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Nanofertilizer use for Sustainable Agriculture

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Abstract: There will be higher pressure on global agricultural systems to provide food security for the growing world population with environmental security in the coming years. The chemical fertilizers lead to the loss of nutrients from agricultural fields via leaching and gaseous emissions that create environmental pollution and climate change. Advanced nano-engineering is used to boost sustainable crop production while reducing chemical fertilization's negative impacts on the environment. Nanotechnology enhances agricultural production by increasing the efficiency of inputs while decreasing the relevant losses due to its wider specific surface area nature of the nanomaterials. The nanomaterials carriers the agrochemicals to increased crop protection by controlled delivery of nutrients. The nanofertilizers lead to higher productivity and nutritional quality of field crops via enhanced nutrient use efficiency (NUE) and decreased nutrient losses. This review summarized the recent attempts and formulation of smart fertilizers and the utilization of nanotechnologies in agriculture, which may help provide solutions for current and future chemical fertilization problems.

Index Terms: agriculture, fertilizer, nanotechnology, slow-release

1 INTRODUCTION

The growing population and a narrowing cultivatable land base and water resources create the demand in agriculture for greater efficiency in food production. Natural or synthetic fertilizers are utilized in the soil–crop systems to fulfil the essential macronutrients and micronutrients nutrient requirement of the plants and boosting crop yield [1]. Farmers applied commercial fertilizers to crop plants for the last 50 years for optimum plant growth that maintain the balanced distribution of the three primary macronutrients such as nitrogen (N), phosphorous (P), and potassium (K) and three secondary macronutrients like Sulfur (S), magnesium (Mg), and calcium (Ca). However, micronutrients like selenium (Se), boron (B), molybdenum (Mo), manganese (Mn), chlorine (Cl), copper (Cu), iron (Fe), and Zinc (Zn) are needed in low amounts for plant growth. The primary macronutrients are required to apply externally due to their inadequate nature in soil [2]. The most used commercial fertilizers are urea, triple superphosphate (TSP), diammonium phosphate (DAP), single superphosphate (SSP), monoammonium phosphate (MAP), and nitrogen−phosphorous−potassium (NPK), which contain essential plant nutrients such as nitrogen, potassium, and phosphorus [3]. Nitrogen is the first and foremost required nutrient for crop plants among mineral nutrients that is the integrant of many enzymes and proteins and chlorophyll thus critical to vegetative growth of crops. Unfortunately, modern profit-oriented farming systems have been reported the utilization efficiency of nitrogenous fertilizers is only 45–50%, and for phosphorous fertilizers is only 10–25% [4]. It has been reported as in early 1970, only 27 kg NPK ha^{-1} was needed for one ton of grain production, whereas in 2008 increased to 109 kg of NPK ha−1 to gain the same amount of production. The International Fertilizer Industry Association (IFIA) reported that world consumption of fertilizer has been rising sharply, and in the year 2016–2017, demand was projected to 192.8 Mt [5]. That runoff overdosing of chemical fertilizers leads to eutrophication in aquatic ecosystems, i.e. the growth of algal on the water surface due to the enriched nutrients on water, which make a barrier to oxygen supply to living organisms into water. Commonly, the utilization efficacy of mineral fertilizers or applied chemicals has remained below 30% [4].

Inefficient fertilizer management leads to environmental pollution, climate change, and economic consequences. For example, approximately half of the applied nitrogen fertilizer lost from agricultural fields to air, water, and other processes that lead to a negative impact on the environment like N-oxides release into the atmosphere thus being as greenhouse gases and lead global warming, and nitrates leached into marine ecosystems [1].

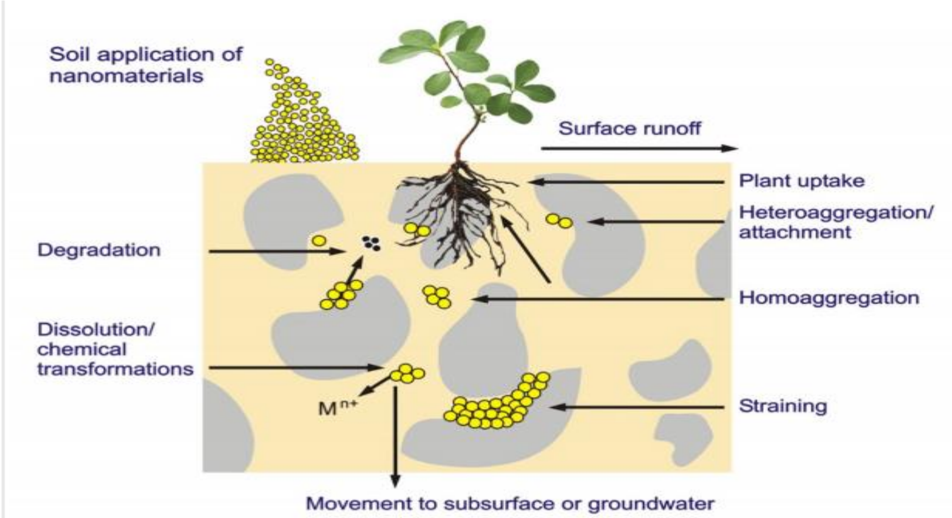

Fig. 01. The fate of nanomaterials in soil system [6]

Ammonium ions form the ammonia gas with alkaline rainwater that creates environmental pollution via escape to the atmosphere [4]. Furthermore, long-period usage of large-scale commercial fertilizers is also not a good way to increase crop productivity because that leads to soil structure, soil microbial flora, plants, and the ecosystem [3]. Not only those effects, but consumers also face problems due to the excess of nitrogen. Many ammonium and nitrates ions accumulate into the leaves of plants, especially in leafy vegetables that become dangerous to human health.

Numerous human diseases like gastric cancer, methemoglobinemia, and bladder were also reported due to nitrate-rich diets. Hence, consumers and environmentalists recommend reducing synthetic fertilizers usage to overcome pollution and protect agro-ecosystems [4]. Nanotechnology deals with matters with a length scale of 1–100 nm. Already nanotechnology used in several field innovations like material science electronics, and medicine. There are a lot of researches that exist for enhancing agricultural productivity via the use of nanotechnology. Nanomaterials can enhance the release profiles, interaction, and efficient uptake of plant nutrients for crop fertilization due to their small size, large surface area nature, catalytic reactivity, and shape, which also increase the environmental and economic benefits [1]. The utilization of nanotechnology in the plant production systems known as “Phyto nanotechnology”. One of Phyto-nanotechnology applications is crop fertilization, that known as “nanofertilizer” (Fig .02) [7]. However, fertilizers with nano-size can deliver required plant nutrition and enhance the sustainability of crop production without compromising the yield of the crop.

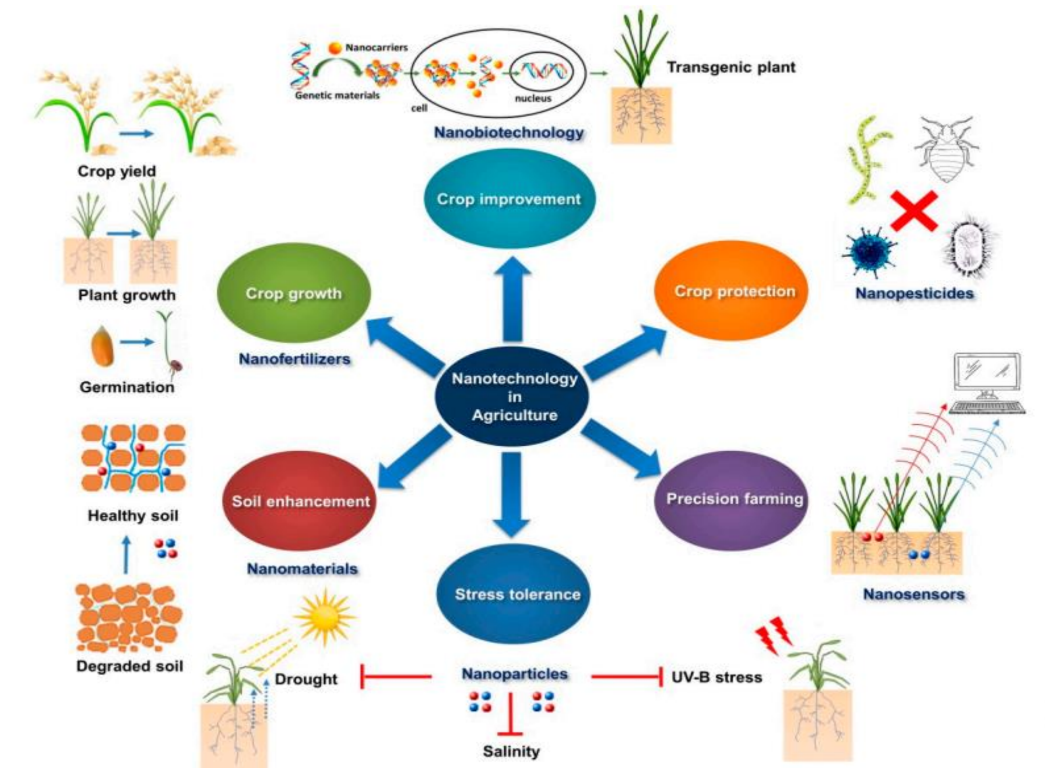

Fig. 02. Applications of nanotechnology in agriculture[6]

The ultimate goal of synthesizing and assess of nanofertilizers is enhancing the nutrients uptake and efficiency of nutrients usage while minimizing the loss of nutrient via gaseous emissions and leaching along with preventing the risk of nutrient toxicity for food security, higher productivity, facilitate the site-targeted controlled delivery of nutrients, and enhance the economic turnouts by doing the sustainable farming processes [4]. Additives with nanoscale used to fertilizer to provide antimicrobial properties or pest resistance. Some fertilizers are encapsulated by nanoscale films or keep in nanoscale pores or spaces within a host material. They are worked as a medium for nutrient adsorption and fertilizers able to protected from decomposition by microbes, heat, and sunlight within the nanosized interlayer space, and reducing fertilizer loss [1].

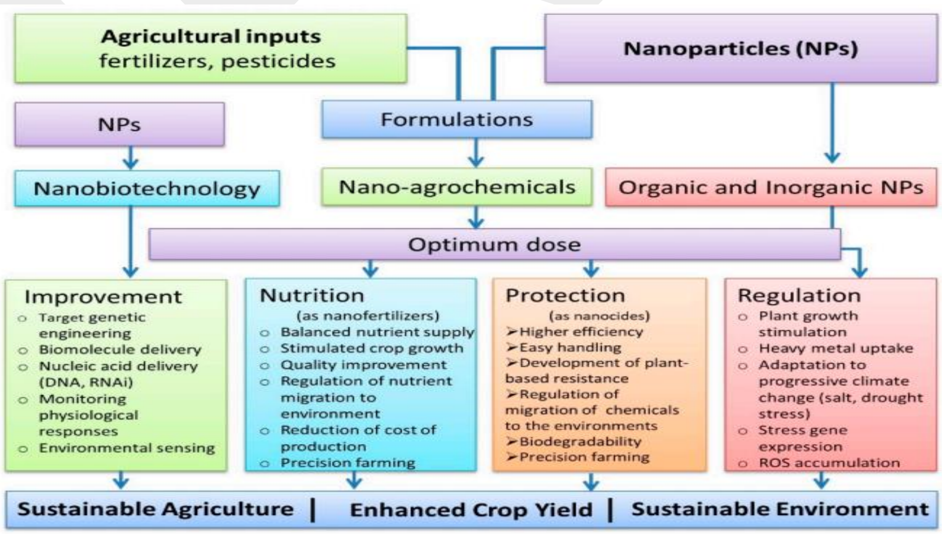

Fig. 03. Overview of potential applications of nanomaterials in sustainable agriculture production [5]

2 POTENTIAL DEVELOPING SMART NANOFERTILIZERS OF NANOTECHNOLOGY

Slow-release fertilizers are the chemical compounds that are gradually and slowly brake down and soil microbial population due to their slight solubility nature in water or other solvents [4]. Slow-release fertilizers can supply nutrients gradually over a specific period (Fig. 04). Advantages of such slow-release fertilizers are higher uptake efficiency of plant nutrients, minimizing capital and labour outlay, less frequent application, improved handling, reduced environmental pollution from leaching of nutrients and storage properties, and flexibility on release periods (40–90 days) [8].

Controlled release fertilizers are higher solubility chemical compounds that are coated with nanomaterials that make an exposure barrier to active ingredient with the solvent resulting in the controlled delivery of nutrients through diffusion. The encapsulation of nutrients with nanomaterials and can be accomplished in three distinct ways;

1. Nutrients with different chemical compositions nature can be encapsulated within the nanomaterials. The Initial nanomaterials are prepared using both chemical (bottom-up) and physical (top-down) approaches.
2. Nanomaterials are applied as a thin layer coating like polymer film on nutrient particles.
3. Nutrients are delivered as emulsions form that's particle having nano range dimension.

Examples for some other available nanofertilizers designs are given below [6],

1. Quick release nanofertilizers- They release nutrients via breakdown of nanoparticle shell when contact with a surface like striking a leaf.
2. Specific release nanofertilizers- They release nutrients via the breakdown of nanoparticle shells when in contact with a specific chemical or enzyme.
3. Ultrasound release nanofertilizers- They release nutrients via nanoparticle shells' breakdown when in contact with an external ultrasound frequency.
4. Magnetic release nanofertilizers release nutrients via the breakdown of magnetic nanoparticle shell when exposed to a magnetic field.
5. Moisture release nanofertilizers- They release nutrients via the breakdown of nanoparticle shells when in contact with water.
6. Heat release nanofertilizers- They release nutrients via nanoparticle shell breakdown when contact with exceeds temperature than set point.
7. pH release nanofertilizers: they release nutrients via breakdown of nanoparticle shell when contact with specified acid or alkaline conditions.

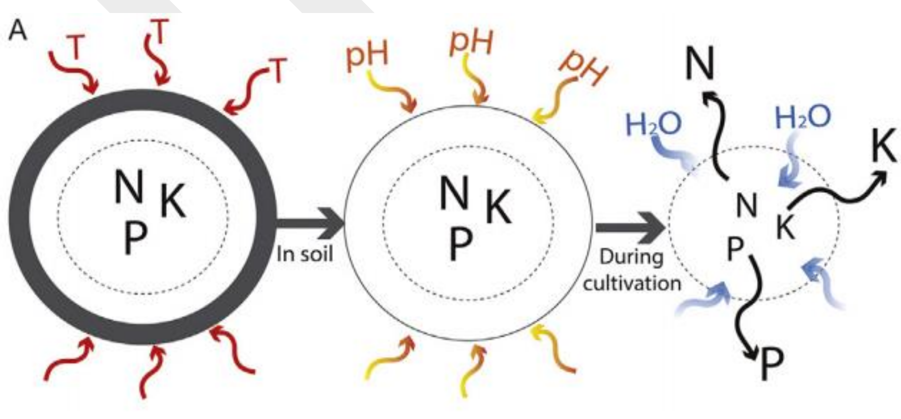

Fig. 04. Schematic representation of smart fertilizer delivery systems [9]

3 BIOLOGICAL MECHANISMS OF NANOFERTILIZERS ACTION

Many facets of plant biology structures like the nutrient gateway to the plant and plant roots are on a nanometer scale. Plant cell walls have 5 to 20 nm diameters range pore. one to a few tens of nanometers pores in diameter have been detected in roots for ionic and molecular transport processes (Fig. 05). However, nanofertilizers could uptake through these nano-scale pores, or uptake by complexation with root exudates or molecular transporters via new pores creation, or by the exploitation of ion channels endocytosis [1].

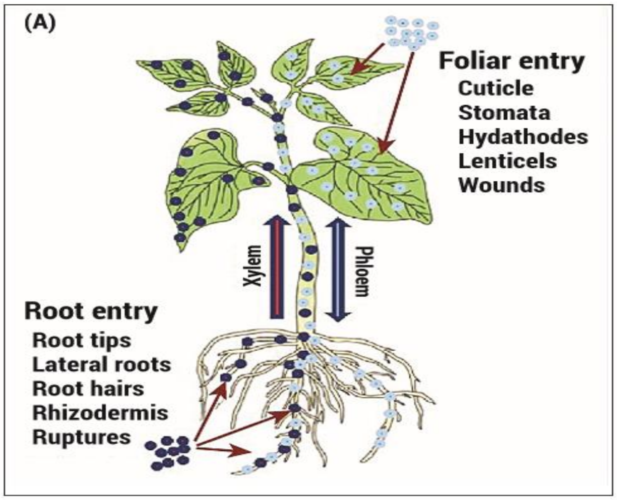

Fig. 05. Potential entry points of nanoparticles of nanofertilizers into plants [8]

The plant leaves also have stomatal openings and nanopores that easily uptake nanomaterial and penetrate deep inside leaves, facilitating the higher nutrient use efficiency (NUE)[4]. The plasmodesmata facilitate cell-to-cell transport within a plant that is nanosized (50–60 nm) channels and are between cells. Fertilizers with nanoscale effectively transport and release nutrients to various transport channels and plant surfaces through plasmodesmata due to their small size [1]. Hence, nanofertilizers enhance productivity (6–17%) and the nutritional quality of field plants via higher NUE and lesser nutrient losses [4].

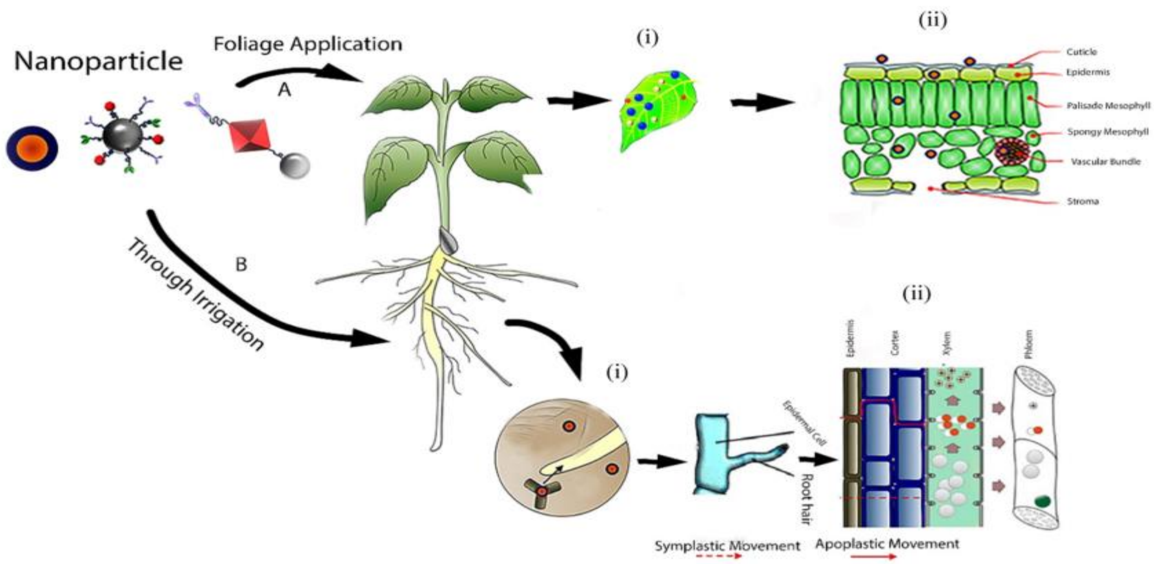

Fig. 06. Uptake and translocation mechanisms of nanoparticles in a plant through leaf and roots[10]

The above Fig. 06 shown as (A) is nanomaterial uptake by foliage application where (i) and (ii) exhibit the way of nanomaterial penetrates leaf cuticle enters into palisade and spongy mesophyll through epidermis layer and finally penetrates vascular bundles respectively. (B) indicate the way of nanomaterial uptake by plant roots when applied through irrigation where (i) and (ii) exhibit the way of penetration of nanomaterial into root hairs and enters into xylem and phloem through epidermis and cortex by apoplastic and symplastic pathways respectively [10].

4 ADVANTAGES OF NANOFERTILIZERS OVER CONVENTIONAL MINERAL FERTILIZERS

Nanofertilizers offer lots of benefits for sustainable and eco-friendly crop production more. Some of the advantages are [4];

1. Nanofertilizers lead to the absorption and utilization of efficient nutrients without higher losses.
2. Nanofertilizers reduce the risk of environmental pollution via reduce the losses of nutrients.
3. Comparatively nanofertilizers have higher diffusion and solubility than conventional synthetic fertilizers.
4. Nanofertilizers deliver nutrients gradually to crop plants in a controlled manner which is in total conflict withthe spontaneous and rapid delivery of nutrients from chemical fertilizers.
5. Nanoparticles can be easily uptake into plants via nano-sized porous, and by molecular transporters as well as root exudates. Nanoparticles uptake higher nutrient by plants via using various ion channels.
6. Smaller amounts of nanofertilizers are enough to apply than synthetic fertilizers due to their small loss nutrient nature.
7. Polymer-coated fertilizers prevent premature contact with water and soil, and negligible loss of nutrients.
8. Nanofertilizers improve soil fertility and develop a feasible environment for microorganisms [3].

Table 1 shown below the difference between conventional fertilizers and nanofertilizers.

Table 1. The difference between conventional fertilizers and nanofertilizers

Index	Conventional fertilizer	Nanofertilizer
Loss rate	High loss rate via drifting, leaching, run-off	Low loss of fertilizer nutrients
Controlled release	Excess release of nutrients lead to high toxicity and soil imbalance	Rate of release and release pattern precisely controlled
Solubility	Low	High
Bioavailability	Low	High
Dispersion of mineral micronutrients	Lower solubility due to large size particle	Improved dispersion of insoluble nutrients
Effective duration of release	Used by the plant at the site and time of application; the rest is converted into an insoluble form	Effective and extended duration
The efficiency of nutrients uptake	It is not available to roots and the efficiency of nutrients uptake is low	Enhanced uptake ratio and saves fertilizer resource
Soil adsorption and fixation	High	Reduced

5 FIELD EVIDENCE OF NANOFERTILIZERS USE FOR SUSTAINABLE CROPS PRODUCTION

Chaitaly Tarafder et al., a new formulation of a hybrid nanofertilizer (HNF) was proposed for the sustainable and slow release of plant nutrients into water and soil. That was synthesized by the incorporation of nanoparticles like zinc, copper, and iron into urea-modified hydroxyapatite to enhance the efficiency of the fertilizer. The developed HNF has experimented on the ladies' finger (*Abelmoschusesculentus*) plant. The results showed slow-release nature, enhancement of nutrient uptake like Zn^{2+}, Fe^{2+}, and Cu^{2+}, eliminate the leaching problem, minimize the nutritional deficiencies of the crop, production nutrient-rich fruits, and increment in the physicochemical properties such as water retention and absorption capacities and swelling ratio, which made the fertilizer more attractive and beneficial than the commercial fertilizer (Fig. 07). Finally, HNF is suggested as a potential fertilizer with great advantages like a slow and sustainable nutrient release, nutrient-rich fruits, negligible land contamination, low cost, and low dosing (50 mg/week) [4].

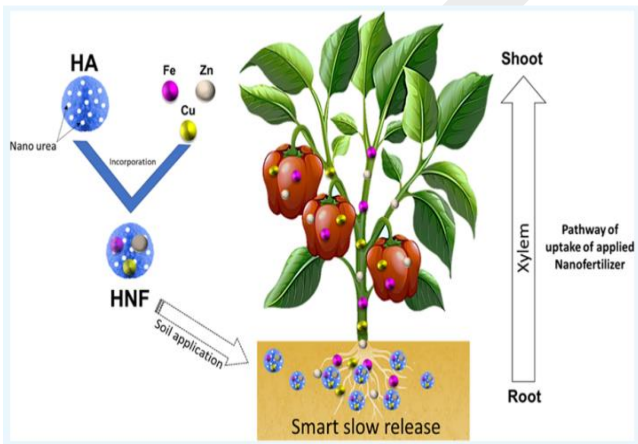

Fig. 07. The diagram description of HNF fertilizer

De Silva et al., a slow-release novel nitrogen material with higher urea content of 36% (w/w) and approximately 83% loading efficiency was developed. Where urea-silica nanohybrids were prepared by the modified in-situ sol-gel route and the higher nitrogen loading was synthesized by silica nanoparticles surface modification with urea via a greener synthetic process. Silica nanoparticles act to deliver silicon micro plant nutrients to crop growth and carrier matrix for urea. However, aforesaid observations were proved the sustained and slow release behavior is done by nanohybrids in water for more than ten days to prevent the urea from a premature loss that due to the strong bonds between the nanoparticles and urea molecules via interaction between surface hydroxyl groups of silica nanoparticles and urea through amine and carbonyl groups by forming of H-bonds without any structural adjustment of nanoparticles. Finally, developed urea-silica nanohybrids proved as a potential candidate for slow-release nitrogen fertilizers over a period of more than 10 days with a rapid and quick release of all nitrogen in urea that can be applied to plants for precise and effective delivery of silica and nitrogen [11], [12].

Kottegoda et al. also focused on the synthesis of low solubility urea via incorporation into a matrix of hydroxyapatite nanoparticles in a urea ratio to hydroxyapatite of 6:1 by weight [13]. Hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$)nanoparticles (HA NPs) offered excellent biocompatibility and act as a rich phosphorus source. The weak interactions of urea with HA NPs lead to a slow release of urea nature for up to 1 week in urea-HA NP nanohybrids, enhancing the nitrogen agronomic use efficiency (NAE) plants and reduce the rate of urea decomposition in soil. This proposed nanofertilizer experimented in a better rice crop at a 50% lower urea concentration [14]. This fertilizer exhibited a slow release of Nitrogen release than pure urea due to the interaction between urea and HA NPs by carbonyl and amine groups [15].

Kottegoda et al. demonstrated a novel fertilizer composition developed via hydroxyapatite adsorbed nitrogen-containing macronutrient on the Surface. The proposed fertilizer composition exhibited a slow release of nitrogen-containing macronutrients to soil[16].

Another research was done by S. Raguraj et al. regarding urea–HA nanohybrid fertilizer on the quality and yield of tea in farmer's fields from three climatic zones in Sri Lanka as Low Country, Mid Country, and UVA regions for three years' period. Results showed nanohybrids increased the yield in Low Country, Uva, and mid-country respectively 10–17%, 14–16%, and 2–3% and reduced the number of fertilizer applications. Further, proposed urea–HA nanohybrids fertilizer enhanced leaf N, soil P, and P concentration in low country tea yields, reduce the urea fertilizer usage, increased the quality parameters like total amino acids, brightness, and total polyphenols in the resulting tea leaves and positive effect during unfavourable climatic conditions[8].

The research on the effects of various HA NPs stabilized with carboxymethylcellulose (CMC) was experimented on seedling growth, germination, and metabolism of SolanumLycopersicum L. by Luca Marchiol et al. HA NPs selected to this research due to the biodegradability and biocompatibility nature. In this work, Hoagland solution and CMC were used to suspend the HA NPs to produce stable colloidal suspensions of nanoparticles that were utilized on tomato plants. The results showed the germination percentage of S. Lycopersicum is not affected by rising HA NPs concentrations, while the elongation of the root is strongly stimulated. Further, tomato plants grown in hydroponics in the availability of HA NPs have not affected phytotoxic effects. However, HA NPs had nontoxic nature on their model plant and that could be applied as a P supplier and carrier of other elements and molecules[7]. In parallel, Pabodha et al. was been able to successfully coat maize using urea coated nanohydroxyapatite composite as a seed coating. In her study, it was proven that the germination of seeds were accelerated by the nano HA-urea coating [17].

Rathnaweera et al. did research to produce efficient, scalable nitrogen fertilizer with cost-effectiveness, which had a nitrogen minimum of 5 times solubility nature than pure urea to sustain future food security. The calcium carbonate (CC) renders enhance the biocompatibility and non-toxic nature that made as a bio inspired material. In this work, urea-CC nanohybrid was produced in the cubic plate-like nanoparticles by an in-situ rapid carbonation method. Proposed novel urea fertilizer nanohybrids exhibited controlled targeted delivery of nitrogen release properties than pure urea due to the bonding interactions between urea and CC nanoparticles. Which novel nanofertilizer system also offered low energy consuming, scalable, and cost-effective method[18].

Kottegoda et al. also researched to produce effective nitrogen-containing macronutrient solid fertilizer for the soil. In this work, solid fertilizer is produced via absorption of nitrogen-containing macronutrient hydroxyapatite phosphate nanoparticles on their Surface. The ratio of the nitrogen-containing macronutrient to the hydroxyapatite phosphate is between 1:1 and 10:1. Proposed nano nitrogen fertilizer showed slowly release of nature for efficient crop production[16].

Samavini et al. developed an efficient Phosphorous (P) nutrient system with increased solubility and plant availability via produced citric acid (CA) Surface modified hydroxyapatite (CMHANPs) by wet chemical precipitation to overcome the problems of current P fertilizers. This research exhibited the optimum release of P in corn due to P's high availability on nanohybrids in the presence of an organic acid than rock phosphate and pure hydroxyapatite nanoparticles. That enhanced the growth and crop productivity than conventional P fertilizers like ERP or TSP[19], [20].

Kottegodaet al., plant uptake of two plant nutrient nanocomposites were developed based on urea nutrient coated by hydroxyapatite and potassium encapsulated into (i) a nanoclay, montmorillonite (MMT) or(ii) cavities present in *Gliricidiasepium* stem that is resulting in a wood chip containing macronutrients. Both nanocomposites formulations exhibited slow release behaviour over a period of 60 days, particularly to nitrogen and improved nutrient use efficiency than conventional formulations. Encapsulated nutrients in nanoparticles enhance the uptake efficiency via creating a barrier to environmental conditions and plant demand. Nano plant nutrient formulations increased the P availability and uptake efficiency due to high surface area and small-size HA NPs that also enhance P solubility [21].

Avinash C. Pandeyab et al. researched to utilized nano-ZnO (NPs) used during the seed germination and root growth of *Cicer arietinum*. Where ZnO nanoparticles are produced by the hydrothermal method. The research demonstrated the effect of ZnO NPs on the seed germination and growth of root of *C. arietinum* seeds. The ZnO NPs affect the phytostimulatory actions via reaction on phytohormonesespecially indole acetic acid (IAA). Zinc-rich ZnO NPs micronutrient enhanced the IAA level in roots (sprouts) due to oxygen vacancies and increase the plant growth rate. ZnO NPs had a high soluble nature in soil and the ability to efficiently uptake by plant root than bulk zinc oxide (ZnO) due to the increased surface-to-volume ratio of ZnO NPs. However, the proposed ZnO NPs very suitable for seed germination and high plant growth rate [22].

Sabir et al. demonstrated the effect of nanocalcite ($CaCO_3$-40%) application with nano Fe_2O_3 (1%), MgO (1%), and SiO_2 (4%). Research exhibited the improvement on Fe, Mg, and Ca uptake and increased the p with micronutrients Mn and Zn intake also. This study did an excellent effort to utilize nanomaterials in better crop production over traditional fertilizers [23].

Abdel-Aziz et al. researched the chitosan-NPK fertilizer application (chitosan nanoparticles loaded with nitrogen, phosphorus, and potassium) for wheat plants via foliar uptake. The chitosan-NPK fertilizer exhibited easy application on leaf surfaces, easy transmission to stomata via gas uptake, and prevent direct interaction with soil systems. The experimented wheat plants showed an increment in crop index, harvest index, and mobilization index of the determined wheat yield variables on sandy soil with nano chitosan-NPK fertilizer over normal fertilized NPK. Further, nanofertilizer also reduced the period of the life cycle of wheat plants than normal-fertilizer with the ratio of 23.5% i.e. 130 days compared with 170 days for yield production from date of sowing. However, nanofertilizers accelerate plant growth and productivity in order to increase the efficiency of agricultural practice and fertilizer usage [24].

Kale et al. also researched the nano zinc oxide application with other fertilizers in zinc-deficient soil. The result showed the enhancement in nutrient use efficiency and increased barley's productivity by 91% than normal fertilizer, whereas traditional bulk ZnSO4 raised productivity by 31% than normal fertilizer[25].

Liu and Lal researched synthetic apatite nanoparticles' effect on soybean (Glycine max) as a greenhouse experiment. The results of the study showed the nanoparticle application enhanced the growth rate by 32.6% and seed yield by 20.4% of soybean (Glycine max L.) than the regular P fertilizer (Ca(H2PO4)2). The biomass productions also increased by 41.2% (below-ground) and18.2% (above-ground). However, apatite nanoparticle usage increased the agronomical yield while reducing water eutrophication [26].

Juan et al. researched the effect of nano-bentonite coated urea utilization on cabbage for growth and nitrogen use efficiency. In this study, a soil pot experiment was carried to demonstrate Nano-bentonite coated urea's effects on the nutrient absorption, leaf chlorophyll content; nitrogen fertilizer uses efficiency, yield, and quality indexes of cabbage. The results of nano-bentonite coated urea utilization exhibited an improvement in the accumulation of nutrients, nitrogen use efficiency, and cabbage yield. The applied 15% nano-bentonite coated urea sample with the content of nitrogen decreased about 10%, and 20% showed the improvement about 7.9%, 8.3% respectively and the applied 20% nano-bentonite coated urea sample with the content of nitrogen decreased about 10% and 20% showed the nitrogen use efficiency improvement about 3.6%、12.6% respectively over pure urea. The cabbage chlorophyll content of applied nano bentonite coated urea had a higher amount than conventional urea, but the difference was not significant[27].

Rehab H. Hagab Yousra et al. studied the effect of the utilization of 50, 75, and 100% of the recommended rates of nano-zeolite zeolite phosphorus (8% P2O5), phosphorus (20.9% P2O5), and the ordinary superphosphate fertilizer (15.5% P2O5) to seeds of peanut crop in the sandy soil. The study investigated the nutrients content, uptake by straw, level of available nutrients, and the yield components. The result of the nano-zeolite phosphorus application exhibited included the 3.48, 1.89, 1.46-ton fed-1, and 53.2 % for straw, pod, seeds crop, and oil content. However, the fertilizers with nano sources can enhance the recovery efficiency of P and crop productivity via higher nutrient contents and uptake by peanut while reducing the number of wasted chemicals and pollution hazards through improving the use efficiency of the ordinary source[28].

Hiyasmin Rose et al., a greenhouse experiment was carried to study the effects of nanofertilizer application on polished rice. The total phenolic content (TPC), yield, and antioxidant activity of rice cv. Ilpum. The obtained results exhibited the enhancement in agronomic parameters, promoted the growth, development TPC, increased yield with high nutritional value, and antioxidant activity in rice. Further, the recommended rate of conventional and nanofertilizer (FRR-CF+FRR-NF) increased the chlorophyll content, plant height, number of reproductive tillers, panicles, and spikelets [29].

S.L. Laware et al. carried study to demonstrate the effect of zinc oxide nanoparticles (ZnO NPs) on onion (*Allium cepa L.*). Where the Six months rested onion bulbs (half) were planted in pots and ZnO NPs sprayed three times at the interval of 15 days along with a sticker. The plant height and number of leaves per plant were studied at the time of flowering. ZnO NPs with 20 and 30µg ml-1 concentration showed better growth and flowered 12-14 days earlier over control. Further, which showed higher values for seed weight per umbel, seeded fruit per umbel, and 1000 seed weight than control plants. Finally, the utilization of ZnO NPs could be decreased the flowering period in onion by 12-14 days and produce healthy seeds [30]. Pierre, Ketsira also researched the effect of urea coated with zinc nanoparticles on tomato plants to improve the uptake and dispersibility of zinc. The results exhibited a higher number of leaves and several fruits set than the control plant[31].

Ping et al. researched NanoTiO_2 Photo semiconductors' effects on Photosynthesis of Cucumber Plants, which act like artificial photosynthesis. TiO_2 semiconductor produced by sol-gel methods and effects on leaf cell malondialdehyde contents, root systems, and photosynthesis after different spray concentration of nano-TiO2 sol on cucumber leaves. The nano-TiO_2 sol formed perfectly transparent, adhesive, continuing, and stable films on the leave surfaces, which promoted the root system's activities and net photosynthetic rates. However, nanoTiO_2 could be utilized as an effective ingredient in agricultural research [32].

Jian et al. studied the nanobiotechnology application to Increase Vegetable Production. The carbon with 5 to 50 nm used as the Nanofertilizer on eggplant, leek crops, radish, tomatoes, cabbage, cabbage, and peppers. The results exhibited promoted the crops' growth with better quality and increased the yield 20% to 40%. Further, the content of VC in chili enhanced 1.5 times. However, nano-carbon could act as non-toxic materials in vegetable production[33].

Shujuan et al. researched to enhance the nitrogen fertilizer efficiency and growth of cabbage. Where, a soil pot experiment carried to study the effects of nano-preparation on the nutrient absorption, leaf chlorophyll content, production, nitrogen fertilizer use efficiency, and some quality indexes of cabbage. The study demonstrated the usage of nano-hydroquinone and nano-tea-polyphenols in nitrogen fertilizer in order to enhance the production, the number of nutrients (N,P,K) absorption, nitrogen fertilizer use efficiency, and leaf chlorophyll content of cabbage, where nano-preparation with 4% tea-polyphenols acted as the best effective treatment among other treatments that production and nitrogen fertilizer use efficiency of cabbage enhanced by44.5% and 134.1% respectively, but the content of Vc had no change. However, nano-preparation could enhance crop yields and improve fertilizer efficiency [34].

Siddiqui et al. experimented with the effects of nano silicon dioxide (nSiO2 with 12 nm size) on the tomato (*Lycopersicumesculentum Mill*. cv Super Strain B) to seed germination. The results exhibited the increment characteristics of seed germination (Fig. 08), which showed improved percent seed germination, seed germination index, seed vigor index, mean germination time, seedling fresh, and dry weight. This proposed fertilizer provides an alternative source for conventional fertilizer system that may enhance sustainable agriculture via increase effectiveness for the growth and yield of crops [35].

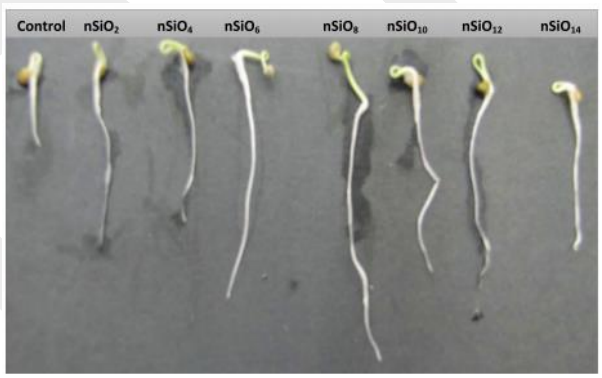

Fig. 08. Effect of nSiO2 on seeding growth of tomato [32]

Mattiello et al. investigated the phytotoxic and genotoxic effects of titanium dioxide NPs ($nTiO_2$) and cerium oxide NPs ($nCeO_2$) in seedlings of Hordeumvulgare L. Caryopses, where that seeds exposed to an aqueous dispersion of $nTiO_2$ and $nCeO_2$ at 2000 mg l^{-1} and0, 500, 1000 mg l^{-1} respectively for 7 days. Genotoxicity was carried by mitotic index on root tip cells and Randomly Amplified Polymorphism DNA (RAPDs). Total Ti and Ce concentration in seedlings was identified and the presence of aggregates of $nTiO_2$and $nCeO_2$ within root cells of barley. The $nTiO_2$ and $nCeO_2$ suspensions were not affected the seed germination and were not allowed to enter the seed coatings. This research verified the presence of both $nTiO_2$ and $nCeO_2$ in the root cells, where an increase in oxidative stress occurred [36].

Haghighi et al. studied the effect of carbon nanotubes (CNTs) on the seedling growth and germination of onion (*Allium cepa L. cv*. ‘Yellow Sweet Spanish’), radish (*Raphanussativus L. cv*. ‘Small radish’), tomato (*Lycopersicumesculentum Mill. cv*. ‘Falcato’), and turnip (*Brassica rapa L. cv*. ‘Toria’). Seeds were germinated in Petri dishes at four concentrations of CNTs (0, 10, 20, and 40 mg L^{-1}) under laboratory conditions, where the effect on germination percentage (GP), mean germination time (MGT), growth, seedling fresh and dry weight, seedling length, and germination rate (GR) were measured. CNTs at 10 - 40 mg L^{-1} enhanced the germination of onion and tomato than turnip and radish. CNTs at 40 mg L^{-1} had a toxic and deleterious effect on radish and onion seed germination. The increment of CNT concentration decreased the fresh weight of radish seedlings. The effectiveness of CNTs SEM may depend on the plant species and the distribution of CNTs on the testa and root surface. However, CNTs could be utilized to improve seed germination and seedling growth-related characteristics[37].

Husen et al. demonstrated that the carbon nanotubes, C_{60}, and fullerene increased the biomass, water-retaining capacity, and fruit yield in plants up to ~118%. This study showed the enhancement in fullerene treated bitter melon seeds on the phytomedicine contents such as lycopene (82%), insulin (91%), cucurbitacin-B (74%), and charantin (20%). Further, 50 μg mL^{-1} of carbon nanotubes increase the production of tomatoes by about 200%. The functionalized multi-wall carbon nanotubes decreased the toxic nature of both plants and animals. The penetration of carbon nanotubes into the plant system made changes in metabolic functions to enhance the fruit/grain yield and biomass. Table 2 shown below the usage of carbon nanomaterials in agriculture to increase crop production [38].

Table 2. Effects of carbon nanomaterials on plants

Nanoparticle	Size (nm)		Plant	Concentration	Effect
C_{60} Fullerenes	1450-1900		Corn, Soybean	500 mg kg−1	Reduced biomass
Fullerol [C_{60} $(OH)_{20}$]	1.5 ± 0.2-5.00 ± 0.7		Bitter melon	0.943, 4.72, 9.43, 10.88 and 47.20 nM	Increased biomass yield, water content, fruit length, fruit number, and fruit fresh weight, increased two anticancerousphytomedicines, cucurbitacin-B and lycopene, and two antidiabetic phytomedicines, charantin and insulin
Functionalized carbon nanotube	8		Lettuce	104, 315,1750 mg L^{-1}	Reduced root length at longer exposure
Functionalized single-walled carbon nanotube	8		Cabbage, carrot, lettuce, onion, tomato	9, 56, 315, 1750 mg L^{-1}	No effect
Multiwalled carbon nanotube			Zucchini	1000 mg L^{-1}	Reduced biomass
			Lettuce	2000 mg L^{-1}	Reduced root length
	Diameter range: 10-30		Rice	20, 40, 80 mg L^{-1}	Chromatin condensed inside the cytoplasm and caused cell death, plasma membrane detachment from

					cell wall and cell shrinkage
			Tomato	10-40 mg L^{-1}	Significant increase in germination rate, fresh biomass, and length of stem significantly enhanced moisture content inside tomato seeds
			Corn, cucumber, radish, rapeseed, ryegrass, lettuce	2000 mg L^{-1}	No effect on germination
			Ryegrass	2000 mg L^{-1}	Increased root length
			Zucchini		No effect on the germination
	Internal dimension: 110-170		Wheat	100 mg L^{-1}	No significant effect on root or shoot growth
	10-25		Tomato	50-200 μg L^{-1}	Significant increase in plant height, flower and fruit formation
Single-walled carbon nanotube	1.19 (major), 18, 722		Rice	400 mg L^{-1}	Delayed flowering, decreased yield
	8		Tomato	104, 315, 1750 mg L^{-1}	Most sensitive in root reduction
	8		Cucumber onion	104, 315, 1750 mg L^{-1}	Increased root length
	8		Cabbage, carrot, lettuce	104, 315, 1750 mg L^{-1}	No effect

Khodakovskaya et al. researched the effect of multi-walled carbon nanotubes (MWCNTs) on the tomato plant from the germination to the flowering stage. The obtained results showed that the plants treated with carbon nanotubes had higher tomato plant height than plants treated with activated charcoal. Further, the tomato plants treated with carbon nanotubes bore twofold flowers compared to the control and those treated with activated charcoal, which enhanced the tomato production by 200%. Carbon nanotubes influenced the reproductive system in tomato plants also [39].

Pandey et al. researched the effects of two carbon-based nanomaterials (CBNs) such as multi-walled carbon nanotubes (CNTs) and graphene on biomass production and germination of two major bioenergy crops such as switchgrass and sorghum. The results showed that the CNTs and graphene-enhanced the rate of germination on switchgrass seeds and led to early germination of sorghum seeds, where the 28% total biomass of switchgrass increased than untreated plants when exposure to (200 mg/l) graphene. CBNs could be decreased the reduce symptoms of salt stress imposed by the addition of NaCl into the growth medium [40].

Liu, X et al. studied the effects of $CaCO_3$ NPs (20–80 nm, 160 mg L^{-1} as Ca) application on peanut (Arachishypogaea) seedlings grown as a Ca nutrient in the sand with Hoagland solution for 80 days. The results showed Ca-NPs significantly 15% enhanced from 4.42 g per plant to 5.07 g per plant the seedling growth than the control. Nonetheless, Ca-NPs could be absorbing Ca source and transport by the plant roots to shoots, where the Ca content in seedling roots and 1.58% and 3.04 respectively. Therefore, Ca-NPs have a large potential as Ca fertilizers for field crops [41].Table 3 shown below some already reported different nanomaterials with growth and yield boosting impact [4].

Table 3. Impact of nanofertilizers on the productivity of different crops under varying pedo-climatic conditions

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

Delfani et al. researched the foliar application Fe-NP and Mg-NP solutions to black-eyed pea (*Vignaunguiculata*). The results showed the 7% of weight enhancement of 1000-seed by the usage of a combination of 0.5 g L−1 of Mg-NP and Fe-NP. The treatment with the combination of 0.5 g L−1 of regular Fe salt and 0.5 g L−1 of Mg-NPs has increased the13.5% yield over the control, and the foliar applications of these two elements enhanced the plant's photosynthetic efficiency. However, Mg-NPs application alone was decreased the ~6% yield over the control. The Mg-NPs application increased the Mg uptake due to its higher availability and mobility of Mg-NPs in plant leaves and stems than regular Mg salt usage [42].

Ghafariyan et al. demonstrated that the superparamagnetic Fe-NPs with low concentrations enhanced the chlorophyll contents in sub-apical leaves of soybeans. The results showed that the Fe-NPs could be used as the source of Fe and decreased chlorotic symptoms of Fe deficiency in a greenhouse test under hydroponic conditions [43]. Pradhan et al. researched the effects of metallic Mn-NPs on mung bean (*Vignaradiata*) as a better micronutrient source of Mn where mung bean seedlings were then incubated for 15 days in an inert media (perlite) with Hoagland solution in growth chambers. The observed results showed better growth and augmented its photosynthesis of mung bean than the commercially-available MnSO4 salt. The 0.05 mg L−1Mn-NPs application enhanced the maximum growth than controls in shoot length by 38%, fresh biomass by 38%, root length by 52%, number of rootlets by 71%, and dry biomass by 100% [44].

Mahajan et al. researched the effects of ZnO-NPs on the growth of mung bean and chickpea (*Cicer arietinum*) seedlings. The results showed the enhancement in the growth of mung bean and chickpea seedlings at low concentrations, where the concentration of 20 mg L−1 of ZnO-NPs increased 42% in length or 41% in biomass exhibited for root and 98% increment in length or 76% in biomass for the shoot in the mung bean seedlings over the control. Further, the concentration of 1 mg L−1 of ZnO-NPs increased 53% in length or 37% in biomass exhibited for root and 6% increment in length or 27% in biomass for the shoot in the chickpea seedlings over the control. However, ZnO-NPs enhanced roots' growth rates and shot f mung bean and chickpea seedlings [45]. Zhao et al. studied the effect of ZnO NPs application on cucumber (*Cucumissativus*) growth through a life cycle analysis of the plant in a greenhouse. The results exhibited ZnO NPs at that 400 and 800 mg kg−1 concentration to a soil mixture increased the growth of cucumber. Further, the plant root dry mass was increased 1.1 and 1.6 times higher and the dry weight of the fruits was enhanced by only 0.6 and 6% than the control. The application of ZnO-NPs also enhanced glutelin's contents by 0.9–2 times, Zn by 1.7–2.5 times, and the starch by 1.1–1.6 times in the harvested cucumber fruits. However, ZnO-NPs could be utilized to enhance crop yield [46].

Taran et al. studied the effect of the Mo-NPs solution on chickpea as a Mo micronutrient source in loamy soil. The chickpea seeds were treated to gain plant root nutrition by supplying Mo and by increased microbiological fertilization of plants. The results showed that the root number and nodule mass per plant were higher than control under this treatment, which also increased the activity of an antioxidant enzyme in chickpea by 2–3 times and increased resistance to plant pathogens. Therefore, Mo-NPs application alone or with the microbial treatment could increase the yield, performance, and disease resistance of legume and other crop species [47].
Yang et al. researched the effects of Ti-NP solution on spinach (*Spinaciaoleracea*) seeds. In this study, spinach seeds soaked in 2.5 g L−1Ti-NP solution under light for 2 days before sowing them in an inert growth medium then the solution was leaf-sprayed on these germinated seedlings in a greenhouse once a week for 35 days. The results exhibited about 2 times enhancement of fresh and dry weights of the plants than controls. Further, the proposed method enhanced the contents of total N by 23%, chlorophyll by 34%, and protein in leaves by 13% over the controls [48].

6 LIMITATIONS OF NANOFERTILIZERS

Nanofertilizers have certain limitations due to the lack of legislation, absence of rigorous monitoring, and research gaps. A few drawbacks and limitations of nanofertilizers for sustainable crop production are listed below [4]. This adverse behavior of nanomaterials should be thoroughly investigated before their release.

1. The higher cost of nanofertilizers is restricted to utilize for crop production under varying pedo-climatic conditions.
2. The problem occurs with gain a uniform size of nanoparticles (1–100 nm).
3. The lack of recognized standardization and formulation leadsto contrast effects of the same nanomaterials under different pedoclimatic conditions.
4. The limited availability and production of nanofertilizers in required quantities.
5. The limitation with nanofertilizers related to risk management and legislation in promoting and advocating nanofertilizers for sustainable crop production.
6. Nanomaterials have a toxic effect on plants and several soil microorganisms including bacteria, yeasts, and fungi [7].
7. Currently, the small size of nanoparticles can easily enter cells, tissues, and organelles and effect functional biomolecularstructures like DNA, ribosomes.

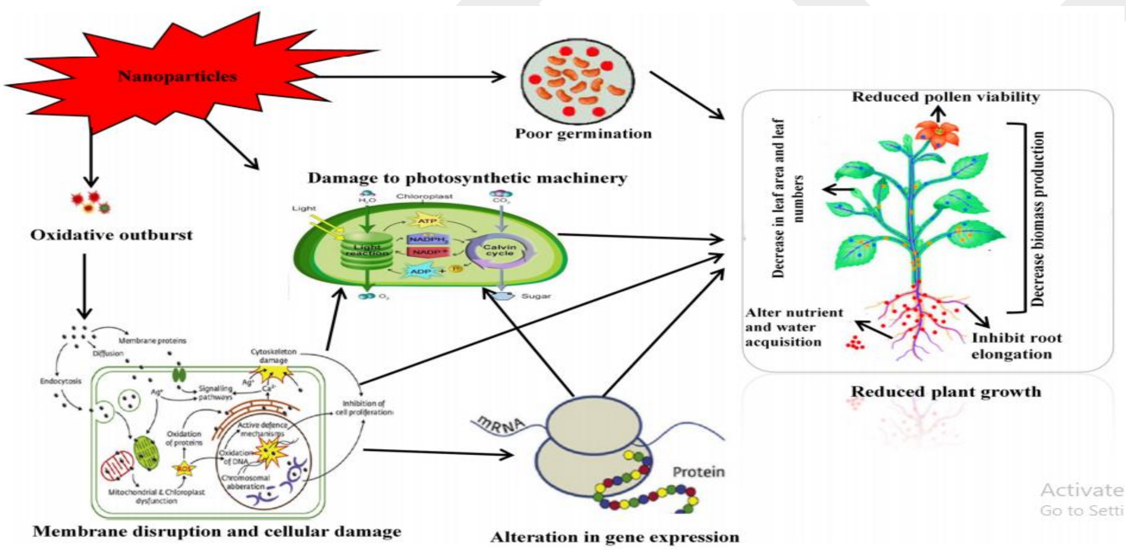

Fig. 09. Toxic effects of nanoparticles on plant growth and development [26]

The above Fig. 09 shown the adverse effects of nanoparticles on plant growth and development. Where higher concentration nanoparticles lead to alteration in physiological and morphology processes of crop plants. higher concentration nanoparticles in the root zone restrict root development, and nutrient and water uptake decreases biomass production and leaf development and inhibits seed germination. Further, the toxicity of nanomaterial leads to oxidative outburst resulting in cellular damage, membrane disruption, altered gene expression, reduced photosynthesis, and chloroplast disorganization.

7 CONCLUSION

Nanofertilizers are utilized alone or in conjunction with organic materials to efficiently boosting nutrients to crop plants while reducing environmental pollution via minimize nutrient loss and enhance the higher absorption rate. Several types of research with different nanomaterials were recorded to enhance the root development, plant height, germination rate, number of roots, and fruits antioxidant and leaf chlorophyll contents. Smart nanofertilizers release nutrients as per the requirements of plants for sustainable crop production. Lastly, researchers and regulators should be responsible for the risk and limitation of nanofertilizer usage in order to take full advantage of nanofertilizers for sustainable crop production under changing climate while reducing the risk of causing environmental pollution.

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