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REVIEW

Exploring Metal Based Nanoparticles for Boosting Plant Tolerance to Heavy Metals and Trace Element Contamination

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ABSTRACT

Heavy metal pollution in agricultural soils is a significant challenge for global food production and human health with the increasing industrialization and urbanization. There is a concern about introducing innovative techniques that are eco-friendly, cost-effective, and have the potential to alleviate metals, enhance crop growth, and protect plants against various environmental threats. For this, nanotechnology is one of the promising solutions having various applications in almost every field of life. This review explores various nano-based strategies that use nanoparticles (NPs) to lessen the harmful effects that heavy metals have on plants. Incorporated literature including published research and review papers from the year 2015 to 2023. This review paper gives a thorough review of the current situation regarding heavy metal contamination in agricultural soils and how it affects plant health. The necessity of finding practical and eco-friendly ways to address these issues is emphasized, paving the way for the introduction of NPs. Then, it highlighted the mechanistic route of heavy metal toxicity alleviation in plants by their application as well as their long-term efficiency and prospects. This review also elaborated on various synthesis methods (physical, chemical, and green), but the emphasis on the green synthesis of NPs by utilizing plant extract offers dependable and sustainable benefits over traditional physicochemical techniques. Under trace element stress, NPs application enhances plant antioxidant defense system, ameliorating structural changes, immobilizing trace elements in growth media, and improving the physio-chemical properties of soil as well. However, there are still numerous limitations present on how these materials are synthesized, applied, and appropriately absorbed by plant cells. It is recommended to promote and fund long-term research to assess the long-term effects of using NPs on plant development, soil health, and possible environmental repercussions.

KEYWORDS

Nanotechnology; heavy metals toxicity; agriculture; physio-chemical attributes; crop yield

1 Introduction

In recent years, due to the fast industrial and urban expansion, there has been rising concern about the potential buildup of heavy metals (HMs) in agricultural soil [1,2]. Mainly HMs are the polluting agents [3] present in different environmental components. They also have deleterious effects on vegetation, animals, and humans because of their persistent, non-biodegradable, and poisonous nature [4–9]. In soil, HMs can be found in many different forms with a wide range in solubility and bioavailability [10,11]. Their excessive buildup in plant tissue interferes with several biochemical, physiological, and morphological functions either directly or indirectly, which affects crop productivity [12,13]. It depends on plant type, HM content, and exposure duration, which directly has a significant effect on the bioavailability of HMs. In various plants, they also can cause oxidative stress and decreased chlorophyll content, which results in photosynthesis reduction [14]. Abiotic variables and climate change are creating uncertainty in agriculture productivity by altering growing conditions such as temperature and water availability that affect crop yield. MTEs are beneficial in trace amounts, but their elevated concentrations during germination are dangerous because they can cause seed death and subsequently lessen plant germination overall [15,16]. Hence, environmental cleanup of these toxic HMs is of the utmost importance [17], such as the application of nanotechnology [18], particularly green technology, which holds great promise for resolving these issues.

Nanotechnology refers to the application of materials generally at the nanometer scale, typically between 1 and 100 nanometers, to attain distinctive properties. Recent nanotechnology advancements have facilitated the widespread use of nanoparticles (NPs) in a variety of science fields, industrial firms, and research. NPs have been identified in agricultural soil, including metals and their oxides, carbon compounds, zeolites, and bimetallic NPs [19,20]. The plants may be able to produce NPs, which are natural substances used to enhance plant morphology without having any adverse consequences. Recently, the application of NPs for abiotic stress conditions has obtained more attention [21]. According to studies, NPs can be applied to decrease the MTEs toxic effects in plants [22,23]. They can enhance morphogenesis of plants like metallic ones, including zinc-oxide (ZnO), and copper-oxide (CuO), the most prevalent NPs used in agriculture and industry. However, due to a lack of mechanisms that have not been clarified or further researched, some of the potential of NPs remains still hidden [9]. This comprehensive review investigates how nanotechnology can be applied to treat plants that harbor HMs in comparison to traditional methods. This article extensively analyzes and deliberates upon the benefits, hurdles, opportunities, and limitations linked to utilizing NPs to extract HMs from plants. Its objective is to furnish environmentalists with an enriched understanding of nanomaterial capabilities and their potential application in studies ranging from laboratory-scale to large practical scales. This review stands as an invaluable asset for researchers and practitioners interested in exploring nanotechnology-driven remedies for the effective and sustainable remediation of heavy metals, all while carefully considering the wider environmental impacts.

It is hypothesized that the use of NPs, which are distinguished by their special physicochemical qualities, is thought to be able to lessen the harmful effects of HMs toxicity and stress on plants via several different processes. These strategies could involve the production of defensive biochemical responses, modification of metal absorption and translocation pathways, and manipulation of plant physiological processes using NPs.

The objectives of this review are to thoroughly examine the effects of HMs on plants and the role of ROS in influencing plant health and growth with a specific focus on their interactions within soil. Additionally, aims to investigate nano-based approaches especially, the use of green synthesized NPs to improve plant resistance and mitigate stress and adverse effects on plant development. This study is significant because it has the potential to address a pressing environmental issue, HMs toxicity of agricultural soils. The results of this review could guide sustainable agriculture practices since HMs pollution seriously jeopardizes ecosystem health and food security. The work aids in the creation of environmentally friendly techniques for soil remediation and crop improvement by clarifying the processes of NPs action in plants.

It also highlights the necessity of conducting additional studies to investigate the combined use of NPs in agricultural systems, as this could improve crop resilience in contaminated settings and support sustainable agricultural productivity.

2 Applications of Nanotechnology for Environmental Remediation

Anthropogenic and natural activities are the two main causes of the complex problem of HMs pollution in the environment [24]. High concentrations of HMs in the air, water, and soil are a result of the fast expansion of industry and metropolitan areas, which has also amplified emissions, released pollutants, and raised resource demand [25]. During industrial activities, HMs are discharged into the atmosphere and can come back to the ground via depositions causing adverse effects as shown in Fig. 1. Wastewater discharges, including home sewage and industrial effluents are also an alarming environmental source of HMs [26–30]. Soils are the major repository of HMs in terrestrial ecosystems. Additionally, HMs are notorious for their significant toxicity in flora and fauna [2,31]. Lead (Pb), copper (Cu), and zinc (Zn) contaminated soils, all individually limit microbial biomass and enzymatic activities. These metals primarily concentrate in plants, where they transform into harmful forms that can infect people and other animals with deadly diseases. In addition to affecting plant growth, toxic HMs can alter the physiological and biochemical processes, resulting in structural damage and deformation [32–34]. The presence of HMs in the food web results ultimately in food chains has been the subject of numerous research in developed countries.

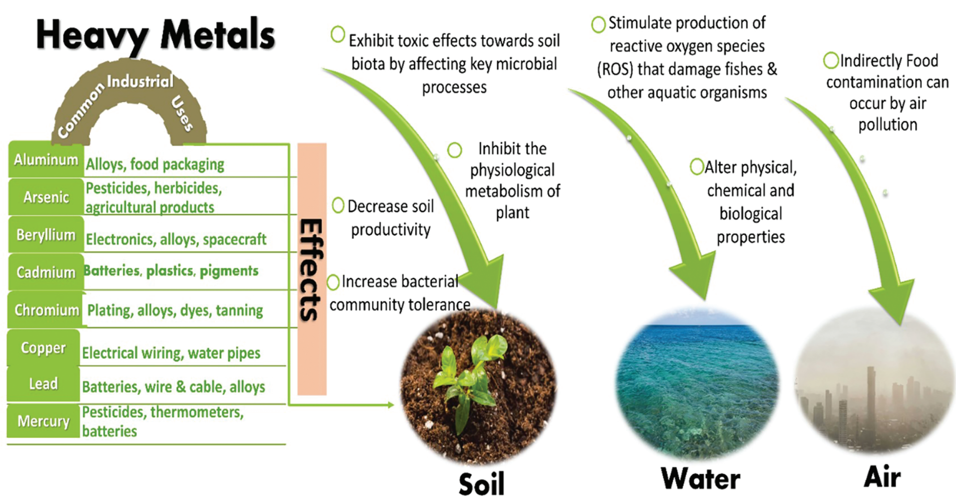

Figure 1: Anthropogenic sources of heavy metals and their key consequences on environment (air, water & soil)

Nanotechnology is also one of the innovative technologies that have promise for raising agricultural output using effective nano-pesticides and nano-herbicides to enhance soil properties and pathogen mitigation. The unique qualities and characteristics of NPs provide a huge potential for their various applications in therapeutic [35] and agriculture [36,37]. However, to address the safety and health issues posed by their application, more research/investigation is necessary. NPs play a pivotal role in alleviating HMs toxicity in plants through several mechanisms. Primarily, NPs can bind and immobilize HMs in the soil, reducing their availability for plant uptake. They also facilitate the breakdown or transformation of toxic metals into less harmful forms. Additionally, NPs can enhance the plant's defense mechanisms, boosting its ability to tolerate and detoxify HMs by triggering antioxidant production or stimulating stress-response pathways. Overall, NPs are contributed to mitigate HMs toxicity in plants by reducing uptake, transforming toxic forms, and enhancing the plant's natural defense mechanisms [38,39].

Metals and metal-oxides NPs are also the most explored NPs for environmental remediation [40]. Cerium oxide (CeO) NPs have been applied in a variety of soil remediation and agricultural applications as they are cost-effective and maintain their catalytic characteristics under stressful environments. The ability of CeO NPs to switch between valence states allows them to mimic the functions of certain enzymes like superoxide dismutase (SOD), catalase (CAT), phosphatase, and phosphotriesterase (PTE) to reduce the oxidative stress harmful effects [41]. The NPs could be used in the agricultural sector to treat plant diseases and enhance growth and nutrient contents [42–45]. Novel nanotechnological techniques are being developed to improve the characteristics of NPs that are being applied in agriculture for sustainable growth (Fig. 2). These methods should be environmentally friendly and can boost plant and crop growth without affecting the surrounding environment.

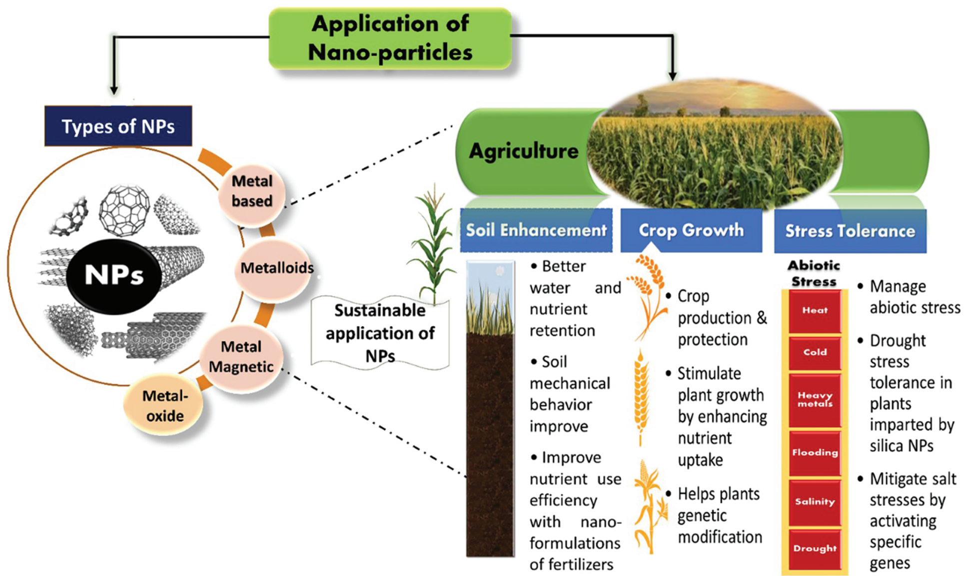

Figure 2: Eco-friendly applications of metal based nanoparticles for sustainable agriculture

3 Synthesis of Nanoparticles: Green *vs.* Physio-Chemical Methods

Physical and chemical NPs synthesis methods use materials and innovative equipment, which can harm the environment. To support the expanding use of NPs across a variety of industrial facilities, the field of nanotechnology have thus switched towards environmentally sustainable and economically feasible "green" synthesis over the past ten years. In contrast to conventional synthetic procedures, green synthesis offers dependable and sustainable ways to produce NPs [46]. The biological method of synthesizing NPs includes the utilization of microorganisms such as fungi, yeast, and plant parts extract as reducing agents of the metal ions [47,48]. Traditional methods have been utilized for a long time, but studies have shown that green method by plant extract seems more efficient because they have fewer failure risks and are less expensive [49]. Plant-based synthesis of NPs was quite simple as a metal salt is made with plant extract, and the process takes only a few minutes to a few hours at standard room temperature [50].

In general, top-down and bottom-up approaches are the two main ways to synthesize NPs [51–53]. The top-down approach incorporated the change of bulk materials to thinner crystallites through a physical pathway including milling and ionic sputtering (enormous mechanical energy sources) [54]. However, this strategy results in some drawbacks, causing secondary impressions, surface chemistry, and physicochemical properties alteration of synthesized NPs [55]. More notably by this approach, NPs are mostly unfeasible. Meanwhile, the bottom-down strategy involves particle formation through building block creation from ultra-small particles followed by assembling them [56,57].

The NPs synthesis using plant extracts is an environmentally friendly method as chemical synthesis might have unfavorable negative consequences on the environment. A wide range of vegetal species from different families have been used for the synthesis of NPs, such as *Garcinia cambogia* extract [58] and flower extract of Japanese honeysuckle (*Lonicera Japonica*) [59] in Ag & gold (Au) NPs synthesizing, respectively. *Cacumen platycladi* leaf extract can also be employed for Au NPs production [60]. Synthesized NPs by this method have been used leaf extracts as biological reducing agents and isolated their active ingredients. Plant extracts also have been widely used to produce copper oxide (CuO) NPs by using *Punica granatum* peels extract [61], *Azadirachta indica* plant extract [62,63], *Abutilon indicum* leaf extract [64], *Rheum palmatum* L. root extract [65] and aqueous extract of *Hyptis suaveolens* L [66]. Consequently, extracts of plants showed an ideal source for NPs production. Plant-based fabrication processes show less energy consumption and improved NPs stability [67].

4 Mechanistic Approach behind Metal Based Nanoparticles Interaction with Soil and Plants

The mechanisms by which NPs interact with soil and plants are complex and depend on their physicochemical properties and environmental conditions. In soil, NPs can interact with soil particles, organic matter, and microorganisms, which can affect their mobility, bioavailability, and toxicity to plants. For example, the surface charge and hydrophobicity of NPs can influence their adsorption and aggregation on soil particles.

Inside plants, NPs can enter plant tissues through various pathways, such as root uptake and foliar application. Once inside, NPs can interact with cell membranes, organelles, and metabolic pathways, which can affect their uptake, translocation, and toxicity to plants. For example, the size, shape, and surface chemistry of NPs can influence their penetration and translocation in plant tissues [68]. As smaller NPs tend to penetrate plant tissues more easily, surface alteration can increase or inhibit their uptake. The mechanism of mode of action of NPs also depends on the target organism and exposure route. In general, NMs can interact with biological membranes and proteins, disrupt cellular functions, generate ROS, and induce inflammation or other immune responses. For example, AgNPs can interact with bacterial cell membranes and disrupt their functions, while carbon nanotubes can induce oxidative stress and inflammation in lung cells.

5 Effects of NPs on Metals Uptake and Metalloids Reduction in Food Crops

Reducing the uptake of toxic metals and metalloids by food crops is crucial for ensuring food safety and preventing potential health risks. Preventing the uptake of metals by NPs is also important for ensuring food safety and preventing potential health risks. To achieve this, it is important to carefully evaluate the physicochemical properties of NPs and their interactions with plants and soil.

The interaction between NPs and HMs in plants is complex and can have both positive and negative effects on plant growth and physiology. Under metal stress, NPs can help to mitigate their toxic effects on plants by reducing their uptake and accumulation in plant tissues while enhancing photosynthesis and nutrient uptake, as shown in Table 1. For example, zinc oxide nanoparticles (ZnO NPs) have been shown to increase the accumulation of zinc in plants, which can help alleviate the toxic effects of HMs such as cadmium (Cd) and lead.

Regarding antioxidant enzymes, NPs can potentially alter the plant defense system under metal stress. For instance, rice seedlings were grown in hydroponic experiments under Cd stress, TiO_2 NPs treatment boosted SOD, CAT, and peroxidase (POD) activity. The antioxidant enzyme activities in a variety of plants under Cd stress, including wheat [69] and rice [29] were dramatically increased with a foliar spray of ZnO NPs [22]. On the other hand, researchers also demonstrated the potential of TiO_2 NPs negative impacts on the physiology and growth of maize. Increased TiO_2 NP treatments dramatically decreased the chlorophyll contents of maize crops.

CeO_2 NPs can promote root growth, activate the antioxidant enzymes [70–72] and can persuade oxidative stress. They also improve agronomic features, photosynthetic pigment content, and antioxidant enzymes in plants exposed to salinity stress and enhanced parameters of growth. Various plants react in different ways towards the presence of CeO_2 NPs. For instance, wheat (*Triticum aestivum* L.) treated plants with approximately 500 mg kg^{-1} CeO_2 NPs in the soil results in increased growth, more grain yield, and shoot biomass [73–75]. Contrarywise, it was observed that CeO_2 NPs suppressed photosynthesis in barley by lowering transpiration and stomatal conductance at 1000 mg kg^{-1} [76].

The uptake of TEs by plants depends merely on their chemical form as well as NPs effectiveness. For instance, in cucumber plants, selenium (Se) application can reduce the Cd concentration in roots. Researchers have demonstrated that for reducing plants' TEs uptake levels, selenite has shown more effectiveness than selenate. The Cd concentration reduction by using ZnO, Fe and Si NPs on wheat has also been studied [22,29,69]. These NPs have significantly increased wheat growth, biomass, and photosynthesis rate.

The effect of NPs on metal bioavailability in the environment is largely dependent on their speciation. Metal sorption and desorption can be impacted by the surface chemistry of NPs, including their coating and functional groups [77–79]. The binding or release of metals may be facilitated by functional groups on NPs, which could impact the metals' bioavailability. The size and surface area of NPs can change when they aggregate, which can affect their reactivity with metals. Due to their limited mobility, aggregated NPs may lower the bioavailability of metals. However, the release of metal ions during NPs dissolution can boost bioavailability [80,81]. NPs and metal ions in the surrounding environment have the potential to form complexes [15]. These complexes' characteristics may affect the speciation of metals and their consequent bioavailability. Metal binding and release can also be influenced by ligand exchange events that occur between NPs and the surrounding ligands.

6 Effects of Nanoparticles Seed Priming and Foliar Application on Plant Growth

Nano-priming can be applied to seeds to protect them during storage, enhance germination, boost plant growth, as well as to increase crops' resistance to biotic or abiotic stress conditions. It is an efficient procedure that can modify the signaling pathways of seeds and the whole plant lifespan. Seed priming is often classified as either abiotic or biotic priming, depending on the priming agent used. Abiotic priming, which covers both traditional and advanced methods of seed priming, is described as the use of non-living chemical and physical agents. Additionally, biofortification of seeds by nano-priming can be employed to encourage an improvement in food quality and production. Using these metal-based NPs for seed nano-priming has significant promise for use in agriculture. For instance, Kumar et al. [82] discovered that ZnO NPs promote germination and seedling development (shoot and root length). At high concentrations, seed priming with ZnO and FeO NPs promoted plant development, boosting spike length, plant biomass, leaves chlorophyll levels, and photosynthetic parameters [19]. Maswada et al. [83] demonstrated that seed priming with iron oxide nanoparticles (Fe_2O_3 NPs) of sorghum plants increased seed germination and plant growth. Photosynthetic pigments and biomass increased after treatment at 500 mg/mL.

Despite significant advancements, the application of physical techniques for NPs seed priming still requires extensive research in terms of priming protocols, appropriate dose, dose rate, and exposed period. On the other hand, several studies showed that foliar application of NPs was better than seed priming treatment [84,85]. This is further demonstrated by Abdel-Aziz et al. [86], who investigated effects of applying either carbon nanotubes (CNTs) or nanochitosan (Cs) unaccompanied or combined with NPK as fertilizers to french bean plants. Foliar treatment reduced the time to harvest as 80 days (37.5%) without affecting yield when related to seed priming treatment & control as 110 days. The NPs applications for foliar and seed priming have both been shown in various studies to have multiple benefits for plant growth. Raj et al. [87] has conducted an experiment on the growth, yield, and economics of Bt cotton using nano-zinc seed treatment and foliar application. Nano ZnO foliar application (@1000 ppm) showed sophisticated productivity as 2718 kg ha^{-1} in seed cotton, an increase in plant height as 190.1 cm, and soil plant analysis development (SPAD) chlorophyll meter value than other concentrations. Various studies have shown positive effects of seed nano-priming and foliar applications like enhancing the growth of plants and development, improving yield, and nutritional food quality but still limitations present for their use. Under some conditions, foliar application of NPs alleviates metal toxicity under metal stress as compared to seed priming. NPs, when combined with additional amendments like farmyard manure (FYM), charcoal, and bio-nanocomposites, also play a key role in reducing metal toxicity, promoting plant development, and affecting the bioavailability of TEs. For instance, Ali et al. [29] assessed the effectiveness of ZnO NPs at various concentrations in Cd-contaminated soil to test Cd alleviation on rice plants alone and with biochar (1.0 w/w). The findings demonstrated that either independently or in combination with biochar, rice plant biomass and photosynthesis were enhanced by Zn NPs. In general, both seed priming and foliar application of metal-based NPs have the potential to improve plant growth and productivity. However, further research is needed to determine the optimal concentration and timing of NPs application for different plant species and growth stages, as well as the potential long-term effects on soil health and the environment.

7 Mechanisms of Trace Elements Tolerance in Plants

7.1 Nanoparticles' Influence on Plant Attributes Focuses on the Tes Absorption and Translocation

Plants that are exposed to an environment polluted with metals suffer significant effects on their vegetative and reproductive development, which ultimately affects agricultural productivity and performance [88,89]. The complicated physiological characteristic of TE absorption and subsequent accumulation in plants is primarily controlled by the element transporters and metal chelators present in the plant system [80]. When present in optimal quantities, these advantageous components raise the nutritional content of plants and have an impact on several processes vital to healthy plant development and productivity. When they are present in excess, though, they become poisonous to plants and cause them to become less able to absorb and accumulate other non-essential elements [90,91]. Several strategies were used to reduce these emerging pollutants' phytotoxicity in the soil plant system [92,13]. The nexus of nanotechnology and plant science has attracted a lot of attention lately, especially when it comes to comprehending how NPs affect plants' ability to tolerate TE toxicity [93]. Because of their distinct physicochemical characteristics, NPs provide opportunities as well as problems to the field of plant biology.

7.2 Antioxidant Defense Systems Enhancement

In plants, mostly HMs can cause oxidative stress that results mainly in reactive oxygen species (ROS) production [94,95]. In such a situation, the application of NPs was observed to be more effective on plants in enhancing the antioxidant defense system and reducing ROS. The ROS have been shown in recent years to be signals that control a variety of developmental ways and responses to the environment [96,97]. Additionally, an increase of TEs in plants might result in oxidative bursts due to enhancement in ROS generation and lipid peroxidation. In this case, NPs reduced the toxicity that TE induced in the plants. To enhance plant development in wheat and lower oxidative stress and Cd content, an experiment was conducted by Latif et al. [19] using Zn and Fe NPs. Both NPs enhanced Fe and Zn concentrations in wheat while reducing oxidative stress and Cd concentrations. Arsenic toxicity in plants can result in the production of ROS, which can harm cells oxidatively and disrupt metabolism. For instance, the MDA concentration (17.5%–30.8%) of rice under arsenic stress was decreased by 10−100 mg L^{-1} ZnO NPs amendment [98]. Similar research has demonstrated that Fe_3O_4 NPs have good impacts on root growth and integrity of membranes by lowering the MDA contents in maize grown in soil amended with NPs (50, and 500 mg/kg) for the duration of 28 days compared with control [99]. The growth, chlorophyll content, and antioxidant activity of basil plants were enhanced by the foliar application of ZnO NPs alone or in combination with Cu and Mn NPs [100]. Foliar application effects of Si and TiO_2 NPs on oxidative burst and Cd uptake by rice was observed by [19]. Nanoparticles lessened EL, and MDA and improved SOD, POD, CAT, and ascorbate peroxidase over the treatment. Thus, findings showed that foliar application of NPs was successful in lowering oxidative burst and enhancing antioxidant defense. Jalil et al. [101] examined the mitigating effects of SiO NPs as well as the physiological and molecular responses of rice genotype "9311" to Cd stress. The study highlights that rice plants' physiological functions are enhanced by the SiO NPs applications and their tolerance to Cd stress as well. Foliar application under abiotic stress can enhance chlorophyll content, increase K^+ absorption, modify Na^+ levels, and lessen damage in cell wall compared to untreated plants. The effective strain response of tomato subjected to CuO NPs depends on hydrogen sulphide (H_2S)-mediated persulfidation of antioxidize [102]. And show that it controls CAT, APX, and POD activity, improving the plant's reaction to oxidative stress. On the other hand, Se may protect plants against various hazardous TEs by regulating their intake and transport in plant parts and can be beneficial to promote plant growth and photosynthesis and control ROS at low-concentration applications. But the reverse scenario can also be observed at high quantities that do not show benefits of reducing oxidative stress [103].

7.3 Plants Morphological and Physiological Alterations by TEs

Plant structural changes brought on by TEs stress result in decreased growth and yield. For example, in the presence of manganese (Mn), Cu, nickel (Ni), leaves turn pale in color, pale pink between veins and leaf chlorosis happens respectively in plants [104,105]. By modifying gene transcription, enhancing antioxidant defense mechanisms, and generating structural alterations, NPs prevent TEs from moving from roots to shoots in plants.

Pérez Velasco et al. [106] assessed the impacts of ZnO NPs application practices, surface modification, and morphology on the growth and biomass on tomato plants. The findings have shown that ZnO NPs treated tomato plants meaningfully boosted in height, stem diameter, and its dry weight. Maraei et al. [107] assessed the impacts of treated TiO_2 NPs on the nutritional worth and broccoli's growth. The results have shown that TiO_2 foliar treatments had a satisfactory impact on vegetative growth as compared to the control. Hussain et al. [108] results demonstrated that Ti NPs application has a considerable effect on the plant's growth, and significantly increases the soybean diameter. Lower TiO_2 NP concentrations (2 and 10 ppm) have also been revealed to be advantageous as enhance the shoots length of wheat seedlings, though with the higher TiO_2 NP concentrations exposed, neutral effects and the repressive effects have also been detected at bulk/greater concentrations of TiO_2 NPs. As 53% shoot length, 33% root length, 44% dry weight, and 48% fresh weight of wheat have also enhanced when calcium phosphate and TiO_2 NPs (both 40 ppm) are used together in contrast to the controls [109]. An experiment was carried out to induce Cd stress tolerance in maize by the exogenous application of silicon nanoparticles (Si NPs). Three levels of Cd (0, 15, and 30 ppm) and five dosages of Si NPs (0, 100, 200, 300, and 400 ppm) were used for the maize hybrid (SF-9515). The biochemical measurements and morphological characteristics of maize were among the response factors. The findings showed that, for maize plants, a Cd level of 30 ppm remained the most severe, as measured by minimal characteristics such as shoot length (39.35 cm), shoot fresh weight (9.52 g), and shoot dry weight (3.20 g) [110].

Table 1: Nanoparticles effects on plant growth under HMs

Plant species	NPs type	NPs size & dose	Experiment type	Mode of NPs exposure	Metal treatment	Duration	Effects	References
Rice (*Oryza sativa* L.)	Mg O NPs	38–57 nm 50, 100 and 200 mg kg^{-1}	Pot	Soil	As	30 days	Substantially increase biomass and reduce As s concentration in roots.	[2]
Rice	Si NPs + TiO_2 NP	Si NP 50 nm ≥ size TiO_2 NP 20–30-nm Si NPs (50, 100 mg/L), and TiO_2 NPs (25, 50 mg/L)	Pot	Solution	As	21 days	NPs upregulate plant antioxidant enzymes' activities and improve growth. The treatment with 100 mg/L Si-NPs had the greatest beneficial impact on rice growth.	[111]
Rice	ZnO NPs	15–137 nm 100 mg kg^{-1}	Hydroponic	Solution	As, Cd	45 days	Without impacting growth of rice, NP lessen the concentration of Cd and As in grains, particularly As (III).	[112]
Maize (*Zea mays* L.)	SiO_2	170 ± 10 nm 10 μM	Hydroponic	Solution	As	7 days	Plant growth and photosynthesis rate enhanced. While oxidative stress and As concentrations decreased.	[113]
Maize	TiO_2 NPs	6.5 ± 0.76 nm 0, 100, 250 mg/L 0, 50 and 500 mg/kg	Hydroponic	Foliar	Cd contaminated	14 days	Alleviate Cd-induced toxicity via increasing SOD and GST activities. Decrease Cd concentration in maize plant tissues.	[114]
Maize	Fe_3O_4 NPs	30 nm	Greenhouse exp.	Suspension	————	4 weeks	The maize plant's roots lengthened greatly, and its MDA level dropped, showed the beneficial impacts on root growth and membrane integrity.	[99]
Maize	CeO_2	Size: ——— 500 mg kg^{-1}	Pot	Solution	Cd	30 days	CeO_2NPs promoted the corn growth and development and also has positive impact on root and leaf biomass.	[115]
Maize	TiO_2 NP	(<100 nm) 0, 5, 10 and 20 mg L^{-1}	Hydroponic	Solution	————	20 days	Except for Fe, applications of TiO_2 NP had a favorable impact on N, P, K, Zn, Mn & Cu concentrations. Boost maize's uptake of nutrients.	[116]
Wheat (*Triticum Aestivum* L.)	ZnO + Fe NPs	Size:——— Zn NPs (0, 25, 50, 75, and 100 mg L^{-1}) Fe NPs (0, 5, 10, 15, and 20 mg L^{-1})	Pot	Seed priming	Cd contaminated Soil	24 hr	Positive influence on wheat photosynthetic. The biomass and nutrition increase while Cd toxicity have decrease.	[22]

(Continued)

Table 1 (continued)

Plant species	NPs type	NPs size & dose	Experiment type	Mode of NPs exposure	Metal treatment	Duration	Effects	References
Wheat	CuO NPs	8–12 nm 25, 50, 75 and 100 mg/L	Pot	Foliar	Cd contaminated soil	121 days	Reduced oxidative stress, raised specific enzyme activity, promoted wheat growth and physiology under Cd stress, and lowered malondialdehyde levels.	[39]
Wheat	ZnO NPs	Size:——— 0, 25, 50, 75, and 100 mg kg^{-1}	Pot	Foliar	Cd contaminated soil	125 days	Enhanced photosynthesis and grain production. Reduce Cd contents in shoots and roots.	[69]
Wheat	ZnONPs	Size:—75 mg/kg	Pot	Foliar	Cd contaminated soil	125 days	Improve the leaf chlorophyll contents and antioxidant enzyme activities.	[117]
Wheat	CuO NP	28 ± 14 nm 50 mg/kg	Pot	Soil treatment Solution	Cu	28 days	In wheat rhizosphere, NPs upsurge the microbial community health.	[118]
Wheat Seedlings	CuO NP	50 nm 0.001...0.1 g/L	Petri plates	Suspension	———	7 days	Positive effect on seed germination capacity and increase in root and stem length observe at 0.01 g/L.	[119]
Wheat	CuO NP	>95 nm 0, 0.5, 1, 2, 4 and 6 mg mL^{-1}	Petri plates	Suspension	Cu	——	Enhance vigor, plumule and radicle length, germination with upsurge in phytochemical compounds biosynthesis in wheat shoots at 0.5 mg mL^{-1}.	[120]
Wheat	Fe_3O_4 NPs + CuO NPs	25 nm Fe_3O_4 NPs and 25 nm CuO NPs 7, 35, and 70 mg/L	Hydroponic	Solution	——	Two-week	Fresh biomass, Shoot and root length of wheat plant increase through Fe_3O_4 NPs.	[121]
Wheat	S NPs CuO NPs	CuO (40 nm) and S (47 nm) S NPs, 200 mg/L CuO NPs, 25 and 50 mg/L	Hydroponic	Solution	Cu	10 days treatment	Increase plant growth and biomass. Also Alleviate Cu toxicity in seedlings by decreasing its buildup in plant tissues.	[122]
Wheat	FeO	25, 50 and 100 mg kg^{-1}	Soil	Solution	Cd	60 days	At all treatment levels, NPs enhance the nutrient contents and alleviate Cd uptake in roots.	[123]
Soya bean *(Glycine max* L.)	CeO_2	41.7 ± 5.2 nm 0, 500 mg kg^{-1}	Pot	Solution	Cd 0, 0.25, 1 mg kg^{-1}	30 days	Increases the plant light energy use efficiency by photosystem II. In soya bean, did not affect Cd accumulation, but significantly upsurge Ce in plant tissues, solely in roots and older leaves.	[124]
Soya bean		20 nm 25 µM ZnO	Hydroponic	Solution	As 25, 50, 100 200 µM	Seeds germinated on moist sterile	As stress decrease in root and shoot tissues and encourage plant growth.	[125]

(Continued)

Table 1 (continued)

Plant species	NPs type	NPs size & dose	Experiment type	Mode of NPs exposure	Metal treatment	Duration	Effects	References
	Se-NPs + ZnO-NPs	25 µM Se NP				vermiculite for 10 days		
Soya bean	Ti NP	0,125, 250, 500, 1000 mg L^{-1}	Field	Foliar	———	4 months	Significantly benefit to plant growth. Enhance diameter and stem strength, SPAD values in comparison to control. Besides, foliar application meaningfully rise photosynthetic rate.	[108]
Carrot (*Daucus carota* L.)	GO + ZnO	≤40 nm avg. particle size 0.05 mg ml^{-1} & 0.10 mg ml^{-1}	Pot	Foliar	———	90 days	Significant increases growth, chlorophyll, carotenoid and proline contents of plant.	[126]
Coriander (*Coriandrum sativum* L.)	Si NPs	20–35 nm 0, 500, 1000, and 1500 mg/kg	Greenhouse exp Plastic boxes	Foliar	Lead spiked soil	4 months after seeds sowing	Reduce Pb concentration in plants and improve defense system.	[127]
Coriander	Se NPs	10–40 nm 0, 20, 40, and 60 mg L^{-1}	Pot	Foliar	Cd contaminated soil	15 days	Improve shoot and root weight, chlorophyll (Chl), and RWC.	[128]
Coriander	Si NPs	10–20 nm 0, 0.75, 1.5 and 2.25 mM 10–20 nm	Pot	Foliar	Cd contaminated	————	Improve the growth and EO yield under Cd stress at 1.5 or 2.25 µM Si-NPs.	[129]
Spinach Beet (*Beta vulgaris* var. bengalensis)	TiO_2, ZnO, P NP	<100 nm ZnO (0, 5, 10, 15, 20, 25 ppm), P (10, 20, 30, 40, 50 ppm) TiO_2 (10, 20, 30, 40, 50 ppm)	Field	Foliar	————	150 days	All NPs treatments positively affected germination and seedling growth of spinach beet by ZnO, P and TiO_2 NPs occurred with 12.48% 13.01% and 10.93% respectively compared to control.	[130]

Note: RWC = Relative Water Content; MDA = Malondialdehyde.

Fe NPs were administered in a variety of ways to strengthen the wheat crop. Fe NPs seed priming, however, was found to be more effective in increasing the contents of proline, chlorophyll a, b, and total chlorophyll in wheat plants when applied topically at concentrations of 10, 20, and 30 mg L^{-1} [131]. CeO_2 NPs meaningfully enhanced fruit weight at doses of 10 mg L^{-1}, whereas increasing the stem elongation at doses of 1 to 10 mg L^{-1} [132,133]. Thus, fewer studies have compared the functional variations in plants in the response towards metals and NPs, therefore, more comprehensive research would be crucial to understand the metals tolerance mechanism.

8 Interaction between NPs and Trace Elements

The interaction between NPs and soil TEs is a complex and dynamic process that can affect the mobility, bioavailability, and toxicity of both NPs and TEs in soil. Through adsorption and desorption, NPs can absorb soil particles, organic matter and TEs. This can affect the mobility and bioavailability of them in soil, as well as the potential for uptake by plants. NPs with high surface reactivity can interact more strongly with TEs in soil, leading to increased adsorption and reduced bioavailability. However, this can also increase the potential for the release of TEs under certain conditions, such as changes in pH or ionic strength.

8.1 TE Bioavailability Alteration in Soil

NPs due to their high sorption capacity, may diminish and/or limit the bioavailability TEs in plants. Depending on the concentration and NPs used, as well as how long NPs and TEs interacted, NPs may immobilize TEs in growth media as shown in Fig. 3. However, soil characteristics are essential for NP dispersion, aggregation, stability, transport, and bioavailability as well as their release into the soil. Labile TE fractions can easily be changed into stable TE fractions using NPs. Due to their nanoscale properties, the mobility, bioavailability, and toxicity of co-existing contaminants like TMs and hazardous organics in the soil environment could all be affected by NPs. The bioavailability of TEs in the soil is influenced by both metallic and organic NPs. ZnO NPs impact on soil TEs concentration has been studied by Baysal et al. [134]. According to the study, ZnO NPs exposure caused a decrease in the amount of Al, Mg, Ca, and Cu in the soil as well as the adsorption of TEs into soil. However, the exposure of ZnO NPs enhanced the Fe content while not affecting Cu or Ni. The impact of nanoscale zerovalent iron (nZVI) and ferrous sulphide (FeS NPs) supported by biochar on the availability of Pb and Fe, as well as the micro-ecology in lead-contaminated soil was examined [135]. In excessive Pb-contaminated alkaline soil, nZVI @ BC exhibited the best immobilization effect on Pb, although Fe_3O_4-NPs toxic consequences on soil micro-ecology was only marginal. According to Rossi et al. [136], on soybean CeO_2 NPs did not affect Cd accumulation, but it markedly boosted Ce accumulation within tissues of plants, particularly in older leaves & roots.

8.2 Soil Physicochemical Properties Enhancement

On soils, limited data showed that metal oxide nanoparticles affect biochemical parameters. By changing the speciation of TEs and altering the physiological, biochemical, and biological characteristics of soil, NPs successfully immobilized TEs in soil solution. If kinetic limitations are removed, NPs, particularly ZnO NPs, dissolve chemically in the soil's aqueous phase can either directly or indirectly change the soil's properties. In the same way, using maize as the test crop, Verma et al. [137] carried out a model experiment in a greenhouse to investigate how ZnO NPs interact with soil. When ZnO NPs were applied, soil pH and organic carbon levels significantly decreased, EC significantly increased, and P, Zn, and Fe availability significantly increased. Through the consumption of reductive material and increased quantity of NPs, Zhang et al. [138] detected an upsurge in soil redox potential after the use of ZnO NPs and CuO NPs. The detrimental effects of TEs on soil lead to a decline in soil quality.

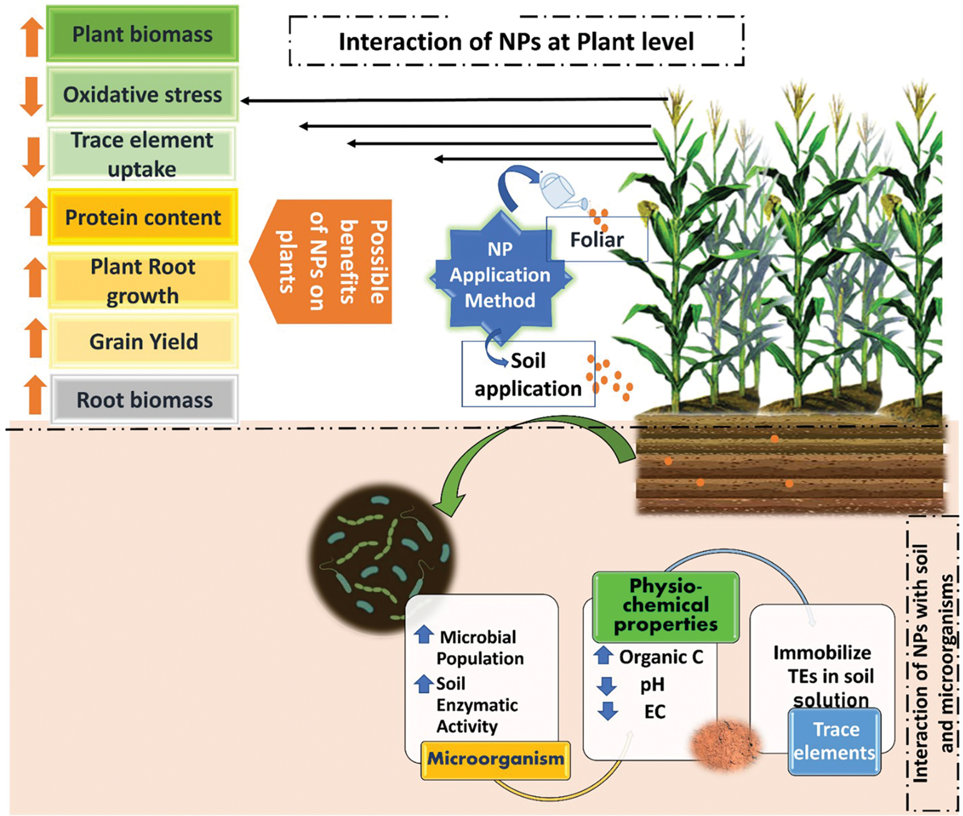

Figure 3: Mechanism and interaction of nanoparticles with the plants and soil and its positive effects on plant growth and soil properties

8.3 Effect on Biological Properties of Soil

The biological characteristics of the soil are influenced by the presence of HMs. Pb, Cu, Cr, and Cd concentrations in soil have an impact on biomass, soil respiration, and enzyme activity. They have been shown to alter microbial colonies and biomass, may have a positive impact on rhizospheric microorganisms and biomass content, and can increase soil fertility. Rajput et al. [139] studied both CuO and ZnO NPs applications and have shown that they promoted bacterial and fungal communities in soil through increasing bacterial and fungus groups. However, at higher concentrations than 250 mg/kg soil, the beneficial effects of NPs on soil microorganisms were hampered [71]. On the sunflower plant cultivated under Cr stress, the administration of CeO_2 NPs greatly increased the enzymatic activities [140]. So, based on previous research findings, it can be demonstrated that NPs, because of their distinctive characteristics and useful applications in various agricultural soils have drawn a lot of interest, but limited studies highlight their role in improving biological properties of soil. So, more work has to been done in future regarding that.

9 Limitations of Using Metal based NPs

The presence of metallic NPs in soil is a serious problem because they can cause secondary contamination, which increases the hazards to the environment and public health. Due to their small size and larger surface area, they are more mobile and can easily leach into groundwater or travel through the air, causing accidental dispersion beyond the original location of pollution [141,142].

Metal-based NPs effectiveness is often concentration-dependent as their dosages may not result in substantial benefits, in contrast, high dosages can be toxic to plants. This may complicate NPs application, in order to determine their optimal dosage for improving plant growth without causing remains a challenge [143]. The mechanisms through which NPs alleviate HMs stress are still not fully understood. While some research indicated that NPs could lower oxidative stress and increase antioxidant enzyme activity, further research is needed to determine the precise molecular interaction between NPs, HMs, and plant physiology [144]. This ambiguity may make it more difficult to develop NPs formulations that work well for agricultural applications. The efficacy of NPs can be affected with their interaction with soil and environmental conditions. Factors including soil chemistry, pH and organic matter can change NPs behavior, result in different outcomes in various soil types [23]. In the food chain, concerns exist with respect to metal-based NPs bioaccumulation. While NPs can assist plants in tolerating HMs, their own potential toxicity and the risk of entering the food supply necessitate careful evaluation to ensure food safety [41]. The damage can be lessened by creating substitute, eco-friendly NPs, but it is crucial to fund studies on remediation strategies. Advanced remediation techniques integrate biological and nanotechnological remediation techniques, whereby the manipulation of nanoscale processes facilitates the adsorption and degradation of contaminants.

10 Conclusions and Future Perspectives

Heavy metal contamination of agricultural soils has recently been a difficult problem for global food security. Nano-remediation strategies, including various metal-based NPs applications, are promising solutions to enhance plant growth and reduce metal uptake. The review highlighted how green synthesized NPs increased agricultural crop yields in several ways, with significant improvements shown in plant height and chlorophyll content, as well as reduced oxidative stress, raising specific enzyme activity under metal stress. Due to their lower cost, eco-effectiveness, and increased plant tolerance to a variety of biotic and abiotic stimuli, it is anticipated that their usage in agriculture will continue to increase. In TEs condition, NPs application at their best treatment level enhances the plant antioxidant defense system, ameliorating the structural changes, immobilizing TE in growth media, and improving the physio-chemical properties of soil as well. There is a significant research gap in understanding the molecular mechanisms underlying the interaction between green-synthesized NPs and plants, hindering the optimization of strategies for mitigating metal stress and enhancing plant growth. While existing studies show positive effects, a comprehensive understanding of the specific physiological processes activated by NPs is lacking. Investigating these mechanisms is crucial for establishing a more robust foundation for the practical application of green-synthesized NPs in sustainable agriculture. For this, it is recommended to promote and fund long-term research to assess the long-term effects of using NPs on plant development, soil health, and possible environmental repercussions.

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