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REVIEW

Biofertilizers, Bionanofertilizers and Nanofertilizers: Ecofriendly alternatives for crop production

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The demand for food resources has been steadily rising over the past century, along with rapid population expansion even after the rise in food grains production by the green revolution. The increased use of synthetic fertilizers on land has led to environmental pollution, long-lasting alterations in the ecology of the soil and altered physicochemical conditions. Therefore, it is important to implement sustainable farming techniques that can increase crop yield without the overuse of chemical fertilizers. It has raised interest in the use of nanofertilizer and bio-fertilizers as an alternative to conventional chemical fertilizers for enhancing plant nutrition. Nano- and bio-fertilizers are crucial tools in agriculture for enhancing crop growth, yield and quality metrics, while also increasing nutrient usage efficiency, lowering fertilizer waste and cultivation costs. In this context, green biomass can be reduced to nanoscale levels with the appropriate shape, size and structure, as well as the optimal surface qualities to create modern agro-nanofertilizers that are more effective and drastically reduce our dependence on synthetic fertilizers. Furthermore, nanofertilizers may also be used in combination with microorganisms (also known as nanobiofertilizers), which provides several additional benefits. However, it is crucial to thoroughly investigate the effects of these nanofertilizers on ecosystems. This review summarizes the potential applications and benefits of nanoparticle and biofertilizer based fertilizers for precision and sustainable agriculture.

Keywords: Biofertilizer, Bionanofertilizer, Nanofertilizer, Sustainable agriculture

INTRODUCTION

Agriculture is the most significant and stable sector of the world economy. Agricultural productivity must increase along with global population growth toprovide food for the expanding population. Global agricultural cropping systems use a lot of chemical fertilisers, insecticides and herbicides to increase crop productivity.

Currently,farmers engaged in agricultural production face challenges such as water scarcity, reducing organic matter in soils, soil degradation, low input use efficiency, decreasing crop yield,developing resistance to different weeds, diseases, insects, decreasing income from productionand toxicity to different beneficial living organisms (Chen and Yada, 2011).

Other environmental problems include climate change, environmental pollution (soil, waterand air pollution), declining arable land due to urbanization and logistical issues, including runoff, fertilizer accumulation and pesticide toxicity. Despite these issues, it remains difficult to feed the world's expanding population. Many new technologies have been scientifically developed as potential solutions to improve productivity, reduce resource costs and environmental issues related to agricultural productionamong the setechnologies, nanotechnology is emerging as a promising alternative (Chen and Yada, 2011).

Nanoparticles with a size of less than 100 nm can be used as fertilizers for effective nutrient

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*Correspondence : pushpa.gehlot1212@gmail.com management, making them more ecofriendly and reducing environmental contamination. Therefore, the value chain of the entire agricultural production system can utilize these agriculturally useful nanoparticles developed with the aid of nanotechnology. Nanoscience and nanotechnology have the potential to reform a wide range of fields such as chemistry, physics, medicine, food production and agriculture, using numerous applications that affect human life (Linkov *et al.* 2011). Nanotechnology has enormous potential for upgrading agricultural practices with novel nanotechnological strategies that control plant disease, improve crop growth, yield and quality parameters by increasing nutrient use efficiency, reduce wastage of fertilizers and cost of cultivation as precision farming techniques,support land and water conservation (Prasad *et al.* 2017). The availability of nutrients to the assimilatory apparatus of crop systems can be increased through nanofortification by applying nanocoats to traditional fertilizers. Nutrients, either applied alone or in combination, are bound to nanodimensional adsorbents, which release nutrients much more slowly than conventional fertilizers (El-Saadony *et al.* 2019; 2021; Reda *et al.* 2020; 2021).

The benefits of combining nanomaterials with biofertilizers such as *Bacillus* spp. and *Pseudomonas* spp. as prospective biofertilizers have been demonstrated by Karunakaran *et al.* (2016). This approach is not only increasing nutrient utilization efficiency, but also minimizes nutrient leaching into groundwater.

Biofertilizer inoculation is another viable technique to increase crop yields, decrease the use of chemical fertilizers and create environment friendly sustainable agriculture (Basu *et al.* 2021; Mohanty *et al.* 2021). Various plant growth-promoting microbes have been characterized for their beneficial traits. These microbes play a significant role in modulating phytohormones, suppressing plant diseases, alleviating abiotic stresses, and improving the accessibility of nutrients such as N, P, K, Znand S. (Glick and Gamalaro, 2021). The application of individual or consortia of beneficial microorganisms has been found to improve plant biomass and crop yield under greenhouse and field conditions (Santoyo *et al.* 2021b). Currently, these beneficial biofertilizer strains are modified with organic materials, cell protectants and nanoparticles to increase their survival potential and efficacy, leading to improvements in crop production. Furthermore, a potent tool to improve the production and release of PGP metabolites by helpful bacteria was made possible by sequencing a large number of microbial genomes and the identification of certain genes (Bakker *et al.* 2012; Köberl *et al.* 2015).

Although nano-fertilizer is highly innovative, recent articles have shown that there is still much work to be done before the technique can be used on farms. The delivery of almost all essential nutrients using nano-adsorbents has been attempted. In most cases, clay and other aluminium silicates have been used as effective adsorbents to deliver nutrients. It has been clearly demonstrated that size reduction by physical or chemical methods increases the surface mass ratio thereby, nutrients are adsorbed and desorbed slowly and steadily for an extended period of time (Khan *et al.* 2021).

The results of several researchersdiscussed in this review, suggest that some nanofertilizers may boost agricultural yield by promoting stress tolerance, seed germination, seedling growth, photosynthesis, nitrogen metabolism and protein and carbohydrate synthesis. Among other benefits, nanofertilizers can be used in relatively smaller amounts, which ultimately lowers transportation costs and improves application ease. However, nanofertilizers may also have some disadvantages that can limit their full implementation in the market (Zulfiqar *et al.* 2019).

Chemical fertilizers or Conventional fertilizers

Chemical fertilizers (CFs) are often made of developed non-organic materials and are synthetic. Farmers use CFs in higher quantities to enhance crop yields. CFs can be in granular or liquid form with the same composition, are cheaper and work faster than organic fertilizers because they dissolve immediately in water. Most applied CFs dissipate into the atmosphere or surface water bodies causing serious environmental problems (Singh *et al.* 2015). For example, excess phosphorus is fixed in the soil where it forms chemical bonds with other elements such as Ca, Mg, Al, Fe and Zn, making it unavailable for plant uptake. Similarly, Nitrogen is largely inaccessible as it forms NH_3, N_2O, or NO in the effluent (Raliya *et al*. 2018). Approximately 80-90% of P and 40-70% of N applied to agricultural land is lost to the environment through runoff or becomes rock.Excessive use of inorganic fertilizers such as N, P and K poses a major challenge to agriculture as they can be leached by runoff. This can lead to eutrophication, contribute to the accumulation of heavy metals in soil, water and air, creating serious hazards for the environment and human health (Savci, 2012). Over the past 40 years, the nutrient utilization efficiency (NUE) of crops has remained constant despite relentless efforts.In addition to low nutrient efficiency, agriculture in developing countries, including India, faces problems such as low organic matter content, unbalanced fertilization and low response to fertilization and ultimately lead to stagnation in crop yields (Biswas and Sharma, 2008). Over-fertilization is the most common problem associated with these fertilizers, as these compounds contaminate water bodies and accumulate in crops, inhibiting plant growth and causing leaf scorch, consequently making plants more sensitive to pests and diseases. In regards to human health, the effects of chemical fertilizers are serious, both with their direct toxic effect, or in the indirect effects that are related to decreasing the nutrient density in the consumed plants.High levels of nitrates and nitrites in chemical fertilizer may cause some diseases. Some fertilizers contain heavy metals like cadmium and chromium and high concentrations of radionuclidesis cause of respiratory and excretory disease.In addition, CFs fails to provide the nutrients needed by plants, depleting soil fertility, stripping moisture of soil, increasing field salinity and reducing beneficial living organisms that help to improve soil quality (Alhrout *et al*. 2018).

Sustainable agriculture

The use of chemical fertilizers to increase agricultural productivity has been a common practice for many years. Over the past decade, however, scientists have become concerned about the associated adverse effects, such as environmental toxicity and the long-term residual effects of excessive use of chemical fertilizers. This has made it imperative to seek non-toxic and environmental friendly alternatives to achieve the desired goal of improving agricultural productivity without the associated side problems. In recent decades, bio- and nanofertilizers have been preferred over chemical fertilizers to ensure biosafety in agriculture (Dhir, 2017). Biofertilizer is mainly consist of live formulations of beneficial microorganisms such as plant growth-promoting rhizobacteria, i.e., *Rhizobium,* blue-green algae (BGA), the fungal mycorrhizae, bacteria *Azotobacter*, *Azospirillum* and phosphate-solubilizing bacteria such as *Pseudomonas* sp. and *Bacillus* sp., which augment the nutrient supply to crops by increasing biological nitrogen fixation and solubilization of insoluble complex organic matter to a simpler form making them biologically available to plants. It increases the water holding capacity of soil, improving the availability of soil nutrient (nitrogen and phosphorus) to the plants and keeps the soil relatively healthier via enrichment of soil microbial status and helps soil aeration and natural fertilization. However, this exciting approach also has some serious problems, such as poor shelf life, lowers the stability in the field, performance in different environmental conditions (sensitivity to temperature, radiation and pH), unsuitability in the long term, lack of beneficial bacterial strains, susceptibility to desiccation, and most importantly, the high dosage requiredfor a wide coverage area (Mishra *et al*. 2017). Interestingly, nanoparticlebased formulations of biofertilizers have shown superiority in solving these problems (El-Ghamry *et al*. 2018). Thus, modern agriculture adopts the innovative approach of nanobiotechnology to develop nanobiofertilizers to address key issues of crop production, food security, sustainability and eco-safety (Khan *et al*. 2017). In nano-biofertilizer formulations, biofertilizers (containing nutrients and plant growth-promoting bacteria) are coated with nanoscale polymers (nanoencapsulation) (Golbashy *et al*. 2017). Nanoencapsulation technology can be used as a versatile tool to protect biofertilizer components containing PGPR, improve their durability and dispersion in fertilizer formulations and enable the controlled release of PGPR (Vejan *et al*. 2016).

This allows nutrients to be delivered to the crop slowly and steadily without being inadvertently lost(Gouda *et al.* 2018).Nano-biofertilizers have a significant impact on farmers'profits by improving the nutrient release characteristics and field performance and reducing economic expenses not only by cost reduction but by reducing application losses as well. It is an eco-sustainable, renewable approach that can accelerates nutrient use efficiency (N, P and K), enriches the soil with beneficial microbial populations, improves the activity of associated enzyme systems, comprehensively improves soil fertility and improve disease resistance of crop. All of these methods of fertilizationof soil are eco-friendly alternative to chemical fertilizers therefore could be used to achieve sustainable development goal-2 *i.e.,* end hunger, achieve food security and improved nutrition and promote sustainable agriculture.

Biofertilizer

Maintaining food security for the growing population in an ecofriendly and cost-effective manner has generated a great deal of interest in the use of biofertilizers over the last few decades (Mukhtar *et al.*2017). Consumption of microorganism's living or latent cells comes under the term bio-fertilizers". These are the most effective because of their positive effects on plants, the agro-system and the health of living beings. Biofertilizers are eco-friendly alternatives to chemical pesticides that are safe for humans and animals and stimulate plant growth. The history of bio-fertilizers started in the initial 19th century with the discovery of a laboratory culture of *Rhizobium* followed by various other microorganisms (Chatterjee and Bandyopadhyay, 2017). These are biologically active single or multiple living microorganisms or microbial inoculants used to enhance crop productivity through nitrogen fixation, phosphate solubilization, or cellulolytic activities (Arriola *et al.*2015). These processes are considered to encourage growth and production by upgrading the accessibility of soil nutrients in the rhizosphere region (Mazid *et al.* 2011). Biofertilizers comprise different microorganisms, such as bacteria, fungi, blue green algae (cyanobacteria), and their metabolites (Mensah *et al.*2018). These may be defined as artificially manufactured cultures of soil microbes or soil inoculants that increase the richness, fertility, and efficiency of soil and plants to enhance productivity (Singh *et al.*2018). When microorganisms based biofertilizers applied to the soil, they colonize in the rhizosphere and stimulate growth by accelerating the availability of essential nutrients to the host plant (Chatterjee *et al.*2017). These biofertilizers also improve the physicochemical and biological characteristics of soil (Tejada *et al.* 2016). Different mechanisms have been proposed to explain the influence of biofertilizers on crop growth and productivity. These mechanisms can be categorized into direct and indirect. The direct mechanism involves mineral solubilization and enhanced plant nutrient uptake (Hajieghrari and Momammadi, 2008). Nitrate, phosphate, and zinc solubilizations are important processes that promote plant growth in nitrogen- and phosphorus-deficient soils. Biofertilizers are used to break down or convert insoluble/complex forms of essential nutrients such as N, P, K, and Zn into soluble forms by different organic acids, such as malic acid, acetic acid, oxalic acid, citric acid, and gluconic acid (Mukhtar *et al.* 2017). This process eases the uptake of vital nutrients and enhances crop growth and productivity. Nitrogen-fixing microorganisms form symbiotic associations with plants and are usually present in biofertilizers, which help in biological nitrogen fixation by transforming inorganic nitrogen into organic forms. These microorganisms are recognized as "diazotrophs". Whereas indirect mechanisms involve siderophores and phytohormones (IAA, cytokinins, gibberellins) production that help in different metabolic activities like photosynthesis, respiration, transpiration, nutrient uptake and transportation etc. which result in improved plant growth (Abbasi *et al.* 2011; Lavakush *et al.* 2014). Additionally, production of antibiotics, acquisition of rhizospheric iron, production of antifungal metabolites, lytic enzymes, competition with pathogens, and induced systemic resistance results in the enhancement of plant growth (Abbasi *et al.* 2011).Microorganisms are important in agriculture to promote the circulation of plant nutrients and reduce the need for chemical fertilizers and pesticides. Plant growth-promoting rhizobacteria or fungi (PGPR/PGPF) are a group of root-associated bacteria and fungi that intimately interact with plant roots and, consequently, influence plant health and soil fertility.

PGPR (Plant Growth Promoting Rhizobacteria)

Depending on their existence and their relationship with host plants, PGPR may be either rhizospheric or endophytic. Rhizospheric PGPR colonize the intercellular spaces of plant roots, whereas endophytic PGPRs colonize the apoplastic spaces inside host plants (Bhattacharyya and Jha, 2012). PGPR contain nitrogen-fixing and symbiotic bacteria such as *Azospirillum*, *Azotobacter*, *Mycobacterium*, *Bacillus*, *Azobacter*, *Serratia*, *Xanthomonas*, *Proteus*, *Pseudomonas*, and *Clostridium* (Abbasi *et al*. 2011; Cortivo *et al*. 2017). *Serratia plymuthica* C48, *Serratia marcescens*, *Paenibacillus* spp., *Streptomyces* spp., and *Pseudomonas stutzeri* produce chitinase enzymes that degrade the mycelia of fungal pathogens (Singh *et al*. 2019). â-1,3-glucanase produced by *Streptomyces*, *Paenibacillus*, and *Bacillus* spp. degrades fungal cell walls. These microbes fix atmospheric nitrogen into organic forms and make it available to the plants. These bacteria colonize the rhizospheric region and promote plant growth through various activities, such as nitrogen fixation, siderophore production, phosphate solubilization, IAA production, enhancement in resistance to biotic and abiotic stresses, 1-Aminocyclopropane-1-carbxylate deaminase (ACC), quorum sensing (QS) signal interference, and disease suppression (Elekhtyar, 2015; Cortivo*et al*. 2017).

PGPF (Plant Growth Promoting Fungi)

PGPFs are non-pathogenic saprophytes that exert advantageous effects on plants. They are known to enhance plant growth and suppress plant diseases (Verma, 2019). These comprise different species of *Aspergillus*, *Penicillium*, *Fusarium* and *Trichoderma*. These fungi establish symbiotic relationships with plant roots in the form of mycorrhiza and aid in the absorption of essential nutrients from the soil, which stimulates the growth and development of plants (Hossain *et al*. 2017; Mensah *et al*. 2018). PGPR and PGPF secrete various organic and inorganic substances and antibodies that reduce pathogen attacks and help in the growth and development of plants (Tyagi *et al*. 2018). Further, PGPR and PGPF produce several enzymes and antibodies that hydrolyze cellulose, hemicelluloses, chitin, and proteins present in the cells of pathogens. The production of chitinase enzymes by PGPFs helps lyse the hyphal cell walls of fungal pathogens and protects host plants, whereas esterase enzymes vitiate cutin and suberin in plant cuticles (Meena *et al*. 2017; Mensah *et al*. 2018). The production of siderophores by PGPRs and PGPFs generates competition for iron intake among plants, microbes, and pathogens that inhibit pathogens (Hoyos-Carvajal *et al*. 2009). In addition, these microorganisms also compete with pathogens for nutrients, space and inhibit their multiplication in the rhizosphere. The Use of various species of *Trichoderma* spp. for their antagonist nature toward different pathogens has increased in the past few years.

PGPR and PGPF help in the production of phytohormones, such as IAA, cytokinin, ethylene, gibberellins, ABA, salicylic acid, jasmonates and ethylene, which play important roles in the defence mechanisms of plants, as they provide strength to the induced systemic resistance (ISR) and systemic acquired resistance (SAR) of complex regulatory networks (Bukhat *et al*. 2020).

Previous studies on *Rhizobium* spp., (Saikia and Jain, 2007), *Azotobacter* spp., (Saritha and Tollamadugu, 2019), *Azospirillum* spp., (Brusamarello-Santos *et al*., 2017), *Herbspirillum* spp., (Abbey *et al*. 2019), *Pseudomonas* spp., *Bacillus* spp., *Micrococcus* spp., *Aspergillus* spp., *Fusarium* spp. etc. (Saritha and Tollamadugu, 2019) have reported successful application of PGPR and PGPF as biofertilizer.

Biofertilizers are normally applied directly to seeds, plant surfaces, or soil, where bacteria infiltrate the rhizosphere or interior parts of the plant. Microorganisms or biofertilizers promote the growth and productivity of host plants either by increasing availability of principal nutrients or by controlling phytopathogens by regulating or hindering their growth (Ahemad and Kibret, 2014).

They also help in the degradation and decomposition of organic matter, mineralization, nitrogen fixation and denitrification in soil systems. Plant growth-promoting bacteria, blue-green algae, and arbuscular mycorrhizal fungi are frequently used as biofertilizers.

The most commonly used biofertilizers are plant growth-promoting microorganisms (PGPMs), that is, plant growth-promoting rhizobacteria (PGPR)and plant growth-promoting fungi (PGPF). PGPR live in the rhizospheric region of plants, where they encourage the growth and development of their hosts through direct and indirect mechanisms (Arrudaa*et al*. 2013; Mukhtar *et al*. 2017). PGPR favour plant growth and productivity directly or indirectly by stimulating the production of phytohormones such as indole acetic acid (IAA), gibberellic acid, cytokinins, ethylene, siderophores, HCN, solubilization of minerals (P and Zn), and breakdown of complex organic substances into simpler forms for easy accessibility to plants and also for their own consumption (Mukhtar *et al*. 2017). Generally, solubilization of minerals by PGPRs involves the release of low-molecular-weight organic acids. These acids contain hydroxyl and carboxyl groups that chelate cations bound to minerals and convert them into soluble forms (Panhwar *et al*. 2011). Currently, PGPRs have been applied as biofertilizers as an efficient substitute for chemical fertilizers because they are ecofriendly and reduce the chances of environmental pollution and the cost of crop production.

The PGPFs may be boon for sustainable development in the field of agriculture and help to reduce the nutrients losses from agricultural sector. The more efficiently used PGPF are different strains of *Trichoderma*, for example, *T. viride*, *T. asperellum*, *T. virens*, *T. harzianum*, and *T. atroviride*, which demonstrated increased growth and productivity of different crops, such as tomato (Molla *et al*. 2012), cucumber (Akter *et al*. 2013), cabbage and red beet (Topolovec-Pintariæ *et al*. 2013), lemon balm (Kowalska *et al*. 2014), and wheat Chen *et al*., 2017). *Trichoderma* spp. used as a plant growth promoter to solubilize nutrients and make them accessible to plants. Furthermore, they secrete various vitamins and enzymes, including phytohormones and siderophores, which enhance the growth and productivity of various crops (de Santiago *et al*. 2013). Siderophores are produced by different bacterial and fungal species that function in iron solubilization, mobilization, transportation, and/or storage (De Hita *et al*. 2020). Fungal siderophores also participate in the suppression of pathogens and diseases. Furthermore, PGPF species produce multiple compounds, such as cell-wall-diminishing enzymes and secondary metabolites, which increase root development and resistance to biotic and abiotic stresses. Thus, PGPF-enriched biofertilizer may be applied as an alternative to chemical fertilizers and pesticides.

Biofertilizers are normally prepared with carrier-based inoculants, with peat being the most commonly used carrier (Hong-yuan *et al*. 2015). Other carriers include coal, clays, inorganic soil and organic substances such as compost, soybean meal, wheat bran, and sawdust, and inorganic materials such as vermiculite, perlite, kaolin, bentonite, and silicates (Naik *et al*. 2020). These carriers should be easy to handle and inexpensive so that they can be practically used by farmers of lower economic backgrounds with reasonable and adequate shelf lives of at least two or three months. Microbial biofertilizers with efficient carriers should have high moisture absorption capacity, proper aeration, and good buffering capacity (Rivera-Cruz *et al*. 2008).

Bionanofertilizer

Chemical synthesis of NPs often involves chemicals such as organic solvents and reducing agents. These hazardous chemicals limit the use of these NPs in various fields due to their toxicity (Pattekari *et al*. 2011). This has led to the concept of 'green nanotechnology' with less chemicals and cost effectiveness. Nano-biofertilizers consist of biofertilizers encapsulated in nanoparticles. Encapsulation is the process of encasing biofertilizer cells into nanomaterial capsules.It involves the use of starch with a non-toxic, biodegradable substance like calcium alginate. The bacterial strains growth is accelerated by starch (Du *et al.* 2018). The most often used nanoparticles for the development of nanobiofertilizers include silicon, zinc, copper, iron, and silver

(Honaryet *al*. 2012; Akhtar *et al*., 2013; Hassan *et al*., 2018). For instance, the plant growth-promoting microorganisms (PGPM) have a wide range of uses as nanobiofertilizers due to their considerable growth promotion and antagonistic properties. In agriculture set-up, soils, plants, microbiomes and nano-biofertilizers often affect each other and their ecosystems. Nano-biofertilizers containing beneficial microorganisms improve plant growth by improving nutrient availability.These nanobiofertilizers may also include N-fixing biofertilizers, P-solubilizing nanobiofertilizers, P-mobilizing biofertilizers, micronutrient biofertilizers and plant growth promoting rhizobacteria. The application of these PGPM nano-biofertilizers can improve structure and function of soil, crop morphological, physiological, biochemical and yield related properties. It also involves in crop protection during both abiotic and biotic stress conditions through their bioactive compounds. The synergistic mechanism of action of biofertilizers and nanoparticles enhances the response when applied to plants. It activates various mechanisms in plants that are responsible for better plant development and yield. They also reduce the negative effects of toxic chemicals and suppress the growth of pathogens in the rhizosphere of plants. Nanobiofertilizers aid bioremediation and replenish the soil with essential nutrients. They upregulate genes involved in the production of antioxidants, osmolytesand stress-related proteins, reduce the detrimental effects of ROS on plants, and maintain cell structure and function. They also preserve membrane transporters which enhanced hormonal production and their activities (Vedamurthy *et al*., 2021; Shcherbakova *et al*., 2017). This production of NPs involving biological systems is highly successful, clean, cheap, controlled release, effective and environmentfriendly (Sambangi *et al*., 2022).Bionanofertilizercan improve the health of the soil and crops while reducing the need for chemical fertilizers. However, as nanotechnology becomes more advantageous and affordable, a growing number of scientists and agriculturalists are turning to their diverse range of applications in present agricultural practices. It has been reported that organic waste such as flowers, cow dung and kitchen waste can also be combined with nanoparticles to create potent nanobiofertilizers that improve soil fertility. Organic waste was washed with water to remove impurities, crushed into small pieces and subjected to decomposition or pyrolysis. This partially decomposed or pyrolyzed waste was combined with nanoparticles to produce nanobiofertilizers (Singh *et al*. 2019). Apart from many advantages use of nanotechnology challenges the nanoparticles (NPs) dosage, toxicity and their environmental footprint in the agricultural soils over a long time.

Nanofertilizer

Fertilizers are chemical compounds used to promote plant growth and yield (Behera and Panda, 2009). Fertilizers are commonly applied either through the soil (for absorption by the plant roots) or by spraying the leaves. Inorganic fertilizers constitute a huge proportion of fertilizers used to provide extra nutrition to plants. The inorganic fertilizers are artificially synthesized and formulated in appropriate concentrations or ratios that usually supply three main nutrients: nitrogen, phosphorus, and potassium (N, Pand K) to various crops. Nitrogen promotes leaf growth and forms proteins and chlorophyll. Phosphorus contributes to the development of roots, flowers and fruits. Potassium contributes to stem and root growth and protein synthesis (Mandal *et al*. 2009). Approximately 30–60% N, 10–20% P, and 30–50% K of the applied fertilizer is utilized by plants and the rest is lost to the environment. This results in significant economic and resource losses, as well as severe soil and water pollution.The application of nanotechnology can minimize these shortcomings of conventional fertilizers in order to utilize the majority of the chemical dosage.This can be achieved by encapsulating nutrients in nanomaterials, coating them with thin protective films, or delivering them as emulsions or nanoparticles (de la Rosa *et al*., 2010). Nano-based slow-release or controlled-release fertilizers have the potential to increase nutrient uptake efficiency and significantly reduce waste. Nanotechnology can be applied for soil nutrition by developing formulations in two ways *i.e.*, first fertilizers can be coated, encapsulated or embedded in nanomaterialsandsecondnanoforms of fertilizers and other growth-promoting materials (Khan and Rizvi, 2017).

Nitrogen

Nitrogen is an important nutrient for plant growth and biomass production. However, considering the energy requirement for synthesis of nitrogen fertilizers and they have high monetary value. 50-70% of the nitrogen applied in conventional fertilizers is lost to the soil through leaching. Attempts to improve NUE (Nitrogen Use Efficiency) in conventional fertilizer formulations have been less effective. On the other hand, the new nano-strategy suggests that due to its high surface area-to-volume ratio, nano-nitrogen is expected to be much more effective than conventional controlled-release nitrogen fertilizers coated with polymers (Hossain *et al*. 2008; De Rosa *et al*. 2010).

Phosphorus

Agriculture is a major user of mined phosphorus (P), accounting for 80-90% of the world's phosphorus requirements (Childers *et al*. 2011). Population growth, growing preference for meat-based dietsand increased demand for bioenergy crops will increase future demand for P fertilizers. However, the application of phosphorus fertilizer leads to the problem of eutrophication of surface water (Carpenter, 2005; Conley, 2009).

Key properties of nanofertilizersare that they increase nutrient utilization efficiency. Nanofertilizers have a larger surface area, primarily due to the very small size of the particles, which provides more space to facilitate various metabolic processes in the plant system and also photosynthesis. Their high surface area and very small size make them highly reactive with other compounds. It shows high solubility in various solvents such as water. The particle size of nanofertilizers is less than 100nm, which facilitates the penetration of nanoparticles into plants through the application at surfaces such as soil and leaves.Nanofertilizers have a very high surface: volume ratio and particle size smaller than the pore size of plant roots and leaves, which can enhance the penetration into plants from the application surface and improve the absorption and nutrient utilization efficiency of nanofertilizers. Nanoparticle increases the chances of contact with the nanofertilizer and improves nutrient penetration and absorption (Shukla, 2019).Nanoparticle-encapsulated fertilizers increase nutrient availability and uptake by crops. Zeolite-based nanofertilizers can slowly release nutrients to crops, increasing nutrient availability during the crop growing season, preventing nutrient loss through denitrification, volatilization, leaching and soil binding, especially NO_3-N and NH_4-N. Nanoparticles can be used as fertilizers for efficient nutritional management, being environmentally friendly and reducing pollution (Manikandan and Subramanian, 2014).The Main reason for the great interest in fertilizers are mainly their penetration capacity, size and very large surface area which differs from the same material usually found in bulk form. One of the reasons for this is nano particles show a very high surface: volume ratio. Therefore, the reaction surface area is proportionally overrepresented for nanoparticles compared to larger particles. Particle surface area increases with decreasing particle size and the surface free energy of a particle is a function of its size (Singh, 2017). Thus, there are classically two types of nanofertilizers: micronutrient nanofertilizers and macronutrient nanofertilizers.

Macronutrient

Fertilizer is one of the most important inputs, accounting for almost one-third of cultivation costs. Bulk macronutrient fertilizers (primarily N, P, and K fertilizers), known as N-P-K fertilizers or compound fertilizers, are intentionally blended to increase the production of food, fiber and other commodities.Total global consumption of macronutrient fertilizers ($N+ P_2O_5+ K_2O$) is expected to increase to 263 million tons by 2050 (Alexandratos and Bruinsma, 2012).

Intensive production of nitrogen fertilizers and rapid depletion of reserves of phosphate and potash fertilizers are of great importance for various countries where energy security has not yet been achieved (Schader, 2009). Macronutrients like nitrogen (N), phosphorus (P), potassium (K), magnesium (Mg), sulfur (S) and calcium (Ca) have been combined with nanomaterials to deliver a precise amount of nutrients to crops and reduces their bulk requirements with the extra benefit of decreasing purchasing and transportation costs (Li *et al*. 2017).Growing population concerns will increase demand for food, which increases need for macronutrient fertilizers (Wang *et al*. 2015). Therefore, from a practical point of view, there is an urgent need for research to develop new nutrient-efficient and environmental friendly alternatives to conventional macronutrient fertilizers. These macronutrient nanofertilizers contain one or more nutrients in an encapsulated form with a specific nanomaterial.

Nitrogen is an important nutrient and is deficient in almost all agricultural soils. N is a major component of plant cells and is required for structural, genetic, metabolic and chlorophyll (photosynthetic) compounds. Due to their high solubility, leachability and denitrifying properties, a wide range of slowrelease nitrogen fertilizers (SRF) such as montmorillonite, zeolites, bentonite and halloysite have been developed using synthetic or biopolymers. Many approaches, such as sulfur-, neem-, and polyolefin-resin-coated urea, have been used to control the release of N to reduce leaching during fertilization. Compared to traditional bulk fertilizers, urea–hydroxyapatite nanohybrid fertilizers release N slowly and uniformly to improve plant growth and development (Kottegoda *et al*. 2011). Recently, polymer-coated urea has been used as a slow-release N fertilizer to improve crop quality, yieldand hydroponic productivity and reduce environmental risks of soil nitrogen (Li *et al*. 2017). Porous nanomaterials such as zeolites, clay and chitosan significantly reduce nitrogen loss by effecting demand-based nitrogen release and increasing plant nitrogen uptake (Abdel-Aziz *et al*. 2016).

Phosphorus is also an essential nutrient for all living things. The main problem is the high solubility of phosphorus fertilizers such as mono-superphosphate and triple-superphosphate, which have low nutrient absorption efficiency. In addition, there are global environmental problems related to eutrophication due to increased phosphorus concentrations in water (Richardson, 2001; Shenoy and Kalagudi, 2005). Nanotechnology is an excellent choice for producing phosphorus fertilizers with high phosphorus absorption efficiency. Biosafe nanofertilizer is the first phosphate nanofertilizer with a particle size of 60-120 nm and is the primary source of phosphorus. Application of nano-zeolite-P in peanut crops increases plant productivity and minimizes pollution risk compared to using other nanomaterials (Hagab *et al*. 2018).

K is also essential for photosynthesis, photosynthetic translocation, protein synthesis, ion balance regulation, plant stomata regulation, water utilization, enzyme activation, and many other processes. Potassium is also known as a quality nutrient because it has a significant impact on quality factors such as size, shape, color, taste, shelf life, fiber quality, and other quality indicators. Zeolites contain large amounts of exchangeable K+ and can promote plant growth in potting media. A recent study showed that foliar application of Lithovit supplemented with nano-K fertilizer improved the growth, yield, quality and quantity of pepper. Similarly, foliar treatment of wheat plants with K-loaded chitosan NPs significantly increased plant growth and productivity (Abdel-Aziz *et al*. 2016).

Sulfur (S), calcium (Ca) and magnesium (Mg) are secondary nutrients that are required in good amounts for plant growth. Although many plant species have higher Ca requirements than Phosphorus, whereas S and Mg are required by plants in approximately the same amounts as phosphorus. Li and Zhang (2010) studied the ability to use surfactant-modified zeolite (SMZ) as a fertilizer additive to control sulfate release in batch. Secondary nutrients are less studied because deficiencies are very few or found in isolated products.

Micronutrient

Micronutrients are trace elements that are required in small amounts (100 ppm) but are essential for physiological, anatomical and morphological processes in plants (Broadley *et al*. 2007; Sharonova *et al*. 2015). The micronutrients are boron (B), copper (Cu), iron (Fe), manganese (Mn), molybdenum (Mo), zinc (Zn) and chloride (Cl). Adverse effects of stress from micronutrient deficiencies in plants include reduced crop yield and quality, imperfections in plant morphological architecture (such as reduced xylem vessels), widespread infestation by various diseases and pests, decreased siderophore activation and declined fertilizer use efficiency (Malakouti, 2008). Zinc (Zn) is an essential trace element required for proper growth and development. The maximum cultivated land is Zn deficient because its availability is restricted to the root zone, which reduces nutrient uptake by the plants. Due to their ultra-small size and large surface area, Zn nanoparticles can be easily transported into plant systems. (Pandey *et al*., 2010; Dimkpa*et al*. 2019; Raliya *et al*. 2016; Shankar and Rhim, 2019). Iron (Fe) is an essential nutrient for plant growth and development as it plays a role in electron transport chain (ETC) (Lindsay and Schwab, 1982). Nanoparticles such as Fe oxides have been widely used in catalytic processes (Laurent *et al*., 2008; Madhura *et al*., 2019) and significantly enhanced several crop traits such as chlorophyll content, photosynthesis, light absorption, nitrogen and phosphorus metabolism, and fruit and biomass yields. Boron (B) is involved in the biosynthesis of the cell wall and various other physiological processes (Davarpanah *et al*., 2016). Therefore, boron and zinc nanochelates are applied to fruit crops to achieve higher yield with better quality. A study showed that low level of B and Zn nanofertilizers at 34 and 636 ppm respectively, increased the yield by 30 percent in *P. granatum* cv. *Ardestani* (Davarpanah *et al*. 2016). The application of 10 ppm zinc oxide nanoparticles in *Coffea arabica* L. increased the net photosynthetic rate by up to 55% and improved fruit set and quality (Rossi *et al*. 2019). Similarly, application of 2000 ppm nanoiron chelate improved leaf area, chlorophyll content, catalase enzyme activity, total soluble solids, ascorbic acid, and total phenol content in *Cydonia oblonga* (Rahemi *et al*., 2020).

Nanofertilizer production and formulations

One of the main characteristics of nanofertilizers is that they can be synthesized using chemical, physical and biological methods. Nutrient-rich bulk forms of fertilizers can be degraded into small (nanoforms, ideally 1–100 nm) units through a variety of mechanophysical (top-down) and chemical and biological (bottom-up) pathways, which ultimately affects plant nutrient uptake, thereby reducing nutrient-related toxicity and losses.Top-down is the physical process of milling of material. In a top-down approach, adsorbent or substrates used in the synthesis of nanofertilizers, such as zeolites and other carriers, are ball milled for several hours to reach nanoscale dimensions.Although the physical methods of nanoparticle synthesis are very simple, the products are heterogeneous and the particles often aggregate. Stabilizers such as polymers and surfactants have been used to prevent aggregation. A bottom-up approach starts at the atomic or molecular level and builds nanoparticles through chemical reactions. Synthesis of plant biomass and microbial-derived nanonutrients is environmentally friendly and simple compared to other approaches (Abd-Elsalam *et al*. 2021). The biological technique is also known as "green synthesis" because many bacteria, algae, fungi and angiosperms have been used in the synthesis of nanonutrient. It is a more energy-efficient, saferand less wasteful method than other methods (Prasad *et al*. 2017).

Recent applications of nanotechnology in agriculture have successfully demonstrated the utility of nanomaterials as potential plant growth regulators, but the practical application of nanomaterial-based fertilizers on agricultural lands requires appropriate substrate to efficiently disperse the nanomaterials (Kumar *et al*., 2018). The types of nanofertilizers includes (a) Nitrogen fertilizers, (b) Potash fertilizers, (c) Zinc nanofertilizer, (d) Nanoporous zeolite, (e) Nanoherbicides and (f) Nanopesticides.

Characterization of Nano-fertilizers

The synthesized nanofertilizers were characterized using a particle size analyzer (PSA), zeta analyzer, Fourier transform infrared spectroscopy (FTI-IR), Raman spectroscopy, X-ray diffraction (XRD), scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDAX), transmission electron microscopy (TEM), and atomic force microscopy (AFM) to confirm their size, shape, charge distribution, functional groups, elemental composition, surfactant attachment and sulfate attachment.

Table.1: Nanoparticle synthesis from biological system

Biological System Type	Types of nanoparticles	References
Algae		
Amphiroa anceps	Ag-NP	Roy and Anantharaman, 2018
Sargassum cinereum	Ag-NP	Mohandass *et al*., 2013
Gracilaria corticate	Ag-NP	Marimuthu *et al*., 2011
Acanthophoraspecifera	Ag-NP	Ibraheem *et al*., 2016
Turbinariaconoides	Ag-NP	Kumar *et al*., 2012
Plants		
Panicum miliaceum	Silver oxide (Ag_2O)	Velsankar*et al*., 2022
Paspalum scrobiculatum	ZnO	Velsankar*et al*., 2022
Vaccinium floribundum	ZnO, MnO-NPs, FeO, ZnO-NPs	Murgueitio-Herrera *et al*., 2022
Cinnamomum camphora	Ag-NPs, Au-NPs	Syed *et al*., 2013
Bacteria		
Azospirillum	Nano-zinc oxide	Manivannan *et al*., 2021
Pseudomonas rhodesiae	AgNPs	Hossain *et al*., 2019
Streptomyces capillispiralis	CuNPs	Hassan *et al*., 2018
Paenibacillus polymyxa	AuNPs	Ratti *et al*., 2008
Fungus		
Aspergillus terreus	CuONPs and CuNPs	Mousa *et al*., 2021
Penicillium funiculosum	AgNPs	Ramos *et al*., 2020
Aspergillus flavus	ZnSNPs	Uddandarao, 2016
Trichoderma citrinoviride	TiO_2	Arya *et al*., 2021

Table.2: Synthesis, characteristics and nutrient release from nano-fertilizers/formulations

Nutrient	Absorbent	Method	Size	References
Nitrogen	Zeolite	Physical	25-30 nm	Thubsuang*et al.*, 2023
	Zeolite	Chemical	20-200 nm	Saritha *et al.*, 2022
	Zeolite	Physical	420 µm	Li et al., 2003
	Zeolite	Physical	20-60 nm	Tran *et al.*, 2022
	Zeolite	Chemical	7–10 nm	Mohanraj, 2013
	Montmorillonite	Physical	35-40 nm	Mani and Mondal, 2016
	Montmorillonite	Chemical	50 µm	Bortolin*et al.*, 2013
	Surface crosslinked superabsorbent (hydrogels)	Chemical	40–80 nm	Oladosu *et al.*, 2022
	Hydroxyapatite nanoparticles + *Gliricidiasepium*	Biological	19–25 nm	Raguraj *et al.*, 2020
Phosphorus	Zeolite	Physical	25–30 nm	Subramanian and Sharmila Rahale, 2013
	Zeolite	Chemical	2–3 µm	Bansiwal *et al.*, 2006
	Montmorillonite, bentonite	Physical	35–40 nm	Subramanian and Rahale, 2013
Potassium	Zeolite	Physical	25–30 nm	Subramanian and Rahale, 2013
	Montmorillonite, bentonite	Physical	35–40 nm	Subramanian and Rahale, 2013
NPK	Nano-coating of sulfur layer Chitosan	Chemical	78 nm – 100 nm	Manjunatha *et al.*, 2016
Nanocomposite	Kaolinite	Chemical	70–80 nm	Wanna *et al.*, 2013
Iron	Zeolite	Chemical	1-3 nm	Jahangirian *et al.*, 2020
Sulphur	Zeolite	Physical	70–93 nm	Thirunavukkarasu, 2014
	Zeolite	Physical	420 µm	Li and Zhang, 2010
Boron	Zeolite	Physical	60 nm	Preetha and Balakrishnan, 2017
Zinc	Nano-Zn	Chemical	35 nm	Nair *et al.*, 2010
	Nano-ZnO	Chemical	20 nm	Burman *et al.*, 2013

Extensive studies have been conducted to characterize nitrogenous (Subramanian and Sharmila Rahale, 2013; Mohanraj, 2013; Manikandan and Subramanian, 2014), phosphatic (Bansiwal *et al.*, 2006; Adhikari, 2019), potassic (Subramanian and Rahale, 2012), sulfatic (Preetha *et al.*, 2014; Thirunavukkarasu and Subramanian, 2014), and zinc (Subramanian and Rahale, 2012) fertilizers.

Nanoparticles are composed of organic and inorganic nanomaterials. Moreover, their syntheses also differ in terms of the physical, chemical or biological methods used. Inorganic nanomaterials include metal oxides, such as ZnO, TiO_2, MgO, and AgO. On the other hand, the organic nanomaterials include lipids, polymers and carbon nanotubes. Nanoparticles of different materials are generally classified into four types. Silver, gold, alloys, magnetism such as Fe_3O_4 (magnetite) and Fe_2O_3 (maghemite). In this regard nanofertilizers are classified according to their nutrient categorization (Naseem and Durrani, 2021).

Modes of nanofertilizer application

The plant cell wall acts as a barrier for the entry of any external agents like nanoparticles because

Table.3: Commercially available Nanofertilizers and their Components

Nanofertilizers	Constituents	Manufacturer
Nano max NPK fertilizer	Multiple Organic acids (protein -lacto-gluconates) based chelated major nutrients (N-P, Os -K, O) (min. 4 -4-4%) along with amino acids @ 6.00 %(min), Organic Carbon@ 10.00% & formulated with Organic micro nutrients / trace elements — vitamins and probiotic.	JU Agri Sciences Pvt. Ltd., India
Nano fertilizer (Eco Star)	Organic matter, N, K, C, and N Humic + Amino Acid + Fulvic Acid + + Atonic + Natural Brassino + Seaweed (Plant Energizer, Flowering Stimulant & Yield Booster)	Shan Maw Myae Trading Co., Ltd., India
Nano ultra-fertilizer	Organic matter, N, P, K, P, K, and Mg	SMTET Eco-technologies Co., Ltd., Taiwan
Plant nutrition powder (Green Nano)	Combination of N, P, K, Ca, Mg, S, Fe, Mn, Cu, and Zn	Green Organic World Co., Ltd., Thailand
Nano calcium (Magic Green)	Combination of Ca, Mg, Si, K, Na, P, Fe, Al, S, Ba, Mn, and Zn	AC International Network Co., Ltd., Germany
Hero super nano	Combination of N, P, K, Ca, Mg, and S	World Connect Plus Mayanmar Co., Ltd., Thailand
Nano green	Extracts of corn, grain, soybeans, potatoes, coconut, and palm	Nano Green Sciences, Inc., India
Supplementary powder (The Best Nano)	Combination of N, P, K, Ca, Mg, S, Fe, Mn, Cu, and Zn	The Best International Network Co., Ltd., Thailand
PPC nano	Combination of M protein, N, P, K and diluent	WAI International Development Co.,Ltd., Malaysia
TAG NANO fertilizers	Proteino–lacto–gluconate chelated with micronutrients, vitamins, probiotics, seaweed extracts and humic acid	Tropical Agrosystem India (P) Ltd., India
Biozar nano-fertilizer	Combination of organic materials, micronutrients and macromolecules	Fanavar Nano-PazhooheshMarkazi Company, Iran
Nano capsule	Combination of N, P, K, Ca, Mg, S, Fe, Mn, Cu, and Zn	The Best International Network Co., Ltd., Thailand
IFFCO nanofertilizer	Nano N—potential to cut the requirement of urea by 50% Nano Zn —10 gm would be sufficient for a hectare of land Nano Cu — provides both nutrition and protection to the plant	Indian Farmers Fertilizer Cooperative Ltd., India

of the pore diameter of cell wall ranging from 5 to 20 nm (Fleischer *et al.*, 1999). Therefore, only nanoparticles with a diameter smaller than the pore size can easily pass through the cell wall and reach the plasma membrane. There is also the possibility of pore enlargement or induction of new cell wall pores upon interaction with engineered nanoparticles, which facilitates nanoparticle uptake. Further internalization occurs during endocytosis with the help of cavity-like structures that form around the nanoparticles across the plasma membrane. They can also cross membranes using embedded transporter proteins or ion channels.They enter through stomatal openings or bases of trichomes and then migrate into various tissues. However, accumulation of nanoparticles on the photosynthetic surface causes foliar heating, which results in alterations in gas exchange due to stomatal obstructions that produce alterations in various physiological and cellular functions of plants (Fernandez and Eichert, 2009). One of the key strategies for building new formulations is nanoencapsulation, which aids in the controlled release of nutrients and minerals. This is necessary to reduce nutrient dosages and improve fertilization efficiency and soil microflora.Such multipartite interactions between plant systems, microorganisms, soil, and nanofertilizers require further in-depth investigation for a fundamental understanding. At the time of application and post-administration, it is important and notable that during fertigation, the properties of the nanofertilizer such as stability, persistence, reduced toxicities, solubility, assimilatory efficiency, release properties etc., normalized over time. Therefore, the application method of nanofertilizer is the most important and can be divided into foliar application and soil application (Fatima *et al.*, 2021).

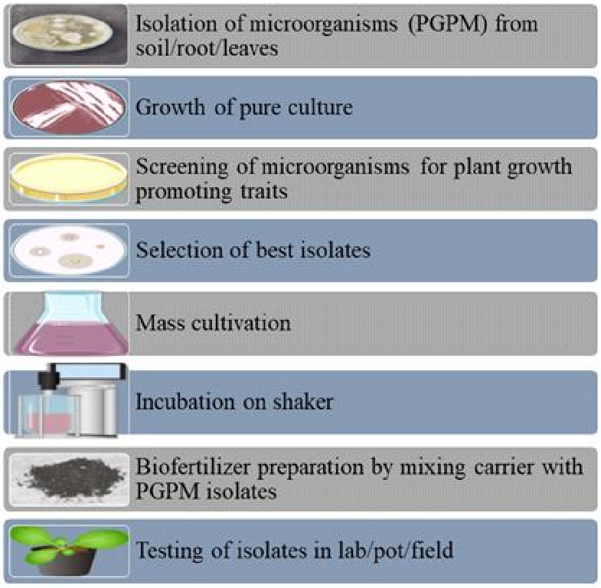

Fig. 1: Major Steps for Isolation and Development of Biofertilizer

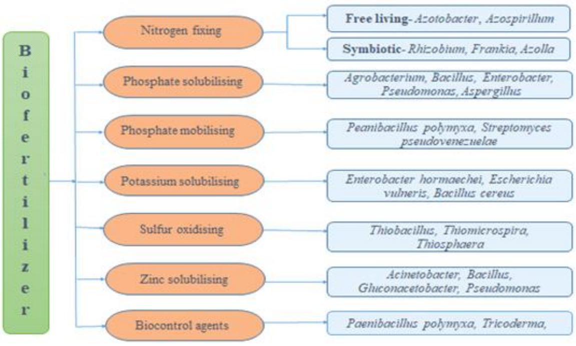

Fig. 2: Various Plant Growth Promoting Activities of Biofertilizer and Their Example

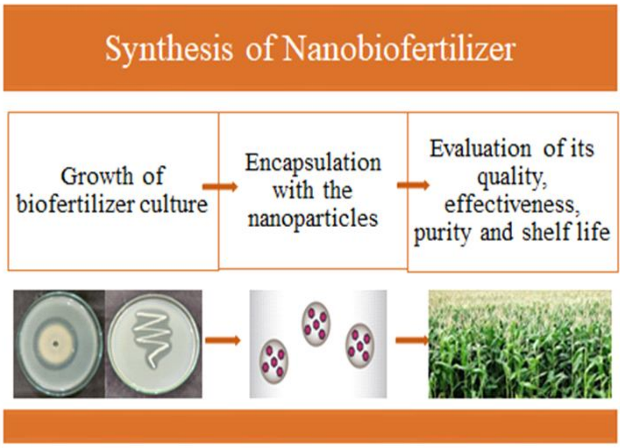

Fig. 3: Procedure for synthesis of nanbiofertilizer

Nanoparticles can be applied in two ways-(i) Foliar-based applications/phyllosphere and (ii) Soil-based application/rhizosphere.

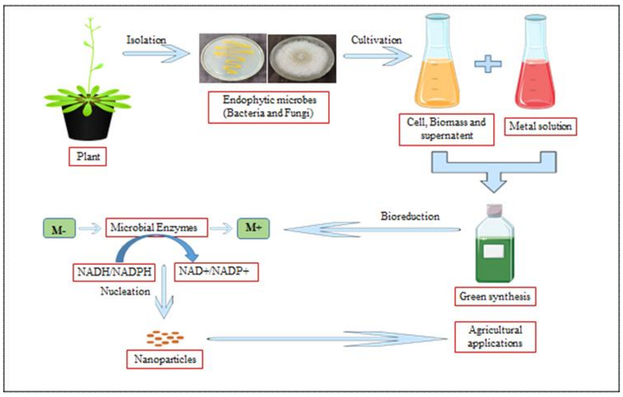

Fig. 4: Diagrammatic representation of overall steps of green synthesis of nanoparticle from microorganisms. (Image Source: Bogas *et al*., 2022).

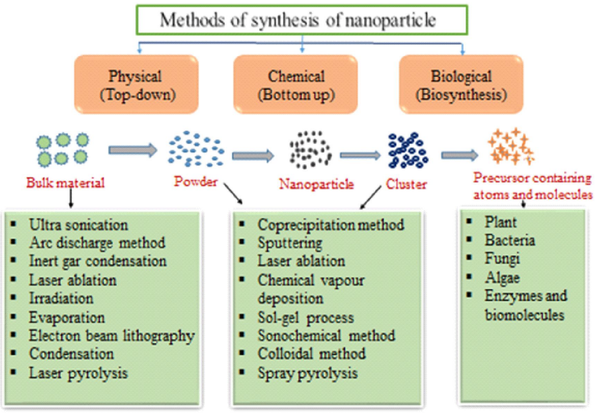

Fig. 5: Synthesis Methods for Nanoparticles

Nanofertilizer toxicity

Although the use of NPs as fertilizers to enhance plant nutrient availability and increase agricultural production has received great attention in last decade, but some toxicity associated issues are matter of concern. Indeed, the toxicity, safety and environmental impact of nanoparticles remain uncertain. This is because smaller particles have a greater ability to penetrate biological systems and therefore a greater potential risk that has not yet been evaluated (Li *et al*. 2016). The intrinsic properties of many nanoparticles are considered potential human health risks due to their size, shape, surface area and charge, solubility, crystalline phases, coatings, material types and dosage concentrations.In addition, environmental factors such as temperature, pH, ionic strength, salinity and organic matter can collectively affect NP behavior, transport and toxicity. Recent studies have revealed the negative effects of NPs on soil organic matter dynamics with different reaction conditions, soil properties and dosages used in the experiments (Schlich and Hund-Rinke, 2015; Rahmatpour *et al*. 2017; Shi *et al*. 2018). NPs synthesized by chemical and physical methods are more toxic than those produced using biological methods; however, the toxicity of biologically synthesized NPs is still under intensive investigation. Metal and metal oxide NPs are more harmful to soil microorganisms than organic nanomaterials; in particular, ZnO NPs prevent thermogenic metabolism, reduce the levels of nutrient-fixing *Azotobacter* and phosphate and potassium-solubilizing bacteriaand also inhibit enzymatic activities (Chai *et al*. 2015). CuO NPs inhibit wheat plant growth and at high concentrations affect plant photosynthesis and respiration processes (Lu *et al*. 2020). Ag NPs penetrate plant roots at high concentrations (Rastogi *et al*. 2017). In conclusion, the use of NPs to provide essential nutrients and improve agricultural production is gaining attention; however, additional studies on the toxicity of newly developed NFs should be conducted to mitigate public concerns about issues related to nanotoxicity.

Further research and strategies to cope with toxicity problems

Nanofertilizers represent a huge opportunity in agriculture, but strategies need to be addressed to manage their accumulation and potential risks to human health and the environment while enjoying the benefits of nanoparticle use in crops. This new field of research pursues important goals and offers opportunities for the future. Thus far, *in vitro* assays have been developed to help standardize the correct dose and type of nanofertilizer recommended for each application and crop species to minimize potential toxicity to the environment, crops and food (Sharma *et al*. 2021). Another important aspect that needs to be, but not yet fully understood, is not only the specific accumulation of NPs in edible plant parts, but also the bioavailability of the accumulated NPs to the next trophic level. In this regard, specific research on the bioavailability of nanoparticles in edible parts is urgently needed for the safe use of nanofertilizers.

DECLARATIONS

Conflict of interest: Author declares no conflict of interest.

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