Interactions of Metal-based and Metal-oxide-based Nanoparticles (MBNPs and MONPs) with Crop Plants: A Critical Review of Research Progress and Prospects

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Interactions of Metal-based and Metal-oxide-based Nanoparticles (MBNPs and MONPs) with Crop Plants: A Critical Review of Research Progress and Prospects

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Abstract: Over the past decade, the production and applications of metal-based and metal-oxide nanoparticles (MBNPs/MONPs) have increased significantly due to their enhanced physico-chemical properties and biological activities when compared with their bulk parent materials. Once MBNPs and MONPs enter agricultural soil via direct or indirect pathways, they can interact with crop plants and thus pose a threat to both animal and human health through food chain pathways. Although many review articles on engineered nanoparticles have been published, few have focused on the interaction between MBNPs/MONPs and crop plants, and their current applications. Therefore, we reviewed the sources and behaviors of MBNPs/MONPs in agricultural soil, physiological and biochemical effects of MBNPs/MONPs on plants, uptake, translocation of MBNPs/MONPs in crop plants, factors affecting the interaction of MBNPs/MONPs-plants, and the applications of MBNPs/MONPs. Lastly, we propose where the future research priorities should be focused to provide a better understanding of MBNPs and MONPs. This review will help to promote scientific research regarding MBNPs and MONPs, and understand the risk and benefits associated with them to plants and will contribute to the advancement of nanotechnology.

Keywords: metal-based nanoparticles (MBNPs); metal-oxide nanoparticles (MONPs); crop plants, uptake and translocation; interaction
1. Introduction

Nanoparticles (NPs) can be defined as particles with at least one dimension in the size < 100 nm (Nel et al. 2006). They have been widely applied in medicines, agriculture, electronics, chemistry, energy, diagnostics and environmental remediation due to their unique chemical and physical characteristics (Chen 2018; Du et al. 2017; Lowry et al. 2019; Montes et al. 2017; Nair 2018; Pagano et al. 2018). Nanoparticles are mainly classified into the following types: (1) carbon-based NPs, including single-walled carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs), (2) metal-based NPs (gold, silver, aluminum, and zero-valent iron), metal oxides NPs (TiO$_2$, ZnO, Al$_2$O$_3$, Fe$_3$O$_4$, Fe$_2$O$_3$, NiO, CuO, CeO$_2$, etc.) and metal salts NPs (nanosilicates and ceramics), (3) quantum dots (CdSe and CdTe), and (4) dendrimers (nanosized polymers) and composites (compounds of different NPs or NPs with larger, bulk-type materials) (Hatami et al. 2016; Srivastava et al. 2015; Verma et al. 2018).

Metal-based and metal oxide nanoparticles (MBNPs and MONPs) have exhibited different physicochemical properties and biological activities compared to their bulk parent materials (Chen 2018; Rastogi et al. 2017). The production and use of MBNPs and MONPs has increased in the past decade, they have been mainly used in different commercial applications including medicines, cosmetics, sunscreens, water treatment, and electronics (Keller and Lazareva 2014; Rajput et al. 2018; Servin et al. 2017). It is estimated that titanium dioxide (TiO$_2$) and silicon dioxide (SiO$_2$) have the highest MONPs production rates with 88,000 and 95,000 metric tons/year, respectively.
Similarly, iron oxides (FeO$_x$), aluminum oxides (AlO$_x$), and zinc oxides are produced at rates of 42,000, 35,000 and 34,000 metric tons/year, respectively. Production of cerium dioxide (CeO$_2$) is estimated to be at a rate of approximately 10,000 metric tons/year (Keller et al. 2013). About 8–28% of the above mentioned MONPs are released into the soil environment (Medina-Velo et al. 2017). Figure 1 shows the industries with extensive use of MBNPs and MONPs and their release into the soil environment.

Soil is an important source as well as the primary sink for the accumulation of NPs in the environment (Ma et al. 2018), and the concentration of NPs in soil has been reported to be higher than that in the atmospheric and aqueous environment (Nair 2018). The accumulation of MBNPs and MONPs in agricultural soil may provide the most significant exposure pathway for the entry of MBNPs and MONPs into the food webs (Du et al. 2017). MBNPs and MONPs are integrated into agricultural soils directly (agricultural products) or indirectly (bio-solids) (Cota-Ruiz et al. 2018). The use of MBNPs and MONPs in agricultural products is increasing, including fertilizers, soil remediation additives, herbicides, insecticides and growth regulators (Gogos et al. 2012; Khot et al. 2012; Pan and Xing 2012), and thus directly impacts crop plants (Priester et al. 2017). Crop plants belong to the primary trophic level in the agricultural ecosystem and represent the base of the food chain for animals and human beings (Ruotolo et al. 2018). Thus, it is important to understand the interaction of MBNPs and MONPs with crop plants in order to predict their accumulation in the food chain and their fate in terrestrial environments (Gardea-Torresdey et al. 2014).
Even though a number of reviews on terrestrial plant interaction with engineered nanoparticles (Du et al. 2018; Ghosh et al. 2019; Tolaymat et al. 2017), metal-based nanoparticles (Lv et al. 2019) and metal oxide nanoparticles (Conway et al. 2015; Golbamaki et al. 2015; Rastogi et al. 2017; Zhu et al. 2019) have been published, they do not provide comprehensive information on the potential toxicity of both MBNPs and MONPs on crop plants and their current applications. This highlights the need for critical reviews focused on the interaction of both MBNPs and MONPs with crop plants. Here, we reviewed MBNPs and MONPs in agricultural soil, the effects of MBNPs and MONPs on seed germination, root elongation, plant growth, pigment content, photosynthetic activity, oxidative stress, plant hormones, and their uptake and translocation in crop plants. In addition, the complete mechanism of plant uptake, translocation, and accumulation of MBNPs and MONPs, the most important factors which affect the interaction of MBNPs and MONPs with plants, and applications of NPs in different fields are also discussed. Specifically, we have compared the current and early studies to better understand plants-NPs interactions. Lastly, we suggest future research priorities that will increase our knowledge on MBNPs and MONPs. This review aims to contribute to the advancement of nanotechnology and promote scientific research regarding MBNPs and MONPs, and their associated risks and benefits.

2. MBNPs and MONPs in agricultural soil

2.1 Source of MBNPs and MONPs in agricultural soil

Agricultural soil has been a major sink for the released MBNPs and MONPs. These NPs can enter the agricultural environment via direct and indirect pathways.
(Chen 2018). The major source of indirect NP input is through the sewage sludge land application. In wastewater treatment plants (WWTPs), MBNPs and MONPs tend to be retained and accumulated in the sewage sludge, rather than in the treated wastewater effluent (Durenkamp et al. 2016). It has been confirmed that up to 99% of the MBNPs and MONPs entering the WWTPs are retained within the sewage sludge (Johnson et al. 2011). Direct input of NPs into agricultural soil is mainly performed via the application of nano-agrochemicals, including nanofertilizers, nanopesticides and nanofungicides (Chhipa 2017; Prasad et al. 2017), additives for soil remediation, and growth regulators (Du et al. 2017). Despite the increased focus on NPs in the agricultural environment, the quantity of NPs entering agricultural soil system via direct and indirect pathways, and their potential risks remain unclear (Chen 2018).

2.2 Behavior of MBNPs and MONPs in agricultural soil

The environmental behavior of the released MBNPs and MONPs exerts a critical role in their mobility, toxicity, reactivity and potential risks in agricultural soil. Upon entering the soil matrix, MBNPs and MONPs may undergo aggregation and agglomeration, interaction with dissolved organic matter (DOM), hetero-aggregation with inorganic colloids, and transformation via dissolution and chemical transformations (Chen 2018). Soil colloids, operationally defined by a size between 1 nm and 1 μm, are composed of minerals (clay, iron oxides, etc.) and/or organic components, and play an important role in determining the behavior, mobility and fate of MBNPs and MONPs in soil (El Hadri et al. 2018; Goswami et al. 2017). Agricultural soil generally has plenty of DOM, and the effect of DOM on the aggregation of MBNPs
and MONPs mainly lies in the characteristics of MBNPs, MONPs, DOM and the environment matrix. DOM can be absorbed on the surface of MBNPs and MONPs, thus can usually decrease their aggregation via increased electrostatic stabilization or increased hydrophobicity (Dickson et al. 2012; Ghosh et al. 2010). It is noteworthy that DOM can also enhance aggregation of MBNPs and MONPs through a bridging effect or by changing the critical characters of MBNPs and MONPs aggregation behavior (Mohd Omar et al. 2014). Dissolution of MBNPs and MONPs mainly depends on their particle size, surface coating, surface morphology, soil matrix such as solution chemistry, and the presence of natural organic matter or colloids (Chen 2018).

3. Uptake, and translocation of MBNPs and MONPs in plants

Nanotechnology is rapidly developing and its applications are increasing the risk of MBNPs and MONPs discharge into the environment, particularly to the plant-soil systems. NPs which are discharged into the environment have a greater tendency to interact with terrestrial plants through soil, atmosphere, and water (Rico et al. 2013). Two main pathways—sewage sludge, which usually contains ZnO, Ag NPs, TiO₂ and SiO₂, and nano-agrochemicals (nano-fertilizers, nano-pesticides) are mainly responsible for the introduction of NPs into the soil-plant system (Gottschalk and Nowack 2011; Kah et al. 2018). NP uptake and translocation are related closely to the toxicity induced by NPs to plants. Studies regarding the uptake and translocation of NPs in plant roots and shoots have been carried out in recent years. An overview of those studies will be discussed here. Moreover, a graphical representation of NP uptake and translocation by the plant has been illustrated in Figure 2.
3.1 Plant uptake of MBNPs and MONPs

Plants take up NP by root to leaf and leaf/fruit to root pathways (Ma et al. 2015). NP interferes with the metabolism of plants in different ways such as through plant oxidative processes in plants resulting in an oxidative burst, by providing micro-nutrients to plants, or through gene regulation (Hossain et al. 2015; Liu and Lal 2015).

Generally, the uptake of MBNPs and MONPs occurs when an NP breaches the cell wall. The cell wall of plant cells regulates the particle traffic through pores (Chen et al. 2010; Kurepa et al. 2010). Some NPs are known to produce bigger pores in the cell wall through which NPs with larger sizes can enter (Kurepa et al. 2010), although NP uptake in plants may vary with the species of plant and the conditions of growth (Li et al. 2014; Servin et al. 2012).

Conflicting data exists regarding the uptake of MBNPs and MONPs by plants. Some authors found that TiO$_2$ nanoparticles could not be absorbed by plants, as the average particle exclusion diameter of the root cell wall pores was reduced from 6.6 to 3.0 nm due to prior nanoparticle treatments (Asli and Neumann 2009). Moreover, exposure of plants to well-characterized nanoparticle suspensions in irrigation water also resulted in no detectable translocation (Birbaum et al. 2010). However, it was found that the seedling of *Arabidopsis thaliana* took up TiO$_2$ NP (< 5 nm), which was mixed with Alizarin red S nano-conjugate, and distributed it in cells and tissues. A mucilage that formed a pectin hydro-gel capsule was released by *Arabidopsis thaliana* roots, indicating that roots either facilitate or inhibit the entry of TiO$_2$ NP (Kurepa et al. 2010). The roots of cucumber (*Cucumis sativum*), and wheat (*Triticum aestivum*) could
take up 30–120 nm of Ag$_2$S NP, which can then be transferred to the shoots (Wang et al. 2017b). Zhu, et al. (2008) studied the uptake of Fe$_3$O$_4$ NP (magnetite, 20 nm) by hydroponic pumpkin seedlings and reported that NPs were detected in the leaves, roots and stems. However, no uptake was detected when these seedlings were grown in soil, indicating that the growth medium also plays an important role in the uptake of NP (Zhu et al. 2008). López-Moreno, et al. (2010) examined the uptake of ZnO NP (500–4000 mg/L range) in soybean (Glycine max) seeds and reported that the uptake of Zn was higher at 500 mg/L but uptake was reduced at higher concentrations (1000–4000 mg/L). Ag NPs in zucchini (Cucurbita pepo) plant shoots were found to be 4.7 times higher than plants that were treated with the same concentration of bulk Ag powder and can be explained by ions being released from the Ag NPs in shoots (Stampoulis et al. 2009).

3.2 Translocation and transformation of MBNPs and MONPs

NPs are transported inside the cell through apoplastic or symplastic pathways, and are transported from one cell to another cell through plasmodesmata (Rico et al. 2011) (Figure 2). Apoplastic transport also occurs through cell walls and intercellular air spaces (Sattelmacher 2001; Wang et al. 2012a). The symplastic pathway moves water and other substances between the cytoplasm of adjacent cells (Roberts and Oparka 2003). NPs enter root cylinders and then advance to aerial parts of the plant using the apoplastic pathway (Sun et al. 2014). NPs are also transported to the endodermis (layer of cells which surround the transport system of the plant) inside the root which has a barrier called Casparian strip that limits the entry of solutes and water into the xylem.
The nature and type of the NPs and plant species significantly affects the translocation in plant tissues. Several studies have been carried out regarding the translocation and transformation of NPs in plants. A study about the translocation of ZnO and CeO NPs in soybean plants indicates that CeO NPs were translocated in the form of NPs and transported via xylem from roots to shoots, whereas Zn was bio-transformed into Zn citrate (Hernandez-Viezcas et al. 2013). In another study, bean plants were exposed to CeO$_2$ suspension and it was found that Ce was present in roots in the form of CeO$_2$ NPs, ionic Ce (tri-valent form) and tetra-valent Ce (Ce-IV). Additionally, results also showed the crossing of the Casparian strip by CeO$_2$ NPs and reaching the xylem, thereby enabling further transportation (Majumdar et al. 2014). Similarly, ZnO and TiO$_2$ NPs accumulated in the leaves and stems of the tomato plant (Raliya et al. 2015). It was found that when the pumpkin plant (C. maxima) was exposed to Fe$_3$O$_4$ NPs (20 nm and 0.5 g/L), 1.3% of the total NPs were translocated to its leaves (Zhu et al. 2008).

In contrast, some plant roots did not translocate MBNPs and MONPs to their aerial parts (Wang et al. 2013a). For example, CeO$_2$ NPs (suspension) applied to maize leaves resulted in their absorption, but the NPs were not translocated to the new leaves (Birbaum et al. 2010). Likewise, Wang, et al. (2011) indicated that Fe$_3$O$_4$ NPs were not translocated into the shoots of pumpkin and ryegrass (Wang et al. 2011).

4. Physiological and biochemical effects of MBNPs and MONPs on plants

MBNPs and MONPs are extensively used in numerous products that are released into the environment, therefore it is necessary to study the impacts of these
nanoparticles on plant physiology and biochemistry (Figure 3). Studies have shown both positive and negative impacts of NPs on plants’ physiological and biochemical parameters.

4.1 Effects of MBNPs and MONPs on seed germination

NPs can affect seed germination positively or negatively, depending on the size of the NP, plant species, and exposure level (Rizwan et al. 2017). Several studies regarding seed germination have shown that the size of NPs affects phytotoxicity; the smaller the size of NPs, the more toxic they are to plants. TiO$_2$ NPs at concentrations of 2 and 10 mg/L can enhance the shoot and seedling growth, respectively (Feizi et al. 2012). CuO NPs could badly inhibit *Brassica nigra* seed germination and seedling growth (Zafar et al. 2017). After soaking seeds in 2000 mg/L before incubation, ZnO and Zn NPs were found to inhibit the seed germination of corn and ryegrass (Lin and Xing 2007). The level of seed germination decreased as the size of Ag NPs increased (Thuesombat et al. 2014). However, Yasur and Rani (2013) observed that Ag NPs (up to 4000 mg/L) had no effect on the seed germination in the castor bean (*Ricinus communis* L.). A summary of the effects of MBNPs and MONPs on seed germination and root elongation is depicted in Table 1.

4.2 Effects of MBNPs and MONPs on plant growth and root elongation

MBNPs and MONPs are phytotoxic, inhibit plant growth, and alter the biochemical, physiological and genetic traits. Growth inhibition related phytotoxicity occurs in the form of reduced root elongation, root biomass, leaf growth, decreased yield and delayed flowering (Tripathi et al. 2017a). In contrast to its negative effects on
plant growth, NPs can also be used as nano-fertilizers, nano-pesticides, and growth stimulators (Rastogi et al. 2017; Ma et al. 2015; Wang et al. 2016b). For example, exposure of *Arabidopsis thaliana* to a low dose of Ag NPs ($\leq 2.5$ mg/L) increased plant growth, whereas at a higher dose ($\geq 5$ mg/L), plant growth decreased significantly (Kaveh et al. 2013). Similarly, Cu NPs facilitated the tri-carboxylic acid cycle, glycolysis, and starch degradation in wheat which enhanced plant growth (Yasmeen et al. 2017). ZnO NPs, Au NPs, and TiO$_2$ NPs are reported to enhance plant growth by improving the uptake of nutrients and other essential elements (Singh et al. 2017).

On the contrary, inhibition in plant growth was found in tobacco plants when exposed to TiO$_2$ NPs ($< 25$nm) (Frazier et al. 2014). ZnO NPs ($< 50$nm) decreased the plant growth and altered the anatomy of leaves and root in rapeseed (*Brassica napus* L.) (Kouhi et al. 2015). Similarly, Lee, et al. (2012) have examined the effects of Ag NPs in crop plants (*Phaseolus radiatus* and Sorghum) and found that NPs inhibited plant growth only in agar media but not in soil media (Lee et al. 2012). It is reported that the possible reason for the negative effect on the growth parameters of plants is the release of toxic metal ions from these NPs.

Similarly, roots are the primary target of certain NPs, and the root apex is found to be the most sensitive zone. A study by Kim et al. (2014) revealed that nZVI (zero-valet-iron) enhances the root elongation by 150–200% by encouraging the OH radical to stimulate the loosening of cell wall, while Al$_2$O$_3$ NPs were reported to reduce the root elongation by 40% (5 mg/ml) and 55% (50 mg/ml) in *Triticum aestivum* (wheat) (Yanik and Vardar 2015). CuO NPs are reported to reduce the root growth in chickpea
and soybean (Dimkpa et al. 2012). Moreover, ZnO NPs at concentrations of 400 and 800 mg/kg did not affect the root growth and biomass of corn plants (Zhao et al. 2013), but a higher concentration (2000 mg/L) of ZnO NPs has been reported to cause the inhibition of root elongation in maize and rice (Yang et al. 2015). Table 1 demonstrates the effects of MNBP scouring MNP scoping and MNO P scoping on growth and root elongation.

### 4.3 Effects of MBNPs and MONPs on pigment content and photosynthetic activity

Many studies have shown that MBNPs and MONPs can influence the pigment content and photosynthetic activity in terrestrial plants (Mirzajani et al. 2013; Perreault et al. 2014; Qian et al. 2013; Rao and Shekhawat 2014; Shaw et al. 2014; Tripathi et al. 2017b). TiO$_2$ NPs enhanced the pigment content and photosynthesis in maize (Zea mays) at the reproductive stage (Tan et al. 2018a). When treated with 100 mg/L of CuO NPs for 21 days, negative effects on the photosynthetic activity and pigment content were found in Mung bean (Vigna radiate L.) (Nair and Chung 2014b). Similarly, ZnO NPs (24 ± 3 nm) at 800 mg/kg could reduce photosynthesis, and chlorophyll content but showed no effects at a concentration of 400 mg/kg (Zhao et al. 2015). However, Fe$_2$O$_3$ (6 nm) enhanced the photosynthetic rate in Glycine max (Alidoust and Isoda 2013). Similarly, Ag NPs reduced chlorophyll production and photosynthesis in a marine diatom (Thalassiosira weissflogii) (Miao et al. 2009). The seedling of mung bean (Vigna Radiata) incubated with Mn NPs solution showed improved growth and photosynthetic activity (Pradhan et al. 2013). Table 2 summarizes the effects of MBNPs and MONPs on the photosynthetic activity and pigment content in plants.

### 4.4 Effects of MBNPs and MONPs on oxidative stress and plant hormones
MBNPs and MONPs can produce an excess amount of reactive oxygen species (ROS), thus causing oxidative stress in terrestrial plants (Faisal et al. 2013; Nair and Chung 2014d). The elevated levels of Fe$_3$O$_4$ NPs increased the ROS levels of plant species such as ryegrass (*Lolium perrenne*) and pumpkin (*Cucurbita mixta*), which affected the membrane stability (Wang et al. 2011). High oxidative stress was measured when *Brassica rapa* was treated with 1000 mg/L CeO$_2$ NPs (Tan et al. 2018b). Onion roots (*Alliuim cepa*) showed enhanced generation of ROS when exposed to 0.2, 0.4, and 0.8 g/L of Zn NPs (Ghosh et al. 2016). Some studies have suggested that TiO$_2$, (rutile and anatase) can increase the ROS activity in plants (Fenoglio et al. 2009). Rutile and anatase are two crystal phases of TiO$_2$ (Markowska-Szczupak et al. 2011), which are of great industrial importance. Due to their higher bandgap energy, UV light is sufficient to activate the anatase and rutile phases (3.2 eV for anatase and 3.0 eV for rutile phase) (Shah et al. 2017). Generally, the anatase phase is more toxic than the rutile phase, but unfortunately, it is being used abundantly (Iswarya et al. 2015).

Moreover, some NPs can also affect plant hormones. Plant hormones are organic compounds, which are produced due to the metabolism of plants, and control the reproduction, growth, and development of a plant (Santner et al. 2009). Ag NPs could affect plant hormones such as auxin and cytokinin (Vinković et al. 2017). While on the other hand, CeO$_2$ NPs (500 mg/L) had no significant effect on the hormones of conventional cotton (Nhan et al. 2015). Another study reported that CeO$_2$ NPs had no significant effect on Gibberellic acid (GA), indole-3-acetic acid in the leaves of transgenic cotton but trans-zeatin-riboside (t-ZR) decreased up to 25% when
conventional cotton was treated with 500 mg/L (Le et al. 2014). The effects of different MBNPs and MONPs on oxidative stress and plant hormones are described in Table 3.

5. Factor affecting the interaction of MBNPs and MONPs with plants

The main factors influencing the interaction of MBNPs and MONPs with plants are the size, concentration, and coating material of the nanoparticles, species of plants, and growth medium (Du et al. 2017; Klaine et al. 2008; Mueller and Nowack 2008). Different factors that mainly influence the toxicity/interaction of MBNPs and MONPs have been presented in Figure 4.

5.1 Nanoparticle size and concentration

NP size and concentration are the main parameters that can affect the uptake and translocation of NPs. NPs of the same metal having different sizes and concentrations may have different behaviors toward the physiological processes of the plant. MBNPs and MONPs have particularly drawn considerable attention due to their small-sized particles (e.g. TiO$_2$, NPs, Ag NPs, CuO NPs) and amplified toxicity (Chen 2018). For instance, an A. thaliana plant can take up 20–40 nm of CuO NPs but cannot take up 1500 nm of bulk CuO (Wang et al. 2016c). Likewise, smaller sized TiO$_2$ NPs can penetrate the cell walls of Cucumis sativus (Servin et al. 2012) and Triticum aestivum (Larue et al. 2012) as compared to larger sized NPs (Du et al. 2011). Moreover, smaller sized Zn NPs caused higher toxicity in wheat plants (Dimkpa et al. 2012).

Interaction of plants with MBNPs and MONPs is also concentration-dependent, for instance; ZnO NPs and CeO$_2$ NPs at lower concentrations (50 and 100 mg/kg) have affected the accumulation of certain nutritional elements in soybean plants (Peralta-
Videa et al. 2014), while Ag NPs at a concentration of 50 mg/L decreased the hydrogen-peroxide, proline, and malondialdehyde (MDA) content, thus improving the growth of *Brassica juncea* (Arora et al. 2012). On the contrary, a higher concentration of Fe$_3$O$_4$ NPs (400, 2000, 4000 mgL$^{-1}$), showed increased negative effects on the root length of *A. thaliana* (Lee et al. 2010).

5.2 Surface coating

Surface characteristics of NPs are important in reference to the phytotoxicity of NPs. When basil (*Ocimum basilicum*) was cultivated in hydrophilic (coated with glycerol and aluminum oxide), and hydrophobic (coated with dimethicone and aluminum oxide) TiO$_2$ amended soil, its agronomic parameters and nutritional quality were affected when compared to the unmodified particles (Tan et al. 2017). When lettuce (*Lactuca sativa*) was sprayed by foliar paint (having aged TiO$_2$ NPs [hydrophobic]), TiO$_2$ NPs infiltrated through leaf stomata and translocated into all tissues of the lettuce plant (Larue et al. 2016). CeO$_2$ NPs (coated with citric acid) affected the nutritional components of tomato (*Lycopersicum esculentum*) as compared to uncoated CeO$_2$ NPs (Barrios et al. 2017). Similarly, Zn NPs (coated with alginate) increased the chlorophyll content in the seedling of maize (*Zea mays*) cultivated in soil (Zhao et al. 2013).

5.3 Plant species

Different plant species have different roles in their interactions with MBNPs and MONPs because they have dissimilar morphology and growth habitats (Dev et al. 2018). It was found that the application of CeO$_2$ NPs (500 ppm) could increase the yield of
wheat grain by 36% (An et al. 2008), while no seeds were formed when barely seedlings were exposed to CeO$_2$ NPs (500 ppm) (Rico et al. 2015). *Arabidopsis thaliana* does not tolerate Ag NPs with concentrations above 300mg/L (Sosan et al. 2016). Similarly, ZnO NPs (500 mg/kg) resulted in damage to the leaves of soybean (*Glycine max*) (Priester et al. 2017), whereas leaves of alfalfa (*Medicago sativa*) showed less toxicity upon exposure to ZnO NPs (Bandyopadhyay et al. 2015).

5.4 Growth medium

Interaction of plants with MBNPs and MONPs is not only affected by the properties of NPs (size, concentration, and surface coating) and plant species but is also affected by the media in which these plants/seedlings are cultivated or grown (Montes et al. 2017; Rizwan et al. 2017; Tolaymat et al. 2017). For example, radish (*Raphnus sativus* L.) showed higher growth in CeO$_2$ NPs (1000 mg/kg) introduced in sandy loam as compared to silty loam (Zhang et al. 2017). Phytotoxicity due to ZnO NPs increased when wheat plants were grown in acidic soil but showed no effects when grown on alkaline soil (Watson et al. 2015). The uptake rate of Fe$_3$O$_4$ NP in pumpkin plants (*Cucurbita maxima*) is higher in the hydroponic medium as compared to plants grown in soil (Zhu et al. 2008). CuO NPs resulted in the reduction of root elongation in both lettuce and alfalfa in the hydroponic growth medium (Hong et al. 2015). While in soil medium, the root and shoot length of lettuce increased after 15 days (Shah and Belozerova 2009).

6. Applications of MBNPs and MONPs

Contrary to their negative impacts and toxicity, nanoparticles can also have
positive impacts on people's lives (Geraci et al. 2015). MBNPs and MONPs have a wide range of applications in various industries including chemical industries (Yin and Talapin 2013), agricultural and food industries (Chen et al. 2014), cosmetic industries and electronics industries (Mishra et al. 2017). Apart from the wellbeing of people, MBNPs and MONPs also have many positive impacts on plants such as increasing plant growth (Alidoust and Isoda 2013), enhancing resistance of plants to certain diseases (Anusuya and Sathiyabama 2015), protection of photosynthesis from ROS (Wu et al. 2017) and improving the rate of photosynthesis (Giraldo et al. 2014). Our latest study recommended that foliar application of TiO$_2$ NPs could significantly decrease Cd content in maize (Zea mays) shoots and has a major influence on the alleviation of Cd-induced toxicity to plants. In the long run, MBNPs and MONPs will have more applications in different fields, few of them are discussed below (Lian et al. 2020).

6.1 Applications in agriculture

Natural resource systems, sustainable agriculture, and food are the most important areas of human activity. The rapidly growing population is a massive challenge for the current agricultural system because the population is expected to reach 9 or 10 billion by 2050, which will need an increase of about 30–70% of current food production (Hunter et al. 2017). Therefore, it is needed to accelerate science and technological advancement and find solutions to address these challenges (Scott et al. 2018). A large number of NPs cause toxic effects, but many others act as growth regulators increasing, biomass, and nutritional quality, and heralding their applications in agriculture as nano-fertilizers (Tripathi et al. 2017a). Figure 5 illustrates the comparison between nano-
fertilizers and bulk-fertilizers on plants. Studies suggest that nanotechnology is essential to tackle problems like nutrient deficiency (Achari and Kowshik 2018; Sekhon 2014).

MBNPs and MONPs can enhance the growth of various plants by increasing mineral nutrition, levels of antioxidant enzymes, chlorophyll content and resistance to pests (Achari and Kowshik 2018; Khot et al. 2012; Reddy et al. 2016). Similarly, MBNPs and MONPs due to their small size, permeability, biodegradability, and solubility can be used as Nano-pesticides (Achari and Kowshik 2018; Khot et al. 2012). These particles can target pathogens in different ways including ROS generation, penetration of cells, and binding to metabolites (Slavin et al. 2017). ZnO NPs can increase microbial community, rhizosphere, and activity of certain enzymes (dehydrogenase, alkaline phosphatase, acid phosphatase, and phytase) (Raliya et al. 2016). Similarly, Fe$_2$O$_3$ NPs and CuO NPs can improve seed germination, and enhance seedling growth (Li et al. 2013; Shah and Belozerova 2009). A combination of Cu and Zn NPs can enhance the leaf area and photosynthetic activity during drought stress (Taran et al. 2017). It is reported that TiO$_2$ NPs (rutile, and anatase phase) have increased photosynthesis and chlorophyll content in tomato and cucumber, and have improved biomass, methionine and cysteine contents of Lactuca sativa plants, while decreasing stress in some plants (Servin et al. 2013; Tiwari et al. 2017; Zahra et al. 2015; Rao and Shekhawat 2016; Tiwari et al. 2017). Al$_2$O$_3$ NPs are also known to improve plant growth, photosynthetic light reactions, enhance antioxidant enzymes, and inhibit certain pathogens in plants (Duhan et al. 2017).
6.2 Applications in phytoremediation of contaminated soil

NPs not only cause toxicity to plants, but are also effective in removing metals from contaminated sites through the phytoremediation technique, thus enhancing plant growth (Singh and Lee 2016). Phytoremediation is a plant-based technique used for removing, degrading, and stabilizing a wide range of soil contaminants and an interesting phenomenon in considering plants-nano interaction for promoting plant growth, increasing the phyto-availability of pollutants, and removing toxic pollutants from contaminated soil (Liang et al. 2017a; Liu et al. 2011). Phytoremediation technologies which are used for soil pollution are rhizodegradation, phytodegradation, phytoextraction, phytovolatilization, and phytostabilization (Song et al. 2019). Phytoextraction is considered to be one of the vital phytoremediation techniques for the removal of lead (Ali et al. 2013), and the application of nanoparticles with plants has been reported effective for enhancing the lead phytoextraction. For example, a study reported that the co-application of nano-hydroxyapatite and ryegrass, removed 30% of lead in the soil after one month and 44.39% after 3 months, respectively (Liang et al. 2017b). Similarly, phytostabilization is used to abate arsenic contamination in soil. Vitkova, et al. (2018) reported that applying nZVi NPs can have a positive effect on the stabilization of arsenic in sunflower rhizosphere. They added nZVi NPs to contaminated soil, after the growth period of five weeks, the concentration of arsenic in the soil decreased by over 80%, and the Ar accumulation in the roots and shoots decreased by 47 and 24% respectively (Vitkova, et al. 2018).

Moreover, studies using biotechnology and NPs have been conducted to
investigate the remediation techniques for contaminated soils and to deal with soil pollution (Gardea-Torresdey et al. 2014; Gong et al. 2018). For example, TiO\textsubscript{2} NPs in combination with phytoremediation (using soybean) can increase the bioaccumulation of Cd from Cd contaminated soil (Singh and Lee 2016). Plants provide a possible route for NPs which further promotes the accumulation of NPs into the food chain. The interaction of NPs and plants often takes place in the roots (Gong et al. 2018). Yang and Watts (2005) reported that the combined use of phytoremediation and NPs not only stabilize pollutants but also decrease the toxicity of NPs in plants. It has been reported that plant exposure to NPs regulates gene expression, oxidative stress, and photosynthetic activities (Nair and Chung 2014a), which might be helpful for phytoremediation of contaminated soils. However, further studies are required in order to understand the effects of NPs on plants under contamination stress using phytoremediation and NPs for removing contaminants from soil. Studies regarding MBNPs and MONPs enhancing the phytoremediation of contaminated soil is demonstrated in Table 4.

6.3 Applications in sustainable renewable energy

Securing long term supply of energy for global development is a major issue facing people nowadays (Alonso et al. 2012). We are mainly dependent on fossil fuels, which is our current source of energy, as a result of which major environmental issues in the form of global warming, acid rain, deforestation, ozone depletion, air pollution and emission of radioactive substances occur (Ramsurn and Gupta 2013). As these fossil fuels are finite, the development of new technologies in the power sector or reduction
in energy consumption becomes more important (Vidu et al. 2014). Nanoscience researchers are presently working to improve the efficiency of photosynthesis and their main goal is to create artificial photosynthesis for promoting crop production on marginal lands and reduction of atmospheric CO₂ (Faunce 2012). Solar energy is a clean and renewable source of energy, Nano-structured photovoltaic cells improve the efficiency of solar energy devices by converting photon energy to electricity by separating the excited electron-hole pairs (Li and Somorjai 2010). Various NPs (MBNPs and MONPs, nanotubes, nanofibers) are reported to produce biofuels (Sekoai et al. 2019). Hydrogen is not a source of energy but is useful as an atomic energy carrier.

Alenzi, et al. (2010) studied the production of hydrogen from the decomposition of water and methanol using Ag/TiO₂ Nano-composite films and concluded a higher production of hydrogen for more than a month. Moreover, the use of films was more convenient as compared to powders and easy to recycle (Alenzi et al. 2010).

Nanotechnology can be used in wind turbines to improve its efficiency and reduce energy loss through low friction coatings and Nano-lubricants (Ahmadi et al. 2019).

7. Conclusion and future perspectives

A thorough review of current and previous literature showed that uptake of MBNPs and MONPs can have both beneficial and toxic effects on the physiological and biochemical processes of a plant such as photosynthesis, water uptake, transpiration, and respiration, which can lead to disparities in seed germination, root elongation, and plant growth. These impacts are mainly influenced by factors like the size, concentration, and coating material of the nanoparticles, plant species and growth medium. It is also evident that MBNPs and MONPs in excess are toxic to plants
whereas in a small amount, they can be advantageous. Interestingly, MBNPs and MONPs can be used in the agriculture sector (micronutrients, Nano-pesticides, Nano-fertilizers), production of sustainable renewable energy and phytoremediation of contaminated soil. Therefore, as mentioned above, further studies are needed to deeply understand the mechanisms of interaction between MBNPs/MONPs and plants, which are discussed below.

Experimental conditions differences. Most of the current studies were carried out in strict environmental conditions (greenhouse or laboratories), the results of which are sometimes unreliable and even contradictory. For this purpose, further studies needed to be carried out in normal environmental conditions/field conditions (e.g. sandy soil), in order to better understand the positive and negative impacts of MBNPs and MONPs.

Further understanding of the environmental behavior of MBNPs and MONPs. The environmental behavior of MBNPs/MONPs largely determine their reactivity, phytoavailable, toxicity and potential risks to the plant-soil system. Up to now, it remains challenging to fully understand and predict the environmental behavior of MBNPs/MONPs, due to the presence of soil organic matter, colloids, plants and microorganisms in soil-plant system (Chen 2018). Therefore, subsequent studies on the fate and transport of MBNPs/MONPs in soil-plant system are still needed to reduce their potential risks.

Exposure time and mode differences. Uptake and translocation of MBNPs and MONPs in plants depend on their concentration, bioavailability, and exposure time (Verma et al. 2018). Very few studies have been carried out covering the long term
impacts of MBNPs and MONPs on the life cycle of plants. Therefore, it is necessary to carry out long term studies on MBNPs and MONPs toxicity and absorption by plants. More attention needs to be paid to whole life span experiments. Moreover, the differences between the foliar exposure and root exposure modes also need to be deeply explored in the future.

Studies on the trophic transfer and transgenerational effects of MBNPs and MONPs. There are few studies regarding the trophic transfer of certain MBNPs and MONPs including CuO NPs, ZnO NPs CeO$_2$ NPs, and CNTs. Due to foliar application of NPs as a fungicide, and bactericide they could become entrapped and accumulated in the food chain which can affect human and animal health. Therefore, it is urgent to investigate the trophic transfer of MBNPs and MONPs in our terrestrial food chain. Moreover, few studies have been carried out to reveal the transgenerational effects of MBNPs and MONPs. For example, water transpiration and biomass decreased in the second generation of tomato seedlings exposed to 10 mg/L of CeO NPs (Wang et al. 2013b). Similarly, in the third generation of Brassica rapa, higher ROS activity, and lower seed production were reported when treated with 1000 mg/L of CeO$_2$ NPs (Ma et al. 2016b).

Co-exposure of mixed MBNPs and MONPs and/or with heavy metals to plants. It is reported that toxicity caused by single NPs can be alleviated by mixing two NPs (Joško et al. 2017). Few studies with NPs mixtures have been carried out including Ni-TiO$_2$-ZnO NPs, Ag-TiO$_2$-ZnO NPs, CuO-TiO$_2$ which show various effects on plants (Josko and Oleszczuk 2013; Joško et al. 2017; Wang et al. 2017a). A latest study
indicated that certain MBNPs/MONPs can alleviate heavy metal-induced toxicity to plants (Lian, et al. 2020). However, more studies are still needed to reveal the effects of co-exposure of MBNPs/MONPs and heavy metals on heavy metals uptake in terrestrial plants and their potential risks.

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**Notes**

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Tables

Table 1
Effect of MBNPs and MONPs on seed germination, root elongation and plant growth

Table 2
Effect of MBNPs and MONPs on pigment content and photosynthetic activity

Table 3
Effect of MBNPs and MONPs on oxidative stress and plant hormones

Table 4
Phytoremediation of contaminated soil enhanced by MBNPs and MONPs

Figure Captions

Figure 1
Usage and disposal of MBNPs and MONPs from industries to soil

Figure 2
Graphic representation of possible NPs uptake through stomata, root and translocation by xylem and phloem which leads to oxidative stress and genotoxicity in plants
Figure 3
Graphical representation of different impacts of NPs on the physiological and biochemical parameters

Figure 4
Graphical representation of factors which affect the interaction of NPs with plants

Figure 5
Comparative analysis of pros and cons between conventional, bulk-fertilizer mediated and Nano-fertilizer mediated agriculture production.
Figure 1.
Figure 2.
Figure 3.
Figure 4.
Figure 5.
### Table 1 Effect of MBNPs and MONPs on seed germination, root elongation and plant growth

<table>
<thead>
<tr>
<th>MBNPs</th>
<th>Size</th>
<th>concentration</th>
<th>Plant species</th>
<th>Medium</th>
<th>Duration</th>
<th>Effects</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au</td>
<td>10-20 nm</td>
<td>0, 10, 25, 50, 100 mg/kg</td>
<td>Mustard (<em>Brassica nigra</em>)</td>
<td>Field conditions</td>
<td>50-70 days</td>
<td>Improved growth, increased the number of leaves, improved redox status and sugar content.</td>
<td>Arora et al. (2012)</td>
</tr>
<tr>
<td>Au</td>
<td>10 nm</td>
<td>10 µg/mL</td>
<td>Barely (<em>Hordeum vulgare</em>)</td>
<td>Hydroponic</td>
<td>14 days</td>
<td>Reduced root growth.</td>
<td>Feichtmeier et al. (2015)</td>
</tr>
<tr>
<td>Au</td>
<td>24 nm</td>
<td>10, 80 ppm</td>
<td>Thale cress (<em>Arabidopsis thaliana</em>)</td>
<td>MS growth medium</td>
<td>15 days</td>
<td>Improved seed growth germination and free radical scavenging activity.</td>
<td>Unrine et al. (2012)</td>
</tr>
<tr>
<td>Au</td>
<td>--</td>
<td>0.013% (w/w)</td>
<td>Lettuce (<em>Lactuca sativa</em>)</td>
<td>--</td>
<td>15 days</td>
<td>Shoot to root ratio increased by 57% as compared to control.</td>
<td>Shah and Belozerova (2009)</td>
</tr>
<tr>
<td>Ag</td>
<td>5, 10, 20 nm</td>
<td>0, 125, 250, 500 mg/L</td>
<td>Radish (<em>Raphanus sativus L.</em>)</td>
<td>In-vitro</td>
<td>5 days</td>
<td>No effect on seed germination, reduced shoot length and water content.</td>
<td>Zuverza-Mena et al. (2016)</td>
</tr>
<tr>
<td>Ag</td>
<td>35 and 40 nm</td>
<td>50, 75 mg/L</td>
<td>Wheat (<em>Triticum aestivum</em>)</td>
<td>Foliar application</td>
<td>40 days</td>
<td>Relatively, no effect on wheat, improved growth in cowpea at 50ppm, and improved shoot parameters in brassica at 100ppm</td>
<td>Pallavi et al. (2016)</td>
</tr>
<tr>
<td>Ag</td>
<td>200, 800 nm</td>
<td>1 mg/L</td>
<td>Fenugreek (<em>Trigonella foenum-graecum</em>)</td>
<td>Agar medium</td>
<td>5 days</td>
<td>Enhanced plant growth, and synthesis of diosgenin was observed.</td>
<td>Jasim et al. (2017)</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>150 nm</td>
<td>400-4000mg/L</td>
<td>Thale cress (<em>Arabidopsis thaliana</em>)</td>
<td>MS agar</td>
<td>18 days</td>
<td>No toxic effects observed, influenced root elongation.</td>
<td>Lee et al. (2010)</td>
</tr>
<tr>
<td>MBNPs</td>
<td>Size</td>
<td>concentration</td>
<td>Plant species</td>
<td>Medium</td>
<td>Duration</td>
<td>Effects</td>
<td>References</td>
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<tr>
<td>Al₂O₃</td>
<td>13 nm</td>
<td>2 mg/ml</td>
<td>Corn, Cucumber, Soybean, Cabbage (<em>Brassica oleracea</em>), Carrot (<em>Daucus sativus</em>)</td>
<td>Milli-Q water</td>
<td>24 hours</td>
<td>Inhibited root elongation in all crops</td>
<td>Yang and Watts (2005)</td>
</tr>
<tr>
<td>CeO₂</td>
<td>20±1.9 nm</td>
<td>0.1, 1, 10 mg/L</td>
<td>Tomato (<em>Solanum lycopersicum</em>)</td>
<td>Hydroponic</td>
<td>4 days</td>
<td>No effect on seed germination</td>
<td>Wang et al. (2012a)</td>
</tr>
<tr>
<td>CeO₂</td>
<td>8 nm</td>
<td>62.5, 125, 250, 500 mg/kg</td>
<td>Cilantro (<em>Corriandrum sativum</em> L.)</td>
<td>Soil</td>
<td>30 days</td>
<td>Enhanced root elongation at 125 mg/kg, and decreased biomass at 250 mg/kg</td>
<td>Morales et al. (2013)</td>
</tr>
<tr>
<td>CeO₂</td>
<td>8±1 nm</td>
<td>125, 250, 500 mg/kg</td>
<td>Wheat (<em>Triticum aestivum</em>)</td>
<td>Soil</td>
<td>94 days</td>
<td>Improved plant growth, shoot biomass, and grain yield at 500 mg/kg</td>
<td>Rico et al. (2014)</td>
</tr>
<tr>
<td>CeO₂</td>
<td>10, 30 nm</td>
<td>10 mg/L</td>
<td>Radish (<em>Raphnus sativus</em>)</td>
<td>Hoagland solution</td>
<td>35 days</td>
<td>No effect on root and shoot biomass</td>
<td>Zhang et al. (2015)</td>
</tr>
<tr>
<td>CuO</td>
<td>20-40 nm</td>
<td>100 µg/mL</td>
<td>Maize (<em>Zea mays</em>)</td>
<td>Hydroponic</td>
<td>15 days</td>
<td>Seed germination was not affected but seedling growth was inhibited.</td>
<td>Wang et al. (2012b)</td>
</tr>
<tr>
<td>CuO</td>
<td>&lt;50 nm</td>
<td>0, 50, 100, 200, 400 and 500 µg/mL</td>
<td>Soybean (<em>Glycine max</em> L.)</td>
<td>Murashige and Skoog medium</td>
<td>14 days</td>
<td>Reduced root, shoot growth, weight, and chlorophyll content at 500 mg/kg, and fresh weights were significantly decreased at all concentrations</td>
<td>Nair and Chung (2014c)</td>
</tr>
<tr>
<td>CuO</td>
<td>&lt;100 nm</td>
<td>0, 1000 mg/kg</td>
<td>Wheat (<em>Triticum aestivum</em>)</td>
<td>Agar culture</td>
<td>2 days</td>
<td>Seedling growth decreased with increasing concentration.</td>
<td>Lee et al. (2008)</td>
</tr>
<tr>
<td>MBNPs</td>
<td>Size</td>
<td>concentration</td>
<td>Plant species</td>
<td>Medium</td>
<td>Duration</td>
<td>Effects</td>
<td>References</td>
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<tr>
<td>Fe$_3$O$_4$</td>
<td>25 nm</td>
<td>30, 100, 500 mg/L</td>
<td>Rye grass (<em>Lolium perenne</em>) pumpkin (<em>Cucurbita mixta</em>)</td>
<td>Hydroponic</td>
<td>18 days</td>
<td>No uptake, increased root elongation, caused oxidative stress.</td>
<td>Wang et al. (2011)</td>
</tr>
<tr>
<td>Fe$_3$O$_4$</td>
<td>7 nm</td>
<td>116 µg/mL</td>
<td>Cucumber (<em>Cucumis sativus</em>), Lettuce (<em>Lactuca sativa</em>)</td>
<td>--</td>
<td>7 days</td>
<td>No toxicity on seed germination.</td>
<td>Barrena et al. (2009)</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>25±0.6 nm</td>
<td>0, 100, 250, 500, 750, 1000 mg/kg</td>
<td>Tomato (<em>Solanum lycopersicum</em>)</td>
<td>Pots with soil</td>
<td>40 days</td>
<td>Enhanced plant growth, root length and biomass at 250 mg/kg, increase in chlorophyll content at 750 mg/kg</td>
<td>Raliya et al. (2015)</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>14, 25, and 40 nm</td>
<td>100 mg/L</td>
<td>Rape seed (<em>Brassica napus</em>), Wheat (<em>Triticum aestivum</em>)</td>
<td>Hydroponic</td>
<td>7 days</td>
<td>14nm particles were absorbed by <em>Brassica napus</em> plant, slight or no effect on plant growth</td>
<td>Larue et al. (2012)</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>100 nm</td>
<td>10 g/kg</td>
<td>Wheat (<em>Triticum aestivum</em>)</td>
<td>Loamy day soil</td>
<td>7 months</td>
<td>Reduction in biomass, NPs found on root surface.</td>
<td>Du et al. (2011)</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>27±4 nm</td>
<td>0, 250, 500, 750 mg/kg</td>
<td>Cucumber (<em>Cucumis sativus</em>)</td>
<td>Sandy loam soil</td>
<td>150 days</td>
<td>Enhanced K and P availability in fruit.</td>
<td>Servin et al. (2013)</td>
</tr>
<tr>
<td>ZnO</td>
<td>25 nm</td>
<td>1000 mg/L</td>
<td>Peanut (<em>Arachis hypogaea</em>)</td>
<td>Soil</td>
<td>3 hours</td>
<td>Improved seedling vigor and seed germination</td>
<td>Prasad et al. (2012)</td>
</tr>
<tr>
<td>ZnO</td>
<td>&lt;10 nm</td>
<td>0, 1000 g/mL</td>
<td>Maize (<em>Zea mays</em>)</td>
<td>Agar media</td>
<td>7 days</td>
<td>Reduction in root length, and alteration in root anatomy.</td>
<td>Pokhrel and Dubey (2013)</td>
</tr>
<tr>
<td>ZnO</td>
<td>&lt;50 nm</td>
<td>0, 5, 10, 25, 50, 75, 100, 125, 250 and 500 µg/mL</td>
<td>Rape seed (<em>Brassica napus</em>)</td>
<td>Petri-dishes</td>
<td>6 days</td>
<td>Decreased root shoot length and dry massed of plant</td>
<td>Mousavi Kouhi et al. (2014)</td>
</tr>
<tr>
<td>MBNPs</td>
<td>Size</td>
<td>concentration</td>
<td>Plant species</td>
<td>Medium</td>
<td>Duration</td>
<td>Effects</td>
<td>References</td>
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<tr>
<td>ZnO</td>
<td>20±5 nm</td>
<td>10, 20, 50, 100, 200, 1000 mg/L</td>
<td>Ryegrass (Lolium perenne)</td>
<td>Hydroponic</td>
<td>--</td>
<td>Inhibition of root elongation (dose dependent), decrease in seedling biomass was observed at above 20 mg/L concentration.</td>
<td>Lin and Xing (2008)</td>
</tr>
<tr>
<td>ZnO</td>
<td>20±5 nm</td>
<td>10, 20, 50, 100, 200, 1000 mg/L</td>
<td>Cattail (Typha latifolia)</td>
<td>Hydroponic</td>
<td>4 weeks</td>
<td>Increased plant growth at low concentration, caused toxicity at higher concentration</td>
<td>Ma et al. (2013)</td>
</tr>
<tr>
<td>ZnO</td>
<td>20±5 nm</td>
<td>10, 20, 50, 100, 200, 1000 mg/L</td>
<td>Rice (Oryza sativa)</td>
<td>Moist filter paper</td>
<td>14 days</td>
<td>Increased seed growth, root and shoot length</td>
<td>Guha et al. (2018)</td>
</tr>
<tr>
<td>MBNPs</td>
<td>Size</td>
<td>concentration</td>
<td>Plant species</td>
<td>Medium</td>
<td>Duration</td>
<td>Effects</td>
<td>References</td>
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</tr>
<tr>
<td>Ag</td>
<td>10-15 nm</td>
<td>0, 100, 1000 mg/L</td>
<td>Tomato (<em>Solanum lycopersicum</em>)</td>
<td>Hydroponic</td>
<td>6 days</td>
<td>Decreased root growth and chlorophyll content</td>
<td>Song et al. (2013)</td>
</tr>
<tr>
<td>Ag</td>
<td>&lt;100 nm</td>
<td>0, 100, 500 mg/L</td>
<td>Pumpkin (<em>Cucurbita pepo</em>)</td>
<td>Hydroponic</td>
<td>14 days</td>
<td>Decreased the rate of transpiration, and biomass by 66 – 84%.</td>
<td>Musante and White (2012)</td>
</tr>
<tr>
<td>CeO₂</td>
<td>&lt;25 nm</td>
<td>50, 100, 1000 mg/L</td>
<td>Lettuce (<em>Lactuca sativa</em>)</td>
<td>Soil</td>
<td>30 days</td>
<td>No effect on chlorophyll content</td>
<td>Gui et al. (2015)</td>
</tr>
<tr>
<td>CeO₂</td>
<td>10-1 nm</td>
<td>400, 800 mg/kg</td>
<td>Maize (<em>Zea mays</em>)</td>
<td>Soil</td>
<td>20 days</td>
<td>No effect on rate of photosynthesis, and transpiration</td>
<td>Zhao et al. (2012)</td>
</tr>
<tr>
<td>CeO₂</td>
<td>10-30 nm</td>
<td>10mg/L</td>
<td>Radish (<em>Raphanus sativus L.</em>)</td>
<td>Hoagland solution</td>
<td>35 days</td>
<td>Decreased relative chlorophyll content, but no effect on the average quantum yield of photosystem II</td>
<td>Zhang et al. (2015)</td>
</tr>
<tr>
<td>CuO</td>
<td>10-15 nm</td>
<td>1.0 mg/L</td>
<td>Duckweed (<em>Landoltia punctate</em>)</td>
<td>Hoagland nutrient</td>
<td>9 days</td>
<td>Decreased chlorophyll content, caused oxidative stress, inhibited growth</td>
<td>Shi et al. (2011)</td>
</tr>
<tr>
<td>CuO</td>
<td>&lt;50 nm</td>
<td>500 mg/kg</td>
<td>Wheat (<em>Triticum aestivum</em>)</td>
<td>Sand matrix</td>
<td>14 days</td>
<td>Reduced chlorophyll content, root, shoot length and biomass. Increased POD and CAT activity in roots</td>
<td>Dimkpa et al. (2012)</td>
</tr>
<tr>
<td>CuO</td>
<td>&lt;50 nm</td>
<td>20, 50, 100, 200, 400, 500 mg/L</td>
<td>Indian mustard (<em>Brassica juncea</em>)</td>
<td>Murashige and Skoog medium</td>
<td>15 days</td>
<td>Decreased total chlorophyll and carotenoid content</td>
<td>Nair and Chung (2015)</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>6 nm</td>
<td>50-2000 mg/L</td>
<td>Soybean (<em>Glycine max</em>)</td>
<td>Potting soil</td>
<td>8 weeks</td>
<td>No adverse effects at any growth stage, increased photosynthetic rate, stomatal opening, positive effect on root elongation</td>
<td>Alidoust and Isoda (2013)</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>22-67 nm</td>
<td>4 mg/kg</td>
<td>Thale cress (<em>Arabidopsis thaliana</em>)</td>
<td>Agar medium</td>
<td>56 days</td>
<td>Decreased chlorophyll, and plant biomass.</td>
<td>Marusenko et al. (2013)</td>
</tr>
<tr>
<td>TiO₂</td>
<td>14 nm</td>
<td>100 mg/L</td>
<td>Wheat (<em>Triticum aestivum</em>)</td>
<td>Vials containing NPs solution</td>
<td>15 days</td>
<td>No effect on seedling growth, photosynthesis and transpiration</td>
<td>Larue et al. (2012)</td>
</tr>
<tr>
<td>TiO₂</td>
<td>27 nm</td>
<td>50, 100, 500, 1000, and 5000 mg/L</td>
<td>Tomato (<em>Solanum lycopersicum</em>)</td>
<td>Hydroponic</td>
<td>7 days</td>
<td>No effect on chlorophyll content</td>
<td>Song et al. (2013)</td>
</tr>
<tr>
<td>TiO₂</td>
<td>25±0.6 nm</td>
<td>0, 100, 250, 500, 750, 1000 mg/kg</td>
<td>Tomato (<em>Solanum lycopersicum</em>)</td>
<td>Pots with soil</td>
<td>40 days</td>
<td>Enhanced plant growth, root length and biomass at 250 mg/kg, increase in chlorophyll content at 750 mg/kg</td>
<td>Raliya et al. (2015)</td>
</tr>
<tr>
<td>MBNPs</td>
<td>Size</td>
<td>concentration</td>
<td>Plant species</td>
<td>Medium</td>
<td>Duration</td>
<td>Effects</td>
<td>References</td>
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</tr>
<tr>
<td>TiO₂</td>
<td>27±4 nm</td>
<td>250, 500, 750 mg/kg</td>
<td>Cucumber (Cucumis sativus)</td>
<td>Soil</td>
<td>150 days</td>
<td>Increased chlorophyll content at 750 mg/kg</td>
<td>Servin et al. (2013)</td>
</tr>
<tr>
<td>ZnO</td>
<td>10 nm</td>
<td>125, 250, and 500 mg/L</td>
<td>Green pea (Pisum sativum)</td>
<td>Soil</td>
<td>25 days</td>
<td>Decreased chlorophyll content by 77%</td>
<td>Mukherjee et al. (2014)</td>
</tr>
<tr>
<td>ZnO</td>
<td>10 nm</td>
<td>400, 800 mg/kg</td>
<td>Cucumber (Cucumis sativus)</td>
<td>Soil</td>
<td>53 days</td>
<td>No effects on growth, chlorophyll content and gas exchanges</td>
<td>Zhao et al. (2013)</td>
</tr>
<tr>
<td>ZnO</td>
<td>3.8 nm</td>
<td>10 mg/L</td>
<td>Cluster bean (Cyamopsis tetragonoloba)</td>
<td>Soil</td>
<td>--</td>
<td>Improved chlorophyll content and total leaf protein</td>
<td>Raliya and Tarafdar (2013)</td>
</tr>
<tr>
<td>ZnO</td>
<td>10 nm</td>
<td>100, 200, 400, 800 mg/L</td>
<td>Corn (Zea mays)</td>
<td>Soil</td>
<td>30 days</td>
<td>Increased chlorophyll a at 400 mg/L in the presence of alginate</td>
<td>Zhao et al. (2013)</td>
</tr>
<tr>
<td>ZnO</td>
<td>90±10 nm</td>
<td>400, 800, 1600, and 3200 mg/kg</td>
<td>Maize (Zea mays)</td>
<td>Soil</td>
<td>8 weeks</td>
<td>Decreased chlorophyll a, b and carotenoid content at 3200 mg/kg</td>
<td>Wang et al. (2016a)</td>
</tr>
<tr>
<td>ZVI</td>
<td>10, 20, 40, 80, 160 mg/L</td>
<td>Rice (Oriza sativa)</td>
<td>Moist filter paper</td>
<td>14 days</td>
<td>Increased photosynthetic pigments, and biomass</td>
<td>Guha et al. (2018)</td>
<td></td>
</tr>
</tbody>
</table>
### Table 3 Effect of MBNPs and MONPs on oxidative stress and plant hormones

<table>
<thead>
<tr>
<th>MBNPs</th>
<th>Size</th>
<th>Concentration</th>
<th>Plant species</th>
<th>Medium</th>
<th>Duration</th>
<th>Effects</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag</td>
<td>&lt;10 nm</td>
<td>10 mg/kg</td>
<td>Wheat <em>(Triticum aestivum)</em></td>
<td>Germination occurred on moist filter paper</td>
<td>5 days</td>
<td>Decrease in biomass, root and shoot length. Alteration of proteins, mainly those which were involved in metabolism,</td>
<td>Vannini et al. (2014)</td>
</tr>
<tr>
<td>Ag</td>
<td>60 nm</td>
<td>12.5, 25, 50, 100 mg/L</td>
<td>Broad bean <em>(Vicia faba)</em></td>
<td>Hydroponic</td>
<td>--</td>
<td>Increase in the number of chromosomal aberrations, decrease mitotic index</td>
<td>Patlolla et al. (2012)</td>
</tr>
<tr>
<td>Ag</td>
<td>10 nm</td>
<td>0.5, 1.5, 2.5, 3.5, 5 mg/kg</td>
<td>Wheat <em>(Triticum aestivum)</em></td>
<td>Pots with sand</td>
<td>14 days</td>
<td>Reduced root and shoot length, while 2.5 mg/kg increased root branching, ROS formation</td>
<td>Dimkpa et al. (2013)</td>
</tr>
<tr>
<td>Ag</td>
<td>6 and 20 nm</td>
<td>0.5, 5, 10 mg/L</td>
<td><em>(Spirodela polyrhiza)</em></td>
<td>Hydroponic</td>
<td>--</td>
<td>Increase in ROS, superoxide, dismutase and peroxidase activity</td>
<td>Jiang et al. (2014)</td>
</tr>
<tr>
<td>CeO₂</td>
<td>10-30 nm</td>
<td>250-1000 mg/L</td>
<td>Thale cress <em>(Arabidopsis thaliana)</em></td>
<td>1/2 MS Agar</td>
<td>5-25 days</td>
<td>Amount of ROS increased, disrupted uptake of nutrients</td>
<td>Ma et al. (2016a)</td>
</tr>
<tr>
<td>CeO₂</td>
<td>10±1 nm</td>
<td>400, 800 mg/kg</td>
<td>Corn</td>
<td>Soil</td>
<td>20 days</td>
<td>Increased H₂O₂ generation, CAT, and APX activities, no effect on MDA content or ion leakage</td>
<td>Zhao et al. (2012)</td>
</tr>
<tr>
<td>CeO₂</td>
<td>8±1 nm</td>
<td>100 and 400 mg/kg</td>
<td>Wheat <em>(Triticum aestivum)</em></td>
<td>Soil</td>
<td>7 months</td>
<td>Increased SOD and CAT activities, no changes in MDA content</td>
<td>Du et al. (2015)</td>
</tr>
<tr>
<td>CuO</td>
<td>&lt;50 nm</td>
<td>0, 0.5, 1, 2, 5, 10, 20, 50, 100 mg/L</td>
<td>Thale cress <em>(Arabidopsis thaliana)</em></td>
<td>Agar culture</td>
<td>21 days</td>
<td>Reduced root elongation, plant biomass, and increased generation of ROS.</td>
<td>Nair and Chung (2014b)</td>
</tr>
</tbody>
</table>
Table 3 (continued)

<table>
<thead>
<tr>
<th>MBNPs</th>
<th>Size</th>
<th>concentration</th>
<th>Plant species</th>
<th>Medium</th>
<th>Duration</th>
<th>Effects</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuO</td>
<td>&lt;50 nm</td>
<td>0.01, 0.02 ppm (root exposure) 8 ppm (foliar spray)</td>
<td>Maize (Zea mays)</td>
<td>Hoagland solution</td>
<td>3 weeks</td>
<td>GPX, CAT and succinate dehydrogenase activities reduced at 0.02 ppm and 8 ppm foliar spray, but SOD activity increased</td>
<td>Adhikari et al. (2016)</td>
</tr>
<tr>
<td>CuO</td>
<td>&lt;50 nm</td>
<td>0.5, 1, and 1.5 mM</td>
<td>Barely (Hordeum vulgare L.)</td>
<td>Cotton pads soaked with NPs suspension</td>
<td>20 days</td>
<td>Biomass, root, and shoot length decreased. Antioxidant activities H$_2$O$_2$ and MDA content increased in plant at higher concentrations</td>
<td>Shaw et al. (2014)</td>
</tr>
<tr>
<td>Fe$_3$O$_4$</td>
<td>50-60 nm</td>
<td>10, 20 mg/L</td>
<td>Lettuce (Lactuca sativa)</td>
<td>Hydroponic</td>
<td>15 days</td>
<td>Increased the activities of antioxidant enzymes, affected water entrance, decreased chlorophyll content.</td>
<td>Trujillo-Reyes et al. (2014)</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>7-40 nm</td>
<td>2, 10 mg/kg</td>
<td>Chick pea (Cicer arietinum)</td>
<td>Soil</td>
<td>35 days</td>
<td>5 mg/kg concentration caused reduction in leakage of electrolyte and MDA content.</td>
<td>Mohammadi et al. (2014)</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>27±4 nm</td>
<td>0, 250, 500, 750 mg/kg</td>
<td>Cucumber (Cucumis sativus)</td>
<td>Sandy loam soil</td>
<td>150 days</td>
<td>Enhanced K and P availability in fruit.</td>
<td>Servin et al. (2013)</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>90-98 nm</td>
<td>12.5, 25, 50, 100 mg/L</td>
<td>Onion (Allium cepa)</td>
<td>Hydroponic</td>
<td>--</td>
<td>Increase in ROS activity and genotoxic effects (concentration dependent)</td>
<td>Pakrashi et al. (2014)</td>
</tr>
<tr>
<td>ZnO</td>
<td>&lt;50 nm</td>
<td>0, 2000 mg/L</td>
<td>Cucumber</td>
<td>Loamy sand soil</td>
<td>8 weeks</td>
<td>Decreased enzymes activity, biomass, shoot and root length, and Zn concentration increased</td>
<td>Kim et al. (2011)</td>
</tr>
<tr>
<td>ZnO</td>
<td>&lt;100 nm</td>
<td>0, 200, 500, 1000, 1500 µg/mL</td>
<td>Indian mustard</td>
<td>Hydroponic</td>
<td>96 hours</td>
<td>Decreased root, shoot length and biomass, ROS and antioxidant enzymes activity increased</td>
<td>Rao and Shekhawat (2014)</td>
</tr>
<tr>
<td>ZnO</td>
<td>10 nm</td>
<td>125, 250, 500 mg/L</td>
<td>Green pea</td>
<td>Soil</td>
<td>25 days</td>
<td>Downregulated APX in root and leaves, and CAT in leaves</td>
<td>Mukherjee et al. (2014)</td>
</tr>
<tr>
<td>ZVI</td>
<td>10, 20, 40, 80, 160 mg/L</td>
<td>Rice (Oryza sativa)</td>
<td>Moist filter paper</td>
<td>14 days</td>
<td>Decrease in antioxidant enzymes activity</td>
<td>Guha et al. (2018)</td>
<td></td>
</tr>
</tbody>
</table>
### Table 4 Phytoremediation of contaminated soil enhanced by MBNPs and MONPs

<table>
<thead>
<tr>
<th>MBNPs</th>
<th>Pollutants</th>
<th>Plant species</th>
<th>Effects</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al₂O₃</td>
<td>Phenanthrene</td>
<td><em>Cucumis sativus, Zea mayz, Daucus carota, Glycine max, and Brassica oleracea</em></td>
<td>Phenanthrene successfully loaded on Al₂O₃ NPs, which in turn reduced the inhibition of root elongation</td>
<td>Yang and Watts (2005)</td>
</tr>
<tr>
<td>Ni/Fe</td>
<td>PBDEs</td>
<td>Chinese cabbage (<em>Brassica rapa</em>)</td>
<td>Ni/Fe NPs Promoted translocation of PBDEs from soil to plants, and decreased toxicity of PBDEs, increased germination rate, root shoot length, and plant biomass</td>
<td>Wu et al. (2018)</td>
</tr>
<tr>
<td>Si</td>
<td>Cr</td>
<td>Chickpea (<em>Cicer arietinum</em>)</td>
<td>Improved plant growth, nitrogen, protein and chlorophyll content, decreased ROS production and Cr accumulation in plants</td>
<td>Tripathi et al. (2015)</td>
</tr>
<tr>
<td>TiO₂</td>
<td>Cd</td>
<td><em>Chlamydomonas reinhardtii</em></td>
<td>Lower Cd bioavailability, alleviated Cd induced growth inhibition, reduced free Cd ion contents</td>
<td>Yang et al. (2012)</td>
</tr>
<tr>
<td>TiO₂</td>
<td>Cd</td>
<td>Soybean (<em>Glycine max</em>)</td>
<td>Increased Cd uptake, but decreased plant oxidative stress in plants</td>
<td>Singh and Lee (2016)</td>
</tr>
<tr>
<td>TiO₂</td>
<td>Cd</td>
<td>Maize (<em>Zea mays</em>)</td>
<td>Foliar application decreased Cd concentration in shoots increased superoxide dismutase (Alidoust and Isoda) and glutathione S-transferase (GST) activities and upregulated several metabolic pathways</td>
<td>Lian et al. (2020)</td>
</tr>
<tr>
<td>ZnO</td>
<td>Cd²⁺, Pb²⁺</td>
<td>Jumbay (<em>Leucaena leucocephala</em>)</td>
<td>Reduced toxicity on plant growth</td>
<td>Venkatachalam (et al. 2017)</td>
</tr>
<tr>
<td>ZVI</td>
<td>As</td>
<td>Barley (<em>Hordeum vulgare</em> L. cv. Pedrezuela)</td>
<td>Decreased As availability and uptake in Barley, increased plant growth and the biomass of plant</td>
<td>Gil-Díaz et al. (2016)</td>
</tr>
</tbody>
</table>