxicity of ZnONPs was less in alkaline soil. Nanoparticles of Ag, CuO and ZnO showed toxicity to P. putida KT2440, a beneficial environmental microbe, suggesting that the NP (B1 mg Ag/L, &10 mg Cu, Zn/L) application may put negative impact on soil microbial processes [24]. CuONPs and AgNPs caused cell death, whereas ZnONPs had bacteriostatic properties [10]. Furthermore, these bulk nanoparticle components lacked inhibitory function, implying that aggregating nanoparticles into larger particles could limit non-target effects also. Therefore, studies on the soil environment that can promote aggregation of nanoparticles may lessen their toxic activity. In comparison to the research cited above they found that metal-based nanoparticles were hazardous to soil beneficial organisms, whereas nano formulations of the commercial fungicide hexaconazole had no such effect. For instance, nitrogen-fixation, nitrogen assimilation, indole acetic acid (IAA) production and phosphate solubilization of nitrogen-fixing blue green algae (BGA) and bacteria was found to be significantly inhibiting in the presence of commercial hexaconazole [27], whereas stimulatory to slightly inhibitory effect on the growth by Nano hexaconazole was used to observe the organisms' quantifiable properties [20,33].Nano hexaconazole was also discovered to be more stable, with no significant negative effects on soil nitrifiers, was preferable to regular hexaconazole usage. All these findings suggest a complex interaction of nanoparticles with soil organisms where different soil types, soil factors and nanoparticle size and type may play significant roles in determining the environmental fate of nanoparticles [36]. Beneficial microbial populations are one of the most important key factors that influence soil ecosystem processes, especially by decomposing soil organic matter, nutrient recycling, disease suppression and growth enhancement etc. Therefore, any factor that induces significant negative effects on soil microbial populations would certainly deteriorate soil quality and sustainability [24]. Thus, intentional application of nanoparticles, particularly in crop protection is a prime concern and identification of safe nanoparticles, procedures for their safe application, following up of mitigation and remediation strategies, if found hazardous, should be a priority. Estimation of beneficial microbial communities in soil must be considered as a crucial factor while investigating the impacts of nanoparticle exposure in soil [24]. Evidences also support the inhibitory effect of AgNPs on soil exoenzyme activities that are crucial to support the soil biochemical processes [22]. Despite of some the nanoparticles that are synthesized from natural polymers or chemicals are bioconvenient and biodegradable, even being fewer toxic plants the compatibility with the soil and environment and its mechanism, interaction with the plant does not provide much nutrients and the growth of the plant is hampered due to lethal oxidative stress.

Ecofriendly Green Nano Fertilizers

The green synthesis preparation of metal and metal oxide nanoparticles from plant materials is also being followed extensively because adequate no. of plants have viable and inexhaustible supply of energy when estimated/analyzed with microbes and enzymes, because they have the capacity to transform almost around 75%

of the chemical energy from light energy and consist of antioxidants and sugars that are helpful for the synthesis of nanoparticles [33, 34]. The prior accumulated light energy that is generated from the plant can be utilized for the synthesis of food for the plant [5]. The bioengineered NPs obtained from plant molecules, cells and organs are helpful in analyzing methods such as catalytic potential, electrical conductivity, magnetic behaviour or biological reactivity are used to characterize the chemical, physical, and biological properties of nanomaterials in addition to many factors such as size, shape, surface charge, chemical structure, surface area, and coagulation properties of nanoscale distinct materials that help in overcoming environmental and bioremediation problems [36].

Plant parts most preferably the leaf extracts that can reduce to corresponding metals in the absence of chemicals is the preferred choice for the manufacture of NPs. Many noble metals such as gold (Au), silver (Ag), platinum (Pt), and palladium (Pd), copper (Cu) and nickel (Ni) which are characterized by their optical, electronic, mechanical, magnetic and chemical properties have reducing properties and also behave as reducing agents [13, 21, 26]. Plants with various reducing agents are helpful for the synthesis of MNPs and MONPs [25]. The green synthesis of metal and metal oxide from plant extracts in nanoparticle synthesis have significance of flavonoids, vitamin B2, ascorbic acid and phenolic compounds that help in the MNP and MONP synthesis. One such derivative used mostly for MNP and MONPs synthesis is Ascorbic acid (vitamin C). It functions as a reducing and capping agent that surrounds the material and prevents the uncontrolled growth of the particles to micron – sized dimensions that makes the plant for its proper growth and survival. The main purpose of the green nanoparticle synthesis is to completely utilize its practical approach for the synthesis from plant extracts that are not harmful and also overcome the use of hazardous substances as most often seen in chemical synthesis of nanoparticle formation. Due to more accumulation of the MNPs and MONPs in the soil and plants, animals gazing the plants for fodder also face serious health issues, also the plants that are accumulated with hazardous substances randomly enter the human food chain [5]. Keeping in view of the health and safety concern management, preference for a better approach in formulating and design of standardized methods for synthesis of MNPs and MONPs from plant extract resources is recommended (fig. 1) [19, 36]. The adequacy to restrict the surface activity and prevent aggregation of the MNPs and MONPs, simultaneously protecting smaller agglomerate sizes for effective conductivity to the root region for an effective and functional uptake to the plant in an improved and perfect nanoparticle delivery system is essential [28,30]. For such nanoparticles, coatings or encapsulated nanomaterials obtained from plant organic sources are recommended [37]. Natural organic matter (NOM), dissolved organic carbon (DOC) and soluble humic acid (HA), or fulvic acid (FA) are some of the natural, environmentally friendly surface coatings that may provide NP agglomeration support through extra steric hindrance, increased electrostatic repulsion, and higher hydrophobicity [28, 37]. The prevalence of such coated nanoparticles not only enables complete conductivity to the root zone but also avoids risks with aggregation corresponding to loss of material during adsorption or through ground water runoff [37].

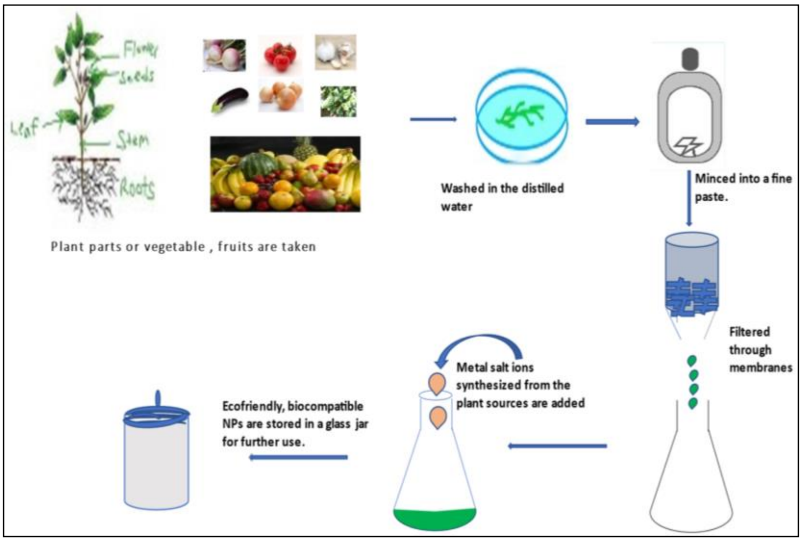

Fig 1: An illustrated diagram showing the process of Ecofriendly green particle synthesis.

Risks of Nanoparticles

Because of their ubiquitous use, nanoparticles have sparked concerns about environmental hazards that effect organisms, animals and humans through food chain and may alter the entire biodiversity system. Thousands of tonnes of nanomaterials have already been dumped into the environment, despite mounting scientific evidence of potential dangers. According to the most trustworthy data on environmental contamination, between 260,000 and 309,000 metric tonnes of worldwide engineered nanomaterials (ENMs) generated in 2010 ended up in water bodies (0.4–7%), landfills (63–91%), soils (8–28%), and the atmosphere (0.1–1.5%).

Conclusion

Global pesticide demand is predicted to increase significantly in the years to come. The use of nano fertilizers in agriculture attempts to reduce pesticide, conventional fertilizer applications and increase yields by suppressing fertilizer and optimising nutrient management. Nanoparticles of ZnO, TiO_2 and especially Ag are intentionally used in many applications and recent studies also highlighted their potential use in plant disease management [13]. Moreover, while nano-herbicides and nano fertilizers, green nano fertilizers have shown to have a bright future in the following years [5, 34], a thorough understanding of their possible risks is essential before products are released. Scientific studies have indicated toxicity of some nanoparticles to different environments including humans; therefore, there should be a strict regulation for the manufacturers to correctly represent the composition and the characteristics of their developed nanopesticide formulation. Current scientific understanding does not allow for a reliable assessment of the associated advantages and risks of nano pesticides; lack of adequate information and methodologies are further obstructing comprehensive risk assessment.

Nano-quantitative toxicity–toxicity relationship (nano-QTTR) models for interspecies cytotoxicity correlation have recently been created to extrapolate data between species [3]. Furthermore, it has been reported that surface-enhanced Raman spectroscopy (SERS) indicator molecules are effective in identifying AgNPs in environmental and biological materials. It's worth noting that ferbam had the best ability to bind AgNPs, detecting as little as 0.1 mg/L AgNPs in natural surface water and 0.57 mg/L in spinach juice. The knowledge on the behaviour of nanomaterials in different environments is rapidly evolving, but is still limited by the lack of robust and integrative research. Collaborative research among different laboratories on the effect of a particular nanoparticle type on different biological systems can make a significant impact for developing safer synthesis of nano fertilizers. Each biological system provides a unique environment to investigate the fate of nanoparticles; consequently, pooling knowledge of nanoparticle behaviour across multiple ecosystems is a key step in defining mankind’s future safety.

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Declarations

Conflict of interest: No conflicts of interest to declare.

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