Nanobiotechnology Approaches for Crop Protection

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Abstract

Modern agriculture uses nanobiotechnology development as one of the most valuable tools. Using biomolecules in nanotechnology provides new agrochemical nanostructured formulations with different action mechanisms to increase crop productivity and improve their protection decreasing chemical pesticide use. Sustainability and safety of agriculturally cultivated crops are achieved by application of nanoformulations used for control of plant disease related with microorganisms, insects and environmental factors. Nanostructures are also applied for controlled release of nutrients and growth regulators. Safety of nanomaterials use and their environmental impacts are the important factors to acceptance of these new technologies by consumer and agricultural companies.

1.1 Introduction

Nanobiotechnology applied for crop production and protection is a relatively recent subject in comparison with pharmaceutical nanotechnology (Corradetti and Ferrari 2016). As nanobiotechnology tools are considered nanosystems that contain biomolecules (nanoparticles obtained from biochemical compounds, or coated with biopolymers, nanoformulations from plant extracts and metal or metal oxide nanoparticles) (Elemike et al. 2017; Kumar et al. 2015; MubarakAli et al. 2011; Narendhran and Sivaraj 2016). Nanobiotechnology alludes to the comprehension

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and regulation of this content at the nanoscale. These tools have the potential to protect plants against microbial diseases and insects, stimulate plant growth, enhance food quality, reduce wastes, and control environmental contamination. Nanosystems are characterized by size dimensions up to 100 nm. It is well known that the properties of nanomaterials differ on scale. Also a material having particles or constituents of nanoscale dimensions is known as a nanomaterial. Moreover, as nanosystems are considered manufactured or natural materials which contain unbound or agglomerated particles with size distribution on at least one dimension between 1 and 100 nm for 50% or more particles (Corradetti and Ferrari 2016). Nanoscale materials that have one dimension are surface coatings or thin films (extended in two dimensions). Nanoscale that are in two dimensions are recognized as nanowire and nanotubes. At the same time, materials with nanosized in three dimensions are fullerenes, colloids, particles, and dendrimers, among others. The improved properties of nanomaterials originate principally from their amplified specific surface area and quantum effects. Different biological molecules have nanodimensions: proteins, cell membranes, sugars, and polysaccharides.

Nanobiosystems applied in agriculture may be useful for improving use water by plants, as well as effect of pesticides, fertilizers, and growth regulators. Nanobiotechnology use may bring potential benefits for crop production, protection, and environmental preservation. Nanobiotechnology approaches include nanomaterials for controlled-release and effective application of water, nutrients, and fertilizers, nanocapsules for products distribution, and antimicrobial nanoemulsions for control of pathogen contamination (Prasad et al. 2014, 2017; Bhattacharyya et al. 2016). Nanobiotechnology attempts are focused on to decrease the unfavorable effect of agrochemical products in crops and surroundings and human well-being. In addition, nanobiotechnology aims to solve problems related to the use of water, soil, water, impacts on the environment and the health of field workers. The present overview is intended to demonstrate potential uses and benefits of nanobiotechnology.

1.2 Nanoparticles Against Pathogens

In the last years, many types of research have been carried out in the field of nanotechnology, since their properties are linked to their size and morphology. Nanoparticles are characterized by being highly reactive and possessing a large surface area. The nanotechnology has undergone fast growth in divergent fields, incorporating microbiology and infectious diseases. Especially, nanostructures carry enormous prospect as effective drug distribution method to tend microbial infections as they display more advantages as compared to standard antibiotic formulations (Aziz et al. 2015, 2016). Nanotechnology points to new solutions of different problems which are faced by humanity, and it promises benefits of all kinds, to mention a few: innovations in medical applications, solutions to environmental problems such as pollution and water treatment, food processing, transgenic foods obtaining, molecular thermal changes, and computer science.

Foodborne illness is the product of consumption of food contaminated with a broad range of pathogenic microorganisms, their toxins, or chemicals. Therefore, there is a need to find methods that contribute to the control of these pathogens in food during processing, packaging, and distribution. One of the most striking applications of nanotechnology has focused on the production of modified packages with silver nanoparticles (AgNPs) (Jo et al. 2009). Thus, the nanoparticles are a classification of materials mixed using different metals or using the nonmetal elements with clear features and large uses in various branches of scientific research. Nanoparticles have possible biological roles and applications, like biosensing the small amount, catalytic reactions, drug delivery, visual representation, and nanodevice fabrication, and may be utilized as antimicrobial representatives (Faraz et al. 2018). The synthesis of NPs utilizing chemical and physical technique has been exhaustively all over society, although these techniques are frequently environmentally poisonous, strictly arduos, and financially costly. Appropiately, biological techniques for synthesis using plants, plant extracts, microbes, and their enzymes have been recomended as great environmental friendly substitutes (Prasad 2014; Prasad et al. 2016, 2018). The use of vegetal extracts as reducing agents during NP synthesis or covering agents of NP is useful over other biological procedures. In this case, the procedures of cultivation and conservation of biological cells are not required, as in the case of tissues or cell cultures, and the nanoparticle synthesis procedure can be scaled. Altogether, plant-mediated synthesis of nanoparticles is a less expensive process, ecologically sustainable, and a one-phase technique for biological synthesis procedures that is secured for different individual curative and nutritional-based applications. Recently, the application of industrial and agricultural waste in the biosynthesis of dissimilar kinds of metallic nanoparticles has been broadly considered (Patra and Baek 2017; Sangeetha et al. 2017). These pathogens which are drug resistant are more pathogenic having enhanced rate of transience compared to that of wild or non-mutated strain. The scientific society is constantly investigating for novel types of decontamination methods and approaches that could act effectively against the potential pathogens.

Numerous researchers on the effectiveness of nanoparticles systems with plant extracts have been published (Table 1.1). The main nanoparticle systems are silver, copper, and zinc; these nanoparticles are capable of decrease microbial growth and also are excellent inhibitors of pathogens. Dhand et al. (2016) reported the synthesis of silver nanoparticles (AgNP), using *Coffea arabica* (seed) extract. These NPs have been tested against pathogen like *E. coli* and *S. aureus* and an excellent antibacterial activity was observed. Extracts of *Vernonia cinerea* (L.) Less. (Asteraceae) were tested and highly efficient against *Xanthomonas campestris* pv. Malvacearum (pathogen of the cotton plant) (Sahayaraj et al. 2015). Rao et al. (2016) reported the action of crude root extract of *Diospyros paniculata* against *B. subtilis*, *E. coli*, and *P. aeruginosa*. Use of peel aqueous extract of citrus (Citrus × clementina) has also been tested and has demonstrated its effectiveness to inhibit *E. coli*, *B. cereus*, and *S. aureus* (Saratale et al. 2017) and extract of *Dodonaea viscosa* against *E. coli*, *K. pneumonia*, *P. fluorescens, S. aureus*, and *B. subtilis* (Kiruba et al. 2013). In the same way, extract of *Tamarindus indica* fruit was used to synthesize AgNP through

Table 1.1 Plant extract used in synthesis of nanoparticles

Plant material	Nanoparticle	Action against pathogen	References
Mentha piperita	AgNPs	*Escherichia coli*	MubarakAli et al. (2011)
Caesalpinia coriaria (leaf)	AgNPs	*E. coli*, *P. aeruginosa*, *K. pneumoniae*, *S. aureus*	Jeeva et al. (2014)
Lippia citriodora	AgNPs	*S. aureus*	Elemike et al. (2017)
		B. subtilis	
		S. typhi	
		E. coli	
		C. albicans	
Tamarind (fruit extract)	AgNPs	*Bacillus cereus*, *Staphylococcus aureus*	Jayaprakash et al. (2017)
		Micrococcus luteus, Bacillus subtilis	
		Enterococcus sp., *Pseudomonas aeruginosa*, *Salmonella typhi*	
		Escherichia coli	
		Klebsiella pneumonia	
Mangifera indica, *Eucalyptus tereticornis*	AgNPs	*Aeromonas hydrophila (aquatic pathogen)*	Mahanty et al. (2013)
Carica papaya			
Musa paradisiaca			
Zingiber officinale (root extract)	AgNPs	*Staphylococcus* spp., *Listeria* spp.	Velmurugan et al. (2014)
Lantana aculeata Linn leaf	ZnO NPs	*Aspergillus flavus*, *Fusarium oxysporum*	Narendhran and Sivaraj (2016)
Brassica rapa L	AgNPs	*Gloeophyllum abietinum*, *G. trabeum*, *Chaetomium globosum*, and *Phanerochaete sordida*	Narayanan and Park (2014)
Mangifera indica, *Eucalyptus tereticornis*, *Carica papaya*	AgNPs	*Aeromonas hydrophila* (fish pathogen)	Mahanty et al. (2013)
Musa paradisiaca			
Salvadora oleoides	ZnO NPs	*Bacillus cereus* (BC) ATCC11778, *S. aureus* (SA) ATCC29737	Padalia et al. (2017)
		C. rubrum (CR) ATCC14898	
		E. coli (EC) NCIM2931	
		P. aeruginosa (PA) ATCC9027	
		K. pneumoniae (KP) NCIM2719	
		S. typhimurium (ST) ATCC23564	
Aloe vera (leaf extract)	CuO NPs	*Aeromonas hydrophila*, *Pseudomonas fluorescens*, and *Flavobacterium branchiophilum*	Kumar et al. (2015)

(continued)

Table 1.1 (continued)

Plant material	Nanoparticle	Action against pathogen	References
Citrus × clementines (peel extract)	AgNPs	*Escherichia coli*	Saratale et al. (2017)
		Bacillus cereus	
		Staphylococcus aureus	
Psidium guajava	AgNPs	*P. aeruginosa* MTCC 741	Bose and Chatterjee (2016)
Dodonaea viscosa	Cu and Ag nanoparticles	*Escherichia coli*	Kiruba et al. (2013)
		Klebsiella pneumoniae, *Pseudomonas fluorescens*, *Staphylococcus aureus*, and *Bacillus subtilis*	
Sargassum wightii (brown marine seaweed)	AgNPs	*S. aureus*	Shanmugam et al. (2014)
		K. pneumoniae	
		S. typhi	
Diospyros paniculata (root extract)	AgNPs	*B. subtilis*	Janmohammadi et al. (2016)
		E. coli	
		P. aeruginosa	
		K. pneumonia	
		S. pyogenes	
		S. aureus	
		B. pumilus	
		P. vulgaris	
Parthenium hysterophorus L.	ZnO NPs	*Aspergillus flavus*, *A. niger*	Rajiv et al. (2013)
Coffea arabica (seed extract)	AgNPs	*E. coli* and *S. aureus*	Dhand et al. (2016)

microwave irradiation (Jayaprakash et al. 2017). Narayanan and Park (2014) managed to synthesize AgNPs using turnip extract and tested its action against fungal pathogens of genera *Gloeophyllum*, *Chaetomium*, and *Phanerochaete* obtaining excellent results. Papaya leaf extract synthesized AgNPs has been reported to achieve inhibition of *Aeromonas hydrophila* an important aquatic pathogen (Mahanty et al. 2013).

Other investigations using an extract substance of brown marine seaweed (*Sargassum wightii)* showed a significant potential antibacterial action against *Staphylococcus aureus*, *Klebsiella pneumoniae*, and *Salmonella typhi*, surpassing twice its action compared to the control of antibiotic (Shanmugam et al. 2014). Even extract of *Cordyceps militaris*, a fungus medicinal, was employed in the synthesis of AgNPs and its antibacterial action against clinical infectious agents like *Escherichia coli*, *Staphylococcus aureus*, *Pseudomonas aeruginosa*, and *Bacillus subtilis* (Wang et al. 2016). Until now, for nanoparticles production, most of the methods reported synthesis with only aqueous extract (Rajan et al. 2015).

Copper oxide nanoparticles were synthesized utilizing a watery solution extract of *Acalypha indica* leaf and tested against *E. coli*, *P. fluorescens*, and *C. albicans* showing inhibition (Sivaraj et al. 2014). Thatoi et al. (2016) evaluated the impact of ZnONPs with two extracts of plant species of mangrove on different pathogenic bacteria; nanoparticles only showed action against *Shigella flexneri*. Also, extract of *Aloe vera* (leaf) was used to synthesized copper oxide nanoparticles; its potential to inhibit *P. fluorescens*, *A. hydrophila*, and *F. branchiophilum* was tested (Kumar et al. 2015).

Furthermore, fabrication of zinc oxide nanoparticles (ZnONPs) has been reported, and different natural extracts are used, for example, extract of *Parthenium hysterophorus* L. showed an excellent inhibition of *A. flavus* and *A. niger* (Rajiv et al. 2013); ZnONPs with extract of *Salvadora oleoides* (leaf) show action against bacteria such as *E. coli B. cereus*, *S. typhimurium*, *S. aureus*, and *C. rubrum*, among others (Padalia et al. 2017). *Anchusa italica* (flower extract) showed that Gram-positive bacteria have an increase of susceptibility than Gram-negative bacteria to the system of ZnO nanoparticles (Azizi et al. 2016). Other reports have described effect of ZnO nanoparticles against fungus in the presence of an extract of *Suaeda aegyptiaca* plant with achieving *Candida albicans* and *Aspergillus oryzae* inhibition.

1.3 Nanoparticles for Plant Disease Suppression

Nanotechnology has the possibility to transform the food and agricultural industries by developing new instruments for the management of plant diseases. It is possible that in the coming days nanostructured catalysts will advance the effectiveness of pesticides and insecticides and will also lower the doses level needed for crop plants (Khan and Rizvi 2014; Servin et al. 2015). The use of nanostructured materials in plant disease management is a novel approach that has the potential to act against pathogens like bacteria, fungi, and nematodes (Gupta et al. 2018; Abd-Elsalam and Prasad 2018). Table 1.2 shows various nanostructured materials utilized against diverse crop pathogens.

The agriculture production is influenced worldwide yearly due to plant pathogens; therefore, several investigations have been realized in an effort to control these plant diseases. Among methods of control or protection of crops against pathogens, the use of nanotechnology is a suitable alternative to protect crops from several pathogens. In this field, silver nanoparticles have been studied and applied as antibacterial material. Recently, Jo et al. (2015) used Ag nanoparticles of 7.5 nm against *Gibberella fujikuroi* in order to protect rice seedlings. Also, Cromwell et al. (2014) studied the application of silver nanoparticles to soil and control the propagation of the nematode *Meloidogyne* spp. and protect Bermuda grass plants. Small Ag nanoparticles (4–8 nm), were sprayed to pepper leaves plants to control the fungus pathogen *Colletotrichum* sp. (Lamsal et al. 2011).

Moreover, other nanostructured materials have been studied as crop protection alternatives. Kanhed et al. (2014) evaluated the antifungal efficacy of copper nanoparticles of 5–10 nm against potential plant pathogenic fungi such as *Alternaria alternata*, *Phoma destructiva*, *Fusarium oxysporum*, and *Curvularia lunata*. In the study, they found that Cu nanoparticles are better than the

Table 1.2 Examples of nanoparticles utilized against crop pathogens

Nanoparticle	Particle size	Mode of exposure (conc.)	Plant	Pathogen	References
DNA-directed AgNPs grown on graphene oxide	5, 18 nm	Sprayed (16, 50 and 100 ppm)	Tomato	*Xanthomonas perforans*	Ocsoy et al. (2013)
Ag ions and NPs	20–30 nm	Sprayed (25–100 ppm)	*Lolium perenne*	*Bipolaris sorokiniana* and *Magnaporthe grisea*	Jo et al. (2009)
SiO_2–Ag	20, 100 nm	Sprayed (0.3–100 ppm)	Cucumber, pansy, and green squash	Fungus: *Botrytis cinerea*, *Rhizoctonia solani*, *Colletotrichum gloeosporioides*, *Magnaporthe grisea*, and *Pythium ultimum* Bacteria: *Escherichia coli*, *Bacillus subtilis*, *Pseudomonas syringae*, *Xanthomonas campestris*, *Azotobacter chroococcum*, and *Rhizobium tropici*	Hae-Jun et al. (2006)
AgNPs	4–8 nm	Sprayed on the leaves (10, 30, 50, and 100 ppm)	Pepper	*Colletotrichum* sp.	Lamsal et al. (2011)
AgNPs	n/a	Applied to soil (1.5, 3, 13, 30 and 150 μg/ml)	Bermuda grass	*Meloidogyne* spp.	Cromwell et al. (2014)
AgNPs	~7.5 nm	Seeds submerged in AgNPs suspension (150 μg/ml)	Rice seedlings	*Gibberella fujikuroi*	Jo et al. (2015)
SeNPs	49–300 nm	–	*Pennisetum glaucum*	*Sclerospora graminicola*	Nandini et al. (2017)

commercial fungicide. Selenium nanoparticles result to be an accurate alternative to protect pearl millet plants against the *Sclerospora graminicola* (Nandini et al. 2017). Rajiv et al. (2013) synthesized zinc oxide nanoparticles and report its antifungal action against the plant pathogens *Aspergillus flavus* and *Aspergillus niger*.

1.4 Nano-encapsulated Phytoextracts for the Control of Pest

This information offers an existing viewpoint and trend of the futuristic prospective of agricultural nanotechnology to improve the effectiveness of botanical insecticides by encapsulating phytoextracts to control insects or plagues, the so-called green technology. Agricultural nanotechnology promises not only new products but also a vast potential as "upgrading technology" in combination with current technical solutions and nano-encapsulation trends of secondary compounds called active phytochemicals of plant extracts. Phytoextract is a plant extract of complex substances of bioactive chemical compounds obtained by physicochemical or microbiological processes (Medina 2001). The use of phytoextracts is known from remote times. They were applied as treatment of common diseases such as indigestion or pneumonia as well as as food preservatives. Numerous phytochemical compounds are considered as plant secondary derivatives or metabolites which were created during evolution to support different functions such as a defensive and protective barrier for the plants, or prevention against attack of microorganisms or insects, between others.

These substances are alkaloids, phenolics, terpenoids, and many others, the secondary metabolites are present in the whole plant in different proportions, and for that reason they are analyzed and obtained by the process of extraction with different organic or aqueous solvents. The application of nanotechnology provides a way to develop novel preparations and systems capable of improving the effectiveness of this kind of insecticides, to be incorporated into the ecosystem, as discussed below with the help to encapsulate this phytoextracts.

The advantage of the nanotechnology strategy is attractive since it can contribute to the benefits of the phytochemical compound in the ecosystem and to anthropoid health as it is easy to assimilate and nontoxic; also its advantages are biodegradability and high structural diversity, which can delay the occurrence of resistance (Raskin et al. 2002).

As a consequence or outcome of several research findings in this field from the study of phytoextracts for insect control, the foremost areas of opportunity to be studied are the scalability of the production of nano-carrier systems before commercializing this technology completely. However, in the manufacture of isolated extracts and active ingredients, a good amount is necessary to regulate some agrarian production in the presence of a pest. The prospective of these systems is to resolve difficulties that will associate the advantages of phytoextracts with nanotechnology, in a potential preparation that will be more efficient for the environment in general.

There are active compounds extracted and widely employed in agricultural sector to control the proliferation of devastating insects, harmful nematodes, and pathogenic fungi and bacteria. Conversely, on the other hand, some may lose their activity in a short period. On the other hand, some of them may lose their activity in a short period. Due to the current trend is focused to the remediation of land, aquifers, and natural systems associated with compounds that affect them, it is intended to increase the use of alternatives based on natural products and pest control agents that are more compatible with the new ecological policy (McSpadden and Fravel 2002). However, these products so far represent a small percentage of the total of the inputs used. Faced with this and the lack of a wider range of active ingredients, these have been gaining and begin to have an important participation not only in small-scale production systems in development with nano-encapsulation of this type of active compounds for their greater stability and effectiveness in the application. The encapsulation of phytoextracts in the encapsulated particles offers an effective potential for future agricultural applications. If the efficiency encapsulation is greater than 90%, the profile will be excellent and will be taken into consideration for the application compared to others that are already on the market that is harmful.

In general, reported results for pesticide-based formulations are encouraging, though more research work will be required to manufacture actual products that are benign, safe, and affordable.

There are comparatively very few reports in the scientific literature regarding the alliance of phytoextracts with encapsulated nanoparticles, and it would be essential to develop accessible systems appropriate for use in agricultural sector in general or green agriculture for pest control.

The next step in the encapsulated phytoextracts will be the activity in the soil and in the plant material of application, together with an efficient carrier system, also against an effect in conjunction with active agents extrinsic to the system that is applied.

The formulations are characterized by particle size and analyzed by scanning electron microscopy (SEM), differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), atomic force microscopy (AFM), and transmission electron microscopy (TEM). All these analyze and verify the potential of the nanoparticles and the availability of the vegetative material.

There are active compounds such as phenylpropanoids, monoterpenoids, and sesquiterpenoids (Nigam and Purohit 1962; Gupta et al. 1985; Ramos et al. 1986) that could be investigated for the development of nano-encapsulates for pest control. Valdés et al. (2006) evaluated the phytoextracts effect on *Scyphophorus acupunctatus* pest. Treatment with Dysphania ambrosioides extract led to 40% mortality in larvae and pupae of *S. acupunctatus*, with *Castela tortuosa* extract on 70% and *Tagetes erecta* at 48%. Moreover, larvae weight decrease was also reported that was considered as growth inhibition.

Table 1.3 shows studies reporting a comparison of phytoextracted compounds reported for botanical pesticides extracted from plants using the encapsulated micro- and nanosystems.

Table 1.3 Studies reporting a comparison between phytoextracts biological active complexes, their resources, and carrier systems employing nano- or microtechnology

Bioactive compound	Source	Carrier system	References
Azadirachtin	Chiefly extracted from the leaves and seeds	Microcapsules of the poly(vinyl acetate)	Riyajan and Sakdapipanich (2009)
	Azadirachta indica (Meliaceae) insecticidal and acaricidal activity	Capsules of sodium alginate/glutaraldehyde	Riyajan and Sakdapipanich (2009)
		Carboxymethyl chitosan/ricinoleic acid-coated nanoparticles	Feng and Peng (2012)
		Sodium alginate spheres	Jerobin et al. (2012)
		Polymeric nano- or microparticles	Forim et al. (2013)
		Polymeric nanocapsules	Da Costa et al. (2014)
Rotenone	Found in *Derris* genera species, *Lonchocarpus*, and *Tephrosia* (Fabaceae) insecticidal and pesticidal activity	Chitosan nanoparticles	Martin et al. (2013)
		Polymeric microparticles	Keawchaoon and Yoksan (2011)
Carvacrol	Present in oregano and thyme essential oils	Nanoparticles of chitosan	Higueras et al. (2013)
	Insecticidal and bactericidal activity	Chitosan/β-cyclodextrin	Higueras et al. (2013)
Thymol	Present in thyme and pepper-rosmarin essential oils. Display bactericidal and insecticidal activity	Film of nano clay	Lim et al. (2010)
		Polymeric microparticles	Guarda et al. (2011)
		Zein nanoparticles	Zhang et al. (2014)
Eugenol	Found in clove, cinnamon, myrrh, and sassafras essential oils. Display bactericidal, nematicidal and insecticidal activity	Cyclodextrins	Choi et al. (2009)
		Solid lipid nanoparticles	Garg and Singh (2011)
		Chitosan/β-cyclodextrin	Sajomsang et al. (2012)
	The active component of turmeric (*Curcuma longa* Zingiberaceae)	Zein nanoparticles	Gomez-Estaca et al. (2012)
Curcumin	Insecticidal action	Nanoparticles of hydroxypropyl cellulose	Bielska et al. (2013)
Limonoids	Anti-food effects on insect pests belonging to Lepidoptera	Phytoextract particles	Suresh et al. (2002)

Research has evaluated the use of synergism based on phytoextracts, used in formulations of natural pesticides observed an appreciable increase in the mortality of the pests.

1.5 Nanoparticles in Bioremediation

Heavy metals affect human, animals, and plants because of they are not biodegradable. Metabolic activities in plans are directly affected by heavy metals leading to people's health affectation and the decreasing of food production (Singh and Prasad 2015).

Dixit et al. (2015) cited that the presence in the environment of heavy metals comes from anthropogenic sources, such as pesticides, paints, fertilizers, tanneries effluents, and steel industries among others, and from natural sources, such as erosion and volcanic activities, particles released by vegetation, and forest fires. On the other hand, heavy metals have toxic effects on the human health producing skin damages, cardiac arrhythmias, and respiratory, fertility, and gastrointestinal problems.

Agrochemicals are the principal source of heavy metal contamination, phosphate fertilizers being the principal source. Getting heavy metal from soil, plants produces exudate which chelates metal ions and facilitates their solubility and extraction (Mustafa and Komatsu 2016).

Vegetables contaminated with heavy metals are a risk to the human health. It is important to know the concentration of these metals in vegetables to avoid human contamination. For instance, it was found a high concentration of heavy metals in vegetables sold in markets at Riyadh, Saudi Arabia, and Varanasi, India, which is a problem to people that consumed these vegetables. This pollution could be originated from industries and vehicles, and they could be deposited on the vegetable surfaces (Ali and Al-Qahtani 2012).

Nanotechnology gives to plants tools to treat diseases and take nutrients from soil leading to increasing crop production. Nanoparticles can be absorbed onto the clay lattice improving soil health and efficient use of nutrients by plants. Polymeric carriers in nanostructures can enhance soil stability and hydraulic characteristics to remove sodium from the soil. Nanoscale gypsum particles encapsulated in polymers would be better to improve the ground quality than gypsum used alone (Patra et al. 2016).

Bioremediation is a microbe-mediated and promising technology to remove heavy metals in polluted water and lands. Some microorganisms use different detoxification methods such as biosorption, bioaccumulation, biotransformation, and biomineralization (Ali and Al-Qahtani 2012).

Nanoparticles used for metal remediation is an attracting idea because of their properties such as unique electrical property, high chemical stability, and large specific surface area (Singh and Prasad 2015).

Nanostructures help to improve crop productivity using nano-nutrients, nano-pesticides, and nano-fertilizers. Nano-pesticides keep a long effect in the plant producing some advantages such as the reduction of the utilization of dangerous traditional chemical pesticides. On the other hand, nano-fertilizers improve the crop growth and productivity (Subramanian et al. 2016; Singhal et al. 2017).

On the contrary, nanosystems are introduced in agriculture and in other applications such as nutrients delivery systems and antifungal and bactericidal uses. Currently, nutrients applied in soils can be incorporated into nanotubes and nanopores, using a coat polymer film. Also, nutrient could be made at nanoscales (Robles-García et al. 2016), and they could be incorporated into the soil.

Bradfield et al. (2017) cited that metals such as zinc and copper had an adverse effect on tuber biomass of potato at the highest concentration analyzed. On the other hand, low and high concentration of cerium did not affect the yield; besides its high levels have a positive effect on tuber diameter. The bioavailable of these metals to the plant was increased from zinc to cerium.

Aluminum is not essential for plants; its toxicity is caused by the trivalent ion which has an adverse effect at high concentrations in acidic soils. It avoids cellular processes, interacting with PO_4^{3-}, SO_4^{2-} and carbonyl groups. Cadmium accesses plant roots as a divalent ion, and it affects plants inducing the oxidative stress and replaces zinc, iron, and calcium in the prosthetic groups of many proteins. Animals and plants need zinc as an essential micronutrient, and it is presented in the 10% of protein binding sites, but higher concentrations have adverse effects in plants provoking growth inhibition. At this high concentration, zinc reduces root growth and increase root thickening amount affectations. Copper is also a micronutrient for the plant, but it is toxic at a high concentration because it is capable of catalyzing Haber-Weiss and Fenton reactions producing cellular damage. Arsenic appears in soils due to pesticides applications changing the properties of soils and reducing crop growth and productivity. Other metals such as chromium, iron, and mercury have appreciable affectations over crops (Mustafa and Komatsu 2016). The Table 1.4 describes the nanosystems effect over the crop-soil surrounding system and their characteristics.

1.6 Nanosystems in Biofertilizers

The use of indiscriminate of pesticides and fertilizers has been causing irreversible damages to the environment. Our communities are being exposed to serious problems such as the pollution of the environment, appearance of agricultural pests and pathogens, and loss of diversity in biology. These problems have led scientists to explore the agriculture area, especially for the protection of the plants and productions (Ghormade et al. 2011).

Introductory studies show the capacity of nanomaterials (in different sizes and shapes) in enhancing of the seed sprouting and development, plant conservation, pathogen recognition, and pesticide/herbicide residue recognition. The use of nanomaterials in these fields has been successful and safe. These improvements are the foundation for future engineering allowing to generate unique properties aiming in a direction of specific applications (Khot et al. 2012).

Table 1.4 Nanosystems effect over the crop-soil surrounding system

Nanosystem	Characteristics/effect	References
TiO_2 and CuO magnetic nanoparticles	Nanoparticles change the nutrient bioavailability reducing the microbial biomass in flooded paddy soil, the total phospholipid fatty acid, and enzymes activities	Xu et al. (2015)
$CoFe_2O_4$	$CoFe_2O_4$ did not have any affectation over germination and growth of plants. 1000 mgL^{-1} of $CoFe_2O_4$-NPs significantly increases the tomato roots compared to the control (30%). However, the micronutrient uptake was affected	López-Moreno et al. (2016)
CeO_2	Although exposition to 2000–4000 mgL^{-1} of CeO_2-engineered nanoparticles increased peroxidase activity in roots and the highest CeO_2 treatments increased the antioxidant enzyme activity, the treatment with nanoparticles provoked a reduction in micronutrients	Hernandez-Viezcas et al. (2016)
Attapulgite micro-nano-network	A high-energy electron beam irradiation of thiosulfate sodium supported by attapulgite network was used as a remediation agent on soil contaminated with chromium VI. In this work, the inhibition effect, on the corn growth, of this ion was reduced	He et al. (2015)
Silicon	The effect of silicon nanoparticles to decrease the chromium (VI) phytotoxicity on the decline the pea growth was studied. Authors, also suggested the use of this information against heavy metal toxicity to understand the interaction mechanism amount silicon nanoparticles and chromium VI in plants	Kumar et al. (2015)
Magnesium hydroxide nanoparticles [Mg $(OH)_2$NPs]	Magnesium hydroxide nanoparticles affect levels of cadmium toxicity on *Brassica juncea*. These nanoparticles, synthesized by sol–gel methods, had a protected effect over cadmium toxicity improving the chlorophyll and carotenoids content, the root–shoot length, seedling size germination percentage, and biomass accumulation. Also, the authors concluded that zinc oxide nanoparticles increase the tolerance mechanisms of *Brassica juncea* contaminated with cadmium	Bohra et al. (2016)
Nanosilica Schiff-base copper (II) bactericide	This environment-friendly bactericide has an excellent antimicrobial activity against four bacterial. At the same time, this nanosystem intensified disease resistance and reduced the phytotoxicity and genotoxicity of copper in plants as a cucumber	Zhang et al. (2014)
Nanoparticles of zinc oxide	They were synthesized to control on rice blast fungus (*P. guise*) and rice brown spot fungus (*H. oryzae*) in vitro under greenhouse conditions. The average ratio of these nanoparticles was around 6.5–71.4 nm, and they have better antifungal effect than zinc oxide	Kalboush et al. (2016)

Nanotechnology, by nanomaterials related property, has agrarian biotechnology applications capacity to mitigate such matters. Reports regarding the function of nanotechnology in soil and plant systems reveal that nanomaterials may help in the following: (1) the regulated release of agrochemicals for nutrition and preservation toward pests and pathogens, (2) distribution of genetic component, (3) fragile identification of pollutants and plant disease, and (4) conservation and development of soil composition (Ghormade et al. 2011).

For example, biodegradable polymeric chitosan (78 nm) and porous silica (15 nm) nanoparticles show steady discharge of enclosed fertilizer and pesticide, appropriately. Furthermore, nano-sized gold particles (5–25 nm) distributed DNA to the plant cells, while the iron oxide (30 nm)-based nano-sensors discovered pesticides at molecular degrees (Ghormade et al. 2011).

The evaluation of the consequences of nitroxin and nanosilver on produce and yield elements of the mini potato tubers raised in the field concludes that by application of nitroxin, the quantity of mineral nitrogen fertilizer can be diminished to half building positive environmental influence. Fascinatingly, the use of nanosilver in merging with nitroxin produce notably higher tuber yield probably attributable to its antimicrobial cause. This antimicrobial effect of nanosilver may have lend seed tubers to remain in healthier condition for an extended period of time in the soil and eventually generated healthier plants. On the other hand, the fabrication of diverse antibiotics by the bacteria existent in nitroxin in rhizospheres of roots may avert the invasion of the root and seed tuber by infectious soilborne organisms and nematodes and expand the defense of plants to these harmful agents (Davod et al. 2011).

Potassium nano-fertilizer and nitrogenous bioinoculants has a positive effect on yield and components of the red bean (*Phaseolus vulgaris L.*), on enlarging the leaf area ratio, grain weight, and number of grain per pod of the treatment. Subject on the testing results, combined application of N biofertilizer and Khazraa K chelate Nano-fertilizer (KKCNF) has a better result on red bean productivity than the lone application of the above inoculants. As a result, chemical fertilizers can be substitute by these fertilizers for more effectiveness. They are more inexpensive and environmental friendly and have more useful crop execution (Farnia and Ghorbani 2014).

The effects of seed sowing date and nano-biofertilizers (Biozar®) containing *Azotobacter* and *Pseudomonas* bacteria and nano-fertilizers such as Fe, Zn, and Mn on yield and yield components of wheat indicate that late seed sowing decreases wheat vegetative growth and growing period length, which are the main reasons for yield loss. The addition of nano-biofertilizer application (4-l ha-1) increased spike length, spike number in m^2, seed number in m^2, seed number in spike, and seed weight some days until physiological maturity. However, there was no further increase with increasing nano-biofertilizer application, except for seed weight, some days until physiological maturity. In sum, early seed sowing and application of 4-l ha-1 nano-biofertilizer are recommended to gain the desirable yield (Farnia and Omidi 2015).

Results of evaluation of effect of nanoparticles and biofertilizers on the chlorophyll and carbohydrate content in forage sorghum (Speedfeed hybrid) show that these treatments allow to synergistic effect of nourishments, can provide the necessary plant nourishment and preserve soil microbes, providing the better condition for plant development without environmental contamination (Mir et al. 2015).

The result of zinc doses and seed treatment with biofertilizer on quality and amount of produce and soybean nodulation shows that the utilization of biofertilizers and zinc performs a major part in yield produce and amount of soybean produced.

Therefore, the raised nodules weight per plant, quantity of plant pods and weight of grains per plant, and the oil content were acquired via application of high quantity of zinc and *Bradyrhizobium japonicum* inoculation along with the plant growth-enhancing bacteria. Also, the stearic and palmitic acids (saturated fatty acids) decrease in the seeds implanted with bioinoculants besides the uninoculated control, whereas in linoleic, linolenic, and oleic acids, the common unsaturated fatty acids were found to be increasing. Therefore, it provides a notion that appropriate quantities of zinc (i.e., 0.9 g L^{-1}) used and inoculation of *Bradyrhizobium japonicum* and plant growth-promoting rhizobacteria (PGPR) can be suggested for succesful lucrative production of soybean (Sharifi 2016).

The evaluation of the impact of biofertilizers and nano-fertilizers under full and deficit irrigation on growth, plant yield, and yield components of maize was performed in northwest of Iran. With the efficiency of biological and nano-fertilizers under various moisture levels, deficit irrigation (25 and 50% of field capacity (FC)) was applied during the reproductive growth stage. Findings showed that although the utilization of biological fertilizers increased growth and some of the yield components under the well-irrigated condition, they failed to maintain their superiority under deficit irrigation. Our results revealed that a maize hybrid (704 single-cross) is well suited for rational deficit irrigation applied during the reproductive growth stages in northwestern Iran. The fundamental aim of the irrigation deficit technique is to increase water use efficiency by reducing the volume of water at each irrigation level. Also, our results indicate that application of bulk NPK, nano-chelated Zn, and nano-fertilizers of complete micronutrients under mild deficit irrigation (50% FC) could significantly improve plant performance. With increasing pressure on limited water resources and growing water shortage, the need for application of deficit irrigation will be more sensible, especially in dry and semidry areas (Janmohammadi et al. 2016). Table 1.5 describes the different applications of nano-biofertilizer system and their application mode.

1.7 Conclusions

The application of nanotechnology in modern agriculture is an invaluable tool for the crop protection. The use of biomolecules to develop nanostructured systems permits elaborate new agrochemical formulations with enhanced action mechanisms that provide crop protection against several pathogenic organisms, increase the crop production, and also reduce the utilization of agrochemicals. Nanotechnology is an appropriate alternative to protect plants from pathogens like bacteria, fungi, and

Table 1.5 Different applications of nano-biofertilizer system

Nanosystem	Application mode	References
Nanosilver	The irrigation method was sprinkler raining systems	Davod et al. (2011)
Khazraa K chelate Nano-fertilizer (KKCNF)	Foliar application	Farnia and Ghorbani (2014)
Fe, Zn, and Mn	Foliar application	Mardalipour et al. (2014)
Nano-zinc chelate	Foliar application	Farnia and Omidi (2015)
Iron chelate nano-fertilizer, potassium chelates nano-fertilizer	Mixed by soil before the sowing	Mir et al. (2015)
Nano zinc oxide and five biofertilizer	Mixed by soil before the sowing	Sharifi (2016)
Nano-chelated boron, nano-chelated zinc, and biofertilizer	Foliar application	Janmohammadi et al. (2016)

nematodes. Diverse nanosystems have been studied in plants and over pathogens to evaluate its activity. In several cases, the use of nanostructured materials exhibits better activity against pathogens than industrial chemicals. The use of nanomaterials improves the growth of crops and seed germination, which makes these nanostructured systems an advantage alternative to protect and promote plant growth.

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