Chapter 8
Benefits and Potential Risks of Nanotechnology Applications in Crop Protection

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8.1 Introduction

Due to the increasing number of human population and changing climatic conditions, it is increasingly difficult to provide sufficient food for the population. With global hunger on the rise again, the Food and Agricultural Organization of the United Nations (FAO) has issued a sobering forecast on world food production. FAO says that if global population reaches 9.1 billion by 2050, the world food production will need to rise by 70%, and food production in the developing world will need to double. The FAO's forecast does not take into account any increase in agricultural production for biofuels. The projected 70% increase in food production will have to overcome rising energy prices, growing depletion of underground aquifers, the continuing loss of farmland to urbanization and increased drought and flooding resulting from climate changes (Population Institute 2017; FAO 2009). From the report of FAO, it results that crop yields would continue to grow but at a slower rate than in the past. Therefore, one of possible strategies is better protection of crops, although crop protection from pests and diseases can only reduce the amount lost after the potential for increased food production has been attained by proper utilization of all means possible. According to the data of FAO, every year the damage done to crops by pests and diseases constitutes ca. 20% of the potential world yield of food crops (FAO 2009). Crop protection becomes even more important in intensive agriculture, where increased fertilization, genetically uniform, high-yielding varieties, increased irrigation, and other methods are used. Crop losses due to

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diseases and pests not only affect national and world food supplies and economies but also affect individual farmers even more, whether they grow the crop for direct consumption or for sale. Because operating expenditures for the production of the crop remain the same in years of low or high disease incidence, harvests are lost due to diseases and pests lower the net return directly (Agrios 2005).

Crop protection can be defined as "the science and practice of managing invertebrate pests and vertebrate pests, plant diseases, weeds and other pest organisms that damage agricultural crops and forestry. Agricultural crops include field crops, vegetable crops and fruit and horticultural crops. Crop protection encompasses (*i*) pesticide-based approaches such as herbicides, fungicides and insecticides; (*ii*) biological pest control approaches such as cover crops, trap crops and beetle banks; (*iii*) barrier-based approaches such as agrotextiles and bird netting; (*iv*) animal psychology-based approaches such as bird scarers; and (*v*) biotechnology-based approaches such as plant breeding and genetic modification" (Crop Protection Definitions 2017). It is estimated that the discovery and development of a new agent costs about 150–200 million USD. A new product must be tested thoroughly for its action and its safety for the environment. It takes an average of 10–15 years to do this, so it is small wonder that worldwide, only about 12 agrochemicals are introduced each year. However, these chemicals are crucial for the efficient production of food (Essential Chemical Industry 2017).

As nanotechnology is one of the key technologies of the twenty-first century (Wennersten et al. 2008) that is able to provide "a new dimension", new properties to many current materials (Borm et al. 2006; Buzea et al. 2007; Jampílek et al. 2013, 2014, 2015; Vaculíková et al. 2016a, b; Jampílek and Kráľová 2017a, 2018a), it has been also widely used in food industry and for production of a new generation of agrochemicals (Chaudhry and Castle 2011; Rashidi and Khosravi-Darani 2011; Khot et al. 2012; Sekhon 2014; Parisi et al. 2015; Jampílek and Kráľová 2015, 2017b, c; Nuruzzaman et al. 2016; Fraceto et al. 2016). Thus, the use of nanotechnologies can significantly contribute to sustainable intensification of agricultural production (Garcia et al. 2010; Pérez-de-Luque and Hermosín 2013; Prasad et al. 2014, 2017; Sekhon 2014; Jampílek and Kráľová 2015), and vice versa, the agricultural production and food industry belong to important areas of nanotechnology application (Ghormade et al. 2011; Coles and Frewer 2013; Raliya et al. 2013; Chen et al. 2014a; Mukhopadhyay 2014).

Based on the definitions of the European Commission and/or US National Nanotechnology Initiative, nanomaterials/nanoparticles (NPs) can be generally classified as materials with a particle size less than 100 nm in at least one dimension (European Commission 2011; National Nanotechnology Initiative 2008). Pesticide nanosystems formulated into this particle size (similarly as nanoformulations of drugs) acquire enhanced bioavailability, targeted delivery, controlled release, protection against degradation and higher potency, and when currently applied and approved pesticides are used, a rapid and economically favourable solution is provided. Nanoformulations of pesticides can be classified either according to the nature of the nanocarrier, organic polymer-based formulations, lipid-based formulations, nanosized metals/metal oxides, metalloids, clay-based nanomaterials, etc. or according to various structures and morphologies of the nanosystem: nanocapsules, nanospheres, nanomicelles, nanogels, nanoemulsions, nanofibers, nanoliposomes, solid lipid nanoparticles, etc. (Balaure et al. 2017; Jampílek and Kráľová 2017a, b, 2018a). Alone pesticides, i.e. herbicides, fungicides and insecticides, can be divided into natural or synthetic and of inorganic or organic nature. In some cases, also a stabilizer/matrix of the nanosystem shows effectivity against phytopathogens, and thus it can be used alone or with a pesticide and amplify its potency.

In this chapter, advantageous effects of nanomaterials/nanoformulations of various herbicides, fungicides, bactericides and insecticides on weed and phytopathogens are discussed in detail, and special attention is devoted also to risks of applications of nanopesticides.

8.2 Nanoherbicides

Modern agriculture and land management uses chemical agents, i.e. herbicides for the control of unwanted vegetation. Although many compounds used for the control of unwanted vegetation were designed and applied, currently new agrochemicals more effective for specific weeds resulting in less damage of desirable vegetation, i.e. safer to human and the environment, are desirable. Since these herbicides of new generations should be affordable, attention is focused not only on nanoformulations of used current herbicides but also on nanosystems containing metals effective against weeds and their combinations. In addition, some polymers used in nanoformulations as excipients were found to potentiate effectivity and selectivity of herbicidal-effective organic compounds.

8.2.1 Synthetic Nanoherbicides

8.2.1.1 Nanoscale Phenoxyacetic Acid Herbicides

Nanohybrids of 2-chloro- (2-CPA) and 2,4,5-trichlorophenoxyacetic acids (2,4,5-T) prepared by hybridization of phenoxyacetic acid herbicides into zinc-aluminium-layered double hydroxide (Zn-Al-LDH) interlamellae, in which the successful intercalation of the herbicides into the layered double hydroxide inorganic interlayers was confirmed by basal spacing expansion from 8.9 Å in the layered double hydroxide to 18.5 and 26.2 Å, respectively, were reported by Sarijo et al. (2010a). The release process was found to be pH-dependent in the order of pH $12 > 3 > 6.25$, and longer release time estimated for 2,4,5-T compared to 2-CPA indicated stronger interaction of 2,4,5-T with the layered double hydroxide inorganic interlayer. The obtained results suggested that two-dimensional-type layered structure consisting of thin crystalline inorganic layers with a thickness of a few nanometers such as Zn-Al-LDH represents a suitable matrix for the controlled release formulation of agrochemicals based on halogen-substituted phenoxyacetic acid such as 2-CPA and 2,4,5-T. In another study, Sarijo et al. (2010b) investigated the release of chlorophenoxy herbicides, namely, 2-CPA, 4-chlorophenoxyacetic acid (4-CPA) and 2,4,5-T, from their nanohybrids into various aqueous solutions, carbonate, sulphate and chloride, whereby the release was found to be controlled by pseudo-second-order rate expression. The calculated $t_{1/2}$ values for 2-CPA were 71, 77 and 103 min in carbonate, sulphate and chloride aqueous solutions. The $t_{1/2}$ values of 79, 97 and 146 min and 210, 282 and 442 min were estimated for 4-CPA and 2,4,5-T for carbonate, sulphate and chloride, respectively, indicating that the percentage of the saturated amount of 4-CPA and 2,4,5,T released decreased in the following order: carbonate > sulphate > chloride. Thus, the release of phenoxyacetic acid herbicides into the media is preferred if the available anion in the media has higher affinity towards the Zn-Al-LDH inorganic interlayers, and, therefore, the exchangeable anions, either they are in the release media or in the nanohybrid, can be exploited as a means to tune the release properties. On the other hand, for all the media the percentage of saturated release decreased in the following order: 2-CPA > 4-CPA > 2,4,5-T. This can be connected with the fact that electrostatic forces with the host in the molecule of 2,4,5-T having three chlorine atoms attached to the benzene ring are stronger than in 2-CPA, which results in more difficult release of 2,4,5-T compared to 2-CPA; the release from the interlayer of the inorganic host could be also affected by the bulkier structure of 2,4,5-T. Easier release of 2-CPA compared to 4-CPA is connected with the fact that in 4-CPA, the chloride substituent in position 4 becomes more negatively charged and therefore held stronger in the interlayer. The inorganic Zn-Al-LDH was also used as a matrix for 2,4-dichlorophenoxyacetic acid (2,4-D) by Hussein et al. (2005) who found that the release rate of the 2,4-D anion from the interlamellae of the nanocomposite depended on the type of anion and its concentration in the release media, the release from the carbonate solution being more effective than from chloride solution or distilled water. Initially, the release of the guest 2,4-D into aqueous solutions containing chloride, carbonate and distilled water was rapid, followed by a more sustained release thereafter, and this behaviour was dependent on the type of anions and their concentrations in the release medium (aqueous solution). While in distilled water and NaCl aqueous solutions the layered structure of the nanohybrid was not destroyed by the release of 2,4-D anions for at least 24 h, in the presence of carbonate in aqueous solution, the release of 2,4-D ions from the nanohybrid resulted in the formation of two new phases, LDH and ZnO. This indicates higher affinity of carbonate towards the LDH inorganic interlamellae compared to chloride. However, independently on the structure of the resulting controlled release formulation, the release of 2,4-D anions from Zn-Al-LDH inorganic lamella was controlled by the first-order kinetic at least at the beginning of the deintercalation up to 12 h.

Using montmorillonite (MMT)-gelatin composites, Alromeed et al. (2015) prepared slow-release formulations of the (4-chloro-2-methylphenoxy)acetic acid (MCPA) herbicide, which could reduce the environmental risk associated with herbicide application by more effective reduction of leaching and improved bioactivity in the upper soil layer compared with a commercial product. MCPA was released much more slowly from the MMT-gelatin formulations prepared at lower pH than from those prepared at higher pH values. For all formulations, the herbicide was completely released after 48 h, and no fraction was bound irreversibly to the clay-gelatin matrix. The highest release was obtained for the formulation prepared at pH close to the isoelectric point of the protein (7.9–9.0). Increasing of pH results in the increased labile fraction of MCPA due to the reduction of strong electrostatic interactions involved in the retention of the herbicide in the clay-gelatin matrix at pH value exceeding the value of isoelectric point; this effect is counteracted by the presence of mostly exfoliated clay particles acting as a barrier to the diffusing out of herbicide molecules. By application of glycerol, the interaction of the herbicide within the clay-gelatin matrix can be modified by enhancing hydrogen bonding over stronger electrostatic interactions, which results in enhanced release of the herbicide. The slower release rate of 2,4-D in water and soil was estimated also from carboxymethyl cellulose gel formulation containing some modified bentonites prepared by intercalating inorganic or organic cations in interlayers of Na^+-saturated bentonite. The $t_{1/2}$ corresponding to the time when 50% of 2,4-D has been released in water varied from 8.8 to 19.8 h, and the largest value was shown by the formulation incorporating hydroxy-iron intercalated bentonite showing the highest sorption capacity to 2,4-D. Such gel formulations could also be used for controlled release of 2,4-D herbicide when applied to a thin soil layer (Li et al. 2009).

Formulations of herbicides 2,4-D and picloram which were anchored on porous gel of hexagonal mesoporous silica modified with carboxylic acid showing a nanometric structure with spheres <50 nm and porous diameter of 10 nm exhibited the controlled release of herbicides, which was lower for picloram than for 2,4-D (Prado et al. 2011).

Nanostructured liquid crystalline particles (NLCP) containing 18% (w/w) of phytantriol with the size of ~250 nm, polydispersity index of 0.22 and zeta potential of −15 mV, which are able safely interact with plant leaf cuticular surfaces with minimal impact on epicuticular waxes, were used to deliver 2,4-D to weeds, crops and model plants. In field trials, such nanoformulation used for the control of the invasive weed wild radish (*Raphanus raphanistrum* L.) in wheat was found to be effective at lower concentrations (0.03% and 0.06%) as compared with commercially available herbicide formulation (Estercide 800), while crop yield remained similar for nano- and commercial preparations. In a separate trial, the phytotoxicity on the crop *Hordeum vulgare* was assessed, along with the herbicidal effects on the weed *R. raphanistrum*, and the obtained results were consistent with earlier observations made on *Triticum aestivum.* High-concentration spray applications of 2,4-D NLCP resulted in greater epicuticular wax solubilization effects, and it was estimated that the area of epicuticular waxes was the highest for untreated controls and significantly decreased with the increase in the concentration of NLCP. This indicates that NLCP can reduce the risk of cuticle damage while still efficiently delivering the active ingredient, which can result in increased yield. The application of NLCP can also eliminate adverse environmental effects as well as negative effects on nontarget plants observed with the overuse of surfactants in agrochemical formulations (Nadiminti et al. 2016).

Sustained release and enhanced herbicidal activity against the tested target plant (*Brassica* sp.) were shown also by nanosized rice husk loaded with 2,4-D, while the nontarget plant *Zea mays* L. was not affected, and better herbicidal efficiency of this formulation as compared with that of the commercial 2,4-D could be connected with the reduced soil sorption or increased bioavailability of 2,4-D in the soil (Abigail et al. 2016).

8.2.1.2 Nanoscale Triazine Herbicides

Solid lipid NPs (SLNPs) prepared using glycerol tripalmitate and poly(vinyl alcohol) (PVA) containing atrazine (ATZ) and simazine (SMZ) showing the hydrodynamic diameter of 255 nm and encapsulation efficiency (EE) of 89.7 ± 0.02% of ATZ and 97.3 ± 0.05% of SMZ were prepared by de Oliveira et al. (2015). PVA used during the preparation of the formulations was adsorbed on the surface of the particles, creating a layer that provided steric stabilization. The SLNP formulations showed negative zeta potential values that were not affected by encapsulation of the herbicides, and after 30 days of storage, a mean value of −15 mV was estimated. The release of herbicides from SLNPs was slower compared to that of the free herbicides, which was reflected in significantly lower $t_{1/2}$ values corresponding to 50% release that were 2.5 h (ATZ) and 5.3 h (SMZ) compared to $t_{1/2}$ values estimated for free herbicides, namely, 52.9 h for ATZ and 51.1 h for SMZ. The values of the release constants showed that atrazine was released faster than simazine. The encapsulated herbicides showed decreased cytotoxicity when compared with the commercial formulation, and they were also investigated for pre- and postemergence treatments applied to a target species (*R. raphanistrum*) and a nontarget species (*Z. mays*) at concentrations equivalent to 0.3 and 3 kg/ha. SLNPs containing herbicides caused greater phytotoxic effects on both the aerial parts and roots of plants, compared to the commercial formulation, and they remained effective also at tenfold lower concentration than the recommended concentration. At postemergence treatment, SLNPs loaded with herbicides showed comparable phytotoxic effects on aerial parts and roots at both studied concentrations, and the interaction of SLNPs with *R. raphanistrum* was found to be species-specific, because no toxic effects of SLNPs were observed in assays with *Z. mays*.

Treatment with poly(ε-caprolactone) (PCL) nanocapsules containing ATZ induced faster and more severe development of toxicity symptoms, faster inhibition of photosystem (PS) II photochemistry and greater lipid peroxidation in *Brassica juncea* leaves compared with the commercial ATZ product, and it was very effective also when the tenfold diluted concentration of nanoformulation was used. The herbicidal effectiveness of nanocapsules containing ATZ could be connected (*i*) with the protection of the encapsulated active compound against physicochemical degradation; (*ii*) with the interaction of hydrophobic nanocapsules with the leaf cuticle resulting in increased delivery of herbicide to the plant tissues and decreased loss of the herbicide to the environment; and (*iii*) with slow release of ATZ from PCL nanocapsules, which can promote a gradual contact between the herbicide and the plant. Thus, PCL nanocapsules could be considered as an efficient carrier system for ATZ enabling the application of lower dosages of the herbicide and could be used as an effective tool in the postemergence control of weeds. Oliveira et al. (2015) evaluated also postemergence herbicidal activity of PCL nanocapsules containing ATZ with the average size of 240.7 ± 2.9 nm using mustard (*B. juncea*) as target plant species model. After 7 days also the leaves of the plants treated with tenfold diluted nanoformulation containing ATZ revealed similar symptoms of leaf wilt, yellowing, and necrosis as the commercial atrazine at the recommended dosage, and a strong reduction of the shoot dry weight was observed. Pereira et al. (2014) evaluated PCL NPs containing ATZ in terms of their herbicidal activity and genotoxicity and found that the encapsulation of the herbicide resulted in harmlessness to a nontarget organism (*Zea mays*), but it enhanced the effectiveness against a target organism (*Brassica* sp.), compared to the use of the free herbicide, which could be connected with increased herbicide bioavailability. At application of nanoencapsulated herbicide, the mobility of ATZ in the soil column was found to be increased because of reduced soil sorption, which led to better effectiveness of ATZ against the target organism. Moreover, the nanoformulations containing ATZ were less genotoxic, compared to the free herbicide, which would contribute to the improved level of safety in agricultural applications. Clemente et al. (2013) performed ecotoxicological evaluation of PCL nanocapsules containing ametryn and ATZ. The encapsulation of the herbicides in nanocapsules resulted in lower toxicity to the alga *Pseudokirchneriella subcapitata* and higher toxicity to the microcrustacean *Daphnia similis* compared to the herbicides alone. The cytogenetic tests employing human lymphocyte cultures showed that formulations of nanocapsules containing the herbicides were less toxic than the herbicides alone. The suitability of polymeric PCL nanocapsules containing three triazine herbicides (ametryn, atrazine and simazine) as controlled release systems that could reduce environmental impacts was studied also by Grillo et al. (2012), and the obtained results supported the previous findings that the use of PCL nanocapsules is a promising technique that could improve the behaviour of herbicides in environmental systems.

Controlled release formulations prepared by incorporation of ATZ in ethylcellulose, in which allophanic clays and nanoclays were incorporated as matrix-modifying agents, were designed by Cea et al. (2010), and their effect on the emergence and growth of field mustard (*Brassica campestris* L.) was evaluated under greenhouse conditions. The controlled release formulations effectively reduced the seedling emergence and caused greater death of seedlings than the commercial formulation, especially when nanoclays were added into the formulation, and they were characterized also by prolonged bio-efficiency enabling longer applications intervals and in this way minimizing the harmful impact of ATZ on the environment.

Metribuzine entrapped within a sepiolite-gel-based matrix with one of two proportions of clay/herbicide and used as either a gel or powder after freeze-drying remained active longer than commercial formulation, avoiding the need to use more frequently herbicide applications (Maqueda et al. 2009).

8.2.1.3 Other Nanoscale Aromatic-Type Herbicides

Paraquat encapsulated in the formulation of AgNPs in the chitosan (CS) matrix with the particle size of 100 nm and the entrapment efficiency of 90% exhibited steady release of herbicide in the early hours, and a total release of about 90% was estimated at 24 h. Surface treatment of the cut pieces of *Eichhornia crassipes* with 0.5, 10 and 25 μg/mL of this formulation resulted in greater necrotic lesions than at application of free paraquat at doses 10 and 25 μg/mL. The application of the nanoformulation did not affect soil physicochemical parameters and soil enzymes activity; nanoherbicide-treated seeds showed 90.1% seed germination, and no plant growth parameters of the nontarget plant *Vigna mungo* were adversely affected (Namasivayam et al. 2014). CS/tripolyphosphate (TPP) NPs loaded with paraquat showing 62.6 ± 0.7% association of the herbicide with the NPs exhibited delayed release of paraquat in laboratory conditions compared to the free herbicide (70% vs 90% within 350 min), and the diffusion and relaxation of the polymeric chain might be a factor affecting paraquat release. The encapsulation did not affect the herbicidal activity of paraquat in cultivations of maize (*Z. mays*) and mustard (*Brassica* sp.), and herbicide bound to NPs caused less chromosome damage compared to its free form (Grillo et al. 2014). Less chromosome damage in samples treated with nanoparaquat compared to conventional paraquat was estimated also by Nishisaka et al. (2014), indicating that the nanoformulation of paraquat loaded into NPs prepared from CS and TPP can be used to minimize damage caused by bulk herbicide and is suitable for safer control of weeds in agriculture. Silva et al. (2011) studied the release profile of paraquat from alginate (ALG)/CS NPs with particle size of 635 nm, zeta potential −22.8 ± 2.3 mV and entrapment efficiency of 74% and compared it with that of the free herbicide. They estimated that the complete herbicide release from NPs was extended by 2 h compared to free paraquat, which allows to reduce the amount of the herbicide resulting in lower environmental risk and lower energy costs. The release process was governed by mechanisms displaying non-Fickian kinetics, and it could be assumed that the release of paraquat from ALG/CS NPs is connected with the rupture of ionic bonds between paraquat and polymeric ALG chains. In another experiment, Silva et al. (2010) loaded clomazone herbicide into ALG/sodium bis(2-ethylhexyl) sulfosuccinate (AOT) or ALG/CS NPs and found that the association of the herbicide with the NPs prolonged the release time: in the time period of 240 min ca. 70% of clomazone was released, while from ALG/AOT or ALG/CS NPs within the same period, this amount was only 50% and 20%, respectively, indicating that ALG/AOT NPs have higher rates of association of the herbicide clomazone than ALG/CS NPs. The release of clomazone was also found to be governed by non-Ficknian kinetic processes, and the kinetic constant value (k) indicated a faster release for herbicide of the ALG/CS NPs ($k = 1.96$ min^{-1}) compared to ALG/AOT NPs ($k = 1.12$ min^{-1}).

Poly(butyl methacrylate-diacetone acrylamide)-based formulation used for controlled release of acetochlor showed improved herbicide incorporation and slower release, obviously due to potential interactions between the herbicide and the polymer (Guo et al. 2014). The evaluation of application of pretilachlor microemulsion and herbicide encapsulated monolithic dispersion with average particle size in the range of 1−100 nm against *Echinochloa crus-galli* in rice fields performed 30, 60 and 90 days after transplantation confirmed that tested nanoformulations were superior compared to the commercial pretilachlor formulation Rifit® 50 EC (Kumar et al. 2016).

Metsulfuron methyl-loaded pectin nanocapsules with particle size ranging from 50 to 90 nm, zeta potential value of −35.9 mV and 63 ± 2% EE, which applied on a weed (*Chenopodium album*) grown in a wheat crop were found to be more effective at a reduced dose than commercial formulation, showed less toxicity and longer lasting effects, while wheat crop was unaffected. The dry biomass of *C. album* treated with nanoformulation containing the herbicide was 5 g/m^2, while it reaches 48 g/m^2 at controls and 19 g/m^2 at application of the normal herbicide (Kumar et al. 2017). Subabul stem lignin was used as a matrix material in a controlled release nanoformulation of diuron with particle size ca. 166 nm and 74.3±4% EE. This nanoformulation exhibited a nonlinear biphasic release profile for diuron, and its application into soil caused earlier signs of leaf chlorosis and mortality in *Brassica rapa* seedlings compared to seedlings grown on soil supplemented with a commercial diuron preparation or bulk diuron (Yearla and Padmasree 2016). Isoproturon-loaded carboxymethyl starch/MMT composite microparticles showing about 75% EE demonstrated a significantly reduced release rate of herbicide than its commercial formulation, releasing 95% isoproturon after 700 h compared to 24 h estimated with the commercial formulation. Moreover, leaching in soil from composite formulations was relatively slower than release in water, which could positively affect the environmental pollution (Wilpiszewska et al. 2016).

Kanimozhi and Chinnamuthu (2012) fabricated manganese (II) carbonate core-shell NPs, in which the $MnCO_3$ core was coated with a single bilayer of the polyelectrolytes sodium polystyrene sulphonate and polyallylamine hydrochloride using a layer-by-layer method. The particle size distribution of the $MnCO_3$ core and core-shell was 126 and 250 nm, respectively. Then the NPs were treated with diluted hydrochloric acid to prepare inorganic/organic hollow spheres, which were subsequently loaded with pre-emergence herbicide pendimethalin programmed to release smartly upon requirements. Porous hollow-shell material could be considered as suitable also for loading of other active ingredients, e.g. fertilizers for conditional release.

The interlayer spaces of the methoxy-modified nanosized tubular halloysite (mHal) and platy kaolinite (mKaol) were found to be suitable for the effective intercalation of amitrole herbicide, which substantially promoted amitrole loading. The slow herbicide release from amitrole-loaded mKaol was connected with the restricted diffusion of the intercalated herbicide caused by the lamellar structure of mKaol as well as with the long diffusion path of the intercalated herbicide due to the large size of mKaol particles compared to mHAL particles (Tan et al. 2015).

ALG/CS and CS/TPP NPs with particle size <400 nm and zeta potentials of −30 and + 26 mV, respectively, were found to be suitable to encapsulate the herbicides imazapic and imazapyr with 60% EE. The treatment of target weed species, *Bidens pilosa* (blackjack), with a dose equal to that used in the field (400 g/ha) resulted in reduced growth compared to the control; the herbicides maintained adequate herbicidal activity, but their toxicity to nontarget organisms was reduced, and the researchers emphasized that the encapsulation of two herbicides in one carrier system could improve the activity and reduce the impacts on the environment (Maruyama et al. 2016). A natural smectite (SW) modified with CS or with Fe^{3+} cation was tested as an adsorbent or a carrier for controlled release formulations of imazamox, an herbicide used for the control of root-parasitic plants *Orobanche* spp. The herbicide release into water was inversely related to the strength of imazamox-clay interactions, whereby the herbicidal activity of the weak complex imazamox-SW modified with CS was comparable with that of commercial formulation, however showing a reduction in the total soil leaching losses (15%) and the peak maximum concentration in soil column leachates (40%) (Cabrera et al. 2016). The co-exposure of AgNPs (100 μM) and chiral herbicide imazethapyr (IM) (0.2 μM) to model plant *Arabidopsis thaliana* showed that the use of (*R*)-enantiomer led to preferential Ag uptake by plant roots, and also higher metal amount in shoots was estimated compared to co-exposure of AgNPs with (*S*)-enantiomer. A significant increase of free amino acids (except cysteine) following exposure to racemate IM, (*R*)-IM or their co-exposure with AgNPs resulted in increased release of Ag^+ due to formation of amino acid adducts with Ag^+ ions, which was then reflected in the toxicity enhancement under co-exposure of AgNPs and (*R*)-enantiomers. Treatment of roots with (*S*)-IM led to reduced production of reactive oxygen species (ROS) compared to the control, while the administration of (*R*)-IM and herbicide racemate as well as their co-exposure with AgNPs resulted in enhanced ROS formation compared to the control, indicating enantioselective ROS production (Wen et al. 2016).

8.2.1.4 Nanoscale Organophosphorus Herbicides

A nanoemulsion system consisting of long-chain fatty acid methyl esters (LFAMEs)/mixed surfactant (long-chain alkyl polyglucosides and ethoxylated 3-(3-hydroxypropyl)-heptamethyltrisiloxane (organosilicone))/water and glyphosate isopropylamine (IPA) herbicide was designed by Lim et al. (2012). The pre-formulation concentrate with less than 20% (w/w) of inerts (LFAMEs + mixed surfactant) appeared as a polymerized multi-connected network, and the dilution of the pre-formulation with water resulted in the destruction of the polymerized network and formation of dispersed NPs of nanoemulsion formulation. Because the emulsion particles had incorporated glyphosate IPA, the herbicide bioactivity, bioavailability and delivery efficiency were improved. Similar oil-in-water nanoemulsions incorporating glyphosate IPA with particle sizes of diameter <200 nm applied on narrow-leaved weed *Eleusine indica* showed lower ED_{50} (0.40 kg a.e./ha) compared to those estimated using Roundup® (0.48 kg a.e./ha), which indicates that the nanoemulsion system could increase penetration and uptake of glyphosate IPA (Jiang et al. 2012). The nanoemulsion formulations containing glyphosate IPA displayed a significantly lower spray deposition on creeping foxglove (2.9–3.5 ng/cm^2), slender button weed (2.6–2.9 ng/cm^2) and buffalo grass (1.8–2.4 ng/cm^2) than

Roundup® (3.7–5.1 ng/cm^2). At 3 and 7 days after treatment, the order of the mortality rates of the investigated weeds was buffalo grass > slender button weed > creeping foxglove, but the control rates were the same at the 14th day for the three weeds. Thus, the different cuticle permeability and foliar structures considerably affected the absorption rates of the herbicide and so its bioefficacy. Fourteen days after treatment with nanoformulation, the visible injury rates were comparable with that of Roundup® indicating the enhanced bioactivity of the nanoemulsion formulations (Lim et al. 2013).

8.2.2 Metal-Based Nanoherbicides

Adverse effects on plants are exhibited also by metal and metal oxide NPs because of stress or stimuli caused by the surface, size and/or shape of the particle, while inside the cells they might directly provoke alterations of membranes and other cell structures and molecules as well as protective mechanisms. The change of membrane permeability connected with the damage of cell membranes due to the production of ROS by metal NPs contributes to the enhanced probability of entry of NPs into the cell (Nel et al. 2006; Nair et al. 2010). Due to increasing environmental pollution with metals, numerous papers are devoted to the study of the negative effects of metal NPs on plants. On the other hand, some NPs of essential metals (e.g. Cu, Zn, Fe) used in appropriate concentration and also alumina and TiO_2 NPs were found to exhibit positive effects on plant growth. The beneficial and adverse effects of metal and metal oxide NPs were comprehensively reviewed by several researchers (e.g. Masarovičová and Kráľová 2013; Ma et al. 2015; Masarovičová et al. 2014; Du et al. 2017; Rizwan et al. 2017; Siddiqi and Husen 2017). However, metal NPs could be considered as non-selective herbicides, because they can damage not only undesired weeds but also crops, and therefore in agriculture selective herbicides targeting the weed without affecting nontarget crops are preferred.

8.3 Nanofungicides and Nanobactericides

There are approximately two million different species of fungi on Earth (Gauthier and Keller 2013). The vast majority of known fungal species are strict saprophytes (De Lucca 2007), but it is estimated that 270,000 fungal species can attack plants, such as genera *Botrytis*, *Sclerotinia*, *Aspergillus*, *Fusarium* and *Verticillium* (Sharon and Shlezinger 2013). Of the over 15,000 species of bacteria, about 200 species of phytopathogenic bacteria were identified, such as genera *Erwinia*, *Acidovorax*, *Pseudomonas*, *Ralstonia*, *Rhizobacter*, *Xanthomonas*, *Agrobacterium*, *Xylella*, *Arthrobacter*, *Clavibacter* and *Streptomyces* (Agrios 2005). Thus fungi and bacteria can cause crop losses worldwide (Gauthier and Keller 2013; Fisher et al. 2012; Carris et al. 2012; Jampílek 2016). Fungicides and bactericides are a specific type of pesticides that control fungal/bacterial diseases by specifically inhibiting or killing the fungus/bacteria that causes the disease (Jampílek 2016; Bhattacharyya et al. 2016; Ismail et al. 2017). As in other classes of pesticides, also dynamic development in the field of inorganic and organic nanofungicides and nanoscale bactericides can be recorded.

8.3.1 Natural and Synthetic Organic Nanoscale Fungicides and Bactericides

Zataria multiflora essential oil (ZEO)-loaded SLNPs with ca. particle size 255 nm, zeta potential approximately −37.8 ± 0.8 mV and EE 84 ± 0.92%, showed in vitro antifungal activity against pathogens such as *Aspergillus ochraceus* (MIC 200 ppm), *Aspergillus flavus* (MIC 200 ppm), *Alternaria solani* (MIC 100 ppm), *Rhizoctonia solani* (MIC 50 ppm) and *Rhizopus stolonifer* (MIC 50 ppm). These formulations showed higher potencies than those with pure essential oil (Nasseri et al. 2016). ZEO encapsulated in CS NPs with the mean particle size of 125–175 nm demonstrated a controlled and sustained release of ZEO for 40 days in vitro, and in vivo investigation showed that the encapsulated oil at 1500 ppm concentration considerably decreased both disease severity and incidence of *Botrytis*-inoculated strawberries during 7 days of storage at 4 °C followed by 2–3 more days at 20 °C. Increasing of the initial ZEO content in CS NPs led to a decrease of ZEO encapsulation and loading efficiency (Mohammadi et al. 2015). Encapsulation of thyme essential oils (TEO) in self-assembled polymer of CS and benzoic acid nanogel notably increased the half-life and the antifungal properties of TEO, and the estimated MIC of encapsulated TEO was 300 mg/L at unsealed and 500 mg/L at sealed condition compared to 400 mg/mL and 1000 mg/mL, respectively, determined for free TEO. Good antifungal effects of encapsulated TEO at concentrations >700 mg/L were confirmed also in in vivo experiment (Khalili et al. 2015). Similar results were obtained also with *Mentha piperita* essential oils encapsulated in CS-cinnamic acid nanogel showing MIC values of 500 ppm against *A. flavus* under sealed condition, while the corresponding MIC value for free oils was 4.2-fold higher. A test under non-sealed condition showed that treatment with 800 ppm of uncapsulated oil resulted in complete inhibition of fungal growth, while the same effect could be obtained only with 3000 ppm of free oils (Beyki et al. 2014). As environmentally friendly alternative products for postharvest disease control, polyethylene terephthalate punnets containing thyme oil and sealed with CS/boehmite nanocomposite lidding films were designed, which significantly reduced the incidence and severity of brown rot caused by *Monilinia laxa* in artificially inoculated peach fruits (cv. Kakawa) held at 25 °C for 5 days and caused considerable reduction of the brown rot incidence to 10% in naturally infected fruits stored at 0.5 °C and 90% relative humidity for 7 days and at simulated market shelf conditions at 15 °C for 3 days (Cindi et al. 2015). β-D-glucan (isolated from the cell wall of *Pythium aphanidermatum*) NPs prepared using sodium TPP, in which phosphoric groups of TPP were linked with

OH group of β-D-glucan with the size 20−50 nm showing spherical, smooth and almost homogenous structure, were found to inhibit the growth of *P. aphanidermatum*, suggesting that they could be used in crop protection against this devastating fungus (Anusuya and Sathiyabama 2014).

The CS NPs inhibited the growth of phytopathogens, namely, *Pyricularia grisea*, *A. solani* and *Fusarium oxysporum*, but they were able also to promote germination %, seed vigour index and vegetative biomass of chickpea seedlings. For example, CS NPs inhibited the radial growth of *P. grisea*, and their application delayed blast symptom expression on fingermillet leaves for 25 days compared to 15 days in control plants, which could be connected with the induction of ROS and the enhanced activity of peroxidase (reaching maximum at day 50) in leaves of fingermillet, which might be the reason for the delayed symptom (Sathiyabama and Manikandan 2016). ROS can directly act at the site of infection or function indirectly as second messengers (Arasimowicz and Floryszak-Wieczorek 2007), and H_2O_2, which could diffuse through the membrane, is considered to serve as a signal molecule under stress (Mittler 2002), while peroxidases, the scavengers of H_2O_2, are one of the pathogenesis-related proteins which are implicated in plant defence system against pathogenic fungi (Hiraga et al. 2001). Moreover, the disease incidence in CS NP-treated fingermillet plants was lower compared to control plants (Sathiyabama and Manikandan 2016), and CS NPs showed also potential in suppressing blast disease of rice, which can be used further under field conditions to protect rice plants from the devastating fungus (Manikandan and Sathiyabama 2016). Nanoemulsions prepared using 1.0% of low molecular weight CS showing 600 nm droplet size inhibited conidial germination and reduced dry weight of mycelia and sporulation of *Colletotrichum gloeosporioides* in vitro, and they could be used as biofungicide for controlling anthracnose of dragon fruit plants in the future (Zahid et al. 2013). CS and CS NPs characterized with low toxicity towards mammalia were also found to be effective for the control of *Fusarium* head blight disease in wheat (*Fusarium graminearum*), and greenhouse experiments showed that plants can be protected from the disease by spraying them at anthesis. CS and CS NPs showing polycationic properties can affect membrane permeability and leakage of cellular contents resulting in disorganized hyphae associated with inhibition of fungal growth. Moreover, application of CS to plant tissues often results in its agglutination around the penetration sites, and isolation of the penetration site through the formation of a physical barrier could prevent the pathogen from spreading and invading other healthy tissues (Kheiri et al. 2016).

The CS NPs prepared of CS having low (LMW) and high molecular weight (HMW) and *N*-trimethyl CS (TMCS) exhibited zeta potential ranging from +22 to +55 mV, and higher values of zeta potential were obtained when HMW CS was used. The CS NPs were tested against *Fusarium solani* and *Aspergillus niger*, and it was found that the smallest HMW CS NPs (CS concentration of 1 mg/mL) showed the best antifungal activity against *F. solani* (MIC = 0.5−1.2 mg/mL), the effect of particle size on the activity being higher than their surface charge. On the other hand, *A. niger* was found to be highly resistant to CS, and inhibition was observed only at treatment with CS solution (MIC = 3 mg/mL) and NPs prepared at high concentration (2 and 3 mg/mL) of HMW CS (MIC = 1.71−2.43 mg/mL). Unlike other types of CS NPs, TMCS NPs had no inhibitory activity against *F. solani* (Ing et al. 2012). Sulphonated CS showed antifungal activities against *Arthrinium sacchari* (MIC, 64.00 mg/mL) and *Botrytis cinerea* (MIC, 0.25 mg/mL), and it was found to damage and deform the structure of fungal hyphae (Sun et al. 2017). Oleoyl-CS NPs with the particle size of about 297 nm were tested against six plant pathogenic fungi in a mycelium growth experiment, and it was found that *Alternaria tenuissima*, *Botryosphaeria dothidea* and *Nigrospora sphaerica* were CS-sensitive in contrast to *Gibberella zeae* and *Fusarium culmorum*, which were CS-resistant. Increasing the NP concentration resulted in an increase of the antifungal index of CS-sensitive fungi, whereby their plasma membranes contained lower levels of unsaturated fatty acid than those of CS-resistant fungi (Xing et al. 2016).

In addition, CS can be also used as a matrix for loading and stabilizing various fungicides. For example, hexaconazole nanocapsules prepared using naturally occurring CS and TPP through ionotropic gelation showed 73% slowing down of the release of the active ingredient compared to a commercial preparation, and this effect was greater at pH 7 and pH 10 than at pH 4, and a release study in soil confirmed that this nanoformulation is suitable for alkaline soil. Also the antifungal activity of nanocapsules against *R. solani* exceeded that of the commercial preparation, and they showed lower toxicity on nontarget cell lines (Chauhan et al. 2017). The study of the effect of nanohexaconazole on the phenotype and pathogenicity of *R. solani* f. sp. *sasakii* causing banded leaf and sheath blight in maize showed that at the application of 1 ppm, it inhibited growth and sclerotial body formation similarly to commercial hexaconazole, while in vivo it exhibited notable restriction of lesion formation in insusceptible cultivar Vivek QPM-9 and also reduced the disease rating caused upon inoculation with the fungus *R. solani* exposed to 0.1 and 0.01 ppm of nanohexaconazole (Bheemaraya et al. 2014). Biodegradable CS-lactide copolymer (CS-PLA) NPs loaded with pyraclostrobin with particle sizes ranging from 77 to 128 nm prepared by varying the feed mass ratio of CS-PLA to fungicide from 50:1 to 5:1 exhibited an initial burst followed by sustained and pH-controlled pyraclostrobin release and better fungicidal activity against *Colletotrichum gossypii* Southw than 25% pyraclostrobin emulsifiable concentrate (Xu et al. 2014). Nanoformulations of carbendazim loaded into polymeric NPs (CS and pectin) with mean particle size of 70−90 nm applied at concentration 0.5 and 1.0 ppm caused complete inhibition of *F. oxysporum* and *Aspergillus parasiticus*, while the antifungal effectiveness of pure carbendazim was lower (80% and 97.2% inhibition at 0.5 and 1.0 ppm concentrations, respectively, against *F. oxysporum*; 86.0% and 100.0% inhibition at 0.5 and 1.0 ppm concentrations, respectively, against *A. parasiticus*), and even the inhibitory effect of commercial formulation WP 50 (50.5% and 70.0% inhibition at 0.5 and 1.0 ppm concentrations, respectively, against *F. oxysporum*; 42% and 58% inhibition at 0.5 and 1 ppm concentrations, respectively, against *A. parasiticus*) did not reach the effectiveness of carbendazim nanoformulations (Sandhya et al. 2017).

Besides CS, also other natural polysaccharides, synthetic polymers or inorganic materials have been used as stabilizers/matrices. Application of nanochitin suspension (0.001% (w/v)) exhibited synergistic effects on inhibition of tobacco root rot when mixed with metalaxyl mancozeb and thiophanate methyl fungicides indicating its protecting effects on tobacco plants from tobacco root rot diseases and suggesting that its co-administration could reduce the amount of chemical fungicides in tobacco plantations (Zhou et al. 2017). PEG 400 was used as the surface-stabilizing agent to prepare nanohexaconazole with a size of about 100 nm showing not only better fungicidal potential than the conventional registered formulation, but also it did not affect adversely the soil nitrifiers (Kumar et al. 2015a). Controlled release nanoformulations of carbendazim prepared using PEG-based functionalized amphiphilic copolymers released the fungicide between the 10th and the 35th day, while the release from a commercial preparation lasted only to the 7th day, and the half-release ($t_{1/2}$) values of the nanoformulation ranged between 9.47 and 24.20 days, showing increased release of the maximum amount of carbendazim with increasing PEG molecular weights. For antifungal activity of the most active formulations against *R. solani*, ED_{50} values ranging from 0.40 to 0.42 mg/mL were estimated (Koli et al. 2015). Azomethine-based nanofungicides with the particle size of 100 nm prepared using technically pure azomethines and PEG as a surface stabilizer exhibited twofold higher antifungal activity against *R. solani*, *R. bataticola* and *Sclerotium rolfsii* compared to bulk azomethines, and they were found to be better antifungal formulations than the conventional preparation also in pot experiments (Mondal et al. 2017).

NPs prepared by encapsulation of thiamine dilauryl sulphate (TDS), a vitamin B1 derivative, into lecithin NPs with a mean diameter of 136 nm exhibited better efficacy on the inhibition of mycelial growth and spore germination of *F. oxysporum* as TDS, and their inhibitory effect at a dosage of 100 ppm was similar or even better than that of the commercial herbicide dazomet (Cho et al. 2013).

Mesoporous SiO_2 nanospheres with the mean particle diameter of 162 nm and mean pore size of 3.2 nm loaded with metalaxyl exhibited sustained release of fungicide and significantly delayed its release in soil, while compared to 76% of free metalaxyl, which was released in soil within a period of 30 days, fungicide release from the mesoporous framework was only 11.5% (Wanyika 2013). Validamycin-loaded nanosized calcium carbonate was found to improve germicidal efficacy against *R. solani* compared to conventional technical validamycin after about 7 days, and it extended the release time of the pesticide to 2 weeks (Qian et al. 2011).

8.3.2 Carbon-Based Nanofungicides and Nanobactericides

Several carbon nanomaterials (CNMs), e.g. single-walled (SWCNTs) or multi-walled carbon nanotubes (MWCNTs), graphene oxide (GO), reduced graphene oxide (rGO), fullerene (C_{60}) and activated carbon (AC), were tested on their activity against phytopathogens (Wang et al. 2014, 2017; Chen et al. 2014b; Sarlak et al. 2014; Sawangphruk et al. 2012). Wang et al. (2014) studied the antifungal activity of six different CNMs against *F. graminearum* and *F. poae* and found that it decreased in the following order, SWCNTs (128 nm) >>> MWCNTs (78.8 nm) > GO (68.06 nm) > > rGO (105.7) nm, while C_{60} (220.6 nm) and AC (190.1 nm) showed no significant antifungal activity. Because in the antifungal activities of carbon nanomaterials their direct contact with spores may play an important role, in the case of C_{60} and AC, lack of tight or direct contacts is responsible for their low antifungal activity. The CNMs could inhibit spore germination just by interfering with the process of water uptake before inducing plasmolysis. After the deposition of spores on CNMs, the CNMs may cause the blockage of the water channels of spores. Superior toxic effect on *Alternaria alternata* fungi was shown also by zineb and mancozeb encapsulated into hybrid materials prepared by polymerization of citric acid onto the surface of oxidized MWCNTs (Sarlak et al. 2014). The estimated IC_{50} values related to the inhibition of the mycelial growth of *F. oxysporum*, *A. niger* and *A. oryzae* by reduced GO nanosheets were estimated as 50, 100 and 100 μg/mL, respectively. The effective inhibition of mycelial growth by reduced GO having sharp edges is connected with its direct contact with the cell walls of fungi and a subsequent chemical reaction of the reactive oxygen-containing functionalities of small rGO nanosheets with the organic functional groups of chitin and other polysaccharides on cell walls of fungi (Sawangphruk et al. 2012).

Covalent functionalization of MWCNTs by lysine and arginine under microwave radiation resulted in improved antifungal activity of functionalized MWCNTs against *A. niger* and *F. culmorum* compared to pristine MWCNT reaching a 1.9- and 1.1-fold increase, respectively, for MWCNTs-lysine, and 2- and 1.7-fold increase, respectively, for MWCNTs-arginine (Zare-Zardini et al. 2013). Nitrogen-doped carbon nanohorns (NCNHs) with the size of 50−60 nm applied at a dose of 150 μg/mL inhibited *R. solani* after 72 h. It could be assumed that in the toxic effect against *R. solani*, primarily the interaction of NCNHs with the pathogens by mechanically wrapping could be considered, which may be one of the major toxicity actions of NCNHs against *R. solani*, and targeting of the endochitinase of *R. solani* by NCNHs results in deactivation of the enzyme (Dharni et al. 2016).

The application of 500 μg/mL GO was found to kill about 90% of *Pseudomonas syringae* and *Xanthomonas campestris* pv. *undulosa* and repress 80% macroconidia germination along with partial cell swelling and lysis in *F. graminearum* and *F. oxysporum*. It could be supposed that GO interwinds the bacteria and fungal spores with a wide range of aggregated GO sheets causing the local perturbation of their cell membrane with a subsequent decrease of the bacterial membrane potential and the leakage of electrolytes of fungal spores. Thus, the toxic effect of GO on phytopathogens is caused by its interaction with these pathogens by mechanical wrapping and local damaging the cell membrane, which finally results in cell lysis, and therefore GO could be successfully used also for resisting crop diseases (Chen et al. 2014a, b). Wang et al. (2017) developed GO-Fe_3O_4 nanocomposites that efficiently repressed the germination of sporangia of *Plasmopara viticola* and inhibited the development of downy mildew, showing also potent curative effects. The GO-Fe_3O_4 nanocomposites applied at concentration 50 μg/mL exhibited superb protective and fungicidal activities, and treatment of grapevine leaves in the field with a dose of 250 μg/mL could result in a notable decrease of the severity of downy mildew.

8.3.3 Metal-Based Nanofungicides and Nanobactericides

Copper belongs to elements that are essential for plants, and benign fungi occurring in the roots of plants could detoxify the excess of copper uptaken by plants (Vitanovic 2012; Anjum et al. 2015). Nanoscale Cu was also found to suppress the growth of bacterial pathogen *Xanthomonas axonopodis* pv. *punicae* causing bacterial blight of pomegranate at 0.2 ppm, i.e. >10,000-fold lower concentration than the usually applied Cu-oxychloride, resulting in cell wall degradation in nano-Cu treated bacterial cells that failed to colonize plant tissues and to produce water-soaked lesions (Mondal and Mani 2012). Ghasemian et al. (2012) studied the antifungal effect of CuNPs of the average particle size of 8 nm on filamentous fungi by agar dilution method and estimated following MIC values: ≤40 mg/L for *Penicillium chrysogenum*, ≤60 mg/L for *A. alternata*, ≤60 mg/L for *F. solani* and ≤80 mg/L for *A. flavus*, suggesting that fungal sensitivity to CuNPs varies depending on the fungal species. Also, Giannousi et al. (2013) tested three different Cu-based (Cu_2O, CuO and Cu/Cu_2O) NPs of similar sizes (11–14 nm) and nearly spherical shape in the field against *Phytophthora infestans* on tomato and found that all the tested Cu-based NPs were more effective in lower formulated product and active ingredient rate than the four registered copper-based agrochemicals Kocide 2000, Kocide Opti, Cuprofix Disperss and Ridomil Gold Plus, without causing any deleterious effect on plants.

Cu-CS NPs with particle sizes ranging from 180.0 to 487.9 nm and zeta potential of +88 mV applied at 0.1% concentration caused notable inhibition of the growth of phytopatogenic fungi *A. alternata* (89.5%), *Macrophomina phaseolina* (63.0%) and *R. solani* (60.1%) in vitro and also exhibited 87.4% inhibition of spore germination of *A. alternata*. The antifungal effectiveness of Cu-CS NPs is connected with their appropriate surface charge density (zeta potential of +88 mV) providing them greater binding affinity for negatively charged fungal membrane as well as with the production of toxic H_2O_2 at the reduction of Cu(II) to Cu(I) in fungi causing destruction of the cell viability (Saharan et al. 2013). Cu-CS NPs with hydrodynamic diameter 374 nm and zeta potential of +22.6 mV applied at concentration 0.12% caused 70% and 73% inhibition of mycelia growth and inhibition of spore germination in *A. solani* (70% and 61%, respectively) and *F. oxysporum* (73% and 83%, respectively). In pot experiments at the treatment with the same concentration of Cu-CS NPs, the observed percentage efficacy of disease control in tomato plants was 88% in early blight and 61% in *Fusarium* wilt. The higher antifungal activity of Cu-CS NPs in pot experiments as compared to Petri plate experiments could be connected with strong elicitor properties of CS in the plant defence mechanism and with the fact that during infection of plants by fungi, different levels of acids produced by fungi decreased the pH resulting in the protonation of CS NH_2 groups and subsequent release of Cu^{2+} ions from Cu-CS nanoformulation, and also highly reactive hydroxyl radicals were produced which caused serious damage of biomolecules (Saharan et al. 2015). Cu(II)-loaded CS nanohydrogels, in which the formation of a Cu(II)-CS complex significantly depends on pH (the decrease of pH results in the release of Cu(II)) and the hydrogels are a suitable substrate for CS hydrolytic enzymes showed a notable synergistic effect between CS and Cu in inhibiting *F. graminearum* growth (Brunel et al. 2013).

The ultrafine colloidal CuNPs (2−5 nm in diameter) prepared using PVA capping polymer and citrate dispersant were found to exhibit notable antifungal activity against *Corticium salmonicolor*, a fungus causing pink disease in citrus and coffee and rubber trees, and showed high killing ability at concentration of 7 ppm and 10 ppm, respectively. A single spraying of 10 ppm CuNPs completely killed *C. salmonicolor* fungi, and treating diseased rubber trees with ultrafine CuNPs resulted in significant reduction of the disease index after twice spraying (Cao et al. 2014). Copper bionanoparticles with spherical shape and the size ranging from 5 to 15 nm synthesized using leaf aqueous extract of *Datura innoxia* effectively inhibited *Xanthomonas oryzae* pv. *oryzae*, the causative organism of bacterial leaf blight of paddy (Kala et al. 2016).

CuNPs prepared using the cetyltrimethylammonium bromide exhibited antifungal activity against three different crop pathogenic fungi that decreased in the following order: *Fusarium equiseti* > *F. oxysporum* > *F. culmorum* (Bramhanwade et al. 2016). The significant antifungal activity of CuNPs coated by cetyltrimethylammonium bromide with particle size ranging from 3 to 10 nm against plant pathogenic fungi *Phoma destructiva*, *Curvularia lunata*, *A. alternata* and *F. oxysporum* was observed by Kanhed et al. (2014). The antifungal activity of CuNPs, which was found to be better than that of the commercially available fungicide bavistin against all the four plant pathogenic fungi, could be connected with their large surface area to volume ratio.

Mageshwari and Sathyamoorthy (2013) designed 3D flower-shaped CuO microspheres with the average diameter of about 1−2 μm, and it was observed that flower-shaped hierarchical microspheres are composed of interpenetrating 2D nanosheet subunits as building blocks, which were self-organized to form spherical assemblies, and the spacing among the nanosheets in the flower-like superstructure favours greater interaction of microbes with the NPs, thereby enhancing the antimicrobial activity. These flower-shaped CuO nanostructures showed antifungal activity against *Mucor*, *Penicillium notatum*, *A. flavus*, *A. niger*, *A. alternata*, *Rhizopus oryzae*, *Cladosporium carrionii* and *A. flavus*. Spherical CuO NPs with the mean diameter of 28 ± 4 nm biosynthesized using *E. crassipes* leaf extract as reducing and capping agents exhibited antifungal activity against plant pathogens that decreased in the following order: *F. culmorum* > *A. niger* > *F. oxysporum* > *A. flavus* > *A. fumigatus* (Vanathi et al. 2016).

Mishra and Singh (2015) in their review paper highlighted the potential applications of AgNPs in the agricultural sector, particularly for plant disease management, focused attention on major interactions of AgNPs with soil, soil biota and plants and analysed the toxicity-determining factors which could be associated with their usage in agriculture. Spraying of 500 kg of colloidal Ag solution with a concentration of 10 ppm on 3306 m^2 large area polluted by rose powdery mildew resulted in fading out (>95%) of the white rose powdery mildew after 2 days, and it did not recur for a week (Kim et al. 2008). AgNPs caused also detrimental effects not only on fungal hyphae but also on conidial germination of ambrosia fungus *Raffaelea* sp. that has been responsible for the mortality of a large number of oak trees in Korea (Kim et al. 2009). Also AgNPs were found to increase the antifungal activity of fluconazole against *Phoma glomerata*, while no significant enhancement of activity was observed against *Phoma herbarum* and *Fusarium semitectum* (Gajbhiye et al. 2009). AgNPs with particle size <5 nm in the commercial product Pyto-patch® exhibited strong inhibition of spore germination rate and mycelial growth of *C. gloeosporioides*, *B. cinerea* and *Sclerotinia sclerotiorum* in vitro; the germination rate of spore of *C. gloeosporioides* dipped in 5 ppm phyto-patch dilute was suppressed to 13.2%; and a dose of 10 ppm proved to inhibit mycelial growth for 2 weeks. While in the field test in untreated plot, the anthracnose development after 21 days reached 40%, treatment with 4 ppm phyto-patch reduced it to 7%, and application of Pyto-patch® spraying (10 ppm) every 7 days in heavy rainfall season was found to ensure the potent control of pepper anthracnose (6% infected fruits compared to 95% in untreated plot). On the other hand, even though during drying period the effectiveness of Phyto-patch® was slightly lower (the portion of diseased fruits was 24.2%), however, in the untreated plot all pepper fruits were completely destroyed within 3 days. These findings indicate that mulching textile coated with AgNPs represents a suitable preparation for the potent prevention of late blight of pepper and it could delay the occurrence of the disease for about 1 month (Il and Kim 2012). AgNPs significantly inhibited the colony formation of *Bipolaris sorokiniana* and *Magnaporthe grisea*, whereby the corresponding IC_{50} values estimated for *B. sorokiniana* were higher than for *M. grisea*. The application of AgNPs exhibited also considerable reduction of fungal diseases on perennial ryegrass (*Lolium perenne*) caused by these two phytopatogens, and for the most effective reduction of disease severity, treatment at 3 h before spore inoculation was necessary (Jo et al. 2009). Kim et al. (2012) investigated the antifungal activity of AgNPs against 11 different plant pathogenic fungi, which were cultivated on potato dextrose agar (PDA), malt extract agar and corn meal agar plates. The most significant inhibition of plant pathogenic fungi was observed on PDA: concentration of 100 ppm caused 100% inhibition of *B. cinerea*, *Cladosporium cucumerinum*, *Corynespora cassiicola*, *Cylindrocarpon destructans*, *F. oxysporum* f. sp. *cucumerinum*, *F. oxysporum*, *Fusarium* sp., *Glomerella cingulata*, *Monosporascus cannonballus*, *P. aphanidermatum* and *Pythium spinosum* and >90% inhibition of *A. alternata*, *Alternaria brassicicola*, *A. solani*, *Didymella bryoniae*, *F. oxysporum* f. sp. *lycopersici*, *F. solani and Stemphylium lycopersici*. AgNPs affected the metabolism and toxicity of moulds and when applied in a higher concentration decreased the mycotoxin production of *Aspergillus* sp. (81–96%), and the highest decrease of mycotoxin amount was noticed for ochratoxin A (*A. westerdijikiae*). In the presence of AgNPs in the culture medium, a decrease in the organic acid production from the 3rd day of incubation was estimated, and the production of organic acids was inhibited to a greater extent in *P. chrysogenum* than in *A. niger*. The most intensive suppression was estimated for oxalic acid and the lowest one for malic acid production. Moreover, treatment with AgNPs resulted in a change in the extracellular enzyme profile of *A. niger* and *P. chrysogenum* and an increase of the total enzymatic activity (Pietrzak et al. 2015). Circular AgNPs with the mean particle size of 30–90 nm prepared using cow milk applied at concentration 2 mM exhibited 87%, 86% and 84% inhibition of the growth of *Colletotrichum coccodes*, *Monilinia* sp. and *Pyricularia* sp. (Lee et al. 2013). Spherical AgNPs of the size 40−60 nm exhibited reduction in the growth of six different *R. solani* anastomosis groups infecting cotton plants in vitro using PDA and Czapek Dox agar (CDA), while generally, higher suppression of fungal radial growth was noticed at a concentration of 1.9 mmol/L (Elgorban et al. 2016a). A notable *F. culmorum*-induced reduction in wheat seedling blight was estimated following treatment with AgNPs, and a serious disintegration of the cell membranes of roots was observed as well. Increased quantum efficiency of energy trapping in the PSII reaction centre (F_v/F_m) with a simultaneous decrease in energy dissipation in the form of heat due to treatment with AgNPs resulted in the higher total dry weight of plants (Gorczyca et al. 2015). Incubation of *F. culmorum* (W.G. Smith) Sacc. (FC) spores with AgNPs resulted in a considerable reduction of mycelial growth, which did not depend significantly on the AgNPs concentration up to 2.5 ppm, and the number of spores formed by mycelia increased in the culture after contact with AgNPs relative to control samples, mainly on the nutrient-poor PDA medium (Kasprowicz et al. 2010). The application of 100 ppm AgNPs effectively inhibited the growth of fungal hyphae as well as conidial germination of *Colletotrichum* species in vitro compared to the control, while in field trials the application of AgNPs before disease outbreak on pepper plants resulted in the considerable inhibition of fungi (Lamsal et al. 2011a). On the other hand, the application of 100 ppm AgNPs in the field tests showed the highest inhibition rate both before and after the outbreak of powdery mildew disease on cucumbers and pumpkins, and this dose of AgNPs also exhibited maximum inhibition for the growth of fungal hyphae and conidial germination in in vivo tests (Lamsal et al. 2011b). Coating of wheat seeds with AgNPs did not reduce seed germinability, and even soil conditions did not affect seed protection provided by AgNPs against fungi, which was comparable to the effect of a conventional preplanting fungicide Carboxitiram, suggesting that also this nanocoating may be considered as potential preplanting fungicide (Karimi et al. 2012).

Biosynthesized spherical AgNPs with the size ranging from 5 to 30 nm exhibited considerable antifungal activity against white mould (*S. sclerotiorum*) and grey mould (*B. cinerea*) in strawberry (*Fragaria x ananassa*), treatment with 150 ppm of AgNPs being the most effective (Elgorban et al. 2016b). Bioactive bile salt sodium deoxycholate-capped AgNPs tested against *C. gloeosporioides* exhibited fivefold higher inhibitory effect than their bioactive capping agent without causing phytotoxicity to treated plants (Muthuramalingam et al. 2015). AgNPs biosynthesized using aqueous extract of *Artemisia absinthium* and applied at the dose of 10 μg/mL inhibited the mycelial growth of *Phytophthora parasitica*, *P. infestans*, *P. pabnivora*, *P. cinnamomi*, *P. tropicalis*, *P. capsici* and *P. katsurae* in vitro, being very efficient against *P. parasitica* and *P. capsici* with IC_{50} values 2.1–8.3 μg/mL and showing complete inhibition (100%) of mycelial growth, zoospore germination, germ tube elongation and zoospore production, and in greenhouse experiments AgNPs prevented *Phytophthora* infection and improved plant survival (Ali et al. 2015). Biosynthesized AgNPs prepared using *Descurainia sophia* applied at concentration 25 μg/mL inhibited the mycelium growth of *R. solani* (>86%), and the minimum inhibitory concentration and the minimum bactericidal concentration of these AgNPs against *Agrobacterium tumefaciens* (strain GV3850) and *A. rhizogenes* (strain 15,843) were estimated as 4 and 8 μg/mL, respectively (Khatami et al. 2016a). Treatment with 40 ppm of spherical AgNPs (mean particle size of 17 nm) biosynthesized using *Trifolium resupinatum* (Persian clover) seed exudates resulted in 94.1% and 84% inhibition of fungal growth of *R.* solani and *Neofusicoccum parvum*, respectively (Khatami et al. 2016b). AgNPs synthesized using *Acalypha indica* leaf extract as reducing agents applied at a dose of 15 mg/10 μL on fungi cultivated on PDA medium showed excellent inhibitory activity against six plant pathogens (*A. alternata*, *B. cinerea*, *C. lunata*, *M. phaseolina*, *R. solani* and *S. sclerotiorum*) (Krishnaraj et al. 2012). Biosynthesized spherical AgNPs with particle size ranging from 7 to 21 nm exhibited notable antifungal activity against plant *F. oxysporum* at the concentration of 8 μg/mL (Gopinath and Velusamy 2013). AgNPs biosynthesized using *Serratia* sp. showing spherical shape and particle size ranging from 10 to 20 nm applied at concentrations 2, 4 and 10 μg/mL caused complete inhibition of conidial germination of *B. sorokiniana*, while in the control the conidial germination was 100%, and these AgNPs also significantly reduced *B. sorokiniana* infection in wheat plants under greenhouse conditions (Mishra et al. 2014). Balashanmugam et al. (2016) reported that using *Cassia roxburghii* aqueous leaf extract stable AgNPs with mean particle size 35 nm and zeta potential of −18.3 mV could be synthesized which could be used as effective growth inhibitors in controlling various plant diseases caused by fungi such as *R. solani*, *F. oxysporum* and *Curvularia* sp. (Balashanmugam et al. 2016).

A nanosized Ag–irradiated fungal CS composite showed strong botryticidal activity (MIC = 125 μg/mL), and its application to the grey mould fungus *B. cinerea* Pers resulted in an alteration in the mycelial shape and moderate lysis in fungal hyphae, which lysed into small and elastic fragments at prolonged treatment. Coating of strawberries using solution containing this nanocomposite effectively eliminated grey mould infection signs even in 90% of the contaminated fruits after 7 days of storage, securing the fresh-like appearance of strawberries in the whole storage period (Moussa et al. 2013). Ho et al. (2015) prepared Ag core−CS shell nanoclusters via chemical reduction using 3,4-dihydroxyphenyl acetic-conjugated oligochitosan as a reducing and protecting agent by its surface adhesion to 3,4-dihydroxyphenyl acetamide moieties. The size of Ag core was 26 ± 9 nm and shell layer thickness was 18 ± 8 nm. These nanoclusters applied at the dose of 9 ppm showed 80% inhibition of *P. capsici* growth, and IC_{50} value estimated for the growth of *Phytophthora nicotianae* and *P. colocasiae* was about 6 ppm. It could be assumed that the CS-based shell layer could act as an active targeting site and results in increasing interaction of the cationic CS shell layer on the Ag core in the nanoclusters and phospholipid layer on bacterial membrane via electrostatic interaction, and the sustained release of Ag^+ ions from nanoclusters situated on the surface of the microbes could kill the fungi. Ag/CS Janus particles applied at the concentration of 0.02 mg/mL suppressed the growth and germination of *B. cinerea* in vitro and in vivo (Jia et al. 2015).

It was estimated that Tween 80 is a preferable stabilizer of AgNPs due to the beneficial synergistic effects of AgNPs and the surfactant related to antibacterial activity against phytopathogenic bacterium *Ralstonia solanacearum*, and Tween 80-stabilized AgNPs caused more severe damage in direct contact with cells, causing mechanistic injury to the cell membrane and strongly modifying and destructing the cellular proteins; also in pot experiments the Tween 80-stabilized AgNPs showed high control efficiency on tobacco bacterial wilt representing 96.7% at 7 days and 84.2% at 21 days, respectively (Chen et al. 2016). A stable nanosized silica hybrid silver complex, in which AgNPs (3−10 nm) representing core part were loaded onto the outer parts of SiO_2 NPs (5−20 nm), decreased the growth of *R. solani* by more than 90% at treatment with 6 μg/mL concentration (Kim et al. 2011). The antifungal efficiency of Ag-SiO_2 NPs synthesized by γ-irradiation, in which AgNPs of about 7 nm were attached to the surface of SiO_2 NPs of approximately 350 nm, applied against *B. cinerea* at doses of 50 and 100 ppm was 99.9% (Oh et al. 2006). Protonated $H_2Ti_3O_7$ nanotubes of ca. 11 nm in diameter and four layers with surface areas 300 m^2/g functionalized with AgNPs (5 nm) effectively inactivated *B. cinerea* isolated from tomato infection under visible light, and cell death was connected with plasmalemma invagination due to oxidative stress and serious morphology damage expanding the conidia (Rodriguez-Gonzalez et al. 2016). In an in vitro experiment, the DNA-directed AgNPs grown on graphene oxide (GO) applied at the dose of approximately 10 μg/mL killed all bacterial cells of Cu-tolerant *Xanthomonas vesicatoria*, *X euvesicatoria* and *X. gardneri* strains and Cu-sensitive *X. perforans* strains in suspensions containing approximately 10^3 CFU/mL within 15 min, and the treatment of tomato plants with this nanoformulation (75 or 100 μg/mL) prior to artificial inoculation resulted in significant reduction of disease severity compared to Cu-mancozeb and negative controls (Strayer et al. 2016). The application of such nanocomposite at 100 ppm on tomato transplants in a greenhouse experiment considerably reduced the severity of bacterial spot disease caused by *Xanthomonas perforans* compared to untreated plants, showing comparable efficiency to current grower standard treatment and no signs of phytotoxicity (Ocsoy et al. 2013).

The investigation of the antifungal effect of AuNPs applied at concentration 0.05−0.2 mg/L in PDA media against *Fusarium verticillioides*, *Penicillium citrinum* and *A. flavus* that was evaluated at 2, 4, 6 and 8 days after incubation showed that not even the concentration of 0.2 mg/L was able to completely inhibit fungal growth; however, in contrast to the untreated control, damaged hyphae and unusual bulges were observed in the fungi structure, suggesting that AuNPs affected the production of toxins by these pathogenic fungi (Savi et al. 2012). AuNPs synthesized using seed aqueous extract of *Abelmoschus esculentus* with nearly spherical shape and particle size ranging from 45 to 75 nm showed higher antifungal activity against *Puccinia graminis tritici* and *Candida albicans* than against *A. flavus* and *A. niger* (Jayaseelan et al. 2013).

Commercially available Zn NPs (264 nm) and ZnO NPs (19.3 nm) were found to inhibit spore germination and infectivity on tobacco leaves resulting from exposure to the fungi-like oomycete pathogen *Peronospora tabacina*, and treatment with these NPs at 8 and 10 mg/L markedly inhibited leaf infection, and considerable higher dependence of these inhibitory effects on the concentration was estimated than could be readily explained by the presence of dissolved Zn (Wagner et al. 2016). Rajiv et al. (2013) biosynthesized spherical (27 ± 5 nm) and hexagonal (84 ± 2 nm) ZnO NPs using different (50% and 25%) concentrations of *Parthenium hysterophorus* L. leaf extracts that exhibited size-dependent antifungal activity against plant fungal pathogens *A. flavus*, *A. niger*, *A. fumigatus*, *F. culmorum* and *F. oxysporum*, showing the highest effectiveness against *A. niger* and *A. flavus*, and the antifungal activity of smaller-sized ZnO NPs exceeded that of larger NPs. The antifungal effectiveness of spherical biogenic ZnO NPs with the mean particle size of 12 ± 3 nm prepared using *Lantana aculeata* leaf extract against *A. flavus* and *F. oxysporum* was reported also by Narendhran and Sivaraj (2016). The antifungal activity of ZnO NPs prepared using reproducible bacteria *Aeromonas hydrophila* as an eco-friendly reducing and capping agent against *A. flavus* was described by Jayaseelan et al. (2012). ZnO NPs were reported to be also suitable for the control of rice blast and brown spot diseases. Spraying of ZnO NPs with the concentrations of 0.2% and 0.5% 5 days before inoculation with a spore suspension of *P. grisea* was effective in controlling rice blast disease, while spraying of ZnO NPs 2 days before inoculation with a spore suspension of *Helminthosporium oryzae* gave the best effect in controlling rice brown spot disease (Kalboush et al. 2016). ZnO NPs applied at the concentration of 100 mM were found to completely inhibit the growth of *Penicillium citrinum* and significantly reduced the growth of *F. verticillioides* and *A. flavus,* and the conidia production of all fungi also was reduced. In treated fungi, hyphae morphological alterations showing hyphae damage as a result of ROS production were observed (Savi et al. 2013; Savi and Scussel 2014). ZnO NPs with sizes of 70 ± 15 nm applied at concentration 3 mmol/L notably inhibited the growth of *B. cinerea* and *Penicillium expansum*, *P. expansum* being more sensitive to the treatment, and it was found that the growth inhibition of *B. cinerea* is connected with the alteration of cellular functions caused by ZnO NPs, while in *P. expansum* the ZnO NPs prevented the development of conidiophores and conidia, causing eventually the death of fungal hyphae (He et al. 2011). In addition, ZnO NPs in the presence of visible light exhibited strong antifungal activity, and treatment with a suspension at the concentration of 5 mM ZnO NPs and incubation time of 24 h resulted in 58% photoinactivation of *B. cinerea* (Kairyte et al. 2013). The antifungal activity of ZnO NPs against *S. rolfsii* and *Pythium debaryanum* was reported by Sharma et al. (2011), and antifungal effectiveness depended on the size, morphology and contact of ZnO NPs with the fungal cell. Polyurethane membranes modified by ZnO NPs were found to exhibit important antifungal properties against *Aspergillus brasiliensis* (ATCC 16404 strain of *A.*) (Vlad et al. 2012). The antifungal activity of ZnO NPs with the size of 35–45 nm against *M. phaseolina* was reported by Shyla et al. (2014).

ZnO NPs were found to be twofold more effective against *Aspergilus niger* than ZnO microparticles (MIC values of 2.5 and 5 mg/L, respectively), and the MIC value of 1.25 mg/L estimated for the antifungal efficiency of ZnO NPs doped with 5% nano-Pd suggested that the antifungal activity of nanoscale ZnO could be improved by loading with nano-Pd (Gondal et al. 2012). The CdSe/ZnS quantum dots coated with 3-mercaptopropionic acid were found to be considerably taken up by the fungal hyphae of *F. oxysporum*, showing their potential for the development of novel control approaches of *F. oxysporum* and related pathogenic fungi following appropriate functionalization (Rispail et al. 2014).

A CS/TiO_2 nanocomposite at the ratio of 1:5 exhibited effective inhibition of the growth of rice bacterial pathogen *Xanthomonas oryzae* pv. *oryzae*, which exceeded that of the two individual components under both light and dark conditions (Li et al. 2016). A CS/TiO_2 hybrid film exhibited excellent antifungal activity against *Bipolaris maydis* under both visible-light irradiation and in a dark environment and showed superior antifungal efficacy of 100% even after 4 h under the irradiation of visible light. A large amount of positive charges on the structure of the hybrid film, which interacted with the negative charges from the cell as well as the detrimental effect of hydroxyl radicals generated by photocatalysis of TiO_2 contributed to the strong antifungal efficacy of the CS/TiO_2 hybrid film (Huang et al. 2013a). Pure and Ag-doped solid and hollow TiO_2 NPs exhibited antifungal activity against *F. solani* causing *Fusarium* wilt disease in potato, tomato, etc. and *Venturia inaequalis* causing apple scab disease, hollow NPs being the most active, and the activity was greater under visible-light exposure due to generation of harmful ROS during photocatalysis causing damage of cell wall with consecutive cell death.

Moreover, in the presence of Ag, stable Ag−S and disulphide bonds (R−S−S−R) in cellular proteins could be formed, which also results in cell damage. It was also observed that at a very low dose (0.015 mg/plate), the NPs successfully arrested the production of toxic naphthoquinone pigment for *F. solani*, which is related to the fungal pathogenicity, and the NPs were found to protect potatoes affected by *F. solani* from spoiling (Boxi et al. 2016). In greenhouse experiments, light-activated Zn-doped nanoscale TiO_2 formulations applied at doses 500−800 ppm considerably reduced bacterial spot severity in tomato transplants artificially infected with *Xanthomonas perforans* compared with untreated and Cu control. They exhibited similar protection as the grower standard, Cu + mancozeb, and also notably reduced disease incidence in three of four trials compared with untreated transplants and Cu control, whereby their effect was comparable or better than that of the grower standard (Paret et al. 2013). Visible-light-activated Pd-modified nitrogen-doped TiO_2 NPs strongly adsorbed onto the surface of *F. graminearum* macroconidium could contribute to the photocatalytic disinfection of these macroconidia causing cell wall/membrane damage by formed ROS (Zhang et al. 2013a).

8.3.4 Other Inorganic Nanofungicides

Maize plants treated with SiO_2 NPs (20−40 nm) showed a higher expression of phenolic compounds and a lower expression of stress-responsive enzymes against both tested fungi (*Aspergillus* spp. and *Fusarium* spp.), and treatment with 10 and

15 kg SiO_2 NPs/ha resulted in significantly higher resistance in maize than treatment with bulk SiO_2, and maize plants expressed more resistance to *Aspergillus* spp. than to *Fusarium* spp. (Suriyaprabha et al. 2014).

Sulphur NPs with the particle size of 35 nm effectively prevented the fungal growth of *F. solani* and *Venturia inaequalis*, and the fungicidal effect was connected mainly with the deposition of NPs on the cell wall and the subsequent damage of the cell wall (Rao and Paria 2013). Orthorhombic (spherical; ~10 nm) and monoclinic (cylindrical; ~50 nm) sulphur NPs significantly reduced the total lipid content of treated isolates of *A. niger*, caused notable downregulation of the expression of various desaturase enzymes (linoleoyl-CoA desaturase, stearoyl-CoA 9-desaturase and phosphatidylcholine desaturase) and noteworthy high accumulation of saturated fatty acids with depleted lipid layer, which could be one of the major reasons of sulphur NP-mediated fungistasis (Choudhury et al. 2012). Surface-modified sulphur NPs prepared using PEG 400 as a surface-stabilizing agent showed promising inhibitory effect on fungal growth and sporulation and significantly reduced phospholipid content in *A. niger* and *F. oxysporum* (Choudhury et al. 2011).

8.4 Nanoinsecticides

Insecticides are compounds that are able to kill insects in various stages of development/growth, i.e. can be applied against insect eggs, larvae or adult insects. Insects represent a class of invertebrates, and among these, there are some insect pests that destroy crops and infest stored grains. Thus, application of nanoscale pesticides can be helpful in the management of insect pests in agriculture without harming the nature (Jampílek and Kráľová 2015, 2017b). An overview regarding the prospects for the development of nanoencapsulated pesticides in sustainable agriculture was presented by Grillo et al. (2016). Agents with activity against insects can be classified according to origin as natural (pure compounds or mixtures) and synthetic or, according to their composition, as organic insecticides and inorganic compounds (metal-based substances, metalloids, clays). The last ones can be used as carriers, or they possess own intrinsic insect-killing effect.

8.4.1 Nanoinsecticides Based on Plant Extracts and Essential Oils

Insecticidal activity of colloidal suspensions of PCL NPs containing neem (*Azadirachta indica*) products as well as nanocapsule spray-dried powders was tested against *Plutella xylostella* by Forim et al. (2013). On day 9, the control neem oil and the colloidal suspension of neem-loaded NPs caused 100% larval mortality, while NPs in powder caused 91.7% larval mortality, and all neem treatments were found to be more efficient than the control insecticide deltamethrin 25 EC after day

5 of the experiments. The nanoformulation also exhibited the improved stability of neem products against ultraviolet radiation and increased their dispersion in the aqueous phase. Giongo et al. (2016) offered corn leaves treated with nanoformulations of neem in colloidal suspension or powder, containing PCL, poly(β-hydroxybutyrate) or poly(methyl methacrylate) in capsules or spheres to first instar larvae of fall armyworm during 10 days and observed that some nanoformulations caused mortality and sublethal effects up to 3 and up to 7 days after spraying; however the residual effect of commercial neem oil was not outperformed. Although all treatments showed phagodeterrence at day 1 after spraying, this was lost over time indicating limited or no release of active ingredient by NPs. Microcapsules of sugarcane bagasse lignin loaded with organic extracts of neem tested as potential bioinsecticides against *Spodoptera frugiperda* and *Diatraea saccharalis* were found to have increased thermal and photo stability compared to the control, and following their administration, for 100% mortality of insects, shorter time was needed than in the controls, indicating that neem extracts loaded into microcapsules not only retained their biopesticidal activity but also exhibited better resistance against the abiotic factor (Costa et al. 2017).

Comparison of the insecticidal activity of NPs loaded with neem products and enriched botanical extract was performed by da Costa et al. (2014). Nanoformulated neem products in the form of powder, soluble powder prepared with neem oil and neem oil emulsifiable concentrate tested against bean weevil *Zabrotes subfasciatus* showed that the treatment of the insect with 1000−4000 ppm neem oil in emulsifiable concentrate resulted in the highest mortality, while the greatest UV stability was observed with nanoformulated neem products in powder. Jamal et al. (2013) investigated the efficacy of nanoencapsulated formulation of essential oil from *Carum copticum* seeds on feeding behaviour of *Plutella xylostella* (Lep.: Plutellidae) larvae and observed that the increase of oil concentration resulted in a decrease of relative consumption rate, relative growth rate, efficacy of conversion of ingested food and efficacy of conversion of digested food, and 72 h after feeding, also a notable reduction of digestibility was estimated indicating that application of this nanoformulation could result in an increase in post-ingestive toxicity of the insect. *Carum copticum* essential oil-loaded myristic acid-CS nanogel was found to exhibit considerably higher toxicity against *Sitophilus granarius* and *Tribolium confusum* than pure oil even after 48 h, being ca. nine- and fourfold more toxic than the pure oil against *S. granarius* and *T. confusum*, respectively. Moreover, as far as the effectiveness of pure oil decreased in the early days of application, this nanoformulation lost its insecticidal effectiveness after 21 days post-application for *S. granarius* and 33 days in the case of *T. confusum* (Ziaee et al. 2014a).

Cuminum cyminum L. oil-loaded myristic acid-CS nanogels exhibited higher toxicity against beetle pests *S. granarius* L. and *T. confusum*, and after 12 days these nanoformulations lost about 60% of their activity when applied against *S. granarius* and 15% for *T. confusum*, while at the same period the complete loss of *C. cyminum* oil insecticidal activity was estimated (Ziaee et al. 2014b). Spherical nanocapsules of essential oil from *C. cyminum* L. with the particle size of about 30 nm in diameter exhibited significantly higher fumigant toxicity against 1–3-day-old adult insects of

Tribolium castaneum (LC_{50} = 16.25 ppm) than pure essential oil (LC_{50} = 32.12 ppm) after 7 days of exposure (Negahban et al. 2012).

PEG NPs containing geranium or bergamot essential oils (EOs), in which the ratio EO:PG was 10%, were characterized with mean diameter <235 nm and loading efficacy >75%, and good stability enhanced the EO contact toxicity and altered the nutritional physiology of both stored product pests *T. castaneum* and *Rhyzopertha dominica*. Due to slow and persistent release of the active ingredients, they considerably increased also residual contact toxicity (Gonzalez et al. 2014). PEG-coated NPs loaded with garlic essential oil with the average diameter <240 nm showing slow and persistent release of active components from the NPs preserved over 80% of their control efficacy against adult *T. castaneum* even after 5 months, while for the free garlic essential oil applied at similar concentration (640 mg/kg), it achieved only 11%. It could be noted that the abundance and percentage content of the major components of nanoencapsulated and free oil were found to be practically the same (Yang et al. 2009).

A nanoemulsion of purslane essential oil exhibited notable strong insecticidal activity against almond moth (*Ephestia cautella*) causing mostly a complete inhibition of moth's emergence, which is attributed to the sterilizing effect of purslane oil on the moths as well as its toxicity to the deposited eggs and adult emergence during storage intervals up to 125 days. The adverse effect of essential oils nanoformulations against larvae of *E. cautella* decreased in the following order: purslane oil > mustard oil > castor oil (Sabbour and Abd El-Aziz 2016a). Also in another experiment focused on the testing of the insecticidal activity of these three oils applied in a nanoform against the granary weevil *S. granarius* under laboratory and stored conditions, the nano-purslane was found to show the highest sterilizing effect, which was reflected in a significant reduction of the mean number of eggs/female compared to control. After 125 days of storage, the percentage of emerged weevils was 7% for treatment with nano-purslane, while at application of bulk purslane, it was 21% and for the untreated control even 98% (Sabbour and Abd El-Aziz 2016b).

For nanoemulsions of essential oils from *Ageratum conyzoides*, *Achillea fragrantissima* and *Tagetes minuta* plants showing significant ovicidal, adulticidal and residual activities against the cowpea beetle, *Callosobruchus maculatus*, which were tested as fumigants, estimated LC_{50} values 96 h after treatment ranged from 16.1 to 40.5 μL/L air and 4.5–243 μL/L air against eggs and adults, respectively, and the insecticidal activity of nanoformulations notably exceeded that of bulk oils (Nenaah et al. 2015). Rani et al. (2014) prepared formulations of α-pinene and linalool with SiO_2 NPs and evaluated their antifeedant activity against the tobacco cutworm (*Spodoptera litura* F.) and the castor semilooper (*Achaea janata* L.) in laboratory bioassays. The hydrodynamic parameters of nanoformulated α-pinene (APSI) and linalool were 46 nm and 48 nm, respectively, and the zeta potential of both nanoformulations was −39.7 mV. Both nanoformulations showed higher antifeedant activity than the corresponding essential oils, and 0.1% nanoformulations of α-pinene and linalool showed 100% feeding deterrence at a dose of 0.1 $\mu L/cm^2$, while the parent terpenes produced <50% activity even at 2 $\mu L/cm^2$. The antifeedant activity of α-pinene against both species was higher than that of linalool formulations. Compared to the effect of parent terpenes, the nanoformulation was found to be 25-fold more effective against *S. litura* and 10-fold more effective against *A. janata*, while SiO_2 NPs alone did not produce any antifeedant effect on tested insects even at higher concentrations (15 μL/cm^2). The nanoformulations prolonged the shelf life of the terpenes. The observed death of larvae 3 days after treatment suggested that larvae died from starvation. On the other hand, nanoformulations did not exhibit repellent activity, since larvae had reached the treated leaf surface and even attempted to feed at all doses tested.

The insecticidal properties of formulations based on *Ocimum gratissimum* and montmorillonite-Na$^+$ (MMT-Na) as well as cetyltrimethylammonium-modified MMT-Na (MMT-Na-CTMA) were tested against the maize weevil *Sitophilus zeamais* (Nguemtchouin et al. 2013). While 7 days following treatment, the mortality of *S. zeamais* treated with essential oil without adsorbent application was not estimated, it decreased from 100% to 87% for the essential oil adsorbed on unmodified clay and to 95% for the essential oil adsorbed on modified clay. The complete loss of insecticidal activity of the formulation prepared with unmodified clay was observed after 30 days, while the formulation with organo-modified clay retained 40% of its full insecticidal efficiency at the same time. The amount of formulation required to kill 50% of *S. zeamais* adults was estimated as 1.01 g and 0.69 g for MMT-Na-*O. gratissimum* and MMT-Na-CTMA-*O. gratissimum*, respectively, indicating higher toxicity of MMT-Na-CTMA, probably due to the incorporation of more compounds with insecticidal activity (i.e. terpenic components) in this formulation.

The entomocidal activity of powders and extracts of medicinal plants *Azadirachta indica*, *Zanthoxylum zanthoxyloides*, *Anacardium occidentale* and *Moringa oleifera* against *Sitophilus oryzae* (L), *Oryzaephilus mercator* (Faur) and *Rhyzopertha dominica* (Fabr.) was reported by Ileke and Ogungbite (2014). Findings focused on the effectiveness of plant extracts, essential oils, their isolated pure compounds and plant-based nanoformulations as well as their mode of action against storage insects with special reference to maize were summarized by Soujanya et al. (2016). Preparation methods related to the encapsulation of vegetable oils and applications of encapsulated vegetable oils as antimicrobials, insecticides, pesticides and pest repellents were summarized by Sagiri et al. (2016).

8.4.2 Synthetic Nanoinsecticides

Functional nano-dispensers of imidacloprid (IMI) encapsulated in PLGA with particle sizes 5–10 μm were found to cause equivalent mortality of Asian citrus psyllids (*Diaphorina citri*) as a current commercial formulation, however at a dosage 200-fold lower (Meyer et al. 2015). Kumar et al. (2014) performed field evaluation of IMI-loaded sodium ALG NPs with particle size ranging from 50 to 100 nm, 98.66% EE and 2.46% loading. Although the pesticide content in the nanoformulation was only 2.46%, its application in the form of spray on leaves of *Abelmoschus esculentus* was found to be effective up to the 15th day in reduction of leafhopper population and exhibited not only better insecticidal activity but also lower toxicity than pure pesticide. Guan et al. (2008) prepared photodegradable insecticide by direct encapsulation of IMI microcrystals with CS and sodium ALG through layer-by-layer self-assembly using sodium dodecyl sulphate (SDS)/Ag/TiO_2 as an effective photocatalyst. The IMI microcrystals had the mean length of 7 μm and the zeta potential of −37.5 mV. The IMI-loaded microparticles showed encapsulation efficiency 81.57 ± 0.96%, and the percentage of the drug-loading content was approx. 56.15 ± 0.96% after encapsulated for ten polyelectrolytes layers. The release rate of the IMI microcrystal decreased with an increase in the layer number of microcapsules, and the total release time for the corresponding microcapsules with 4, 10 and 20 layers was approximately 2-, 4- and 8-fold longer, respectively, than that of the uncoated pesticide.

Amphiphilic nano-polymers synthesized using different molecular weight PEGs (300, 600 and 1000) as a hydrophilic head and aliphatic diacids (glutaric acid, adipic acid, pimelic acid and suberic acid) as a hydrophobic moiety were used to prepare controlled release formulation for IMI. The micelle size of the polymers ranged from 127 to 354 nm, the loading capacity of the polymers ranged from 6.8% to 8.9% and the encapsulation efficiencies for different formulations were in the range from 75.0% to 97.9%. The value of half-life $t_{1/2}$ (i.e. time taken for 50% release) of IMI encapsulated in polymers ranged from 2.3 to 9.3 days, being higher for the formulation containing PEG 1000 than for polymers having PEG 300 and PEG 600 moiety, and $t_{1/2}$ was found to increase with the increasing molecular weight of PEG for diacids, namely, adipic acid and suberic acid. Thus, imidacloprid applications can be optimized to achieve insect control for the desired period using a suitable matrix of the polymer (Adak et al. 2012).

Memarizadeh et al. (2014) encapsulated IMI into ABA triblock linear-dendritic copolymers composed of polycitric acid (PCA) as A block and polyethylene glycol (PEG) as B block, the encapsulation process being performed by self-assembly of PCA-PEG-PCA in the presence of IMI in different solvents. The morphology of nano-IMI varied from fibre-like to globular and tubular, while its size varied from 10 nm to several mm, depending on the type of solvent, time and concentration. The loading capacity of the copolymers at pH 7 was estimated as 53% and, at pH 10, it was 80%. While IMI release at pH 7 slowly increased for 6 h and then remained constant, its release rate into phosphate-buffered saline solution with pH 10 increased up to 24 h, and higher percentage of pesticide was released than at pH 7. The insecticidal efficiency of nano-IMI and bulk insecticide diluted in water was investigated by leaf-dip bioassay tests on the *Glyphodes pyloalis*. The LC_{50} values estimated for the nano-IMI decreased over free IMI as exposure time increased, and after 4 and 5 days of exposure, they were five- and ninefold lower, respectively, than those observed for the bulk form. In the topical bioassay, the performance of nano-IMI prepared in ethanol was tested. Comparison of LC_{50} values observed at 24, 48, 72 and 96 h showed that at all periods of exposure, the LC_{50} values were considerably lower for the nanopesticide formulation than for free IMI. The increased penetration of the effective compound by means of citric acid molecules to the metathoracic tergum membrane cells of *G. pyloalis* larvae contributed to the higher effectiveness of nano-IMI prepared with ethanol. The higher loading capacity and the slower release rate of the pesticide from nano-IMI formulation at pH 10 corresponding to optimum pH of *G. pyloalis* gut compared to neutral pH suggest its selective and controllable action. Lower doses of nano-IMI compared to its bulk form required for pest control can also significantly reduce the environmental risk.

In contact toxicity bioassay using adult *Martianus dermestoides*, the 142-h LC_{50} values estimated with 50% nano-SDS/Ag/TiO_2-IMI were 9.86 mg/L compared to 13.45 mg/L observed with 95% IMI. The use of bentonite and/or activated carbon sorbents reduced the release rate of IMI and isoproturon in comparison with the technical product and with ALG formulation without modifying agents. The formulation with the highest percentage of activated carbon exhibited the highest decrease in the release rate, and the release rate was higher in imidacloprid systems than in those prepared with isoproturon (Garrido-Herrera et al. 2006).

Neonicotinoid acetamiprid-loaded nanocapsules prepared by polyelectrolyte complexation of ALG and CS showed controlled release in vitro, with maximum release at pH 10, the released amount decreasing with decreasing pH, and a controlled release pattern was observed also in soil, indicating that such nanoformulation could reduce the frequency of application of pesticides and reduce their side effects (Kumar et al. 2015b). Amphiphilic copolymers prepared from PEGs and various aliphatic and aromatic diacids, which self-assemble into nanomicellar aggregates, were used to prepare controlled release formulations of thiamethoxam, a systemic insecticide from the class of neonicotinoids exhibiting a broad spectrum of activity against many types of insects. The average micelle size of different formulations was approx. 138 nm, and the size of pyridalyl was <100 nm. The release of the insecticide from these nanoformulations was slower than from a commercial formulation with $t_{1/2}$ values ranging from 3.5 to 6 days, and the formulations showed non-Fickian transport (Sarkar et al. 2012).

The toxicity of the suspension of ALG nanocapsules containing pyridalyl against the larval stage of *Helicoverpa armigera* was tested using the leaf dip as well as the topical methods and compared with the toxicity of a technical material and a commercial formulation. The excellent insecticidal activity of the nanoformulation was confirmed by the estimated LC_{50} values of 40 and 80 μg/mL using the two above-mentioned methods. In the form of the nanoformulation, pyridalyl was found to be ca. two- and sixfold more effective against *H. armigera* as stomach poison than the technical product and the commercial formulation, respectively, while the LC_{50} values estimated by the topical method were 80, 150 and 250 μg/mL for nanoformulation, technical material and commercial formulation, respectively. The higher insecticidal effect of the nanoformulation could be connected with the better penetration of NPs through the epithelial lining of digestive tract and better penetration in capillaries to get into the systemic circulation, affecting the tertiary structure of protein, resulting finally in the malfunctioning and the death of the insect (Saini et al. 2014).

Organophosphate insecticide chlorpyrifos loaded CS-PLA-1,2-dipalmitoyl-sn-glycero-3-phosphoethanolamine copolymer NPs with the particle size of 100−300 nm exhibited controlled release by adjusting the ratio of copolymer to chlorpyrifos, showed an initial burst release and then a steadier release profile, the released amount depending on the amount of chlorpyrifos entrapped in the NPs, and the increased amount of the insecticide within NPs resulted in its decreased release (Zhang et al. 2013b). A nanohybrid prepared by intercalation of a chlorpyrifos inclusion complex with carboxymethyl-β-cyclodextrin into the interlayer of Zn-Al-layered double hydroxides showed distinct slow release, unlike to nanohybrid, in which sulphonated hydroxyethyl-β-cyclodextrin was used for chlorpyrifos inclusion complex and the kinetic process of pesticide release could be fitted well by the pseudo-second-order and the parabolic diffusion models (Liu et al. 2016). A nanocomposition prepared by encapsulation of organophosphate acephate with the particle size of 80–120 nm and irregular shape showed high efficacy against *S. litura*, *Lipaphis erysimi* (mustard aphid) and *Bemisia tabaci* (whitefly) both in vitro and in vivo and was found to be more effective than a commercial bulk formulation. Treatment with this nanocomposite at 300 ppm resulted in approximately 100% mortality of *S. litura* within 7 days, and at application of 240 ppm and 180 ppm almost 75% and 20% larvae, respectively, were killed. Higher concentrations also reduced the fecundity of larvae when they reached adulthood. Treatment with 300 ppm of nanocomposite caused about 100% mortality of the mites after 5 days of treatment. In the field study, foliar spray of a nanocomposition at 180 ppm, 240 ppm and 300 ppm ensured the superior control of *S. litura* and *Lipaphis erysimi* compared to the commercial one. Reduced acetylcholinesterase activity due to nanoacephate treatments indicated more binding of the active constituent of acephate with thiocholine, which could be a probable reason for breaking resistance in lepidopteron pest. Consequently, it could be expected that this nanoformulation might overcome the problem of reduced target site sensitivity, one of the major causes of resistance development in insects (Pradhan et al. 2013).

The toxic effect of urea-based insecticide novaluron NPs (50−200 nm) on Egyptian cotton leaf worm *Spodoptera littoralis* larvae was found to be similar to that of the commercial formulation (Elek et al. 2010). The effects of two nanotypes of pyrifluquinazon and a non-nanotype of this insecticide which modifies insect behaviour by rapidly stopping feeding so that insects starve to death on the mortality of the green peach aphid *Myzus persicae* were investigated using concentrations of 25, 50 and 100 ppm. The nanoformulations of pyrifluquinazon were prepared using a different molecular weight CS as coating material (CS 30,000 (0.1%) and CS 3000 (0.3%). The best controlled release feature was observed with the CS 3000, 0.3% nanotype pyrifluquinazon. Both CS-containing nanoformulations were effective against *M. persicae* at 14 days after treatment, and the reaction time slowed from 14 to 30 days after treatment in the aphids treated with CS 3000 (0.3%), while the best lethal efficiency of non-nanotype insecticide applied at 50 and 25 ppm was estimated at 2 days after treatment (Kang et al. 2012).

Liu et al. (2008) reported flash nanoprecipitation using a multi-inlet vortex mixer as the technology to produce bifenthrin NPs suspensions with sizes between 60 and 200 nm, the stability of which depended on the properties of the polymeric stabilizer. The most stable NPs with the narrowest size distribution were prepared using a block copolymer of polyacrylic acid and polybutylacrylate, but stable NPs were fabricated also with polyvinylpyrrolidone and polyvinyl alcohol. Bang et al. (2011) prepared CS-coated nanoliposomes containing etofenprox or α-cypermethrin using different types and concentrations of CS to regulate the mean size and the surface charge and found that as the CS concentration (0.1−0.5%, w/v) and the degree of deacetylation increased, surface charge also increased, and the release period of the entrapped insecticide could be prolonged by increasing the intrinsic surface charge or concentration of the coating material. By encapsulation of β-cyfluthrin in PEGs of different molecular weights (600, 1000, 1500 and 2000), insecticidal controlled release nanoformulations were prepared, and their effect on the mortality of *C. maculatus* (Coleoptera: Bruchidae) was tested. The approximate EC_{50} values of different test formulations against *C. maculatus* for 1, 3, 7, 14, 21 to 30 days in water after 24 h exposure of each day were estimated. At the 7th day, the formulations with PEG 600 and PEG 100 showed lower EC_{50} values than PEG 1500 and PEG 2000 due to faster release of the pesticide. The formulations prepared with PEG 1500 and PEG 2000 showed minimum EC_{50} on 14th day (2.20 and 1.58 mg/L, respectively) and mean EC_{50} value during 30 days (36.98 and 32.23 mg/L, respectively), whereby all prepared nanoformulations were more effective than a commercial preparation with the mean EC_{50} value of 124.29 mg/mL during 30 days (Loha et al. 2012).

Biocompatible oil-core silica-shell nanocapsules designed for sustained release of fipronil insecticide, in which release of insecticide can be tuned through control of the silica-shell thickness (i.e. 8−44 nm), showed insecticidal effect against economically important subterranean termites (Wibowo et al. 2014). Guo et al. (2015) fabricated enzyme-responsive emamectin benzoate microcapsules based on a copolymer matrix of SiO_2-epichlorohydrin-carboxymethyl cellulose showing excellent protection of the active ingredient against photo- and thermal degradation, notable cellulase stimuli-responsive properties as well as sustained insecticidal efficacy against *M. persicae*, and their genotoxicity was less than that of grade emamectin benzoate. Because mineral particles can scratch the exoskeletons of insects resulting in wounds, block their spiracles, reduce activity and cause strong dehydration of the insect resulting in death, they are used in the protection of plants against tiny insects.

8.4.3 Insecticides Based on Nanoscale Metals

The investigation of the impact of AgNPs on the life history parameters of two agricultural pest insect species, *Heliothis virescens* (tobacco budworm) and *Trichoplusia ni* (cabbage looper), and a beneficial predatory insect species, *Podisus maculiventris* (spined soldier bug), showed that AgNPs retarded the development, reduced the adult weight and fecundity and increased mortality in the predator, although they practically did not affect the developmental times, pupal weights and adult emergence. Thus, the adverse effects of AgNPs on the beneficial insect species require considering carefully the risk of their widespread application in insect pest management (Afrasiabi et al. 2016). The application of AgNPs with the particle size ranging from 42 to 98 nm prepared using *Sargassum muticum* extract resulted in significant changes in the protein profile of hemolymph, morphology of hemocytes and deteriorated midgut inclusions such as lumen, basement membrane, fat body and gastric caeca of *Ergolis merione*. In treated larvae, the hemocytes had thin or no outer membrane, and in the fat body, the lipid content was denatured and washed out, which led to opening its inclusion to the lumen of the midgut and attaining irregular shape and size (Moorthi et al. 2015). Yasur and Pathipati (2015) investigated the susceptibility of two lepidopteran pests of castor plant (*Ricinus communis* L.), asian armyworm, *S. litura* F. and castor semilooper, *A. janata* L. to polyvinylpyrrolidone (PVP)-coated AgNPs with particle size <100 nm and zeta potential of 22.3 ± 5.78 mV. They fed larvae with castor leaves treated with AgNPs or $AgNO_3$ and observed a decrease in larval and pupal body weights of both insects as well as changes in the antioxidative and detoxifying enzymes of the treated larva indicating that exposure of larvae to AgNPs led to induction of oxidative stress, which was countered by antioxidant enzymes. The LD_{50} and LD_{90} values of AgNPs synthesized using aqueous leaves extracts of *Euphorbia prostrata* having the rod shape and the size of 25−80 nm with the average size of 52 nm against *S. oryzae* L. were estimated as 45 mg/kg and 168 mg/kg, respectively, and they were found to be significantly lower than the corresponding values estimated for $AgNO_3$ (248 and 2675 mg/kg, respectively). Moreover, no fresh insect infestation was found in the AgNP-treated stored rice even after 2 months of treatment, indicating the superb potential of AgNPs as a stored grain and seed protecting agent if applied with proper safety measures (Zahir et al. 2012). Remarkable pesticidal activity on *S. oryzae* was shown also by AgNPs (15−25 nm) synthesized using *Avicennia marina* (Sankar and Abideen 2015). Rouhani et al. (2013) reported LC_{50} values related to insecticidal effect of AgNPs on the cowpea seed beetle, *C. maculatus* F. (Coleoptera: Bruchidae), as 2.06 g/kg (adults) and 1.00 g/kg (larvae), respectively. The experiments with a model insect *Drosophila melanogaster* showed that the activity of Cu-dependent enzymes, namely, tyrosinase and Cu-Zn superoxide dismutase, significantly decreased following the consumption of AgNPs, despite the constant level of Cu present in the tissue, which resulted in cuticular demelanization, because tyrosinase activity is essential for melanin biosynthesis (Armstrong et al. 2013). In the third instar larvae of *D. melanogaster* that were fed with a diet of standard cornmeal media mixed with AgNPs at the concentrations of 50 and 100 μg/mL for 24 and 48 h, the AgNPs induced heat-shock stress, oxidative stress, DNA damage and apoptosis (Ahamed et al. 2010).

AuNPs showing multiple irregular shape, crystalline nature and particle size in the range 20−50 nm prepared using latex of *Jatropha curcas* inhibited catalytic potential of trypsin due to the formation of trypsin−AuNPs complex because of covalent and electrostatic interactions of AuNPs with proteins and binding to −SH groups of aminoacids. This finding was supported also by investigations performed in vivo on serum of several vectors and agriculturally important pests (Patil et al. 2016). The citrate-capped AuNPs exhibited significant in vivo toxicity in the model insect *D. melanogaster* upon ingestion, which was reflected in a significant reduction of the life span and fertility, presence of DNA fragmentation as well as a significant overexpression of the stress proteins (Pompa et al. 2011).

As a safe alternative to insecticides in protection of rice grains against *S. oryzae* (Linnaeus), natural rock powder and ZnO NPs could be used (Hamza 2012). Shu et al. (2012) investigated the response of *S. litura* to zinc stress and found that the treatment with 50–500 mg Zn/kg resulted in notable induction of both metallothionein content and metallothionein gene expression in the midgut as well as changes in cell ultrastructure (mainly the presence of electron-dense granules in the cytoplasm of the midgut cells), showing significant positive correlation with Zn accumulation in the midgut, which could be considered as effective detoxification mechanisms in the common cutworm. Derbalah et al. (2014) tested the insecticidal activity of ZnO NPs and SiO_2 NPs against the pink bollworm *Pectinophora gossypiella*, which is one of the key pests of cotton in the world, and compared it with that of conventional insecticide pyriproxyfen. In these tests the effects of individual materials on some liver function enzymes, carbohydrate hydrolyzing enzymes, total protein and total lipids of the 4th instar larvae of the *P. gossypiella* pest were also investigated, and it was found that ZnO NPs were the most effective against the newly hatched larvae.

Biosynthesized NiNPs with cubical shape and the average particle size of 47 nm showed insecticidal activity against agricultural pest *Callosobruchus maculatus* resulting in 97% mortality (Elango et al. 2016).

8.4.4 Insecticides Based on Nanoscale Metalloids

Amorphous SiO_2 NPs (15–30 nm) were found to be highly effective against insect pest *S. oryzae* causing more than 90% mortality, indicating the effectiveness of SiO_2 NPs to control insect pests (Debnath et al. 2011). Spherical amorphous SiO_2 NPs with the size 70−80 nm were also found to be highly effective against stored grain pest *Corcyra cephalonica*, causing 100% mortality, suggesting their potential to control insect pests (Vani and Brindhaa 2013). The study focused on the cellular uptake of amorphous SiO_2 NPs (<30 nm) in the midgut of the third instar larvae of *D. melanogaster* that were exposed orally to 1−100 μg/mL of SiO_2 NPs for 12−36 h showed considerably increased expression of hsp70 and hsp22 along with caspase activation, membrane destabilization and mitochondrial membrane potential loss (Pandey et al. 2013). The experiment with adults of *R. dominica* F. and *T. confusum* Jacquelin du Val. that were exposed to SiO_2 NPs Aerosil® and Nanosav at the rate of 0.2 mg/cm^2 for 1 and 2 days on filter paper inside plastic Petri dishes confirmed the significant toxic effects of SiO_2 NPs on both insects, *R. dominica* being more susceptible. At low concentrations, Aerosil® was more effective than Nanosav, and the effectiveness of SiO_2 NPs in wheat grains was higher than in barley (Ziaee and Ganji 2016). Santo-Orihuela et al. (2016) tested bare SiO_2 NPs (14, 380 and 1430 nm) and amine-modified SiO_2 NPs (131 and 448 nm) on the viability of *S. frugiperda* cells (Sf9 cell line) and found that 14 nm NPs were the most effective. Exposure to 0.12 mg/mL SiO_2 NPs during 24 h resulted in the reduced viability of the cells by 60% compared to the control, and activity of cells was lowered also in the presence of other negatively charged NPs. On the other hand, positively charged NPs applied at concentrations 0.12 and 0.6 mg/mL were found to promote the proliferation of the cells, while the effect of higher concentrations (7.2 mg/mL) was comparable with that of the control. Silica NPs caused mortalities to carmine spider mite and two-spotted spider mite with mean lethal concentrations 317, 116 and 112, 83 ppm, 7 days after treatment, for *Tetranychus cinnabarinus* and *Tetranychus urticae* adult females and eggs, respectively, as well as the mortality of their predatory species *Stethorus punctillum* (97%), *Phytoseiulus persimilis* (35%) and *Orius insidiosus* (32%) (Hala and Elsamahy 2016). Soil and foliar treatments with SiO_2 NPs led to 37% and 44% feeding inhibition rate in oriental armyworm *Mythimna separata* (Walker) and elongation of the larval stage period to 31 days compared to 26 days observed in the control, and mortality percentages of larvae at SiO_2 NPs administration in the form of spray was 67%, while in the control it represented only 10% (Mousa et al. 2014). Rouhani et al. (2013) investigated the insecticidal effect of SiO_2 NPs on the cowpea seed beetle, *C. maculatus* F. (Coleoptera: Bruchidae), and estimated LC_{50} value of 0.68 g/kg on adults and 1.03 g/kg on larvae, respectively, and the high efficiency of SiO_2 NPs on adults was also reflected in 100% mortality. *Capsicum annuum* proteinase inhibitor immobilized on SiO_2-based nanospheres and rods showed bioactive peptide loading 62% at acidic pH and 56% of peptide release at pH 10, simulating gut milieu of the target pest *H. armigera*, and in vivo study showed that on the 8th day after feeding with this nanoformulation, about 40% reduction in insect body mass was estimated compared to control insects. This indicates the potential of peptide nanocarriers in delivering diverse biologically active complexes specific to gut pH of *H. armigera* (Khandelwal et al. 2015).

Spherical SiO_2 NPs synthesized by sol-gel method and surface functionalized in situ with 3-mercaptopropyltrimethoxysilane (MPTS) and hexamethyldisilazane (HMDS) with the size ranging from 15 to 20 nm for HMDS and from 29 to 37 nm for MPTS were found to exhibit insecticidal activity against the second instar larvae of *S. litura*, and their application at a dose 125 mg/cm^2 resulted in 58% (HMDS) and 64% (MPTS) mortality. Treatment with 0.25 mg/cm^2 of MPTS functionalized SiO_2 NPs killed all insect larvae, while the application of HMDS functionalized SiO_2 NPs resulted in 84% insect mortality at the same dose, and no survivors were estimated after application of both SiO_2 NPs at a dose of 0.5 mg/cm^2. The dead bodies of the insects were found to be remarkably dehydrated indicating that abrasion or, to some extent, also the absorption of lipids present in cuticle caused by SiO_2 NPs damaged the cuticular water barrier of *S. litura* resulting in the loss of water from the body and subsequent death due to desiccation (Debnath et al. 2012).

Amorphous nanosilica and nanoalumina were also found to be highly effective against mustard aphid *Lipaphis pseudobrassicae* (Debnath et al. 2010). Goswami et al. (2010) applied solid SiO_2, Al_2O_3, TiO_2 and ZnO NPs at doses 0.5, 1.0 and 2.0 g/kg against rice weevil *S. oryzae* and found that on the first day the treatment with 1 g/kg of hydrophilic SiO_2 NPs was the most effective. At application of 2 g/kg of SiO_2 NPs and Al_2O_3 NPs, the mortality on day 2 represented 90%, and after 7 days of exposure, 95% and 86% mortality was obtained with hydrophilic and hydrophobic SiO_2 NPs at 1 g/kg, while the treatment of rice with lipophilic SiO_2 NPs at 1 g/kg resulted in approximately 70% mortality, and Al_2O_3 NPs killed almost all the insects using a dose of 0.1 g/kg dose.

The experiments of Buteler et al. (2015) who tested the effect of three unique types of nanoalumina dust with particles <50 nm as an insecticide against 0–6-week-old adults of the rice weevil *S. oryzae* and the lesser grain borer *R. dominica*, two species that differ in their susceptibility to inert dusts, showed that insecticidal activity depended on particle size, particle morphology and surface area; however minimizing particle size and maximizing surface area were not the sole dominant factors influencing the efficacy. All dust types were more effective on *S. oryzae* than on *R. dominica*, and the dust synthesized using a modified glycine-nitrate combustion process consistently yielded greater mortality rates. In general, the superb efficacy of the dusts for both insect species was observed at low humidity, which decreased significantly at elevated humidity indicating that dusts can adsorb either water or cuticle waxes and thus atmospheric water reduces the effectiveness of all the tested dusts by competing with the cuticle hydrocarbons. The inert dusts absorb epicuticular hydrocarbons by capillary forces, and dusts with smaller particle size will cause greater insect mortality. Stadler et al. (2010a) tested insecticidal activity of nanostructured Al_2O_3 applied as dry dust against *S. oryzae* L. and *R. dominica* (F.), which are major insect pests in stored food supplies. Exposure of the insects to *T. aestivum* plants treated with nanostructured Al_2O_3 reduced survival in both species, whereby mortality in both species increased with increasing exposure interval and product concentration. While after 3 days of continuous exposure to 500 mg/kg, the mortality of *S. oryzae* and *R. dominica* adults represented 20% and 40%, respectively, at treatment with 250 mg/kg during 9 days, 80% of the adults of both species were dead. The LD_{50} values estimated after 9 days of exposure were 149 mg/kg (*R. dominica)* and 177 mg/kg (*S. oryzae*), respectively. It is suggested that nanoalumina kills arthropods by adsorbing epicuticular lipid layers through capillarity, causing excessive water loss through the cuticle (Stadler et al. 2010b), and those with a small particle size and high surface areas having a composition conducive to wetting of the specific hydrocarbons present on the surface of the insect could be suggested as the most effective dusts. In addition, nanostructured alumina particles were found to be more effective in killing *S. oryzae* than dry dust applications of Protect® diatomaceous earth, were equally toxic to *R. dominica* and caused also the reduction of progeny production, and *S. oryzae* showed higher susceptibility to inert dusts than *R. dominica* (Stadler et al. 2012). Huang et al. (2013b) investigated the effect of Al_2O_3 NPs on the rhythmic activities in the antennal lobe of *Drosophila* using patch clamps to record electrophysiological activities and found that 15 min after their application the average frequencies of spontaneous activities were significantly decreased compared with control groups indicating that these NPs might have adverse effects on the central nervous system in *Drosophila*.

8.4.5 Other Inorganic Nanoinsecticides

The estimated LC_{50} values at application of a 20% calcium carbonate suspension concentrate with particle sizes about 100 nm and a 95% bulk calcium carbonate powder (>1 μm) on infestations of peach aphids (*M. persicae*) were 2685 and 93,036 ppm, respectively, indicating that in controlling peach aphids, the 20% calcium carbonate suspension concentrate was the most effective (Liu et al. 2014). The study of the influence of temperature and humidity on the insecticidal effect of three diatomaceous earth formulations (Protect-It, PyriSec and DEA-P) against larger grain borer *Prostephanus truncatus* (Horn) (Coleoptera: Bostrychidae) adults in stored maize (*Z. mays* L.) at three temperatures (20, 25 and 30 °C) and 55% and 75% relative humidity levels showed that DEA-P was the most effective and caused complete mortality to the exposed insect, even at the lowest dose rate (75 ppm), completely suppressed progeny production, and its efficacy was continuously high in all temperatures and relative humidities examined (Athanassiou et al. 2007). The acaricidal effect of different diatomaceous earth formulations (SilicoSec, PyriSec, Insecto, Protect-It and DEA-P) applied at the dose 0.2 and 0.5 g/kg against *Tyrophagus putrescentiae* on stored wheat was investigated by Iatrou et al. (2010) by measuring the mortality of mite individuals after 5 days of exposure and checking for *T. putrescentiae* offspring on the treated wheat after 30 days. The application of 0.2 or 0.5 g/kg caused mortality of both adults and immatures >78%, and treatment with the dose 0.5 g/kg resulted in 100% mortality. The immature stages of the insect were less tolerant to diatomaceous earth formulations than the adults, and PyriSec was found to be the most effective against adults, whereby increasing of the dose led to considerable reduction of progeny production.

8.5 Risks of Nanopesticide Applications

In recent decades, advances in nanotechnology engineering have given rise to the rapid development of many novel applications in various industrial fields. Nanoscale materials exhibit unusual physical, chemical and biological properties, differing in important ways from the properties of bulk materials and single atom or molecule (National Nanotechnology Initiative 2008; Medina et al. 2007; Dolez 2015; Borm et al. 2006; Buzea et al. 2007; Fröhlich 2013). It is no wonder that nanotechnology has also found its use in agriculture and the food industry. Nanosystems/nanomaterials have been used for plant protection and nutrition in the form of nanopesticides or nanofertilizers or other plant growth-stimulating nanoscale materials (Jampílek and Kráľová 2015, 2017b, c; Masarovičová and Kráľová 2013; Masarovičová et al. 2014; Kookana et al. 2014; Bleeker et al. 2015). Various nanocomposites have been applied for protection of different foodstuffs, smart active or responsive packaging materials and edible coatings. Diverse nanosensors applicable for monitoring of food quality, safety and integrity can be found as well (Kookana et al. 2014; Bleeker et al. 2015; Jampílek and Kráľová 2015, 2018b). Thus, the application of nanotechnology for sustainable intensification of agricultural production, such as crop protection agrochemicals, but also agents facilitating the protection of plants against pesticides, enhancing plant growth, securing rise of global food production, guaranteeing enhanced food quality and minimizing the waste, can be considered as an excellent solution, but the most critical is stability and degradability all these nanomaterials (Prasad et al. 2014, 2017; Bleeker et al. 2015; Jampílek and Kráľová 2015, 2017b; Andronescu et al. 2016; Sangeetha et al. 2017a, b, c).

Due to their direct and intentional application in the environment, nanoagrochemicals may be regarded as particularly critical in terms of possible environmental impact, as they would represent the only intentional diffuse source of engineered NPs in the environment (Kah et al. 2013; Kah 2015). Although many nanomaterials showed benefits, nanosystems used in agriculture and the food industry, especially when they are exceedingly stable in the environment, can contaminate water resources and/or ground and return to the life cycle. On the other hand, they can contaminate food products by residues of packaging materials/edible coatings. Thus, NPs can be associated with some risks (toxicity) for human and environmental health. Possible routes of entry into the body include inhalation, absorption through the skin or digestive tract (Jampílek and Kráľová 2015, 2017a, b, c, 2018a; Khan 2013; Bleeker et al. 2015; Andronescu et al. 2016).

Different permeation through cell walls/membranes into cells is probably the most affected and the most valuable parameter in case of nanopesticides and their application for crop protection. In this context, especially particles with particle size <100 nm are critical, because they are able to practically unlimitedly permeate through biomembranes. In general, the ability of NPs "to permeate anywhere" is connected primarily with their particle size and shape (Hagens et al. 2007; Buzea et al. 2007; Keck and Müller 2013; Nehoff et al. 2014). These NPs may be more easily taken up by any organism, which could result in their longer persistence in environmental systems. The small size (an extrinsic property) of NPs influences these effects more significantly than a unique nanoscale property representing an intrinsic property (Buzea et al. 2007; De Jong and Borm 2008; Auffan et al. 2009; Kumar et al. 2012; Brayner et al. 2013; Janrao et al. 2014). Mainly adverse effects of NPs accumulated in the cell leading to intracellular changes such as disruption of organelle integrity, gene alterations, etc., or cytotoxic effects by generation of ROS as well as reactive nitrogen species resulting in the damage of plasma membrane, cell organelles and intracellular proteins are critical. Considering the potential toxicity of NPs and different nanomaterials on living organisms and also on human health, it is indispensable to minimize their entry into the environment (Ventola 2012; Berkner et al. 2016; Vestel et al. 2016).

Based on particle size definitions of NPs (European Commission 2011; National Nanotechnology Initiative 2008), a classification of NPs (Sioutas et al. 2005) according to biodegradability (ability of a compound to degrade in organism/environment) into four classes was suggested as follows: (*i*) size >100 nm and biodegradable, (*ii*) size >100 nm and non-biodegradable, (*iii*) size <100 nm and biodegradable and (*iv*) size <100 nm and non-biodegradable (Keck and Müller 2013). Logically, the last class of NPs is considered as the most dangerous for human health. Toxicological properties of NPs are affected by particle shape, size, surface area, surface charge and the adsorption properties of the material as well as by abiotic factors such as pH, ionic strength, water hardness and the presence of organic matter (Handy et al. 2008). While inside cells, NPs might directly provoke alterations of membranes and other cell structures and molecules as well as protective mechanisms, NPs can exhibit also indirect effects depending on their chemical and physical properties, e.g. physical restraints (clogging effects) or production of ROS (Navarro et al. 2008).

In the light of these facts, some multinational corporations, such as BASF, Bayer, Monsanto, DuPont and Syngenta, focused among others on pesticide production and started to invest in the development of nanopesticides, concealing this development before public, because prefix “nano” cannot be currently perceived so positively (Suppan 2013), which does not, however, mean that the first nanopesticides cannot be already applied (Gewin 2015). On the other hand, many nanoagrochemicals described in the scientific literature do not meet the cost-benefit requirements, and their production is not profitable (Aschberger et al. 2015).

It is also important to note that nanopesticides offer many advantages, such as increased efficacy, dose reduction, lower exposure to nontarget organisms or lower risk of resistance development. It can be stated that launched nanoagrochemical products mostly consist of “nano” formulations of already registered ingredients, and thus they are very similar to many agrochemical products currently available on the market (e.g. emulsions, suspensions) (Aschberger et al. 2015; Gewin 2015; Kah 2015).

Due to the above-mentioned facts, regulatory authorities will play a crucial role in the future development of other nanoagrochemicals. The facts that NPs are more efficient or that their application has some benefits for crop protection have been proven and are unexceptionable. Several international organizations coordinated seminars on nanotechnology applications for agriculture (e.g. FAO 2010, 2013; JRC-IPTS 2014). The activities of governments and regulatory authorities dealing with the development of legislation adapted to nanoagrochemicals vary considerably (FAO 2013; APVMA 2014). The extent to which nanoagrochemicals are developed will be strongly influenced by the regulatory system that controls their entry into the market. There are currently great geographic discrepancies that can influence applications in a given market (Watson et al. 2011). There are considerable issues relating to the definition of NPs and how the proposed criteria can be applied to nanopesticides (Kah et al. 2013; EC 2014; JRC-IPTS 2014).

When considering all the nanoproducts that appear in the agriculture and food sectors, there is a generally accepted consensus that there has been currently insufficient reliable data and the level of knowledge to allow a clear safety/risk assessment (FAO 2013; JRC-IPTS 2014). However, prohibiting the application of nanopesticides until they are proven entirely safe is unrealistic, as all pesticides are inherently toxic (at least to the target pest) and, thus, associated with some risk. When considering only nanoagrochemicals, a conventional approach to risk assessment – the hazard×exposure paradigm – would result in a number of pitfalls (Kookana et al. 2014). The exposure assessment is based on investigations into the environmental fate of a compound. There have been a limited number of studies investigating nanoagrochemicals (Kah et al. 2013; Kah and Hofmann 2014). It is also probable that endpoints of fate and dangers are not sufficiently determined by the use of protocols previously developed for other types of chemicals (Kah et al. 2014; Kookana et al. 2014). Thus, a fair assessment of nanopesticides should be focused on the evaluation of both the risks and benefits associated with their use relative to current solutions. While this may not be possible when considering all products discussed so far in literature, restricting the analysis to products that are likely to emerge in the next decade shows that a fair assessment may be possible (Kah et al. 2015).

The effects of agrochemical formulations on the environment and the effect of active ingredients have been evaluated within the EU under Directive 91/414. The new EU pesticide regulation (1107/2009) states that the impact of formulations should be taken into account, but it also comes with recommendations that it is reasonable to assume that "formulation does not affect the fate and behaviour of the active ingredient in the environment" (e.g. European Commission 2009). The authorization of pesticides has long been the subject of a rigorous and constantly protective regulatory risk assessment. Safety factors are commonly used to uncover uncertainties and provide a margin of safety. It is likely that the effects of formulations (nano or not) fall within this boundary. This is probably the reason why a representative of the European Crop Protection Association considered that "under the current procedure for traditional crop protection products, the safety of nanomaterials would also be properly assessed" (JRC-IPTS 2014), although the current scientific paradigm cannot be reasonable.

The use of the highly conservative risk assessment strategy mentioned above does not support the level of R&D investment needed to design risk-reducing formulations. Impacts of (nano) formulations on fate and effects of active substances have been repeatedly reported in scientific literature, but the relevant mechanisms remain poorly understood (Jampílek and Kráľová 2018c). Elucidation of these processes and the analysis of environmental impacts require the use of experimental protocols, analytical techniques and theories that differ from typical applications to agrochemicals. Kookana et al. (2014) discussed that combining and adapting approaches developed for pesticides and NPs could in many cases provide a reasonable assessment of the risks associated with nanopesticides. The same approach could be used successfully in assessing the impact of formulations that can exhibit colloidal behaviour in application (whether or not designated as "nano" according to criteria used in research, public or industrial) (Kah 2015).

8.6 Conclusion

It can be stated that plant protection plays an extremely important role in increasing the production of agricultural crops and in protecting them. Nanotechnology and nanoscale science afford unambiguously a great potential in innovative and improved solutions. Nanosized materials change their physical, chemical and biological properties in comparison with bulk materials, and some of them can really help to improve and innovate some pesticides for a more efficient combat against plant diseases, weeds and various pests. The requirements of the latest EU directive regarding a better evaluation of formulations should not be perceived as constraints, but as a tool that should prevent nanopesticides to become the next emerging category of contaminants of environment and human health risks associated with agriculture. To investigate nanopesticide risks, i.e. to minimize nanopesticide impacts on environment and human, cooperation among expert teams at all stages of the development and evaluation of nanopesticides (e.g. formulators, botanists, agricultural scientists and nano(eco)toxicologists) should originate and be intensified to result in the development of successful products, meeting the multiple constraints of the agrochemical sector, and this would bring an added value in relation to existing products.

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