Chapter 10
Nanopesticide: Future Application of Nanomaterials in Plant Protection

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10.1 Introduction

Pests and disease often limit agricultural production and have significant impact on farmers' incomes. The loss can occur on the crops in the field and in the storage. Farmers mostly use synthetic pesticides to manage pests to maximize crop yields and/or manage stored-product insect pests and disease, posing potential risks for workers, consumers, and the environments. It has been estimated that about 2.5 million tons of pesticides are used on crops each year and the worldwide damage caused by pesticides reaches $100 billion annually (Mohan et al. 2011). Furthermore, many of the chemical nematicides have been banned (91/414/EEC) or are under evaluation (2009/1107/EU) by strict legislations in European Union countries (Ntalli et al. 2011).

For the above reasons, there is a need to search for cheaper, nonpersistent, and less toxic alternative control measures on crop pest insects and disease pathogens. The essential oils (EOs) extracted from plants are suitable as they are economically reasonable and have high activity in certain cases, and are also biodegradable (Silva et al. 2008; Sukumar et al. 1991). And also, a new approach by modern technology that plays an important and effective role in plant pests and disease control to avoid chemical pesticide hazards is nanotechnology. Nanotechnology has emerged as a promising area for innovative products, including pesticides. Nanotechnology offers great promise on the development of new formulations called nanoformulation, especially with nanoparticle application as an alternative to pesticides or assistant factor in preparation of pesticides (Martinelli et al. 2014; Abdellatif et al. 2016), as new formulations are able to improve the effectiveness and stability of botanical insecticides (Gogos et al. 2012; Scott and Chen 2012; Ghormade et al. 2011; Perlatti et al. 2013) and offer the ability to release the active compound to the target organism and then provide controlled release of the molecules at the site of action (Duran and Marcato 2013; Gogos et al. 2012; Perlatti et al. 2013; Prasad et al. 2019).

This chapter summarized the recent approach of nanotechnology in plant pest and disease management through developing nanopesticide and controlled release formulation of pesticides, and their strategic field application in minimizing the environmental impact. This review focuses on the enabling contribution of (1) nanomaterials to the use of metal as a pesticide active ingredient; (2) nanoemulsions to the use of EOs as natural pesticide agents, specifically addressing the formulation of stable EO nanoemulsions; and (3) small engineered structure as controlled release agent of agrochemical pesticidal properties and bioactive agent.

10.2 Developing Nanopesticide

10.2.1 Definition and Concept of Nanomaterials in Developing Nanopesticide

A nanomaterial is one millionth of a millimeter (mm) of materials that is engineered through nanotechnology manufacturing system. The term nanotechnology was described first by Professor Norio Taniguchi of Tokyo Science University in 1974 to illustrate precision manufacturing of materials at the nanometer level with the size of 1–100 nanometers (nm) (Taniguchi 1974). These materials display different properties from bulk materials due to their size. Nanomaterials show novel surface chemistry properties, physical strength, and distinct thermal, biological, electrical conductance, magnetism, and optical properties/effects associated with their atomic strength and are useful to enhance sensitivity, reduce response times, and improve detection limits and can be used in multiplexed systems (Johnston 2010; Merkt 2008). The nanoparticles (NPs) have a high surface to volume ratio that increases their reactivity and possible biochemical activity (Dubchak et al. 2010). Nanoparticles are of different shapes and many times smaller than bacterial cells. The particle size is even smaller than a virus particle like tomato mozaik virus (300 nm length and 10–18 nm diameter). Over many decades, nanotechnology and nanomaterials have been used as conductors and semiconductors, medical devices, sensors, coatings, catalytic agents, and also as pesticides (Bhattacharyya et al. 2010). Nanotechnology and nanomaterials are developing pesticides through nanoformulation technique.

10.2.2 Pesticide Nanoformulation

According to Athanassiou et al. (2018), nanoformulations are like other common pesticide formulations, they aid in increasing the apparent solubility of a poorly soluble active ingredient or in releasing the active ingredient in a slow or targeted manner, thus protecting the active ingredient against premature degradation. Pesticides developed from nanoformulation technique are called nanopesticides. Nanopesticides are prepared either by very small particles of pesticidal active ingredients or some other nanostructured molecules with pesticidal properties. Researchers have developed different types of nanopesticides like nanocapsulated formulations, nanoemulsion, nanogel, nanospheres, and metal and metal oxide nanoparticles (Kah and Hofmann 2014).

Merkt (2008) found that targeted nanoparticles often exhibit novel characteristics like extraordinary strength and more chemical reactivity and possess a high electrical conductivity. Nanomaterials used for formulating nanopesticides have desired properties such as biodegradability, solubility, permeability, and thermal stability (Bouwmeester et al. 2009). Targeted nanoparticles for pesticidal active ingredients often show a broad spectrum of activity against plant pest and disease pathogenic. Metal and plant essential oils/plant oils exhibit such broad-spectrum characteristics. Other pesticidal active ingredients targeted by nanoformulation recently being developed as nanopesticides are agrochemical pesticides and biopesticide organisms.

The applications of nanoemulsions in nanopesticide formulation and botanical pesticide formulation using plant essential oil for delivery of antimicrobials active/bioactive components have gained interest recently due to an extremely small droplet diameter in the range of 20–200 nm, high physical stability, high bioavailability, and optical transparency compared with other conventional emulsions (Solans et al. 2005; McClements 2012). According to Shafiq-un-Nabi et al. (2007) and Sakeena

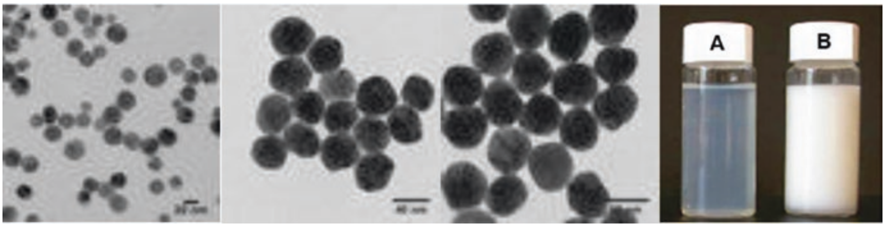

Fig. 10.1 Metal nanoparticles and essential oil nanoemulsion. Silver nanoparticles (left to right: 100 nm, 250 nm, 400 nm). (Oldenburg and Saunders 2018): (A) nanoemulsion, (B) macroemulsion. (Shafiq-un-Nabi et al. 2007)

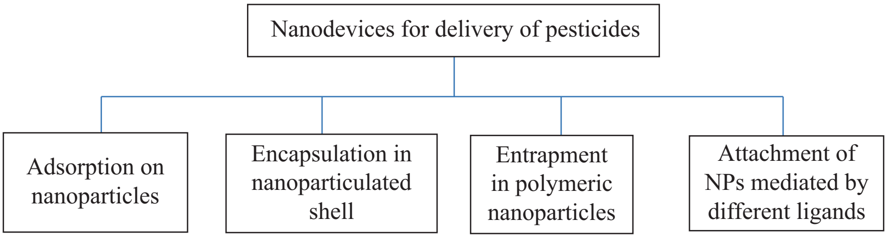

Fig. 10.2 Different nanodevices for delivery of pesticide. (Kaushik and Djiwanti 2017)

et al. (2011), nanoemulsions are clear, transparent, isotropic, and thermodynamically stable solutions of oils, surfactant, and cosurfactant with droplet size of less than 100 nm (Fig. 10.1). The surfactants are chosen from "Generally Regarded as Safe" category from FDA for use in food and pharmaceutical preparations. Other colloidal system devices, i.e., lipid carriers, including liposomes, solid lipid nanoparticles, and nanostructured lipid particles, may be used in essential oil nanoencapsulation. Nanoemulsions (NEs) were also developed to improve solubility, spreadability (better dispersion), and wettability, found helpful in less degradation and volatilization of active ingredient, and improve their bioavailability for a long time period, which implied to improve efficiency and reduction of effective pesticide concentration (Guillette and Iguchi 2012; Bergeson 2010a; Anton et al. 2008; Mason et al. 2006).

Nanopesticide formulations constitute the process and delivery methods of active ingredient into the nanomatrix. The process of absorption, attachment, encapsulation, or entrapment of the active ingredient into the nanomatrix occurs in nanopesticide formulations (Fig. 10.2). Nanoemulsions, nanoencapsulates, nanocontainers, and nanocages are some of the nanopesticide delivery methods which have been widely applied in nanoformulations (Bergeson 2010b).

Controlled release technology has emerged as an alternative approach with the promise to solve the problems accompanying the use of some agrochemicals, while avoiding possible side effects with others (Han et al. 2009). The ability to delay or control delivery of pesticides to the target organisms is achieved by these nanopesticide delivery methods (Singh et al. 2015). Nanoencapsulation of agrochemicals provides effective concentration of the active ingredient with high stability and site-targeted smart delivery with reduced collateral damage and less ecotoxicity (Nair and Kumar 2012). Nanoencapsulation and entrapment of agrochemicals pesticides and other active substances by using polymers, dendrimers, surface ionic attachments, and other mechanisms may be used in controlled and slow release of agrochemicals, which allows the slow uptake of active ingredients and in turn reduces the amount of agrochemical application by minimizing the input and waste (Chowdappa and Gowda 2013).

10.3 Metal-based Nanopesticide

Copper (Cu), mercury (Hg), zinc (Zn), chromium (Cr), nickel (Ni), cobalt (Co), tin (Sn), iron (Fe), titanium (Ti), magnesium (Mg), gold (Au), and silver (Ag) are the metals used as base for inorganic and organic fungicides. Among them, significant research and application have been done on silver and gold, against several plant pests and disease pathogens.

In the last decade, among nanostructures which possess and display variation in properties as compared to bulk metal, and due to their unique photocatalytic photothermal, optical, and electrical properties and stability, the silver and gold nanoparticles have gained much significance in research. Ultrasmall size and very high reactivity nanomaterials will affect the activity of pests and pathogens. Pesticides in nanosize can include either nano-/very small particles of pesticidal active ingredients or other nano-/small engineered structures with useful pesticidal properties (Bergeson 2010b). Important steps in metal-based nanoformulation are synthesis of metal nanoparticles or nano-/small engineered structures, characterization of the metal nanoparticles/nanomaterials, and exploring their antimicrobial activity against pests and disease pathogens.

10.3.1 Metal Nanoparticle Synthesis

The synthesis deals with the conversion of the matter of the macrosize into the particles of the nanosize, 1–100 nm. Metal nanoparticles could be synthesized by chemical, physical, and biological methods. Biosynthesis of particles at nanoscale using microorganisms and plants (including algae) has become popular recently due to the increase of the chemical, physical, and biological properties created by these method practices, in addition to their use as reducing and stabilizing agents (Abdellatif et al. 2016; Jain and Kothari 2014; Ahmed et al. 2015; Sharma et al. 2017; Mandal et al. 2006; Mohanpuria et al. 2007; Prasad et al. 2016). Microorganisms play an important role in diminishing the toxic metals by reduction of metal ions. Fungi have a number of advantages for NP synthesis in relation to other microbes and plant material. The use of fungi in the synthesis of NPs is potentially important since they produce large quantities of enzymes and are simpler to handle in the laboratory (Mandal et al. 2006, Mohanpuria et al. 2007; Prasad 2016, 2017; Prasad et al. 2018; Abdel-Aziz et al. 2018). A number of fungi, i.e., *Alternaria alternata*, *Fusarium oxysporium*, and *Amylomyces rouxii*, were screened to generate silver nanoparticles (AgNPs) (Gajbhiye et al. 2009; Musarrat et al. 2010; Al-Askar et al. 2013). Thakur and Shirkot (2017) reviewed various bacteria that have been reported with the ability to synthesize silver and gold metal nanoparticles [*Bacillus licheniformis*, *Bacillus subtilis* (culture supernatant), *Bacillus cereus*, *Bacillus* sp., *Bacillus flexus*, *Morganella* sp., *Escherichia coli*, *Proteus mirabilis*, *Corynebacterium* sp., *Staphylococcus aureus*, actinomycetes (*Thermomonospora* sp.)]. Biogold nanoparticle syntheses by various biological organisms including bacteria are becoming popular as these overcome the disadvantages (Zhang et al. 2016). Highly stable AuNPs of different sizes and shapes can be synthesized using bacteria, fungi, actinomycetes, and yeast. Ahmed et al. (2015) reviewed a plant diversity to be utilized toward a rapid and single protocol to produce silver nanoparticles and described their antimicrobial activities. Gholami-Shabani et al. (2017) reviewed about 130 more plant species extracts that could be used to synthesize metals at nanoscale and described their schematic protocol. Some plant species from aromatic herbs and spices, fruits, and algal (*Turbinaria turbinate*, *Ulva lactuca*) and pesticidal source plants effectively synthesized metals at nanoscales (1–100 nm). Now bioiron nanoparticles synthesized by various biological organisms such as bacteria, fungi, viruses, algae, and higher plants are becoming popular as these overcome the disadvantages of various physical and chemical methods (Bansal et al. 2014). Bacteria with their ability to reduce various metals grab target Fe^{2+} ions from the environment and convert these into FeO by iron reductase enzyme.

Green and biosynthesis of metal nanoparticles methods offer an easy, inexpensive, environmentally friendly, and appropriate setup for large-scale nanoparticles such as silver NP production compared with conventional chemical methods of production, in spite of increasing the antipathogenic activity (Hassan et al. 2016; Shankar et al. 2003). Induced systemic resistance was derived from *F. oxysporum*-biosynthesized AgNPs, because Nep1-like proteins secreted from *F. oxysporum* trigger plant defense responses and cell death (Veit et al. 2001). Combining green silver nanoparticle (GSN) with algae such as *T. turbinata* that supplements the GSN nematicidal effect may increase its applicability. Additionally, the mechanism in the nematicidal action of GSN also permits improvement of GSN effectiveness by adding natural compounds (i.e., algae formulations) (Abdellatif et al. 2016).

10.3.2 Mode of Action

Different types of inorganic nanomaterials like copper (Cu), zinc (Zn), titanium (Ti), magnesium (Mg), iron (Fe), gold (Au), and silver (Ag), aluminum (Al), and metal oxide-based polymers zinc oxide (ZnO) and titanium dioxide (TiO_2) have been developed for pests and disease management. DNA-tagged nanogold was effective to control the armyworm, *Spodoptera litura* (Chakravarthy et al. 2012a,

Table 10.1 Antimicrobial effect of metal nanoparticles on various plant pests, disease pathogens, and postharvest pests reported by researchers

Metal/metal oxide nanoparticles	Reducing and stabilizing agent	Efficacious pests and pathogens	References
Biogenic iron nanoformulations (70 nm)	Bacterial isolate (*Stenotrophomonas maltophilia* KBS 2.4) supernatant solution	*Meloidogyne incognita* in Okra	Sharma et al. (2017)
Biosilver nanoparticles	Fungus *Alternaria alternata*-mediated synthesis	*Phoma glomerata* of fungal pathogen of Ascochyta blight disease on pea	Gajbhiye et al. (2009)
Biosilver nanoparticles	Fungus *Fusarium oxysporium*	Antifungal activity (*Alternia alternata*, *Fusarium oxysporum*, and *Aspergillus flavus*)	Al-Askar et al. (2013)
Biosilver nanoparticles	Water extracts of the fungus *Amylomyces rouxii* strain KSU-09	Soil-borne fungus *Fusarium oxysporum*	Musarrat et al. (2010)
AgNPs	*Fusarium oxysporium* bioproduction	The antibacterial activity (*Erwinia carotovora*, *E. amylovora*, *P. wasabiae* Hf569027, *P. carotovorum atrosepticum* 1007, *D. chrysanthemi* Dsm4610, *P. wasabiae* 33, and *D. dadantii*)[54]	Al-Askar et al. (2013)
AgNPs (10–20 nm)	Aqueous leaf extract preparation biosynthesis-AgNPs	Sunhemp rosette virus (SHRV), on bean	Jain and Kothari (2014)
Green silver nanoparticles (8–19 nm, spherical shape)	Algal *Turbinaria turbinata* synthesized AgNP solution	*Meloidogyne javanica* in egg plant	Abdellatif et al. (2016)
Green silver nanoparticles	*Aristolochia indica* plant extract	Crop pest *Helicoverpa armigera*	Siva and Kumar (2015)
Ag and Zn nanoparticles	Chemical synthesis	*Aphis nerii* Boyer De Fonscolombe (Hemiptera: Aphididae)	Rouhani et al. (2012)
Al_2O_3 and TiO_2	Chemical synthesis	*Sitophilus oryzae* (store pest)	Sabbour (2012)
TiO_2	Photocatalysis	Bacterial pathogen *Xanthomonas perforans*	Paret et al. (2013)
AgNPs	Chemical synthesis	*Spodoptera litura*	Yasur and Usha Rani (2015)
Gold NPs	DNA-tagged nanogold	*Spodoptera litura* Fab. (Lepidoptera: Noctuidae)	Chakravarthy et al. (2012a, b)
Nanoparticles CdS, nano-Ag and nano-TiO_2 against	Chemical synthesis	*Spodoptera litura* (Fabricius) (Lepidoptera: Noctuidae)	Chakravarthy et al. (2012a, b)

(continued)

Table 10.1 (continued)

Metal/metal oxide nanoparticles	Reducing and stabilizing agent	Efficacious pests and pathogens	References
AgNPs	*Euphorbia prostrata*	Postharvest pest *Sitophilus oryzae*	Zahir et al. (2012)
	Avivennia marina	*Sitophilus oryzae*	Sankar and Abideen (2015)
Zinc oxide nanoparticles (ZnO NPs) (70 ± 15 nm)		Postharvest pathogenic fungi, *Botrytis cinerea*, and *Penicillium expansum*	Bryaskova et al. (2011)
Cu NPs		Four-order higher activity against bacterial blight *Xanthomonas axonopodis* pv. punicae on pomegranate at 10,000 times less concentration of recommended Cu	Mondal and Mani (2012)
$CuSo_4$ and $Na_2B_4O_7$ NPs		Rust disease of field peas	Singh et al. (2013)

2012b) (Table 10.1). An active preparation of FeNPs is well-known to possess nematicidal properties and thus used in fields of agriculture and horticulture (Sharma et al. 2017). The laboratory assays attested significant nematicidal effect of FeNP and the field evaluation demonstrated its benefits for mitigating damage caused by root-knot nematode. Biologically synthesized iron nanoparticles by a reaction of 2 mM $FeSO_4$ with 50 ml of selected bacterial isolate (*Stenotrophomonas maltophilia* KBS 2.4) supernatant solution were used as a potential nematicide in in vitro (>99% nematodes became inactive after 10 hrs) and in vivo experiments (88% of nematodes and root-knot numbers were reduced after 30–40 days of exposures) (Sharma et al. 2017).

However, silver nanoparticles have proved to be most effective as they exhibit potent antimicrobial efficacy against fungi, bacteria, virus, and parasitic nematodes. Silver nanoparticles are nanomaterials being applied as active ingredients in controlling plant pathogenic bacteria and fungi (Al-Askar et al. 2013; Musarrat et al. 2010; Gajbhiye et al. 2009) and their toxicity due to their induction of oxidative stress in the cells of targeted nematodes (Lim et al. 2012), due to affection in the function of membrane-bound enzymes in the respiratory chain to inhibit the oxygen metabolism leading to suffocation and subsequent cell death of bacteria and fungi (Puebla et al. 2004), and due to inhabiting replication of viral nucleic acid (Jain and Kothari 2014); AgNP has a microbial and nematicidal activity which may provide an alternative to high-risk chemical pesticides.

Review from some research results (Table 10.1) revealed that direct application of silver nanoparticles significantly suppressed the plant pests and disease pathogens such as fungi (i.e., *Alternia alternata*, *Fusarium oxysporum*, *Aspergillus fla-*

vus, *Phoma glomerata*), bacteria (i.e., *Erwinia carotovora*, *E. amylovora*, *P. wasabiae* Hf569027, *P. carotovorum atrosepticum* 1007, *D. chrysanthemi* Dsm4610, *P. wasabiae* 33, and *D. dadantii*), viruses (Sunhemp rosette virus (SHRV)), parasitic nematodes (i.e., *Meloidogyne incognita*, *M. javanica*), and crop pests (i.e., *Spodoptera litura*), including postharvest/stored-product pests (i.e., *Sitophilus oryzae*). This review indicated that silver nanoparticles have potential prospects and application in the management of plant pests and diseases.

Metal oxide NPs (Al_2O_3, TiO_2, ZnO) and $Na_2B_4O_7$ NPs showed insecticidal bioactivity and potential to use in managing stored-product pest (*Sitophilus oryzae*), crop pest (*Spodoptera litura*), bacterial pathogen *Xanthomonas perforans*, postharvest pathogenic fungi (*Botrytis cinerea*, *Penicillium expansum*), and rust disease of field peas (Table 10.1).

Nanoparticles possess distinct physical, biological, and chemical properties associated with their atomic strength (Merkt 2008). Due to their ultra submicroscopic size, nanoparticles gain the high degree of reactivity and sensitivity and thus have potential to prove very useful in controlling the pests and pathogens, as chemical and physical properties of nanoparticles vary greatly as compared to larger form.

Researchers have discussed and reviewed many modes of actions, but the exact mechanism by which silver NP control and prevent pests and disease pathogens is partially understood. Antimicrobial mechanisms were mostly studied and observed on bacterial pathogens. Basically, mode of toxicity of AgNPs is independent of silver ions but toxicity could be derived from a combination of silver nanoparticles and silver ions that are released during application of silver nanoparticles (Navarro et al. 2008; Asharani et al. 2008a). Small sizes of silver nanoparticles have the ability to pass through the membrane to interact with internal structures and become lodged within the membrane (Asharani et al. 2008b). Silver nanoparticles deposited in the membrane can affect the regulation of solute movements, exchange of proteins, as well as cell recognition. However, the mode of action of AgNPs against microbial pathogens is not very specific, and different mechanisms involve disrupting multiple cellular mechanisms, e.g., plasma membrane permeability, ATP synthesis, and response to oxidative stress in both eukaryotic and prokaryotic cells (Roh et al. 2009; Ahamed et al. 2010; Lim et al. 2012; Lara et al. 2011; Meyer et al. 2010; Sondi and Salopek-Sondi 2004; Morones et al. 2005; Lok et al. 2006; Choi and Hu 2008; Aziz et al. 2015, 2016). Subsequently, it leads to inhibition of respiration and other metabolic reactions as well as morphological and physical damages (Bragg and Rainnie 1974; Thurman and Gerba 1989). It was revealed that silver ions after penetrating the cell intercalate with bacterial DNA, consequently, inhibiting the proliferation and replication of the pathogen and ultimately killing the cell (Woo et al. 2009). Morones et al. (2005) observed that silver nanoparticles have impacts on the defense system of fungal pathogens in AgNP-treated cells.

The antimicrobial activity and property of the nanoparticle depend on the forms/shapes, size, and concentration of the nanoparticles. The silver nanoparticles with different shapes have different effects on bacterial cell (Rai et al. 2009). Truncated triangular nanoparticles reveal bacterial inhibition with silver content of 1.0 (one) µg, while spherical nanoparticles are needed with silver content of 12.5 µg, and the rod-shaped particles are needed with silver content in the range of 50–100 µg. Furthermore, the antimicrobial property of the silver nanoparticles is size and concentration dependent (Xia et al. 2016; Morones et al. 2005; Gavanji et al. 2012; Kim et al. 2012; Papp et al. 2010). Nanometer-sized silver possesses different properties due to morphological, structural, and physiological changes (Nel et al. 2003). The smaller silver nanoparticles have more significant antibacterial activity and more ability in DNA change. Silver ions release rate is a function of silver nanoparticle size (Oldenburg 2017). Generally, inhibition of plant pathogens is directly proportional to the concentration of AgNPs. Armstrong et al. (2013) reported that silver nanoparticles, like almost all nanoparticles, are potentially toxic beyond a certain concentration because the survival of the organism is compromised due to scores of pathophysiological abnormalities past that concentration. AgNP effect may be subtle and chronic at low concentrations applied in the field (Taha 2016). Toxicity of sub-lethal doses of AgNP to parasitic nematodes *M. incognita* could result in reproduction inhibition with 20, 40, and 50 ppm/ml of AgNP (Meyer et al. 2010; Taha 2016). However, in high concentration, nanosilver effect may cause toxicity to beneficial entomopathogenic nematodes, *Heterorhabditis indica*, *Steinernema arenarium* and *Steinernema abbasi* (Taha and Abo-Shady 2016), and *Caenorhabditis elegans* (Meyer et al. 2010; Lim et al. 2012). Syu et al. (2014) investigated the effects of the size and shape of AgNPs on growth, antimicrobial activity, and gene expression of *Arabidopsis* plant. Decahedral AgNPs (45 nm) exhibited the highest stimulation of root growth, while spherical ones (8 nm) did not stimulate root growth but induced uppermost levels of anthocyanin accumulation in plants. On the other hand, the highest antimicrobial activity was observed with triangular (47 nm) and spherical AgNPs. Moreover, AgNPs were found to activate *Arabidopsis* gene expression involved in cell proliferation, metabolism, and hormone signaling pathways. The toxic impact of AgNPs on plants, similarly to the effects of other metal NPs, is connected with their chemical composition enabling the release of toxic Ag^+ ions as well as with stress caused by some specific properties of these NPs, such as surface, size, and shape (Masarovičová and Kráľová 2013; Masarovičová et al. 2014).

10.3.3 Metal Nanoformulation

Silver-based organic and inorganic composites were developed for application against plant pest and disease pathogens (Table 10.2). Formulation stability is an important parameter for the biosafety of nanomaterials (Liu et al. 2008b). Some polymer and biopolymer stabilizers have been used in metal nanoformulation as stabilizer compounds. Hassan et al. (2016) used polyvinylpyrrolidone (PVP) as a stabilizer compound of silver nanoparticles against nematode *Meloidogyne incognita* on tomato. Cromwell et al. (2014) and Taha and Abo-Shady (2016) used starch

Table 10.2 Metal-based nanopesticide, their nanoformulation pesticidal, and antimicrobial activity

Metal and metal oxide nanoparticles	Nanoformulation method	Targeted pests and disease pathogens efficacious	References
Silver nanoparticles	Nanosized silica-silver	Bacterial pathogen *Pseudomonas syringae* and *Xanthomonas compestris* pv. *vesicatoria*	Park et al. (2006)
Silver nanoparticles (7–25 nm)	AgNP compound in colloidal suspension (7–25 nm particle size, 10,000 μL/mL silver content, pure water solvent)	Plant-pathogenic fungi on PDA (*Alternaria alternata*, *A. brassicicola*, *A. solani*, *Botrytis cinerea*, *Cladosporium cucumerinum*, *Corynespora cassiicola*, *Cylindrocarpon destructans*, *Didymella bryoniae*, *Fusarium oxysporum* f.sp. *cucumerinum*, *F. o*. f.sp. *lycopersici*, *F. solani*, *Fusarium* sp., *Glomerella cingulata*, *Monosporascus cannonballus*, *Pythium aphanidermatum*, *P. spinosum*, *Stemphylium lycopersici*)	Kim et al. (2012)
AgNPs (10–15 nm)	Chitosan–AgNp composite (size 10–15 nm)	Complete inhibition of conidial germination in *Colletotrichum gloeosporioides*	Chowdappa and Gowda (2013)
Silver nanoparticles (5 nm)	DNA-directed silver nanoparticles on graphene oxide (Ag@dsDNA@GO) composite	Xanthomonas *perforans* of tomato	Ocsoy et al. (2013)
Silver nanoparticles	AgNP was synthesized by a redox reaction of silver nitrate with sodium borohydride ($NaBH_4$) as a reducing agent using 0.2% starch (polymeric carbohydrate) as a stabilizer	In vitro study, J2 of *M. incognita* and *M. graminis* on turfgrass, reduced gall formation in the roots in 2 years without phytotoxicity	Cromwell et al. (2014)
Silver nanoparticles	Starch-stabilized Ag nanoparticles	*M. incognita*	Taha and Abo-Shady (2016)
Silver nanoparticles	Silver nanoparticles–PVP (polyvinylpyrrolidone) as stabilizer compound	*Meloidogyne incognita* on tomato	Hassan et al. (2016)
Ag+, Cu_2+, Zn_2+, Mn_2+,	Ag+, Cu_2+, Zn_2+, Mn_2+ loaded chitosan NPs	Antibacterial activity	Du et al. (2009)
Cu	Cu–chitosan NPs nanohydrogel	Antifungal pathogen *Fusarium graminearum*	Brunel et al. (2013)

(continued)

Table 10.2 (continued)

Metal and metal oxide nanoparticles	Nanoformulation method	Targeted pests and disease pathogens efficacious	References
Cu	Cu–chitosan NPs	Antifungal pathogen *Alternaria solani* and *Fusarium oxysporum*	Saharan et al. (2015)
Cu NPs	Soda-lime glass powder containing copper nanoparticle	Antimicrobial activity against Gram-positive, Gram-negative bacteria, yeast, and fungi	Esteban-Tejeda et al. (2009)
AgNP dust	AgNP dust stabilized with polyvinyl pyrrolidone	For control of castor semilooper, *Achaea janata* (L.) (Lepidoptera: Noctuidae), and the oriental leafworm moth, *Spodoptera litura* (F.) (Lepidoptera: Noctuidae) on *R. communis* leaves	Yasur and Usha Rani (2015)
Nanoalumina	Nanoalumina dust	Postharvest pests *Sitophilus oryzae* and *Rhyzopertha dominica*	Buteler et al. (2015)

as a stabilizer compound of silver nanoparticles against nematode *Meloidogyne* spp. Appropriate modification of chitosan nanomaterials by functionalizing them with metal compounds could significantly enhance their bioactivity toward plants through improvement of physical and chemical properties (Choudhary et al. 2017) (Table 10.2). Biopolymers such as starch, cellulose, alginate, chitin, and chitosan have been used for the development of new materials with environmental sustainability and desirable functionality (Babu et al. 2013).

Nanoform of copper (Cu) showed four order higher activity against bacterial blight on pomegranate at 10,000 times less concentration of recommended Cu (Mondal and Mani 2012). Titanium dioxide nanoparticles were also explored for bacterial spot disease of tomato and rose in pristine form or doped with zinc and silver (Paret et al. 2013). Alumina nanoparticles exhibited greater mortality against different postharvest pests (Buteler et al. 2015) (Table 10.2).

Other metal nanoformulations, such as Ag^{+}-, Cu^{2+}-, Zn^{2+}-, and Mn^{2+}- loaded chitosan nanoparticles, and Cu- and Zn-based chitosan NPs were found to possess broad-spectrum antimicrobial activity, act as plant defense booster, and enhance plant growth with regard to controlling plant diseases. Metals Cu and Zn have traditionally been used as components of agrochemicals. Cu and Zn, as components of nanoparticulate system, may reduce the risk of hazardous agrochemicals for crop improvement and protection. Due to high metal chelation ability of chitosan, metallic-based chitosan nanomaterials can be developed to fulfill antimicrobial action (antifungal activity and antibacterial activity (Saharan et al. 2013; Qi et al. 2004; Du et al. 2009; Ali et al. 2011), the deficiency of micronutrient/nanofertilizers (Corradini et al. 2010), and plant growth-promoting activity (Van et al. 2013; Saharan et al. 2016). As chitosan also has insecticidal properties (Sahab et al. 2015), metal-based chitosan NP composites will produce broad-spectrum microbial and insecticidal nanopesticides. Some researchers included Cu- and Zn-based chitosan NPs into agrochemical nanopesticides. However, as metals Cu, Zn, or Mn were not in the form of salts of metals, thus Cu- and Zn- or Ag- or Mn-based chitosan NPs may be included into metal-based nanopesticide.

Recently, considerable researches have been focused on various metal-based chitosan nanomaterials as potential antimicrobial agents. Nanochitosan acquired remarkable advantage over bulk chitosan due to large surface area and small size. Being nanosize of chitosan, it can easily interact with plant as well as microbial system that will lead to enhanced plant immune system, growth promotion, and antimicrobial activity (Van et al. 2013; Saharan and Pal 2016). More surface area and positively charged nanomaterials of Cu and Zn chitosan could interact easily to negatively charged cellular components of bacteria and fungi. This interaction provides an excellent antimicrobial activity. Cu-chitosan NPs exhibited higher antifungal activity compared to bulk chitosan, saponin, and $CuSO_4$ (Saharan et al. 2013). In another study, Cu-chitosan NPs are found to be effective against *Alternaria solani* and *Fusarium oxysporum* than the bulk chitosan and $CuSO_4$ (Saharan et al. 2015). Similarly, Zn-loaded chitosan NPs showed a wide spectrum of effective antimicrobial activities against various bacterial species including *E. coli*, *S. choleraesuis*, and *S. aureus*, which showed higher antibacterial activity than bulk chitosan, chitosan NPs, and Zn ions (Du et al. 2009). Similarly, for antifungal and antiviral activity, the negatively charged components of fungal and viral surfaces like protein and glycoprotein also interact with chitosan (Sudarshan et al. 1992). In general, Gram-negative bacteria were found to be more sensitive than Gram-positive bacteria.

It is observed that discharge of considerable amount of nanoparticles into environment due to increasing use of silver nanoparticles and widespread geographic distribution is increasing (Nam et al. 2014). Silver nanoparticle is now used in hydroponics systems and planter soils to eliminate unwanted microorganisms. As ultrasmall size nanoparticles have immense applications, the same characteristic is responsible for adverse effects on the environment, human beings, animals, and plants; thus some disadvantages and risks are involved in using nanoparticles (Khan and Rizvi 2014). All studies of toxicity on zebrafish and human cell indicated concern of potential risk (Nam et al. 2014; Verano-Braga et al. 2014; Ahamed et al. 2010; Johnston et al. 2010). Silver nanoparticle has been found to cause genotoxic, oxidative, inflammatory, cytotoxic consequences (Johnston et al. 2010). This finding indicated that production and field application of metal nanoparticles should be carried out with cautions and biosafety of metal nanoparticle-based pesticide is not yet accepted practically in plant protection area. It needs more research to evaluate the influence/impact of this new technology on all environmental components (Sharon et al. 2010). Several aspects of silver nanoparticles with relation to plants, viz., their half-life in soil, their toxicity effects on plants, and the optimum dosage for application in the field, need to be determined (Patel et al. 2014). However, to control the manufacturing and application of nanomaterials, several international programs, e.g., OECD (Organization for Economic Co-operation and Development), sponsorship program for the testing of manufactured nanomaterials to test nanoparticles, have been established (www.oecd.org/science/nanosafety/) (Nam et al. 2014). Moreover, some eco-friendly, cheap technologies such as green and biosynthesis of nanoparticles and biomaterials for matrices in nanoformulation have been developed and should be supported in developing metal nanopesticide.

10.4 Essential Oil-based Nanopesticide

Phytochemicals extracted from different parts of plants such as alkaloids, flavonoids, essential oils, glycosides, limonoids, quassinoids, saponins, and phenolics become promising tools as fungicides, bactericides, and nematicides (Suruyavathana et al. 2010; Khalil 2014). Plant essential oils have been recognized as an important natural source of insecticide and pesticides and promising alternatives for chemical insecticides now (Isman 2006; Rajendran and Sriranjini 2008).

10.4.1 Plant Essential Oil

Essential oils (EOs) are a group of ethereal lipophilic compounds, extracted from herbs, spices, and aromatic plants such as thyme (thymol), oregano (carvacrol), and clove (eugenol), citronella grass (sitronellal dan geraniol), eucalyptus (eucalyptol), camphor (D-camphor, linalool, cineole), rosemary (1,8-cineole, camphor, β-myrcene, α-pinene, verbenone, borneol, camphene), and cinnamon (cinnamaldehyde) (Burt 2004). Essential oils contain large proportions of volatile terpenes and compounds such as terpenoids and phenolic compounds which have insecticidal, bactericidal, virucidal, fungicidal, antiparasitical, and nematicidal activities with the different mechanisms of action and other medicinal properties such as analgesic, sedative, anti-inflammatory, spasmolytic, and locally anaesthetic remedies (Elgengaihi et al. 2016; Fernandes et al. 2014; Lee et al. 2012; Chen et al. 2014; Bilia et al. 2014; Toure et al. 2007). These compounds involved in plants may act as repellents, attractants, hatching stimulants or inhibitors, as well as nematotoxicants (Chitwood 2002). Many plant essential oils show a broad spectrum of activity against plant pest insects, disease pathogens, and a range of stored-product pests and antivector activities and larvicidal properties (Mohan et al. 2011; Conti et al. 2010).

The exact mechanisms of antimicrobial activities of EOs are still not clear although several modes of actions have been proposed and studied (Lambert et al. 2001; Sikkema et al. 1994). A generalized model is related to the hydrophobic nature of EO components, which enables them to insert into the cell membrane, disturbing the structure and increasing its permeability and resulting in the leakage of cell contents such as ions, ATP, nucleic acids, and amino acids (Burt 2004).

Some essential oils such as clove oil, citronella grass oil, eucalyptus oil, camphor oil, and oregano oil showed fumigant activity and/or contact toxicity against post-harvest and/or crop pest and disease (pest insects, bacterial, fungal, viral pathogen, and parasitic nematodes) (Ho et al. 1994; Cimanga et al. 2002; Batish et al. 2006; Su et al. 2006; Liu et al. 2008a; Lee et al. 2012; Djiwanti and Supriadi 2012; Huang and Lakshman 2010; Wang et al. 2010; Prasad et al. 2010; Balfas and Mardiningsih 2016; Mariana and Noveriza 2013; Katooli et al. 2012; Patel and Jasrai 2015; Ravi et al. 2014; Laquale et al. 2018; Šegvic Klaric et al. 2007).

It has been reported that clove oil was successfully used as pesticide (Isman 2000; Jiang et al. 2012). Eugenol (4 allyl-2-methoxy phenol; $C_{10}H_{12}O_2$) is a major constituent of clove essential oil and is an organic phenol compound. In 1998, clove oil (CAS # 8000-34-8) as pesticide was registered under United States Environmental Protection Agency (USEPA). Also, clove oil is classified as a minimum-risk pesticide and is not subject to federal registration requirements because its active and inert ingredients are evidently safe for human use (USEPA 2011). All of these products have been approved for use in organic food production.

Phytochemicals like essential oils and secondary metabolites face problems of cost-effectiveness and stability (pesticidal activity). Essential oil from *Artemisia arborescens* L. faced the problem of instability during pesticidal activity against *Aphis gossipy* (citrus fruit pest), adult and young *Bemicia tabaci*, and *Lymantia dispar* (cork plant pest) (Lai et al. 2006). Neem oil has been reported to show antifeedant, repellent, insecticidal, grain protectant, and growth-inhibiting activities against these insects; because of having large droplet size, nonavailability of suitable spraying equipment at farmers' level, and phytotoxicity at higher doses, it did not show encouraging results for its commercial applications (Prakash and Rao 1997). EOs have poor water solubility and this is a technological problem for their application as pesticidal products. Also, the use of essential oils as fumigant agent in large scales encountered some problems such as low vapor pressure that could be solved using some formulations such as control released formulations (Rajendran and Sriranjini 2008).

Currently, there is a new trend in using the natural plant extracts as well as EOs as natural pesticides to control pests with nanoformulations, by encapsulation of bioactive compounds in aqueous solutions through the production of nanoemulsions (Duarte et al. 2015; Ebadollahi 2011).

10.4.2 Essential Oil Nanoformulation

The encapsulation of essentials oils using nanoemulsified systems has potential application in nanopesticide products for antimicrobial delivery systems providing control released manner. A variety of EOs delivery systems have been developed in two categories of nanocarriers, i.e., (1) polymeric nanoparticulate formulations, which resulted in significant improvement of the essential oil antimicrobial activity, and (2) lipid carriers, including liposomes, solid lipid nanoparticles, nanostructured lipid particles, and nanoemulsions (Bilia et al. 2014).

Nanoemulsions are colloidal nanodispersions of oil and water being thermodynamically stabilized by interfacial layer of surfactant/cosurfactant (Chen et al.

2006). EOs have to be associated or combined with surfactants in order to enhance the antimicrobial activities by increasing the solubility of EOs in the aqueous phase. Surfactants also prevent shear induced coalescence during emulsion process (Chen et al. 2006). Nanoemulsion consists of surfactant aggregates that are in the range of 1–100 nm. Nanoemulsions were characterized by droplet size, transmittance, and stability. In this nanotechnology, it is needed to develop nanoformulations with particle size ranging from 20 to 200 nm that improved insecticidal activity and emulsion stability (Hamdi et al. 2015).

Surfactants play a main role in lowering the surface tension between oil and water interfaces and are essential for stable droplet size. Most EO nanoemulsions are currently prepared with synthetic (nonionic) surfactants (Tween 80, Span® 80, and Polysorbate 80). Ionic (polymeric) surfactants are not generally preferred due to toxicological limitations (Garg and Kumar 2014; Gupta et al. 2016). Tween 80 is low molecular weight surfactant, has a high hydrophilic and lipophilic balance, and it is efficient in minimizing droplet size better than polymeric surfactants (Ghosh et al. 2013). Tween® 80 and Span® 80 are commonly used as safe surfactants because of their high degree of compatibility with other ingredients and low toxicity, Span® 80 as a viscous, lipophilic, emulsifying liquid agent. Tween® 80, hydrophilic in nature, is a derivative of Span® 80. Mixture of Span® 80 and Tween® 80 was used having stable nanoemulsion. These nonionic surfactants as uncharged molecules are also known as safe and biocompatible products; they are not affected by any pH changes of the mixture (Lv et al. 2014; Mahdi et al. 2011; Sagiri et al. 2012). Ionic (polymer) surfactants (e.g., sorbitan monoesters) are hydrophobic and tend formation of water-in-oil type. Sometimes, mixtures of both hydrophilic and hydrophobic surfactants are used for nanoemulsion formation. Lecithins, polaxamer, and polysorbates are some of the most preferred surfactants for use. Organic solvents such as propylene glycol, polyethylene glycol, ethanol, and glycerol are also generally preferred (Garg and Kumar 2014; Gupta et al. 2016). Molecular complexes such as cyclodextrin inclusion complexes also represent a valid strategy to increase water solubility, stability, and bioavailability and decrease volatility of essential oils (Bilia et al. 2014).

The common methods involved in nanoemulsion preparation include high energy methods (high pressure homogenization and ultrasonication) and low energy methods (phase inversion temperature and emulsion inversion point). The high-energy method utilizes mechanical devices to produce strong disruptive forces to break the oil and water phase to obtain nanoemulsions. The low-energy method utilizes the stored internal energy for the formation of small droplets. Emulsions are obtained by changing the process parameters like temperature, composition, and others that affect the hydrophilic–lipophilic balance (HLB) (Nirmala and Nagarajan 2017). However, each of these examples has certain limitations, e.g., high energy emulsification is used to prepare nanoemulsions and large quantity of surfactant required for formulating microemulsions. However, now some reports are available for the formation of essential oil nanoemulsion with low energy emulsification. Ultrasonication emulsification method has considerable advantages for production of clove oil nanoemulsion as a green pesticide with the nanoemulsion droplet size of 43 nm

(Shahavi et al. 2015). In preparation of nanoemulsion, Tween® 80/Span® 80 as nonionic surfactants via ultrasonic emulsification method was used.

10.4.3 Mode of Action

The nanoemulsion formulation of essential oils showed higher efficacy as pesticidal and antimicrobial. Nanoemulsion caused high mortality, and toxicity was increased by 35.6% compared to the EOs (Mossa et al. 2017). Regarding applications of essential oils in healthcare using nanoemulsions, the effect of rosemary oil was amplified more than 100-fold in 200 times lower than the concentration of the raw essential oil (https://www.doterra.com/US/en/blog/science-safety-physiology-nanoemulsion-essential-oils%202018). Some essential oil nanoformulations have been studied and assessed against some crop and storage pests and disease pathogens (Table 10.3).

In the current study, camphor nanoemulsion (oil-in-water) (5%) was prepared using Polysorbate 20 as a nonionic surfactant, camphor EO, and deionized water. Nanoemulsion of camphor EO (oil-in-water) (5%) with droplet diameter 99.0 nm was formulated by ultrasonic emulsification for 40 min using Polysorbate 20 as a nonionic surfactant, camphor EO, and deionized water. Nanoemulsion showed high insecticidal activity against wheat weevil, *Sitophilus granarius*, with LC_{50} 181.49 μg g^{-1}. From Gas Chromatography-Mass Spectrometry analysis, phytochemicals such as 1,8-cineole, β-cimene, D-limonene, α-pinen, and α-terpineol were found in camphor EO which could play a role as insecticidal activity. Camphor nanoemulsion did not show any effect on germination or seedling growth. Acute and sub-chronic toxicity studies showed no signs of toxicity or biochemical alterations in liver biomarkers of male rats (Mossa et al. 2017). Camphor leaves EO also had strong fumigant (LC_{50} 2.5 mg L^{-1}) and contact toxicity (LD_{50} 21.25 μg/adult) against *Lasioderma serricorne*. Camphor EO from stem barks, leaves, and fruits had highly fumigant and contact toxicity against *Tribolium castaneum* and *Lasioderma serricorne* (Gonzalez et al. 2014).

Nanoemulsion of eucalyptus essential oil on polyvinyl alcohol (PVA) pellet formulation with fumigant active ingredient had been developed. The pellet making chamber was completely sealed (Chiellini et al. 2003). Its water solubility, reactivity, and biodegradability make it a potentially useful material in biomedical, agricultural, and water treatment areas (Gohil et al. 2006). Insecticidal efficacy of produced pellets was investigated against adults (1–3 days old) of *Tribolium castaneum* (Herbst), *Callosobruchus maculatus* (F.), *Rhyzopertha dominica* (F.), *Oryzaephilus surinamensis* (L.), and *Sitophilus oryzae* (L.). A representative pesticide, NeemAzal (neem oil), was encapsulated into polyvinyl alcohol/alginate-montmorillonite (PVA/Alg-MMT) nanocomposite capsule beads, by cross-linking with glutaraldehyde. The addition of sodium MMT to these formulations was found to have a profound inhibitory effect on the release of NeemAzal and has the potential for controlled release of pesticide (Rashidzadeh et al. 2014) (Table 10.3).

Table 10.3 Some nanoformulations of essential oils reported effectively against plant pest and disease

Essential oils nanoemulsion	Nanoformulation loaded/ method	Pest and disease target	Reference
Eucalyptus EOs (1,8-cineole (eucalyptol)/fumigant toxicity	Nanoemulsion of eucalyptus essential oil on PVA pellet formulation with fumigant active ingredient	Storage pests *Tribolium castaneum* (Herbst), *Callosobruchus maculatus* (F.), *Rhyzopertha dominica* (F.), *Oryzaephilus surinamensis* (L.), and *Sitophilus oryzae* (L.)	Chiellini et al. (2003); Gohil et al. (2006)
Thyme essential oil (p-cymene, 1,8-cineole) and other thymol constituens)	Thyme oil-in-water nanoemulsions stabilized by a nonionic surfactant	Postharvest fungi: *Aspergillus*, *Penicillium*, *Alternaria*, *Cladosporium*, *Rhizopus*, *Trichoderma*	Šegvic Klaric et al. (2007)
Garlic essential oil	Polyethylene glycol	Postharvest pest *Tribolium castaneum*	Yang et al. (2009)
Artemisia arborescens L essential oil	*Artemisia arborescens* L essential oil-loaded solid lipid nanoparticles		Lai et al. (2006)
Citrus peel essential oil nanoformulations	Nanoformulations	Tomato borer, *Tuta absoluta*	Campolo et al. (2017)
Camphor (*Eucalyptus globulus*) essential oil (α-Pinene, (b) β-Cymene, (c) D-Limonene, (d) 1,8-Cineole, and (e) α-Terpineol)	Camphor essential oil nanoemulsion (droplet size 99.0 nm)	Insect stored grains wheat weevil, *Sitophilus granarius*	Mossa et al. (2017)
NeemAzal/neem oil (azadirachtin, nimbidin)	Encapsulated into polyvinyl alcohol/ alginate-montmorillonite (PVA/Alg-MMT) nanocomposite capsule beads by cross-linking with glutaraldehyde	Insecticide, nematicide	Rashidzadeh et al. (2014)

Liposomal encapsulation was also promising technology in essential oil nanoparticulate system. Liposomes are colloidal particles associated from amphiphilic lipids usually phospholipids as bilayer vesicles, which can be used to incorporate hydrophobic or hydrophilic bioactive components within the nonpolar regions and the interior aqueous core, respectively (McClements 2012a; São Pedro et al. 2013). Thymol, carvacrol, and their mixture all showed significantly enhanced antimicrobial activities after liposomal encapsulation (Liolios et al. 2009). Enhanced antimicrobial and antioxidant activities of EO from citrus lemon after encapsulation in liposomes were also reported (Gortzi et al. 2007). Eugenol loaded in nanoliposomes exhibited improved storage stability and sustained release but the antimicrobial activities of eugenol were reduced because the good protection of liposomal encapsulation also reduced the contact of antimicrobial with bacteria (Peng et al. 2015). Clove oil in liposomes showed sustained release of eugenol and maintained good quality and stability during storage (Akrachalanont 2008).

The green pesticide technology uses oil-in-water nanoemulsions as a nanopesticide delivery system to replace the traditional emulsifiable concentrates (oil). Nanoemulsion is used due to highly stable product for long duration. The main reasons to use oil in water as nanoemulsion are reducing the use of organic solvent and increasing the dispersity, wettability, and penetration properties of the droplets. Oil-in-water nanoemulsions are for the improvement of biological efficacy and reducing the dosage of pesticides (Shahavi et al. 2015); they would be a useful strategy in green pesticide technology. These green and nanopesticides are safe and low to mammalian toxicity and have many sites of toxic actions in pests, which lead to high selectivity and low resistance development (Ehsanfar and Modarres-Sanavy 2004; Elaissi et al. 2012).

10.5 Agrochemical and Bioactive Agent/Material-based Nanopesticide

Agrochemical nanoformulations may be developed by two pathways, directly processed into nanoparticles and using nanomaterials as carriers to formulate smart delivery systems or controlled release mechanisms (Cui et al. 2018), and the controlled use of biological active compound nanoformulation may be developed by using bionanomaterials as carriers to formulate smart delivery systems.

10.5.1 Agrochemical Pesticide Nanoformulations

Pesticides are still a component of integrated pest management and used in certain conditions. Problems in their applications are improper delivery of agrochemicals and management, only 0.1% of the chemicals used in crop protection reach the target pest while the rest are lost, and they enter the environment and may cause hazards to nontarget organisms, including humans (Pepper 2008). Safe application of conventional agrochemicals is a major concern.

Safe application of those chemicals is replaced by application of various nano-based formulations that are similar to conventional formulations developed with improved features of increased rate of solubility, stability, permeability, and biodegradability and decreased rate of agrochemical spreading with uniform dispersion (Kah et al. 2013; Kah 2015), recently called as controlled release technology. The composition of many conventional insecticides is mostly water soluble and requires a delivery system for their application in the field (Das et al. 2014). This involves formulating the pesticide with a carrier, such as lipid or polymer based (nanoemulsions), or other systems including silica and nanoclays.

Basically, the nanoformulations should degrade faster in the soil and slowly in plants with residue levels below the regulatory criteria in foodstuffs (Khan and Rizvi 2014). Due to better kinetic stability, smaller size, low viscosity, and optical transparency, nanoemulsions can serve as better pesticide delivery systems (Xu et al. 2010). Such formulations may greatly decrease the amount of pesticide concentration and associated environmental hazards. Nanopesticides shall reduce the rate of application because the quantity of the chemical actually being effective is at least 10–15 times smaller than that applied with classical formulations; hence much smaller than the normal amount could be required to achieve satisfactory control of the disease. The nanoemulsion, as a carrier for pesticide delivery, can improve the solubility and bioavailability of the active ingredients of the chemical. Since all the propagules/spores of a pathogen do not approach/invade the host at one time, rather they attack intermittently, hence persistence or slow/gradual release of active ingredient in the root zone shall enhance the effectiveness of the formulation (Khan et al. 2011). Thus, such nanoformulation pesticides may decrease adverse environmental and human effects as compared to classical pesticides. Shi et al. (2010) studied the toxicity of chlorfenapyr (nanopesticide) on mice. It was reported that the chlorfenapyr nanoformulation from 4.84 to 19.36 mg kg^{-1} was less toxic to mice than the common formulation.

Some agrochemical nanopesticides have shown more efficiency in controlling plant pest and disease (Table 10.4), and are used in nanoformulations. Some examples are given below

1. Imidacloprid nanocapsule and nanoparticle
2. Nanocapsule for carbaryl, itraconazole, bifenthrin, fipronil, and lansiumamide B
3. Insecticide-coated liposome of imidacloprid, thiamethoxam, carbofuran, thiram, β-cyfluthrin, and mancozeb
4. Carbofuran nanomicelle
5. Beta-cypermethrin nanogel
6. Imidacloprid or cyromazine nanogranule and nanoclay
7. Silica nanoparticle-controlled release of chlorfenapyr and nanocalcium carbonate and silica-controlled release of validamycin
8. Silica nanoparticle-coated 3 mercaptopropyltriethoxysilane
9. Imidacloprid or cyromazine nanogranule and nanoclay

Table 10.4 presents some controlled release formulations of agrochemical pesticides employing novel nano-ranged amphiphilic polymers. Polymer-based nanoformulations have been exploited for the encapsulation of most of the insecticides. Different polysaccharides (e.g., chitosan, alginates, starch) and polyesters (e.g., poly-ε-caprolactone, polyethylene glycol) have been considered for the synthesis of nanoinsecticides (Das et al. 2014). Liu et al. (2008a) studied that polymer stabilizers

Table 10.4 Some controlled release formulations of agrochemical pesticides and their bioactivity

Chemical pesticide	Nano/microencapsulation method	Bioactivity	Reference
Imidacloprid	Imidacloprid nanocapsule (lignin–polyethylene glycol–ethylcellulose copolymer) suspension	Insecticide	Flores-Cespedes et al. (2012)
Imidacloprid	Controlled release formulations of imidacloprid employing novel nano-ranged amphiphilic polymers (liposome)	Insecticide	Chhipa 2017b
Imidacloprid	SDS (sodium dodecyl sulfate) -modified silver/titanium dioxide (Ag/TiO_2) along with chitosan and alginate by microencapsulation technique to increase the photodegradation	The sodium dodecyl sulfate (SDS) can play a role to enhance the photodegradation of the NPs in soil	Guan et al. (2010)
Imidacloprid	Imidacloprid nanoparticle [chitosan–poly(lactide) copolymer]	Insecticide	Li et al. (2011)
Carbaryl	Insecticide nanocapsule (carboxymethylcellulos)		Isiklan (2004)
Itraconazole	Insecticide nanocapsule acrylic acid-buacrylate		Goldshtein et al. (2005)
Bifenthrin	Bifenthrin nanocapsule [synthetic polimers: polyvinylpyrrolidone (PVP), polyvinyl alcohol (PVA), and poly (acrylic acid)-b-poly(butyl acrylate) (PAA-b-PBA) and polyvinyl alcohol (PVOH)]	Insecticide	Liu et al. (2008a)
Thiamethoxam	Insecticide-coated liposome (polyethylene glycol polymer)	Insecticide	Wibowo et al. (2014)
Carbofuran	Insecticide-coated liposome [poly (ethylene glycol) polyvinyl pyrrolidone]	Systemic and contact insecticide, nematicide	Yin et al. (2012), Grillo et al. (2016)
Carbofuran	Carbofuran nanomicelle (polyethylene glycol dimethyl esters polymer)		Shakil et al. (2010)

(continued)

Table 10.4 (continued)

Chemical pesticide	Nano/microencapsulation method	Bioactivity	Reference
Thiram	Insecticide-coated liposome (polyethylene glycol polymer)	Fungicide, ectoparasiticide to prevent fungal diseases in seed and crops and similarly as a animal repellent to protect fruit trees and ornamentals from damage by rabbits, rodents and deer	Fraceto et al. (2016)
β-Cyfluthrin	Insecticide-coated liposome (polyethylene glycol polymer)	Pyrethroid insecticide (low aqueous solubility, semi-volatile) against pest *Callosobruchus maculatus*	Loha et al. (2012)
Mancozeb	Insecticide-coated liposome (polymeric nanoformulation)	Dithiocarbamate nonsystemic agricultural fungicide with multisite, protective action on contact	Amenta et al. (2015); Venugopal and Sainadh (2016)
Carbofuran	Carbofuran nanomicelle (polyethylene glycol dimethyl esters polymer)		Shakil et al. (2010)
Beta-cypermethrin	Beta-cypermethrin nanogel (methyl methacrylate and methacrylic acid with and without 2-hydroxy ethyl methacrylate crosslinkage)		Rudzinski et al. (2003)
Chlorfenapyr	Silica nanoparticle as controlled release	Twice insecticidal activity	Song et al. (2012)
Fipronil	Oilcore silica-shell nanocapsule for fipronil nanoemulsion	Insecticide	Wibowo et al. (2014); Gutierrez et al. (2008)
Lansiumamide B	Lansiumamide B biocompatible silica nanocapsules	Nematicidal activity	Yin et al. (2012)

(continued)

Table 10.4 (continued)

Chemical pesticide	Nano/microencapsulation method	Bioactivity	Reference
Validamycin	Nanosized calcium carbonate and porous silica as controlled release	More active for longer period fungicide *Rhizoctonia solani*	Qian et al. (2011)
3 mercaptopropyltriethoxysilane coated	Silica nanoparticles coated with 3 mercaptopropyltriethoxysilane	More efficient insecticide	Liu et al. (2006)
Metribuzin	Alginate controlled release formulations		Pepperman et al. (1991)
Aldicarb	Aldicarb nanogel (lignin)		Kok et al. (1999)
Imidacloprid or cyromazine	Imidacloprid or cyromazine nanogranule (lignin)		Fernandez-Perez et al. (2011); Ragaei and Sabry (2014)
Imidacloprid or cyromazine	Insecticide nanoclay (alginate-bentonite)		Fernandez-Perez et al. (2011); Ragaei and Sabry (2014)

like PVP, PVA, poly(acrylic acid)-b-poly(butyl acrylate) (PAA-b-PBA), and polyvinyl alcohol (PVOH) were able to use them in formulating a stable (bifenthrin) nanopesticide. Pepperman et al. (1991) have proved that biodegradable microbial polymers like polyhydroxyl alkanates were effective for controlled release of pesticides.

The controlled use of agrochemicals could be also possible by the development of smart delivery system using biomaterials. Encapsulation of various agrochemicals in chitosan, silica, alginate, and calcium carbonat is an option for controlled and sustained delivery (Choudhary et al. 2017; Song et al. 2012; Qian et al. 2011; Guan et al. 2010). Nanoformulations of silica nanocapsule for chlorfenapyr, fipronil nanoemulsion, lansiumamide B, and validamycin; imidacloprid–chitosan-poly(lactide) copolymer; and three mercaptopropyltriethoxysilane-coated silica nanoparticles showed higher insecticidal, nematicidal, and fungicidal activities (Table 10.4).

Biomaterials as components of nanoparticulate system may reduce the risk of hazardous agrochemicals for crop improvement and protection. Nanoparticles prepared from natural sources and biopolymers have some merits of biocompatibility and biodegradability. Khodakovsky et al. (2000) reported that when they planted tomato seeds in a soil that contained carbon nanotubes (CNTs), these CNTs could not only penetrate into the hard coat of germinating tomato seeds but also exerted a growth-enhancing effect. They envisaged that the enhanced growth was due to increased water uptake caused by penetration of the CNT. This could be an advantage for using CNT as a vehicle to deliver desired molecules such as chemicals or other pesticidal properties into the seeds during germination that can protect them from the diseases. Since it is growth promoting, it will not have any toxic or inhibiting or adverse effect on the plant. Carbon nanotubes are allotropes of carbon, whose nanostructure is cylindrical in shape.

However, ultrasmall-sized toxic pesticide materials, similar to metal nanoparticles, are also a big concern towards human health and environment, as their higher ability in contact to animal, aquatic biota and human in compared to conventional pesticides.

10.5.2 Bioactive Agent Nanoformulation

Biocontrol agents such as natural enemies of pests and pathogens also could play a role as pesticidal properties of biopesticide products (Bhattacharyya et al. 2016). There are some biological control agents such as entomopathogen, rhizobacteria, endophytic microbe, fungi (enthomopathogen), bacteria (rhizobacteria), viruses, and nematode (entomonematode) which are used against insect pests and disease pathogens. Mycopesticides (fungal biocontrol agents) are promising biological pesticides as there is no need of ingestion; instead, they act by contact, are very specific, and can be easily mass-produced (Baric et al. 2008). Microbial products such as enzymes, antibiotics, inhibitors, and toxins are also promising as biopesticides against plant pathogens and pests (Bhattacharyya et al. 2016).

Similarly, biopesticides developed from inorganic and organic minerals nanomaterials had been paid attention from researchers. Inorganic mineral such as amorphous nanosilica obtained from various sources such as phytoplankton, volcanic soil is used as a biopesticide useful against stored grain, fungal organism, and worms/nematode (Liu et al. 2008b); and organic mineral such as chitosan and its derivative (chitin) nanoparticle is used as a biopesticide useful against crop pests (Sahab et al. 2015). Silica nanoparticles were developed as active ingredients and as nanostructured silica as a stored pulse protector and showed insecticidal activity and potential to use in managing crop pest (*Spodoptera litura*) and stored-product pests/postharvest pests (i.e., *Sitophilus oryzae*, *Callosobruchus maculatus*) (Table 10.5). Bionanomaterial of nanodiatomaceous earth (DE) was found effective to manage postharvest pests, confused and red flour beetles *Tribolium confusum* and *Tribolium castaneum* (Sabbour and Abd El-Aziz 2015), and can be useful as biopesticide. Amorphous silica is considered to have low toxicity, but prolonged inhalation causes changes to the lungs (https://www.cdc.gov/niosh/pel88/68855-54.html). However, today's common DE formulations are safer to use, as they are predominantly made up of amorphous silica and contain little or no crystalline silica

Table 10.5 Some inorganic/organic minerals nanomaterial and their mode of action against pests

Inorganic minerals nanomaterials	Targeted pests and pathogens	References
SiNPs	*Spodoptera litura*	Debnath et al. (2011)
Silica NPs	*Sitophilus oryzae* (L.).	Debnath et al. (2012)
Silica nanoparticles (SNPs)	Reduction infestation of stored pulse beetle, *Callosobruchus maculatus* on seeds of *Cajanus cajan*, *Macrotyloma uniflorum*, *Vigna mungo*, *Vigna radiata*, *Cicer arietinum*, and *Vigna unguiculata*	Arumugam et al. (2015)
Nanostructured silica as a stored pulse protector	Bruchid beetle, *Callosobruchus maculatus* (Coleoptera: Bruchidae	Arumugam et al. (2015)
Nanodiatomaceous earth	Postharvest pests, confused and red flour beetles *Tribolium confusum* and *Tribolium castaneum*	Sabbour and Abd El-Aziz (2015)
Chitosan (CS)-g-poly (acrylic acid) PAA nanoparticles	*Aphis gossypii*	Sahab et al. (2015)
Chitosan nanoparticle-coated fungal metabolite	Crop pest *Spodoptera litura*	Chandra et al. (2013)

(Subramanyam and Roesli 2003). A chitin derivative (N-(2-chloro-6- fluorobenzyl-chitosan), chitosan, has also been found to show strong insecticidal activity in some plant pests (Qian et al. 2011; Liu et al. 2006).

Microbial-based and other biopesticide formulations need stabilization and directed delivery mechanism toward identified targets. Formulations prepared from organisms and/or biomaterials are usually susceptible to desiccation, ultraviolet light inactivation, or even heat. Nanoformulations may provide new ways to enhance the stability of these biological agents. The controlled use of biological active compounds (as same as of agrochemicals) could be possible by the development of smart delivery system using biomaterials. Chitosan and clay being biocompatible nanomaterials can be used as stabilizing and delivery agents and, hence, have potential applications in the development of biopesticide formulations. Chitosan nanoparticle-coated fungal metabolite (CNPCFM), uncoated fungal metabolite (UFM), and fungal spores (FS) of entomopathogenic fungi *Nomuraea rileyi* (F.) Samson were evaluated against pest *Spodoptera litura* (Chandra et al. 2013). Results showed that among the tested materials, CNPCFM was found to be more effective than UFM and FS. Chitosan itself has insecticidal properties/bioactivity, i.e., chitosan (CS)-g-poly(acrylic acid) (PAA) nanoparticles reduced egg laying of *Aphis gossypii* (20.9 ± 9.1 and 28.9 ± 9.2 eggs/female for laboratory and under semi-field conditions, respectively) than control (97.3 ± 4.9 and 90.3 ± 4.9 eggs/female for laboratory and under semi-field conditions, respectively) (Sahab et al. 2015). The use of chitosan NPs as stabilizer and delivery agent in biopesticide nanoformulation will improve their plant pest and disease effectivity and safety as well.

The exploration of inorganic/organic mineral (biomaterials) nanoparticles and nanobiopesticide bioactivity toward other disease pathogens and nematode suppression should be investigated, as their activity on these pathogens has been reported, and as nanostructure for controlled release of microbial-based and other biopesticide formulations. Chitosan, a hydrophilic biopolymer industrially obtained by *N*-deacetylation of chitin, can be applied as an antimicrobial agent against fungi, bacteria, and viruses and as an elicitor of plant defense mechanisms (Rabea et al. 2003).

10.6 Commercial Product and Uses of Nanopesticide

Plant protection products containing nanomaterials that alter the functionality or risk profile of active ingredients (nano-enabled pesticides) promise many benefits over conventional pesticide products, such as better targeting of pest species, increased efficacy, lower application rates, and enhanced environmental safety (Walker et al. 2017). Nanosilver is the most studied in suppression of pest and disease impact on crops. The advancement of silver nanomaterials manufacture especially in silver nanoformulation, were making them have already been in the market for several years apparently. Several approaches are being investigated continuously to develop silver nanoformulations to increase their antimicrobial activity, and biosafety as well.

Recently, one of the products of nanosilver-based formula is "Alstasan Silvox" nanosilver hydrogen peroxide under Chemtex Speciality Limited Company. The product was commercialized as a safe and an eco-friendly "biodegradable disinfectant" (www.silverhydrogenperoxide.com, accessed in 2018). However, the product was manufactured also for effective and efficient broad-spectrum fungicides, antibiotics/bactericides, virucides, and nematicides. The product can also be used in the prevention and treatment of various agricultural diseases like root-knot nematodes, bacterial blights, and powdery mildew. The product, owing to its nonfoaming nature, is suitable for both cleaning and disinfecting, effective over a large range of microorganisms, eco-friendly, biodegradable, colorless, odorless, noncarcinogenic and nonmutagenic in nature, with no danger of microbial resistance, nonpolluting, and nonstaining in nature, does not emit any harmful fumes (unlike chlorine, bromine, formalin, and aldehydes), can be used in multimedia sanitation (air, water, soil, surface), and stably works over a wide range of pH and temperature. This silver peroxide destroys biofilms; provides rapid sterilization unlike other traditional methods; is a cold sterilant; does not change/alter any physical properties of the medium; is nonflammable, minimizing transportation and storage risks; has high thermostability; maintains easy handling and dosing; is free of carcinogenic aldehydes; and has no gaps in efficacy. This silver peroxide works on a short contact time and provides long-lasting disinfection with no toxic residues. The product is claimed safe for human consumption upto a concentration of 25 ppm. This product is in transparent liquid form and can be applied by four different methods, namely, Clean-in-place (CIP) method, dip method, spray method, and fill and soak method.

In this product, the nanosilver has stabilizer function, activator function, and oligodynamic action of the hydrogen peroxide (chemical naturally used as an antiseptic).

Nanoformulation of metal such as silver has a broad spectrum of antimicrobial activity and has been broadly applied as an active disinfecting and sterilization agent and in various fields such as water preservation, food and beverage storage, pharmaceutical, cosmetics, treatment of various human diseases, and agriculture; it would appear that their manufactured product is categorized as safe with broad utility application and cannot be categorized as an agro-nanopesticide only. Even in this product, the nanosilver has been applied as a stabilizer and activator and has oligodynamic action of the hydrogen peroxide. With all those characteristics described above, this nanosilver product seems to meet the criteria of desirable and ideal for its safe, efficient, and effective applications in agriculture. According to Khot et al. (2012) and Sangeetha et al. (2017), the advancement of nanomaterials with intense dispersion and interaction between the fluid and solid phases, with well-understood toxicodynamics and toxic kinetics, biodegradability in soil and environment, less toxicity and more photogenerativity, and smart and stable application in agriculture sector, would be desirable and ideal for their efficient and effective applications in agriculture.

Eventhough the duration or expiration of the long-term effect of the nanosilver (in the product) was undetermined and its long time of higher reactivity of nanosilver exposure by continuous application requires consideration of a bioaccumulation risk assessment, this nanosilver product offers effective and efficient broad-spectrum nanopesticides against plant pest and disease. However, this product shown that developing metal-based nanopesticide, is creating and designing the nanoformulation contained nanometal as pesticidal ingredient or as stabilizer and activator of the formula product.

Another nanopesticide product is nanochemical pesticide. One of the first nanoindustrial applications is the development of nanochemical pesticides (or nanopesticides) which contain nanoscale chemical toxins (Kuzma and Verhage 2006). Leading agrochemical companies developing nano-based pesticides are BASF, Bayer Crop Science, Monsanto, and Syngenta. However, the marketing of smart pesticides is currently constricted, especially through environmental groups/risk assessors opposing their introduction or potential risks associated with nanoscale materials, because the impacts of nanoparticles on the environment and human health are still largely unknown and unpredictable (Annex E 2018, http://www.nanotechproject.org/). Some of the nanopesticides issued in the market recently are mentioned in Table 10.6.

Table 10.6 Nano-based product on the market (Annex E 2018, http://www.nanotechproject.org/)

Company	Product	Mechanism
Syngenta	PRIMO Maxx and KARATE ZEON	Inhibit neural system
Nano Green	Nano Green	Attack respiratory apparatus
Agro Nanotechnology Corp	Nano Gro	Mimics stress conditions, increasing crop activity and yield

10.7 Future Prospects and Challenges of Nanopesticide Formulation and Application in Plant Pest and Disease Management

Nanomaterials give plant pest- and disease pathogen-targeted applications in plant protection through nanopesticide formulation of (1) nanoparticles (metal, EOs, agrochemicals), as an alternative pesticidal active ingredient to conventional pesticides, and (2) nanostructures providing pesticidal ingredient (agrochemicals, bioactive agent, EOs, metals) as controlled release mediator. Potential pesticidal ingredient-targeted applications are metal nanoparticles (silver and gold), essential oil nanoemulsion (clove, citronella grass, eucalyptus, camphor, thyme, *Monarda* spp.), agrochemicals (toxic pesticide), and bioactive agents (microorganisms, biomaterials, microbial products).

Nanomaterials and nanoencapsulation were solutions of the problem associated with pesticidal ingredients of metal, essential oil, agrochemicals, and bioactive agent and their application. The bulk metals have low antimicrobial and insecticidal effect. Silver nanoparticles, which have a high surface area and high fraction of surface atoms, have high antimicrobial effect as compared to the bulk silver (Patel et al. 2014). Chemical pesticides are ineffective to solve the problem of nematodes, as nematode population increased several months after the nematicidal is used (Thakur and Shirkot 2017), and of devastating disease pathogens such as viruses and bacteria. Controlled release technology from nanocarrier of nano-based formulations has emerged as an alternative approach with the promise to solve the problems accompanying the use of some agrochemicals while avoiding possible side effects with others (Han et al. 2009). Small engineered structure which provides pesticidal properties has shown slow degradation and controlled release of active ingredient for a long time period, making them environmentally safe and less toxic in comparison to chemical pesticide (Chhipa 2017a). The ability to delay or control delivery of pesticides to the target organisms is achieved by these nanopesticide delivery methods (Singh et al. 2015). Without encapsulation, EOs face the problem of instability during pesticidal activity, nonavailability of suitable spraying equipment at farmers' level since EOs have large droplet size, and low vapor pressure when used as fumigant agent in large scales. Nanoemulsions or nanoencapsulation of essential oil could solve the problem of water solubility and low vapor pressure, respectively. Nanoformulations may enhance the stability of these biological agents and biomaterials from desiccation, UV light inactivation, or heat stimuli. The controlled use of biological active compounds (as same as of agrochemicals) could be possible by the development of smart delivery system using nano-biomaterials. In order to keep the residue level below the critical limits as permissible by the regulatory criteria in foodstuffs, the nanoformulation should be degraded fast in the soil but slowly in plants (Khan and Rizvi 2014). These nanostructures have shown slow degradation and controlled release of active ingredients for a long time period in plants.

At present there is growing interest to utilize antifungal properties of AgNPs for plant disease management (Karimi et al. 2012; Aziz et al. 2016), because well-dispersed and stabilized AgNP solution can act as excellent fungicide due to good adhesion on bacterial and fungal cell surface (Kim et al. 2008), and so contribute to healthy plant growth. Metal nanoparticles offer a lot of potentials to effectively control pest population through their targeted approach; nanoparticles mediate higher penetration of active ingredients with a minimum concentration of chemicals used, as they penetrate easily through the cell wall and produce maximum effect (Thakur and Shirkot 2017). The nanotechnology has the immense potential prospect of applications in agriculture and plant pest management in particular direct application of nanoparticles to soil or seed or foliage to protect plants from different types of pathogen invasion by suppressing them as by the chemical methods (Thakur and Shirkot 2017). Silver nanoparticle is now used in hydroponics systems and planter soils to eliminate unwanted microorganisms. Using nanopesticides will contribute to effective and efficient spraying and, thus, decrease splash losses which are often evident with conventional pesticide and EOs spraying, since the droplet size is diminished also by this nanoformulation system (Bergeson 2010a). Moreover, silver is an excellent plant growth stimulator (Oldenburg 2017). Silver nanoparticles have merits over common chemical antimicrobial agents causing multidrug resistance (Guzman et al. 2009). Nanosilver-based compounds give promising broad-spectrum pesticides, as silver metallic nanoparticles exhibited bactericidal, fungicidal, virucidal, nematicidal, and insecticidal activities (Park et al. 2006; Jo et al. 2009; El-Shazly et al. 2017; Abbassy et al. 2017; Siva and Kumar 2015; Sankar and Abideen 2015; Sharma et al. 2017). Further these nanoparticles are free of toxic chemicals and hence are compatible with biological entities and safer to use. Moreover, AgNP may provide an additional benefit of managing multiple plant pathogens, as complex diseases often occur in the field. These effects may be due to its mode of action being not specific but associated with multiple cellular mechanisms. For this reason, AgNP is a wide-spectrum antimicrobial agent capable of affecting plant-pathogenic fungi and bacteria (Park et al. 2006; Jo et al. 2009). For example, it is possible that AgNP has an antifungal effect on several root-associated fungal pathogens (e.g., *Gaeumannomyces graminis* and *Rhizoctonia solani*). Pathogens treated with AgNP may become more tolerant to root-knot nematode damage because of some protection from additional stress by these other pathogens (Taha 2016).

From the viewpoint of the advantage of silver nanoparticles, nanopesticides offer promising higher effectiveness and safety and could be alternative to conventional pesticide. However, controversion of their biosafety to ecosystem had been addressed to their field application. The discharge of considerable amount of nanoparticles in the environment observed due to the increasing use of silver nanoparticles and the widespread geographic distribution is increasing (Nam et al. 2014). The AgNP antimicrobial activity is not specific and has higher reactivity; thus its mode of action could come in contact with plants, soil, and aquatic biota including fish, animals, and human beings and affect adversely the beneficial microorganisms. Colman et al. (2013) found that nanosilver treatment led to changes in microbial community composition, biomass, extracellular enzyme activity, and affected some ground plant species.

Since the mechanism of metal nanoparticle (e.g., AgNPs) toxicity remains undetermined, the use of AgNP-based pesticides may cause contamination in soil and water due to longer persistence, enhanced transport, and higher reactivity of nanoparticles (Khan and Rizvi 2014). Biodegradation of pesticides/nanopesticide is very important to remove the toxic compounds from the natural ecosystem. The application of silver and agrochemical-based nanoparticle product should be followed with soil and water remediation measurements (which usually applied for conventional chemical pesticides) to minimize the adverse effect of toxic NPs. Pesticide-contaminated soil and water are generally treated using phytoremediation, biodegradation, photochemical processes, and oxidation processes. Some literatures revealed that both chemical and biological nanomaterials also have a substantial role in crop protection as in irrigation water filtration and remediation of harmful pesticides (Patil et al. 2016). Iron nanoparticles occupy an important place among nanomaterials due to their enormous applications in environmental remediation and waste water treatment (Ali et al. 2016). Pesticides like chlorpyrifos and atrazine can be degraded using nanosized zerovalent iron. Similarly, some pesticide residues can also be photocatalytically decomposed using TiO_2 doped with Fe_2O_3 either incorporated into the pesticide formulations or sprayed directly on crops (Sasson et al. 2007). Iron oxide was a catalyst and adsorbent for natural and synthetic micropollutants (Xu et al. 2012; Rajabi et al. 2012). A potential bioremediation treatment is slowly gaining popularity. Some plant species have shown capability to accumulate heavy metals and other toxic subtances. The essential oil plant, citronella grass, showed ability in phytoremediation for the decontamination of metal-polluted soil (Handique and Handique 2009). Biochars also have shown ability to alleviate the soil function and decrease the biomass emission, binded carbon, and heavy metal substances (Juhaeti et al. 2005). Ramadass and Thiagarajan (2017) reviewed the microbes which play a major and important role in biodegradation. Common genera of bacteria such as *Bacillus*, *Pseudomonas*, *Flavobacterium*, *Sphingomonas*, *Brevibacterium*, and *Burkholderia* possess the inherent ability to utilize specific chemical groups in the pesticides as their sole source of either carbon and/or nitrogen and consequently achieve their conversion into nontoxic end products. Then, applied nanopesticide (of metal and agrochemical) as a component of integrated pest management (IPM) concept, which consequently lowers the volume of nanopesticide that will be applied, may minimize volume and spread of such nanopesticide, consequently lowering the impact on the environment.

Essential oils and bioactive agent-based nanopesticides were practically accepted as effective and safe nanopesticides. EOs-based nanopesticides are considered active, safe, and alternative to synthetic pesticides to control pest and disease pathogens, including storage pests, without producing adverse effects on seed germination and ecosystem (Khan and Rizvi 2014; Williams 2002; Dhekney et al.

2007). These oils have broad spectrum of pesticidal and insecticidal activities against many pests and disease pathogens due to the presence of many active components including volatile subtances, which had different sites and mechanisms of toxic action from highly fumigant and contact toxicity against crop pest and storage pests. One bioactive agent such as chitosan is few of the promising candidates in the future for nanopesticide formulation as alternative safe and effective pesticidal active ingredients, and or the nanostructure for controlled release delivery system of pesticidal ingredients, due to its unique properties such as abundance, biocompatibility, biodegradability, hydrophilicity, safety, and Nontoxicity. These bioactive agents have been used in several applications including antifungal activity (Saharan et al. 2013), antibacterial activity (Qi et al. 2004; Du et al. 2009; Ali et al. 2011), plant growth-promoting activity (Van et al. 2013; Saharan et al. 2015, 2016), and nanofertilizers (Corradini et al. 2010).

Great efforts are required in the commercialization of nanomaterials for agricultural applications (i.e., metal, agrochemicals), which require proper protection needs, testing priorities, risk assessment, and regulatory guidance at the global level (Chen and Yada 2011). Otherwise, the development and commercialization of essential oil and bioactive agent-based nanopesticides as green pesticides are prospects and challenges in future research and industry. The plant-based pesticides are in high demand, because they are sustainable in the environment and they are safe and are also pleasant to use (Maia and Moore 2011). The wide availability of essential oils from the flavor and fragrance industries, well received by consumers for use against home and garden pests, proves effective in agricultural situations for organic food production, and the allowed component of IPM has made it possible to fast track the commercialization of essential oil-based pesticides (Mohan et al. 2011). However, much work is needed to prepare effective, low-cost, and scalable nanoemulsions for nanopesticide application. The efficacy of EOs is greatly affected by many factors, such as plant's ripeness period, cultivation area, and essential oil distillation method/technology; different results can be observed (Ozdemir and Gozel 2017). In nanoformulations, nanoparticles prepared from natural sources (silica, chitosan, clay) and biopolymers have some merits of biocompatibility and biodegradability.

10.8 Conclusion and Suggestion

Developing nanopesticides includes developing application of nanomaterials as pesticidal active agents and as nanocarriers for developing delivery systems, improving conventional pesticide and bioactive agent nanoformulations. Nanomaterial applications in pesticide formulation increased their efficacy, efficiency, stability, durability, solubility, and targeted delivery, and controlled release rates of pesticidal agent, leading to protection against their adverse effect to environment.

Some potential green technologies and biomaterials useful for preparation of effective and safe pesticidal ingredients and structures of pesticidal nanoformulations should be considered and supported by researchers and the industry in the future design and fabrication of new metal, essential oils, agrochemicals, and bioactive agent-based nanopesticides. Future silver and metal nanopesticide manufacturing should consider size and concentration of nanoparticles, which are effective to pests and pathogens but less toxic to nontarget organisms. Future studies on EOs pesticide nanoformulation could focus on determining GAP (Good Agricultural Practice) of EOs plants, their postharvest measures, and distillation method in order to obtain highly active ingredient content and effective and efficient scalable nanoemulsions for application.

Nanopesticides significantly affect pest and disease pathogen suppression because of their specific physical and chemical properties and being environmentally safe and less toxic in comparison to excess use of agrochemical pesticides. However, their undetermined long-term effect of ultrasmall size of metal and agrochemicals, and as some product of their formula increased; its long-term exposed field and water are better being ameliorated through, i.e., ameliorant/bio-ameliorant filter, phytoremediation plants, and their application as component of IPM concept.

Strategic application and research of bioremediation plants and microorganisms, along with determination of the biodegradation rate of contaminants/pollutans, including exploration of new and improved nanostructures and nanomaterials for safe, effective, and efficient nanopesticide formulation, may support mitigation and suppression of possible adverse effects of harmful metal and agrochemical nanopesticides and environmental protection in the future.

Since the environmental fate of nanometal and agrochemical pesticide remains undetermined, utility of nanopesticide is a matter of choice for the government and/or farmer/consumer considering the harmful effects in the ecosystem and human health. However, in the future, nanopesticide safe use uniform should be considered and specifically designed as nanopesticide differ from conventional pesticides.

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