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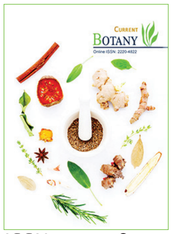

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Engineered nanomaterials in plant protection: their controlled, site-directed delivery and phytotoxicity

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ABSTRACT

Engineered nanomaterials (ENMs) are being produced and utilized in certain nanoformulations almost in every sector of development including agriculture. The diverse groups of engineered nanoparticles (ENPs) provide numerous benefits in agriculture, but their bulk and direct delivery pose a serious risk to the plants and ecosystem for a long time. The harmful effects on all the exposed living systems are owing to the variable shape, size, behaviour and toxic properties of ENPs. The accumulated ENMs in plant tissue may lead to biomagnification at a higher trophic level causing severe toxicity. The hazardous effects of these entities can be minimized with their controlled, specified and targeted delivery to the crop plants. Such smart-delivery systems as Ehrlich's '*magic bullets*' are being demonstrated for nutrients and growth enhancers, fertilizers, pesticides and weedicides; as well as biomolecules in plant genetic engineering. This review summarizes the benefits of ENMs and ENPs in plant protection to increase crop productivity, their targeted delivery suggesting sustainable utilization, and the available information on phytotoxicity.

KEYWORDS: Nanoformulations, Controlled delivery, Crop protection, Crop improvement, Nanotoxicity

INTRODUCTION

The economy of countries purely based on the agricultural sector is driven by the amount of crops produced. So, the responsibility rests not only with the government but also on the shoulders of farmers who work hard in fields to raise their crop yield. This economic backbone can be helped with the recently evolved nanodiscipline which finds its scope to address different issues in agriculture and crop productivity. For this, a large number of nanomaterials (NMs) are being explored for their potential use in agronomy and food science by maintaining a sustainable environment (Kaphle *et al*., 2018). In the last decade, the global use of Si, Ti, Al, Fe, and ZnO ENMs were found at a higher level (Keller *et al*., 2013), and are still being used in electronics, textiles, pharmaceutics, cosmetics and biomedicine, agriculture, biotechnology and plant genetic engineering, energy sector and microbial fuel cells, food packaging and preservation technology, and environmental applications such as bioremediation (Gogos *et al*., 2012; Arruda *et al*., 2015; Parisi *et al*., 2015; Baker *et al*., 2017; Hayles *et al*., 2017; Cunningham *et al*., 2018; Ojha *et al*., 2018; Islam *et al*., 2019; Pang *et al*., 2021; Kamali *et al*., 2022; Umapathi *et al*., 2022). Modarresi *et al.* (2020) observed increased concentrations of secondary metabolites (total alkaloids and flavonoids) and the content of glaucine, quercetin, and kaempferol in Iranian species of *Nigella arvensis* L. when exposed to different concentrations of TiO_2, Al_2O_3, and NiO nanoparticles (NPs). Soil enriched with selenium (Se) ENMs increases yield and improves the nutritional quality of *Brassica chinensis* (Wang *et al*., 2022). So, the properties of these NPs can be used in pharmaceutics for their possible exploitation in drug development. However, Ahmed *et al.* (2013) attracted scientific diaspora towards the scope and possible utilization of nanomaterials in crop protection. They also urged people to evaluate the penetration, transportation, and internalization of bio-nanoparticles within the plants. The ability of various NMs in agriculture production and crop protection has already been reviewed sustainably (Khot *et al*., 2012; Zulfiqar *et al*., 2019). In the agriculture system, nanotechnology has promising applications in pest management through nano-based smart pesticide formulations (Hayles *et al*., 2017; Khan & Rizvi, 2017; Kumar *et al*., 2019). These smart nano(bio)pesticides and other

NMs (plant growth regulators, fertilizers and pesticides) can be released in a controlled manner and targeted specifically for the insect-pest management and advancement of plant growth as well as yield (Balaure *et al.*, 2017; Jampílek & Kráľová, 2017; Lade *et al.*, 2019). Such biopesticides will certainly scale down the use of synthetic pesticides being used on a large scale.

The nanofertilizers have several advantages over conventional fertilizers but still, there is a worry to use these due to a lack of appropriate knowledge of their recognition mechanisms at the ecosystem level (Maghsoodi *et al.*, 2019). Furthermore, the cost of nanoformulation production is much higher which does not allow its trials on a large scale in the field condition (Pérez-de-Luque, 2017). Likewise, the NPs interaction with plants may result in several morphological, physiological, biochemical and genotoxic effects on their growth and development which may vary with the properties of ENMs, their mode of action and the plant species (Nair, 2016; Du *et al.*, 2017; Rizwan *et al.*, 2017; Siddiqi & Husen, 2017; Verma *et al.*, 2018). The fate, behaviour and toxic effects of NMs in the environment have been critically reviewed (Lead *et al.*, 2018), and the mechanisms of their (ENPs) uptake, accumulation, translocation and transformation in plants have also been studied (Lv *et al.*, 2019). Thus, nanotechnology provides many opportunities in the agriculture sector but will surely pose a handling risk with potent toxic implications (Iavicoli *et al.*, 2017). This review deals with the use of ENMs in crop protection, their controlled and site-directed delivery, and phytotoxicity.

NANOMATERIALS IN PLANT PROTECTION AND IMPROVEMENT

From the beginning of 21st century, scientific publications and patents on plant protection and agro-nanomaterials increased exponentially in which Western countries (USA and Germany) ranked in patents whereas Asian countries released most scientific articles (Gogos *et al.*, 2012). These studies were aimed to upgrade existing agro-techniques for the betterment and elevated agricultural production. It is also clear that the demands and food security of an exponentially increasing global population can only be fulfilled with the use of nanotechnology and nanomaterials in the near future (Rajwade *et al.*, 2020), and thus the nanotechnology provides new tools for sustainable agro-development with great potential in precision agriculture and plant sciences thereby minimizing the occurrence of infections, increasing crop productivity and maintaining beneficial microflora in soil (Chen & Yada, 2011; Mukhopadhyay, 2014; Wang *et al.*, 2016; Duhan *et al.*, 2017; Ojha *et al.*, 2018; Singh *et al.*, 2020b; Ghosh & Kikani, 2023; Salem & Husen, 2023). The crops exposed to ENMs were also found to show better adaptation towards different stresses like salt and drought stresses (Ahmad *et al.*, 2023; Amna *et al.*, 2023; Weisany & Khosropour, 2023). Several nanoplatforms (*e.g.* nanoparticles, nanoformulations, nanosensors, quantum dots, nanobarcode assay, nanoimaging, nanopore DNA sequencing tool, *etc.*) are available for rapid detection and tackling of the plant pathogenic fungi in the farm itself (Abd-Elsalam, 2012; Khiyami *et al.*, 2014; Hussain, 2017; Ojha *et al.*, 2018; Sharon *et al.*, 2010).

Most nanoparticles being used in plant disease management are synthesized from different metal oxides, nonmetals and metalloids. These ENMs find their intense use in the agricultural sector including biosensors designing for plant disease diagnosis, management of phytopathogens and insect pests, agrochemicals delivery and molecular manipulations (Figure 1) (Sharon *et al.*, 2010; Rai & Ingle, 2012; Elmer & White, 2018; Khan *et al.*, 2019a; Kumar *et al.*, 2020;). They have relatively higher efficiency than those of conventional agrochemicals (Kusiak *et al.*, 2022). Several attempts have been made to develop nano(bio)sensors such as quantum dots to support smart agriculture to meet with the increasing global food demand (Sharon *et al.*, 2010; Antonacci *et al.*, 2018). In one such innovative method, an electrochemical immunosensor-based selective method has been found very effective in detecting citrus canker (Haji-hashemi *et al.*, 2018). Likewise, Tu *et al.* (2019) designed a simple technique, by using cysteamine-modified AuNPs, for the rapid *in situ* detection of as low as 0.001 mg/L glyphosate pesticide on the plant tissue.

Although nanotechnology offers new benefits to the varied sectors but poses an inevitable risk to human and environmental health (Prasad *et al.*, 2017). The continuous use of pesticides in the agricultural sector not only contaminates the agricultural ecosystem but also poses a serious risk to human health. To reduce the substantial effects of agrochemicals, bio-engineered NMs are becoming progressively essential to deliver nutrients, fertilizers and pesticides for plant growth promotion and protection (Jayarambabu & Rao, 2019), as well as to minimize the ecological imbalance. Achari and Kowshik (2018) documented both positive and negative effects of nanofertilizers on plants and associated microorganisms when applied through foliar and soil routes. Adisa *et al.* (2019) critically reviewed the action mechanisms of nano-enabled fertilizers and pesticides on crop yield.

The procedures followed in the chemical synthesis of NPs are hazardous from an ecological point of view. Thus, alternative methods such as green synthesis are usually preferred by the research communities. The wide range of plant extracts and soil microbes have the potential and scope to synthesize eco-friendly NPs (Khan & Rizvi, 2014). On application, the penetration and reactivity of NPs depend on the size (Zhang *et al.*, 2013) and other characteristics too. The use of nanotechnology in agriculture and crop protection has been extensively reviewed (Chowdappa & Gowda, 2013; Shang *et al.*, 2019; Usman *et al.*, 2020). The commonly exploited NPs in agriculture and scientific studies in the allied sector are discussed here.

Gold (Au) NPs

A comprehensive review of the fabrication and engineering of plant-based AuNPs and their wide demand in the fields of sustainable agriculture, environmental science, and bionanotechnology proved their everlasting value (Khan *et al.*, 2019b). The green AuNPs synthesized using *Terminalia arjuna* leaf extract was found to induce mitotic cell division in *Allium cepa* and pollen germination in *Gloriosa superba* plants (Gopinath *et al.*, 2013). Abdel-Raouf *et al.* (2017) evaluated the activity of AuNPs synthesized using ethanolic extract of marine

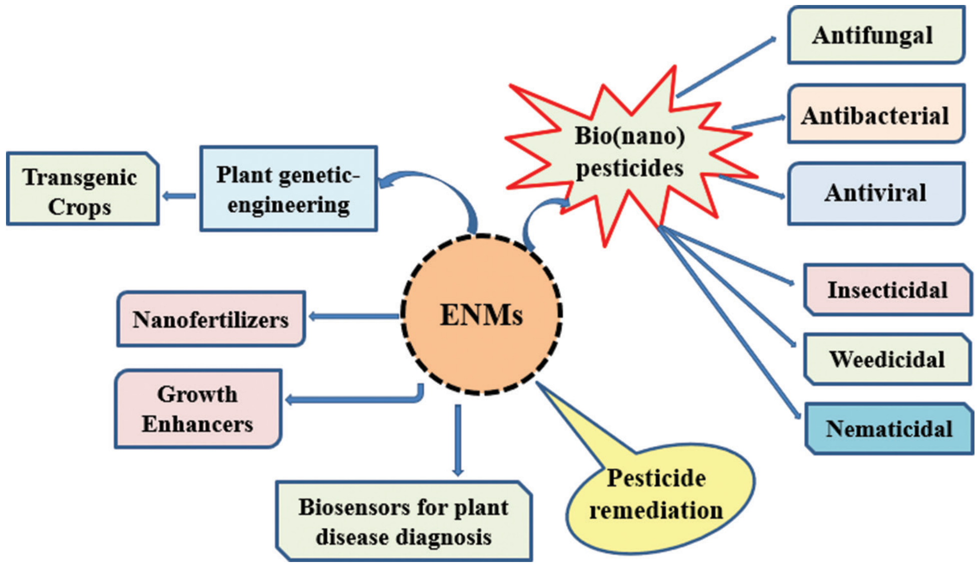

Figure 1: The use of ENMs in agriculture improves and elevates the crop yield several folds, and also minimizes the use of chemical pesticides causing environmental pollution

red alga *Galaxaura elongata* against *Escherichia coli*, *Klebsiella pneumoniae*, *Staphylococcus aureus* and *Pseudomonas aeruginosa* with significant inhibition zones. The AuNPs synthesized and activated by the leaf extract of *Salix alba* L. exhibited effective activity against *Alternaria solani*, *Aspergillus niger*, and *Aspergillus flavus* (Islam *et al.*, 2019); whereas, *Pongamia pinnata* leaf extract synthesized AuNPs showed fungicidal potential against the plant pathogenic fungus - *Pythium ultimum* (Khatua *et al.*, 2020). The AuNPs synthesized using *Coleus aromaticus* leaf extract and coated with cotton fabric showed protection against UV rays and antibacterial activity against *Staphylococcus epidermidis* and *E. coli* (Boomi *et al.*, 2019). The foliar applications of AuNPs to *Brassica juncea* plants under field conditions demonstrated positive effects on growth profile and optimal increase in productivity (10 ppm), thereby presenting an alternative to the genetically modified (GM) crops (Arora *et al.*, 2012). More recently, the calixarene coated AuNPs with antifungal, phytotoxic and mild cytotoxic activities have been demonstrated (Khalid *et al.*, 2020), and can again be refined to use in the agriculture sector.

Silver (Ag) NPs

The *Acalypha indica* leaf extract based AgNPs have effective inhibitory activity at 15 mg concentration against *Alternaria alternata*, *Sclerotinia sclerotiorum*, *Macrophomina phaseolina*, *Rhizoctonia solani*, *Botrytis cinerea*, and *Curvularia lunata* (Krishnaraj *et al.*, 2012). Cvjetko *et al.* (2018) observed reduced phytotoxicity of AgNPs to the *Nicotiana tabacum* L. plants than $AgNO_3$ in terms of oxidative stress. The NPs synthesized using leaf extract of *Melia azedarach* demonstrated excellent antifungal activity against *Verticillium dahliae* in brinjal plants (Jebril *et al.*, 2020).

Silica-silver (Ag-SiO_2) Composite

Silver (Ag) and silica (SiO_2) both are eco-friendly and are also safe from human health issues. Silica-based nanosystems play a pivotal role in sustainable agriculture. They are being used as nanofertilizers, nanopesticides, and nanocarriers for various biomolecules (Rajiv *et al.*, 2020). The silica is previously known to induce defence responses in *Lolium perenne* L. against a gray leaf-spot disease caused by *Magnaporthe oryzae* (Catt.) B.C. Couch (Rahman *et al.*, 2015). The nanosized Ag-SiO_2 composite is many folds effective against a wide range of plant pathogenic fungi (*Blumeria* spp., *Sphaerotheca* spp., *Phytophthora* spp., *Rhizoctonia* spp., *Colletotrichum* spp., *Botrytis* spp., *Magnaporthe* spp. and *Pythium* spp.) at 3.0 ppm concentration when compared to the commercial fungicides (Park *et al.*, 2006). The application of 1-10 ppm Ag-SiO_2 on *Arabidopsis thaliana* promoted its growth in soil, but higher doses (100 ppm) resulted in the formation of curled leaves (Chu *et al.*, 2012). Similarly, a 1 ppm Ag-SiO_2 hybrid in Murashige and Skoog (MS) medium stimulated rooting in *Arabidopsis* seedlings, which was found inhibiting at a 10 ppm concentration of the hybrid complex (Chu *et al.*, 2012). However, 10 ppm exposure of the said complex induces resistance against the pathogen *Pseudomonas syringae* pv. *tomato* DC3000 (Chu *et al.*, 2012).

Copper (Cu) and Coper Oxide (CuO) NPs

Many times, soil composition shows its influence on the phytotoxicity of NPs. However, an application of 300 mg CuNPs/Kg of alkaline soil (pH 8.3) does not show any phytotoxic effect on the growth of *Triticum aestivum* indicating the influence of soil chemistry on plants' life (Anderson *et al.*, 2017). This supports the possible use of metal oxide fertilizers to deliver essential metals to plants growing in metal deficient soil. The foliar application of CuO-NPs (at 200 mg/L) on *Cucumis sativus* seedling leaves showed increased fruit weight when compared with control (Hong *et al.*, 2015). The recent findings of CuNPs or CuO-NPs application (1:1, v/v) on *Cucurbita pepo* for three weeks showed a reduction in the activity of ascorbate peroxidase (APX) and catalase (CAT) enzymes suggesting its beneficial effects in stress management (Tamez *et al.*, 2019). The CuO-NPs show *in vitro* toxic effects against *Escherichia coli*, *Bacillus subtilis*, and *Streptococcus aureus* (Baek & An, 2011). The CuO-NMs at 50 mg/L exhibited antifungal activity towards *Rhizopus stolonifer* causing soft rot disease in *Solanum tuberosum* (Pang *et al.*, 2021).

Iron (Fe) and Iron Oxide (Fe_2O_3) NPs

The plant-mediated synthesis methods of Fe NPs under controlled reaction conditions and their applications in various fields have been studied (Ebrahiminezhad *et al.*, 2018). The biological effects of Fe NPs additive concentrations on the growth of *Capsicum annuum* plants showed varied results. The lower concentrations promoted plant growth by altering leaf structure to accumulate the high number of chloroplasts with increased grana stacking, and developed vascular bundles; while, higher concentrations lead to their aggregation at cell walls blocking the transport of Fe nutrients (Yuan *et al.*, 2018). The Fe_2O_3 NPs release iron gradually in a broad pH range (pH 3-11) serving as a good source of iron to the plants (Askary *et al.*, 2017). An exposure of *Mentha piperata* to 30 μM Fe_2O_3 NPs concentration increases plant biomass and the Phosphorus, Potassium, Iron, and Zinc content; however, it decreases the antioxidant activity under salinity stress (Askary *et al.*, 2017). The dose and time dependent increase in growth and productivity of *Spinacea oleracea* was increased due to the uptake of Fe in hydroponics supplemented with Fe_2O_3 NPs (Jeyasubramanian *et al.*, 2016). The nano-iron oxide treatment to *Glycine max* (L.) Merr. crop increases grain yield by 48% with no significant effects on other traits of the plants (Sheykhbaglou *et al.*, 2010).

Aluminium Oxide (Al_2O_3) NPs

Aluminium is an abundantly occurring non-essential, toxic element in the earth's crust. The lower doses of Al_2O_3NPs (101.8 μM in 700 mL Hoagland solution, a basal salt mixture containing macro- and microelements) have been found to boost the physiological parameters (seedling growth, pigments, protein content) in *Brassica oleracea* var. capitata seedlings (Amist *et al.*, 2017). Investigations on the hydroponically-grown *Lactuca sativa* L. revealed the positive influence of Al_2O_3 NPs on biomass production (0.4 mg/mL) (Hayes *et al.*, 2020); while a study on *Arabidopsis thaliana* showed a significant effect on root elongation at the concentrations of 400, 2,000, and 4,000 mg/L (Lee *et al.*, 2010). A study on an alga *Scenedesmus obliquus* demonstrated the reduced toxicity of Cu in the presence of Al_2O_3 NPs (Li *et al.*, 2016). The decrease in Cu-toxicity was attributed to the phenomenon of adsorption whereby the Cu adsorbs onto Al_2O_3 NPs reducing the availability of Cu for uptake (Li *et al.*, 2016). Thus, the toxic effects of Cu on aquatic life can be minimized to a certain extent with the addition of Al_2O_3 NPs in water bodies.

Nickel Oxide (NiO) NPs

An *Aegle marmelos* leaf extract synthesized NiO-NPs showed *in vitro* antibacterial activity against Gram positive (*Streptococcus pnemonia*, *Staphylococcus aureus*) and Gram negative (*Escherichia hermannii*, *E. coli*) bacterial strains (Ezhilarasi *et al.*, 2018). The NPs cause cytotoxicity and apoptosis in A549 cell culture and also demonstrate effective photocatalytic degradation of 4-chlorophenol (an endocrine disrupting chemical) between 50-250 mg/L (Ezhilarasi *et al.*, 2018). The NiO-NPs in Luria-Bertani agar plate medium show toxic properties against *E. coli*, *B. subtilis*, and *Streptococcus aureus* (Baek & An, 2011), while the NPs at a concentration of 1000 μg/mL show synergistic antibacterial effects when combined with amoxicillin against *E. coli* and *S. aureus* instead of using either pure amoxicillin or pure NiO-NPs (Khashan *et al.*, 2017). Similarly, the NPs demonstrate cell inhibition activity against both Gram-positive and Gram-negative bacterial strains in the agar well diffusion method (Kannan *et al.*, 2020). Exposure of yeast *Saccharomyces cerevisiae* to the NiO-NPs induces the accumulation of reactive oxygen species (ROS) inside the cell causing viability loss (Sousa *et al.*, 2018).

Zinc Oxide (ZnO) NPs

Zinc is present abundantly in the earth's crust and is essential for the biological processes of living systems. The literature on the beneficial uses of ZnO-NPs on plants has been scrutinized by Pullagurala *et al.* (2018) and suggested the extension of studies to the flower and fruit-bearing plants because most of the studies have been predominantly focused on vegetable-based plants. The 10 and 25 mg/L concentrations of ZnO-NPs show enhanced seed germination and seedling growth in *Vicia faba* (Youssef & Elamawi, 2018). Furthermore, the adverse effects of ZnO-NPs on soil bacterial communities, agricultural plants and their harvest can be reduced to 50% by growing *Glycine max* plants in soils contaminated with nano-ZnO (Ge *et al.*, 2014). The ZnO-NPs synthesized using flower extract of *Nyctanthes arbortristis* show antifungal activity (Jamdagni *et al.*, 2018); whereas, the ZnO-NPs synthesized using *Solanum nigrum* leaf extract demonstrated effective activities against *Staphylococcus aureus* (Gram-positive) and *Salmonella paratyphi*, *Vibrio cholera* and *E. coli* (Gram-negative) bacterial strains (Ramesh *et al.*, 2015).

Carbon Nanomaterials (CNMs)

The CNMs possess great versatile properties owing to which they have drawn great attention in biomedical engineering for orthopaedic coatings, drug delivery, medical device fabrication and diagnosis (Bhong *et al.*, 2019; Maiti *et al.*, 2019). Due to the detection capacity of biomolecules, they can be used in carbon-based sensor technology for the cheap production of commercial products (Yang *et al.*, 2010; De Volder *et al.*, 2013). Some of the advantageous properties of CNMs include biocompatibility, surface uniqueness, chemical, mechanical, optical, electrochemical, electrical and thermal properties like other advanced materials. Considering the above properties, the CNMs can be used in regulating plant growth and development (Khot *et al.*, 2012). In a study, penetration and accumulation of non-biological nanostructures like single-walled carbon nanotubes (SWCNTs) inside the chloroplasts *in vivo* augmented the photosynthetic activity by three times than that of controls (Giraldo *et al.*, 2014).

Graphene Oxide (GO)

Single-bilayer graphene oxide sheet (GO) is a water-soluble derivative of graphene (made up of single-layer of sp^2-hybridized carbon atoms) often used as a 2D-NP composite (Geim, 2009; Xu & Wang, 2012). The GO at 400 and 800 mg/L improved the health status of *Vicia faba* L. (Anjum *et al.*, 2014). It also shows elevated activity of antioxidant enzymes (APX, CAT) and proline levels (30 μmol/g of fresh weight) (Anjum *et al.*, 2014). Contrarily, the *V. faba* L. shows increased sensitivity towards three GO concentrations (1,600> 200> 100 mg/L) with decreased glutathione redox ratio and glutathione pool (Anjum *et al.*, 2013). Likewise, application of GO in μg/L concentration neither influences seed germination and shoot/root development in seedlings, nor it induces the formation of oxidative stress and the activity of antioxidant enzymes (Zhao *et al.*, 2015).

Other Metal Oxide Nanoparticles

Several engineered metal oxide NPs with significant potential can be used to selectively inhibit weeds and harmful fungi from the crop fields (Wu *et al.*, 2012). Wang *et al.* (2012) observed a 10% increase in *Solanum lycopersicum* L. yield with 10 mg/L Cerium Oxide (CeO_2) NPs solution treatment. Likewise, exposure of *Lactuca sativa* L. plants to CeO_2 NPs shows elevated activity of antioxidant enzymes such as superoxide dismutase (SOD) and peroxidase (POD) to resist with the antioxidant stress induced by the NPs (Zhang *et al.*, 2013). Khot *et al.* (2012) focus on the potential use of various nanomaterials in seed germination and growth, crop protection, as well as detection of pathogen and pesticide residues in plants and their products. Fe_2O_3 NPs inhibit the plant height and root length in *Bt*-transgenic cotton while promoting the formation of root hairs and elevated biomass in non-transgenic cotton plants. Furthermore, nutrients (Na and K) and hormones increase in the roots of *Bt*-transgenic cotton at low concentrations of Fe_2O_3 NPs exposure whereas, a decrease in Zn content and the hormones occur at higher concentrations (Nhan *et al.*, 2016). Thus the FeOx-NPs demonstrate positive effects in the agricultural sector as they stimulate plant growth at low concentrations of 5-20 ppm (Liu *et al.*, 2016). The *Vigna radiata* (L.) R. Wilczek on exposure to manganese nanoparticles (MnNPs) shows enhanced photosynthetic rate and growth, but do not have any toxic effect at higher doses (Pradhan *et al.*, 2013). Similarly, MnOx-NPs stimulate the seedling growth of *Lactuca sativa* by 12-54% (Liu *et al.*, 2016). The interaction study of antimony (Sb(III) and Sb(V), at 50 mg/L) with CeO_2 NPs (at 50 mg/L) shows a significant reduction in the accumulation of CeO_2 NPs in *Glycine max* (L.) Merrill. seedlings compared to exposure of CeO_2 NPs alone (Cao *et al.*, 2020). The exposure of *Foeniculum vulgare* Mill to nanosized Titanium dioxide (TiO_2) at 40 ppm shows increased seed germination time (31.8%) compared to the untreated plants (Feizi *et al.*, 2013). Thus, TiO_2 NPs can be used to overcome the difficulties in seed germination of certain plants.

CONTROLLED AND SITE-DIRECTED DELIVERY OF ENMs

The inefficient delivery of conventional pesticides and agrochemicals resulted in the contamination of soil, water and air while increasing resistance to pests and pathogens (Goswami *et al.*, 2017). So, the researchers are looking towards a wide variety of nanoformulations which could be the safer and environment-friendly option against plant pathogens and their management (Banik & Sharma, 2011). Crop production and productivity can be increased by using site-directed applications of nanomaterials in controlling pests and plant diseases with the least damage to the ecosystem (Nair & Kumar, 2013; Wang *et al.*, 2016; Raliya *et al.*, 2017). Kamle *et al.* (2020) pointed out the use of nanoparticles in monitoring plant growth and delivering fertilizers, and hormones to raise the productivity of crops by some folds. Thus, these nano-encapsulated pesticide formulations serve as nanocarriers (Figure 2) and can potentially be used as controlled release systems to deliver agrochemicals at the specified sites of the living system without any premature degradation (Nuruzzaman *et al.*, 2016; Jalil & Ansari, 2020). The plant bioengineers have successfully exploited various NPs as vehicles to overcome cell wall barriers in delivering biomolecules at the specified sites (Cunningham *et al.*, 2018).

The principle of drug delivery lies in the slow release of chemicals at the target site for specific and prolonged effects. The same nanotechnology-based principle can be applied in agriculture to deliver nutrients to plants. P. Ehrlich called these NPs as '*magic bullets*' to be used as smart-delivery systems or carriers in the field of life sciences (Himmelweit, 1960). The carriers loaded with agrochemicals for plant disease resistance, nutrition and growth enhancement hold the capacity to release agrochemicals at specific sites in plants with the least damage to the ecology (Nair *et al.*, 2010). The nanosystems (solid NPs, dendrimers, nanoemulsions, polymeric micelles, carbon nanotubes, nanoshells, *etc.*) possess wide characteristics (size, morphology, crystal structure, chemical composition, *etc.*) that promote their use in sustained release of pesticides, herbicides and other agrochemicals or nucleic acids to target specific plant tissues or areas of infection (Luque & Rubiales, 2009; Cunningham *et al.*, 2018; Pérez-de- Singh *et al.*, 2020a). Sometimes, these smart nano-formulations can be used for efficient delivery and distribution of bioactive compounds thereby protecting later from cellular metabolic processes (Martínez-Ballesta *et al.*, 2018).

A wide variety of nano-sized carbon materials have a promising capacity to deliver genetic material into living cells (Khodakovskaya & Lahiani, 2016). These target delivery systems can sustainably be used by optimizing their capacities for the positive effects on targeted plants and are expected to reduce their early degradation due to various environmental effects (Kumar *et al.*, 2019). Khodakovskaya *et al.* (2009) for the first time demonstrated penetration of *Lycopersicum lycopersicon* L. seed coats by carbon nanotubes (CNTs) which supports water uptake and increased germination rate.

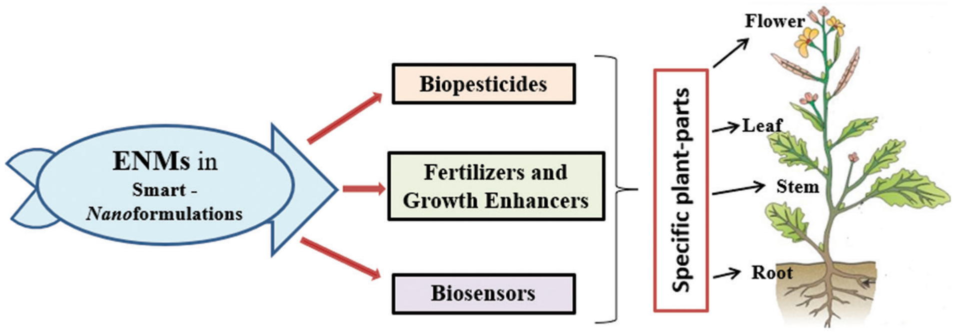

Figure 2: Controlled and site-directed delivery of ENMs can reduce the risk of ecological toxicity

Besides plant protectants, several other NPs can also be used as carriers to entrap or adsorb an active agricultural formulation against insects, fungi, herbs, weeds, *etc*. These carriers include silica NPs, chitosan NPs, Solid lipid nanoparticles (SLNs) and Layered double hydroxides (LDHs) (Worrall *et al*., 2018). The controlled-release fertilizer (CRF) is specifically designed to release functional nutrients to the plants but purely in a controlled, delayed manner facilitating their efficient uptake (Shaviv, 2005). CRFs are economical in their use which checks the nutrient loss, seed toxicity, hazardous emissions, leaf burning, dermal irritation, and inhalation problems. Due to the low cost of urea, its easy handling and high nitrogen content (46%), it is the top-ranking fertilizer in use (Trenkel, 2010). Moreover, the agricultural crop plants facing specific nutrient deficiency and that are non-treatable with common agricultural nutrients can be treated by *nano*therapeutic technique (Karny *et al*., 2018). The *Solanum lycopersicum* var. *cerasiforme* plants suffering from an acute deficiency of Fe and Mg when treated with foliar application of liposomes carrying Fe and Mg showed positive growth response without any toxicity (Karny *et al*., 2018). So, the controlled release coated urea (CRCU) can be produced by entrapping urea granules in a suitable coating material to enhance the nitrogen use efficiency of plants thereby reducing nitrogen loss due to volatilization and leaching (Azeem *et al*., 2014). The uptake and translocation of nano-chitosan loaded with nitrogen, phosphorus and potassium (NPK) by the *Triticum aestivum* plants through foliar spray induced a significant increase in its harvest index (Abdel-Aziz *et al*., 2016). Similarly, Kalia *et al*. (2019) observed the slow and prolonged (approx. 30 days) release of urea from chitosan-urea NP (CS-Urea NP) formulation in controlled conditions. The application of CS-urea NP formulation at 75% on *Solanum tuberosum* L. var. 'Kufri Pukhraj' enhanced tuber yield by 7.23% compared to the conventional urea or CS-NP formulation alone.

Recently, Phan *et al*. (2019) evaluated the effects of hydroxyapatite [$(Ca_{10}(PO_4)_6(OH)_2$] nanoparticles (HA-NPs) based multimicronutrient nano-systems on *Asparagus officinalis* seed germination. The study shows a faster germination rate (46.4±1.2 mm/10 days) compared to the control (35.3±0.8 mm/10 days) suggesting the promising application of nanofertilizers in agriculture. Similarly, Kottegoda *et al*. (2017) demonstrated the slow release of nitrogen from urea-HA nanohybrids resulting in a better crop at 50% less application of pure urea. The functionalized urea-HA nanohybrids exhibit slow release of N_2 up to one week in an aquatic medium, compared to pure urea which is expended within minutes.

Nanocapsules can generally be considered as large containers carrying a wide array of nanomaterials. The natural biopolymer chitosan and its derivatives, due to their common occurrence and properties, rank first in manufacturing encapsulations and drug delivery (Prashanth & Tharanathan, 2007). The systemic herbicide (Joel, 2000) germination stimulants (López-Ráez *et al*., 2008), natural metabolites such as mycotoxins (Vurro *et al*., 2009) can be entrapped in the nanocapsules for their systemic delivery to the specific target. Similarly, mesoporous silica nanoparticles can successfully deliver DNA and other chemicals for the expression of transgene into plant cells (Torney *et al*., 2007).

Moreover, nanobiotechnology researchers are investigating plant viruses as carriers in pharmacology and medicine (Loo *et al*., 2007; Singh *et al*., 2007; Steinmetz & Evans, 2007). The virus comprises of a protein coat as a capsid enclosing its nucleic acid and can serve as a carrier with the features of a drug delivery system. The capsid assembly for certain viruses can be managed *in vitro* by changing the external conditions such as pH to open and close the nano gates for entry or exit nano-substances (Steinmetz & Evans, 2007). The amino acid (lysine) functionalized AuNPs can be used as effective transfection vectors to deliver DNA efficiently in a controlled manner without any cytotoxic effect (Ghosh *et al*., 2008).

Magnetic nanoparticles are being used in the biomedical fields to target specific organs to detect and treat diseases (Mornet *et al*., 2004; Ali *et al*., 2016). Substantially, Jurgons *et al*. (2006) successfully targeted the drug-loaded magnetic iron nanoparticles to treat the artificially induced tumours in rabbits. However, the first report on smart delivery of magnetic nanoparticles was given by González-Melendi *et al*. (2008) suggesting the possible introduction and concentration of charged nanoparticles in the desired areas of plants using magnets. The study on *Cucurbita pepo* L. plants revealed the penetration of magnetic nanoparticles and translocation of bioferrofluid through the vascular system to other areas of the plant.

PHYTOTOXICITY OF ENMs AND NANOFORMULATIONS

Although the ENMs have several positive and beneficial effects in the agro-economy through the fertilizer industry, they may have hazardous effects on the environment, and the physiology of plants, animals as well as human beings (Khan & Rizvi, 2014). Both, direct and indirect effects of different NPs have been observed on algae, plants and fungi (Navarro *et al.*, 2008). The widespread use of ENMs in agriculture and other consumer formulations led to their release into the aquatic ecosystems interacting with certain abiotic factors, undergoing various transformations causing toxicity to the aquatic plant species (Kansara *et al.*, 2022; Kumar *et al.*, 2022). The toxic effects of these nanoparticles are mainly due to their chemical nature and surface reactivity. Their large surface-to-volume ratio makes them highly reactive than the large-sized particles with the same chemical composition (Oberdörster *et al.*, 2005). Patel *et al.* (2021) reviewed the various methods to evaluate the effects of ENMs being used in several applications.

The uptake, translocation, accumulation and phytotoxicity of ENMs depend not only on their size, shape, chemical composition, functionalization and stability (Rico *et al.*, 2011; Khodakovskaya *et al.*, 2012), coating material composition but also on the environment and physicochemical nature of the plant species (Wu *et al.*, 2012; Ruttkay-Nedecky *et al.*, 2017). The uptake, penetration, and accumulation of ENPs in biological systems are deeply reviewed (Ma *et al.*, 2010a; Chichiriccò & Poma, 2015) and their phytotoxic effects in staple food crops have also been summarized (Ma *et al.*, 2010a; Chun *et al.*, 2020). Yang *et al.* (2017) documented both enhancive and inhibitory effects of various NPs on physiological indices, hormones and the quality of crop plants, whereas, Tripathi *et al.* (2017) discussed the toxicity of NPs at morphological, anatomical, physiological, biochemical and molecular levels of the plant's life cycle. However, most of such phytotoxicity studies have been carried out in hydroponic cultures. The possible type of phytotoxicity has been depicted in Figure 3, and the various NPs causing plant toxicity are reviewed as under:

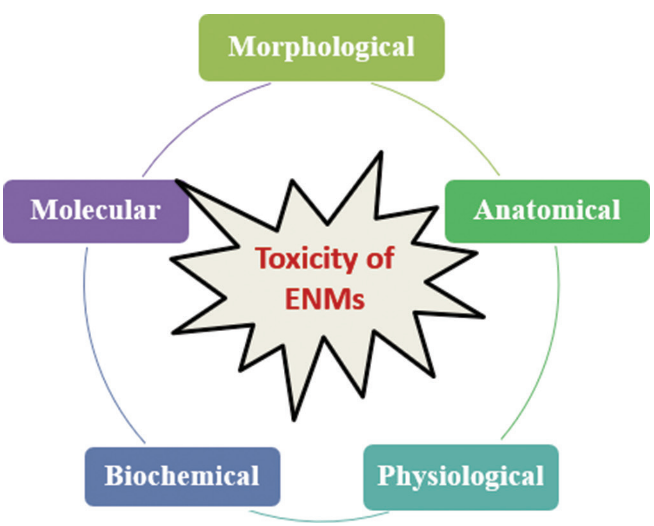

Figure 3: Possible toxicity of ENMs to plants

Metal Nanoparticles

Gold (Au) NPs

The *Phaseolus vulgaris* seedlings exposed to 5 mg/L AuNPs, irrespective of their surface coatings, show no significant impact on plant biomass, transpiration, root-shoot elongation and chlorophyll content compared to uncoated AuNPs and control plants (Ma & Quah, 2016). However, in the roots of polyethylene glycol coated (PEG) AuNPs treated plants CAT activity was significantly higher than other enzyme antioxidants. Taylor *et al.* (2014) demonstrated the uptake of gold by *Arabidopsis thaliana* L. in ionic form leading to up-regulation of plant stress genes (glutathione transferases, cytochromes P450, glucosyltransferases and peroxidases) and down-regulation of specific metal transporters (Cu, Cd, Fe, Ni^{+}, *etc.*) to restrict the gold uptake.

Silver (Ag) NPs

Yan and Chen (2019) reviewed the detrimental effects of AgNPs on plants at morphological, physiological, cellular and molecular levels; whereas, their toxicity to aquatic life forms has been documented by Domingo *et al.* (2019). The size-dependent toxicity of AgNPs reveals hazardous effects on photosynthetic efficiency and increased generation of ROS in leaves the of *Vicia faba* (Falco *et al.*, 2019). The AgNPs remarkably reduced the root biomass of *Cucumis sativus* L. at 50 and 100 mg/L; whereas in *Triticum aestivum* L., it was significantly decreased for shoots at higher concentrations of 20-100 mg/L (Cui *et al.*, 2014).

The AgNPs exposure to *Glycine max* L. seedlings leads to the increased oxidative burst evidenced from the appearance of dark blue spots on leaves after nitroblue-tetrazolium (NBT) staining; and loss of root cell viability indicated with the increased uptake of Evans blue by AgNPs (Hossain *et al.*, 2016). Similar results were observed in *Arachis hypogaea* L. plants at the elevated level of antioxidant isozymes with consistent activity (Rui *et al.*, 2017). The comparative impact study of plant-mediated AgNPs and silver nitrate ($AgNO_3$) on *Brassica* sp. plants reveal high deleterious effects of $AgNO_3$ on seedling growth (Vishwakarma *et al.*, 2017). The plants treated with 3 mM $AgNO_3$ show reduced content of proteins, chlorophyll, carotenoids and antioxidant activities (CAT and APX), while a slightly elevated level was seen in AgNPs treated seedlings. The fluorescence microscopy and flow cytometry exhibited harmful effects of $AgNO_3$ on the structural and functional properties of the cell (Vishwakarma *et al.*, 2017).

The surface coating of AgNPs may change its shape, dispersion and optical properties (Pereira *et al.*, 2018). Ding *et al.* (2019) investigated the inhibitory effect of AgNPs on the root/leaf biomass production and induction of ROS leading to damage in the root morphology of *Lemna minor*. These toxic effects were encountered by the interaction of AgNPs with humic acid in aquaculture. The photosynthetic and oxidative toxicity of AgNPs to *Arabidopsis thaliana* at 30 mg/L were found higher than that in 0.12 mg/L Ag^{+} whereas 60% of genes specifically regulated with these treatments (Zhang *et al.*, 2019a).

The phytotoxicity of AgNPs and ionic silver ($AgNO_3$) in *Nicotiana tabacum* leaves is attributed to the proteomic changes showing tissue-specific responses (Štefanić *et al.*, 2019). A study on the exposure of AgNPs to *Actinidia deliciosa* pollen grains decreases pollen viability and performance causing ultrastructural alteration with the unbalanced redox state of the grain (Speranza *et al.*, 2013). The NPs also disrupt the pollen membrane and tube-elongation process.

Copper (Cu) NPs

The phytotoxicity of essential metal (Cu) NPs and its oxide in non-stabilized and stabilized form was tested on the integral index of root growth in *Allium cepa* L. The treatment of colloidal solution (CuNPs with a stabilizer trisodium citrate) strongly suppresses the root growth by 81% in experimental onion bulbs (Konotop *et al.*, 2019).

The CuNPs exposure to germinating seeds of *Cucurbita pepo* show reduced root length by 77% and 64%; while biomass by 90% and 69% relative to unamended controls and bulk Cu powder. However, the germination indices tests alone may not be the sensitive and appropriate methods for phytotoxicity evaluation (Stampoulis *et al.*, 2009). Similar results were reported in *Cucumis sativus* with a significant reduction in biomass by 30.2% on the exposure of 20 mg/L of nano-Cu (Zhao *et al.*, 2016).

Palladium (Pd) NPs

The *in vitro* toxicity studies of Pd showed alarming effects on the reproductive capacity of the *Actinidia deliciosa* pollen grains and consequently on the biological system. The PdNPs accumulated more rapidly in the grains with substantial damage to the plasma membrane and termination of pollen germination (Speranza *et al.*, 2010).

Metal Oxide Nanoparticles

Aluminum Oxide (Al_2O_3) NPs

The Al_2O_3 NPs demonstrated chronic impact on a freshwater alga *Pseudokirchneriella subcapitata* thereby inhibiting growth, membrane integrity, metabolic and photosynthetic activities, and the intracellular accumulation of ROS (Sousa *et al.*, 2019). Chahardoli *et al.* (2020) demonstrated the oxidative stress (elevated concentrations of CAT, POD, APX and SOD) in *Nigella arvensis* L. plants grown in a hydroponic system supplemented with 1000 or 2500 mg/L Al_2O_3 NPs. However, the higher doses of Al_2O_3 NPs (2.17 mM Al_2O_3 NPs in 700 mL Hoagland solution) adversely affect the biochemical parameters as well as nitrate reductase activity of *Brassica oleracea* var. capitata (Amist *et al.*, 2017). The treatment of Al_2O_3 NPs to root cells of *Allium cepa* brought the highest reduction in mitotic index (MI) and the chromosomal aberration at 0.1 mg/L (disturbed metaphase), 10 mg/L (abnormal anaphase) and 100 mg/L (sticky metaphase) as compared to control (Debnath *et al.*, 2020); whereas, it was found responsible for the significant reduction in the germination of *Zea mays* L. seeds (Karunakaran *et al.*, 2016). Similarly, Hayes *et al.* (2020) observed a decrease in biomass by 10.4% (1 mg/mL) and 17.9% (2 mg/mL) in hydroponically-grown *Lactuca sativa* L. plants. Yang and Watts (2005) observed reduced phytotoxicity of phenanthrene-loaded nano-alumina on root elongation of *Zea mays*, *Cucumis sativus*, *Glycine max*, *Brassica oleracea* and *Daucus carota* compared to unloaded ones. The decreased phytotoxicity is linked with the surface characteristics of the nanoparticles.

Copper Oxide (CuO) NPs

The toxicity of CuO-NPs on germination index (combined seed germination and root elongation) of three plant species *viz*. *Lactuca sativa*, *Raphanus sativus* and *Cucumis sativus* have been tested, whereby the lettuce seeds were found most sensitive towards these NPs with the effective concentration (EC) of 13 mg/L. The phytotoxicity of NPs is associated with released free metal ion concentration in the vicinity of germinating seeds and their interactions with the seed/root surface (Wu *et al.*, 2012). The CuO-NPs have inhibitory effects on *Lactuca sativa* seed germination at trace concentrations (<50 ppm) than that of Cu^{2+} ions (Liu *et al.*, 2016); whereas, Yang *et al.* (2015) reported the inhibitory effect of CuO-NPs on seed germination of *Zea mays* L. 95.73%, and *Oryza sativa* L. 97.28%, only at the higher concentration (2000 mg/L). Gao *et al.* (2018) observed a reduction in the root length of *Triticum aestivum* in soil aged with CuO-NPs for 28 days before sowing. The toxicity of these NPs in rhizosphere soil has been correlated with their dissolution rate.

Treatment of *Cucumis sativus* plants with nano-Cu leads to adverse effects on the uptake and translocation of mineral nutrients and metabolic processes. The decrease in concentrations of Na, P, S, K, Mo and Zn has reported in the exposed plants (Zhao *et al.*, 2016). The CuO-NPs also induce DNA damage and significant accumulation of oxidatively modified mutagenic DNA lesions (7, 8-dihydro-8-oxoguanine; 2, 6-diamino-4-hydroxy-5-formamidopyrimidine; 4, 6-diamino-5-formamidopyrimidine), while strong plant growth inhibitions occur in *Raphanus sativus*, *Lolium perenne*, and *Lolium rigidum* under controlled conditions (Atha *et al.*, 2012).

Dimkpa *et al.* (2012) demonstrated the impairment of roots and shoots in sand grown *Triticum aestivum* plants exposed to 500 mg/Kg CuO-NPs. The root extracts of treated plants show oxidative stress with increased POD and CAT activities compared to its bulk counterparts and controlled plants. The induced toxicity by metal oxide NPs may be due to the accumulation of their ions in growing seedlings (Dimkpa *et al.*, 2012; Landa *et al.*, 2016).

The foliar uptake of CuO-NPs by edible leafy vegetables [3773 mg/Kg by *Lactuca sativa* L. and 4448 mg/Kg by *Brassica oleracea* var. capitata L.] cause a decrease in plant dry weight, photosynthetic capacity and the water content (Xiong *et al.*, 2017); whereas, increased application of CuO-NPs in agriculture poses a greater risk of their release into the environment leading to uptake by the *Oryza sativa* L. plants (Liu *et al.*, 2017). The foliar applications of both CuO-NPs and bulk-CuO at 200 mg/L decline molybdenum (Mo) by 51% and 44%, respectively (Hong *et al.*, 2015). Furthermore, the high adsorption capacity (26.9 mg/g) of arsenic (As (III)) by CuO-NPs (Martinson & Reddy, 2009), they may uptake and get concentrated in the *Oryza sativa* L. plants along with CuO-NPs which may pose a serious risk to its consumers (Liu *et al.*, 2017).

Nickel Oxide (NiO) NPs

Baskar *et al.* (2020) studied the dose-dependent phytotoxic effects of NiO-NPs on *in vitro* seedling growth of *Abelmoschus esculentus* plants and found the suppressed plant growth evidenced from the decreased shoot and root lengths. A significant reduction in the content of chlorophyll, anthocyanin, phenolic and flavonoids was also reported with the increased NP concentrations (Baskar *et al.*, 2020). The *Hordeum vulgare* L. plants after 14 days of nano-NiO treatment at increased concentration show a marked decrease in photosynthetic pigments (chlorophyll and carotenoids) leading to reduced productivity (Soares *et al.*, 2016). The treatment at the lowest dose (87.8 mg/Kg) led to a significant elevation of lipid peroxide and superoxide anions causing oxidative stress (Soares *et al.*, 2016). Similarly, the defence systems of *Nigella arvensis* L. get inhibited with exposure to NiO-NPs higher than the concentration of 1000 mg/L exhibiting the toxic effects (Chahardoli *et al.*, 2020); whereas, their concentration as low as 10 mg/L has found effective in inducing genomic instability in *Allium cepa* L. (Manna & Bandyopadhyay, 2017). The exposure of *Brassica rapa* spp. Pekinensis var. Seoul seedlings to the different doses (50 mg/L – 500 mg/L) of NiO-NPs elicits toxic responses including a reduction in plant biomass, chlorophyll, carotenoid and sugar contents; with a significant increase in anthocyanin, proline and the antioxidant enzymes (Chung *et al.*, 2019). Likewise, the comparative toxicity studies on *Lycium barbarum* L. shoots in *in vitro* conditions demonstrate the harmful effects of nano-Ni than its bulk counterpart [Nickel (II) Sulphate, $NiSO_4$] (Pinto *et al.*, 2019). Higher pH and ionic strength promote stability to NiO-NPs thereby forming aggregates and ion release (Ni^{2+}). Such aggregations are found to inhibit the growth of marine algae *Chlorella vulgaris* (Gong *et al.*, 2019). Almost similar kind of toxicity has reported in freshwater alga *Pseudokirchneriella subcapitata* (Sousa *et al.*, 2018). Oukarroum *et al.* (2015) studies on an aquatic plant *Lemna gibba* L. reveal the production of ROS at 1000 mg/L concentration, as an early biomarker of NiO toxicity higher than NiO-bulk. However, the experiments carried out at an elevated concentration of CO_2 (620 ppm) on the growth and physiology of *Triticum aestivum* L. show reduced phytotoxicity of NiO-NPs and also minimized oxidative stress (Saleh *et al.*, 2019).

Iron Oxide (Fe_2O_3) NPs

Generally, the iron NPs are thought to be non-toxic or less toxic to plants. But, the treatment of nano-maghemite (nFe_2O_3) to the roots of hydroponically grown *Helianthus annuus* L. plants causes significant reduction (up to 57% at 50 mg/L concentration) in root hydraulic conductivity and macronutrients (Ca, K, Mg, S) in the shoot (Martínez-Fernández *et al.*, 2015). The reduced macronutrients in shoots decline the chlorophyll content of leaves. Similar effects of nFe_2O_3 have observed in *Solanum lycopersicum* L. plants at 100 mg/L concentration resulting in lowering nutrient immobilization capacity for Mo and Zn in the plant shoots (Martínez-Fernández & Komárek, 2016). The foliar application of 100 ppm Fe_3O_4 NPs shows enhanced growth and physiological parameters in *Zea mays* L. for the first generation. However, the Fe-NPs treated second-generation progenies show less biomass, reduced contents of chlorophyll, protein and calcium, and lower hydrogen peroxide (H_2O_2) scavenging capacity compared to control plants (Jalali *et al.*, 2017). Lee *et al.* (2010) did not find an inhibitory effect of Fe_3O_4 NPs on *Arabidopsis thaliana* seed germination but observed exerted effects on plant development at all three tested concentrations (400, 2,000, and 4,000 mg/L). In similar experiments with *Sinapis alba* L. plants, Landa *et al.* (2016) noticed no toxicity symptoms of Fe_3O_4 NPs on germinating seeds. However, the nano-sized zero-valent iron at higher concentrations (>200 mg/L) was found irregularly accumulated on the root surface of plant species: *Typha latifolia* and hybrid poplars - *Populous deltoids* × *Populous nigra* (Ma *et al.*, 2013). The decrease in transpiration and plant growth rate occurs in both species (Ma *et al.*, 2013).

Zinc Oxide (ZnO) NPs

Lee *et al.* (2010) reported the phytotoxic effects of ZnO-NPs on the developmental patterns of *Arabidopsis thaliana*. The intensity of ZnO-NPs phytotoxicity was due to the NP size, exerting higher toxicity than the corresponding micron-sized particles at the equivalent concentrations (Lee *et al.*, 2010). A similar kind of root elongation inhibitory effects of metal oxide NPs have been observed in *Zea mays* and *Oryza sativa* (Yang *et al.*, 2015). The toxicological effects of ZnO-NPs on plant species have recently been reviewed by Rajput *et al.* (2018). The cytotoxic, genotoxic and biochemical effects of ZnO-NPs on *Allium cepa* bulbs have also been evaluated (Kumari *et al.*, 2011; Ghosh *et al.*, 2016). It shows a dose-dependent decrease in MI; while an increase in the micronuclei (MN) and chromosomal aberration indices in 100 μg/mL ZnO-NPs treated samples (Kumari *et al.*, 2011). Likewise, the activity of ROS producing enzymes in *Vicia faba* and *Nicotiana tabacum* has been found elevated with ZnO-NPs treatment (Ghosh *et al.*, 2016). Dobrucka *et al.* (2020) observed an increased cell death rate in *Betonica officinalis* extract synthesized ZnO-NPs treated plants than its bulk form. The toxicity of ZnO-NPs could be due to the formation of ROS causing lipid peroxidation and the destruction of biological membranes (Kumari *et al.*, 2011). A similar kind of cytotoxic and genotoxic effect of ZnO-NPs (100 and 200 mg/L) has been reported in *Vicia faba* (Youssef & Elamawi, 2018). Recently, Debnath *et al.* (2020) demonstrated the effects of ZnO-NPs on root tip cells of *Allium cepa* producing chromosomal aberration with multiple chromatin bridges.

Lin and Xing (2007) noticed inhibition of *Lolium perenne* seed germination by nano-Zn, and *Zea mays* by ZnO-NPs at 2000 mg/L; whereas, suspension of both the NPs at equivalent concentration terminated root elongation in *Brassica napus*, *Raphanus sativus*, *Lolium perenne*, *Lactuca sativa*, *Zea mays* and *Cucumis sativus*. The toxicity of ZnO-NPs, nanowires and the bulk ZnO is due to the released Zn^{2+} in the cultivation medium and its accumulation in germinating *Sinapis alba* L. seeds (Landa *et al.*, 2016). The toxic Zn^{2+} uptake by *Triticum aestivum* L. increases due to dissolved ZnO-NPs in the soil leading to biomass reduction and the inhibition of soil enzymes (protease, catalase and peroxidase) activity (Du *et al.*, 2011).

An exposure of *Glycine max* L. seedlings to ZnO-NPs shows increased oxidative stress and adverse effects on plant growth, rigidity of roots and root cell viability (Hossain *et al.*, 2016). Mukherjee *et al.* (2014) studied the concentration-dependent effects of ZnO-NPs on *Pisum sativum* L. cultivated in organic matter rich soil. The NPs cause increased root elongation and translocation of Zn in aerial plant parts. The accumulated Zn resulted in an elevated level of H_2O_2 in leaves; thereby reducing the activity of stress enzymes (CAT and APX). After 25 days of growth, a reduction of ~61%, 67% and 77% was observed in the chlorophyll content of leaves at 125, 250 and 500 mg/L ZnO-NPs respectively (Mukherjee *et al.*, 2014).

Furthermore, the phytotoxicity of ZnO-NPs on root elongation of *Zea mays* and *Oryza sativa* has found concentration-dependent but significant (50.45% and 66.75% respectively) at 2000 mg/L (Yang *et al.*, 2015). The phytotoxicity of commercially coated (Z-COTE-HP1®), uncoated (Z-COTE®) ZnO-NPs and the bulk ZnO has evaluated on *Phaseolus vulgaris* L. seedlings (Medina-Velo *et al.*, 2017). The Z-COTE-HP1® shows increased root length (~53%) and leaf length (~18%) at 125 and 250 mg/Kg compared to the control; whereas, bulk ZnO shows a reduction in root length (~53%) at 62.5 mg/Kg concentration.

Carbon Nanomaterials (CNMs)

The mixed effects and toxicity of CNMs exposure on crop plants (*Allium cepa*) lead to enhanced yield, acute cytotoxicity and genetic alteration (Ghosh *et al.*, 2015; Mukherjee *et al.*, 2016). Among the CNMs, carbon nanotubes (CNTs) are the top ranking ENMs being produced (Keller *et al.*, 2013) and have the ability to penetrate the plant cell wall and the cell membrane (Liu *et al.*, 2009). The cylindrical CNTs may possess open or closed ends and based on the number of concentric layers of rolled graphene sheets they are categorized into single-walled (SWCNTs) and multi-walled carbon nanotubes (MWCNTs) (Yang *et al.*, 2010; De Volder *et al.*, 2013). The varied effects of functionalized (fCNTs) and nonfunctionalized (CNTs) SWCNTs exposure on root elongation of six different plant species *viz*. *Brassica oleracea*, *Daucus carota*, *Cucumis sativus*, *Lactuca sativa*, *Allium cepa*, and *Lycopersicon esculentum* have been reported (Cañas *et al.*, 2008). The CNTs have been found toxic to more species than fCNTs. The nanotubes functionalized with poly-3-aminobenzenesulfonic acid (PABS) at a ratio of PABS to CNTs of 65:35 (w/w) which possibly be more biologically available than CNTs because of their water solubility property (Cañas *et al.*, 2008).

A 15-day hydroponic trial exposure of multiwalled carbon nanotubes (MWCNTs) to *Cucurbita pepo* reduces 60% of its biomass (Stampoulis *et al.*, 2009). At the genetic level, Ghosh *et al.* (2015) reported the induction of hyper-methylation in the *Allium cepa* plant system by the MWCNTs.

The natural colloids (nanocolloids, Nc) are common in an aqueous environment and show fast interaction with the graphene oxide (GO), an ENM. These GO-Nc hybrids are much stronger in inducing the generation of ROS, DNA damage, plasmolysis and also cause the inhibition of photosynthesis (Ouyang *et al.*, 2020).

Rare Earth Nanomaterials (RENMs)

The applications of different RENMs have different adverse effects on the physiology of plants such as nutrient uptake, enzyme activity, expression of genes, biomass, *etc*. These are the fundamental causes of phytotoxicity (Feng *et al.*, 2018). The seven rare earth oxides (CeO_2, Er_2O_3, Nd_2O_3, Tm_2O_3, Yb_2O_3, La_2O_3, and Tb_4O_7) are characterized using Raman spectroscopy (Cui & Hope, 2015) and are being used to synthesize nanoparticles to screen their effects in human welfare. According to an estimate, approximately 3000 tons of Titanium dioxide (TiO_2) NPs and 55 tons of Cerium oxide (CeO_2) NPs are produced annually for various uses (Piccinno *et al.*, 2012). Previously, Ma *et al.* (2010b) reported that the nano-suspensions of Lanthanum oxide (La_2O_3), Gadolinium oxide (Gd_2O_3) and Ytterbium oxide (Yb_2O_3) induced root elongation inhibition in the seven higher plant species (*Raphanus sativus*, *Brassica napus*, *Lycopersicum esculentum*, *Lactuca sativa*, *Triticum aestivum*, *Brassica oleracea*, and *Cucumis sativus*) at 2000 mg/L concentration, but CeO_2 show no effect on any of the above species at the same concentration. Similar significant inhibitory effects were observed in *Cucumis sativus* plants with reduced root biomass (≥2 mg/L), shoot biomass (≥20 mg/L), induced ROS and cell death in roots (2000 mg/L) (Ma *et al.*, 2014). Recently, Liu *et al.* (2018) replicated the earlier findings of La_2O_3-NPs toxicity and studied the effect of different concentrations on *Zea mays* L. The treatments show declination in biomass of shoot (≥10 mg/L) and root (≥5 mg/L), while the chlorophyll content decreased by 25.9% at 50 mg/L concentration. The phytotoxicity of La_2O_3-NPs may be due to their higher degree of dissolution and transformation in the plants (Ma *et al.*, 2014).

Most of the studies on CeO_2-NMs demonstrate their non-phytotoxic nature but may produce harmful effects at extremely high concentrations (García-gómez & Fernández, 2019). Zhang *et al*. (2013) investigated the species-specific toxicity of CeO_2-NMs on *Lactuca* species; whereas, Mattiello *et al*. (2015) observed the dose-dependent uptake of CeO_2 and TiO_2-NPs in root cells of *Hordeum vulgare* L. leading to the generation of oxidative stress and chromatin modifications. The elevated concentration of TiO_2 (2000 mg/L) shows a significant reduction in ATP level and the MI of its seedlings. The toxicity of Ce-NPs to *Lactuca* plants may result due to the release of Ce^{3+} ions instead of nano-effect (Zhang *et al.*, 2013) which in turn depends upon the availability of oxygen in a cell system. Similarly, the foliar applications of nano-ceria on *Phaseolus vulgaris* L. were found to have fewer toxic effects on their corresponding C^{3+} concentrations (Xie *et al.*, 2019).

The TiO_2-NPs in low concentrations (0.5–2 g/L) promote the growth and overall health of *Solanum lycopersicum* L. plants; whereas, the higher concentrations (4 g/L) produce increased oxidative stress affecting photosynthetic efficiency, reduced biomass and plant performance on short term exposure in the hydroponic system (Tiwari *et al.*, 2017). The elemental analysis of tissues at lower concentrations revealed significant disturbances in the distribution of essential elements (P, S, Mg and Fe) in the roots and leaves of the *S. lycopersicum* L. plants (Tiwari *et al.*, 2017). Du *et al.* (2011) reported the retention of TiO_2-NPs in soil for a long duration adhering to cell walls of *Triticum aestivum* L. plants causing a significant reduction in biomass. The treatment of TiO_2-NPs (0.1 mg/L) to *Allium cepa* root tips leads to the reduction in MI and generation of chromosomal aberrations (Debnath *et al.*, 2020).

CeO_2-NPs causes oxidative stress, a significant reduction in the chlorophyll content at 125 mg/L nano-CeO_2 and serious damage to the membranes in *Oryza sativa* L. plants (Rico *et al.*, 2013); whereas, CeO_2 and Indium oxide (In_2O_3) NPs at 250 mg/L and 1000 mg/L concentration demonstrate elevated oxidative stress on *Arabidopsis thaliana* plants (Ma *et al.*, 2016). Hong *et al.* (2014) observed the uptake and internalization of CeO_2-NPs by *Cucumis sativus* leaves leading to the reduction in chloroplast number. It could be due to decreased APX activity in leaves which protects the plant from ROS damage. The CeO_2-NPs application on *Solanum lycopersicum* L. plants shows positive effects but their continuous accumulation in fruits may pose a higher risk to human beings and the environment (Wang *et al.*, 2012). The impact of CeO_2-NPs on the second generation of *Solanum lycopersicum* L. seedlings has been studied by Wang *et al.* (2013), where these plants were small and weak with little biomass, lower water transpiration and with a slightly elevated level of ROS. The CeO_2-NPs at 0.1 g/Kg show ill effects on soil bacterial communities in planted soil than in unplanted soils indicating the interaction between plant exudates and the NPs (Ge *et al.*, 2014). The foliar application of CeO_2-NPs at 200 mg/L on *Cucumis sativus* seedling leaves significantly shows a decrease in net photosynthetic rate by 22% and transpiration rate by 11%; whereas, the nutritional analysis of its fruits reveals a 25% reduction in Zn for both, CeO_2-NPs and bulk-CeO_2 (Hong *et al.*, 2015). Zhang *et al.* (2019b) have investigated the ability of different plant species to transform and translocate CeO_2-NPs. The mechanism involved may differ depending on the chemistry of the surrounding solution (like presence or absence of phosphorus, pH, redox state and other ions). Thus, for some plants (*e.g. Zea mays* and *Triticum aestivum*), phosphorus deficiency can lead to the potential toxicity of CeO_2-NPs thereby accumulating Ce^{3+} in plants.

Zhang *et al.* (2012) studied the comparative toxicity of Yb_2O_3-NPs and bulk-Yb_2O_3 on the root elongation and biomass yield of *Cucumis sativus*. Both the treatments higher than 200 mg/L inhibit root elongation; whereas, at the highest concentration (2000 mg/L) root elongation was reduced by 78.1% (Yb_2O_3-NPs) and 46.9% (bulk-Yb_2O_3) respectively. However, treatments >20 mg/L reduce biomass significantly. The Yb_2O_3-NPs inhibit biomass at the exposure of 0.32 mg/L indicating its toxicity to plants and the ecosystem. The reduction in biomass of roots/shoots for Yb_2O_3-NPs and bulk-Yb_2O_3 at 2000 mg/L concentrations were 78.3%/62.9% and 70.5%/53.2% respectively. Recently, Zhao *et al.* (2021) studied the phytotoxicity of Y_2O_3-NPs on hydroponically grown *Oryza sativa* L. seedlings. The higher concentrations (50 and 100 mg/L) caused delayed seed germination, and a reduction in chlorophyll content thereby accumulating Y_2O_3-NPs in the roots.

CONCLUSION

The ENMs have great potential in agriculture especially in plant protection and elevation of the crop yield. To avoid ecological imbalances through their traditional applications in a field they can be targeted and delivered to the specific plant parts in a controlled manner. However, these ENPs show obvious phytotoxicity and ecotoxicological effects on the surroundings. Despite their high production cost, uncertain technical benefits and legislature, public opinion, the promising opportunities from nanotechnology are being actively explored nearly all across the globe. The limitation to use nanocarriers is their high cost and scale of production. They can be produced to apply on high-input crops in controlled environmental conditions. Before the widespread applications of ENPs in the agricultural sector, a thorough evaluation of their phytotoxicity, mechanism of action, accumulation and transformation in plants is needed. The scientific community is in a shortfall of knowledge because most of the literature on the phytotoxicity of ENMs is restricted to their high doses, short exposures and insensitive parameters like germination indices, biomass and pigment production. With the suggestions of Servin and White (2016), more accurate, advanced and ecologically relevant approaches/measurement methodologies have to be designed for plant-ENMs interaction studies with sensitive endpoints. The innovative methods can substantially be used in the assessment/management of environmental risks caused due to ENMs. Furthermore, mechanisms of their absorption from soil, accumulation and retention within the plant parts as well as their direct and indirect effects on human life have to be studied through the regulatory board. For this, policymakers and the respective administrators should understand these pitfalls and release sustained grants for further research. Still, the social acceptance of these novel NMs will be the barrier for their sustainable use in the agro-sector unless and until the risks associated with their handling are minimized to the eco-friendly level.

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