

Recent advances in nanotechnology for the improvement of conventional agricultural systems: A review

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ABSTRACT

Agriculture provides food and raw materials for the construction, energy, textile and pharmaceutical industries. Recently, agriculture is facing several concerns including climate change, soil degradation, decreasing land holding, urbanization, unsustainable use of natural resources, excessive use of agrochemicals, biodiversity loss, air pollution etc. are some of alarming issues which demand immediate interventions. Conventional agricultural practices could not handle these challenges as they are complex, labour intensive, time-consuming, less efficient, large requirements of crop nutrients and non-targeted. Furthermore, the inefficient use of agrochemicals poses a serious threat to the ecosystem. Therefore, scientists, farmers and policymakers are constantly searching for new techniques to combat existing challenges. Nanotechnology is emerging as the new savior of sustainable agriculture. Besides precision farming, nanosensors have been employed for the detection of crop pathogens and chemically harmful analytes in agri-fields. Moreover, nanorobotics and nano-barcodes have also shown a profound impact on agriculture practices to enhance the yield of agriculture. Further, tremendous applications of nanotools in agriculture are extensively implicated in bioimaging, sensing, photocatalysis and agrochemicals delivery. This review comprehensively discusses diverse tremendous applications of nanotechnology in overcoming the challenges of conventional agronomic practices and future prospects of nanotechnology in agriculture.

1. Introduction

The increasing human population and the consumerist nature of man are depleting natural resources at a very fast rate which is a challenge to sustainable development. Several other problems of modern agriculture include overdependence on supplementary irrigation, depleting ground-water levels, soil degradation, pesticides and fertilizers contamination, the lesser interest of youth in agriculture, non-efficient existing agricultural techniques etc. (Gleick, 2014; Rodell et al., 2009). Food and Agriculture Organization (FAO) has reported that by 2050 AD, the global population will be 10 billion which will increase food demand by 50% particularly in developing countries (Usman et al., 2020). At present about 815 million people are malnourished and this number can be 2 billion by 2050 AD. It necessitates intense modifications in the food-producing system at the global level. To increase global crop productivity to the tune of three billion tones, huge quantities of agrochemicals (187 million tonnes of fertilizers for providing efficient nutrients, 4 million tonnes of pesticides to protect crops from attack of insects and pests, 2.7

trillion cubic meters of water and approximately > 2 quadrillion BTS of energy) are required (Kah et al., 2018). The use of these inputs will increase the cost of agricultural production and further deteriorate the environmental quality. As a result, the productivity and sustainability of agriculture will be serious concerns across the globe.

Excessive use of fertilizers and pesticides has increased the risk of eutrophication of surface water bodies and groundwater. Ultimately basic integrity of the ecosystem has been compromised. Moreover, disrupted ecosystem cycles have affected the life cycle of living organisms. Owing to degraded ecosystems, various serious human health issues have emerged in recent times (Hoq et al., 2018).

Addition of biomass (crop residues, green manure etc.) in bulk quantity has improved soil fertility thereby increasing the productivity of crops. It is not efficient in retaining carbon compounds and managing the pollution of nitrogenous compounds. Consequently, it increased the temperature of entire ecosystem (Roberts and Mattoo, 2018). Techniques such as bioremediation and phytoremediation are practically not capable to decompose the heavy metals of soil because they require the relocation of farmers and

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withdrawal of their livelihood (Karn et al., 2009). It is becoming difficult particularly for poor and marginal farmers to face with these emerging challenges. To handle these issues of modern agriculture, researchers have shown their interest in nanotechnology to achieve sustainable development goals 1 and 2 (zero hunger) by increasing the efficiency of agricultural practices for resolving the aforesaid challenges of food productivity and food security. Nanotechnology can have several applications in agriculture systems during vegetative growth of crops, production, processing, storing, packaging, and transportation of agricultural produce (Joshi et al., 2019). The main goal of nano-based agriculture over conventional agriculture systems is the ability of crop plants to survive under varying climatic conditions, water scarcity, saline water, and increased CO₂ levels and thereby enhancing crop productivity (Vermeulen et al., 2012).

In agriculture, nanomaterials are used in the fabrication of biosensors, formulation of nanopesticides, nanofertilizers, genetic transformation of plants and animals with desirable characteristics, and nano plant growth regulators (Singh and Gurjar, 2022). Nanodevices have been developed and used in fields to improve the existing plant breeding and genetic transformation technology (Mukhopadhyay and Sharma, 2013; Prasad et al., 2017). Researchers have reported the encouraging applications of nanosensors in precision farming (Dasgupta et al., 2017). The nanodevices have also been employed for the measurement and evaluation of growth, crop productivity, soil parameters, insect and microbial infections and dissemination of fertilizers to attain a sustainable and eco-friendly environment (Chen et al. 2016). Nanobarcodes have been designed for monitoring the quality of agricultural products (Li et al. 2005). Pandey, (2018) has reported that nanotechnology can increase the 25% growth rate of agri-market. Integration of nano-based approaches in the agriculture system can augment the economic growth of up to three trillion USD in recent years.

Though, previously, several articles have been published which provide a discussion on the role of nanotools in agriculture, however, recently nonetheless review comprehensively explains the key roles of both nanotools and nanodevices for enhancing agriculture productivity. This review deciphers recent agronomic practices and their challenges, detailed account of nanotechnology in overcoming the challenges of conventional agronomic practices, advantages of green nanomaterials over chemically synthesized nanomaterials, tremendous applications of nanotechnology in insect-pest management, efficient use of nanofertilizers and nanoherbicides, crops climatic adaptation, crops genome manipulation by mutation breeding and DNA nanobiotechnology. Besides these, we have also elaborated fabrication of biosensors for the detection of a diverse range of harmful analytes, on-site monitoring of crop health nanosensors in precision farming for remote areas, and future prospects of nanotechnology in agriculture. In this article, the fabrication of various nano-tools, nano-devices and their role in increasing the productivity of agriculture in varying climatic conditions, preventing pathogenic attack by manipulating plant genetic material and proper insect-pest management system, and improving the nutrient content and water holding capacity of soil have been discussed.

2. Agronomic practices used by farmers

Farmers use conventional and modern agronomic practices including molecular farming during the cultivation of crops. In the below section, conventional and modern practices used by farmers are given.

2.1. Conventional practices

Conventional practices increase the yield of crops by increasing the nutrient content in the soil and protecting it from insect pests at affordable prices. Conventional agronomic practices are mainly based on the use of agrochemicals for different purposes such as fertilizers and pesticides. Some chemicals are used for preventing microbial attacks on crops. These agrochemicals are poor in efficiency, stability, costly, required in large quantities and sometimes non-targeted. Moreover, conventional agrochemicals are hazardous to all living beings because they may cause various toxicities like carcinogenicity, mutagenicity and

reproductive toxicity. In addition to these, they also act as pollutants and cause air pollution, water pollution and soil pollution. Consequently, these agrochemicals affect the entire ecosystem by destroying the inter-linked food chains. Therefore, to mitigate aforesaid challenges of conventional agriculture practices, farmers use modern agriculture practices.

Further, these practices are labor intensive, causes toxicity and require large quantity of agrochemicals.

2.2. Modern practices

Modern agriculture practices involve crop rotation, intercropping, and natural fertilizers such as compost from animals, plants and bone meal (Singh and Singh 2017). Sometimes natural predators are also employed to control pests. These modern practices increase the fertility of the soil, and eco-friendly and use natural ingredients. These practices overcome the limitation of conventional agriculture practices as they are more efficient, cost-effective, non-toxic, improve the fertility of the soil by increasing nutrient content and are use-friendly. These modern techniques also have a number of issues such as they are non-targeted and require more manpower and large quantities of active ingredients. Therefore, this necessitated the researchers and farmers to some innovative practices to resolve the aforesaid issues. Researchers have developed various nanotools and devices which exhibit several advantages including unique efficiency, stability, targeted, renewable, user-friendly, and cost-effective.

Conventional and modern agricultural practices are inefficient in the proper utilization of applied agrochemicals (Lowry et al., 2019). Consequently, insects and weeds are resistant to conventional insecticides and herbicides. Agrochemicals have affected biodiversity and impaired the functions of different ecosystems (Beketov et al., 2013). The presence of agrochemicals in potable water is known to cause several ill-effects on the health of human beings (Diaz and Rosenberg 2008; Klarich et al., 2017). Even after the use of agrochemicals, crop yields are reduced by microbial diseases, soil erosion, and vulnerability to climatic parameters like drought, heat stress, salinity, etc. (Lowry et al., 2019). These agricultural practices have shown very little resilience to monocropping, soil erosion, water deficiency and frequent attack of microbes. Hence, there is an urgent need to develop efficient alternatives to resolve these challenges of conventional and modern agricultural practices.

2.3. Molecular farming

Molecular farming is used for the production of genetically engineered proteins in plants which can be used either in purified form or crude extracts without altering the phenology, performance, and metabolism of that plant. Production of antibodies and human serum albumin in plant cell suspension cultures and transgenic plants are some of the initial examples of molecular farming (Schillberg et al., 2021). Various plant species have been used as hosts for the production of biomedicines (Hirsch et al., 2003). Veterinary products synthesized in plants have also aroused the interest of researchers due to the reduced use of antibiotics in food and dairy animals (Scott, 2005, Seeman, 2004 and Tolles et al., 2003). Pharmaceutical products obtained by molecular farming are economically cheaper, have larger scalability and are non-toxic. Some proteins and growth factors that are used as chemical reagents in research, ornamental constituents, sensors, and biocatalysts and bioremediation agents have also been produced by using molecular farming. Presently, several commercially available non-pharmaceutical products of molecular farming are produced using molecular farming in the small to medium range, depending upon the culture conditions. Various approaches of molecular farming used for agriculture practices include nanofabricated gel-free systems and high throughput DNA sequencing, microchips and expression profiling, DNA microarrays and protein microarrays. Scientists are of the view that molecular farming along with nanotechnology can be used for early diagnosis of plant diseases and to increase crop productivity.

Table 1 depicts the comparison of conventional, modern and nano-based practices used for augmenting agriculture productivity.

Table 1
Comparison of conventional, modern and nano based practices used for increasing agriculture productivity.

Aspects of agriculture		Conventional agriculture practices	Modern agriculture practices	Nano-based agriculture practices	Reference
Methods used		These practices are based on use of distinct types of chemicals	These practices involve mixed cropping, crop rotation, companion planting and organic compost.	These practices are based on use of active ingredients in the form of distinct types of nanomaterials	Babu et al., 2022;
Fertility of soil		Poor fertility	Augmented the fertility of soil by improving the nutrients content	Increased the nutrients content of soil thereby significantly augmented the soil fertility	Singh and Singh, 2017
Types of fertilizers		Fertilizers used are mainly inorganic	These practices use organic fertilizers	Both inorganic as well as organic fertilizers are used in these practices	Duhan et al., 2017
Concentration of active ingredients		Agrochemicals are required in very high amount	These practices require moderate amount of agrochemicals	These practices require very low amount of agrochemicals	Lowry et al., 2019
Nutrient content		Soil contain scarce amount of nutrients	Soil contain all nutrients required for growth of crops	Soil is very rich in nutrients	Duhan et al., 2017
Efficiency		These practices show poor efficiency	These practices show high efficiency	These practices show exceptional high efficiency	Mittal., 2020
Targeted/non-targeted		Agrochemicals used in these practices are non-targeted	Agrochemicals used in these practices are also non-targeted	Agrochemicals used in these practices are targeted	Lowry et al., 2019
Stability		Stability of spraying of agrochemicals is very less	Stability of spraying of agrochemicals is better than conventional practices	Stability of spraying of agrochemicals is good	Mittal., 2020
Cost		These practices use very costly agrochemicals in large quantity	These practices use cost-effective	These practices use cost-effective as they are used in minimum quantity	Babu et al., 2022
Toxicity		Very hazardous consequently, increases the risk of cancer, reproductive toxicity and neuronal ailments. These also increase the risk of eutrophication in water bodies.	These practices minimum toxicity	These practices show moderately but green nanomaterials do not cause toxicity	Duhan et al., 2017
Effect on soil		Fertile but soon become infertile due to exploitation.	These practices keep soil fertile but may increase the prevalence of deforestation and soil erosion	Nanomaterials based approaches significantly enhance fertility of soil	Mittal., 2020
Eco-friendly		Non-sustainable as conventional agrochemicals kill beneficial insecticides that causes bio-diversity loss	These practices are sustainable	Green nano based approaches are sustainable as they are compatible with living system	Shang et al., 2019
Animal cruelty		Antibiotics are injected in livestock	These practices do not show animal cruelty	These practices also do not show animal cruelty	Shelar et al., 2023

3. Rationale of Nanotechnology: advantages to significance

Nanotechnology is a branch of diverse sciences including life sciences, material science and information technology, that design and characterize the materials and devices, whose smallest functional entity in at least one dimension, is on the nanometer scale (Joshi et al., 2019; Silva, 2004). It is a promising field of science that resolves problems that otherwise cannot be solved by an engineer or a biologist. The combination of nano-science and technology involves the fabrication and working of material on a nano scale that helps in the manipulation and invention of new tools, materials and structures at the molecular level, by rearranging their atom sequence into functional structures having a size in nanoscale (Ray et al., 2009).

Almost every organism, from microbes to humans is composed of molecular and cellular machinery systems that function at the nano level (Duhon et al., 2017). It is a multidisciplinary research field, which is based on the combined efforts of scientific communities from different branches including chemistry, physics, biology, medical science and engineering. Though, researchers have used nano-based approaches in self-replicating, monitoring, controlling and repairing tools or devices but yet it has not attained their development stages (Scott, 2005; Seeman, 2003). The nanotools/devices have been used in the agriculture sector during the processing of foods, protection of food from harmful agents, in food packing, dairy, transportation of food items, increase shelf-life and maintain the quality of agricultural food (Pandey, 2018).

3.1. Significance of nano based approaches

Nanotechnology has provided solutions to mitigate the challenges of existing agriculture practices. The fundamental components of nanotechnology are nanotools and nanodevices. The nanotools are different types of nanomaterials, viz. carbon-based nanomaterials, mineral nanoparticles, metal and metal oxide nanoparticles which have a very high surface area (Lowry et al., 2019). On the other hand, nano-based devices have improved the existing plant breeding and genetic transformation technology. It has also been reported that engineered nanomaterials (ENMs) based agricultural practices can acclimatize to fluctuating environmental climatic conditions (Mittal et al., 2020). ENMs coated with molecular recognition elements like aptamer or antibodies help in targeted delivery of nutrients. This increases the yield of crops by minimizing the adverse impact on the environment and also led to sustainable use of nutrients. These ENMs have overcome the issues of conventional and modern agricultural practices by enhancing the targeted delivery of agrochemicals and their efficient utilization and management in the fields. ENMs have shown promising sustainable applications in agricultural practices by designing nano-scaled agrochemicals (Gilbertson et al., 2020). ENMs can improve agricultural sustainability by (i) improving the soil texture by restricting the use of nitrogen fertilizers, (ii) coating seedlings with Zn and Cu nanoparticles has augmented the seed germinating rate in comparison to conventional practices with potassium chloride, potassium nitrate and polyethylene glycol (PEG) which have high embodied energy (iii) foliar spray of ENMs including nano Zn, ZnO and TiO₂ has also increased the crop productivity by efficient targeted uptake of agrochemicals. ENMs-based foliar treatment increased crop productivity by augmenting the photosynthetic efficiency of crops by preventing the effect of abiotic stresses on photosynthesis rate, elevating chlorophyll quantity, increasing light absorption efficiency, scavenging reactive oxygen species and supporting effective electron transport system (Lowry et al., 2019). It has been revealed that high photosynthetic rate sometime lower the nutritional value of food. Therefore, spraying of micronutrients of iron, zinc and silica in ENMs form maintain the high nutrient content in foods. Moreover, modification in the surface chemistry of ENMs improves their adherence to leaves and thus increases the nutrient uptake efficiency by cuticle and mesophyll cells. Moreover, these ENMs have

been used in the fabrication of sensing devices to evaluate the health of crops in high spatial and temporal resolution (Giraldo et al., 2019).

In the following section fabrication of various nano-based tools and devices has been discussed (Fig. 1);

3.1.1. Nanofabrication for agricultural purposes

Nanofabrication is the process of designing and manufacturing nano-tools and nano-devices. Nanomaterials can be used to provide more nutritional ingredients to plants which in turn will increase the growth and yield of crops and minimize the release of hazardous components in the environment as compared to traditional practices (Zf et al., 2018). Depending upon the nature of nanoparticles, their introduction into plants may result in some biological and physical alterations (Pandey, 2018). These alterations are due to the chemical interactions between nanoparticles and plants may impact membrane transport action, production of active oxygen species, lipid peroxidation, ion-cell disorder and oxidative- breakage (Pandey, 2018). Fig. 2 shows the applications of nanotechnology in diverse agriculture and its related fields.

3.2. Advantages of nanomaterials over corresponding bulk materials

Nanomaterials have unique properties viz; higher surface area, more cation exchange capacity, better ion adsorption and complexation efficiency. The main difference between nanomaterials and bulk materials is that a large number of atoms are exposed to the surface in the case of nanomaterials which is not possible in the case of bulk materials (Hochella et al., 2008). Nanoparticles also differ in terms of configurations, types, densities, and reactivity, concerning adsorption and oxidation/reduction reactions used for nanoparticles preparation for agriculture purposes (Waychunas et al., 2005). ENMs-based agrochemicals, due to their small size and unique properties, are the emerging platform for the revolution of existing agriculture systems. This is due to their ability to cross biological barriers, enhanced diffusing capability in plant vasculature after root or foliar applications, and enabling new efficient routes of delivery of nutrients and pesticides. They exhibit unique stability as a result of their controlled release of nutrients and antibiotics improve crops resilience to various diseases (Kah et al., 2018). Moreover, configuration and surface modification with diverse functional groups of ENMs also facilitate the targeted and smart release of agrochemicals. Fig. 3 depicts the significance of nanomaterials in agriculture.

3.3. Significance of green NPs in the agriculture system

Various chemical methods have been reported for the synthesis of nanoparticles which require hazardous chemicals that are toxic to living systems. It compels us to develop some eco-friendly practices. So, the adverse impacts of hazardous chemicals can be mitigated. A comparison of green methods, chemical methods and physical methods have been depicted in Table 2. Biological materials such as higher plants bacteria, fungi, and viruses have been used by many scientists for the synthesis of nanoparticles (Kuppusamy et al., 2016). Plants are the chemical reservoirs of nature are cost-effective and require minimum protection. They can detoxify and accumulate heavy metals (Jadoun et al., 2021). Plant based nanoparticles can be synthesized from fruit, leaf, stem and root by washing and boiling of plant parts in distilled water. This is followed by squeezing, filtering, and addition of nanoparticles-specific solutions such as micro-emulsion and macro-emulsion. Addition of these solutions for example silver nitrate solution changes the colour of the solution and reveal the formation of nanoparticles. Various methods of synthesis of green nanoparticles have been depicted in Fig. 4.

Different types of microorganisms, such as diatoms, *Pseudomonas stutzeri*, *Desulfovibrio desulfuricans*, NCIMB 8307 *Clostridium thermoaceticum* and *Klebsiella aerogens* have been reported for the synthesis of

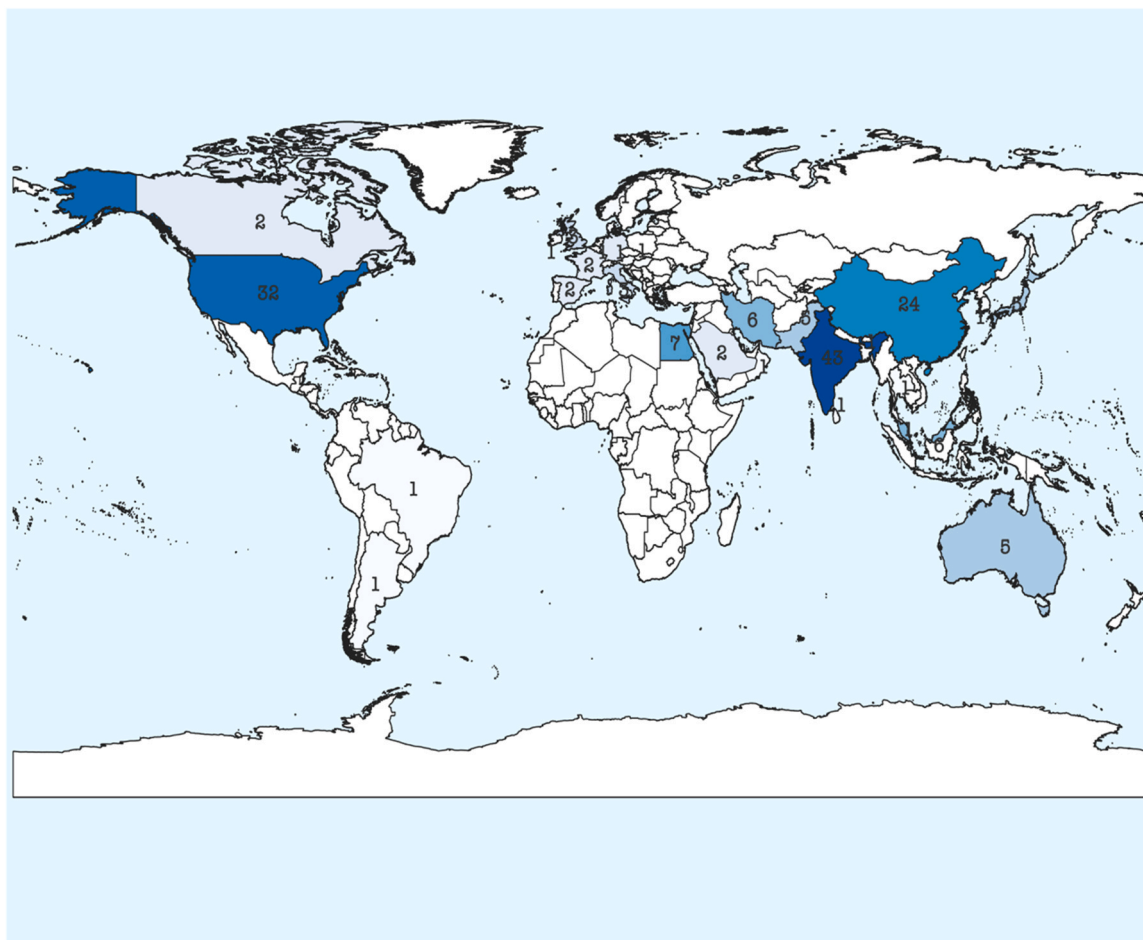


Fig. 1. Country -wise global map of different articles screened from various countries.

Si, Au, ZnS and CdS, respectively. Fungi such as *Verticillium* sp., *Aspergillus* sp., have also been employed for the synthesis of biological nanoparticles. Mahawar and Prasanna (2018) have documented the role of ZnO nanoparticles synthesized from soil fungi as nano-fertilizers. These ZnO nanoparticles have been used to improve the efficiency of nutrient uptake and their transport to different parts of crop plants. Bartolucci et al. (2020) have reported the tremendous applications of distinct types of green nanoparticles in agricultural systems. They have documented that green nanoparticles synthesized from varying plant sources have been used in distinct agricultural applications such as

nanofertilizers, nanopesticides, plant development processes, and regulation of plant hormones. Besides remote sensing applications, green nanoparticles integrated biosensors have also been developed for the detection of pathogens and sensing various plant growth parameters. For the synthesis of Au nanoparticles plants like *Medicago sativa* and *Sesbania* sp. have been used. In addition to these green nanoparticles inorganic nanomaterials of Ag, have also been synthesized using *Brassica juncea* and *Medicago sativa* (Irvani, 2011; Kitching et al., 2015). These silver nanoparticles increased the photosynthetic efficiency of *Brassica juncea* and *Medicago sativa*.

According to a demonstration, exposure of Ag nanoparticles synthesized using *Eucalyptus globules* have shown a profound effect on several physiological processes including germination of seeds, development processes of plants, photosynthetic efficiency of *Zea mays* L., *Trigonella foenum-graecum* L., and *Allium cepa* L. (Soliman et al., 2020). Nanomaterials synthesized from plants are non-toxic, ecofriendly, cost-effective, stable and exhibit improved analytical performance in comparison to microorganisms-based nanoparticles (Bhardwaj et al., 2020).

4. Applications of nanotechnology in agriculture

Nanotechnology has played a significant role in agriculture by enhancing crop productivity. The application of nano-principles in agriculture can combat several challenges related to the environment and sustainability, safety, and security of foods (Pandey, 2018). Nanotechnology has revolutionized the traditional agriculture system in terms of productivity, economics, minimum toxicity and efficient use of nanoproducts. A number of nanoproducts including nanofertilizers and nanopesticides are available commercially and their use in fields offers

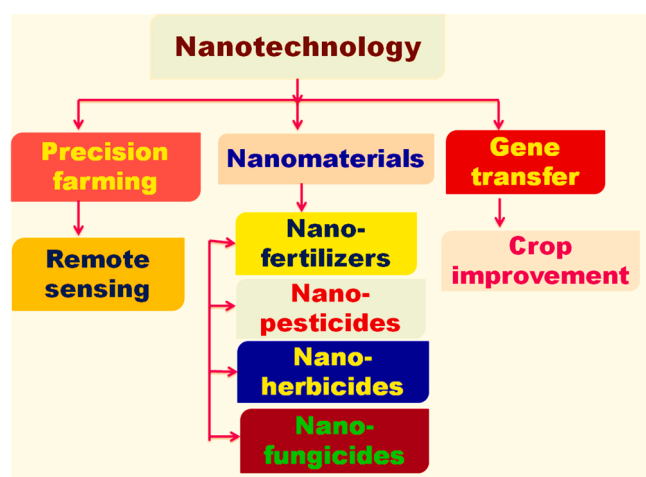


Fig. 2. Approaches for nanotechnology use in agriculture.

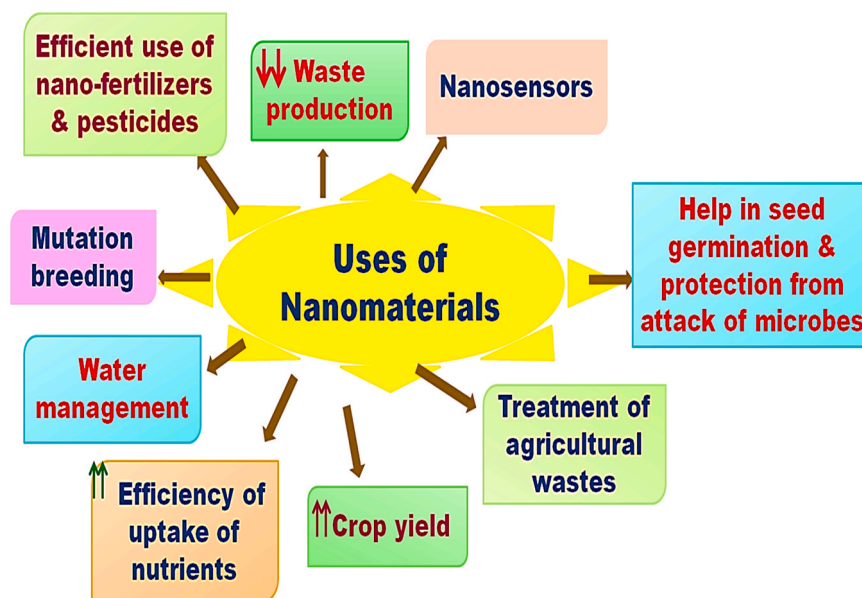


Fig. 3. Diagrammatic representation of uses of nanomaterials in agriculture.

many benefits to farmers. For instance, commercially available nano-fertilizers including Nano-N, Nano-Zn and Nano-Cu are synthesized by Indian Farmers Fertiliser Cooperative Ltd. (Kumar et al., 2020). Nano-max NPK is also a nanofertilizer that was used to enhance the productivity of tomatoes in winter season (Panda et al., 2020). These nanoproducts have significantly raised the net income of farmers as slow and continuous release of these nanoproducts are less labour intensive, stable, site-specific and effective in minute concentration. Further, they show minimum toxicity to living beings in comparison to traditional agrochemicals. The impact of nanotechnology on the net income of farmers has been revealed on 12 crops grown in the winter season. This study revealed twice spray of Nano-N showed 50% reduction of traditionally used urea in fields. Therefore, these nanoproducts are not only augmenting the economic status of farmers but also protecting the environment through their easier degradation.

Researchers have developed nano-robots for various agricultural practices. These nano-robots have exhibited high-speed wire-less connection for scrutinizing the plant capillaries by scanning process (Pandey, 2018; Parisi et al., 2015). The analytical outcomes transferred by these nano-robots help in diagnostic applications in crop fields (Pandey, 2018). Various applications and advantages of nanomaterials are given in Table 3.

4.1. Applications of nano-sized carriers in agriculture

Smart nano-carriers have been developed for the effective intake of fertilizers, pesticides and plant growth regulators. These smart nano-carriers are confined in the vicinity of the roots of the crop plants growing in soil rich in organic matter. Potassium nitrate encapsulated with graphene oxide increased the release of fertilizer in the soil system. Consequently, prolong the stability and cost of fertilizers (Shang et al., 2019). Furthermore, ENMs application in soil systems increases the rhizosphere roots oil- microbiome interaction to enhance crop productivity (R. Zhang et al., 2017). For example, the introduction of metallic ENMs in soil alters nitrogen, phosphorous and carbon cycles. These ENMs either increase the population of useful plant endophytes or their colonization with plant roots by nitrogen-fixing bacteria.

Moreover, nanomaterials of ZnO, TiO₂, MWCNTs, and FeO have increased the growth of several crops including peanut, soybean, mung bean, wheat, tomato and potato (Shojaei et al., 2019). Therefore, this approach has increased consistency and minimized efforts to reduce deformations persuaded by atmospheric factors (Ditta and Arshad, 2016; Ditta, 2012).

4.2. Applications of nano-fertilizers in agriculture

The growth and survival of crops require several essential nutrients including nitrogen, phosphate, potassium, calcium, magnesium, sulfur, iron, manganese, zinc etc. Typically these nutrients are found in soil but in many areas, these are present in very low quantities and hence cause nutrient deficiency in the crops. Using nanotechnology several novel varieties of fertilizers have been developed which have amplified the agriculture yield assumed food security (Iavicoli et al., 2017). Nano-fertilizers are used in small quantities hence reducing the adverse effects of conventional fertilizers on the environment. The nano-fertilizers facilitate the controlled release of nutrients in the soil. Smart nano-fertilizers have a very high surface area which increases their uptake by the plants. The application of nano-fertilizers also reduces the necessity of fertilizer and labor costs. The application of nano-fertilizers minimizes the loss of active ingredients of fertilizers from soil (Ditta and Arshad, 2016). Nanofertilizers can enter inside plant cells effectively via the cell wall and act as sieve because the nanoparticles used for this purpose have a small size than cell wall pores (5–20 nm). Nanomaterials used in these fertilizers are dissolved in soil solution and release soluble nutrients in the form of ions. Plants can efficiently absorb these soluble nutrient ions. It has been found that the rate of solubility and formation of nano satellites in the water/soil solution is more than the bulky nutrients because nanomaterials comprised of large surface to volume ratio (Zf et al., 2018). Nanofertilizers encapsulated with nanomaterials protect and increase the survival of crop plants in polluted soils and ensure the persistent release of nutrients in the soil atmosphere. Due to the unique features of nanofertilizers, researchers have synthesized different types of nano-fertilizers based on carbon-based dendrimers, minerals, metals, and nano-biocomposites (Qureshi and Stansly, 2009). Rastogi et al. (2019) have also reported the significant applications of green Si nanoparticles in nanofertilizers, nanopesticides for controlling weeds pathogenicity and resistance to heat. Surfactant-functionalized zeolites have facilitated the gradual release of phosphate for prolonged bioavailability. Nanocarriers of graphene oxide are used in the form of micronutrients. The nano dimension of micronutrients increased the uptake efficiency of macronutrients (Hofmann et al., 2020).

Wu and Liu (2008) have explained the significance of chitosan-coated NPK-composed fertilizer which assist their regulated release in the soil system as well as increase the water-retention ability that is provided by an internal layer of chitosan, and an external layer of poly (acrylic acid-co acrylamide) (P(AA-co-AM)). In addition, both chitosan

Table 2
A comparison of significance of various methods used for the preparation of nanomaterials.

Characteristics	Green methods	Chemical methods	Physical methods	Reference
Economic Stability	These methods are cost-effective They are highly stable	These are expensive Stability is very less	These are also expensive Stability is very less as they show altered surface chemistry and physicochemical properties	Jiang et al., 2022 Deepak et al., 2019
Eco-friendly	They are easily degradable	Chemicals used in these methods are not completely degradable	They use gases and high very temperature which is harmful for surrounding creatures	Ying et al., 2022
Source Availability	Different types of sources including plants and microbes are easily available in huge amount	Difficult to arrange chemicals used for preparation	Gases used in these methods are sometimes not easily available	Alsaiani et al., 2023; Singh et al., 2018
Compatibility	They show good compatibility with living system	They do not show compatibility with living system	They also do not show compatibility with living system	Hano and Abbasi, 2022
Cumbersome	Process of nanomaterials preparation is very simple	They involve complicated procedure	They involve complicated procedure and require skilled personnel	Satyanarayana and Reddy, 2018
Time	Nanomaterials can be prepared very quickly	Preparation of nanomaterials takes long time	Preparation of nanomaterials takes long time	Bhardwaj et al., 2020
Energy consumption Toxicity	They use minimum energy They do not cause toxicity to living system	They use more energy They are highly toxic to living system	They use extreme high temperature and pressure They are also toxic to living system	Ying et al., 2022 Rafique et al., 2016

and P(AA-co-AM) are easily degradable in soil therefore, these nano fertilizers, polymers and their degraded products are non-hazardous. Liu and co-workers (2009) have reported that the use of nano-calcium carbonate has several benefits including the large surface area of peanut leaves, increased count of leaves, dry weight, the soluble sugar, and peanut protein quantity. Nanoparticles of chitosan have antibacterial activity also. The nanoporous zeolites have high efficiency as well as gradual release of fertilizers (Chinnamuthu and Boopathi, 2009). It has been observed that SiO₂ nanoparticles have elevated the germination of tomato (*Lycopersicum esculentum*) seeds (Siddiqui and Al-Wahaibi, 2014). Kottegoda and co-workers (2011) have demonstrated that modified hydroxyapatite nanoparticles mediated the slow release of nanofertilizers. The impact of TiO₂ nanoparticles has also been studied in growing corn plants. These TiO₂ nanoparticles have augmented the growth of corn plants and amplified the absorption as well as the photo-energy transfer ability of corn plants. SiO₂ nanoparticles and TiO₂ nanoparticles have increased the nitrate reductase activity in soybean plants, and also improved the plant absorption capacity (Changmei et al., 2002).

Anion-responsive nano-system is developed using polyethylenimine-modified hollow mesoporous silica for the release of selenate using a 5 mM phosphate solution. The working of this system was based on the electrostatic interaction between carrier and selenium. The release of fertilizer by this system was increased by valence and the anion content. This nanosystem improved the growth, efficiency and minimum loss of fertilizer in comparison to conventional systems (G. Zhang et al., 2018). Besides, these magnetic nanoparticles have been used for the targeted delivery of hormones, biocides, and drugs for protecting crops from attack of pathogens. Thus, increasing agricultural productivity (Camara et al., 2019).

The iron nano-fertilizers increased the agronomic traits of *Dracocephalum moldavica*, better seed sowing density and also enhanced the quantity of seed essential oil of this plant (Yousefzadeh and Sabaghnia, 2016). TiO₂ nanomaterials elevated the rate of photosynthesis in spinach (Zheng et al., 2005). Fe/SiO₂ nanoparticles enlarged the shoot length of barley and maize plants (Najafi Disfani et al., 2017). Fe₃O₄ nanoparticles increased the chlorophyll content, carbohydrate, essential oil levels, iron amount, height of plant and number of branches/plant, leaves/plant thereby of *Ocimum basilicum* plants (Elfeky et al., 2013). It has been reported that nanomaterials increase the surface area of roots and leaves for nutrient absorption. They improve the efficiency of nutrient uptake either by (i) increasing nanopores formation (ii) enhancing the compatibility of molecular transporters or root exudates by forming new pores or (iv) exploitation of endocytosis or ion channels. Consequently, crops adsorb plenty of nutrients for a prolonged time and enhance the productivity of crops. As a result, farmers can earn more profit by using these nanofertilizers. Therefore, the application of nanofertilizers has been found significant in agricultural practices, particularly regions inclined to drought or unexpected flash flood. Such regions require early maturity of crops essential for sustainable agricultural productivity.

4.3. Applications of nanotechnology in insect-pest management

Insects and pests cause huge losses to crop yield. These have caused a loss of the fauna amounting to Rs. 50,000 crores in India in 2015 (Kumar and Arora, 2020). Therefore, it is important to use pesticides to control weeds, insects, bacteria, fungi, rodents, snails and several other microorganisms (Prasad et al., 2017). To maintain crop productivity the use of agrochemicals is continuously increasing at a global level (Singh et al., 2020). Conventional pesticides are toxic and their improper use can cause morbidity and mortality to living systems. Several other issues associated with conventional pesticides are insects or microbes' resistance to pesticides, lesser effectiveness, cost and sometimes affect non-target organisms. Data provided by European Union has fixed the permissible quantity of distinct types of pesticides and their associated components involving 0.1 µg/L and 0.05 mg/kg in potable water and food obtained from plants respectively (Khairy et al., 2018). It has been

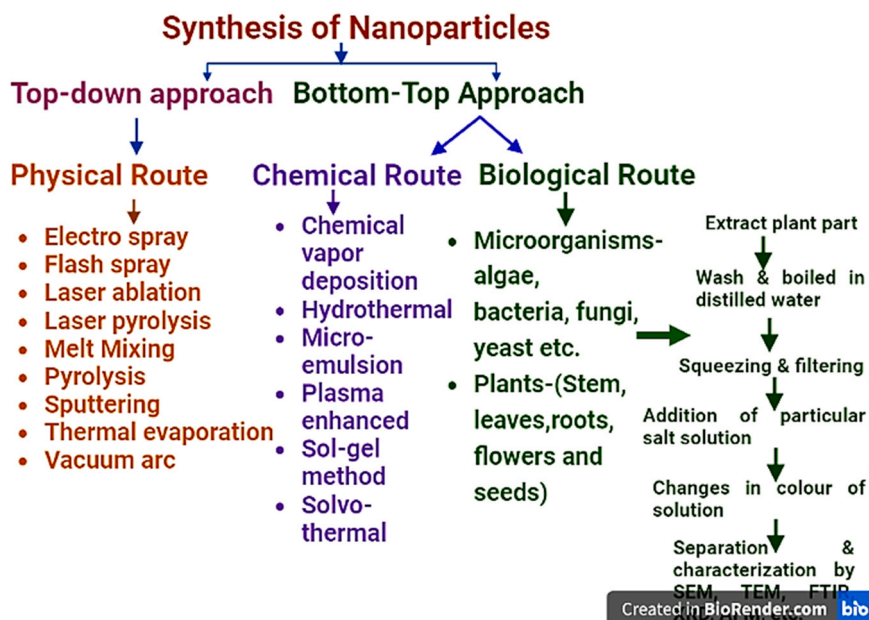


Fig. 4. Various approaches of synthesis of green nanoparticles.

analyzed that a very small amount i.e. 0.1% of exposed pesticides reached targeted pests while a huge amount (99.9%) remained in the environment as pesticide residues (Khairy et al., 2018). Therefore, there is an urgent need to develop some innovative approaches to overcome aforesaid issues. Researchers have formulated nano-pesticides to overcome the limitations of conventional pesticides. These nano-pesticides have been designed by encapsulating the chemical ingredients using nanomaterials. Metal nanoparticles had been found very effective against plant pathogens and used for the formulation of pesticides, insecticides and insect repellants (Barik et al., 2008). For instance, nanomaterials of silica protect the plant from the attack of silkworms by reducing the lipoprotein found in larvae of silkworms, Wu and Liu (2008) have reported the use of Si nanoparticles loaded with validamycin for the protection of host plants against various insecticides in a controlled manner. Nano-emulsion of oil in water has been used for the preparation of pesticides and these nano-emulsions can be used as pesticides against various insects which affect the productivity of crops (Wang et al., 2007). Beside these nano-emulsions, other nano-pesticides

such as essential oil-loaded solid lipid nanoparticles have also been used in agriculture (Shah and Wani, 2016). Nanocarriers of Zein, the storage protein of maize are used for plant pest repellents. These nanocarriers showed significantly high biocompatibility, efficiency and low toxicity. 2,4-dichlorophenoxyacetic acid formulated by AgIdea has also been used as nanopesticides (Hofmann et al., 2020).

Petosa et al. (2017) have reported that nano formulated pesticides integrated with polymers of nanocapsules and the pyrethroid bifenthrin (nC4P4-BIF) take more time for their release, and have more delivery potential in soil and hand water. In these pesticides, nCAP4 acts as a capable transport carrier of pyrethroid pesticides. In addition to these, nanomaterials used in the encapsulation of pesticides have characteristic features like high absorbency, heat resistance, solubility, crystallinity, and easily degradable (Ul Haq and Ijaz, 2019). It has been reported that nanoformulations of pesticides have enhanced systemic acquired resistance (SAR) of crop plants to prevent the attack of insects.

For instance, Si nanosphere formulations have increased the penetration power of pesticides into plants. These Si nanospheres after

Table 3
Various applications and advantages of nanomaterials.

Sr. No.	Nanoproducts	Advantages	References
1	ZnO NPs and TiO ₂ NPs	Augmented antioxidant activities in tomato plants	Hussain et al. (2021); Kolenčik et al. (2020)
2	Recyclable thermoplastic starch (TPS)	Unique mechanical strength with reduced water permeability	Jiang et al. (2020)
3	Precision farming	Nanosensors connected to global positioning system to evaluate soil conditions and crop growth in fields	Sishodia et al. (2020)
4	Nanovaccines, Nanoveterinary medicine, and Nanocapsules	Nanovaccines and Nanoveterinary medicine in the form of nanoparticles, buckyballs, dendrimers, nanocapsules for drug delivery, smart herds and cleaning fish ponds	Pramanik et al. (2020)
5	Macronutrient fertilizers coated with zinc oxide nanoparticles	Enhanced nutrients absorption by plants and the delivery of nutrients at the target sites	Shang et al. (2019)
6	Zeolites and Nano-clays	Increases water holding capacity and gradual discharge of agrochemicals for better absorption in soil	Shang et al. (2019)
7	Silver nanoparticles	Help in removal of <i>Campylobacter jejuni</i> from poultry	Vadalaesetty et al. (2018)
8	Acetamidrid loaded alginate-chitosan nanocapsules	Improved delivery of agrochemicals in the field, better efficacy, and better control of application/dose.	Duhan et al. (2017)
9	Silver nanoparticles	Help in removal of <i>Campylobacter jejuni</i> from poultry	Vadalaesetty et al. (2018)
10	Nanocides	Pesticides encapsulated in nanoparticles for controlled release and more efficiency	Nuruzzaman et al. (2016)
11	Buckyball fertilizer	Help in release of ammonia	Mukhopadhyay and Sharma, (2013)
12	Nanoemulsion	Neem oil (<i>Azadirachta indica</i>) nanoemulsion as larvicidal agent	Anjali et al. (2012)

reaching the cell sap exert a systemic effect that is responsible for controlled sucking insects for example aphids. In addition to SAR effect, nanoformulations have also altered the non-systemic behavior of pesticides (Hou et al., 2016). For example, nonsystemic behavior of ferbam formulated with metallic gold nanoparticles has increased the piercing properties inside the tea leaves.

Patil et al. (2016) have reported the reduced catalytic potential of trypsin (acting as insect protease) by latex-fabricated bioactive Au nanoparticles and thus used for insect control. Shang et al. (2019) reported that generally, herbicides kill above-ground parts of weed plants from the upper part of the ground but do not affect response to below ground parts of the plants like rhizomes or tubers.

The insecticidal activity of nanostructured alumina against two insect pests in stored food viz. *Sitophilus oryzae* L. and *Rhyzopertha dominica* (F.), have been investigated and mortality was observed after 3 days of continuous exposure of nanostructured alumina in treated wheat (Stadler et al., 2010). Table 4 depicts the various nanagrochemicals and nano-materials that are being synthesized for increasing the crops' productivity. Various types of nanoparticles have been developed and used to prevent plant diseases. These nanoparticles include nano forms of carbon, silver, silica and alumino-silicates. Various nanoparticles of silver, aluminium oxide, zinc oxide and TiO₂ have been used for the protection of rice from weevil and grasserie disease in silkworms caused by *Sitophilu soryzae* and *Baculovirus BmNPV* (*B. mori* nuclear polyhedrosis virus), respectively (Goswami et al., 2010). For this, a bioassay based on solid and liquid preparations of these nanoparticles was developed. These preparations of nanoparticles were applied on rice kept in a plastic box with 20 adults of *S. oryzae* and the response was perceived after 7 days. Treatment with hydrophilic silver nanoparticles was effective on the first day however subsequent day about > 90% mortality was seen using Si and aluminium oxide nanoparticles. After one week of exposure to hydrophilic Si nanoparticles, showed approximately 95% mortality while hydrophobic SiNPs showed 86% mortality (Goswami et al., 2010). Application of lipophilic silver nanoparticles on rice causes approximately 70% mortality. Treatment of aluminium oxide nanoparticles exhibited 100% mortality. Goswami et al. (2010) performed an assay for grasserie disease in silkworms. They reported that leaves of *B. mori* treated with ethanolic suspension of hydrophobic alumino-silicate NPs reduced the viral counts up to 86% (Goswami et al., 2010). *In-situ* synthesis of silver nanoparticles on fabric has been revealed on the surface of cotton fabrics and plant membranes using silver nitrate reduced by phenolics and flavonoids (Li and Yan, 2020). Moreover, silver nanoparticles synthesized in-vivo have shown promising applications in agriculture by controlling crop diseases and weeds expansion and increasing crop nutrients absorption.

Carbon is selected as a building molecule for the facile synthesis of nanomaterials. Carbon nanotubes (CNTs) are allotropes of carbon and are cylindrical. These have been used in various fields including agriculture. CNTs introduced into planted tomato seeds in soil, the growth and water uptake efficiency of the plants were improved (Henley et al., 2020). It indicates that CNTs act as vehicles for the delivery of desired compounds into seeds during germination and prevent the attack of pathogens on germinating seeds. CNTs are growth-promoting and not toxic for the plants (Duhan et al., 2017).

Ag nanoparticles have promising inhibitory and bactericidal properties and potent antimicrobial activities. Colloidal nano-Ag solution has shown antifungal activity against powdery mildew caused by *Sphaerothecapannosa varrosae* (Kim et al., 2017). A number of patents have been filed for 'Nano silver for diseases abatement in modern agriculture systems. Singh et al. (2021) have reported the synthesis of Ag nanoparticles from *Dioscorea bulbifera* L. These Ag nanoparticles (100 ppm) showed excellent inhibitory activity against *Fusarium oxysporum* and *Colletotrichum gloeosporioides*. Recently, Dutta et al. (2022) have investigated the antimicrobial activity of Ag nanoparticles synthesized from fruit extract of *Glycosmis pentaphylla* on crop plants. They investigated antifungal activity against *Alternaria alterata*,

Colletotrichum lindemuthianum, *Fusarium moniliforme* and *Candida glabrata* and antibacterial activity against *Bacillus subtilis*, *Streptococcus mutans*, *Escherichia coli* and *Salmonella enterica*. The maximum inhibitory effect of Ag nanoparticles was revealed from *A. alterata* and *B. subtilis*. Moreover, Ag nanoparticles prepared from *Pseudomonas* sp. inhibited bacterial pathogens such as *Acidovorax oryzae* and *Dickeya dadantii*. These bacterial pathogens cause bacterial soft rot and bacterial stripe diseases respectively (Paul and Roychoudhury, 2021). Antibacterial activity of Ag nanoparticles against *Citrobacter freundii*, *Erwinia* sp. and *Pseudomonas syringae* has also been revealed. These bacteria cause various pathogenicities including bacterial cankers, soft, rot, wilt, leaf spots, and discolouration of plant tissues in different plants. Ag nanoparticles exhibit antifungal activity by damaging fungal hyphae to interfere with nutrients absorption, inhibiting growth and spore germination (Kaur et al., 2018). For instance, Ag nanoparticles prepared from yeast inhibit *Penicillium* sp. *Helminthosporium oryzae*, *Rhizopus* sp. and *Botrytis cinerea* (Paul and Roychoudhury, 2021). Moreover, these nanoparticles also inhibit *Phytophthora* sp. and *Gloeophyllum* sp. The antifungal activity of these Ag nanoparticles can be improved by augmenting the quantity of reducing and stabilizing agents such as protein, polysaccharides, organic acids, vitamins and secondary metabolites found in medicinal plants.

The antiviral activity of Ag nanoparticles depends on factors like configuration, surface charge, and crystal charge. Although, the mechanism of action of antiviral is not well understood; however, the antiviral activity of Ag nanoparticles may be due to the attachment of nanoparticles at the virus surface for the interaction between envelope glycoproteins and coat proteins to inhibit virus replication. Ag nanoparticles have shown antiviral activity against sun hemp rosette virus, bean yellow mosaic virus, potato virus, tomato spotted wilt virus etc.

In addition to these, Ag nanoparticles prepared from *Ulva lactuca* and *Turbinaria turbinata* have also shown nematocidal activity against *Meloidogyne javanica* and *Meloidogyne incognita* infestations (Hamed et al., 2019). These nanoparticles inhibit growth, reduced the potency of egg hatching, increase larvae mortality in the juvenile phase and decreased egg production (Paul and Roychoudhury, 2021).

Exposure to Si makes crop plants more tolerant against diseases and stress (Ma and Yamaji, 2006). Aqueous silicate solution has been employed for the treatment of powdery mildew and downy mildew. Besides this, several other beneficial effects were seen including increased growth, physiological activities and resistance to diseases and stress of crop plants (Kanto et al., 2006). Ag is a potent disinfecting agent, therefore, it can destroy microbial populations and inactivates the enzymes involved in metabolic reactions of microorganisms by oligodynamic reaction and also suppress the growth of algae (Kim et al., 2017). The ionic state of Ag is not stable because of its high reactivity and therefore, it is converted into oxidized/reduced forms depending on the conditions of the physiological environment. Thus, Ag does not exhibit constant antimicrobial activity. Ionic states of silver are stable in the environment but have poor antimicrobial activity. Hence, Park et al. (2006) have prepared a hybrid of nano sized Si-Ag for prevention of various diseases in plants. This nano sized hybrid was conjugated with silica molecules. Silica-silver hybrid at 0.3 ppm has shown excellent antifungal activity and also controlled powdery mildews of pumpkin. They have also investigated the 'effective concentration' of nano sized silica-silver to control the growth of various fungi; and found that at 10 ppm there was 100% inhibitory effect on the growth of various fungi such as *Pythium ultimum*, *Magnaporthe grisea*, *Colletotrichum gloeosporioides*, *Botrytis cinerea* and *Rhizoctonia solani*. Nano sized silica-silver has also exhibited the 100% antibacterial activity at concentration 100 mg/L against *Bacillus subtilis*, *Azotobacter chroococcum*, *Rhizobium tropici*, *Pseudomonas syringae* and *Xanthomonas compestris* pv. *Vesicatoria* (Prasad et al., 2017). But higher concentration (3200 ppm) of these nano sized silica-silver has caused chemical injuries on cucumber and pansy plant (Park et al., 2006).

Silica-based nanomaterials have been synthesized using silica which can be used in medicine and drug discovery. Mesoporous silica

Table 4

Effects of various nanomaterials mediated nanofertilizers and nanopesticides used for increasing the productivity of crops.

Nanomaterials/nanoparticles (NPs)		Impact on crops	References
Nanofertilizers	Nano coated phosphate, urea	They meet nitrogen demand of the soil	Pandey (2018)
	Encapsulated nano-silver	They enhance the strength of roots and seed growth	Pandey (2018)
	Chitosan nanoparticles	They facilitate the release of plant growth hormone, 1-naphthylacetic acid	Pandey, (2018)
	Spraying of FeO nanoparticles	They improve productivity, protein content and spike-weight in wheat and work as a source of Fe for soybean plants	Pandey, (2018)
	Au nanoparticles	They help in multiplication of plant-growth promoting bacteria <i>Rhizobacteria</i>	Liu et al. (2012); Shukla et al. (2015)
	Super nano clay capsule comprised of fertilizers and pesticides	Help in release of nutrients gradually	Singh Sekhon, (2014)
Nanopesticides	Fe ₃ O ₄ nanoparticles	They increase quantity of chlorophyll pigment, carbohydrate, essential oil levels, iron amount, height of plant and number of branches/plant, leaves/plant thereby increase in organic matter of <i>Ocimum basilicum</i> plants	Elfeky et al. (2013)
	Urea HAP coated with wood powder fertilizer	Slow release of nitrogen	Kottegoda et al. (2011)
	Primo Maxx Syngenta	Improve the potency functional constituents and reduced frequency of use during growth of plants	Rani et al. (2020)
	Nanoformulated herbicide	Inhibit the growth of weed plants and germinating weedy seeds	Amna et al. (2019)
Crops/plants essential macroelements	Nanoencapsulated herbicides and pesticides	Improved the potency and targeted release of nutrients	Duhan et al. (2017)
	ZnO nanoparticles (Essential Microelement)	More fiber, carbohydrate, fat and ash content in <i>S. oleracea</i> and increased growth, chlorophyll content and yield was observed in <i>A. hypogaea</i> , <i>P. americanum</i> , <i>V. radiata</i> and <i>C. arietinum</i>	Achari and Kowshik, (2018)
	CaCO ₃ nanoparticles (Essential Macroelement)	Increases Ca ²⁺ ions uptake and control of insect pests in <i>Z. mauritiana</i>	Hua et al. (2015)
Crops/plants essential microelements	Mg nanoparticles (Essential Macroelement)	Improved growth and productivity, uptake of minerals and enzyme activity in <i>T. aestivum</i> and <i>V. unguiculata</i> subsp. <i>Unguiculata</i>	Delfani et al. (2014)
	Fe ₂ O ₃ nanoparticles (Essential Microelement)	More carbohydrate content and essential oil concentration in <i>O. basilicum</i> , increases photosynthetic rate, stomatal conductance and transpiration rates in <i>G. max</i> and growth parameters in <i>C. maxima</i> and <i>V. unguiculata</i> subsp.	Achari and Kowshik, (2018)
	Cu-chitosan nanoparticles	Antifungal activity against <i>Alternaria alternata</i> , <i>Macrophomina phaseolina</i> and <i>Rhizoctonia solani</i>	Duhan et al., (2017)
	Ag nanoparticles	Potent antifungal activity against <i>Bipolaris</i> spp., <i>Fusarium</i> spp., <i>Pythium</i> spp., <i>Clindrocarpon destructans</i> , <i>Cladosporium cucumerinum</i> , <i>Glomerella cingulata</i> , <i>Didymella bryoniae</i> , <i>Stemphylium lycopersici</i> and <i>Monosporascus cannonballus</i>	Duhan et al., (2017)
	SiO ₂ nanoparticles (Essential Microelement)	<i>Alternaria alternata</i> , <i>Penicillium digitatum</i> and <i>Alternaria citri</i>	Janmohammadi et al., (2016)
		Increased chlorophyll, protein, phenol contents and redox status in <i>Z. mays</i> , enhanced canopy spread, stem diameter, plant height, ground cover and the number of achenes in capitulum in <i>C. tinctorius</i> , alleviation in cadmium toxicity in <i>O. sativa</i>	
	Au nanoparticles	Antibacterial activity against <i>Klebsiella pneumonia</i>	Malarkodi et al., (2013)
	TiO ₂ and Ag nanoparticles	<i>Lactobacillus</i> spp.	Jha and Biointerfaces, 2010

nanoparticles are used as nanocarriers to enhance the efficiency of conventional pesticides. Nano-Si enhances the efficiency of pesticides by increasing the durability of pesticide release. Moreover, about 1–2.5 g/kg concentration of silicon oxide nanoparticles has been found lethal to *Callosobruchus maculatus*. These nanoparticles either block the spiracles and tracheas or damage the protective wax coating on the cuticle by physical absorption and abrasion (Rastogi et al., 2019). Moreover, silica nanoparticles damage the protecting lipid-water barrier of insect cuticles by physisorption. Consequently, insects die due to loss of water. Moreover, the application of modified hydrophobic nano-Si has also been used to control a wide range of agricultural animal ectoparasites (Singh Sekhon, 2014).

Several commercial-grade nano-pesticides using alumino-silicate nanotubes have been formulated. The spraying of these nano-pesticides on the plants causes quick stacking in the insect hairs and so consumes pesticide filled nanotubes. These alumino-silicate nano-pesticides are highly active and eco-friendly.

Nano-herbicides have been used to control weeds from agricultural fields. Encapsulations of herbicide in polymeric nanoparticles reduce toxicity and become eco-friendly. Nano tools prepared from biochar, attapulgit, azobenzene and amino silicon are used in the encapsulation of glyphosate (Camara et al., 2019). Satapanajaru et al. (2008) reported the efficiency of nano zerovalent iron (nano ZVI) to dechlorinate atrazine (2-chloro-4-ethylamino-6-isopropylamino-1, 3, 5-triazine) in the

contaminated water and soil. Nanoparticles encapsulated with the herbicide have been used for delivery in the roots of weed plants. Consequently, the penetration of encapsulated molecules enters in the root system and from there, these molecules translocate to different cells where they interrupt the physiological processes like pyruvate forming the glycolysis cycle and thus, plants lead to death (Duhan et al., 2017). Various types of nanoherbicides have been synthesized and their effects on the plants have been evaluated such as effect of chitosan nano-emulsion and sodium triphosphate paraquat, clomazone/alginate/chitosan nanomaterials on *Allium cepa*, effect of complex of paraquat, formulation of silver nanoparticles chitosan matrix on *Eichhornia crassipes* and nano-emulsion of glyphosate isopropylamine (GIPA) on *Elwsine indica* (Chaw et al., 2012).

A supramolecular photo-responsive vesicle encapsulated with paraquat was designed using the self-assembly of derivatives of cucurbit, uril, paraquat and azobenzene showed increased herbicidal activity against *Estuca arundinaceae* (Gao et al., 2018). Carboxymethyl chitosan combined with photolabile 2-nitrobenzyl group was used for the delivery of diuron herbicide (Camara et al., 2019). Moreover, photoactive micelles were synthesized by self-assembly of polyethylene glycol (PEG) and the pesticide dichlorophenoxyacetic acid (2,4-d) using photoactive triggering molecule namely 3-nitro-4-bromomethylbenzoic acid (NBA). These micelles released the pesticide in a controlled manner in sunlight (99.6%) and UV radiations (99.5%) for a long duration of 8 h and 9 min respectively (Ding et al., 2016). Coumarin copolymer of acrylate and polyethylene glycol encapsulated with 2,4-d was synthesized. This copolymer showed enhanced herbicidal activity and stability in sunlight and VU-light (Serhan et al., 2019).

Table 5 shows the effect of nano-herbicides on various plants.

4.4. Applications of nanotechnology in climatic adaptation

The development of nanotechnology-mediated products such as nanofertilizers has increased agricultural productivity in adverse environmental conditions as well. It has been reported that stress induced by a saline environment declines crop productivity by 25% globally. Scientists have made efforts to resolve this issue with the help of nanomaterials. Crop sustainability is also attributed to biotic and abiotic stresses using ENMs as they increase the survival ability of plants by resisting or resiliency to a varying range of stresses including temperature, salinity, drought, flood and various microbial/viral infections (Lowry et al., 2019). These ENMs make the crops withstand adverse conditions without decreasing yield and nutritional value by efficient uptake of agrochemicals. They also enhance the bioavailability of macronutrients N and P through the modification of microbial activity, and increasing their abundance (Simonin et al., 2018). Though, ENMs have shown tremendous application in increasing agricultural productivity, however, there is still an urgent need to find precise concentration, exact plant part and time of application of ENMs (Lowry et al., 2019). Besides these, efforts are also needed to understand the mechanism of action of ENMs with plant systems. People should be aware of the beneficial and toxic impacts of ENMs on the commercialization of ENMs-based agrochemicals.

It has been reported that the use of SiO₂ nanoparticles has improved seed germination, increased plant organic matter and photosynthetic chlorophyll pigment by accumulating proline under NaCl stress in tomato and squash plants (Siddiqui and Al-Wahaibi, 2014). Foliar spray of iron sulfate nanoparticles has increased the salinity tolerance level in sunflower harvested fields (Torabian et al., 2017). Additionally, FeSO₄ nanoparticles enlarged the leaf area, increased shoot organic matter, fast CO₂ assimilation rate, more chlorophyll pigment synthesis (36–57%), efficient performance of photosystem II, more iron amount and drastic decrease (15%) in sodium concentration in leaves. Moreover at elevated temperature and saline environment, introduction of CeO₂ nanoparticles has increased the photosynthetic rate by 67% and thereby increasing the agriculture productivity due to their antioxidant properties (Wu et al., 2017).

Table 5
Use of different nanomaterials as nanoherbicide.

Sr. No.	Nanoemulsion/nanomaterials/nanoparticles/ Nanoformulation	Targeted herbs/weeds	Effect on herbs/weeds	Reference
(1)	Ag, Cu, Fe, Zn, Mn nanoparticles	<i>Allium cepa</i>	Inhibit growth of roots	Yan and Chen (2019); Konotop et al., (2014)
(2)	Solid lipid nanoparticles + Atrazine + Simazine	<i>Raphanus raphanistrum</i>		De Oliveira et al. (2015)
(3)	Paraquat + formulation of Ag nanoparticles chitosan matrix	<i>Eichhornia crassipes</i>	Nanoformulation showed the necrotic lesions on the leaves	Karthick Raja Namasivayam et al., (2014)
(4)	CuO and ZnO nanoparticles	<i>Fagopyrum esculentum</i>	Inhibit root growth	Lee et al., (2013)
(5)	Nanoemulsion of Glyphosate Isopropylamine (GIPA)	<i>Elwsine indica</i>	Nanoemulsion causes lower surface tension and thus penetrates effectively due to large surface area	Chaw Jiang et al., (2012)
(6)	CuO and ZnO nanoparticles	<i>Cucumis sativus</i>	Provide defense mechanism against oxidative stress	Kim et al., (2012)
(7)	Cu nanoparticles	<i>Raphanus sativus, Lolium perenne and</i>	Inhibit cell growth and reduced transpiration rate	Hawthorne et al., (2012); Musante and White (2012)
(8)	CuO nanoparticles	<i>Lolium rigidum</i>	Cellular DNA damage	Atha et al., (2012)
(9)	Cu nanoparticles	<i>Elodea densa</i>	Reduced rate of photosynthesis	Nekrasova et al. (2011)

Detoxification of hazardous components, existing in the environment has also been carried out using nanomaterials. Wang et al. (2015) reported that the foliar spray of Si nanoparticles enabled the rice plant to grow under Cd stress environment. Similarly, effectiveness of Si nanoparticles against Pb, Cu, and Zn along with Cd has been reported (Wang et al., 2016). CuO, ZnO, and MgO nanoparticles have presented several plants and soil-borne infections spread by *Botrytis cinerea*, *Alternaria alternata*, *Monilinia fructicola*, *Colletotrichum gloeosporioides*, *Fusarium solani*, *Fusarium oxysporum* fsp *Radicis Lycopersici*, *Verticillium Dahliae*, *Phytophthora infestans* and *Ralstonia solanacearum* (Imada et al., 2016). Devi et al. (2019) have reported the application of *Bacillus thuringiensis* (Bt) nanocomposites as a pesticide. In addition to these, the use of SiO₂ and ZnO nanoparticles enhanced the free proline amino acid concentration, nutritional ingredients, efficient uptake of water and better antioxidant activity. Beneficial effects of ZnO nanoparticles was revealed in plants growing in adverse environmental conditions due to the functional activities of diverse enzymes including superoxide dismutase, catalase, peroxidase, nitrate reductase, and glutathione reductase (Shalaby et al., 2016). ZnO nanoparticles have been used for increasing growth, yield and Zn content (7.9–20%) in wheat crops (K. Singh et al., 2021). Furthermore, these ZnO nanoparticles at 5 mg/kg are found efficient in producing wheat in Zn deficient, neutral and alkaline soil.

Microarray based investigation revealed that Ag nanoparticles application in *Arabidopsis* showed regulated expression of several genes either by increasing or decreasing their expression (Banerjee and Kole, 2016). For example, these nanoparticles increased the expression of genes coding various plant enzymes like cation exchanger, cytochrome P450-dependent oxidase, superoxide dismutase, and peroxidase. Contrary to these enzymes, Ag nanoparticles have reduced gene expression of enzymes responding to pathogens, plant hormone signaling systems like ethylene and auxin and increased the expression of salt stress-related genes up to 4 fold.

Stimuli responsive nanoparticles have been used in soil for targeted and slow release of fertilizers, fungicides, herbicides, and plant growth regulators for increasing crop productivity (Majeed et al., 2018). Agricultural productivity can also be augmented by developing a redox responsive system by encapsulating abscisic acid which increased the level of glutathione for regulating plants' physiological conditions under stress (Sun et al., 2018). Researchers have also demonstrated the application of nanoparticles in increasing the survival capacity of *Arabidopsis* plants in water stress by closing their stomata and enhancing expression of At-GALK2 gene (Camara et al., 2019). Nanoparticles responding to multiple stress have been synthesized for the exogenous delivery of gibberellic acid (GA3) under saline and drought conditions. In this, GA3 was sealed in hollow mesoporous silica covered with Fe₃O₄ nanoparticles functionalized by carboxylatopillar[5]arene ammonium (WP[5]A) (Li et al., 2019). The targeted release of GA3 was regulated by providing various stimuli like acidic/basic pH, polyamines and ultrasound. Furthermore, biopolymers of chitosan were used to evaluate the release of GA3 in varying ranges of temperatures. During regulation of GA3 release temperature changes the viscosity and hydrophobicity of polymers. The release ability of chitosan biopolymers was revealed at 30 °C than 25 °C. Smart release of indoleacetic acid and naphthoxyacetic acid has been achieved by synthesizing a photo-responsive system based on the photo-removable protecting group of coumarin (Camara et al., 2019). Application of this system increased the growth of *Cicer arietinum* by releasing plant growth regulators in a controlled manner.

4.5. Applications of nanotechnology in mutation breeding

Nanotechnology can be employed to modify the genetic material of crop plants thus helping in better crop productivity. Mutations, either natural or induced, play a significant role in agricultural systems. Various conventionally used mutagens including ethylmethanesulfonate (EMS), methylmethane sulfonate (MMS) and X-rays, gamma rays etc. have shown that nanotechnology can provide a new platform to induce new desired traits in the crop plants. In Thailand, Chiang Mai University's Nuclear

Physics Laboratory has developed a novel white-grained rice variety from conventional purple-coloured rice variety called 'Khao Kam' using a nanotechnological approach. The word "Kam" describes dark purple, and this rice variety has gained popularity due to its characteristics stem, leaves and grains which are purple in colour. Scientists have modified the leaves and stems color of Khao Kam from purple to green using nanotechnology and this new rice variety has produced grains of white color. In this method, a rice cell's wall and membrane are punctured at the nanoscale to shoot a nitrogen atom. The hole was formed by a particle beam which was a flow of rapidly moving particles while the nitrogen atom was injected via the hole. The injected nitrogen atom has rearranged the genetic material of the target cell of rice. The plants generated by new rice cells were known as 'Atomically Modified Organisms (AMOs)'. These new plants were modified at the atomic level (Kumar et al., 2016).

Detection of viral pathogens using biomarkers has facilitated the easy identification of viruses in accurate disease stages. Identification of characteristics protein formation in both normal and infected states helps in the detection of proteins produced in the infected cycle (Usman et al., 2020). Current achievements of nanotechnology have been reported in tissue engineering and nanomaterials based transport of CRISPR (clustered regularly interspaced short palindromic repeats)/Cas (CRISPR-associated protein) mRNA, and sgRNA for the transformation of genetic constituents of crop plants (Shang et al., 2019; Zhang et al., 2019). Nanomaterials have also been used for the transport of CRISPR/Cas9 single guide RNA (sgRNA) (Yadav et al., 2021). CRISPR/Cas9 complex composed of redundant spacer arrays of CRISPR and Cas proteins is involved in RNA-directed protection in bacteria by editing plant genetic material. The application of nanomaterials has improved the efficiency as well as specificity of CRISPR/Cas systems by reducing the hurdles of targeted alteration. It has been demonstrated that the cationic arginine gold nanoparticles (ArgNPs) combined with Cas9En (E-tag)-RNP (ribonucleoproteins) and transported sgRNA have enhanced cytoplasmic/nuclear gene editing efficiency in cultured cell lines consequently facilitate future research into crop development (Lahiani et al., 2013).

4.6. Applications of Nanosensors/nanobiosensors in agriculture for the precision farming

Nanobiosensors have been used for analyzing a diverse range of fertilizers, herbicides, insecticides, pathogens, the texture of the soil, and their regulated utilization in agriculture to enhance crop yield (Rai et al., 2012). Singh et al. (2010) have developed an immunosensor based on Au nanoparticles for the detection of *karnal bunt* in wheat plants. Nano plant hormone regulators like auxin assist scientific communities in knowing the mechanism of plant roots to adjust in harsh environments. Thus, nanosensors are anticipated to improve agriculture, food, and environmental sectors. Development of portable nanodevices can analyze insects, diseases, pathogens, and pollutants (Farrell et al., 2010). Razmi et al. (2019) have reported the colorimetric detection of tomato yellow leaf curl virus (TYLCV) in the infected tomato plants using localized surface plasmon resonance based on Au nanoparticles. Kumar and Arora (2020) have reported the development of optical biosensors for the identification of genetically modified plants. They have reported the detection of *Bacillus thuringiensis* (Bt) gene in genetically modified rice plants using Surface Enhanced Raman Spectroscopy (SERS) that was integrated with a barcode composed of bacterial small DNA sequence and silica encapsulated Au nanoparticles as a spectroscopic tags. Furthermore, Fu et al. (2018) have detected the active components found in different tissues of five species of *Lycoris* bulbs namely *L. chinensis*, *L. radiata*, *L. aurea*, *L. sprengeri* and *L. straminea* by designing electrochemical biosensors. Moreover, biosensors are novel analytical devices that can provide constructive information to monitor the quantity of specific metabolites formed during distinct metabolic reactions of a plant (Singh et al., 2020). A comparison of different analytical parameters of different types of biosensors for the detection of pesticides in real samples in Table 6.

Table 6
A comparison of different analytical parameters of different types of biosensors used for agriculture purposes.

Type of biosensor	Name of nanomaterials and immobilization substrate	Target analyte	Advantage	Limit of detection (LOD)	Sensitivity	Response time (Minutes)	Stability (Days)	Reference
Paper based optical	Unicellular green photosynthetic algae <i>Chlamydomonas reinhardtii</i> was immobilised on a paper substrate soaked with an agar thin film and placed in a glass optical measurement cell	Atrazine	Acted as effective support in smart agriculture for on-site, eco- friendly, economic and sensitive for atrazine analysis	4 pM	-	15	21	Scognamiglio et al. (2019)
Electrochemical	<i>Burkholderia cepacia</i> lipase (BCL)@MOF nanofibers and chitosan onto glassy carbon electrode	Methyl parathion	Exhibited high sensitivity, rapid and reliability for detection of methyl parathion residues in vegetable samples	0.067 µM	-	-	21	Wang et al. (2019)
Electrochemical	Acetylcholinesterase (AChE) immobilized on s-SWCNTs wrapped with bovine serum albumin (BSA) immobilized on glassy carbon electrode	Methyl parathion	Showed good repeatability and reproducibility for MP detection	3.75×10^{-11} M	-	15	33	Kumar and Sundramoorthy (2019)
Microfluidic Electrochemical	Paper based screen printed carbon electrode modified with Prussian nanoparticles	Paraoxon, 2,4-dichlorophenoxyacetic acid, and atrazine	3-dimensional origami paper device exhibited quick, inexpensive, efficient and reliable detection of pesticide surface water	10 and 20 ppb	-	2	-	Arduini et al. (2019)
Electrochemical	Acetylcholinesterase adsorbed on chitosan (CS), TiO2 sol-gel, and reduced graphene oxide (rGO) based multi-layered immobilization glassy carbon electrode	Dichlorvos (DDVP)	Detection of DDVP was very reliable, simple and rapid	29 nM	-	25	30	Cui et al. (2018)
Surface enhanced Raman scattering (SERS)	Gold (Au) coated electrospun PVA nanofibers	Deltamethrin, quinalphos and thiocloprid	Showed high reproducibility, stability and reliability	0.01148 mg/L	-	-	-	Chamuah et al. (2018)
Electrochemical	Nickel oxide nanoparticles immobilized on screen printed electrode	Parathion	Displays high electrochemical activity including stability, sensitivity, selectivity and applicability for organophosphate pesticide (Parathion) determination	0.024 µM	-	-	-	Khairy et al. (2018)
Electrochemical impedimetric	Acetylcholinesterase (AChE), chitosan and metal carbides (MXenes) nanosheets immobilized onto glassy carbon electrode	Malathion	Displayed standard reproducibility, satisfactory consistency, and anti-interference ability	0.3×10^{-14} M	-	10	38	Zhou et al. (2017)
Electrochemical	Electropolymerized polypyrrole (PPy)/polyphenol oxidase (PPO)	Atrazine	Provided fast and technically user-friendly detection of atrazine	0.1 ppm	-	60	21	El Kaoutit et al. (2004)
Electrochemical	3D graphene oxide network/ multi-walled carbon	Carbofuran and paraoxon	exhibits good reproducibility and high	-	-	10	20	Li et al. (2017)

(Continued on next page)

Table 6 (continued)

Type of biosensor	Name of nanomaterials and immobilization substrate	Target analyte	Advantage	Limit of detection (LOD)	Sensitivity	Response time (Minutes)	Stability (Days)	Reference
Optical	nanotube composites immobilized on glassy carbon electrode		stability, which demonstrates good efficiency in spinach, cabbage and water samples	0.015 and 0.025 ng/ mL, respectively				
	AChE was immobilised onto the eggshell membrane	Malathion	Displayed high rapidity, simplicity, cost-effective and consistency	0.1 ng/mL		30	31	Kaur et al. (2015)
Electrochemical	-	Paraoxon	Showed high stability and quick response	$6.5 \cdot 10^{-10}$ M	$2.23 \mu\text{A mM}^{-1}$	10	28	Zhang et al. (2014)
Electrochemical	Acetylcholinesterase (AChE) encapsulated with silica matrix and immobilized on a nanohybrid of gold nanoparticles, polypyrrole, and reduced graphene oxide sheets deposited on glassy carbon electrode	Paraoxon-ethyl	high stability and excellent activity together with a fast response to organophosphorus pesticides	0.5 nM	-	15	10	Yang et al. (2014)

It can be inferred from Table 6 that attention has been given to the fabrication of electrochemical biosensors for the detection of biotic and abiotic analytes affecting crops. This may be due to their simplicity, sensitivity, specificity, reproducibility, accuracy, user-friendly, rapidity, cost-effectiveness, and ease of miniaturization (Neethirajan et al., 2018). Miniaturized electrochemical point-of-care devices have offered direct benefits to farmers by quick analysis of targeted analytes to prevent the loss of agricultural yield from harmful analytes of crops (Li et al., 2020). Though, optical biosensors have also been used for miniaturization, however; these sensing systems are based on absorbance, fluorescence, and colorimetric reactions (Mahato et al., 2018). Hence, sometimes they give a false positive or negative performance. Further optical biosensors are more susceptible to environmental interferences, physical injury and poor consistency (Chen and Wang, 2020). For further sensing systems, scientific communities must develop innovative, more sensitive, economical, quick and user-friendly electrochemical nano tools and devices for the simultaneous on-site, automated detection of multiple analytes present in the surroundings of a standing crop by limiting the need for sample pre-treatment procedures.

Several approaches such as imaging, spectroscopy and fluorescence from the visible to the infrared have been used for monitoring physical traits related to crop stress and deficiency (Giraldo et al., 2019). Although these techniques provide necessary information viz. leaf area, chlorophyll content and fluorescence (Zhao et al., 2016), stomatal conductance, transpiration use efficiency (Al-Tamimi et al., 2016), water potential and leaf temperature however, they are not efficient in early detection of stress and nutrients deficiency of individual plants (Giraldo et al., 2019). Chlorophyll fluorescence used for crops' impaired growth due to reduced chlorophyll quantity and leaf surface area is not always reliable for early indication and detection. On the other hand, Raman and infrared spectroscopy shows minimum signal-to-noise ratios but it needs expensive equipment and complicated operation procedures. This technique due to its portability is used for the examination of leaf parameters in the fields. Airborne detecting tools have not been optimized for the investigation of individual plants (Zarco-Tejada et al., 2018). Moreover, these tools are affected by sunlight, low signal-to-noise ratio and interfering environmental factors such as incorporation of alien species (Li et al., 2014). Sensing tools have facilitated the simultaneous monitoring of distinct plants in the fields. Various electrical devices such as mobiles, hyperspectral cameras and automated machines can be conjugated with nanosensors. Because nanomaterials based approaches are used for transducing the imperceptible plant stress-related chemical signals into optical, wireless or electrical signals that can be measured by existing phenotyping instruments like greenhouse, growth room or field scan analyzers. Real-time detection of specific environmental stress can be revealed from distinct chemical traits or signaling molecules of plants.

Researchers have developed several wearable sensors for the monitoring of plant growth, rate of transpiration, plant stress including drought and salinity, and microclimatic parameters such as humidity, temperature and light (Lee et al., 2021). Furthermore, these wearable sensors have also been used for the detection of pesticides. Li et al. (2021) have developed multiplexed wearable sensors using reduced graphene oxide nanosheets functionalized with gold nanoparticles for the real-time detection of plant volatile organic compounds like green leaf volatiles and phytohormones in the ambient environment. This sensor was stable under mechanical perturbations due to wind blowing and hand touching. This sensor was also used for the investigation of temperature and humidity. Moreover, this wearable sensor was used for the *Phytophthora infestans* detection in infected tomato plants in the acute stage. Real-time measurement of mechanical injury due to abiotic stress was also investigated by in-situ monitoring of plant VOCs. Analytical performance of this multiplexed wearable sensor revealed high sensitivity (LOD 0.1–3.4 ppm), accuracy, improved stability, early detection of *P. infestans* (within 4 days) and quick response time (20 s) of plant VOCs detection.

Electronic nose (E-nose) technologies have provided remarkable applications in the efficient management of agricultural practices including cultivation, harvesting, crop production and storage of crops (Seesaard et al., 2022). The working of E-nose system depends on the human olfactory system which consists of three components viz. sample delivery part, detection and computing system. In the sample part, a sample is injected directly into a clean air carrier to the equipment. In the detector part, varying ranges of aroma molecules interact with the embedded sensor chamber at room temperature or high temperature. The computing system removes the background interference, records electrical signal data and detects the desired aroma using pattern recognition algorithms. Plant VOCs have been detected by an E-nose system based on functionalized capacitive micromachined ultrasonic transducer array (Sennik et al., 2021). Polymers, phthalocyanines, and metals were used for the functionalization of E-nose. This E-nose was used to detect diverse VOCs such as 1-Octanol, linalool, p-Xylene, styrene and (Z)-3-hexenol. LOD and response time of this E-nose was 500 ppb and 10 min respectively. The E-nose system has also been used to detect infection caused by *Phytophthora plurivora* and *Pythium intermedium* (Borowik et al., 2021).

Precision farming, based on smart sensors, helps in increasing agriculture productivity through the effective utilization of agricultural ingredients such as water, nutrients, and chemicals, rapid, simple, sensitive, specific, portable and cost-effective. Precision agriculture

makes use of GIS, GPS and to remotely identify crop pests or identify stress like drought. The nanosensors enable to recognize the plants infecting viruses, other pests and nutrient levels in the soil (Brock et al., 2011).

Precision farming, based on nanomaterials, has reduced the cost, labour, improved effectiveness and ecofriendly (Ali et al., 2014). Moreover, nanosensors fabricated for agricultural purposes have exhibited several benefits such as measuring and examining the growth of crop plants and rhizosphere parameters, nutrient ingredients, hazardous effects, and microbial infection. They have also been used to access the release of fertilizers and pesticides into the environment that affect the soil and crop vitality, productivity and safety for sustainable agriculture and environmental system (Fig. 5). In nature, living organisms have been used for sensing the existing parameters of the environment. Therefore sensors fabricated with conjugated living entities and nanomaterials have several advantages as during sensing of any impairments they are more specific, sensitive and give quick responses to sense the impairments (Dubey and Mailapalli, 2016). For instance, real-time assessment of crops has been carried out by nanosensors integrated with global positioning system (GPS). These nanosensors examine the regulated dispersion mechanism through nanoscale carriers involving wireless signals distributed all over the agricultural area. Thus, real-time and inclusive scrutinization of the cultivated fields for growth and valuable information has been provided by these

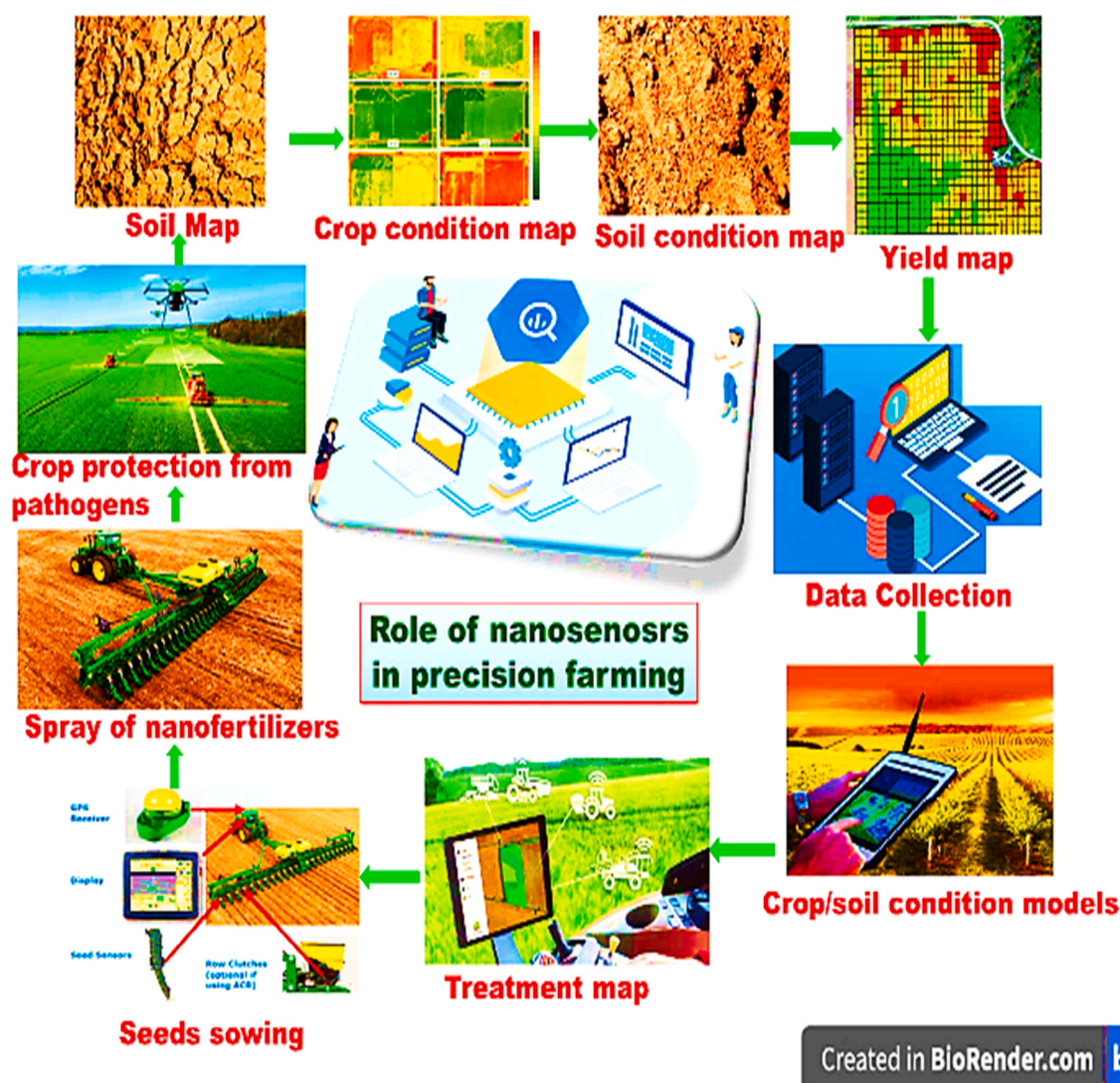


Fig. 5. Pictorial illustration of role of nanosensors in precision farming.

nanosensors. Consequently, provide efficient management approach by reducing overindulge of agricultural ingredients (Chen and Yada, 2011). Computer based irrigation systems have also been linked with sensor technology. Nanosensors have been used for the in-fields assessing of pressure exerted by water residing in soil system connected with independent irrigation control in the water scarced region (Hossain et al., 2020). Afsharinejad and co-workers (2016) have developed a wireless nanosensor that was used for the detection of pest infections. Nano-biosensors have also been employed for the estimation of ground water level in the fields, moisture quantity and nutritional ingredients in soil system (Pandey, 2018).

Recent developments have led to the production of bionic plants. These plants have been produced by incorporating nanoparticles inside chloroplasts of plants to amplify photosynthetic efficiency and are thus used in precision farming (Ghorbanpour and Fahimirad, 2017). The purpose of these plants is to produce an array of wild-type plants which are self-powered light sources and infrared communicating devices and groundwater sensors. Moreover, advanced sensing systems have been designed to provide real-time information on growing plants. These devices can detect chemicals released in air and ground water. Giraldo et al. (2014) have documented that the inserted single-walled carbon nanotubes (SWNTs) in the bionic plants have accelerated the electron transfer rate of light-adapted chloroplasts by increasing photoabsorption from the natural environment. They reported that the insertion of SWNTs has suppressed the formation of reactive oxygen species and increased the rate of photosynthesis (Wong et al., 2017). There are various stress hormones such as jasmonic acid, methyl jasmonate, and salicylic acid which enable plants to withstand stress conditions. Wang et al. (2010) have demonstrated that biosensors based on Cu nanoparticles can detect pathogenic fungus infestation by monitoring the concentration of salicylic acid in oil seed. Besides SWNTs, multiwalled carbon nanotubes (MWNTs) have also been reported for the regulation of plant development by examining the level of auxin hormone and providing information about how plant roots survive in marginal soils (McLamore et al., 2010). Sensing the humidity, using potassium niobate (KNO_3), nanofibers have been developed (Kumar et al., 2016). Fang et al. (2017) have designed a marker free glutathione controlled platform integrated with up conversion nanoparticles (UCNPs)/Au nanoparticles to detect acetylcholinesterase (AChE) activity and hazardous Cd^{2+} in the water sample. These developments indicate that precision farming has promising applications to attain food security (Finger et al., 2019; Roberts and Mattoo, 2019).

Precision farming, involving GPS, helps to monitor the topography of agricultural fields. The uneven crop-fields can be identified easily and may be used for specific purposes (Bobby et al., 2009). This approach can also be used for infield monitoring of yield and soil conditions. But the precision farming is in the developing stage and require many years for collecting ample information for its implementation (Saiz-Rubio and Rovira-Más 2020). Therefore future research should be focused on further improvement based on novel tools and devices that must be user-friendly, economic and quick for achieving.

Engineered nanomaterials are used in the monitoring of various signaling molecules viz. reactive oxygen species (ROS), calcium (Ca^{2+}), glucose, sucrose, nitric oxide (NO) and plant hormones such as abscisic acid (ABA), jasmonic acid, methyl salicylate and ethylene. Therefore, nanomaterials based techniques can help to understand the mechanism of plant stress communication and to monitor the health status of plants. Real-time detection of Ca^{2+} ion levels in entire plants under herbivore attack was revealed by using a fluorescence technique (Toyota et al., 2018). The development of genome specific sensors in plants is based on the formation of transgenic material in standing plants. Distinct sensing mechanism in plants by genetically encoded sensors is based on from protein-protein interactions involving covalent interactions which augment the fluorescence intensity. Sugars (glucose and sucrose) in the leaves and roots of transgenic plants namely *Arabidopsis thaliana* and rice were detected by using sensors

integrated with fluorescence resonance energy transfer under abiotic and biotic stresses (Giraldo et al., 2019). Biosensors are used for the in vivo detection of hydrogen peroxide in chloroplast and nuclei. These biosensors have shown high sensitivities as they can detect slight concentration variation within seconds (10 s). Moreover, nanomaterials integrated biosensors have been used for the delivery of nucleic acid sequences without using genetic techniques (Demirer et al., 2019).

For instance, SWCNT encapsulated with exogenous DNA can penetrate plant lipid bilayers of leaf lamina by passive and spontaneous translocation processes without *Agrobacterium* or gene gun particle bombardment (Giraldo et al., 2019). Furthermore, SWCNTs have also been used to deliver plastid DNA to the chloroplast of various plant species. Most of biosensors are positioned in cell cytosol therefore, the plastid genome provides a platform for developing translatable sensors for wider plant taxa than the nuclear genome (Walia et al., 2018). SWCNTs based nanosensors are used for the detection of different signaling molecules including ROS, NO, calcium, glucose, dopamine, nitroaromatics and proteins (Giraldo et al., 2019). Quantum dots have also been used for the optical detection of glucose in plant tissues. Metal-organic frameworks (MOFs) are three-dimensional structures exhibiting large surface area. In-situ fluorescence emission in plants by these MOFs revealed the presence of acetone content in the air because the presence of acetone in the environment alters the intensity of fluorescence of MOFs by volatile components i.e. acetone (Richardson and Liang, 2018). Fluorescent MOFs generated by plants in situ allowed them to report acetone levels in the air through fluorescence changes in the presence of these volatile compounds (Giraldo et al., 2019).

4.7. Miscellaneous applications of nanotechnology in the agricultural system

The nanotechnology has reformed various areas of the agriculture sector through various materials and devices for the treatment of diseases, fast detection and improving the nutrient absorbing capacity of plants. This has been achieved by developing smart sensors and smart delivery of nano-pesticides at the affected site that can fight infected crops (Aune et al., 2017). Future research is focused on nano-based catalysts which will augment the efficiency of insecticides and herbicides and require them in very low quantity. Nanotechnology has impacted the environment by using renewable energy resources, filters, or catalysts to reduce pollution by absorbing or degrading various pollutants and thus, helped in the protection of the environment (Tungittiplakorn et al., 2005). Bhattacharyya et al. (2010) have reported the relevance of nanotechnology in diverse areas such as nano-foods production, nano-foods packaging and nano-farming. Nanoparticles of polyethylene glycol loaded with garlic essential oil and exhibited insecticidal activity for adult *Tribolium castaneum* found in the stockpiled foodstuffs. It was found that about 80% protection from adult *T. castaneum* had been achieved by continuous and gradual release of the active ingredients from nanoparticles (Yang et al., 2016). Fig. 6 illustrates the tremendous applications of nanotechnology in agriculture.

4.7.1. Applications of nanotechnology in food industries

Nanotechnology has diverse applications in food industries. Nano approaches have been adopted for packaging and protection to smart delivery (Chen and Yada, 2011). Pandey et al. (2018) have reported the significance of nano-composites in food packaging to enhance the safeguarding and life expectancy of agricultural foods by inserting antimicrobial agents. Moreover, these nanocomposites have increased the resistance to temperature, and automated stress and reduced the diffusion of oxygen in plants. Researchers have also documented the addition of nanocapsules encapsulated with precise ingredients like vitamins, color and flavor enhancers into foods where they act as inert components. After consuming such foods, inserted nanocapsules are released into the body according to the need of cells (Katouzian and Jafari, 2016; Pandey, 2018).

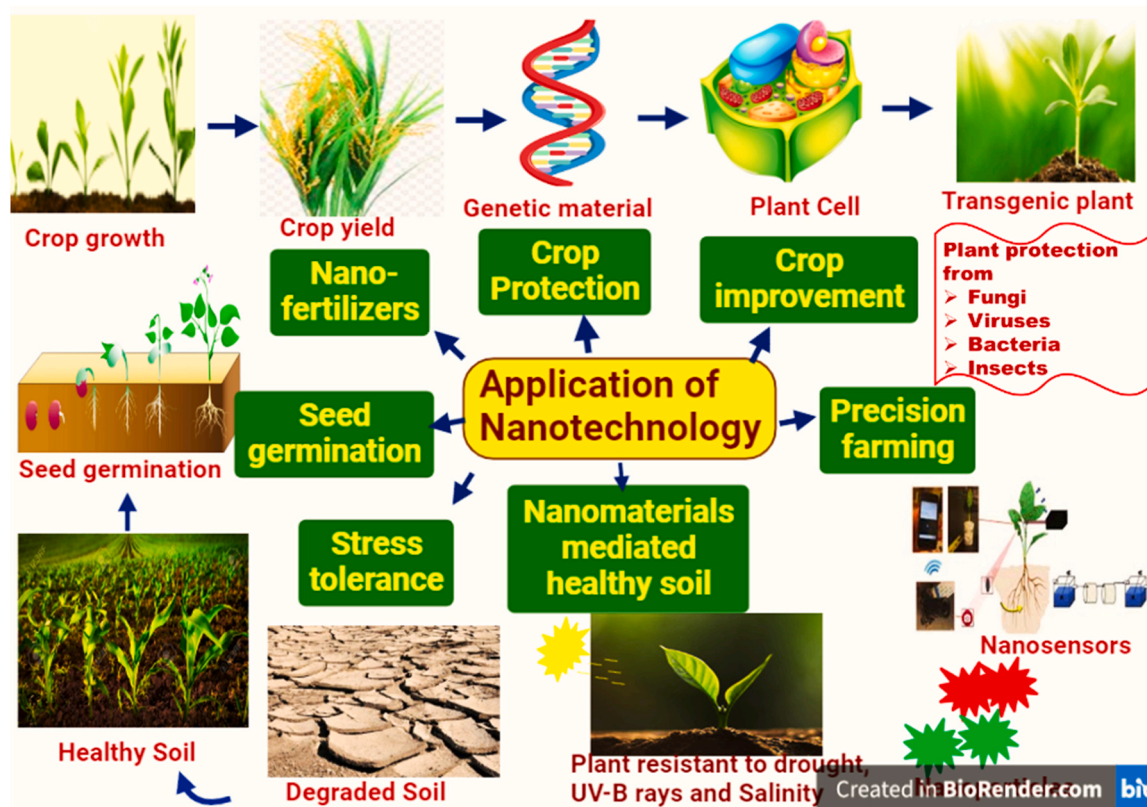


Fig. 6. Diagrammatic illustration of uses of nanotechnology in agriculture.

4.7.2. DNA nanotechnology in agriculture systems

Researchers are giving more attention to reducing the dimensions of biological constituents to the nanoscale to simplify diagnostics and therapeutics strategies. In 1976, Genentech Company developed an automated process for synthesizing DNA and constructed a fully functioning artificial gene and artificial DNA which gave a new direction in the field of genetic engineering in medicine and agriculture (Kumar, 2016). Biological molecules and cell phenomena have offered unique properties that assist nanotechnologists to achieve their goals which are not possible by other methods. For instance, the construction of scaffolds of silicon for nanostructures is not necessary as the helical structure of DNA offers nonscientists a real skeleton for assembling nanostructures. Due to DNA's specific linkage pattern which arranges atoms in a predictable pattern to form a nanostructure (Tolles and Rath, 2003; Tomànek and Enbody 2000). DNA is an important component of nanomachines for the construction of nanostructures. DNA stores genetic information which is acting as the basis of the advanced generation of computers. Microprocessors and microcircuits have been modified to form nanoprocessors and nanocircuits respectively by immobilizing DNA molecules on silicon chips. These modified silicon chips have replaced microchips with electron flow channels found in silicon. Such biochips are DNA-based processors that have exhibited exceptional pieces of information of mounted DNA. Biochips use the properties of DNA to resolve computational obstacles, by simplifying the mathematical calculations. Other biological molecules also store and transmit information in smaller places. Researchers are using light-absorbing molecules, like human eye retinas, to augment the storage capability of CDs by about a thousand folds (Whitesides, 2003). Nanobiotechnology, is a promising field that has opened vast opportunities for nano/microfabrication in conjugation with biotechnology and gives solutions to existing unresolved problems. It congregates all possible applications of genomics including mammalian, plant and microbial sources to provide the fundamental tools for collecting sequence information that are used

to design innovative devices. These devices will solve queries related to genomic information and employ these devices in diverse fields, particularly in the medicine and agriculture sectors (Yasuda, 2004).

5. Challenges associated with nanotechnological interventions in the agricultural sector

Though nanotechnology has the potential to revolutionize agriculture, however, this technology has also raised issues of achieving benefits in the field of agriculture. Lowry et al. (2019) have reported several barriers to rapid spreading of nanotechnology in agriculture including a lack of mechanistic understanding of plant-ENM interactions (These are the interactions by which ENMs directly expose plants to soil, water, and the atmosphere), restricted pathways for the delivery of nanomaterials into plant vascular system and organelles, a partial understanding of hazardous effects to living beings caused by nanomaterials placed into the food chain. Commercialization of nanoproducts used in agriculture has been restricted due to toxicity effects mainly mutagenic effects to living systems. Inefficient use of nanoproducts may cause chronic health issues such as cancer, reduced fertility, cardiac and central nervous system disorders etc. to healthy lives. Nanomaterials synthesized chemically are not eco-friendly as they are not easy to degrade completely. Therefore, the extent of toxicity caused to the living systems depend on the dose and extent of exposure of nanoproducts in the environment. Therefore to overcome toxic effects current investigations are now mainly focussed on plants. Furthermore, the release and interaction of nanoproducts is dependent on climatic conditions. Research is being carried out extensively to understand the mechanism of release and interaction of nanoproducts with crops. Besides, efficient implementation of this technology within the low-profit limits of agriculture relies on their capability to equilibrium arrangement and structure expenses and reimbursements.

6. Conclusion and Future Prospects

Nanotechnology has the potential to revolutionize the agriculture system due to its diverse applications in plant breeding, disease control, fertilizer application and precision agriculture. This article has explained the conventional, modern and nanomaterials based agricultural practices. Nano-based approaches that can improve the quality and quantity of agricultural products by targeted delivery of agrochemicals (fertilizers and pesticides) and their efficient and proper utilization have been explained. Nanoparticles such as Au, Ag, Si, TiO₂ etc. have been used as antimicrobial agents. Nanomaterials-integrated biosensors have been used to prevent the loss of crop yield by detecting various microbial pathogens which cause diseases. Precision farming based on sensors has been used for assessing growth of crop plants and rhizosphere parameters such as groundwater level, moisture content, nutrient ingredients including plant growth regulators/hormones, hazardous effects, and microbial infection. Moreover, this technology has exhibited many advantages such as simple, rapid, cost-effective, sensitive, specific and portable. Hence, nanotechnology provides effective ecological substitutes for the management of insect pests without impairment of flora and fauna. Future efforts are required for the development of highly innovative nanomaterials based devices that must be miniaturized, economical, safe, quick, efficient and user-friendly to mitigate the challenges of existing nanotechniques used in agriculture for enhancing the yield of crops.

Efforts are also needed in the direction of commercialization of nanomaterials based applications. This can be achieved by screening and optimizing nanomaterials for different crops. The efficiency of such optimized nanomaterials can be enhanced by manipulating their properties and consistency. Hence, there is a need to develop some novel nano approaches that must be highly efficient in the absorption of active ingredients of agriculture, better stability, and targeted transport of fertilizers, pesticides and fungicides. Moreover, the efficiency of existing bioremediation techniques can also be improved by integrating them with innovative nanotools and devices. Most of the demonstrations related to the use of nanomaterials in agriculture in a laboratory scale; there are very few reports which documented the on-site use of nano-approaches. Therefore, it would be more beneficial for farmers if this technology is used and demonstrated at the field scale. Researchers are also concerned for toxicity because toxicity caused by nanomaterials may create other health issues such as cancers, respiratory problems, dermatitis etc. Hence, toxicity-related issues can be resolved by synthesizing nanomaterials from biological sources. In the future, nano-technology can play an important role in agriculture by renovating food necessity and their distribution system by increasing crop productivity for achieving ecological sustainability, a green environment and economic consistency.

Ethical Approval

This work was not done on animals.

Data Availability

Data will be made available on request.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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