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Potential role of nanoparticles in Plants Protection

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Abstract: Human population is exploding at an unprecedented rate from the past few decades, causing expansion of industries, shrinkage of arable land, and land urbanization. To feed billions of people, the current agricultural practices like plant breeding and IPM are not sufficient and need smart alternatives that could match our current and future food demands. 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. By employing NPs we can reduce input on plant protective chemicals, minimize nutrient loss, and enhance crop yield. The technology is sufficient in alleviating problems of higher chemical input cost, poor pesticide efficiently, and pesticide contamination in land and groundwater. 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. 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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Introduction

Due to plant disease agricultural production is reduced worldwide every year; therefore, millions of moneys have been invested in efforts to control the plant diseases. Various natural and artificial methods of control for protection of plants from these diseases have been applied. Among methods for disease control, use of pesticides is the most prevalent. In recent years, environmental hazards caused by excessive use of pesticides have been widely discussed; therefore, researchers in the agricultural field are searching for alternative measures against pesticides. Nanotechnological applicability in crop disease protection offers a great promise in the management of insects and pathogens. To safeguard sustainable agriculture and food production, the advanced agronomic application of nanotechnology in plants, termed phytonanotechnology, is of great significance (Wang et al., 2016). Nanomaterials are defined as materials having one dimension less than 100 nm. In contrast to their conventional counterparts, a key advantage that nanomaterials possess is a high surface-to-volume ratio due to their small size. They have unique physicochemical properties: small surface area, atypical surface structure, and increased reactivity due to their small size, surface structure, chemical composition, stability, shape, and agglomeration of nanoparticles. Besides its unique physicochemical properties, nanomaterials are readily amenable to surface conjugation and thus can be developed as versatile platforms with broad applications in plant science. Application of nanotechnology in crop protection holds a significant promise in management of insects and pathogens, by controlled and targeted delivery of agro-chemicals and also by providing diagnostic tools for early detection. Nano-particles can serve as 'magic bullets', containing herbicides, nano-pesticides, fertilizers, or genes, which target specific cellular organelles in the plant to release their content. Nano-particles are highly stable and biodegradable active compounds protected in capsules, they are not degraded by external agents or the crop plant itself, and are not involuntarily dispersed into the soil, allowing the use of a reduced number of active compounds for plant treatments and consequently causing a lower environmental impact. In recent years, various nanotechnology-based products such as nanofertilizers, nanoherbicides, nanopesticides, nanofungicides, and nanoinsecticides have been developed to combat pest-related diseases (Jampílek and kráľová 2015). Important areas of nanopesticide application in the agriculture are precise farming, weed, and nutrient management. In the food sector, the applications involve food processing, packaging systems, and preservation (Chellaram et al. 2014).

Nanotechnology in plant disease management

Silver nano-particles for disease management

The accurate detection and diagnosis of plant pathogens is an important step in proper disease management, and it helps in executing timely application of pesticides for proper management of the disease field. Nanoparticles can be used as biomarkers or as a rapid diagnostic tool for detection of plant pathogenic bacteria (Boonham et al. 2008), viruses (Yao et al. 2009), and fungi (Chartuprayoon et al. 2010). Nanoparticles can be integrated with other biological materials such as antibodies to construct immunosensors to detect bacterial infections. Yao et al. (2009) successfully prepared silica nanoparticle biomarker using silica NPs along with antibodies and developed silica NP probe to detect bacterial spot disease-causing bacteria, Xanthomonas axonopodis pv. vesicatoria. Shipway et al. (2000) constructed gold nanoparticle-based optical immunosensors for detecting Karnal bunt disease in wheat. Lopez et al. (2009) reported that the nanochips made of fluorescent oligo probes can detect single nucleotide change in the bacteria and viruses with high sensitivity and specificity. Similarly, nano-gold-based immunosensor has been prepared to detect Karnal bunt causing pathogen, Tilletia indica in wheat (Singh et al. 2010). The use of the above sensors in the seed certification and plant quarantine may prove highly effective and accurate in detecting the microbial infections. Zhao et al. (2008) have reported that during the recent years, sensor-based approaches with transduction mechanisms such as optical, electrochemical, and mass sensitive measurements have offered an accurate and reliable technology for detection of microorganisms. Gold nanoparticle (gold NP)-based colorimetric biosensing assays have recently attracted considerable attention in detection and diagnosis of microorganisms, because of their simplicity and versatility. The DNA-AuNP probes as a new generation of biosensorbased detection tools offer a promising technology for precision in biological sciences. Wang and Ma (2009) have reported that for having unique optical properties, gold NPs have been extensively explored as probes for sensing/imaging a wide range of analytes and targets such as heavy metallic cations, nucleic acids, proteins, cells, etc. The AuNPbased probes have been successfully used to detect bacterial infections (Gill et al. 2008). Castañeda et al. (2007) have shown that thiols and other functional groups, which have the capacity to strongly interact with gold NPs, could be exploited to immobilize DNA strands on gold NPs. Silver nanoparticles as antifungal and antibacterial agents have role in agricultural crop protection where these particles also regulate proper nutrition to plants. DNA directed silver NPs grown on graphene oxide and studied the antibacterial activity against xanthomonas perforans, a causative agent of bacterial spot in Tomatoes (Polash et al.,2017). The in vitro antifungal activity of AgNPs against nineteen different plant pathogenic fungi is investigated. (Mout et al., 2016) Cationic arginine gold nanoparticles (ArgNPs) assembled Cas9En (Etag)-RNP (ribonucleoproteins) delivery of sgRNA provides about 30% effective cytoplasmic/nuclear gene editing efficiency in cultured cell lines, which would greatly facilitate future research into crop development (Elamawi et al., 2018). The antifungal activity of silver nanoparticles synthesized by trichoderma longibrachiatum, against nine fungal isolates like aspergillus alternate and others (Nadaf et al., 2019). The AgNPs/PVP have also been reported suppressive against different yeasts and molds, such as Candida albicans, C. krusei, C. tropicalis, C. glabrata, and Aspergillus brasiliensis. The hybrid materials showed strong antifungal effects against the above microbes (Bryaskova et al. 2011). The treatment with silver nanoparticles greatly suppressed plant pathogenic fungi, viz., Alternaria alternata, Sclerotinia sclerotiorum, Macrophomina phaseolina, Rhizoctonia solani, B. cinerea, and Curvularia lunata (Krishnaraj et al. 2012). They found that 15 mg/l concentration of NPs greatly inhibited the activity of all the tested fungi.

Copper based nanoparticles

To control the menace of pathogens, copper was used in several formulations since ancient times. Copper sulfate is one of those compounds, which has antifungal properties and is a key ingredient in most of the commercially available fungicides for farm and garden. In a typical formulation, copper sulfate mixed with lime or soda ash in water was sprayed onto the plants. Cu-based fungicides create extremely reactive hydroxyl radicals that may damage lipids, DNA, proteins, as well as other bio-molecules, and thus, play a vital role for the prevention of disease occurring in huge diversity of plant species (Borkow, 2005). Copper oxide is also used as a fungicidal agent in the protection of tea, banana, cocoa, citrus, coffee, and other important plant species from major fungal leaf and fruit diseases, for instance, blight, downy or powdery mildew, and rust, etc. (Kim et al., 2021). Cioffi et al. (2004) reported antifungal activity of polymerbased copper nanocomposites against pathogenic fungi. CuNPs inhibited the colonization of plant pathogenic fungi, Alternari alternata, Fusarium oxysporum, Curvularia lunata, and Phoma destructiva (Kanhed et al. 2014). Bramhanwade et al. (2016) reported that treatment with CuNPs significantly suppressed the colonization of wilt-causing fungi, F. culmorum, F. equiseti, and F. oxysporum. Giannousi et al. (2013) observed that when Cu-based nanoparticles (11–25 nm) at concentration much lower than the commercial formulations were applied on tomato, the infection by Phytophthora infestans was controlled effectively.

Zinc nanoparticles

Among the various metal oxides, ZnO nanoparticles appear to be one of the most propitious candidates as these NPs can be generated through low-cost synthesis techniques in bulk amounts. Further, their better biosafety and lower cytotoxicity indices for mammalian cells have been proven through several cell line studies (Hanley et al., 2008) including the report on the preferential killing of human cancer cells compared to normal cells by ZnO NPs (Premanathan et al., 2011). The antimicrobial action spectrum of Zn nanomaterials includes antibacterial, antifungal, and antiviral characteristics (Reddy et al., 2007). However, plant pathogenic bacteria-Zn nanomaterial interactions have been studied including the reports showcasing the inhibitory effect on the causative agent of citrus canker (*Xanthomonas citri* subsp. *citri*) (Graham et al., 2016), rice leaf blight pathogen (*Xanthomonas oryzae* pv. *oryzae*) (Ogunyemi et al., 2019), tomato bacterial spot pathogen (copper-tolerant strains of *Xanthomonas perforans*) (Carvalho et al., 2019), the causative agent of lentil bacterial leaf spot (*Xanthomonas axonopodis* pv. *phaseoli*) (Siddiqui et al., 2018), the causative agent of bacterial blight of lentil (*Pseudomonas syringae* pv. *syringae*), and eggplant bacterial wilt pathogen (*Ralstonia solanacearum*) (Khan et al., 2019). The antibacterial effect of ZnO-NPs was demonstrated by Ogunyemi et al. (2019) and Hossain et al. (2019) against *Xanthomonas oryzae* pv.oryzae and *Dickeya* dadantii. They observed the growth and swimming motility of the bacteria were significantly affected by ZnO-NPs, reflecting the potent antibacteriality of ZnO-NPs. The antifungal property of ZnO-NPs was further proved by the study of Lahuf et al. (2019) where the growth of the phytopathogenic fungus *Rhizoctonia solani* was significantly reduced by the treatment of ZnO-NPs, thereby reducing the damping off in sunflower plant. The inhibition of *Podosphaera pannosa* infection in rose leaves by increasing the contents of zeatin riboside (ZR), dihydrozeatin ribosid and isopentenyl adenosine under the treatments of NPs also proved that NPs increased plant resistance against fungal infection by regulating phytohormones contents (Hao et al. 2019). The study of Xue et al. (2014) also demonstrated the penetration of the ZnO-NPs into *Phytophthora capsici* cell causing oxidative damage to the fungus, which revealed the antifungal activity of ZnO-NPs. The antimicrobial property of essential metal NPs including ZnO-NPs which inhibited the growth of many bacterial and fungal plant pathogens and eventually caused cell death of the pathogens was also reviewed by Ruttkay-Nedecky et al. (2017). ZnO-NPs can also be used as an effective antiviral agent, which was proved by the study of Cai et al. (2019).

Nanoparticles for insect pests

Nanoparticles have advantages over pesticides, as they increase the surface-to volume ratio, act precisely to target, can be made of eco-friendly material, release slowly from the vector polymer, and are biodegradable: desired results can obtained in a few hours (Luque and Rubiales 2009) that are not hazardous to plants, animals, and humans mainly because of their controlled release in the environment (Li et al. 2007). Silicon nanoparticles applied to wheat (BaCgli et al. 2003) and tomato (El-bendary and El-Helaly 2013) in fields show reduction in pest infestation and increased resistance in wheat and tomato by affecting pest feeding preferences and thus decreasing their population density. Similarly, nanoparticles of carbon, silver, silica, and aluminosilicates effectively protect plants in agricultural fields. Another merit of NPs is that they are small in size and their chemical properties provide a carrier for the pesticide that can enter into plant viruses. Carboncoated iron nanoparticles are transported to the affected area in an organism or insect body with the help of NP magnetic properties and are adsorbed to the molecule of interest such as a drug, chemical, enzymes, or DNA (González-Melendi et al. 2008). Moreover, nanoparticle-mediated plant genetic engineering and the use of nanosensors have opened up a new realm in the field of crop protection. Thus, silver-, zinc-, iron-, gold-, and copper-based nanoparticles are precisely delivered for tackling fungi, insects, and microbes.

Nanoparticles, therefore, are promising as being safer and economically superior to pesticides for plant protection. However, further study must validate their viability in extensive field trials (Sharma et al. 2016). Chitosan has been found to expose robust insecticidal activity in a few plant pests (Zheng et al. 2005; Rabea et al. 2005). Chitosan (i.e., N-alkyl-, N-benzylchitosans) are made to be had through chemical synthesis, their insecticidal activities are being reported using an oral larvae feeding bioassay (Rabea et al. 2005; Badawy et al. 2005). Encapsulated microcrystals of the insecticide imidacloprid (IMI) with the aid of LbL assembly the use of chitosan and sodium alginate accompanied by way of addition of photocatalytic NPs (Guan et al. 2008). The insecticide etofenprox was encapsulated the use of a nanosized chitosan carrier in three types according to a difference in release patterns by adjusting the molecular weight and concentration of chitosan. Release properties of etofenprox and its organic activity aganist Spodoptera litura suggested that such managed-release method is used as a technique for preventing loss of etofenprox, increasing its activity against the target pest (Hwang et al. 2011). The entomopathogenic fungi Nomuraea rileyi were investigated against S. Litura, and chitosan nanoparticle coated fungal metabolite (CNPCFM) showed better pesticidal activity, as compared with Uncoated Fungal Metabolite (UFM) and Fungal Spores (FS) (Chandra et al. 2013). Chitosan nanoparticles integrated insecticidal protein beauvericin (CSNp-BV) became organized by using ionic gelation technique to enhance insecticidal activity against S. litura. Pesticidal interest found out that all lifestyles stages have been susceptible to the CSNp-BV formulation and the maximum mortality was recorded in early larval instars. CSNp-BV treatment reduced pupal and adult emergence (Bharani et al. 2014). Chitosan (CS)-g-poly (acrylic acid) PAA nanoparticles reduced egg laying of Aphis gossypii (20.9 ± 9.1 and 28.9 ± 9.2 eggs/woman for laboratory and below F. A. Al-Dhabaan et al. 367 semi-discipline situations, respectively) than manage (97.3 ± 4.9 and 90.34. Nine eggs/female for laboratory and below semi-subject situations, respectively (Sahab et al. 2015). Chitosan nanoparticles decreased egg laying of Callosobruchus maculatus (10.9 ± 9.9 and 19.9 ± 9. Nine eggs/female laboratory and under semi-storage conditions, respectively (Sahab et al. 2015). Under semi subject situations, the wide variety of Schistocerca gregaria had been notably reduced after the chitosan and nanochitosan remedy, the quantity of infestations with S. gregaria reduced to 29 ± 3.6 and 8 ± 1.1 individuals after 120 days of remedies (Sabbour 2016). Rouhani et al. (2012) used the silver nanoparticles against the oleander aphid, Aphis nerii. The authors compared the effectiveness of silver nanoparticles with the traditional insecticide imidacloprid. The lethal concentration of 50% for insect population (LC50) values was 0.13 µL/mL and 424.67 mg/mL for imidacloprid silver nanoparticles, respectively. The authors recommended that the silver nanoparticles can be used in integrated pest managements. The use of imidacloprid and silver nanoparticles in combination increases the potency of imidacloprid. So, the silver nanoparticles have a synergist action. Babu et al. (2014) synthesized the silver nanoparticles by using marine bacteria Shewanella algae bangaramma in the laboratory. The silver nanoparticles are characterized by using UV–vis spectrum, TEM, FTIR, EDAX, XRD, and AFM analysis. The synthesized silver nanoparticles are spherical, crystalline, and 5–30 nm in diameter. The maximum LC50 and LC90 values were 4.529 and 9.580 mg/mL against the third instar larvae of Lepidiota mansueta (Burmeister). Rouhani et al. (2012) synthesized the silica and silver nanoparticles through a solvothermal method and used different concentrations against Callosobruchus maculatus. In this experiment, the LC50 value for $SiO_2$and Ag nanoparticles was 0.68 and 2.06 g/ kg cowpeas on adults and 1.03 and 1.00 g/kg on larvae, respectively. Sadowski et al. (2008) synthesized the silver nanoparticles from microorganisms (Penicillium strain). The inoculated fungi were put in Petri dish and male extracts added to 0.5% yeast extract in a room temperature. The fungi were grown aerobically in liquid medium containing (g/L): KH_2PO_4 7.0, K_2HPO_4 2.0, $MgSO_4 \times 7H_2O$ 0.1, $(NH_4)_2SO_4$ 1.0, yeast extract 0.6, and glucose 10.0. All of them were inoculated in Erlenmeyer flasks with spores and incubated at 25 °C with shaking (150 rpm) for 72 h. After the cleaning steps, $AgNO_3$ (1 mM of final concentration) was mixed with cell-free filtrate in an Erlenmeyer flask and agitated at 25 °C in dark. Yasur and Rani (2015) tested the effect of silver nanoparticles (AgNPs) on growth and feeding responses of two lepidopteron insects, namely, Asian armyworm, Spodoptera litura, and castor semilooper, Achaea janata L. (Lepidoptera: Noctuidae). The larvae were fed on PVP-coated AgNP-treated castor leaf at different concentrations. The efficacy of silver nanoparticles was compared to that of silver nitrate ($AgNO_3$)-treated leaf diets. Larval and pupal body weights decreased along with the decrease in the concentrations of AgNPs and $AgNO_3$ in both the test insects. On the other hand, Debnath et al. (2012) found that silica nanoparticles (SNPs) could effectively kill second-stadium larvae of S. litura. Araj et al. (2015) synthesized sulfur nanoparticles (SNPs) also, by mixing amount of sodium thiosulfate

($Na_2S_2O_3 + 5H_2O$) dissolved in 100 mL of sterile deionized water in a beaker 250 mL under mild stirring with magnetic stirrer at room temperature and atmospheric pressure. Ten milliliter of aqueous solution of citrus leaf extract acidified with dilute hydrochloric acid (HCl) was added to the aqueous solution of sodium thiosulfate with rate 1 mL/min with mild stirring for allowing the sulfur precipitations uniformly. The suspended sulfur particles produced were separated by centrifugation at 1000 rpm/min for 5 min and then repeatedly washed with sterile distilled water to remove any biological materials. The sulfur nanoparticles are divided into two parts. In the first part, the sulfur nanoparticles remained in the sterile distilled water without any additives added. In the second part, the sulfur nanoparticles after purification were dried in a vacuum at 80 °C for 2 h. Rao and Paria (2013) used sulfur nanoparticles (SNPs) against two phytopathogens, Fusarium solani and Venturia inaequalis. The authors found that the smallsized particles are very effective in preventing the fungal growth. Hunt et al. (2008) found that silica acts on insect pests by reducing its digestibility, not just palatability. Subramanyam and Roesli (2000) hypothesized that silica nanoparticle (SNP)-based insecticide is physically active against some insects and causes damage to the cuticular water barrier of the insects mostly by abrasion and to some extent due to adsorption. Insect death occurs due to desiccation. Silica is suitable for many purposes, while for others chemical processing is needed to make a modification or otherwise more suitability. Silicon (Si) was used in agriculture that has been started since the 1970s (Laing et al. 2006). It can be said that silicon application can significantly act on insect pest and disease resistance in plants and cause yield increases in many crops. Giongo et al. (2016) offered corn leaves treated with nanoformulations of neem in colloidal suspension or powder, containing PCL, poly (βhydroxybutyrate) 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. 2014). 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. 2014). 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. 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 t1/2 (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 t1/2 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).

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2/22/2022