**ABSTRACT**

Application of nanoparticles to address various environmental issues; especially heavy metal contaminated soil restoration is of global interest. Indiscriminate usage of phosphate fertilizer and other anthropogenic activities contribute to Cd contamination of soil, resulting in degradation of soil quality and low crop yield. By the virtue of unique physiochemical characteristics, nanoparticles (NPs) are effective enough for heavy metal stress mitigation. This review has focused on Cd uptake, accumulation and toxicity in plants followed by the successful application of different metallic and non metallic NPs for soil Cd decontamination. Positive impact of NPs as plant growth elicitor under Cd stress has been explored here. Various ways of NP application (soil, foliar, hydroponics), uptake, mode of action and effective treatment concentration have been highlighted. We have collected handful information regarding the use of NPs as nanofertilizer and nanopesticides. The negative effects of NPs have not been considered here. More in depth study to be conducted for better illumination on plant - NPs interaction, mobilization mechanism and biological activities. Though this review summarizes few facts among various aspect of NP but can be counted as a supportive documentation for the better use of NPs in environmental protection in future.

**Introduction**

Rapid industrialization, indiscriminate usage of agrochemicals and fertilizers, excessive mining has led to heavy metal (HM) soil contamination a global burning issue. HM pollution of soil is one of the critical issues hampering crop yield and limiting food security. Being non biodegradable; bioaccumulation of heavy metal (loid)s in soil imparts severe ecological risk to the biome. Cadmium (67th element in order of abundance) is one of the most toxic heavy metals that get deposited in soils through natural or anthropological means like mining, smelting, battery manufacturing etc (1). By the virtue of better water solubility and mobility cadmium (Cd) is easily taken up by plants via ascent of sap in roots followed by transportation to shoot through membrane embedded metal ATPase (2). It can cause potential damage to living organisms, even at very low concentrations, thus considered as the fourth most toxic element in (3) the environment. Cd is ranked third globally, following mercury and lead in the list of most hazardous contaminants by the US Environmental Protection Agency (EPA). Biologically non essential Cd is quite efficient to replace important mineral calcium owes to its similar chemical structure and behaviour (4) resulting easy passage in plant and animal tissues through the food chain.

Continuous persistence of Cd in soil not only interferes in plant physiology but also alters soil properties such as pH, organic matter affecting important minerals (Fe, P, Ca, Mn) uptake by plants (5). The main visible signs of Cd toxicity are chlorosis, leaf rolling, compromised growth and ultimate necrosis in plants under higher concentration (6). Beside occupational exposure, other route of Cd poisoning in human is the ingestion of Cd contaminated foods (cereals, leafy vegetables) which contain more Cd in comparison to animal products (meat, egg, milk) (7). Mainly the accumulation of Cd in staple food rice and its transfer to the successive trophic levels has become a major environmental concern (8). Kidney and livers are the two most affected organs account for the maximum Cd accumulation in the human body (7). The presence of Cd poses serious threat to humans like anaemia, cardiac failure, kidney malfunction and osteoporosis (9). The ‘Itai-Itai’ disease in humans was caused due to consumption of Cd-polluted rice (10). According to WHO the allowable limits of Cd concentration in soil is 0.2 mg/kg (11). Many attempts have been adopted to address the issue of Cd decontamination of soil that
includes chemical clean up, phytoremediation and recently nanotechnology also.

Nanotechnology is a rapidly emerging field of research, which involves the study and development of nanoparticles (NPs) and has gained a huge momentum in remediation of metal contaminated soil and water and environmental protection. According to ASTM standards, Nanomaterials (NMs) is a natural or engineered material, with a dimension of 1-100 nm (12). The small size and a high surface-to-volume ratio of NMs offer better adsorption capacity. Nano-materials like nZVI, carbon nanotubes, nano-silica, graphene or hybrid metal-non-metal nanoparticles are extensively utilized for soil decontamination. The unique physical properties of NPs (small size, porosity, high surface-area and better absorption) provide additional advantages as compared to the traditional methods, as efficient materials for environmental remediation. Due to minimum toxic effect, iron oxide NPs are of maximum use (13). Various studies have proven the effectiveness of NPs in immobilization of heavy metal (loids), thereby decreasing their bioavailability. Several reports indicated the positive impact of NPs on plant seed germination, photosynthesis, antioxidative defense, growth, and crop quality (14, 15). Selenium and silicon NPs mitigates Cd and Pb toxicity in rice via foliar spray (16). Foliar application of TiO$_2$ NPs had better response than soil treatment for Cd toxicity alleviation in maize. Successful use of NPs as nanofertilizers (17, 18) and nanoparticles (19), have been globally accepted but the potential ecological hazards can’t be ruled out (20). This review is a comprehensive summary of many recent studies, with keen focus on the application of various NPs and their effectiveness in the mitigation of Cd toxicity in plants. But the phytotoxicity of NPs has not been considered here in details.

**Cadmium contamination in environment**

Soil and groundwater contamination due to leaching effect of Cd has enough global reports (21). Devoid of any microbial and biochemical degradation, persistence of soil Cd is a continuous threat to the biota. Non-essential heavy metal Cadmium (Cd), is mostly released into the environment through metal industries, mining, smelting and other anthropogenic activities like application of fertilizers, sewage sludge, in various industrial usage such as metal plating and as neutron absorbent in nuclear reactors (22). Having detectable percentage of Cd impurity phosphate fertilizer (4) is a potential Cd donor to soil. Not only MSW but also electrical stress tolerant Cd-Ni batteries are distinct contributors to soil Cd (23). The air-borne source of Cd is burning of fossil fuels and emission through iron and steel factories. Certain plants like rice, potato, tobacco and other leafy vegetables can uptake Cd more avidly as compared to other heavy metals like lead and mercury (24). Safe limit of Cd as suggested by World Health Organization (WHO) is below 200 mg Cd$kg^{-1}$.

**Plant response to bio-available Cadmium**

Cd toxicity has a comprehensive negative interference with all the metabolic pathways including water relations, photosynthetic rate, respiration, transpiration, stomatal conductance (25, 26). Response of plants to elevated soil Cd concentration is cultivar specific as bioaccumulation capacity is genotype dependent (27). Cd mobility is a multivariant component that depends on various physicochemical properties of soil, but most important is the soil pH which is indirectly proportional to Cd bioavailability (28). Root exudates always decrease Cd accessibility to plants facilitating other micronutrients uptake (28). Presence of other cations in soil antagonizes Cd availability as they vigorously compete for the binding site of plants roots (28). Cd is absorbed by roots either as inorganic complexes (Cd$^{2+}$SO$_4$$^-$, CdCl$_2$), or as organic forms (phytometallophore) (4). Cd is absorbed by roots either as inorganic complexes (Cd$^{2+}$SO$_4$$^-$, CdCl$_2$), or as organic forms (phytometallophore) (4). Presence of other cations in soil antagonizes Cd availability as they vigorously compete for the binding site of plants roots (28). Cadmium being a non-essential heavy metal, its presence exerts serious adverse effects in plants (Fig. 1). Acute damage of root and shoot morphology in various crops such as rice and wheat (2, 16, 29) is a well known fact. The stunted growth of Cd treated plants is directly related to reduced nutrient, water availability and enzymatic degradation of respiration, photosynthesis, nitrogen.

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**Fig. 1.** Cd induced reactive oxygen species generation and oxidative stress in plants.
Cadmium tolerance in plants

Plants handle Cd toxicity either by avoidance or by tolerance. Avoidance deals with the minimization of Cd uptake while tolerance (34) includes Cd accumulation followed by sequestration with different chelating molecules (peptides, proteins). Versatile strategies employed by plants to cope up with soil Cd load are; lowering the bioavailability of HM in the soil (52), down-regulating the HM transporter genes (53) and elevating the production of enzymatic and non-enzymatic antioxidant molecules (54). The first line of defense is scavenging of Cd in root vacuole by low molecular weight organic acids, polysaccharides and non-protein thiol (NPT, phytochelatin) compounds (55, 56) preventing its translocation to shoots (3). Sharp rise in the synthesis of Cd chelator low molecular weight peptide Phytochelatin (PC) is well documented in Cd stressed Eichhornia crassipes (55), Oryza sativa (57) and Arabidopsis (58) by upregulating phytochelatin synthase 1 gene. PC is well equipped to scavenge Cd for its detoxification. Plants enhance their tolerance capacity by increasing the production of stress signalling compounds (salicylic acid, jasmonic acid, nitric oxide and brassinosteroids) that are involved in the upregulation of various detoxification pathways during Cd toxicity (59). Plants have evolved various antioxidative enzymes such as catalase (CAT), peroxidase (POD), superoxide dismutase (SOD), glutathione reductase (GR) for direct detoxification of ROS. Studies have revealed that under moderate Cd toxicity rice plant stimulated their anti oxidative system (SOD, CAT) (41, 43), osmoregulation, ion homeostasis as well as increased the production of various signalling molecules (54). Studies revealed various genes involved in Cd tolerance in rice such as the Low Cadmium (LCD) gene responsible for Cd accumulation without hampering growth parameters (60). In Arabidopsis, cadmium stress-responsive gene AtFCl was transcriptionally activated to elevate Cd tolerance by upregulating non protein thiol compound (glutathione and phytochelatins) production, that confers increase in root length, biomass, chlorophyll content with simultaneous decrease in free radicals (61). Subcellular...
compartmentalization and sequestration are mostly practiced in hyperaccumulators without acute visible symptoms of Cd toxicity (62). Positive effect of plant growth regulator (salicylic acid, gibberellin) in Cd remediation by reducing ROS generation and upregulating different antioxidative enzymes like SOD, CAT (63) and heat shock (stress) protein (64) production is a well established proven fact.

**Cd uptake and transport in plants**

Cadmium mainly exists in the soil in the form of divalent cation Cd\(^{2+}\). The bioavailability of Cd depends on the physicochemical characters of the soil, such as redox potential, soil pH, organic matter and presence of other trace elements (65). The entry path of Cd\(^{2+}\) into the root is as follows (Fig. 2).

1. At the plasma membrane of root cells dissociation of H\(_2\)CO\(_3\) into H\(^+\) and HCO\(_3\)\(^-\) followed by the exchange of H\(^+\) with Cd\(^{2+}\) and its absorption (38).
2. Cd\(^{2+}\) enters through ion channels for other minerals Fe\(^{2+}\), Zn\(^{2+}\) and Ca\(^{2+}\) where it combines with transporter proteins and subsequently taken up by root epidermis via symplast pathway.
3. Mugineic acids, a siderophore secreted by plant (Poaceae) roots forms Cd\(^{2+}\) metal ligand complexes under Fe deficiency that facilitates Cd\(^{2+}\) uptake in root epidermis via Yellow-Stripe 1- Like (YSL) proteins (66, 67).

**Genes involved in Cd uptake**

The process of Cd uptake and localization in plants has gathered the attention of scientists worldwide. The recent technologies that are being utilized to detect Cd localization in plants are- ultramicroscopy, radioautography and energy dispersive X-ray microanalysis (EMAX). Several genes, responsible for encoding heavy metal transporters, have been identified in plants. A diverse range of proteins responsible for Cd uptake have been reported such as NRAMP family, P-type ATPase, ABC transporter, ZIP family and LCT transporter. Rice genome expresses several HMA genes, among which, OsHMA2 is of immense importance for Cd uptake. The physiological concentration of heavy metals in plant cell is mainly regulated by the optimum activity of metal transporters embedded in plasma membrane and tonoplast. Details of different genes involved in Cd import into the plants have been listed in Table 1. A diagrammatic representation of various Cd transporter proteins responsible for Cd sequestration is given in Fig. 3.

**Types of nanoparticles**

In modern era, application of nanomaterials is of paramount interest for addressing the problem of rapid increase of Cd contamination in agricultural lands. Nanomaterials have distinctive physicochemical characteristics that offer multifunctional use in plant science, not only to enhance crop productivity but also to ameliorate heavy metal toxicity. Depending on sizes, nanomaterial may be of different types-nanoparticles, nanosheets, nanowires, nanoflowers, nanotubes and nanorods (100). Recently, NPs mediated plant interactions, regarding metal uptake, mobilization and accumulation are of great interest and a few successfully engineered NPs have been
tested positive in this field with the final goal of plant defense elicitation. Polymeric NP is gaining more attention now a days for being biocompatible, cheaper and being responsive to environmental stimuli (101). Commercially available Core NPs are prepared with different combination of organic and inorganic materials. The preference of NPs entirely depends on the ultimate targets and use.

Metallic nanoparticles- These are nano sized particles of dimensions within 100 nm. These are the pure metallic state or oxides of gold, titanium, iron, gold, manganese, copper and many others. Metal oxides are more preferable due to better stability than pure metallic forms. Greater surface area makes them better absorber of small molecules (102).

Non-metallic nanoparticles- Major non-metallic carbon-based nanoparticles are fullerene and carbon nanotubes. Fullerenes are of great commercial value due to their electrical conductivity, high strength and versatility (103). Carbon-nanotubes are slender, elongated tubes of 1-2 nm diameter. They may be single-walled, double-walled or multi-walled carbon nanotubes that act as efficient adsorbents in environmental remediation.

Hybrid nanoparticles- These are formed by a mixture between metallic and non-metallic nanoparticles and by the virtue of improved properties these are preferred more as compared to the singular metallic or non-metallic nanoparticles. A metallic hybrid consisting of ZnO and TiO2 hybrid was

| Function | Name | Annotation | Organ of expression | Plant species | Co-transported ions | References |
|----------|------|------------|---------------------|---------------|---------------------|------------|
| 1) Process of uptake into cell | LCT1 | Low-affinity cation transporters | Roots | Triticum aestivum | Ca, K | 71 |
| | ANN4 | Annexin | Roots | Oryza sativa | | 73 |
| | NRAMP1, NRAMP2 and NRAMP3 | Natural resistance-associated macrophage protein | Roots | Triticum aestivum, Zea mays, Oryza sativa, Arabidopsis thaliana | Fe, Mn, Co | 71, 74, 75, 76, 77, |
| | YSL1 and YSL3 | Yellow-Stripe Like transporter | Vascular bundles and epidermal cells of the roots | Solanum nigrum, Oryza sativa | Fe(II), Cu, Zn, Ni | 78, 79 |
| 2) Efflux out of the cell | MTP9 | Cation-diffusion facilitator (CDF) | Root epidermis | Cucumis sativus | Mn | 80 |
| | PDR9 | ATP-Binding Cassettes | Roots(Hair and epidermis), shoot | Arabidopsis thaliana | Pb | 81 |
| 3) Chelation | MTL | MT-like protein | Roots | Sedum plumtizincicola | | 82 |
| | CDT1 | Cys-rich peptide | Roots, shoots (cell surface, cell-wall) | Digitaria ciliaris, O. sativa | | 83 |
| | CAL1 | Defensin-like protein | Roots | Oryza sativa | | 84 |
| 4) Uptake into vacuole sequestration | HMA3 | P type ATPase family, subfamily HMA(for Heavy Metal Associated) | Vacuoles of roots and shoots | Sedum plumtizincicola, Oryza sativa, Brassica rapa | Zn, Co, Pb | 85, 86, 87 |
| | MRP3 | ATP-Binding Cassettes | Roots, shoots | Hordeum vulgare | | 88 |
| | CAX2 and CAX4 | Cation exchanger | Tonoplast-localized | Arabidopsis thaliana | Ca, Zn, Mn | 89, 90 |
| | BCC3 | ATP-Binding Cassettes | Roots and shoots tonoplasts | Arabidopsis thaliana | Phytochelatin | 91 |
| 5) Efflux out of the cell | NRAMP3 and | Natural resistance-associated macrophage protein | Roots, shoots | Thlaspi caerulescens | Fe, Mn | 92 |
| | NRAMP4 | | | | | |
| 6) Xylem loading | HMA2 and HMA4 | P-type ATPase family, subfamily HMA(for Heavy Metal Associated) | Roots, shoots | Arabidopsis thaliana, Noccaea caerulescens, Oryza sativa | Zn, Pb, Cu | 93, 94, 95 |
| | MTP1 | Cation-diffusion facilitator (CDF) | Roots, Leaves | Oryza sativa | Zn | 96 |
| | CCX2 | Cation/Calcium (Ca) exchanger | Roots, shoots | Oryza sativa | Ca | 97 |
| 7) Phloem loading | LCT1 | Low affinity cation transporter | Shoot | Oryza sativa | K, Mg, Ca, Mn | 98 |
| | HMA2 | P-type ATPase family, subfamily HMA(for Heavy Metal Associated) | Shoot (node) | Oryza sativa | Zn | 99 |
synthesised. This hybrid showed a better adsorption efficiency of Pb (II) and Cd (II) by more than 50%, as compared to ZnO and TiO$_2$ individually (13).

Nanogel: These are ionic and non-ionic hydrogels of nano size made up of polymeric chains (104). NGs are more porous with higher water content (70–90% of the entire structure) and has better load bearing capacity. Chitosan and alginates are commonly used interpenetrated network (IPN) and well known for better stimuli-responsiveness (13).

It is very true that benefits of NPs usage in plant sciences has not been fully explored due to inadequate knowledge of their exact mode of action. Success of nanotechnology depends on the comprehensive knowledge of their bioavailability, uptake and accumulation in plants with simultaneous analysis of their negative impact on plant metabolism and growth. Uptake of NPs by plants is quite unpredictable as it depends on the coordination of multiple factors involving physical features of NPs, way of application and various soil parameters such as soil microbiota, organic matter, water retention capacity and soil texture (16). The route of administration of NPs has great impact on NP availability and uptake capacity of plants. Manufactured NPs are preferably taken up either by roots or the leaves as root exudates facilitate NP adhesion followed by NP internalization on root surface (105). Normally after getting accumulated in cell walls NPs form complex with HM to restrict its bioavailability for plants (11). Soil pH is one of the most important criteria that regulate the interactions of NPs and HM and its mobility. This is evident from the studies of few workers where pH was found to influence the charge of the nZVI and its surface protonation that interfere its uptake and further interaction with the metals (106). Adsorption capacity of CNTs was also affected by pH that alters the potential difference between CNT surface and the ions.

**Role of NP in Cd uptake and ROS mitigation**

NP has been successfully applied to reduce bioavailability of heavy metals. Use of Fe$_3$O$_4$ NPs was proven to be beneficial for immobilization of Cd in rice (107). After 3 years of through field study, the role of MPTS nano silica (mercapto functionalized nano silica) in the reduction of bioavailability and leaching effect of Cd in wheat grain have been established (108). Cd contaminated agricultural soil augmented with nano silica was found to be effective enough for long term Cd stabilization. Moreover, it was reported that hydroxyapatite NP dependent Cd immobilization was attributed to the rise in soil pH due to the release of phosphate in soil (109). Nanozero valent iron was found to be good enough in restricting Cd uptake by inhibiting the expression of various iron transporters in rice exposed to moderate (10 µM) Cd toxicity (110). In a recent study, Cd uptake was withhold due to the suppression of three Cd transporter genes OsLCT1, OsHMA2 and OsHMA3 in Cd stressed rice co treated with different concentration of biofabricated iron NP (111). NP triggers metabolic pathways related to ROS clearance under HM stress (102) to nullify the yield loss. ROS is an unwanted product of oxidative metabolism which in optimum concentrations acts as signalling molecule but has detrimental effect on biomolecules under excess accumulation. DNA damage, lipid peroxidation, protein degradation, membrane damage are common attributes of ROS induced oxidative stress. Photosynthetic efficiency is highly susceptible to heavy metal induced ROS production. Recent study (111) has established the

![Fig. 3. Schematic representation of different transporter proteins involved in Cd uptake in plants. Red and blue arrows show inward and outward movement of Cd.](image-url)
antioxidant capacity of biofabricated (biogenic, eco-friendly, less toxic) iron NP applied against Cd treated rice plant. Maximum increase in antioxidative enzymes (CAT- 32%, POD- 48%, SOD- 32%) with simultaneous decrease in ROS (H$_2$O$_2$: 54%) was recorded in Cd and drought stressed rice seedling with concurrent use of IONP (100 mg/kg soil) and chemically synthesised hydrogel NP. In another study, co-application of 10 µM Cd and 100 mg/l nZVI was proven to be highly efficient in lowering ROS (H$_2$O$_2$) formation in 17 days old rice seedling both in root (27.92%) and shoot (14.15%) with respect to untreated ones (110). They also reported confirmatory visual evidence of ROS reduction via ROS imaging by confocal microscopy. Nanoceria, a family of cerium oxide NPs was found to be an effective ROS scavenger in isolated chloroplast. Antioxidants capacity of nanoceria (CNPs) is based on the redox behaviour of Ce and its ability to shift oxidation states between Ce$^{3+}$ and Ce$^{4+}$ has already been confirmed (112) in green alga Pseudokirchneriella subcapitata. Though there are contradictory reports regarding nanoceria mediated ROS production, but the toxicity deciding factor is the Ce$^{3+}$/Ce$^{4+}$ ratio at the particle surface. Under higher ratio of Ce$^{3+}$/Ce$^{4+}$, nanoceria mimics SOD activity resulting hydrogen peroxide accumulation followed by impaired growth, while lower ratio facilitates catalase activity reducing ROS accumulation. Study revealed ROS scavenging potential of nanoceria inside *in vitro* chloroplast of Arabidopsis thaliana under excess light, heat and chilling stress (113). Poly acrylic acid nanoceria with low Ce$^{3+}$/Ce$^{4+}$ ratio not only reduced ROS production in leaf by 52% but also enhanced photosynthetic efficiency in terms of quantum yield and CO$_2$ assimilation rate in A. thaliana.

**Nanoparticles mediated Cd toxicity amelioration**

NPs serve to mitigate toxicity, enhance plant growth and offer versatile means of Cd immobilization of contaminated soil. Inorganic NPs (Ag, Se, Au, Ce, Fe, Ti, Zn) are most effective due to their unique bioactivities in nanofoms. Fig. 4 depicts different modes of NP administration on plants.

**Titanium oxide NPs**

As TiO$_2$ NPs could serve as a potential tool for agriculturally important crops. Recently use of nTiO$_2$ in plant growth and abiotic stress tolerance is under thorough scrutinization. Due to its large surface area, high adhesiveness, TiO$_2$ NP is successfully used in agricultural field. A greenhouse experiment was carried out (114) to assess the impact of TiO$_2$ NPs on salinity stressed Dracocephalum moldavica L.. 100 mg/l TiO$_2$ NP ameliorated detrimental effects of 100 mM NaCl and improved agronomic parameters by upregulating SOD and APX activities. Further research indicated positive effects of TiO$_2$ nanoparticles on Cd stressed cowpea plants (115) where soil augmentation with nTiO$_2$ (100 mg/kg) upregulated antioxidative enzyme activity (APX and CAT) with simultaneous reduction of membrane damage. This study revealed that TiO$_2$ could be used as a green alternative to ameliorate the Cd toxicity in cowpea plants. The positive impact of TiO$_2$ NP on root length, hormone concentration, antioxidative enzyme activity of Cd stressed rice indicated the healing capacity of this NP though seedling biomass remains unaltered (116). Successful inhibition of Cd absorption by foliar spray of TiO$_2$ NP in maize grown in moderate to higher soil Cd concentration (100-250 mg/l) was also documented (117). Moreover SOD and GST activity was elicited which corresponds to increase in various metabolic routes to mitigate Cd toxicity of maize.

**Selenium NPs**

Being an essential trace element Selenium NPs are easily taken up by plants. Its administration facilitates reduction of Cd contamination in cabbage (*Brassica rapa*) and lettuce (*Lactuca sativa* L.). Multifaceted benefit of Se NPs in Cd stressed *Brassica juncea* includes enhanced uptake of important minerals (Mn and Mg), increase in relative water content (RWC) and activities of anti oxidative enzymes (118). Moreover, elevated proline accumulation, over expression of glutathione reductase (GR) and peroxidase (POX) with subsequent decrease in ethylene, relieved the Cd induced oxidative stress in wheat plant (119). Actually, Se is incorporated as selenocysteine which is a vital amino acid in the active centre of selenoprotein that participates in oxidation reduction reactions (120). Similar observation was reported in pepper plant where Se NP treatment improved the quality and quantity of the pepper fruits and up regulated anti oxidative defense machinery against Cd stress.

**Cerium Oxide NPs**

Literature revealed the effectiveness of low concentration of CeO$_2$ NPs on plant growth due to its higher porosity and better catalytic activity (121). It has been reported that CeO$_2$ NPs (100 mg/kg) enhanced the rate of photosynthesis in soybeans while 500 mg/kg CeO$_2$-NPs lowered the same by 36% (122). CeO$_2$ NPs dependent reduction (70%) of Cd translocation was proven in soybean seedlings (123) grown in hydroponics with co-application of 1.0 mg/l Cd$^{2+}$ + 100 mg l$^{-1}$ CeO$_2$ NP. Over secretion of root exudates was observed due to the co-presence of Cd and CeO$_2$ NPs which enhanced the CeO$_2$ NP dissolution due to the alteration in the chemical environment of the plant rhizosphere. Foliar spray of CeO$_2$ NPs (200 mg/l) significantly elicited antioxidative detoxification capacity in hydroponically grown rice treated with CdCl$_2$: 50 µM and restricted the uptake of Cd (124). Several contradictory reports are available regarding the effect of CeO$_2$ NP in metal accumulation in plant. No significant impact of CeO$_2$ NPs (500 mg/kg) on Cd accumulation in soybeans cultivated in Cd polluted soil (1.0 mg/kg) was noted; rather uptake of Ce in plant was observed (125). This might be due to the combined application of Cd and CeO$_2$ NPs that influenced root apoplastic pathway.

**Silicon dioxide NPs**

As Silicon triggers stress tolerance potential in plants, SiO$_2$ is one of the most famous nanomaterials being used in environmental remediation. Being second most abundant soil element, Si confers tolerance to
plants against abiotic and biotic stress. Silicon NP (SiNP) mediated mitigation of Cd contaminated rice plants is of paramount interest since the last decades. Recent research indicated Si dependent reduction of soil to plant Cd translocation via upregulation of vacuolar transporter OVP1 which was positively correlated with low grain Cd accumulation in two rice cultivars (53). Few workers (11) observed positive effects of silica NPs on rice cells treated with Cd in suspension culture. Result revealed that Cd toxicity amelioration capacity of SiNP was size dependent and indirectly proportional to its effectiveness. The average Cd$^{2+}$ influx in rice cells treated with SiNPs (19 nM, 48 nM and 202 nM) decreased by 15.7-, 11.1- and 4.6- fold respectively on using noninvasive micro test technology. SiNP down regulated the expression of Cd uptake and transporter gene - OsLCT1 and OsNramp5, but elevated the expression of OsHMA3- gene involved in Cd transport into the vacuole and OsLsi1 - gene involved in Si uptake. A hydroponic experiment was designed with foliar application of 2.5 mM nano-silica to reduce Cd stress in rice seedlings which suffered from compromised growth and mineral deficiency (Mg, Fe, Zn) (126). Nano-Si application was found to be beneficial for growth enhancement and mineral uptake of rice seedlings with simultaneous significant increase in GSH content imparting better defense against Cd. It also helped to lower the rate of Cd translocation from roots to shoot. Foliar application of Si NPs was also found to be quite capable in minimizing Cd accumulation in rice grain (127, 128) and quality enhancement. Ali and his team reported Si NP dependent growth restoration of Cd treated wheat seedlings by increase in biomass, pigment content and restricting grain Cd concentration and electrolytic damage (129). Use of Si NP has gained focus in fertilizer formulations due to considerable enhanced bioavailability than conventional Si fertilizers (11).

**Nano-hydroxyapatite (nHAP) NPs**

Application of nHAP is not only cost-effective but also eco-friendly and highly efficient for HM immobilization in contaminated soil due to their better adsorption efficiency, low water solubility, high stability in redox reactions and good cytocompatibility. The nHAP works by exchanging the Ca$^{2+}$ ions present on its surface with the heavy metal ions present in the soil and thereby decreasing the transport of heavy metals to the plants. Application of 30 g/kg nHAP in 10 mgkg$^{-1}$ Cd-treated *Brassica chinensis*, showed a prominent decrease in Cd shoot translocation (62.36%) with increase in chlorophyll and vitamin C content was recorded followed by minimization of MDA content and elevation in anti oxidative enzymes activities (SOD, CAT and POD) (130). Positive effects of nHAP on Cd and Pb co-contaminated soil, was evident from reduction of water-soluble Pb and Cd by 72% and 90% respectively (131). Bioavailability of Pb and Cd also decreased by 12.5–27.5% and 17.7– 34.6% respectively. By releasing phosphate and increasing soil pH, nHAP reduces the phytoavailability of HM in the contaminated soil (109). An increase in the pH of the Cd-contaminated soil (10 mg/kg) was noted after the administration of nHAP (0.2%, 0.5% and 1%) (132).

**Iron NPs**

Iron has pivotal importance in the physiochemical processes of plants. It is essential in photosynthesis...
for synthesis of certain chlorophyll-protein complexes in chloroplasts, respiration, cell’s metabolism and co-factor of enzymes (112). Iron salt application has proved to be effective in enhancing the carbon and nitrogen assimilation in rice plants and also improving the yield (133, 134). Iron NPs act as efficient adsorbents due to their structural uniqueness, electronic features, large surface area, fast reaction speed and strong reduction ability (135). The various ways explored by nano iron for amelioration of heavy metal toxicity is by adsorption of heavy metals on its surface, promoting the formation of root surface iron film, activating the antioxidative defense mechanisms and by detoxifying the ROS. But, the tendency to aggregate and react quickly with the non-target compound reduces the stability of iron NPs (136). The individual and joint effects of citrate-coated magnetite NPs on the bioaccumulation and toxicity of Cd$^{2+}$ and Cr$^{6+}$ on wheat plants was studied for seven days by Lopez-Luna and team (137). The parameters studied were rate of germination, rooting and shooting and metal uptake. A 50% decrease in the root length of wheat at 2.7 mg Cd$^{2+}$kg$^{-1}$ and 5.6 mg Cr$^{6+}$kg$^{-1}$ was observed. However, the root length of plants was found to increase by 25% and 50% when magnetite NPs (1000 mg kg$^{-1}$) was added. A similar and non-interactive joint action of Cd$^{2+}$ and Cr$^{6+}$ was observed, but they strongly inhibited the growth of wheat seedlings. External administration of magnetite NPs diminished the accumulation of cadmium and chromium in the vegetable tissues and also alleviated heavy metal toxicity. Few workers scrutinized different effects of nZVI to alleviate Cd toxicity (138-140). 500 mgkg$^{-1}$ nZVI acts as growth promoter and elevates antioxidative enzyme activities in Cd treated plant. Activities of superoxide dismutase (SOD), catalase (CAT) and peroxidase (POX) were found to be upregulated in roots on administering nZVI but was down regulated in shoot. The soil exchangeable Cd decreased by 74.04% on nZVI treatment. It also helped to increase the proline levels and decreased ROS levels by increasing the levels of anti-oxidative enzymes to combat the abiotic Cd stress in the plants. nZVI unregulated the level of NPSH and restricted Cd translocation in the roots through chelation. Soil treatment and foliar spraying of Fe$_3$O$_4$ NPs was found to be quite effective in lowering electrolytic leakage and grain accumulation of Cd stressed wheat with simultaneous increase in SOD, POX activities and growth parameters (141). Application of starch-stabilized nZVI particles could improve the phytoextraction efficiency of ramie (142). Starch-stabilized nZVI particle (100, 500, 1000 mg/kg) was added to the contaminated sediment before plantation which elevated Cd uptake in the roots (16-50%), stems (29-52%) and leaves (31-73%). Oxidative injury of Cd-stressed ramie was withdrawn by low level (100 mg/kg) of nZVI administration, while the growth of plant was affected under higher nZVI concentration. This indicates that the choice of effective concentration is a prerequisite for phytoremediation success of nZVI. In rice plants exposed to Cd stress, external administration of nZVI suppressed the gene expression of iron transporters (IRT1, IRT2, YSL2 and YSL15) involved in Cd and Fe uptake (110). Moreover, the genes - OSVIT1 and OSCAX4 were over-expressed resulting in Cd sequestration in vacuoles which was further facilitated due to upregulation of phytochelatin synthesis. Though studies have reported that high doses of iron NPs are phytoxic for rice growth in hydroponic system (143, 144) but lower doses of nZVI enhanced seedling (14 days old) vigour in rice cv. Gobindobhog (145). Recent work has suggested the important and commercial role of nZVI as growth and yield enhancer in field grown rice (146). Plants germinated from nanoprimed seeds were reported to have better vitality regarding various agronomic traits (biomass, tiller numbers, broader leaves, photosynthetic efficiencies). Low dosage of nZVI (10 mg/l) was confirmed having no genotoxic effect also.

**Zinc Oxide NPs**

Zinc is an essential micronutrient which plays an integral role in various metabolic processes such as biosynthesis of carotenoids and enhancing the photosynthetic apparatus of the plants. Higher absorption efficiency makes ZnO suitable for soil and water decontamination, but due to its agglomeration at higher concentration it is tough to separate and recover (147, 148). Zinc oxide NP (ZnONP) was found to be very effective in mitigating Cd toxicity when externally applied to Cd-contaminated rice fields (1.0 mgkg$^{-1}$, 2.5 mgkg$^{-1}$, 5.0 mgkg$^{-1}$). The biomass of rice plant was found to increase by 13-22% and 25-43% in the rice fields exposed to 2.5 mgkg$^{-1}$ and 5.0 mgkg$^{-1}$ Cd respectively (149). Cd toxicity amelioration with 50 mg/l ZnO NP in various concentration of Cd stressed (0.4, 0.6, 0.8 mM) tomato was reported (150). Cd induced oxidative burst was relieved by ZnO NPs, which is evident from sharp drop in endogenous H$_2$O$_2$ and superoxide content generation with increase in growth parameters (height, biomass), photosynthetic rates, protein content, nitrate reductase and carbonic anhydrase activities. A study (151) exposed the *Leucaena leucocephala* different concentrations of Pb(NO$_3$)$_2$ - (0, 25, 50, 75, 100, 150 and 200 mg/l) and CdCl$_2$ - (0, 10, 20, 30, 40, 50, 75 and 100 mg/l) in a hydroponic medium. Seven combinations of ZnO NPs and two heavy metals-Cd and Pb was applied, where ZnO NP causes significant increase in chlorophyll content and total soluble protein content with sharp drop in the malondialdehyde (MDA) content. Activities of superoxide dismutase (SOD), catalase (CAT) and peroxidase (POX) were found to be uplifited. It was revealed that positive effect of combined treatment of organic amendments and ZnO NPs foliar spray (100, 200 mg/l) which was effective enough to increase biomass, yield, pigment content and antioxidative enzyme activities in Cd treated wheat (152). Recent workers have suggested that combination of biochar and ZnO NP was found to be more successful than individual application to deal with HM (Cd) toxicity (144, 152, 153). ZnO has enough potential to overcome combined water and Cd stress in wheat by minimizing oxidative damage and bioavailable Cd content in water deficit soil.

**Carbon nanotubes(CNTs) and Modified Carbon Black(MCB)**

Remarkable use of CNTs in nano biosciences is attributed to its light weight, unique electrical, mechanical features, chemical resistance, thermal
stability and higher durability (112). The effect of carbon nanotubes to reduce Cd toxicity was studied in *Spartina alterniflora* (154). The experimental design consisted of two Cd concentrations (50 and 200 mgkg⁻¹) with two CNT levels (800 and 2400 mgkg⁻¹). CNTs reduced Cd stress (200 mgkg⁻¹) by improving shoot growth and retrieving the water content. The effect of 100, 500, 1000 and 5000 mg/kg of Multi-walled Carbon Nanotubes (MWCNTs) was investigated on *Boehmeria nivea* L. seedlings grown in Cd-polluted water sediments (155). Results indicated that 500 mg/kg of MWCNTs successfully alleviated Cd-induced oxidative injuries by growth promotion and up regulating anti oxidative defense response. But poor solubility of CNT in aqueous media or organic solvents is the main constrain of its maximum use (156). The effects of MCB on 5 mgk⁻¹ of Cd-contaminated soil of *Lolium multiform* (Rye grass) and *Beta vulgaris* (Chard), was studied by Cheng and his colleagues (157). Positive results of MCB were reported which indicated increase in dry biomass of shoots of ryegrass and chard by 1.07 and 1.05 times respectively with elevated activity of urease and catalase after 25 days of incubation. In the control set, a decrease in the nitrogen-functional bacteria like *Nitrososphaera* was reported. MCB helped to increase the microflora in the soil and reduced the bioavailability of heavy metals in the soil. This promoted plant growth, by increasing nitrogen concentration in the soil.

**Conclusion and future prospects**

Uninterrupted advancement of technology, has introduced an era of nano bioscience, by the virtue of which several types of smartly designed NPs are available in the market. The matter of concern is the proper determination of nanoparticle’s interaction with plants to explore their ultimate benefit. Considerable effort has been made to enhance the phytoremediation efficiency by combining different strategies or modifying the NPs. Engineered NPs are also extensively utilized for quality crop production, as growth elicitor, nanopesticides, phytoremediating soil and water, nanofertilizers. Application of nanoparticles in plants has been an intricate area of investigation and data published over that last 10 years have been being evidence to this fact. Though there are numerous review articles available on nanoparticle-plant interaction, to our best knowledge, this article is unique being the first comprehensive review on NP mediated alleviation of cadmium inflicted stress in plants. However, regarding limitations, this review article does not discuss the synthesis and characterization of the various NP that have been employed to mitigate Cd stress in plants. Rather, this work mainly highlights the biological aspect of NP application and stress alleviation in plants. The ambiguity of success of NPs in growth promotion, HM remediation depends on various criteria, such as; exposure level, mode of application, optimum concentration. The mode of administration of NPs needs to be addressed more thoroughly in future research. Application of NPs in combination with other materials is a more promising aspect of plant growth booster and immobilization of HM. More advanced research work from various applied aspects is needed to understand the long-term performance of NPs in heavy metal decontamination purpose. It is true that the huge production cost behind NPs is one of the reasons behind their limited use. Therefore, we can suggest and look forward for the synthesis of eco-friendly and economic NPs by integrating the principles of green nanotechnology.

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**Authors’ contributions**

SC made the basic framework. SP1 supervised, curated and drafted the manuscript. SP2 conceived the main idea and scrutinized the manuscript. All authors read and approved the final manuscript.

**Conflict of interests**

Authors do not have any conflict of interest to declare.

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