



Review

Nanotechnology in agriculture: Current status, challenges and future opportunities



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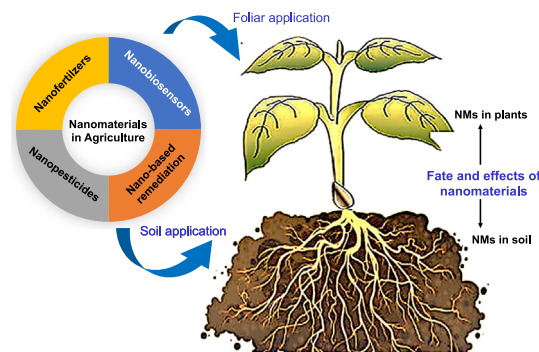
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HIGHLIGHTS

- Nanotechnology could promote sustainable agriculture.
- Different roles of nanotechnology in agriculture are illustrated.
- Comprehensive evaluation of its impacts on soil, plant and environment.
- Perspectives on future challenges and opportunities in nano-enabled agriculture.

GRAPHICAL ABSTRACT



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ABSTRACT

Nanotechnology has shown promising potential to promote sustainable agriculture. This article reviews the recent developments on applications of nanotechnology in agriculture including crop production and protection with emphasis on nanofertilizers, nanopesticides, nanobiosensors and nano-enabled remediation strategies for contaminated soils. Nanomaterials play an important role regarding the fate, mobility and toxicity of soil pollutants and are essential part of different biotic and abiotic remediation strategies. Efficiency and fate of nanomaterials is strongly dictated by their properties and interactions with soil constituents which is also critically discussed in this review. Investigations into the remediation applications and fate of nanoparticles in soil remain scarce and are mostly limited to laboratory studies. Once entered in the soil system, nanomaterials may affect the soil quality and plant growth which is discussed in context of their effects on nutrient release in target soils, soil biota, soil organic matter and plant morphological and physiological responses. The mechanisms involved in uptake and translocation of nanomaterials within plants and associated defense mechanisms have also been discussed. Future research directions have been identified to promote the research into sustainable development of nano-enabled agriculture.

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1. Introduction

Sustainable agriculture is crucial to achieve “Zero hunger” which is among the 17 sustainable development goals of the United Nations. World food production and distribution are facing huge stress due to increasing population, climate change, environmental contamination, and higher demands of water and energy. Present agriculture uses a staggering amount of resources. For instance, global annual crop production exceeds three billion tonnes which requires 187 million tonnes of fertilizer, 4 million tonnes of pesticides, 2.7 trillion cubic meters of water (about 70% of all freshwater consumptive use globally), and over two quadrillion British thermal units (BTU) of energy (Kah et al., 2019). According to Food and Agriculture Organization (FAO, 2017), world's population is projected to reach 10 billion by 2050 boosting food requirements by 50% especially in the developing countries. Moreover, there are approximately 815 million people who are currently undernourished, and it is expected that additional 2 billion people will be in this category by 2050. This situation calls for profound changes in the global food production systems. Recent research has shown the promising potential of nanotechnology to improve the agriculture sector by increasing the efficiency of agricultural inputs and offering solutions to agricultural and environment problems for improving food productivity and security.

Therefore, research concerning applications of nanotechnology for agriculture has gained significant attention during the recent years (Parisi et al., 2015; Kah et al., 2019). Though a great amount of research data is available in this field, a comprehensive review of this topic covering application of nanotechnology in different sectors of agriculture is still missing in literature. Here, we compile the research data from numerous publications dealing with different aspects of the nanotechnology in agriculture. In the first part of this review, different uses of nanomaterials (NMs) in agriculture, such as nanofertilizers, nanopesticides, nanobiosensors and NMs for soil remediation via biotic and abiotic pathways, are critically evaluated. The fate of NMs is highlighted in soil-plant system with a critical evaluation of potential threats to the soil ecosystem. Next sections describe the effect of NMs on soil health and crops with a special focus on nutrient release in target soils, soil biota, soil organic matter and plant morphological and physiological responses. Mechanisms involved in the uptake and translocation of NMs within plants and associated defense mechanisms are also discussed. This review is aimed to provide a unique reference for researchers working in different disciplines of nano-enabled agriculture to highlight the opportunities and future research directions for nanotechnology in agriculture and food security.

2. Application of nanomaterials in agriculture

Nanomaterials have many potential applications in agriculture to enhance crop productivity and to improve the soil health which has been highlighted in this section. Here, we illustrate various developments in the field of nanofertilizers, nanopesticides, nanobiosensors and nano-enabled remediation of contaminated soils.

2.1. Nanofertilizers

During the last five decades, an enormous increase in crops yield, especially that of cereals, played a significant role in meeting the world's nutritional requirements. Increase in use of chemical fertilizers is among the major contributors to boost the crop yield in this regard. Fertilizer-responsive crop varieties have multiplied the use of chemical fertilizers. Use of chemical fertilizers is, however, limited by their poor use efficiency due to the loss of fertilizer (by volatilization and leaching) that contaminates the environment and increases the cost of production (FAO, 2017). For example, 50–70% of the nitrogen applied by conventional fertilizers is lost to the environment (DeRosa, 2010). Therefore, development of alternate strategies to ensure sustainable use of nutrients is gaining significant attention among the scientific community. In this context, nanotechnology is used to reduce the losses of mobile nutrients, to develop slow-release fertilizers, and to improve the accessibility of poorly-available nutrients (Kah et al., 2018). Nanofertilizers are nanomaterials which are either nutrients themselves (micro- or macro-nutrients) or are acting as carriers/additives (e.g. by compositing with minerals) for the nutrients (Kah et al., 2018). Nanofertilizers can also be developed by encapsulating nutrients inside the nanomaterials (DeRosa, 2010).

Nanofertilizers improve crop yield and quality with higher nutrient use efficiency while reducing the cost of production and thus, contribute towards agricultural sustainability. A critical analysis of a dataset of nanofertilizers by Kah et al. (2018) revealed a median efficacy gain of 18–29% by nanofertilizers as compared to the conventional fertilizers (Kah et al., 2018). Application of phosphatic nanofertilizers has also been linked to an increased growth rate (by 32%) and seed yield (by 20%) of soybean (*Glycine max* L.) as compared to those treated with conventional fertilizer (Liu and Lal, 2014). Nanofertilizers also improve the plant metabolism and the uptake of nutrients through nanometric pores facilitated by molecular transporters or nanostructure cuticle pores (detailed in Section 4.3) (Rico et al., 2011).

Introduction of nanotechnology in plant nutrition facilitates the development of slow/controlled release fertilizers which improve the

fertilizer use efficiency and reduce the losses of nutrients to the environment making them ecofriendly (Liu and Lal, 2014). The fertilizer use efficiency of conventional nitrogenous fertilizers is 30–60%, while 8–90% conventional phosphatic fertilizers are lost by chemical bonding in soil and become unavailable to plants (Giroto et al., 2017). On the other hand, nanocomposites of urea and hydroxyapatite offered controlled release of nitrogen, lower NH_3 volatilization and sustained availability of phosphorus after four weeks of incubation (Giroto et al., 2017). Overall, fertilizer amount is reduced by using slow release products. Ideally, nanofertilizers should be able to release the nutrients when and where required by plants restricting the conversion of extra fertilizers to gaseous forms or leaching towards downstream. It can be achieved if the nutrient release is based on plant signaling (DeRosa, 2010) and these intelligent fertilizers are possible by explaining the communicational signals between plant roots and soil microbes (Mastronardi et al., 2015). Nanomaterial containing plant nutrients respond to various chemical and/or physical stimuli which indicate the needs of nutrients for plant growth (DeRosa, 2010). These stimuli may include ethylene production by plants roots and acidification of rhizosphere, which are released in response to P and/or K deficiency in soils (Rop et al., 2019). Application of nanoparticles may modify the internal root signals, as reported by Syu et al. (2014) that affect the ethylene production by Arabidopsis roots. Internal stimuli from roots for nutrient release in response to P and/or N deficiency could be a great breakthrough towards controlled release nanofertilizers. It is evident from the literature that engineered NMs can significantly reduce the amount of fertilizer applied, both applied through soil and foliage, enhancing their efficiency and decreasing release into the environment as compared to the conventional formulations (Adisa et al., 2019). Kah et al. (2019) reviewed and advocated the use of nano-enabled fertilizers and predicated that their social acceptance as nano-formulations will not have any issue for regulatory agencies working in many developed countries.

Nanostructured material such as clay minerals, hydroxyapatite, chitosan, polyacrylic acid, zeolite, etc., is used to develop fertilizers to be used for soil and/or foliar application. Large surface area of hydroxyapatite and its strong interactions with urea lead to slow release of N from urea (Kottegoda et al., 2011). Urea modified with hydroxyapatite nanoparticles release N up to 60 days of plant growth as compared to the other conventional fertilizers (urea, ammonium nitrate) which release N till 30 days (Kottegoda et al., 2011). Ghafariyan et al. (2013) described an increase in chlorophyll content of soybean by using superparamagnetic iron oxide. A 10% increase in chlorophyll content was measured in cowpea (*Vigna unguiculata* (L. Walp.) by applying Fe nanoparticles on foliage as 0.5 g L^{-1} solution with reference to same solution of common forms of Fe (Karami et al., 2014). Application of 1 and 20 mg L^{-1} ZnO-NP spray to mung bean (*Vigna radiata* (L.) R. Wilczek) and chickpea (*Cicer arietinum* L.) improved the plant growth as compared to the conventional fertilizers (Mahajan et al., 2011). Subbarao et al. (2013) also reported that potassic fertilizer coated with polyacrylamide polymer contribute to slow release of K. Slow release K fertilizers are required in sandy soils to decrease the leaching and reduce the K fixation in K fixing soils. Humic substances (HS) stabilize the colloidal Fe by binding iron oxides (Angelico et al., 2014) and inhibit the crystallization of ferric hydroxides (Usman et al., 2018). Therefore, Fe-HS composites have been used as “nanofertilizer” and are mixed with the industrial composite fertilizers containing N, P and K (Sorkina et al., 2014). Furthermore, use of HS as macroligands provides ecological safety as well as better uptake and translocation in the plants as compared to synthetic iron oxide nanoparticles.

Enhanced organic waste decomposition and production of compost can be a significant aspect of nanotechnology in agriculture, however the work is still in infancy and no solid outcome has been presented to date. It is evident from the available information that nanofertilizers can reduce the amount of fertilizers to be applied due to their high use efficiency thus decreasing the environmental impacts due to nutrient losses. This innovation is very timely to ensure world's food security

and environmental safety. Nevertheless, economic feasibility of nanofertilizers still need to be studied for sustainable and profitable agriculture.

2.2. Nanopesticides

Pesticide use is a regular practice in commercial agriculture and development of new, efficient and target-specific pesticides is a continuous process. Therefore, large number of pesticides are screened each year (>1 million according to an estimate in 2009) (Resh and Cardé, 2009). Only very small amount of the applied pesticides (0.1%) reaches the target pests, while the remaining (99.9%) contaminates the environment (Carriger et al., 2006) which has serious consequences on food chain and human health. In addition to the impact on non-target species, ubiquitous presence of pesticides in environment has resulted in the development of pesticide-resistance in weeds, insects and pathogens (Rai and Ingle, 2012). It is, however, important to note that if there were no pesticides in the world, the life losses would exceed by factor of 1000 for each life lost to pesticides (Lomborg, 2002). Biopesticides appeared to reduce hazardous effects of synthetic pesticides but their use is limited by their slow and environment-dependent efficiency against pests. Nanopesticides are showing viable potential to overcome these limitations. Slow degradation and controlled release of active ingredients in the presence of suitable NMs can offer an effective pest control over long time (Chhipa, 2017). Therefore, nanopesticides are important for effective and sustainable management of different pests and have potential to minimize the use of synthetic chemicals and associated environmental risks. The nanopesticides behave differently from conventional pesticides to increase their efficacy (Kah et al., 2019). Nano-sized particles can be transported in dissolved and colloidal states and this type of mechanism underlie different behavior than those for conventional solutes of the same particles (Kumpiene et al., 2008). The solubility of active ingredients could increase mobility and degradation by soil inhabiting microorganisms. As the nanoparticle-based pesticides increase the solubility of the AI so they are also considered to have less harmful impact on the environment as compared to conventional pesticides (Kah and Hofmann, 2014).

Overall, nanopesticides conserve energy and water as they are applied in smaller amount and less frequently than the conventional pesticides. They also enhance pesticide efficiency and crop productivity by higher yields and lower input costs by reducing waste and labor costs. However, nanopesticides may cause health issues (Ragaei and Sabry, 2014) due to different reasons described by environmental protection agency (EPA, USA) as: i) dermal absorption of nanopesticides due to their very small size and they can pass through cell membranes, ii) through inhalation as they can go deep in lungs and translocate to brain by crossing blood brain barrier, iii) durability and reactive potential of some NMs raise environmental concerns, and (iv) dearth of knowledge to gauge environmental exposure to engineered NMs.

There are different types of nanopesticide formulations (Supplementary material, Table S1) and several studies indicated their effectiveness against a wide range of pests (Table S2). For example, imidacloprid (IMI) is a highly effective systemic insecticide against several sucking insects. The in vitro assessment of IMI against *Martianus dermestoides* (Coleopteran, Tenebrionidae) revealed 100% mortality after 142 h but novel 50% nano-SDS/Ag/TiO₂-IMI was significantly more effective (lethal concentration LC50: 9.86 mg L^{-1}) than 95% IMI (LC50: 13.45 mg L^{-1}). In addition, the nano-IMI was also more photodegradable than conventional formulation which indicates its environmental benefits (Guan et al., 2008). Another study revealed an increased uptake of permethrin in nanoformulation than the commercial form against *Aedes aegypti*. Moreover, the adverse effects on soil bacteria and plants were reduced in case of nanopesticides (Kumar et al., 2013). Similar results were observed using polyethylene glycol based nanoformulations of carbofuran and acephate (Pankaj et al., 2012; Pradhan et al., 2013). The lower toxicity of nano-acephate to

non-target organisms was also observed as compared to the commercial product of acephate (Pankaj et al., 2012; Pradhan et al., 2013). It was suggested that efficiency was increased due to slower release of the active ingredients and not because of increased uptake of nanoformulated active ingredients. Chlorfenapyr associated with silica nanoparticles exhibited two times higher insecticidal activity against cotton bollworm than chlorfenapyr associated with microparticles (Song et al., 2012b). These results are promising for the slow release of active ingredients against different crop pests and can serve as effective tools in future pest management practices in agriculture. The recent studies have reported the efficacy of nanosilica to control insect pests of stored grain products (Gamal, 2018). Hashem et al. (2018) also described the increased efficacy and stability of anise (*Pimpinella anisum*) essential oil against red flour beetle (*Tribolium castaneum*) and concluded that nanoemulsions can contribute to reduce the use of harmful synthetic insecticides against insect pests.

The antimicrobial activity of nanoparticles is also well-recognized against bacterial, fungal and viral pathogens. The important inorganic nanoparticles having pesticidal properties are silver (Kim et al., 2012) copper (Gogos et al., 2012) and aluminum (Stadler et al., 2012). A study of silica-silver nanoparticles to control pathogenic fungi (*Rhizoctonia solani*, *Magnaporthe grisea*, *Colletotrichum gloeosporioides*) demonstrated that the disease-causing pathogens disappeared from the infected leaves within 3 days of spraying of the product (Park et al., 2006). Antifungal activity of silver nanoparticles was also observed against *Raffaelea* sp. causing damage to oak trees (Kim et al., 2009). The fungal development was significantly inhibited. The antimicrobial activity of copper nanoparticles revealed significant antibacterial and antifungal activities (Esteban-Tejeda et al., 2009). The development of nanoformulated commercial fungicide (Trifloxystrobin 25% + Tebuconazole 50%) assessment at various concentrations (5, 10, 15, and 25 ppm) against the soil borne fungal pathogen *Macrophomina phaseolina* showed better performance in comparison with commercial compound (Kumar et al., 2016).

Weeds are emerging threats in the modern agriculture. Nano-herbicides rely mostly on biodegradable polymeric substances which could improve the efficiency of herbicides. For example, poly(epsilon caprolactone) has been used to encapsulate atrazine owing to its good physico-chemical properties, enhanced bioavailability and biocompatibility (Abigail and Chidambaram, 2017). The polymeric nanoparticles encapsulated with atrazine were proven effective on target plant (*Brassica* spp.) with enhanced herbicidal activity, stability (for 3 months) and reduced mobility in soil as compared to that of free atrazine (Pereira et al., 2014). The similar trends were observed in other studies (Grillo et al., 2012, 2014) with polymer-based encapsulation of different herbicides (atrazine, ametryn and simazine, paraquat). The increase in bioavailability of herbicides revealed similar to or slightly greater efficacy of glyphosate nanoemulsion than commercial formulation (Jiang et al., 2012; Lim et al., 2013). Atrazine has been known to contaminate surface and groundwater sources. The nanoformulations of atrazine and paraquat were more effective against target weeds than pure compounds while genotoxicity and cytotoxicity assays revealed less toxic impact on non-target plants like onion (*Allium cepa* L.) (Grillo et al., 2014; Pereira et al., 2014). A study on nanoformulation of atrazine foliar interaction with Indian mustard (*Brassica juncea* (L.) Czern.) plants revealed herbicidal activity directly through the vascular tissue of the leaves (Bombo et al., 2019). This showed great potential to maintain herbicidal activity at low concentrations and substantial upsurge in the herbicidal efficacy. Similarly, atrazine-loaded nanocapsules were more effective against slender amaranth (*Amaranthus viridis* L.) and hairy beggarticks (*Bidens pilosa* L.) than commercial atrazine product (Sousa et al., 2018). Thus, nanoformulations have emerged as efficient nanoherbicides to manage the weeds as well.

Little is known about the possible ecotoxicological impact of nanopesticides. The first ecotoxicological life history trait data on earthworms (good indicators of soil health) was published by (Heckmann

et al., 2011). They screened different inorganic nanoparticles (Ag, Cu, Ni, Al₂O₃, SiO₂, TiO₂ and ZrO₂) for toxicity on earthworms and confirmed the toxicity of Ag, Cu and TiO₂ nanoparticles. The total reproductive failure of earthworms was observed with both Ag treatments (Heckmann et al., 2011). The earthworms can also sense and avoid the soils containing Ag nanoparticles which suggest unpredictable effects on the behavior of non-target organisms. The reproduction of earthworms was significantly reduced when they were exposed to AgNO₃ (94.21 mg kg⁻¹) or Ag nanoparticles. However, higher Ag accumulation in tissues was reported when they were exposed to AgNO₃ as compared to the equivalent concentrations of Ag nanoparticles (Shoultz-Wilson et al., 2011). Unrine et al. (2010) investigated the effect of particle size on the oxidation, bioavailability, and adverse effects of manufactured Cu nanoparticles in soils and noted that oxidized Cu nanoparticles had adverse effects in earthworms but only at relatively high concentrations (>65 mg Cu kg⁻¹ soil). The toxicological effects of atrazine on earthworm (*Nsukkadrius mbae*) revealed significantly different concentration dependent LC50 values after different time intervals. Similarly, histopathological manifestations included damage to the chloragogenous layer and the epithelial tissues, prominent vacuolations and pyknotic cells (Oluah et al., 2010). The poly(epsilon-caprolactone) nanocapsules based encapsulated herbicides resulted lower toxicity to the *Pseudokirchneriella subcapitata* and *Prochilodus lineatus* while higher toxicity to the *Daphnia similis* compared to the herbicides alone (Clemente et al., 2014; Andrade et al., 2019). Based on above mentioned risks and other nanoparticle toxicity studies (Unrine et al., 2012; Diez-Ortiz et al., 2015; Pandey et al., 2018; Tiwari et al., 2020), it is obvious that comprehensive risk assessment approaches for nanoparticles are needed to identify beneficial forms of nanopesticides at cellular or molecular level.

2.3. Nano-biosensors for soil-plant systems

Biosensors denote hybrid system of receptor-transducer which are used to sense the physical and chemical properties of a medium in the presence of biological or organic recognition element to detect the specific biological analyte present (Sun et al., 2006). Nanobiosensors are next generation of biosensor which are more compact and linked to sensitized element to detect selective analyte at ultra-low concentration through a physico-chemical transducer. Nano-biosensor technology can help in early detection and rapid decision to enhance crop yields by suitable management of water, land, fertilizers and pesticides. High surface to volume ratio, rapid electron-transfer kinetics, high sensitivity and stability with longer life offer competitive advantages to nanobiosensors over conventional and last generation sensors (Scognamiglio, 2013).

Nanobiosensors contain nano-sized materials that act as bioreceptor on a transducer which provide signal to recognition element to detect single or multiplex analyte. The fascinating features of nanobiosensor are fictionalization, immobilization and miniaturization that integrate biocomponents of a transduction system into complex architecture to improve the analytical performance of NMs (Fig. 1) (Arduini et al., 2016). The nanobiosensors work based on turn off/on mechanism, detect analyte concentration within parts per trillion (ppt) and limits the analyzed matrix based on nano-formulation (Fig. 1) (Antonacci et al., 2018).

The most commonly used nanobiosensors, their sensing strategy and applications in detection of analytes in soil and water bodies are given in the supplementary material (Table S3). Early detection of soil pollutants may help avoid their detrimental effects. Accumulation of potentially toxic metal ions in arable soils and plants above threshold levels is a global problem with serious health hazards. They are detected using optical sensors which are chemical in nature and utilize electromagnetic radiations for detection and their binding with immobilized organic dye in sample changes the optical properties that indicate the concentration of specific analyte (Gruber et al., 2017). Fluorescent and

surface enhanced Raman scattering (SERS) are two common optical sensors using biological macromolecules/reduced metal oxides in their structure for recognition of metal ions in river water or soil bodies. Integration of these nanosystems with microfluid or paper chips strategy can be more promising in deployment of portable nanosensor design for their commercial or industrial application in detection of metal ions (Ullah et al., 2018).

Among pesticides, organo-phosphates, neonicotinoids, carbamates and atrazines are some of dominant classes and their residues even at low concentration persist longer in soil due to low homogeneity. These pesticides are detected using nano-biosensors that employ the piezoelectric transducers with antigen-antibody interaction (Ivask et al., 2002; Přibyl et al., 2006), inhibiting enzymes activity, binding properties of nano-materials and specific anti-bodies. Nonetheless, efficiency of these nano-biosensors may vary according to detection limit and high cost involved in development of antibodies which exist only for about 10% of 800 active ingredients of pesticides hence, may limit their commercial application (Aragay et al., 2012; Liu et al., 2013). Therefore, efficiency of these nano-structured biosensors needs to be improved using pre-treatment and multiple sampling.

Urea is the most-widely used fertilizer for crop production and source of nitrate, nitrite and urease that are ubiquitous contaminants in water causing eutrophication posing environmental implications (Mura et al., 2015; Delgadillo-Vargas et al., 2016). Nanobiosensors are used to detect these contaminants in water and soil based on microfluidic impedimetric and colorimetric assay (Table S1). However, precise and accurate detection of these nitrogenous compounds using

nano-biosensors can provide spatial and temporal variation of nutrients in field to monitor their concentration, fertilizer analysis and their application in precision agriculture.

Some novel materials with improved features of rapid response, sensitivity, stability, and repeated application potential, nano-structured particles are used to monitor soil moisture status. Some of the examples of nanobiosensors coated with ceramic substrate with different range of sensitivity and response fabricated are Ag—Pd interdigitated electrodes and graphene oxide films (Table S1). These sensors exploit properties of NMs and ceramic materials by ion transport and dispersion concentrations of graphene oxide films (Liu et al., 2011; Zhao et al., 2011). In addition, NMs-based biosensor to quantify the soil total carbon, organic matter, sodium chloride, phosphate and residual nitrate are in infant stages for soil analyses, and restricted to in vitro standards and water solutions (Antonacci et al., 2018).

Nanotechnology has also been used to in electronic noses (e-noses) regarded as artificial intelligent systems and next generation of sensors. They have been frequently applied in agriculture to monitor the production processes and to assess the plant diseases, insect infestations and soil/water contaminants (Hu et al., 2019). Although, use of nanotechnology has opened new revolution in smart farming and reduced associated risks, wide use of nanomaterials -based agriculture and food products and less-likely immobilized nano-sensors have raised concerns on human and environmental health. Complexity of nano-bio-eco-interactions limits monitoring their behavior in soils. Therefore, a holistic approach is recommended to understand these interactions in soil-plant-air and ultimately in food chain. Regulatory authorities and

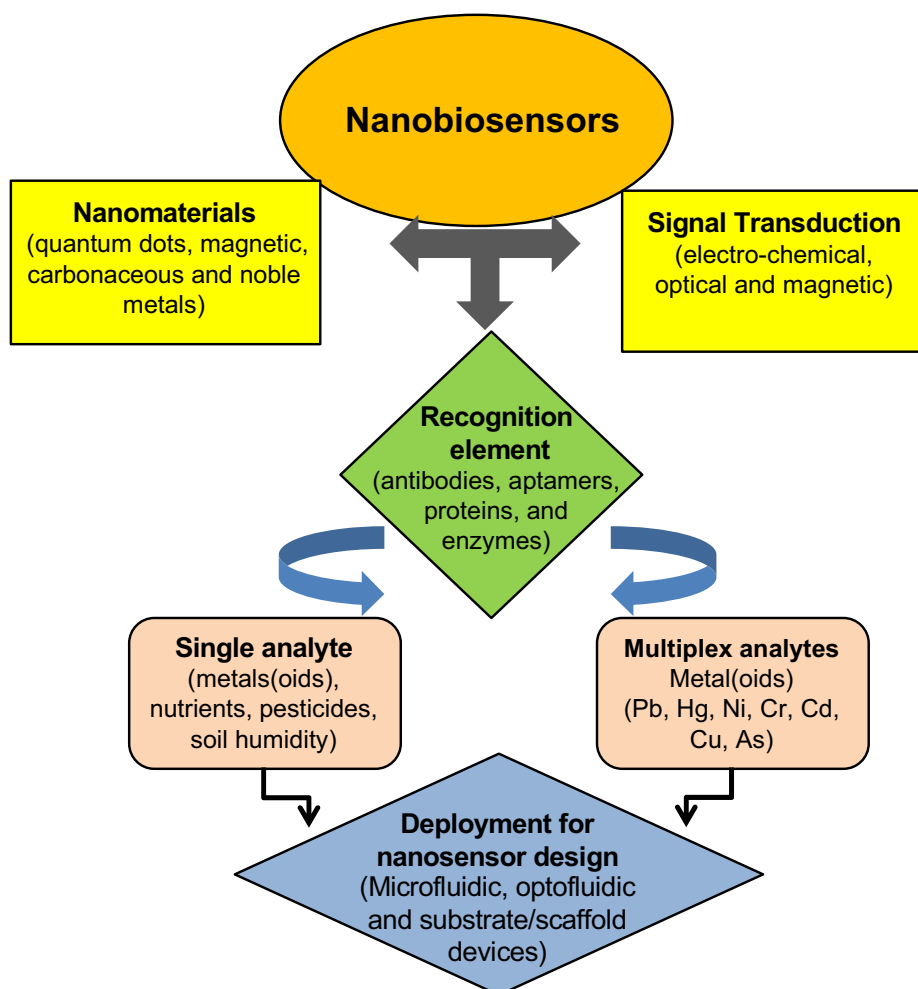


Fig. 1. Mechanistic function of nano-structured biosensors and their designs.

legislation can provide the roadmaps and guidelines for sustainable use of nano-materials to detect, validate and reduce their toxic effects in the whole ecosystem.

2.4. Nanomaterials for soil remediation

This section describes the role of NMs to affect the mobility, transformation and toxicity of various organic and inorganic pollutants. They are widely used in various abiotic and biotic strategies to remove pollutants from contaminated soils. These techniques are detailed in following sub-sections.

2.4.1. Nano-assisted abiotic remediation of contaminated soils

Owing to the smaller particle size, higher surface area and well-established reactivity of NMs, there has been a growing interest in their use to remediate contaminated soils mainly through sorption, reduction or chemical oxidation (Guerra et al., 2018).

Activity and toxicity of soil pollutants, organic and inorganic, is mainly governed by their sorption-desorption reactions with soil constituents (Hamid et al., 2020b). Therefore, amending the contaminated soils with suitable amendments can influence the mobility and toxicity of soil pollutants (Hamid et al., 2019; Hamid et al., 2020a). It proceeds through different sorption processes including adsorption onto mineral surfaces, complexation with organic ligands, ion exchange and surface precipitation (Kumpiene et al., 2008). These amendments are categorized into two groups: (i) mobilization agents which promote the mobility and bioavailability of soil contaminants for an enhanced removal via soil washing and plant uptake, and (ii) immobilizing agents which bind the pollutants in soil and decrease their mobility and bioavailability preventing their entry into the food chain (Robinson et al., 2009). For example, soil washing performance of metal(oid) contaminated soil was improved in the presence of nZVI which adsorbed the metal(oid) and was separated by magnetic separation (Boente et al., 2018). Recovery of adsorbents offers an opportunity to recover the pollutants (for their ex situ treatment or their use as a resource) and reuse of adsorbents in remediation. Moreover, recycling of NMs for its reuse in further treatment cycles is gaining significant attention as it could reduce the remediation cost. Therefore, it is highly demanding to develop NMs which are stable and could retain their treatment efficiency for multiple treatment cycles. It should, however, be noted that regeneration of adsorbents has rarely been reported in context of treatment of contaminated soils as compared to that in wastewater. In this regard, magnetic nanoparticles, owing to high magnetism, offer quick and easy separation from the reaction medium under the magnetic field allowing their recycling or regeneration for further treatment cycles (Usman et al., 2014; Ajmal et al., 2018; Fu et al., 2018). Therefore, magnetic nanoparticles have many potential applications in adsorption and catalytic removal of pollutants (Usman et al., 2018). For example, use of polyacrylamide modified magnetite nanoparticles in soil offered simultaneous control of soil erosion (reduced by 90%) and arsenate leaching (82% immobilization) (Zheng et al., 2020).

In situ immobilization of pollutants has gained significant attention recently as an effective and cost-effective technique to remediate contaminated soils (Hamid et al., 2019). Various amendments based on NMs have been explored in literature to identify a suitable material considering various factors such as cost, efficiency, stability, environmental impacts and reusability of material. Use of nano-hydroxyapatite particles effectively immobilized metal contents in contaminated sediments (Zhang et al., 2010) and soils (Dong et al., 2016) by decreasing their exchangeable fraction which reduced their concentration in pore water (Zhang et al., 2010). For instance, Wang et al. (2014b) reported 80% removal of soil bound Cr(VI) using sodium carboxymethyl cellulose-stabilized nZVI. They proposed immobilization and reduction as the possible removal mechanism based on their XPS findings and elemental distribution data. Further in vitro studies revealed a significant decrease in leaching (82%) and bioaccessibility (58%) of Cr(VI) in the presence of

stabilized nZVI (0.09 g L^{-1}) (Wang et al., 2014a). It also suppressed the bioaccumulation of Cr(VI) in Chinese cabbage (*Brassica rapa* L.) and edible rapeseed (*Brassica napus* L.) by 36 and 61%, respectively after 72 h remediation. Abiotic reductive transformations alone or accompanied by immobilization play a critical role in the fate, mobility, and toxicity of redox sensitive contaminants in soil. For example, addition of nZVI in pyrene contaminated soil resulted in strong reducing conditions to remove pyrene via reduction (Chang and Kang, 2009). Type of ZVI and iron dosage controlled the reaction kinetics as nZVI was more effective ($k = 0.135 \text{ min}^{-1}$) to reduce pyrene than micro-ZVI ($k = 0.103 \text{ min}^{-1}$). Singh et al. (2012) reported complete reduction of Cr(VI) in contaminated soil using nZVI (0.10 g L^{-1}) after 2 h in batch conditions. They also performed soil windrow experiments to test the efficiency of nZVI (5 g L^{-1}) in field where 99% of Cr(VI) was reduced after 40 days (Singh et al., 2012). Owing to the strong reducing capacity, nZVI has been widely used to remediate contaminated soils but it tends to agglomerate rapidly due to its nano-sized particles and magnetic properties which decreases its mobility and remediation efficiency. Therefore, different strategies have been explored to improve its stability in contaminated soil including its stabilization and surface modification by using sodium carboxymethyl cellulose-stabilized nZVI (Wang et al., 2014a), starch (Reyhanitabar et al., 2012), biochar (Su et al., 2016) or by choosing a green synthesis method (Wang et al., 2019).

Nanomaterials are also applied for catalytic degradation and mineralization of organic pollutants in contaminated soils through advanced oxidation processes (AOPs) which use different oxidants. Dosing of hydrogen peroxide (H_2O_2) or persulfate ($\text{S}_2\text{O}_8^{2-}$) along with soluble Fe(II) can generate highly reactive radicals (HO^\bullet or $\text{SO}_4^{\bullet-}$) for an effective oxidative degradation of organic pollutants.

However, these processes are mainly limited by the acidic pH (<4 required to avoid Fe(II) precipitation) and associated demerits including the cost of initial acidification, and adverse effects on the soil quality and microbes. Therefore, instead of soluble Fe(II), use of solid iron phases has been advocated to allow the chemical oxidation without pH modification (Usman et al., 2012a, 2013, 2018). For example, magnetite (Fe(II) Fe(III)₂O₄) catalyzed H_2O_2 and $\text{S}_2\text{O}_8^{2-}$ oxidation systems were very effective to remediate hydrocarbon contaminated soils (>80% treatment efficiency) while soluble Fe(II) exhibited weak catalytic efficiency (<15%) at neutral pH (Usman et al., 2012b, 2012c). However, soil application of these treatments was limited by pollutant availability, organic matter and soil matrix (Usman et al., 2013, 2016a, 2016b). Use of chelating agents is also recommended along with iron particles. For example, (Jorfi et al., 2013) tested iron-nanoparticles along with various chelating agents in Fenton oxidation to remediate pyrene contaminated soil. Oxidation efficiency varied according to the nature of chelating agents and was maximum (93% removal) for sodium pyrophosphate. It is worth mentioning that endogenous Fe can also effectively catalyze the chemical oxidation depending upon the nature of soil and Fe contents (Santos et al., 2018). Iron addition was, therefore, required during Fenton oxidation of gasoline-contaminated soils with low Fe content (1.5 g kg^{-1}) while soils rich in endogenous Fe ($30\text{--}216 \text{ g kg}^{-1}$) did not require any additional Fe (Santos et al., 2018). Despite strong efficiency of chemical oxidation to degrade organic pollutants, application of chemical oxidation can lead to the loss of organic matter while decreasing the soil's revegetation potential and changing the fertility status (Usman et al., 2016b).

The contact between "pollutant/catalyst/oxidant" plays a crucial role to affect the oxidation efficiency, and therefore, catalyst particles with greater mobility have better chances to reach and react at the contaminated targeted areas (Usman et al., 2016b). Mobility of catalyst minerals is strongly related to their particle size (micro or nanoparticles) and composition (Jiang et al., 2010). It should, however, be noted that almost all soil remediation studies, involving chemical oxidation and reduction, were performed in batch slurry system at lab scale whereas immobilization has also been extended to the pot and field. However,

limited data are available in column systems or for field applications which should be focused in future studies. It would require thorough investigation on the fate, mobility and injection mode of nanoparticles in soil. Batch tests are usually the first step to evaluate and optimize the remediation efficiency. On the other hand, column studies are considered as better representative of real field conditions and are performed under water-unsaturated conditions (vadose zone) and water-saturated conditions (aquifer) before lysimeter test in field conditions and ultimate field application of a treatment. These experimental setups are shown in Fig. 2. Thus, upscaling of reduction, immobilization and chemical oxidation strategies based on nanomaterials should be put forward for field application.

2.4.2. Nano-assisted bioremediation of contaminated soils

Bioremediation is an in situ, natural, environment-friendly, cost-effective and adaptable strategy to decontaminate noxious pollutants (organic and inorganic). However, its efficiency may be limited due to long treatment time, poor pollutant availability, low remediation efficiency in highly contaminated soils caused by toxicity of pollutants to biological agents (bacteria, fungi, plants etc.), and formation of toxic by-products (Cecchin et al., 2017). Use of NMs in integration with bioremediation offers solution to overcome limitations associated with this green technology. Although, NMs have been used for chemical decontamination of sites since last two decades (Section 2.4.1), their integration in bioremediation is relatively a new field and is in developmental phase. The integrated (nano-bio) system can be in sequential order or simultaneous to remediate the contaminated soils.

2.4.2.1. Nanomaterials for bioremediation of organic pollutants.

Integration of two very effective remediation methods (nano-bio) is a great breakthrough for decontamination of soils contaminated with organic pollutants. Recalcitrant organic pollutants can be subjected to dechlorination/dehalogenation process by highly reactive NMs followed by bioremediation for an effective remediation. For example, Bokare et al. (2010) studied the integration feasibility of reductive process using palladium (Pd)/Fe followed by bioremediation process for remediation of triclosan (2,4,4'-trichloro-2'-hydroxydiphenyl ether, TCS) contaminated solution (5 g L^{-1}). Pd/nFe caused rapid reductive dechlorination of triclosan under anaerobic conditions with production of 2-

phenoxyphenol as the single dechlorination product. Subsequently, 2-phenoxyphenol was completely oxidized through the application of laccase enzyme produced by *Trametes versicolor* in the presence syringaldehyde, a natural redox mediator. Singh et al. (2013) investigated the treatment of lindane (gamma-hexachlorocyclohexane) contaminated soil using stabilized Pd/Fe⁰ bimetallic nanoparticles (CMC-Pd/nFe⁰) followed by bioremediation using *Sphingomonas* sp. strain. They noted better bacterial growth and degradation efficiency (1.7–2.1 times) of lindane in combined system due to stimulatory impact of nanoparticles on the *Sphingomonas* sp. Strain (Singh et al., 2013). Le et al. (2015) evaluated the coupling potential of chemical oxidation by a nanoparticle and biodegradation for remediation of PCBs (Aroclor 1248). During the first step, 99% tri-, 92% tetra-, 84% penta-, and 28% hexachlorinated biphenyls were dechlorinated using a bimetallic nanoparticle Pd/nFe. During second step, *Burkholderia xenovorans* biodegraded the remaining biphenyls. No toxic impact of nanoparticles to *Burkholderia xenovorans* was observed (Le et al., 2015).

Nanomaterials may also be helpful in bioremediation of organic pollutants from soil by increasing the bioavailability of organic pollutants to the bioagents used for remediation. Pollutants adhered to the NMs could be accumulated by plants simultaneously with small-sized nanoparticles. In addition, altered membrane selectivity due to phytotoxic NMs may also facilitate uptake of organic pollutants (Gong et al., 2018). De La Torre-Roche et al. (2012) investigated the impact of fullerene exposure on accumulation of DDE (a metabolite of DDT) in three plants including winter squash (*Cucurbita pepo* L.), soybean, and tomato (*Solanum lycopersicum* L.) grown in vermiculite medium. Exposure of fullerene increased uptake of DDE significantly (30 to 65%) in all plant species. They suggested co-uptake of NMs and pollutants as one of the possible mechanisms of enhanced uptake.

In addition to affecting the bioavailability/bioaccumulation of organic pollutants, NMs could impact bioremediation though reducing the toxicity of pollutants to bioagents. Wu et al. (2016) studied the impact of Ni/Fe bimetallic nanoparticles on the translocation and toxicity of polybrominated diphenyl ethers (PBDEs) to Chinese cabbage. Application of NMs significantly reduced the phytotoxicity of PBDEs to the plants. This suggests that coupling of NMs and bioremediation could reduce the toxicities of soil contaminants and NMs in the plants simultaneously. Nevertheless, coupling could also aggravate the toxicity of

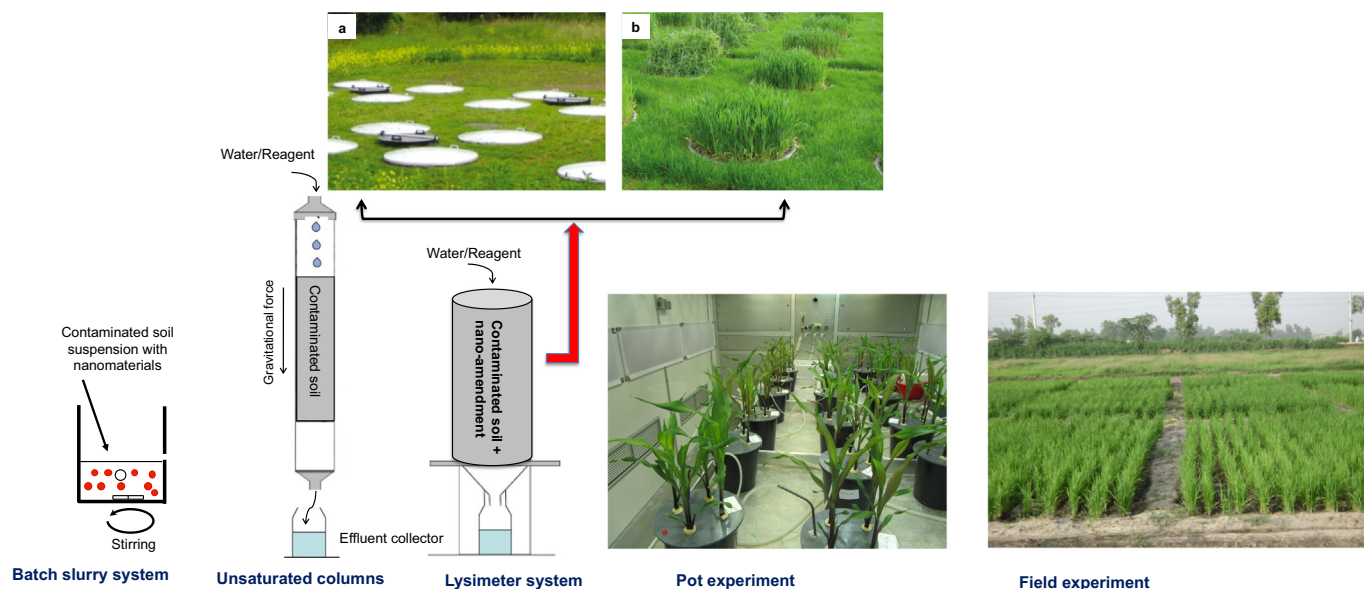


Fig. 2. Different phases of experimental setup used for laboratory to field application to investigate remediation of contaminated soils. Batch tests are used to optimize the remediation efficiency under stirring while column studies are chosen due to better representation of real field conditions. Lysimeter tests are mostly applied in field conditions in large soil columns with bare soil (a) or soil covered by vegetation (b). Pot experiments allow investigations with plants under controlled conditions. Field experiments represent the ultimate studies in real field conditions. Batch and column setups are adapted from Usman et al. (2016b) while images a and b are borrowed from UGT-GmbH.

pollutant by synergistic effect. Schwab et al. (2013) reported negative impact of addition of carbon nano tubes (CNTs) on *Chlorella vulgaris* grown in diuron contaminated soil.

2.4.2.2. Nanomaterials for bioremediation of inorganic pollutants. Nanomaterials can significantly improve the phytoremediation efficiency of heavy metals in contaminated soils. Singh and Lee (2016) investigated the impact of nano-titanium dioxide (TiO₂) on Cd accumulation by soybean plants from soil. The addition of TiO₂ improved uptake of Cd in plants and reduced Cd toxicity to soybean plants by protecting plants from oxidative damage and scavenging free radicals produced due to Cd toxicity. Liang et al. (2017) studied the collective impact of nano-hydroxyapatite (NHAP) and nano-carbon black (NCB) on lead (Pb) phytoextraction by ryegrass (*Lolium temulentum* L.) from soil in a field experiment as an enhanced remediation technique. Application of NHAP or NCB significantly mitigated the phytotoxicity of Pb to the ryegrass and increased phytoextraction potential of ryegrass. NHAP was found more suitable for in situ remediation of soils contaminated with Pb than NCB. Nanomaterials can alleviate metal toxicity in plants through regulation of gene expression associated with metal stress, oxidative stress, water homeostasis, cell wall formation, photosynthetic pathways and cell division (Khodakovskaya et al., 2012; Kaveh et al., 2013; Nair and Chung, 2014). Hu et al. (2015) proposed that NMs could increase accumulation of heavy metals in plants by modulating cell wall permeability, transporter gene expression and co-transportation of heavy metals with NMs. Conversely, negative impacts of NMs on phytoremediation efficiency have also been reported. For example, Tang et al. (2015) reported aggravated Cd toxicity in *Microcystis aeruginosa* by enhancing ROS generation because of combined effects of graphene oxide (GO) and Cd. It is worth noting that different NMs have differential impact on heavy metal uptake or toxicity in plants (Gong et al., 2018).

3. Fate of nanomaterials in soil

Natural colloids and organic and mineral fractions could interact with NMs which would lead to their partitioning in solid and aqueous phase of soil system (Darlington et al., 2009; Ben-Moshe et al., 2010). Limited data are, however, available about fate and behavior of NMs in the soil system as most of the research has been carried out in water systems. As a matter of fact, behavior of NMs in soil systems has been mostly deduced from studies in soil suspensions. Fig. 3 describes various processes involved in the fate of NMs in soil which control their reactivity, mobility, stability and toxicity.

Upon entering soil, NMs can undergo physical, chemical and/or biological transformations depending on their nature and on their interactions with various soil components (organic and inorganic). Aggregation is the major physical process which occurs spontaneously when NMs are introduced into the soil environment. Aggregation reduces the available surface area of NMs which affects their reactivity. Moreover, increase in size of aggregate will decrease their mobility in porous media which will affect reactivity and behavior of NMs (Lowry et al., 2012). There are two distinct forms of aggregation: homoaggregation between the same NMs and heteroaggregation between NMs and another particle in environment (heteroaggregation) e.g., natural colloids (Lowry et al., 2012; Batley et al., 2013). Heteroaggregation is usually more important than homoaggregation because higher concentration of environmental particles than the NMs would favor the heteroaggregation especially at pH region between the PZCs of the natural colloid and NMs (Lowry et al., 2012; Cornelis et al., 2014). Absence of electrostatic repulsion at this pH region and opposite surface charges of NMs and natural colloids favors the heteroaggregation (Kim et al., 2012). However, use of higher contents of TiO₂ nanoparticles (1.0 g L⁻¹) versus kaolin clay (0.13 g L⁻¹) resulted in pronounced homoaggregation (78 ± 16.2%) than heteroaggregation (22 ±

2.2%) but proportion of homo/hetero- aggregation changed in the presence of phosphate or *E. coli* (Xu et al., 2020). For example, presence of *E. coli* changed these values to 51.3 ± 7.9% and 43.7 ± 13.1%, for nTiO₂-nTiO₂ homoaggregates and nTiO₂-kaolin heteroaggregates, respectively. Soil colloids were noted as carriers of strongly adsorbed Zn oxide nanoparticles and their aggregates were visually associated with soil clay minerals by electron microprobe (Zhao et al., 2012). Therefore, heteroaggregation is more likely to control the fate of NMs in natural settings. Despite these arguments, the most aggregation studies focused on homoaggregation. Moreover, heteroaggregation has typically been investigated with high concentrations of NMs in the presence of low concentrations of natural colloids (Batley et al., 2013).

Soil colloids and minerals, particularly clay and iron minerals, are considered as important sink for NMs. Quantification of NMs concentration in different particle-size fractions of soil highlighted the importance of soil colloids with an emphasis on water-dispersible colloids that retained higher amounts of MWCNTs (Zhang et al., 2017) and Ag nanoparticles (Makselon et al., 2018). Han et al. (2008) studied the effect of soil clay minerals (kaolinite and montmorillonite) on the stability of surfactants-stabilized MWCNTs which were deposited in the presence of these minerals. It was suggested that presence of these minerals will hinder the movement and affect the stability of MWCNTs in soils or sediments (Han et al., 2008). Recently, Xu et al. (2020) suggested that titanium dioxide nanoparticles (TiO₂) could preferentially form aggregates with kaolin. However, transport of these aggregates could increase in porous media in the presence of phosphate and *E. coli* due to changes in aggregation state and enhancement in repulsive interactions with the porous media.

Soil organic matter (SOM) is another crucial factor with substantial effects on fate and behavior of NMs mainly through adsorption and stabilization (Lei et al., 2018). Adsorption of SOM would result in surface coverage of NMs and thereby decreasing their active surface area which can significantly mitigate the potential effects of NMs (Li et al., 2008). Toxicity of nC₆₀ was eliminated after adsorption of HS at concentration as low as at 0.05 mg L⁻¹ (Li et al., 2008).

Soil organic matter may exhibit contradictory effects on the mobility and stability of NMs depending upon their nature. On one hand, SOM was observed to accelerate aggregation of NMs by bridging flocculation. On the other hand, it can improve stability of NMs by increasing their electrostatic stability (Philippe and Schaumann, 2014; Klitzke et al., 2015). In a recent study (Gao et al., 2019), increase in SOM was correlated well to an increased solubility of copper oxide NMs in soil highlighting the role of SOM to control the solubility of these NMs. Zhang et al. (2011) found that peat in dissolved form prevented aggregation of MWCNTs through both electrostatic repulsion and steric hindrance in the presence of Na (>4 mM) or in solutions of pH ≥ 4. Contents of SOM and Fe minerals were found responsible to dictate mobility and stability of TiO₂ nanoparticles in three soils characterized by different charges (Zhang et al., 2019). Organic matter may also contribute in bringing negative charge to NMs resulting in electrostatic destabilization of the initially positively charged particles under environmental pH such as magnetite (pH_{PZC} = 8) (Philippe and Schaumann, 2014; Lei et al., 2018). However, Zhang et al. (2012) found very limited deposition of nC₆₀ even at low flow velocities in columns of pure quartz. Transport of nC₆₀ was strongly inhibited in heterogeneous sandy soil with low SOM content. However, Johnson et al. (2009) reported a strong increase in mobility of nZVI through granular media in the presence of SOM. They attributed this effect to reduced sticking coefficient in the presence of sorbed SOM. Addition of humic acid significantly increased the mobility of metal oxide nanoparticles (CuO, Fe₃O₄, TiO₂, and ZnO) in a series of column experiments (Ben-Moshe et al., 2010). Moreover, nature of organic matter fractions and solution chemistry imparts significant alterations in the behavior of nanoparticles (Ghosh et al., 2008). Presence of humic acids greatly enhanced the stability of aluminum oxide nanoparticles at the pH of PZC or above it. However, acidic conditions

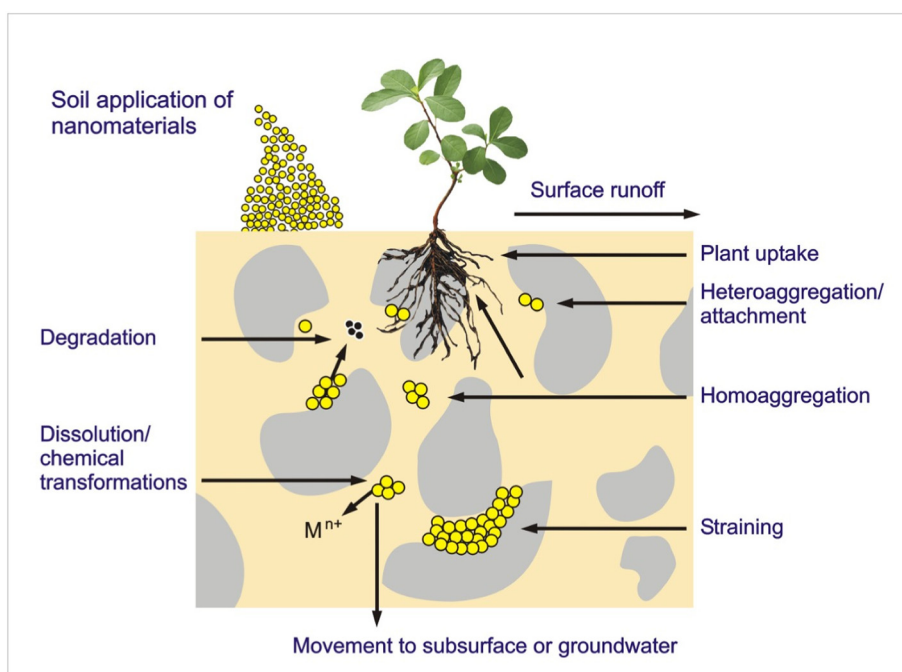


Fig. 3. Fate of nanomaterials in soil system. Adapted from Batley et al. (2013).

resulted in strong aggregation in the presence of HA (Ghosh et al., 2008). Short chained OM showed preferential adsorption on silver nanoparticles as compared to the long-chained aromatic OM (Klitzke et al., 2015). Stabilizing effect were also concentration dependent as silver NMs showed higher stability at higher concentrations of NMs in the presence of organic matter (Klitzke et al., 2015). Very recently, Xu et al. (2019) suggested that heterogeneity of SOM fractions should also be considered in addition to the total SOM contents. They compared the effects of two primary fractions of SOM on the mobility of hydroxyapatite nanoparticles which was inhibited by mineral-associated organic matter due to surface deposition and mechanical straining. On the other hand, dissolved organic matter improved the mobility of hydroxyapatite nanoparticles by increasing electrostatic repulsion among these nanoparticles and soil surfaces (Xu et al., 2019).

Chemical transformations of NMs proceed via biotic or abiotic pathways and involve oxidation, reduction, degradation, dissolution, sulfidation, surface modification, degradation of surface coating etc., (Lowry et al., 2012; Lei et al., 2018). Many NMs are composed of constituents which are sensitive to oxidation-reduction such as silver and iron. Oxidation of mixed-valent Fe(II)-Fe(III) minerals can decrease structural Fe(II) and can alter their stoichiometry (Fe(II)/Fe(III) ratio) (Usman et al., 2018). Stoichiometry of mixed-valent Fe minerals has a crucial role in dictating the reactivity of these minerals for environmental remediation (Usman et al., 2018). Sulfidation of Ag nanoparticles caused a significant decrease in their toxicity due to the lower solubility of silver sulfide which effects their persistence in environment (Levard et al., 2012). Surface coating of NMs can also affect their mobility and retention as it was the case for Ag NMs which showed higher mobility after being coated with citrate and polyvinylpyrrolidone (He et al., 2019). This was associated to the obstruction of surface sites which were initially available to retain Ag NMs. Similar was found true for dimercaptosuccinic acid coated magnetite in a wetland soil that showed different impacts on the mobility of trace elements (Al-Sid-Cheikh et al., 2019). Further investigations are, however, required to better assess the impact of coating of NMs on their fate as well as their efficiency. Uptake of NMs by plants is detailed in Section 4.3.1.

4. Effect of nanomaterials on soil/plant system

4.1. Effect of nanomaterials on soil organic matter

Soil organic matter directly affects soil physical, chemical and biological properties and its accumulation in soil is of great concern for better crop production and to minimize global warming. In agricultural ecosystems, SOM decomposition is directly affected by inherent factors (climate and soil properties) and anthropogenic activities including cultural practices as well as agricultural inputs, especially fertilizers and pesticides (Johnston et al., 2009). The use of nanotechnology in modern agriculture may also have significant impacts on SOM dynamics. But these impacts may vary depending on nature of SOM as it can be either hydrophilic such as HS or hydrophobic (non-humic) and their decomposability in soil also differs because of differences in their biochemical composition (Grillo et al., 2015).

Recent studies demonstrated contradictory effects of ENMs on SOM dynamics because of different experimental conditions, soil properties and ENMs dosage used in the experiments (Schlich and Hund-Rinke, 2015; Rahmatpour et al., 2017; Shi et al., 2018). Using Ag nanoparticles at low dose have non-significant impacts on SOM dynamics (Rahmatpour et al., 2017). Similarly, metal-oxide nanoparticles (CuO and Fe₃O₄) had no effect on total SOM, except changes in biochemical composition (Ben-Moshe et al., 2013). On the other hand, other type of metal oxides, like TiO₂ nanoparticles, helped in stabilizing SOM by photo-oxidatively coupling humic molecules together through covalent bonds (Nuzzo et al., 2016). In general, these TiO₂ nanoparticles do not affect the microbial-derived SOM dynamics but can decrease SOM decomposition by improving its stability due to its complexation with HS (Simonin et al., 2015). In contrast, the application of ZnO nanoparticles reduced litter-derived organic carbon decomposition efficiency up to 130% due to decreased microbial activities (Rashid et al., 2017b). In another study, they found that Fe₂O₃- nanoparticles application also reduced CO₂ emissions up to 30% indicating less SOM decomposition with nano-material application in soil (Rashid et al., 2017a). These NMs can sequester organic carbon in soil by reducing soil CO₂ emissions which can contribute in lowering global warming. While, Shi et al. (2018)

found that higher concentrations of CuO nanoparticles can even result in decreased SOM contents in paddy soils.

4.2. Effect of nanomaterials on soil microbes

Soil microorganisms are very good indicators of soil quality as they directly influence soil quality especially SOM dynamics and nutrient cycling (Dinesh et al., 2012). NMs are localized in soil micro-aggregates (2–53 and <2 μm) and are in direct contact with the most of inhabiting microbial communities as 40–70% of total soil bacteria are present in these micro-aggregates (Vottori-Antisari et al., 2013). It is very important to know how these NMs applied in soil can affect the microbial structure, diversity, and their activities in soil. It is reported that soil microorganisms can be directly affected either due to the toxicity of added NMs or indirectly by amplifying the bioavailability of other toxic compounds already present in soil (Simonet and Valcárcel, 2009). The toxicity of these nanoparticles on microbial activities and functioning is highly variable depending on the type of nanoparticles, as inorganic nanoparticles (metal and metal oxide) have higher toxic potential than organic nanoparticles (fullerenes and carbon nanotubes) (Simonin and Richaume, 2015; Rajput et al., 2018). In general, Gram -ve bacteria are often less sensitive towards ENMs than the Gram +ve bacteria because of their different cell wall structures (McKee and Filser, 2016). Nonetheless, in this respect there is no unanimity in the literature, as Ag nanoparticles are more toxic for Gram -ve bacteria (Ingle et al., 2014). The carbon based nanoparticles had severe impacts on the functional genes and pathways of soil microbial communities (*Archaea, Bacteria and Eukarya*) involved in C and N cycles, but S and P cycles were less vulnerable (Wu et al., 2020). Similarly metals and metal-oxide nanoparticles may also act as antimicrobial agents (Dinesh et al., 2012). In addition, use of these NMs in pure cultures inhibited the growth of plant growth promoting rhizobacteria (PGPRs) and other bacterial species involved in N cycle (Mishra and Kumar, 2009). Nano-sized metal oxides such as TiO₂ and ZnO caused reduction in microbial biomass carbon (MBC), especially Gram -ve bacteria (Ben-Moshe et al., 2013; Rajput et al., 2018; Rashid et al., 2017b). In another study, soils were exposed to different doses of nano-particulates of TiO₂ and ZnO in microcosms for over 60 days, which showed that these NMs reduced MBC and have negative impact on substrate induced respirations, showing reduced microbial activity. Meanwhile, soil bacterial community shifted and diversity declined due to these NMs which affected the enzymatic activities (Ge et al., 2011). Similarly, ZnO and Fe₂O₃ nanoparticles significantly decreased MBC and the cultivable heterotrophic bacterial and fungal colony forming units (Rashid et al., 2017a, 2017b).

Tong et al. (2016) reported the minimal impact of C₆₀ NMs of different particle sizes on MBC as well as their enzyme activities. Other metal-oxide nanoparticles (CeO₂, Fe₃O₄ and SnO₂) also showed no impact on MBC but microbial biodiversity was significantly changed, determined by bacterial/fungal biomass ratios (Ben-Moshe et al., 2013; Vottori-Antisari et al., 2013). In contrast, Fe-oxide nanoparticles stimulated bacterial growth, especially of *Actinobacteria* by enhancing urease and invertase enzyme activities. Although bacterial abundance did not change but there were significant changes in bacterial community structures (He et al., 2011). A recent long-term study for two years also showed a positive impact of applying low concentration of nZnO and nCuO (10 mg kg⁻¹) on microbial population and enzymatic activity (Joško et al., 2019). In another study, denitrification was significantly inhibited (11 fold increase in NO₃⁻ concentration) while use of lower concentrations of nCuO (10 and 100 mg kg⁻¹) did not show any significant inhibitory effect (Zhao et al., 2020). These contrasting effects of nanoparticles on microbial biomass and their activities were mainly dependent on their dose added in soil, as it was revealed that Ag nanoparticles had only negative impact on microbial functioning when high dose of Ag was added in soil (He et al., 2016; Rahmatpour et al., 2017). Published literature also indicated that most of nanoparticles

(Ag, Al₂O₃, TiO₂, CuO, ZnO etc.,) had negative impacts on soil microbial communities, whereas studies with nanoparticles of Si, Fe, Au, Pd, Ag₂S had either no or very little effects (Suresh et al., 2013; Simonin and Richaume, 2015; Rajput et al., 2020). As these effects differ between metals and are not necessarily negative, and they may be nano-specific, it is very important to consider the nanoparticles dose, size and shape as well as soil characteristics while studying the reactions of these nanoparticles with the soil environment.

Nanomaterials may also pose toxicity to the soil microbes. However, this toxicity depends on the nature, particle size, dose, concentration and nature of nanoparticles, and soil type and soil moisture (Chen et al., 2019; Peng et al., 2020). When concentration of NMs exceeds a threshold that may inhibit the growth of many of the soil microbes. This strongly effects the microbial biomass and their community structure (Kang et al., 2019; Peng et al., 2020). Recently, use of biogenic NMs were found less harmful for soil microbial communities compared to their chemically-synthesized analogues and thus, their use has been advocated as an approach to address nanotoxicity in soils (Mishra et al., 2020; Ottoni et al., 2020). Considering very few studies on the use of biogenic NMs in soils, further studies are required to explore their application potential.

4.3. Nano-materials in plants

Application of nanoparticles at pre-optimized rates improves the seed germination, stand establishment, growth and yield formation in several plant species. Nanoparticles also impart tolerance against different biotic and abiotic stresses in plants due to expression of stress-tolerant genes (Van Aken, 2015) and stress proteins (Giraldo et al., 2014). In the following lines, uptake and translocation of NMs in plants has been discussed. The influence of NMs on morphology and physiology of plants is also described.

4.3.1. Uptake and translocation mechanism

The nanoparticles penetrate into the cell membrane and cell wall of the root epidermis through a complex series of events to enter into the plant vascular bundle (xylem), stele and to finally to reach the leaves (Fig. 4) (Tripathi et al., 2017). However, to pass through the intact cell membrane, nanoparticles move through pores on the cell membrane, which is size specific (Rico et al., 2011). Before reaching to the stele, nanoparticles integrate passively through apoplast of the endodermis (Judy et al., 2012). The uptake mechanism of nanoparticles is mostly through active transport and includes other cellular processes as signaling, recycling and regulation of plasma membrane (Etxeberria et al., 2009; Tripathi et al., 2017).

Nanoparticles enter the plant root through osmotic pressure, capillary forces and pores on the cell wall through plasmodesmata connections and/or by symplastic routes (Fig. 4) (Liu et al., 2010; Gao et al., 2011). The NMs enter the plant cell by binding to the carrier protein, through ion channels, aquaporin and endocytosis via formation of new pores (Kurepa et al., 2010). Once the nanoparticles enter the plant cell, it may be transported via apoplast or symplast from one cell to another through plasmodesmata (Hauck et al., 2008). The entry of nanoparticles through cell wall depends upon the pore size of cell wall and smaller size nanoparticles pass through the cell wall easily (Fleischer et al., 1999) while larger size nanoparticles penetrate through stomata, hydathodes and flower stigma (Hossain et al., 2016). The transport of nanoparticles takes place through stomata pores when the particle size is 40 nm or above (Eichert et al., 2008). These nanoparticles accumulate in stomata, instead of vascular bundle and then are translocated to different parts via phloem (Tripathi et al., 2017). The nanoparticles enter through parenchymatous intercellular spaces in seed coat (Lee et al., 2010). However, in the seed coat, the aquaporins are involved in regulating the entry of nanoparticles (Abu-Hamdah et al., 2004).

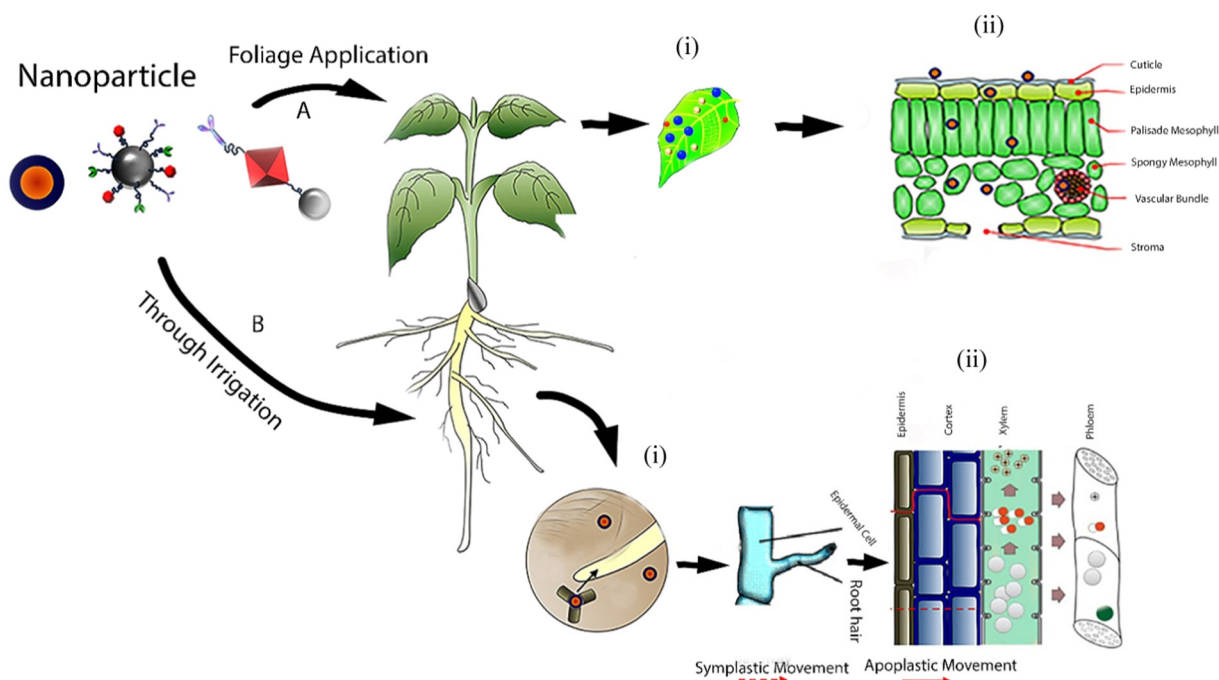


Fig. 4. Uptake and translocation mechanisms of nanoparticles in plant through leaf and roots. (A) uptake of nanomaterial by foliage application (i) nanomaterial penetrates into leaf cuticle (ii) enters into palisade and spongy mesophyll through epidermis layer and finally penetrates into vascular bundles (B) nanomaterial uptake by plant roots when applied through irrigation (i) penetration of nanomaterial into root hairs (ii) enters into xylem and phloem through epidermis and cortex by apoplastic and symplastic pathways.

4.3.2. Influence of nanomaterials on plants

Upon interaction of nano-materials with plants, several morphological changes take place in plants depending on the concentration and nature of nano-material applied (Siddiqui et al., 2015). Therefore, the influence of nano-materials on plants may be positive or phytotoxic (Aslani et al., 2014; Siddiqui et al., 2015).

Nano-growth stimulants help improve the seed germination (Nadiminti et al., 2013) and later growth stages (Aslani et al., 2014). For instance, soybean seed treatment with nano-TiO₂ and nano-SiO₂ increased the nitrate reductase activity, which in turn stimulated the seed germination, combined application of both NMs was more beneficial (Lu et al., 2002). Seed treatment with TiO₂ (0.25%) nanoparticles in spinach (*Spinacia oleracea* L.) improved the nitrogen assimilation and rate of photosynthesis, which resulted in better growth of spinach (44% increase in dry weight over control) (Zheng et al., 2005; Yang et al., 2006). Soaking of pre-germinated wheat seeds in multiwall carbon nanotubes (MWCNTs) solution (at 40–160 µg L⁻¹) for 4 h, resulted in faster root growth and higher vegetative biomass. However, no influence of MWCNTs (Wang et al., 2012). Soaking of Indian mustard seeds in oxidized MWCNT solution (2.3–46.0 µg L⁻¹) for 4 h improved the uniformity and rate of germination, and increased the root and shoot growth of Indian mustard (Mondal et al., 2011) Likewise, seed soaking of watermelon (*Citrullus lanatus* (Thunb.) Matsum & Nakai) in Fe₂O₃ nanoparticles increased the germination and triggered the plant growth and fruiting behavior (Li et al., 2013). Tomato seed treatment with SiO₂ nanoparticles at low concentration improved its germination (Siddiqui and Al-Wahaibi, 2014). Nanomaterials have wider applications in in vitro culture. For instance, use of Zn as ZnO nanomaterial had more pronounced effect on the growth of tobacco (*Nicotiana tabacum* L.) calli and physiological indices compared to other ZnO forms. The calli accumulated more Zn when received that as NMs. In addition to promotion of calli growth, that also resulted in more protein contents (Mazaheri-Tirani and Dayani, 2020).

The foliar application of ZnO nanoparticles (10 mg L⁻¹) increased the chlorophyll, total soluble leaf protein and phosphorus concentration in cluster bean (*Cyamopsis tetragonoloba* (L.) Taub.) (Raliya and

Tarafdar, 2013). Nanomaterials have been found very effective in improving the plant growth through better and quick germination, and improved nitrogen-fixing ability (Hong et al., 2005; Yang et al., 2006). Foliar application of SiO₂ nanoparticles (5–15 nm; 300 µg L⁻¹) improved the sugarcane (*Saccharum officinarum* L.) growth, under chilling stress, by maintenance of effective quantum yield of cyclic electron flow during photosynthesis and photoprotection (Elsheery et al., 2020).

Although, there are several reports of beneficial effects of NMs (Mondal et al., 2011; Raliya and Tarafdar, 2013; Aslani et al., 2014), application of NMs may be phytotoxic as well (Fig. 5) (Mazaheri-Tirani and Dayani, 2020). However, the positive and toxicity effects depend on dose, size and nature of NM, and duration and conditions of exposure (Mazaheri-Tirani and Dayani, 2020; Noori et al., 2020). For example, Yusefi-Tanha et al. (2020) reported that smaller size CuO nanoparticles (25 nm diameter) were more phytotoxic to soybean than the larger size CuO nanoparticles (50 nm and 250 nm) and dissolved Cu²⁺. They also noted that concentration-response curves for smaller size CuO nanoparticles were linear, whereas the relationships were nonlinear for the larger size CuO nanoparticles (Yusefi-Tanha et al., 2020).

The main effect of toxicity of nanoparticles on plant physiological traits is on germination, biomass, leaf number, and root elongation (Lin and Xing, 2007; Racuciu and Creanga, 2007; Doshi et al., 2008; Lee et al., 2010). The nanoparticles may cause reduction in seed germination, plant elongation and sometime cause plant death (Yang et al., 2017). The negative impacts may include slow growth (Colman et al., 2013), alteration in sub-cellular metabolism (Zheng et al., 2005), oxidative damages to biological membranes (Noori et al., 2020), decreased photosynthetic rate (Barhoumi et al., 2015), chromosomal abnormalities (Raskar and Laware, 2014), disturbance in water transport and water status of the plant (Martínez-Fernández et al., 2016), decrease in plant growth hormones (Rui et al., 2014), and changes in transcription profile of genes (García-Sánchez et al., 2015).

The interaction of plant cell with nanoparticles leads to changes in plant gene expression and associated biological pathways which subsequently affect the plant growth and development (Ghormade et al., 2011; Feizi et al., 2013; Moreno-Olivas et al., 2014). Moreno-Olivas

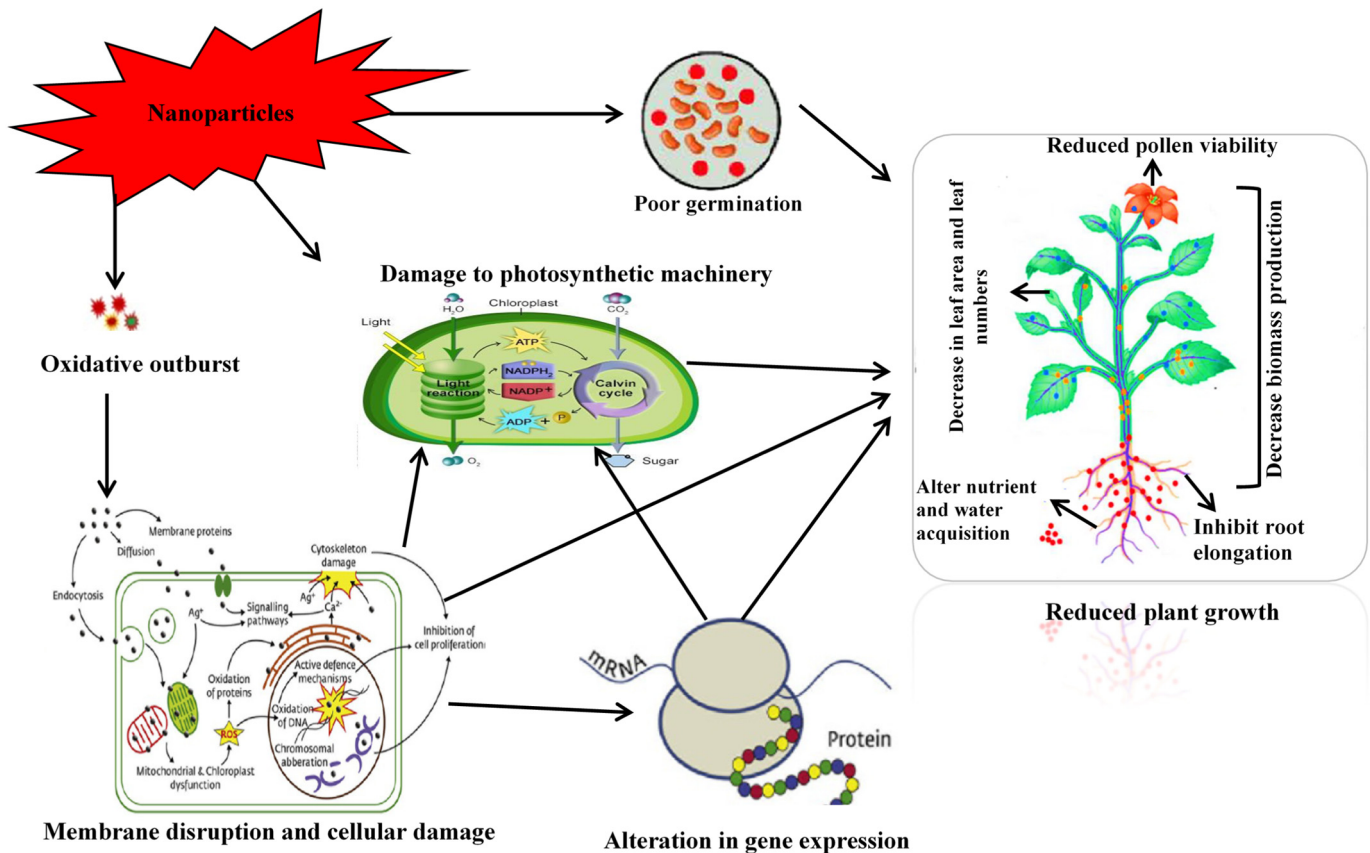


Fig. 5. Toxic effects of nanoparticles on plant growth and development. The higher concentration of nanoparticles causes alteration in morphology and physiological processes of crop plants. Higher concentration of nanoparticles in root zone inhibits seed germination, restricts root development; alters water and nutrient uptake, and decreases leaf development and biomass production. Moreover, nanomaterial toxicity causes oxidative outburst resulting in chloroplast disorganization, reduced photosynthesis, membrane disruption, cellular damage and altered gene expression.

et al. (2014) reported that the use of TiO_2 nanoparticles caused damage to the genomic DNA. Transcriptomic analyses showed the nanoparticles' toxicity in higher plants as these nanoparticles disturbed the link for up and down regulation of genes (Landa et al., 2015). In maize, the exposure of single walled carbon nanotubes upregulated the *SLR1* and *RTCS* genes while, down regulated the *RTH1* and *RTH3* genes (Yan et al., 2013).

The use of fullerene nanoparticles disturbed the pathways of energy and transport of electron by repressing the transcription genes (Hossain et al., 2016). Likewise, the application of nanoparticles up-regulated many genes like genes associated with stresses and water channels (Tripathi et al., 2017). The use of MWCNTs up-regulated the genes *NNtPIP1*, *NtLRX1* and *CycB* that are responsible for water transport, formation of cell wall and cell divisions, respectively (Khodakovskaya et al., 2012). However, application at higher concentration is often toxic. For instance, the application of CeO_2 nanoparticles (2000 and 4000 mg L^{-1}) damaged the structure of DNA in soybean (López-Moreno et al., 2010). Likewise, application of TiO_2 nanoparticles at 2 mM concentration damaged the DNA in tobacco (Ghosh et al., 2010) while at 10 mM damaged the DNA in maize (Ruffini Castiglione et al., 2011). This indicates that pre-testing of NMs for each of the plant species is needed before field application and commercial launch.

4.3.3. Defense mechanism

The exposure of plants to metallic nanoparticles may cause oxidative damage resulting in production of reactive oxygen species (ROS) together with the activation of antioxidant defense mechanism (Rico et al., 2015). The antioxidant defense includes both enzymatic as ascorbate peroxidase, catalase, superoxide dismutase, guaiacol peroxidase and glutathione reductase, etc., and non-enzymatic antioxidants as

glutathione, ascorbate, thiols, and phenolics etc., (Rico et al., 2015; Singh and Lee, 2016). The catalase and guaiacol peroxidase play role in quenching of ROS and peroxy radicals while superoxide dismutase catalyzes the dismutation of superoxide anion into hydrogen peroxide (Rico et al., 2015). The use of TiO_2 nanoparticles may cause photocytotoxicity due to production of ROS, however, these generated ROS radicals may act as signaling molecules to activate the plant antioxidant defense mechanism to detoxify the free radicals (Yin et al., 2012).

In the production of ROS by NMs, the ascorbate peroxidase reduces H_2O_2 into H_2O molecule (Rico et al., 2015). Plants have developed antioxidant potential against nanoparticles-induced oxidative stress (Wei and Wang, 2013). The antioxidant enzymes are activated by several NMs as nFe_2O_4 , nCeO_2 , and nCo_3O_4 induce catalase; nFe_3O_4 , nCeO_2 , nMnO_2 , nCuO and nAu induce guaiacol peroxidase while nCeO_2 , nPt and fullerene induce superoxide dismutase (Tripathi et al., 2017). The application of nTiO_2 in spinach improved the activities of superoxide dismutase, catalase, ascorbate peroxidase and guaiacol peroxidase (Lei et al., 2008). Likewise, Song et al. (2012a) reported enhanced activity of guaiacol peroxidase, superoxide dismutase and catalase. The use of TiO_2 nanoparticles at low concentration (200 mg mL^{-1}) increased the chlorophyll, peroxidase catalase, malondialdehyde contents and superoxide dismutase through the elimination of ROS and at high concentration (500 mg mL^{-1}) TiO_2 nanoparticles causes disruption of cell membrane (Song et al., 2012a).

5. Conclusions and outlook

Nanotechnology has found many applications in agricultural applications such as nanofertilizers, nanopesticides, nanobiosensors or as environmental remediation agents. However, a firm understanding of

nanomaterials' fate and environmental impacts remains a major challenge in agricultural and environmental sciences. Collaborative research among institutes exploring different uses of nanomaterials would be crucial to develop efficient, multifunctional, stable, cost-effective and environment-friendly nanomaterials. This would also facilitate to complete the picture about the role, fate, behavior and ecotoxicity assessment of NMs.

Application of NMs may help improve the growth and yield of crop plants, but response may vary as per plant species. Thus, commercial use of nanomaterials requires thorough investigations into screening and optimization of the nanomaterials for different plant species. Efficiency and behavior of nanomaterials can be tailored by tuning the properties and stability of nanomaterials. Therefore, further progress in the development of innovative and improved synthesis methods with precise control over product composition will be highly useful to improve their efficiency. Role of NMs should also be explored in bioremediation to develop integrated remediation strategies. Moreover, most of the studies on nano-assisted agriculture rely on experiments performed under controlled conditions while limited data is available regarding their field application. More knowledge at field level would be highly useful for large-scale implementation of nano-based strategies.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.scitotenv.2020.137778>.

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