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A Review on Crop Responses to Nanofertilizers for Mitigation of Multiple Environmental Stresses

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ABSTRACT

Over the past years, alterations in the environment have had an adverse impact on the global agricultural system, leading to difficulties in plant growth, physiology, and productivity due to non-living factors. These difficulties pose a significant risk to both global food security and agricultural advancement, necessitating innovative methods for long-term sustainability. Nanotechnology has emerged as a promising solution to address these difficulties by utilizing nanoscale products like nanofertilizers, nanofungicides, nanoherbicides, and nanopesticides. Nanoparticles provide distinct advantages in agriculture due to their small size, ability to easily penetrate cellular barriers, and efficient absorption by plants. Numerous studies have demonstrated that the application of nanoparticles can improve both the quantity and quality of crop yields, even when faced with various biological and environmental pressures. This research study primarily focuses on investigating the impact of non-living pressures on plants and examining how nanoparticles can help alleviate these effects. Additionally, it explores the molecular, metabolic, and anatomical adaptations that plants undergo to thrive in challenging environments. Nonetheless, it is essential to acknowledge that the widespread utilization of nanotechnology raises concerns regarding potential risks to the environment and human health.

Keywords: abiotic stress, nanotechnology, nanoparticles, salinity, drought, heat.

INTRODUCTION

The term "abiotic stress" describes the harmful effects of inanimate objects on living things. (Zandalinas et al., 2021). Global environmental challenges, including drought, salt, heavy metals, extreme temperatures, and climate change-induced factors, pose significant threats to plants (Zandalinas et al., 2021; studies and 2006, 2006; Liang et al., 2013). The response of plants to stress depends on various factors such as the affected tissue or organ, as well as the severity and duration of the stress (Munns and Tester, 2008). Early stress-signaling pathways are activated by plants to mitigate stress, involving the release of second messengers like calcium, reactive oxygen species (ROS), phospholipids, and nitric oxide (NO), as well as protein kinases (Bhatla and Lal, 2018; Zhang et al., 2022). SnRk1 kinases play a role in helping plants recover from disturbances by regulating stress-responsive genes and enhancing stress resistance (Zhu, 2016). Plant hormones, such as abscisic acid (ABA) and ethylene, serve as important signals triggering plant defense responses, including stomatal closure during drought (Zhu, 2016). Plants activate transcription factors and antioxidant molecules to counteract the excessive production of ROS, which can damage critical physiological functions (Zhu, 2016; Zörb et al., 2019). Under abiotic stress, plants increase the synthesis of compounds like phenolics, flavonoids, phytochelatins, and proline to mitigate its effects (Emamverdian et al., 2015; Zulfiqar and Ashraf, 2021). Long-term abiotic stress adversely affects plant growth and development, resulting in significant reductions in agricultural output, with up to half of the yield losses in major crops attributed to abiotic stress (Lowry et al., 2019a). To address these challenges, researchers are exploring various strategies, including genetic engineering, plant breeding, and the application of nanotechnology (Lowry et al., 2019a). Nanoparticles are emerging as a promising approach in sustainable agriculture, as they have the potential to enhance crop yield and improve plant tolerance to abiotic stress (Lowry et al., 2019a). Thus, the utilization of nanoparticles is considered a beneficial and promising strategy to overcome current and future production limitations in sustainable agriculture (Lowry et al., 2019a).

ROLE OF NANOFERTILIZERS IN UPTAKE AND THEIR MOVEMENTS IN PLANTS

The interaction, absorption, and mechanism of nanoparticles within the plant system involve complex processes (Figure 1). Root epidermal regions serve as the primary site for nanoparticle absorption, facilitated by osmotic pressure and capillary forces. Nanoparticles ranging from 3 to 5 nm in size are effectively absorbed through small pores in the root epidermal cell wall (Nair et al., 2010). Despite their larger size compared to typical absorbing pores, nanoparticles can induce the formation of cell wall pores, enabling their entry into the plant system. The initial interaction between nanoparticles and the epidermis is influenced by the particle's charge (Xu et al., 2022). Once inside the plant, nanoparticles can follow two pathways to reach their target tissues: the apoplastic and symplastic pathways. Transport through xylem channels is facilitated by membrane carrier proteins, with any aggregates present in different channel regions being transported back to the roots through the phloem. In leaves, nanoparticles can enter the internal system through both the cuticle and stomata. Particles smaller than 5 nm primarily utilize the cuticular pathway, while larger particles take the stomatal route. The transport mechanism within leaves resembles that of roots. Nanoparticles are transported to shoots, roots, fruits, and other plant parts via the phloem, utilizing both apoplastic and symplastic pathways (Khan et al., 2019a).

Pathways of foliar application for their uptake by plants

During agricultural practices, nanoparticles are commonly applied as a spray onto the leaves. These nanoparticles adhere to the leaf surface

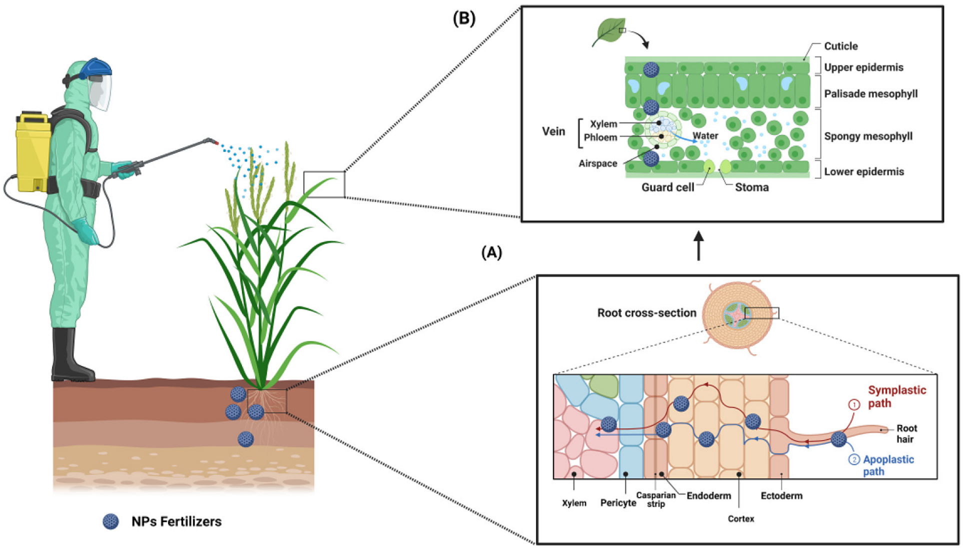

Figure 1. Diagrammatic representation of the application of nanofertilizer (a) root and transport through xylem and phloem vessel and (b) uptake via stomata transport into different parts of plants

and enter the plant through two main pathways: the cuticle and stomata. The leaf's waxy cuticle, which is composed of wax, cutin, and pectin, acts as a natural barrier against nanoparticle penetration while also preventing water loss in developing leaves (Yang et al., 2015). However, the waxy cuticle contains hydrophilic and lipophilic channels with different diameters, ranging from 0.6 nm to 4.8 nm (Avellan et al., 2019; Eichert et al., 2008). Hydrophilic nanoparticles smaller than 4.8 nm can diffuse through the hydrophilic channels, while lipophilic nanoparticles can penetrate the cuticle surface via the lipophilic channels (Bussières, 2014). Recent studies using confocal fluorescence microscopy have shown that carbon dots smaller than 2 nm can enter cotton leaves through the cuticular pathway. It is worth noting that the plant's epidermis has limited capacity to absorb nanoparticles due to the relatively small size of the cuticle pore channels (Hu et al., 2020a). Consequently, nanoparticles may accumulate in the epidermis and vascular tissue after being sprayed onto the leaf surface (Figure 1). However, research suggests that nanoparticles can also be absorbed through the stomatal pathway, allowing them to be transported to other plant organs (Figure 1).

Pathways of foliar application for their uptake by plants

The initial interaction between nanoparticles and plant roots involves the adsorption of nanoparticles onto the root surface. According to Hu et al. (2020a), nanoparticles with positive charges have a higher affinity for accumulation and absorption on the negatively charged root surface, which is attributed to the release of chemicals from root hairs, such as mucus and organic acids. Lateral roots provide an additional surface for nanoparticle adsorption, facilitating their entry into the root column (Peng et al., 2015). While the root epidermis, similar to the leaf epidermis, plays a crucial role in nanoparticle interaction, the epidermis of root hairs and primary/secondary roots is not fully developed, allowing direct contact and penetration of nanoparticles (Khan et al., 2019). Water can pass through the cell wall of the root epidermis, but the presence of small pores restricts the passage of larger particles (Khan et al., 2019). In the absence of the exodermis, nanoparticles can enter the xylem, which is the central column of the root (Su et al., 2019). Furthermore, Wu and Li (2022) suggest that certain nanoparticles can damage the plasma membrane, leading to the formation of new pores in the epidermal cell wall and facilitating the entry of larger nanoparticles. The uptake of nanoparticles by plant cells involves various mechanisms within plant tissue (Wu and Li, 2022). These mechanisms include the ion pathway, endocytosis, protein binding to cell membranes, and physical damage. The hydrophilic pathway has been identified as one route for nanoparticle entry into plant cells. However, due to the small pore size, this pathway is not highly efficient for nanoparticle uptake (Wu and Li, 2022). Another significant pathway is endocytosis, where nanoparticles enter cells through the invagination of the plasma membrane. Endocytosis does not exhibit particle size selectivity, although particles smaller than 1 μm have been demonstrated to be taken up by plant protoplasts (Grillo et al., 2021). For instance, endocytosis has been proposed as the mechanism for the uptake of carbon-based nanoparticles and carbon nanotubes by root cells of Catharanthus roseus. Additionally, plants can uptake nanoparticles by binding to transport proteins in their cuticle.

FACTORS AFFECTING UPTAKE OF NANOFERTILIZER

Size of nanofertilizer

Extensive research has been conducted to explore the size-dependent uptake of metal-based nanoparticles in plants. It has been observed that metal-based nanoparticles smaller than 50 nm in diameter can enter plant leaves through the stomatal pathway (19). The uptake efficiency of leaves decreases as the particle size increases. For example, Zhu et al. (2020) conducted a study using fluorescein isothiocyanate (FITC)-labeled ZnO-NPs (30 nm) applied to wheat leaves. They utilized confocal microscopy to observe the entry of nanoparticles into wheat chloroplasts through the stomatal pathway and subsequent exit from the leaf epidermis. The study also investigated the impact of stomatal opening and closing on ZnO-NPs uptake. It was found that wheat leaf cells had lower zinc concentrations in chloroplasts and cytoplasms when stomatal diameters were reduced. Wheat leaves were also found to absorb coated gold nanoparticles of various sizes (3, 10, and 50 nm), possibly through disruption of the cuticle layer or diffusion through stomata (Avellan et al., 2019). Transmission electron microscopy (TEM) confirmed the uptake of MgO NPs (27–35 nm) by watermelon leaves (TEM). Moreover, nanoparticles composed of silica, polymers, and natural materials exhibited similar absorption behavior by plant leaves as metal-based nanoparticles, with the critical size for absorption varying depending on the nanoparticle type. TEM analysis demonstrated that SiO_2 nanoparticles with a size of 54 nm could enter Arabidopsis thaliana leaves through the stomatal pathway (El-Shetehy et al., 2020). Zhao et al. (2021) demonstrated that cucumber leaves could take up FITC-labeled mesoporous silica nanoparticles (200–300 nm). Another study discovered that polystyrene nanoplastics with a size of 93.6 nm could enter lettuce phloem through trans epidermal transport. Recent findings have shown that rice leaves can absorb and distribute chitosan-based silicon nanoparticles with a size of 166 nm (Jia-Yi et al., 2022).

In terms of root absorption from the soil, nanoparticle size plays a significant role in the process. Previous studies have demonstrated the absorption of gold nanoparticles (3.5 nm) in the roots of *Vicia faba* L. and cerium oxide nanoparticles (81 nm) in maize roots (Zhao et al., 2012). Additionally, research has indicated that the uptake of TiO_2 nanoparticles by wheat roots is directly proportional to particle size. Wheat roots can absorb TiO_2 nanoparticles ranging from 36 to 140 nm, with absorption decreasing as the particle size increases. Wheat roots are unable to absorb TiO_2 nanoparticles larger than 140 nm (Larue et al., 2012). Generally, it is believed that metal-based nanoparticles larger than 100 nm face challenges in being absorbed by plant roots (Banerjee et al., 2019). However, interestingly, nanoparticles larger than 100 nm derived from silicon and natural polymers can still be absorbed. Arabidopsis plants treated with Si nanoparticles (200 nm) were found to have absorbed them in their roots after 6 weeks of exposure (Slomberg and Schoenfisch, 2012). Confocal microscopy and transmission electron microscopy have shown that sugarcane roots can absorb zein nanoparticles with an average particle size of 135 nm (Prasad et al., 2018).

Surface charge of nanofertilizer

The ability of nanoparticles to penetrate plant mesophyll tissue is influenced not only by their size but also by their shape and charge. The shape of nanoparticles affects their surface area and contact angle with the plant surface, thereby influencing their uptake. A study found that rod-shaped gold nanoparticles were more easily absorbed and internalized by Arabidopsis leaves compared to other nanoparticle shapes (Su et al., 2019). Plant leaves have the ability to take up both positively and negatively charged nanoparticles. For example, the absorption of graphene quantum dots (GQDs) with different surface charges (NH2-GQDs and OH-GQDs) on maize leaves was evaluated. It was observed that both positively charged NH2-GQDs and negatively charged OH-GQDs were taken up by maize leaves through stomata (Sun et al., 2022). Similarly, the adsorption of positively charged FITC-labeled F-P-ZnO NPs and negatively charged F-N-ZnO NPs on wheat leaves was confirmed using confocal microscopy. The study demonstrated that positively charged nanoparticles had stronger adsorption in leaves compared to negatively charged nanoparticles (Zhu et al., 2021).

Regarding root absorption, nanoparticle surface charge plays a role due to the negative charge of plant root cell walls. Plant roots are less sensitive to electric charge compared to leaves. Positively charged nanoparticles are electrostatically attracted to the negatively charged cell wall, preventing their penetration into the tissue and keeping them on the root surface (Bosker et al., 2019). Confocal microscopy showed that nanoparticles with different particle sizes (20–100 nm) and surface charges, including negatively and uncharged nanoparticles, were taken up by Arabidopsis thaliana root cells and transported into the root's xylem. However, negatively charged nanoparticles were restricted to the root epidermis and could not penetrate further into the Arabidopsis root (Parkinson et al., 2022).

Crop species

Nanoparticle uptake in plant leaves is influenced by multiple factors, including the plant species (Ha et al., 2021). The distribution, density, and size of pores in the leaves are important factors affecting nanoparticle uptake. Stomata in monocotyledonous plants are more orderly and uniformly shaped compared to dicotyledonous plants. The growth stage and life cycle of plants also affect the rate of nanoparticle absorption in leaves. While some plant species have stomata on both the upper and lower epidermis, this is not typical (Zhu et al., 2020). In cases where both sides of the leaves have stomata, dicotyledon plants tend to have approximately 1.4 times more stomata per square centimeter on the lower epidermis than the upper epidermis. Monocotyledon plants, however, exhibit a similar number of stomata on both sides (Zhu et al., 2020). Abiotic environmental factors, such as temperature, humidity, and light, also influence the rate of nanoparticle absorption (Rani et al., 2022). Dicotyledonous pumpkins have been found to be more efficient in absorbing CeO_2 nanoparticles compared to monocotyledonous wheat (Adrees et al., 2021; Shahbaz and Ashraf, 2013). Tomatoes, when compared to festuca, demonstrate a higher rate of Ce nanoparticle absorption. Recent research by Hu et al. (2020b) reveals that the extracellular space in monocotyledonous plants like maize is insufficient for nanoparticle entry, whereas dicotyledons like cotton, with a higher number of stomata, provide more opportunities for nanoparticle entry.

COMPARISON BETWEEN NANOFERTILIZERS AND TRADITIONAL FERTILIZERS

Singh et al. (2021) propose that the application of nanoscale transporters and compounds holds promise in agriculture for achieving precise delivery of macromolecules and controlled release of agrochemicals. This approach has the potential to decrease reliance on fertilizers and pesticides while still maintaining high crop yields. Commercial fertilizers, in contrast to nanoagrochemicals, exhibit lower efficacy due to their larger particle size and limited ability to penetrate water. Additionally, the repeated use of chemical fertilizers can lead to the accumulation of toxic heavy metals in the soil, resulting in an ecological imbalance (Singh et al., 2021).

The excessive use of chemical fertilizers can result in soil contamination through leaching or the accumulation of leftover fertilizer in plant waste. In order to achieve sustainable agriculture, the use of nanoagrochemicals is important as it improves the efficiency of fertilizers and helps regulate water quality (Fraceto et al., 2016). However, prolonged exposure to and accumulation of nanoparticles (NPs) in plants can have negative effects on human health and food security (Verma et al., 2022). NPs can be absorbed and stored in the edible tissues of crops, disrupting plant physiology by interfering with cellular and subcellular structures and functions. Moreover, the natural accumulation of NPs or metal ions can modify the composition of proteins, lipids, and nucleic acids through the generation of ROS (Ye et al., 2020). The widespread use of NPs in agriculture raises concerns from environmental, ethical, health, and safety perspectives (Rajput et al., 2021).

However, at present, there is only speculation and no concrete evidence supporting the idea that NPs are harmful to human health (Staro et al., 2020). While the application of nanotechnology in agriculture has gained popularity for the development of novel NPs, it is crucial to thoroughly evaluate the specific advantages and disadvantages associated with their use. The proliferation of NPs in the agricultural environment is a direct consequence of the development of nanotechnology, and the safe disposal of large quantities of NPs, which amount to several hundred tons per year, raises concerns among researchers and professionals (Rajput et al., 2021). NPs can be found in various regulated entities, including air, water, soil, hydrobionts, algae, fungi, and the tissues of plants and animals (Rajput et al., 2020b). Limited research has been conducted on the fate and migration of NPs in soil compared to other sources. Despite acting as a sink for NPs, soil also plays a crucial role in providing essential nutrients to food crops (Ghani et al., 2022). This analysis provides insights into the potential impact of NPs on ecological sustainability, human health, and food safety.

NANOFERTILIZERS SYNTHESIS

Nanotechnology enables the manipulation and control of devices at the nanometer scale, allowing for the development of nanostructured materials in “smart fertilizers” (Sivarethinamohan and Sujatha, 2021). These nanofertilizers offer numerous benefits, such as improved nutrient uptake, enhanced soil fertility, increased absorption rates, higher photosynthesis and production rates, reduced soil toxicity, fewer applications, improved plant health, and minimized environmental pollution (Rajput et al., 2020a). Examples of nanomaterials used in these fertilizers include gold nanorods, ZnCdSe/ZnS core-shell quantum dots, InP/ZnS core-shell quantum dots, and Mn/ZnSe quantum dots. The effectiveness of nanomaterials as nanofertilizers depends on factors like size, content, concentration, chemical properties, and the specific crop being grown. When nanofertilizers containing nanoparticles (NPs) come into contact with water, they release their nutrients into the soil (Vishwakarma et al., 2018). To prevent nutrient losses, NPs in nanofertilizers can be encapsulated in polymers or thin coatings. Leveraging the unique characteristics of NPs in nanofertilizers is a strategy to enhance crop productivity while minimizing input costs. The production of nanofertilizers involves combining or adding single nutrients to nanoscale adsorbents. The cationic nutrients are not altered during the physical and chemical processes used to create nanomaterials, while the anionic nutrients undergo surface adjustment (Panpatte et al., 2016). Encapsulating fertilizers within NPs can be done in one of three ways: delivering the nutrient as nanoscale particles or emulsions, coating it with a thin polymer layer, or enclosing it within nanoporous materials (Mittal et al., 2013). Nanofertilizers have diverse applications, including nanoscale measurement control, virtual forecasting modeling, and manipulation of nanoscale matter. Solid NPs also have implications in agricultural areas. Bio-fabrication of NPs through biological processes has become popular as a way to make nanofertilizers that are beneficial to the environment, interact well, and also don't harm people (Al-Mamun et al., 2021). Nanoscale coating fertilizers, nanoscale additive fertilizers, and nanoporous materials are the three types of nanofertilizers that can be prepared based on plant nutrient requirements. Nanofertilizers containing hydroxyapatite can supply plants with calcium and phosphorus due to their high surface area to volume ratio (Yasmin et al., 2021). Improved crop quality and the promotion of sustainable agriculture could be possible with the use of mesoporous silica nanoparticles (NPs) due to their large surface area, mesoporous architecture, biocompatibility, and lack of toxicity. Silica nanoparticles have been shown to promote plant development in salty environments (Pan et al., 2022). Carbon-based nanomaterials like carbon NPs, carbon nanotubes (CNTs), fullerenes, and fullerols act as plant growth regulators by increasing germination, chlorophyll, and protein levels. Different physical or chemical processes are used to create a wide variety of nanofertilizers from organic and inorganic nanomaterials. Nanomaterials can be classified as either organic (such as lipids and polymers) or inorganic (such as metal oxides such as AgO, MgO, ZnO, and TiO_2). Potential agrochemical carriers include polymeric NPs with polymeric cationic properties, such as chitosan, and the ability to interact with negatively charged molecules or polymers. Chitosan utilizes as a biodegradable, natural, and agriculturally safe carrier.

Mechanism of action of nanoparticle-mediated mitigation of Abiotic stress in plants

Several studies have explored the effects of nanoparticles (NPs) on plant growth, and different responses have been observed depending on the concentration and nature of the NPs used. Higher concentrations of NPs have been found to be detrimental to plant growth, while appropriate doses can have beneficial effects (Naderi and Danesh-Shahraki, 2013). NPs can enter plant cells through various pathways in the cellular membrane, including direct penetration. It is proposed that NPs may function as stress signaling molecules, leading to the upregulation of stress-related genes. When plants experience stress, their defense mechanisms are activated, including the expression of regulatory factors. Metal-based NPs can increase reactive oxygen species (ROS) levels above safe thresholds, triggering the plant's defense system to respond to stress. A meta-analysis of plant responses to metal-based NPs revealed common reactions such as changes in root architecture, activation of antioxidant mechanisms, and involvement of unique signaling pathways mediated by phytohormones in response to NPs-induced stress signaling (Rakgotho et al., 2022). The effects were found to be influenced by the characteristics of the NPs and the duration of exposure. For example, the downregulation of genes involved in trichoblast development, a specialized subset of epidermal cells responsible for root hair formation, may explain the observed changes in root architecture following NP exposure. Additionally, genes responsive to indole acetic acid (IAA) and ethylene (ET) have been identified as positive regulators of root hair formation (Li et al., 2022). Treatment with NPs typically induces changes in defense-related cellular processes. Genes encoding proteins essential for maintaining a healthy ROS balance, such as NADPH oxidase, glutathione S-transferase (GST), superoxide dismutase (SOD), and peroxidases (POX), are upregulated in response to NP treatment (Li et al., 2022). NPs can enhance the expression of genes associated with antioxidant enzymes (Massange-Sánchez et al., 2021). For instance, TiO_2 NPs were found to increase the activity of the SOD enzyme in onion seedlings, with the effect being more pronounced at higher NP concentrations. However, high concentrations of TiO_2 NPs inhibited both onion seedling growth and seed germination (Janmohammadi et al., 2016). TiO_2 and SiO_2 NPs have also been shown to enhance germination and growth in Glycine max seeds (Hatami et al., 2016). NPs can act as cytoplasmic signaling molecules or interact with calcium-binding protein (CaBP) complexes within plant cells (Jiang et al., 2021). Upon reaching plant cells, NPs are recognized by NP-specific proteins, which activate the transcription of genes involved in stress response (Jiang et al., 2021). This triggers a series of intracellular signaling pathways that lead to the upregulation of genes involved in enhancing the plant's tolerance to abiotic stress. The sensitive to desiccation (RD20) gene, for example, is upregulated in Arabidopsis thaliana in response to salinity, drought, or abscisic acid (ABA) (Jiang et al., 2021). Furthermore, nanoparticles have been proposed to activate antioxidant enzymes by scavenging ROS. ZnO-NPs were found to significantly increase the expression of Cu/Zn SOD, Fe/Mn SOD, catalase (CAT), and ascorbate peroxidase (APX) in plants under drought stress. Transcriptomics and proteomics analyses have been conducted to gain a better understanding of the interaction between plants and nanomaterials (Hussain et al., 2016). Cu-based NPs (50 nm) were found to influence oxidative stress-responsive genes, genes involved in brassinosteroid production, and genes related to root development (Mittler, 2002). Metabolomic analysis of cucumber plants exposed to 40 nm-sized Cu NPs showed an increased accumulation of secondary metabolites involved in cell signaling and defense responses, while metabolites involved in flavonoid and fatty acid synthesis, riboflavin, and amino acid metabolism were decreased (Mohamed et al., 2022). Transcriptome analysis of tobacco plants treated with TiO_2 NPs revealed higher transcript levels of miRNAs 399 and 395, which are believed to regulate plants' adaptive responses to nutritional stress. Treatment of Arabidopsis thaliana seedlings with 3 nm-sized carbon nanodots resulted in dose-dependent root elongation, with upregulated genes involved in cellular response to phosphate starvation, UDP-glycosyltransferase activity, and stimulus response, while genes associated with chloroplast structure and function were downregulated (Baig et al., 2021). Metabolomics research has also linked the activation of the defense response to increased accumulation of carbohydrate components in the plant cell wall.

NANOFERTILIZERS APPLICATION FOR MITIGATION OF ABIOTIC STRESSES

Indeed, plants are exposed to various stresses such as drought, submergence, flooding, chilling, freezing, and heat stress, all of which have been extensively studied in terms of their impact on plant resilience. The role of plant natriuretic peptides in maintaining salt and water balance in plants has been a topic of recent discussion in relation to multiple plant stresses. The effects of natural variations in multiple abiotic stresses in a hyper-seasonal edaphic savanna and the potential of transcriptomic analysis under various stresses have also been explored, including the impact on plant boron deficiency and toxicity (Lutts et al., 2016). In addition to nanofertilizers, various other materials have been investigated for their roles in mitigating combined stresses and enhancing plant productivity. However, the management of nanofertilizers in the agricultural sector is still in its early stages, as it depends on a wide range of soil and environmental factors. Figure 2 provides an overview of the reactions of cultivated plants to different stresses when nanofertilizers are used. These stresses can be categorized into three types: singular, combined, and multiple. Singular stresses, such as salinity, drought, heavy metals, water stress, and nutrient deficiency, can potentially be alleviated by supplementing the soil with nanonutrients like copper oxide (CuO), selenium oxide (SeO_2), zinc oxide (ZnO), silicon dioxide (SiO_2), iron oxide (FeO_2), and sulfur (S) (Grillo et al., 2021). Combined stresses involve the combination of two different stress factors, such as heat stress and drought, salinity and heat, heat and salinity, salinity and heavy metals, and heat and drought (Lowry et al., 2019b; Rani et al., 2022). In these cases, specific nanonutrients can potentially help mitigate the combined stresses. For example, applied nano-Si has been studied for drought and salinity, nSe for salinity and heat stress, nSi for salinity and drought, nZn for drought and heat stress, and nZn for drought and heavy metals (Younis et al., 2020). However, there is currently a lack of literature on the application

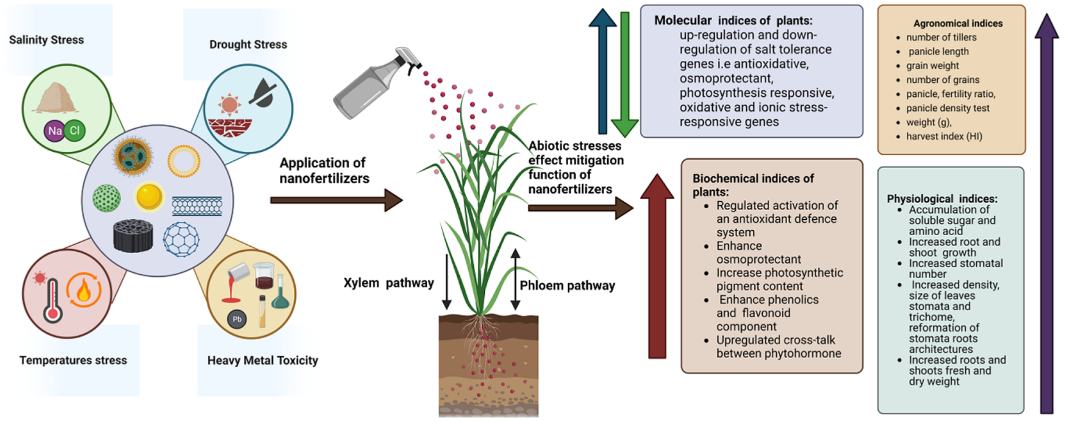

Figure 2. Diagrammatic representation of mode of action of nanofertilizers to mitigating the effect of abiotic stress

of nanofertilizers in situations involving multiple stresses. Further research is needed to investigate the potential of nanofertilizers in alleviating the effects of multiple stresses on plants.

Drought stress

Drought stress, characterized by limited water availability, high temperatures, and reduced water uptake by plants, exerts significant effects on plant development, including seed germination and seed setting stages. Multiple studies have demonstrated the ability of silica nanoparticles (NPs) to enhance drought tolerance in plants, while other types of NPs have also shown similar effects. Silica NPs application has been shown to improve the growth and physiological parameters of hawthorn seedlings even under drought stress conditions. Likewise, Triticum aestivum has exhibited positive outcomes under drought stress, with increased starch and gluten content leading to enhanced growth and yield (Jaberzadeh et al., 2013). TiO_2 NPs have also demonstrated the ability to promote germination and plant growth, contributing to improved drought tolerance. When plants are exposed to drought stress, TiO_2 treatment has been found to increase biomass, maintain relative water content (RWC), and stimulate antioxidative enzymes, thus providing beneficial effects (Faraji and Sepehri, 2020). The use of hydroxyapatite nanoparticles (CaNP) in jute seeds has been found to enhance drought tolerance by regulating proline levels through proline biosynthesis (Das et al., 2016). In the case of maize seedlings, drought stress typically hampers growth. However, a study revealed that treatment with yttrium-doped Fe_2O_3 NPs improved the photosynthetic machinery, as evidenced by increased chlorophyll and carotenoid content. Furthermore, these NPs showed efficacy in mitigating the negative impacts of drought on B. napus (Palmqvist et al., 2017). These findings collectively indicate that various types of nanoparticles, including silica, TiO_2, hydroxyapatite, and yttrium-doped Fe_2O_3 NPs, have the potential to enhance drought tolerance in plants through mechanisms such as improved growth, maintenance of water content, stimulation of antioxidative enzymes, regulation of proline levels, and enhancement of photosynthetic activity. (Jaberzadeh et al., 2013; Faraji and Sepehri, 2020; Das et al., 2016; Palmqvist et al., 2017).

Salinity stress

Crop growth and productivity worldwide are significantly affected by salt stress, which occurs when plants are exposed to excessive sodium (Na^+) and chloride (Cl^-) ions. In response to osmoregulation, a mechanism to maintain normal physiological functions, plants can generate reactive oxygen species (ROS) and experience nutrient imbalances, resulting in oxidative stress. To counteract these effects, plants accumulate organic compounds like amino acids, polyols, sugars, glycine betaine, and quaternary ammonium compounds during osmoregulation. It is crucial for plants to maintain ion homeostasis by reducing Na+ concentration and increasing K^+ concentration in cells to mitigate the effects of ROS and activate enzymatic machinery (Isayenkov, 2012). Nanoparticles (NPs) have been found to alleviate environmental stresses through various mechanisms. They can activate specific genes, facilitate the accumulation of osmolytes, and provide free nutrients and amino acids. Studies have shown that treating Cucurbita pepo with SiO_2 NPs enhances the transpiration rate, water use efficiency (WUE), carbonic anhydrase activity, and resistance to salinity stress (Siddiqui et al., 2022). TiO_2 (anatase) NPs interfere with linolenic acid in the electron transport chain (ETC) and modify photoreduction activity (Siddiqui et al., 2014; Su et al., 2009). In Abelmoschus esculentus, the application of ZnO-NPs to the leaves improves photosynthetic functionality and enzymatic machinery, thereby alleviating the adverse effects of salinity stress. In summary, studies have demonstrated that nanoparticles, such as SiO_2, TiO_2 (anatase), and ZnO-NPs, can enhance plant resilience to salt stress by promoting physiological processes, modulating electron transport, and improving photosynthetic functionality (Siddiqui et al., 2022; Siddiqui et al., 2014; Su et al., 2009).

According to a study conducted by Alabdallah and Alzahrani in 2020, the combined application of ZnO nanoparticles (NPs) and silicon (Si) as a foliar spray on mango seedlings resulted in improved growth. This was achieved by enhancing carbon assimilation and nutrient uptake, leading to increased photosystem II activity and maintaining relative water content, which helped reduce membrane damage. Oprica et al. (2021) found that the application of SiO_2 NPs in plants like Solanum lycopersicum, strawberry, and Ocimum basilicum had several positive effects. These included increased vegetative growth, enhanced epicuticular wax layer, accumulation of proline, and regulation of salt stress-related genes, which effectively alleviated the negative impacts of salinity stress. The potential of silver nitrate nanoparticles (AgNPs) for mitigating salinity stress was proposed by Isayenkov and Maathuis in 2019. They discovered that treating Triticum aestivum with AgNPs increased the accumulation of peroxidase (POD), proline, and sugar, resulting in improved germination. Isayenkov (2012) observed that the application of CeO, carbon nanotubes (CNTs), and graphene NPs to cotton and Catharanthus roseus increased protein and amino acid content during the reproductive stage. This enhancement played a role in improving tolerance to salinity stress. In a study by Torabian et al. in 2016, ZnO NPs were found to enhance salt tolerance in lupine plants. The application of ZnO-NPs reduced malondialdehyde (MDA) and Na+ contents while improving germination in cumin seeds. This helped restore normal osmoregulation, improve the photosynthetic system, and decrease MDA and Na^+ levels, effectively mitigating the harmful effects of NaCl.

Temperatures stress

Temperature stress can have adverse effects on plants, leading to disruptions at the cellular level and even plant death. When plants experience heat stress, they initiate various physiological and biochemical responses to protect cellular structures and restore balance. One of these responses involves the production of heat shock proteins (HSPs) and activation of antioxidant mechanisms to counteract oxidative stress (Zhu, 2016). Nanoparticles (NPs) offer potential solutions for mitigating the negative impacts of heat stress on plants. For instance, the application of selenium NPs to sorghum plants improved their antioxidant mechanisms, enabling them to scavenge reactive ROS generated during heat stress (Djanaguiraman et al., 2018). Similarly, selenium NPs enhanced the tolerance of Lycopersicon esculentum to both high and low temperature stresses, thereby improving the plant's ability to cope with temperature fluctuations. In wheat plants exposed to high-temperature stress, the use of silver nanoparticles (AgNPs) resulted in improved growth parameters. These improvements included increased root shoot length, root number, fresh and dry weight, leaf area, and leaf number (Iqbal et al., 2019). Under chilling stress conditions, the application of zinc oxide (ZnO) NPs in Oryza sativa helped regulate the antioxidative system and chilling response transcription factors. This application potentially enhanced the plant's capacity to tolerate low temperatures (Song et al., 2021).

Heavy metal toxicity

Phytoremediation, the use of plants for sustainable cleanup of polluted areas, has gained popularity as an effective approach. Nanoparticles (NPs) have emerged as valuable tools in phytoremediation due to their interaction with plant metabolism and metal ions (Morales-Díaz et al., 2017). NPs have been found to reduce oxidative stress caused by heavy metals and promote the growth of various plant species, even in toxic environments (Iqbal et al., 2019). The application of silicon dioxide NPs has been shown to increase the tolerance of plants like Acorus pygmaeus to heavy metal stress by enhancing biomass accumulation and the activities of biocatalysts within the plant (Iqbal et al., 2019). Additionally, silicon dioxide NPs facilitate the absorption and accumulation of heavy metals in plant roots, preventing their translocation to the leaves and minimizing toxicity (Rajput et al., 2020a). NPs can immobilize toxic metal ions, and nanofibrous composite membranes based on materials like polyvinyl alcohol and polyacrylonitrile exhibit efficient metal chelation, aiding in the removal of metals such as chromium and cadmium (Lew et al., 2021). The surface charge of NPs influences their effectiveness in metal chelation (136). Furthermore, NPs have been shown to protect the membranes of stressed plants by reducing the accumulation of malondialdehyde (MDA), a marker of oxidative damage. Zinc oxide (ZnO) NPs, for example, increase the activity of antioxidant enzymes such as superoxide dismutase (SOD), catalase (CAT), and ascorbate peroxidase (APX) while decreasing MDA content in plants like Leucaena leucocephala under cadmium and lead stresses (Venkatachalam et al., 2017). Wheat seedlings exposed to heavy metals also exhibit reduced MDA accumulation when supplemented with magnetic nano-Fe3O4, which enhances the activity of SOD and peroxidase (POD) (Konate et al., n.d.). Iron (Fe) NPs have been found to increase the accumulation of phytochelatins and glutathione in rice, leading to upregulated activity of antioxidant enzymes and glyoxalase, thereby enhancing the plant's tolerance to arsenic (Bidi et al., 2021). In finger millet and Gossypium hirsutum exposed to NPs, mineral acquisition and biosynthesis of photosynthetic pigments were restored, aiding in cadmium and lead stress tolerance. Additionally, ZnO NPs showed potential in removing heavy metal-contaminated media in rice (Sinha and Verma, 2021).

TOXICITY CONCERN OF NANOFERTILIZERS

According to Manjunatha et al. (2016), comprehensive risk assessments and nano-toxicological evaluations are necessary for the safe and responsible use of nanoparticles (NPs). While there is evidence suggesting that the nanostructure of a substance may pose higher risks compared to its non-nano form, further research is needed to confirm this hypothesis (Figure 3). Bayat et al. (2020) emphasize the importance of developing scientific approaches to manage the toxicological effects of NP interactions with the environment and biological systems. The interaction between NPs and living systems or cells is regulated by the protein corona (PC), as highlighted by Rajput et al. (2018). Incompatible NP-PC interactions can result in cytotoxic, genotoxic, and pathophysiological effects. The biocompatibility of NPs is influenced by the type of protein forming the PC, as well as the hydrodynamic size and charge of the protein (Rajput et al., 2020a). NPs can exhibit

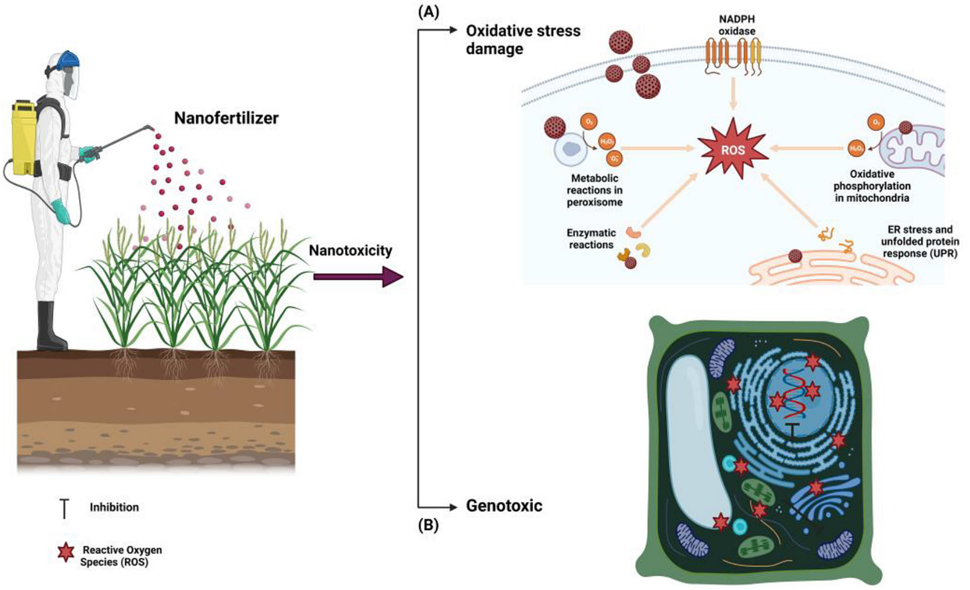

Figure 3. Phytotoxicity effect of nanoparticles based fertilizers accumulation in various plants part that leads to oxidative damage and genotoxic effect on DNA, chloroplasts m mitochondria and other cellular organelles

phytotoxicity, causing various morphological and physiological effects on plants, including reduced root length, damaged root tips, decreased biomass, and chlorophyll degradation. The response to NPs varies among different plant species. For example, Tenzer et al. (2013) observed that cucumber exposed to titanium dioxide (TiO_2) NPs and guar exposed to ZnO-NPs exhibited increased chlorophyll content, while pea exposed to ZnO-NPs and tomato exposed to silver (Ag) NPs showed decreased chlorophyll content. The generation of reactive oxygen species (ROS) by NPs can disrupt normal biophysical functions and abiotic stress response mechanisms, leading to oxidative stress and genotoxic effects through the modulation of stress-related genes (Mirzajani et al., 2013). NPs penetration can result in harmful effects such as ion leakage, cell death, and anomalies in cell membranes due to ROS-induced lipid degradation. Different plant species may exhibit distinct responses to NP-induced lipid peroxidation and ion leakage (Rico et al., 2013). Interactions between plants and NPs can interfere with secondary plant metabolism, hormonal balance, and overall growth and development. NPs treatment can affect gene expression related to phosphate loss, infections, and stress response, thereby impacting a plant's ability to defend against diseases and develop healthy roots (Rico et al., 2013). Moreover, NPs can alter nutrient distribution, hindering growth and development. Servin et al. (2013) found that CeO_2 NPs inhibited rhizobacterial N2-fixation, reducing nitrogen availability and impeding normal plant growth, while TiO_2 NPs increased the accessibility of potassium (K) and phosphorus (P) in Cucumis sativus. Accumulation of NP metal components in the environment and excessive application of certain nutrients can have toxic effects on plants. To mitigate stress caused by these factors, plants employ mechanisms such as upregulation of antioxidant compounds and downregulation of genes responsible for metal transport (Taylor et al., 2014). Studies using omics data in a systems biology approach have demonstrated that metal NPs induce a generalized stress response, particularly the oxidative stress response, in rice, tobacco, and wheat cultivars (Ruotolo et al., 2018). High-throughput investigations of genetic and metabolic responses induced by NP exposure are necessary to understand NP phytotoxicity, even in the absence of observable phenotypic toxicity (Majumdar et al., 2015). The effectiveness of activated detoxification mechanisms in reversing NP-induced biomolecular stress and the precise influence of NP type and interaction on nanotoxicity are still uncertain. Therefore, it is crucial to have a thorough understanding of the properties of synthesized NPs before evaluating their impacts in the plant system to mitigate potential hazards to human health and the environment (Pradhan and Mailapalli, 2017). Proteomic studies aimed at identifying protein indicators (signatures) will contribute to clarifying the toxicities brought about by NPs at the proteome level. To ensure the effective utilization of nutrients with minimal associated toxicity, it is essential to conduct comprehensive in vitro and in vivo phytological testing before commercializing any nano agriproducts (Pradhan and Mailapalli, 2017).

CONCLUSION

The increasing global threat of abiotic stress on green plants and agricultural crops, arising from factors like urbanization, extreme weather conditions, pollution, and habitat loss, has prompted the exploration of nanotechnology as a potential solution. This review focuses on examining the protective effects of nanoparticles (NPs) on crops and their mechanisms of accumulation in plants. NPs, which can exist as fertilizers, herbicides, or pesticides, are readily absorbed by plants due to their small size and reactivity. Their chemical composition, particle size, surface area, and sensitivity play a role in determining their interactions with plants, leading to diverse changes in plant morphology, anatomy, and physiology. These interactions have been observed to enhance plant growth, biomass production, chlorophyll content, sugar levels, accumulation of osmolytes and antioxidants, expression of stress-related genes, and promotion of nitrogen metabolism. However, concerns have been raised regarding the accumulation of NPs in the edible parts of plants and their potential adverse effects on the environment. Therefore, it is crucial to develop reliable evaluation methods to assess the impacts of NPs on both biotic and abiotic components of ecosystems. Additionally, further studies are necessary to determine safe exposure levels for humans and to develop cost-effective, non-toxic, ecologically safe, and biodegradable NPs before the effective implementation of nanotechnology in agriculture can be achieved.

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