CHAPTER

12 Nano-agromaterials: Influence on plant growth and crop protection

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1 Introduction

Nanotechnology is a rapidly flourishing field of science which associates different scientific domains to intrigue and establish technical advances [1, 2]. According to the European Commission, nanotechnology is one of the key enabling technologies which can attribute the sustainable development [3, 4]. The term nano derived from the Greek word which means dwarf and is represented as 10^{-9} [5]. It was in the 1960s the literature cited officially the concept of nano into reality with the famous lecture "There is Plenty of Room at the Bottom," by the physicist "Richard Feynman" at the American Physical Society [6]. Since then the word nano embedded in the literature and gained tremendous interest which was tapped to insight particles beyond the micro and macro levels.

In nanotechnology, particles miniaturization occurs at nanoscale which in turn signifies the physicochemical properties of the nanomaterials [7, 8]. The unique properties of nanoparticles contribute to attenuate desired applicative properties [9]. Some of the prime properties include size-dependent properties which can be classified as zero-dimensional, for example, quantum dots, carbon dots. Further, one-dimensional nanomaterials include nanowires and two-dimensional includes nano-films and three-dimensional nanomaterials can be grouped as metal nanoparticles [10, 11]. Apart from size-dependent properties, nanomaterials exhibit mechanical properties which enhance their adhesion and deformation. The electrical properties can be exploited for developing semiconductors, capacitors, and electromechanical stimulations [12]. The optical properties of nanomaterials such as surface plasmon resonance can be implemented and studied to enhance the luminescence and absorption phenomenon [13, 14]. The nanomaterials also confer

Industrial Applications of Nanomaterials. https://doi.org/10.1016/B978-0-12-815749-7.00012-8

biological properties such as biological sensing, target site delivery, nano-diagnostics, and nano-therapeutics [15]. Overall, these properties become more prevalent at the nanoscale in comparison with bulk materials [16]. Owing to these facts, in recent years, nanoparticles are regarded as particles of the century which are rapidly rooting their applications in myriad industrial sectors [13, 17].

There are innumerable applications of nanoparticles, for instance, nanochips, nanosensors, biosensor, biofuels, biolabeling, semiconductors, and antimicrobials to name a few [10, 18]. In recent years, advances in nanotechnology have paved new horizon in agriculture sciences [19, 20]. The implementation of nanoparticles as novel nano-agromaterials has ushered new dimension to uplift the standards of modern agriculture system [3, 4, 21]. Agriculture is a backbone of all the nations across the globe and there is a huge scope for developing a novel formulation which can improve the crop productivity and minimize the risks associated with the conventional routes in agriculture [22]. There is ever increasing demand for large-scale production of agricultural commodities owing to the fact of a rapidly expanding global population which is growing at an alarming pace [23]. The agriculture production is a vital driving force of the global economy which can offer rich value-added crop production [24]. The extensive usage of chemical agents like pesticides, fertilizers, herbicides, and weedicides has created serious implications both on ecosystem and health of the individual who cultivate it and the population which consumes it [25]. The magnitude of health implications can be gauged with a trace amount of these hazardous chemicals entering the food chain and affecting all forms of life and ecosystem [26].

Hence, there is great demand for developing a novel formulation which can overcome the obstacles faced due to the usage of chemical pesticides and fertilizers. The impact of agriculture production also depends on the natural calamities which directly or indirectly influences the crop yield [27]. Some of the other factors influencing the yield include loss of arable land owing to urbanization, deficient soil due to the treatment of various chemical agents which results in loss of soil fertility [28]. Further, the climatic changes due to global warming, floods which wash away the crop, pest attacks and the resurgence of new pests and damage to crops by a microbial infection caused by phytopathogens and natural resource depletion [3, 4]. Overall the farming communities are facing different challenges. In order to address these implications, the development of new technologies can easily diffuse without tempering the natural resources [29]. Hence, there is a new paradigm shift toward implementation of nanotechnological principles to improve the modern agriculture and food industries [21]. The nanotechnology can offer the driving force for sustainable productivity and protection of crops for both human and animal consumption [22]. Nano-agrotechnology can provide a new formulation which can minimize the risk posed by the chemical agents used in agriculture production [30]. Further, nanotechnological principles can act efficiently against the target without altering the desired crop yields [3, 4]. Use of nanoparticles can be attenuated right from the sowing stage till the consumer acceptance and can also aid in postharvesting storage to increase the shelf life of the food without altering the food quality and retain its nutritive values [31]. The nanoparticles-based packaging system coupled with spoilage detection system can be one of the key factors to favor the consumer acceptance [32]. In recent years, nanotechnology has envisioned potential roles in plant protection, on-site monitoring of infections and pest attack, boost the crop productivity, sustainable management in farming by using nano-filtration for water [33]. The nano-agrotechnology has the potential to deliver the novel strategies by introducing novel nano-formulation which can be used as nano-pesticides [34]. These nano-pesticides reduce the harmful effects on the environment in comparison with the conventional chemical pesticides which are often being banned from usage [35]. Nano-pesticides are being formulated to achieve specific activity and are delivered with a safe route to maintain the environmental sustainability [36]. Similar strategies are being implemented to develop nano-herbicides, nano-fertilizers, nano-microbicides, and for plant growth promotions [3, 4]. These novel formulations have been discussed individually later in this chapter. In the last few decades, there has been extensive research pertaining to improve the nanoparticles standards with multiapplicative properties [15]. It has been estimated that nearly more than 2500 research articles and patents have been published on nano-agrotechnology and most of the formulation have already hit the market and fields' trails are underway [3, 4]. In order to achieve the sustainability of these nano-formulations, the production of nanoparticles plays a vital role. According to the perusal of literature, synthesis of nanoparticles can be grouped into top-down and bottom-up processes. In most cases,

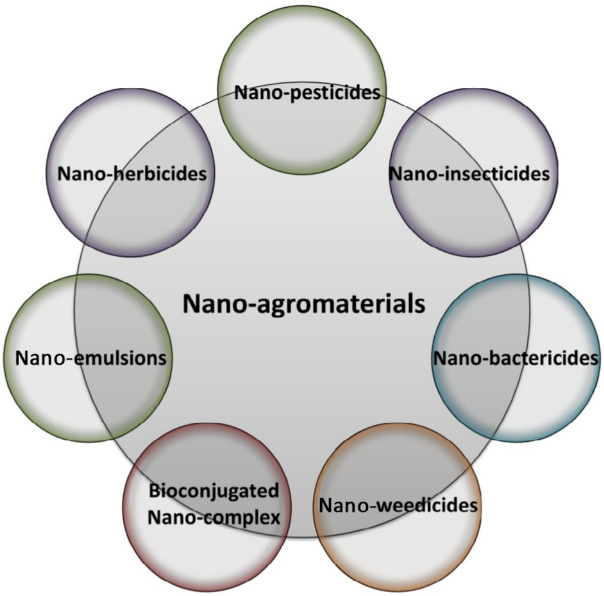

FIG. 1

Different applications of nano-agromaterials.

these methods are employed to achieve desired characteristics to nanoparticles which can behave in accordance to obtain activity [15, 16]. Overall collectively some of the important applications of nano-agroparticles can be cited in Fig. 1.

2 Properties of nano-agromaterials

2.1 Nano-carriers

Nano-carriers are the complex materials at nanoscale which carry the active substance and deliver to achieve target activity with controlled release capacity [37]. The carrier molecules can be of different types such as biodegradable materials which include natural or synthetic polymers, polysaccharides, lipids, and phospholipids [38]. The active substance can be bioactive metabolites, nanoparticles, nanocrystals, peptides, or chemical entities [37]. These nano-carriers form one of the most compatible complexes which serve better advantageous than the sole active substance. They prevent self-degradation, control the delivery process, withstand biotic and abiotic stresses (Fig. 2). The nano-carriers are designed to anchor the plant system by initiating the molecular conformational changes to deliver the designed active components to target sites [39]. The nano-based silicon carriers are developed with

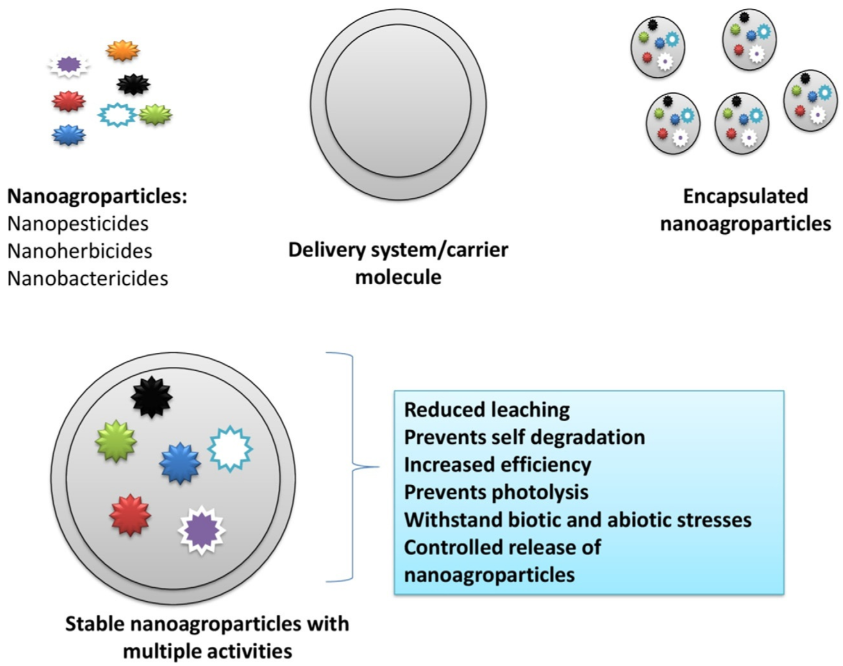

FIG. 2

Development of stable nano-agroparticles for delivery system.

diatom frustules with size ranging between 1 and 100 nm which are used in waste water management system [40]. The nano-carriers are used for delivering agrochemicals such as plant growth promotions, pesticides and herbicides which can produce higher yield and enhanced crop quality compared to its bulk counter parts [41, 42].

2.2 Nanotubes

Nanotubes are cylindrical structures with unique physicochemical and electrical properties [43]. These multiple properties of nanotubes endow them to be one of the most versatile nanomaterials to gain different applications [43a]. Based on the synthesis conditions, nanotubes can be framed into different size and shapes which can predetermine their applicative roles. Carbon nanotubes are one of the best examples which have gained popularity in the recent years. In the agriculture sector, nanotubes are reported to increase the germination rates and influence the seedling growth and modulate the water uptake [44].

2.3 Nanomicelles

The nanomicelles are a self-assembled nano-sized structure with size ranging from 1 to 100 nm [45]. They are colloidal structure mainly in spherical shape and sometimes they can be synthesized into a cylindrical shape [46]. They consist of both hydrophilic and hydrophobic components [47]. They are widely used in delivering drugs to targeted sites especially water-insoluble drugs. In agriculture, they can be exploited to deliver pesticides and insecticides with controlled release property [4].

2.4 Nanowires

A thin nano-sized wire with extraordinary quantum mechanical and physicochemical properties [48, 49]. These wires can be composed of metallic, semiconducting, and insulating components [50]. They are similar to nanotubes with one-dimensional structure and are used in solar cells, nanosensing, semiconductors, etc. [51]. The superior properties of nanowires can be exploited in sensing the on-site of diseases, sanitizing irrigation water, and used repelling of insects [3, 4, 50].

2.5 Nanoemulsion

Nano-emulsions are a biphasic colloidal particulate system which is made up of heterogeneous dispersion of two immiscible liquids [52]. This can be oil in water or water in oil with a size comprising of 100 nm [52]. They have a high surface-volume ratio, highly stable, size, and applicative tunable properties make them one of the superior carrier molecules [53]. In agriculture, nano-emulsions can be prepared for targeted delivery of pesticides, fungicides, and insecticides which are insoluble in water and only soluble in oil [54].

2.6 Nanoparticles

Nanoparticles are ultra-fine particles with at least one dimension at nanoscale such as length, width, or depth at the nanoscale [55]. These particles at nano-size behave completely contrast to their bulk counterpart and exhibit significant and superior properties [51]. They have high stability, a high surface area with respect to volume ratio, tunable optical properties, and size-dependent properties [15]. Some of the important and widely used nanoparticles are mentioned below.

2.7 Silver nanoparticles

Silver nanoparticles are nano-sized silver which has exhibited strong microbicidal properties which have to be explored against a wide range of pathogens [1, 2]. The use of silver-related components can be traced since ancient times and with the invention of nano-silver, the applications have expanded rapidly [10]. In agriculture, they have been used to combat bacteria which are reported to possess drug resistance [4]. The influence of silver nanoparticles on seed germination of corn, water melon, and zucchini was studied. The study was carried out with seven different concentrations ranging from 0.05 to 2.5 mg/mL of silver nanoparticles. The results showed enhancement in the growth and germination rates of all the three crops evaluated [56].

2.8 Gold nanoparticles

Since ages, gold has been used in different sectors and most popularly they have been used as ornament, painting, medicines, etc. The implementation of gold nanoparticles has reported their usage in the delivery system, sensing various analytes such as pesticides, pathogens, and other environmental contaminants. Further, they also possess antimicrobial properties [57]. The use of gold nanoparticles has enhanced the on-site detection system which does not require any sophisticated instrumentation and can be implemented at farm level. For instance, the presence of chlorpyrifos and malathion pesticides is detected using gold nanoparticles-based visual detection system which can detect the presence of ppb level of these contaminants [58]. Similarly, occurrence of DDT in various environmental samples and liquids was detected using gold nanoparticles-based immuno-dipstick method by developing anti-DDT antibodies which were used as sensing elements onto the nitrocellulose membranes. The detection system was reliable with linearity ranging between 0.05 and 1 ng/mL with limit of detection was found to be 0.05 ng/mL [7, 16].

2.9 Copper nanoparticles

The applications of copper-based products are overwhelming with significant properties like magnetic, optical, catalytic, and electric properties [59]. In the recent years, copper nanoparticles have influenced different sector with its potential roles [60]. Studies confer that copper nanoparticles have profound antimicrobial activity [3]. In agriculture, copper nanoparticles are used as fungicidal agents in the treatment of fungal pathogens [61]. The nonionic colloidal solutions if copper nanoparticles were treated on wheat *Pseudocercosporella herpotrichoides* pathosystem which resulted in changes in the dynamic patterns thiobarbituric acid reactive substances with 100% increase in comparison with other wheat varieties and the treatment of nanoparticles showed no impact on the growth and development of the wheat crop [62].

2.10 Zinc oxide nanoparticles

Zinc oxide nanoparticles are considered as one of the most versatile nanomaterials owing to their diverse physic-chemical properties [63]. The large surface area, low toxicity, and the direct band gap of 3.37 eV at room temperature with large quantum efficiency have traded their applications in surface coating, optical communications, sensor, semiconductors, used in fabricating rubber, lubricant, ceramics, cement, and potent antimicrobial properties [50]. Interestingly, zinc oxide nanoparticles possess photooxidation and catalysis which creates an impact on pathogenic microorganisms. Most importantly use of zinc oxide is generally recognized as safe (GRAS) has resulted in rapid expansion of its applications in food and agriculture [64]. The zinc oxide nanoparticles with 25-nm particle size at 1000 ppm were able to promote seed germination, seedling vigor, and influence plant growth system which resulted in increase in the stem and root growth peanuts [64a]. The colloidal solution of zinc oxide nanoparticles was employed as fertilizers which could aid in providing plant nutrition and revive the organic state of the soil with minimal quantity in comparison to its counter chemical fertilizers which requires large quantity [65].

2.11 Titanium oxide nanoparticles

Titanium oxide is one of the extensively studied transition metal oxides with innumerable applications which includes the development of biosensor, electronic devices, batteries, and also evaluated in biomedical applications as a potent antimicrobial agent, toothpaste, and ointments [65a]. These applications are attributed to its unique chemical and physical properties for instances high surface area, refractive index, chemical, and thermal stability, low absorption, and dispersion in spectral regions [65b]. The profound bactericidal activity of titanium dioxide nanoparticles is based on its photocatalytic property which triggers and releases hydroxyl radicals and superoxide ions and significantly decreases the expression of vital genes and proteins which are responsible for regulatory signaling and growth functions [66]. The effect of titanium oxide nanoparticles on spinach seeds reported increase in the germination and growth rates at 0.25%–4% as per the study conducted by Zheng et al. [66a]. The study reported increase in the plant weight along with chlorophyll content, photosynthetic activity along with the improved physiological process.

2.12 Iron oxide nanoparticles

The applications of iron oxides are widespread and have served mankind for centuries especially in diagnostic practices [66b]. The recent implementation of iron oxide nanoparticles has led to innumerable applications owing to the unique properties. The advances in iron oxide nanoparticles-based research are constantly explored and in recent decades in transforming the fundamental knowledge to technological applications for instances in targeted drug delivery, biosensors, magnetic resonance imaging, bioengineering, electrochromic devices, batteries, solar cells, and potent antimicrobial activity against microbial pathogens [66c]. The use of iron oxide nanoparticles at 50 mg/mL on *Citrus maxima* plant significantly enhanced chlorophyll content by 23.2% and root activity was increased by 23.8% as compared to control and ferric ions. The study also highlighted that iron oxide nanoparticles can be used as nano-fertilizers for plant growth [67].

2.13 Bioconjugated nanoparticles

The bioconjugation is based on the interaction between functional sites of nanoparticles and drug molecule thus forming new formulation as an effective antimicrobial agent. Bioconjugation research has to burgeon interest due to various methods of appending biomolecules with other molecules leading toward the bridge between chemistry and biology with valuable progress [68] one such area is bioconjugation of nanoparticles with biomolecules. The choice of the bioconjugation procedure depends strictly on physicochemical and biochemical properties of nanomaterials and bioactive molecules [4]. The interaction between nanoparticles and biomolecules based on the electrostatic forces forms an organization resulting in functionalized nanoparticles in a reversible manner based on the opposite charges (Fig. 3). As nanoparticles possess unique properties which form a base toward developing hybridization with the biomolecules resulting in a specific activity [3]. In recent study, Syed et al. [1, 2] displayed bioconjugation of silver nanoparticles with

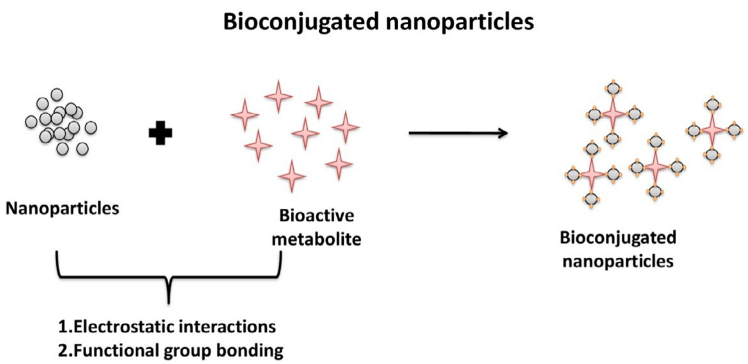

FIG. 3

Bioconjugated nanoparticles for biological activity.

2,4-diacetlyphloroglucinol (2,4-DAPG) to develop nano-complex resulted in enhanced bactericidal property against phytopathogens in comparison with sole 2,4-DAPG and silver nanoparticles.

3 Nano-agromaterials and their role in plant growth promotion

Nano-agromaterials have demonstrated the significant impact on the germination rate and physiological processes [4]. These nano-based particles penetrate the thick seed wall and create pores which supports the sufficient water uptake thus influencing faster germination process and increases the biomass production [22]. Further, the generation of cost-effective coupled with minimal environmental impact is one of the prerequisites to promote nano-agromaterials for plant growth promotion [4]. Nano-agromaterials can be judiciously employed to increase the agriculture productivity [21]. The ideal characteristics for plant growth promotion is directly related to metabolic processes such as photosynthesis, production of phyto-components, signal transduction process, pigment production, chlorophyll content, energy transfer, compatible and effective with the wide range of crops productivity, and decreased phytotoxicity [4].

In the recent years, a wide range of nanoparticles is evaluated for growth promotion activities. For instances, calcium phosphate nanoparticles enhanced the growth promotion of *Zea mays* by influencing and improving chlorophyll content, root proliferation, and balance the symbiotic relationship with plant and their arbuscular mycorrhizal fungi. Similarly, nanosilica was reported to improve seed germination percentage in maize seeds in comparison with the conventional bulk silica source. In addition to this, nanosilica also influences the rhizosphere bacterial colony forming a unit by doubling the population from 4×10^5 to 8×10^5 CFU in per gram of soil. The study concluded with the fact that nanosilica benefited both plant growth and symbiotic bacteria living in close proximity [69]. Carbon nanotubes were reported to increase the germination and growth rates at varying concentration of 10–40 μg/mL on tomato seeds [70]. Effect of silver nanoparticles on seed germination and growth productivity of wheat cultivar NARC2009 was studied with 10–20 nm sized silver nanoparticles at a different concentration from 0 to 150 ppm. The results indicated increased in the seminal roots, leaf area, root biomass, and weight with 25 ppm silver nanoparticles [71].

In some cases, these nanoparticles are capable of acting efficiently to overcome the deficiency of growth promoters, for instances, iron oxide nanoparticles are used to replace the traditional iron fertilizers and add better advantages in comparison to their bulk counterparts. According to the study conducted by Rui et al. [72], iron oxide nanoparticles increased the root length, shoot length, the biomass of *Arachis hypogaea* which is reported to be very sensitive to iron deficiency. The study was conducted in a pot experiment and compared with control. Interestingly, iron oxide nanoparticles were capable of promoting growth and development by regulating phytohormones and enzymatic activities. The study also displayed the adsorption of nanoparticles onto the sandy soil and improved its availability to plants thus overcoming the leaching of fertilizers. Similar findings were observed with exposure of *Triticum aestivum* seeds to iron nanoparticles which increased the germination rate by enhancing the root and shoot length [73]. Influence of combinatorial nanoparticles which comprises of iron oxide nanoparticles and zinc oxide nanoparticles showed increased in the yield of *Daucus carota* L. at a combined concentration of 100 ppm of zinc oxide nanoparticles and 50 ppm for iron oxide nanoparticles [74]. The use of titanium dioxide nanoparticles is widely practiced in the recent years which are reported to have multiple properties like catalysts, increases the pigment production, stimulates the production of carbohydrates, and helps in regulating the phytohormones. Influence of titanium dioxide nanoparticles on Canola seeds was studied by treating with different concentration of titanium dioxide. The study indicated that titanium dioxide improved the radicle and plumule growth of canola seedlings in comparison with the control experiments. The influence of titanium dioxide and zinc oxide nanoparticles was studied for plant growth promotion and photosynthetic pigmentation along with protein content. The results displayed a significant increase in the chlorophyll and protein content with the treatment of zinc oxide nanoparticles than titanium dioxide nanoparticles [75]. Similar findings were observed with zinc oxide nanoparticles on tomato plants. The treatment of different concentration of zinc oxide nanoparticles on seedlings followed by cup experiments showed a significant increase in the growth and photosynthetic efficiency. The study also concluded that enzymatic activity and antioxidant properties were also enhanced at 8 mg/L concentration of zinc oxide nanoparticles.

4 Nano-agromaterials as microbicidal agents against phytopathogens

Nanomaterials are reported to have significant microbicidal properties against a wide range of pathogenic microorganisms [20]. In the recent decades, an upsurge of drug-resistant pathogens have created pathetic conditions across the globe and there is a great demand for developing novel antimicrobial agents which can act efficiently to combat drug-resistant pathogens [57]. According to the WHO 2017, antimicrobial resistance is one of the top priority research in the current scenario. The impact of drug resistant is estimated to be high in hospital-acquired infections [51]. But contrary in the agriculture sector, there has been over usage of fungicides and bactericides which is posing a severe threat to normal flora and fauna [4]. The overusage of these antimicrobial agents is directly or indirectly contributing to increasing and development of drug resistance. In agriculture, microbial infestation accounts for more than 50%–80% of crop diseases which is more than any pest attacks thus causing severe loss and damage to crops [76]. A wide range of economically important cash crops such as rice, maize, cotton, apples, pears, grapes, wheat, etc. are susceptible to microbial infestation [4]. The usages of conventional fungicides are being leached out and are also targeting nonspecific organisms [35]. Hence, there is great scope for nanoparticles-based formulation. The size-dependent properties of nanoparticles are reported to penetrate across the cell wall of targeted pathogens and damage it by causing pits which leads to loss of cellular contents [10]. Studies also report binding of nano-size materials to vital components such as enzymes and proteins which results in disturbing the cellular activities such as suppressing DNA synthesis, protein synthesis, etc. [20]. There are different classes of nanoparticles which are effective against pathogenic microorganisms.

The use of silver against various ailments is well documented but with the implementation of nano-silver the applications of silver have been expanded in different sectors. In agriculture, silver is employed against different pathogens. For instances, silver nanoparticles were tested for in vitro antifungal activity against *Biplaris sorokiniana* and *Magnaporthe grisea* which was evaluated with colony formation. The results indicated that 50% inhibition activity for *B. sorokiniana* than *M. grisea*. Further, growth chamber inoculation assays confirmed silver nanoparticles in reducing the growth of fungal diseases on perennial ryegrass [77]. Biogenic synthesis of silver nanoparticles from endophyte Pseudomonas reported bearing bactericidal activity against a range of human and phytopathogens. The study concluded with *Xanthomonas campestris* to be most sensitive phytopathogens among other agriculture important pathogens tested [51]. A similar observation was reported against *Phomopsis* species by silver nanoparticles synthesized with sodium citrate and stabilized with ammonia. The synthesized nanoparticles were 50 nm in size and were highly efficient in controlling the growth of the test pathogen [78]. The activity of zinc oxide nanoparticles is also reported to suppress the growth of various fungal pathogens and also possess bactericidal properties. For instances, zinc oxide nanoparticles displayed antifungal activity against *Erythricium salmoni* color, a fungal pathogen which is reported to be the causal organism of pink disease. The activity was measured with inactivation of mycelial growth. Electron microscopy revealed deformation in the growth pattern with thinning of hyphae, liquefaction of cytoplamic content, and detachment of cell wall [79]. A similar observation was reported with zinc oxide nanoparticles synthesized from flower extract of *Nyctanthes arbor-tritis*. The synthesized nanoparticles displayed significant activity against pathogens viz., *Alternaria*, *Aspergillus*, *Botrytis*, *Fusarium*, and *Penicillium* species [80]. The in vitro antifungal activity of copper nanoparticles was tested against *Fusarium* species which is reported to be the causative agent of wilt disease in date palm and *Phoenix dactylifera*. The study mentioned the size and shape-dependent activity of synthesized nanoparticles, polygonal copper nanoparticles displayed higher activity than the spherical-shaped copper nanoparticles [80a]. Further, copper nanoparticles with size 20–50 nm were reported to exhibit antifungal activity against *Fusarium* species at a concentration of 450 ppm which displayed 93% of growth inhibition in comparison with control [81].

The antifungal activity of chitosan-copper-based nanocomposite was tested against *Sclerotium rolfsii* and *Rhizoctonia solani*. The study reported the loss of cytoplasm content, damage of hyphae, and cytoplasmic coagulation was confirmed.

The synthesized nanocomposite was reported to be both fungicidal and fungistatic depending on the type of test pathogens [82]. The magnesium oxide nanoparticles acting against bacterial wilt causing bacterium *Ralstonia solanacearum* in tomato was recently reported. The treatment of magnesium oxide nanoparticles significantly reduced the incidence of disease. The study also highlighted generation of reactive oxygen species and series of physiological and enzymatic changes due to magnesium oxide nanoparticles treatment which in turn conferred the resistance in tomato plants against the pathogen *R. solanacearum* [83].

5 Nano-agromaterials formulation as an alternative to chemical pesticides

The term pesticides can be defined in different forms based on their type of applications. For instance, fungicides, insecticides, nematicides, herbicides, weedicides, rodenticides, nematicides, etc. [84, 85]. Broadly, the pesticides are the chemical entities which are employed in agriculture management to achieve the desired activity and increase the crop productivity [86]. The use of large quantities of pesticides across the globe has surfaced controversy and huge impact on ecological niches by affecting nontargeted pests including humans [35, 87]. These pesticides are reported to be highly toxic even at trace levels [25]. The carcinogenic effects of chemical-based pesticides are already well documented with various scientific groups reporting different forms of pesticides and their by-products to enter food chain to cause biomagnification [25]. The harmful effects of pesticides are being discussed and validated at a global level and different governing bodies have banned most of the pesticides which are reported to enter groundwater, persist in environment, easily penetrate the tissues of human and animal to cause deleterious health implications which are at high risk, and is subject of great concern as these health implications are passed onto generations [88–90]. The degree of pesticidal impacts can be gauged at different levels ranging from a simple headache, fever to chronic levels like carcinogenic, disturbing reproductive and endocrine systems [91].

Hence, there is a serious concern to overcome the limitations posed by chemical-derived pesticides. In order to achieve facile and safe management of agriculture, bio-pesticides were implemented [92]. But these pesticides were based on the biological entities like microorganisms or their products. In most of the cases, these potent microbial source used as bio-pesticides often loses the stability and are susceptible for mutation which resulted in low efficiency and failed to attenuate the desired activity. In the recent years, at greater platforms, nano-based formulations are being designed to test their efficacy in agriculture management as the best alternative for pesticides. One of the strengths of nano-based pesticides is their usage at low concentration to achieve desire activities and tuning their applicative properties to target the pest but not the nontarget species. Use of nano-formulation can reduce the drug-resistant kinetics among the pests. There are different scientific groups who are already working on the development of a nano-based formulation for pest management and by far most of the researches have completed the field trails. It can be estimated with traditional records that the use of metallic components are effective in targeting insects and pest. These metallic compounds are synthesized at nanoscale to achieve profound activity at low concentrations which can easily minimize the risks posed by the chemical pesticides. The modern scientific tools and advancement of nanotechnology offer different rational techniques to design the novel formulations which can achieve hassle-free activity irrespective of biotic or abiotic factors. The efficiency can be tuned accordingly based on the type of crop management and targeted pests. The engineered nanoparticles can offer tremendous advantages for instance nanoparticles-mediated gene transfer technology can protect the plants from invading pests and insect. Further, nano-carriers and composites loaded with desired pesticides can be one of the ideal delivery systems which can be controlled and prolong the release of pesticides. The development of water-based nanoformulations can also be effective in repelling the insect and protect the plants without affecting its nutritive components. There are wide ranges of nanomaterials which are effectively employed in the management of pests. The nano-sized aluminum oxide and titanium dioxide were used against *Sitophilus oryzae* and the results showed that aluminum oxide was found highly effective against the pest with a mortality rate at 73.3% compared to titanium dioxide which was found to be 59% under the laboratory conditions [93]. The silver nanoparticles were synthesized from leaf extract of *Aristolochia indica* and tested for pesticidal activity against larvae of *Helicoverpa armigera*. The results showed significant antifeedant and larvicidal activity with LD50 at 309.98 mg/mL [94]. Similar findings were observed with silver nanoparticles and their impact on growth pattern and feeding responses of *Spodoptera litura* F. and *Achaea janata* L. larvae. The nanoparticles were coated with PVP and treated at different concentration and their activity was measured. The transmission electron microscopy revealed the accumulation of nanoparticles in different cell organelles. The study concluded with the fact that silver nanoparticles induced oxidative stress [95].

The controlled release of pesticides is reported to improve the pesticidal efficacy and minimize the adverse effects. For instance, silica nanoparticles have been one of the smart and ideal delivery systems. Recently, amino group functionalization and carboxymethyl chitosan were modified to form pesticide carrier of azoxystrobin. The modified complex exhibited significant fungicidal activity against *Phytophthora infestans* [96]. In the agriculture sector, early weed control is prime important and most of the conventional weedicides are reported to target the weeds along with the normal crops thus causing implications. Hence, nano-based herbicides are introduced to overcome the limitations posed by the conventional pesticides. The nanoparticles-based herbicides penetrate the root system of targeted weeds and inhibit the physiological process which in turns creates the starvation and destroy the weeds. To achieve maximum herbicidal activity, naturally based carriers are employed, for instance, encapsulation of imazapic and imazapyr herbicides were carried out using alginate/chitosan and chitosan/tripolyphosphate. The study determined the release kinetics of the complex and results showed satisfactory encapsulation efficiency at 70% controlled release. The study also determined the cytotoxicity and genotoxicity of the complex which resulted in lesser toxicity and decreased genotoxicity in comparison to the sole herbicides.

6 Challenges of nano-agromaterials in agriculture management

Despite the significant advances of nanotechnology in different sectors, there has been scrawling progress in agriculture sector which is by far in marginal to reach its potential. The scientific wave of nanotechnological discoveries is bound with various regulations [97]. Most of the research with regards to nano-agrotechnology under pipelines and yet to reach the market scale of commercialization and still under academic sectors and research enterprises [98]. The research trends and publications along with large patent ownership on nanomaterials are significantly growing. The big giants and industrial organization are funding the product-oriented nano-agromaterials but the effects of regulations and strict rules are sidelining the beneficial part of the product [4]. The labeling of nano-products has gained moderate acceptance from the consumer owing to the limitations posed by various nano-sized chemical entities which are highly toxic at trace levels as similar to pesticides [22]. Most of these limitations can be well attended by designing the eco-friendly or biomimetic-based nanoparticles which can minimize the risk associated with chemical bound nanoparticles [15]. In the recent years, biological-oriented nano-products are gaining importance which is based on the core element or composition of nanomaterials which can act efficiently with causing the hazardous impact [7]. Further, disseminating nano-agrochemicals is one of the major issues to reach the market [99]. The nano-based materials are lagging to reach its full potential across the globe especially the developing countries which are often facing serious problems. The developed world should step up with the measures to transfer the technologies and train the scientific personnel's from the low-income countries where the flow of knowledge is highly essential. The scientific organization must provide funding for collaborating with partners from different countries which can increase the mobility of researchers and technologies can be easily transmitted and tested under different environmental conditions. The scientific organizations must carryout more scientific conferences to exchange the knowledge and invite the prominent scientific communities under one roof who can motivate the research activities and troubleshoot if the academic research is facing problems. Most of the research on nano-agroparticles work well under sophisticated laboratory conditions and fail to show the same potential on grounds and field trials [100]. These limitations might be owing to myriads abiotic and biotic conditions which can be addressed based on the precise scientific trials and designing the laboratory conditions which can be best suited for facing environmental stress [100a]. Further, special emphasis should be given to low dose and high potential of nano-products which can minimize the over usage of the product [3, 4]. This strategy can be useful and consumer friendly as it can be a cost effective wherein a minimal amount of nano-formulation is applied. The consumer knowledge on the nano-formulation is also an important factor, the consumer must be aware of the principle and the mode of action with the benefits should be ensured and updated with the manual. Minimal instrumentation and usage without any additional equipment are also desirable for consumer acceptance. The ideal nano-agroparticles must meet at least the following standards, for instance, the type of applicative properties attenuating by the developed product, for instance, growth promotion, pesticidal, insecticidal, etc. [101]. Nano-agroparticles must provide adequate information with its interference with the terrestrial environment and food chains. Upon application of nanoproduct, toxicity studies must be carried out to reveal the lethal dose-dependent activities. The scientific studies should provide evidence to reveal the interaction with plants and their translocation to edible plant shoot and roots. Till date, scanty reports are available on the co-contamination of nanoproducts upon exposure [4]. The nanomaterials are highly reactive which can also constitute a negative impact when they react with chemical entities like conventional pesticides and fertilizers [22]. The nonspecific target must be prevented, reports are available that nanomaterials might also influence and act upon the nontarget host especially when they are used as weedicides. Plants are reported to have a symbiotic relationship with the microbial plethora and the association is expected to beneficial to both the partners [57]. In most cases, the rhizosphere microbial flora is in close proximity to the plant roots and influence in growth and development [102].

7 Future prospective of nano-agromaterials

The extensive research on nanomaterials has documented its untapped roles in different sectors including agriculture sector [21]. Agriculture is one of the most vital sectors for any nation, scientific standards to uplift the modern agriculture practices is highly essential [103]. The nano-agromaterials roles can be highly reliable based on their toxicity levels, type of function, and their fate in the ecological niches [104]. It would be highly efficient in near future to bioconjugate the nanomaterials with the natural derivatives which are in the approval list by GRAS and other scientific organization [4]. One of the advantages of tailoring the nanomaterials with biological or natural derivatives is to minimize the risk associated with the conventional agrochemicals which are widely in practice. The bioconjugation tool can aid in developing multiapplicative nanomaterials which can complete the specific activities, also monitor as nanosensor and forecast the early infections [10]. In agriculture, the postharvesting stage is also very crucial to regulate and maintain the nutritive aspects of the crops. In most cases, the crops are exported and every country has its own regulatory system and during such situation, developing nanomaterial-based packaging system is highly desirable which can retain the freshness of the agricultural crop [105]. Further, one of the least studied area with respect to nanomaterials and agriculture is in irrigation system [99]. The role of irrigation system plays a highly important role in the agriculture sector. In most cases, contaminated water used in agriculture system carries various diseases causing pathogens which directly add their deleterious impact on crop [4]. Such a scenario is still practiced in the developing countries where adequate sanitary conditions are still at large. In contrast to this, most parts of the world lack regular water cycle system and are affected by severe drought conditions. In both the conditions, the role of nanomaterials has done be investigated, studies demonstrate the role of nanoparticles in the treatment of sanitary water treatment by designing nanomaterial-based filter systems. The membranes and filters can be designed based on the target water contaminants, for instance, iron oxide nanoparticles are reported to bear high adsorption capacity which can filter most of the major contaminant [106]. Further, magnetic nanoparticles can eliminate the heavy metals and give portable water [4]. These nanoparticles are also considered to have antimicrobial potential which acts upon the waterborne infectious agent. Developing a nano-based model for water purification can be the highly attractive tool in modern agriculture system which can reach the masses especially in the remote areas where developing conventional water treatment plant is not feasible. In recent times, owing to the natural disasters, soil loses its fertility which in turn influences its strength and becomes weak thus unable to cultivate any types of crops. Studies have demonstrated the role of nanoparticles in strengthening the soil. For instances, colloidal silica nanoparticles can easily react with soil and remediate it. Further use of bentonite and laponite-based nanoparticles can retain the soil structure [4]. These are some of the areas which need to be improved with the aid of nanotechnological principle. Funding agencies should encourage the scientific communities by providing funding for nanoparticles research related to agriculture and help the scientific community to collaborate the industrial sector to commercialize the product and bring the science to society.

8 Summary and conclusion

Overall the chapter comprises of different roles of nano-agromaterials in agriculture system. The different properties of nano-agroparticles have uplifted the standards and overcome the limitations posed by the conventional pesticides and fungicides which are reported to usher deleterious impact on the ecosystem and the living entities. The impact has serious health implications which are raised and constantly reported. Hence, nano-agromaterials are employed to improve the efficiency and attenuate the desired activity. The possible implementation of nano-principles is expected to perform well in comparison to its bulk counterparts. Future studies will be highly valuable enough to address the major challenges like food safety and security, improving the crop productivity, prevents postharvest losses, monitoring, and forecasting the disease. Further, degradation of agrochemicals can also achieve using nanoparticles.

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Further reading

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