Potentiality of Metal Nanoparticles in Precision and Sustainable Agriculture

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Abstract

 The world's increasing population has a higher demand for food and a suitable environment. However, using conventional farming methods and industrial agrochemicals leads to environmental risk, which is a significant threat for the next generation. So, nanotechnology can be a blessing for saving our environment and producing risk-free foods at minimal cost in an eco-friendly way. Nanoparticles (NPs) used as nanopesticides, nanofertilizers, nanosensors, nanopriming agents, and other applications in agriculture can help mitigate issues such as high production costs, excessive pesticide and fertilizer requirements, soil depletion, and various biotic and abiotic challenges. A variety of important information from different research findings on metal nanoparticles, their characteristics, the synthesis process, and their roles in precision and sustainable agriculture are included in this article. This literature review discusses the benefits of metal nanoparticles on plant growth and development, the ease of green nanoparticle production over chemical and physical approaches, and the effects of metal nanoparticles on agriculture. Future perspectives for metal nanoparticles are also covered in this article based on these impacts. Metal nanoparticles, used as biosensors and seed-priming materials, can contribute to seed germination even in adverse conditions. So, overall, this review article discusses the potentiality of using metal nanoparticles in lieu of inorganic agrochemicals and their possible contribution to precision and sustainable agriculture.

Keywords: Metal nanoparticles; Sustainable agriculture; Environmental risk; Nanoparticles;

1.Introduction

 Nanotechnology refers to the investigation of substances ranging in size from one to one hundred nanometers (Joudeh & Linke, 2022). Nanoparticles (NPs) are exceedingly minute metal particles that have the capability of integrating diverse active principles to form an integrated system. This integration allows the NPs to operate within an experimental organism, ultimately improving the organism's overall health (Baker et al.,2015). The numerous applications of NPs in agriculture can be attributed to their special characteristics, which include their tiny size, increased surface area to volume ratio, physical strength, reactivity, and optical, electrical, and magnetic properties (Hazarika et al., 2022). In the agriculture industry, these distinctive features of NPs have sparked extreme alarm.

 The number of people in the world is constantly growing, and these restlessly growing people's desire for food is equally increasing. According to the United Nations, there will be 8.5 million people on the planet by 2030, and food production will need to rise by almost 50% in order to feed everyone (Mittal et al., 2020a). Industrialization also became hazardous for the environment, lowering the natural resources for food production. This also increases the need for increasing food production with maintaining the biodiversity. Farmers have long used traditional methods, which have limited agricultural output due to increased fertilizer consumption, environmental contamination, microorganism-causing diseases, and abiotic stressors (Jhing et al., 2022).

 The next green revolution will be built on precision farming, which monitors environmental factors and implements targeted measures to maximize output (economic yield) while limiting input (pesticides, fertilizers, herbicides, etc.) (Panpatte et al., 2016). Nanotechnology is essential for sustainable agriculture development. By implementing innovative approaches that increase plant productivity through the deft addition of nanonutrients for nanoherbicides, nanofertilizers, and nanopesticides by the plants, has the immense potential to completely transform the agricultural sector (Aslam et al., 2022). Metal NPs can be synthesized biologically, chemically, or physically. There are benefits and drawbacks to each of the three ways, but the biological

 synthesis method—also known as "green synthesis"—is the most advantageous. Farmers frequently employ pesticides and fertilizers to boost output, which is primarily lost by leaching, runoff, and other factors (Mittal et al., 2020b). This raises production costs and reduces biodiversity. NPs are employed in agriculture to boost yields while maximizing output, minimizing nutrient losses, minimizing production expenses, and reducing the number of products needed for plant protection (Usman et al., 2020). The most popular metal nanoparticles for antibacterial applications are zinc (Zn), silver (Ag), and copper (Cu). Copper NPs are widely used in agriculture for a range of applications because they are somewhat more cost-effective and readily available (Hazarika et al., 2022). Increased agricultural productivity can be achieved by using NPs as nutrient elements for improved germination, controlling vectors and pests, using nanosensors for pest detection, efficiently dosing water and fertilizer, using nanoporous zeolites for slow release, delivering herbicides via nanocapsules, and creating nanofertilizers (Ditta et al., 2015).

 This research emphasizes the possible use of metal nanoparticles in sustainable agriculture. It addresses metal nanoparticles, their synthesis method, and their advantageous role in enhancing precision agricultural production. The contributions provided by NPs will undoubtedly change the challenges that farmers encounter.

2. Commonly used metal nanoparticles

 The field of science and engineering that studies materials with dimensions of one-hundredth of a nanometer or less are known as nanotechnology (Mody et al.,2010), and there are two categories for this large class of nanomaterials: metallic and non-metallic nanoparticles (Yih and Al-Fandi,2006). Metal-based nanoparticles commonly generated and used include cerium oxide, gold, zinc oxide, copper oxide/dioxide, silver, and titanium dioxide (Rico *et al.,*2015). Besides, iron, magnesium and cobalt are also used (Kumari & Chauhan, 2019; Sharma *et al.,* 2022; Vijayanandan & Balakrishnan, 2018). NPs are the most commonly used conventional farming method because of their small size, high efficiency, ease of handling, portability, and long shelf life (Hazarika et al., 2022). Table 1 shows the many uses of NPs in agriculture. NPs are useful

 for controlling plant nutrition, phytopathogen protection, plant growth regulators, and nanofertilizers (Figure 1).

2.1. Iron oxide nanoparticles

89 Hematite (α -Fe₂O₃), magnetite (Fe₃O₄) and maghemite (γ -Fe₂O₃) are the most frequent types of iron oxides in nature and for biomedical applications the first two are the best option (Ali *et al.*,2016). Spherical-shaped iron nanoparticles are extracted from different plant species, and their size ranges from 0-150nm (Abegunde *et al.,*2020). For many cellular enzymes in organelles, iron is a critical factor in determining their biological activities, and these enzymes are essential for photosynthesis, respiration, and the quality of goods made from plants (Vigani *et al.,* 2013; Briat *et al.*, 2015).

2.2. Titanium dioxide nanoparticles

 There are two types of titanium dioxide based on structure: rutile and anatase (Chen and 98 Mao,). TiO₂ nanoparticles boost the plant's immunity and photosynthetic rate, which raises crop output by 30% (Waghmode *et al.,*2019) and the development of plants is said to benefit from it. Plants can also benefit from its application in nano form to increase production and 101 growth (Faraz et al., 2020). Before sowing, TiO₂ seed treatment increased spinach chlorophyll content, rate of photosynthesis, and dry weight of the plant (Zheng *et al.,* 2005).

2.3. Silver nanoparticles

 The most prevalent metallic nanoparticles with antibacterial properties are silver nanoparticles, and they are utilized to treat plant diseases (Mishra & Singh, 2015) and improve the efficacy of fungicides, plant growth, and fruit ripening in agricultural settings (Mahendran *et al*.,2019). Spherical shaped (1-100nm) silver nanoparticles are extracted from different plant species like *Acalypha indica*, *Allium cepa*, *Allium sativum, Annona squamosa,* etc. (Rajan *et al.,* 2015). Besides, they are slender, round, oval, and triangular, shaped like a flower (Zhang et al.,2016), and their biological impacts are influenced by their coatings' surface charges, which can impact their interaction with living systems (Powers *et al.,*2011).

2.4. Zinc oxide nanoparticles

 Zinc (Zn), a mineral essential to plant development and production, contains a component needed at modest levels for enzyme and protein functions (Al Jabri *et al*.,2022). It is a cofactor for the majority of enzymes, including superoxide dismutase, carboxypeptidase, and carbonic anhydrase (Rizwan *et al*., 2019; Saifullah *et al*., 2016). Zinc nanoparticles can take many forms, including rods, plates, spheres, boxes, hexagons, tripods, tetrapods, wires, tubes, rings, cages, and even flowers (Siddiqi *et al.,*2018).

2.5. Magnesium oxide nanoparticles

 Because of their exceptional physicochemical properties, which include outstanding corrosion resistance, low electrical and high thermal conductivity, exceptional refractive index, physical strength, etc., magnesium nanoparticles (MgO) are environmentally friendly, commercially viable, and industrially significant nanoparticles, and their different shapes (spherical, cubic, nano-flower, rod-like, cluster, hexagonal, etc.) are seen during green synthesis (Abinaya *et al.*,2021). They act as an anti-microbial agent, increase insect tolerance of plants, enhance agricultural production, activate defense signaling pathways in plants, and are suitable for precision farming (Fernandes *et al.,*2020).

2.6. Cobalt oxide nanoparticles

 The magnetic characteristics of cobalt oxide nanoparticles make them useful in a wide variety of technological applications, such as catalysts, energy storage devices, electrochemistry, sensors, magnetic fluids, and biomedicine (Ogunyemi *et al*.,2023). When administered in small amounts, they contribute to plant development in every phase, facilitating crucial chemical and biological interactions (Singhal *et al.,*2023). Additionally, they have been seen to benefit plants during drought stress (Brengi *et al.,*2022).

2.7. Copper oxide nanoparticles

 Variable microelectrode potential, renewable surface area, and a high surface-to-volume ratio make copper nanoparticles popular catalysts (Din and Rehan,2017). Copper nanoparticles (Cuprous oxide and cupric oxide) that include agrochemicals such as herbicides and fertilizers are being used more often in agriculture as substitutes for their traditional forms, and these nanoparticles are crucial micronutrients for crop development. Cuprous oxide and cupric oxide 146 (Bakshi and Kumar, 2021). It is necessary for plant development, and it is also used as a 147 bactericide and fungicide. Studies have shown that it is more effective in preventing a variety of 148 common bacterial and fungal illnesses (Rai *et al.,*2018).

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150 **2.8. Cerium oxide nanoparticles**

 A member of the lanthanide group, Cerium is the most prevalent rare metal with catalytic capabilities (Singh *et al.,*2020a). 5-30 nm sized cerium nanoparticles can be extracted from plant species like *Acalypha indica, Olea europaea, Hibiscus Sabdariffa* etc. Nanoceria have antibacterial, anticancer and antioxidant activity (Rajeshkumar and Naik,2018). In agricultural sector it is used for crop improvement and stress tolerance (Singh *et al*.,2020b).

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157 **2.9. Gold nanoparticles**

 Gold nanoparticles can be synthesized from leaves of *Brassica juncea, Aegle marmelos, Aloe vera, Coriandrum sativum, Euphorbia hirta,* etc., and roots of *Zingiber officinale, Morinda citrifolia, Angelica archangelica,* etc. SPR phenomenon causes gold nanoparticles to absorb strongly in the visible spectrum, with a maximum in the 500–600 nm range (Husen,2017). They have the properties of high mobility and solubility, high adsorption capacity, high reactivity and catalytic capacity (Venzhik *et al*.,2021). Uses of gold nanoparticles include bio-catalysis and pathogen detection, and they are used as biosensors also (Santhosh *et al.,*2022). The beneficial effects of these metal nanoparticles on plants are listed in Table 1.

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167 **Table 1:** Metal nanoparticles and their beneficiary applications/functions on different crops and 168 performance against stress conditions.

Name of metal nanoparticles Applications/functions Sources Iron oxide nanoparticles 1. Wheat grain's protein content was found to be elevated after application to the leaves. Bakhtiari *et al*.,2015 2. At low concentrations, plant cellular growth increased. Yuan *et al.,*2018 3. respiration, redox reactions, chlorophyll synthesis, and leghemoglobin production in nodules Singh *et al.,*2021

172 **3. Synthesis methods of metal nanoparticles**

 Nanoparticle synthesis can be carried out utilizing either top-down or bottom-up logic (Raliya *et al*., 2017). The top-down strategy involves the processing of bulk materials into nanoparticles using techniques such as milling, grinding, sputtering, thermal/laser ablation, and so on (Ndaba *et al.*, 2022). This approach's drawback is its limited ability to manage nanoparticle size and increased number of contaminants (Zulfiqar *et al.,* 2019). By building NPs from small entities through reduction and oxidation processes, the bottom-up approach produces NPs with fewer flaws (Singh *et al.,* 2015). These two approaches include chemical, physical, and biological synthesis methods (Figure 2). However, the stability and monodispersion of the nanoparticle size are two issues with the chemical and physical procedures, despite the fact that they are generally simple to perform (Kaningini *et al.,* 2022). Methods usually used for metal nanoparticle synthesis are described in Table 2.

184 **Table 2.** Different synthesis approaches of metal NPs along with their merits and demerits.

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3.1. Physical method of synthesis

 There are specific impacts of using nanoparticles in agriculture. The process used to synthesize NPs is the primary contributing factor. Physical synthesis requires high temperatures and several hazardous materials. Alterations to the synthesis process, such as catalysts and temperature reductions, could make NPs safer to use. This will lead to a synthesis approach that is both cost- effective and environmentally safe. This led to research on reducing the use of hazardous substances and replacing them with natural molecules, which gave rise to the "green chemistry" movement (Quaresma *et al*., 2009).

Some common methods of physical synthesis from Table 2 are described briefly:

 3.1.1. Evaporation-condensation: The two most crucial physical procedures, evaporation- condensation and laser ablation, guarantee that the NPs are distributed evenly and that the thin films that are produced are free of solvent contamination (Iravani *et al*.,2014). The initial method for creating nanocrystalline metals and alloys was gas condensation. Thermal evaporation sources, such as electron beam evaporation devices or joule-heated refractory crucibles, can evaporate inorganic or metallic materials within a pressure range of 1 to 50 mbar (Rajput N., 2015).

 3.1.2. Laser ablation: The process known as "laser ablation" involves focusing a concentrated laser beam—an acronym for "light amplification by stimulated emission of radiation"—on a specific region of a solid surface with the goal of vaporizing any material that absorbs the light (Kim *et al.,* 2017a). Using this technology, different forms of nanomaterials and nanostructures have been developed with higher chemical, electrical, optical, and magnetic capabilities (Larosi *et al.*,2022). Metal NPs like TiO₂, Au, Fe₂O₃, Ag, etc. can be generated by the laser ablation approach (Kim *et al.,* 2017b).

 3.1.3. Pulse laser deposition: Pulsed laser deposition is another type of physical vapor deposition. In this manner, the material to be deposited is targeted by the pulsed, high-power laser beam. After vaporizing off the target in a plasma plume, this material condenses into a thin layer on a substrate, like a silicon wafer that faces the target. This might occur with a background gas (oxygen, for example), which is commonly employed to deposit oxides and fully oxygenate the films being formed, or it could occur in a completely vacuum environment (Haider *et al.,* 2022).

 3.1.4. Thermal decomposition and ball-milling: Thermal decomposition is the term for the endothermic chemical breakdown brought on by heat, which causes the molecule's chemical bond to disintegrate (Masoud *et al.,* 2008 The breakdown of metal at a particular temperature produces the NPs. Ball milling is the most basic and inexpensive mechanical technique for transferring kinetic energy from the grinding media to the material being reduced. For instance, ZnO, CuO, Ti, and Ag are produced by this process (Ijaz *et al*., 2020).

 3.1.5. Sputtering: During the sputtering process, a powerful gas or gaseous plasma ion bombardment is applied to the target material. This action ejects small particles from the atomic or molecular element's surface. Sputtering occurs via momentum exchange between the element atoms and ions. Sputtering allows for the deposit of films that have the same composition as the target source. It is a flexible method that works with nearly every kind of material (Rane *et al.,* 2018).

 3.1.6. Ultrasonication: The other method used was the ultrasonication of the ultrasonic sound wave frequency in the range of >20 kHz. It was applied to the solution to awaken the homogenous dispersion as it causes an upset of the intermolecular force, decreasing the cluster formation of nanoparticles into the base fluid (Mahbubul *et al*.,2017).

 3.1.7. Inert gas condensation: Inert gas condensation is the process by which metal or inorganic material is evaporated from an evaporating source in the presence of an atmosphere of inert gas and subsequently condensed on a very cold substrate for a substantially shorter amount of time, resulting in the formation of nanoparticles.

 3.1.8. Pyrolysis: In contrast to that, pyrolysis is the process that is used to atomize the liquid solution containing the metal composite that is present. The carrier gas transports the atomized droplets to a furnace. The solvent undergoes a chemical dissociation in the furnace after the solution has been heated to the proper temperature. When the process is being done, then the solution will always get more and more saturated and there will be no solvent left after some time of heating.

3.2. Chemical method of synthesis

 The chemical method of synthesis is a bottom-up approach that produces nanoparticles (NPs) in a liquid medium with various reactants present. Low temperatures are present when the reactions take place. The primary benefit of this process, aside from toxicity, is that it produces nanoparticles (NPs) at low temperatures, which saves manufacturing time and costs while maintaining the desired particle size. Here are some commonly used chemical synthesis techniques discussed:

 3.2.1. Chemical reduction: A major contributing element to the success of the wet chemical synthesis approach is the kinetic and thermodynamic provisions that allow composition, shape, and size to be adjusted to reflect changes in surface, electrical, and optical properties (Nikam *et al.*, 2017). Chemical reduction is an effective wet-chemical procedure for generating zero-valent nanoparticles from chemically reduced aqueous metal salts, such as silver nitrate, in the case of Ag NP manufacture (Nam & Luong, 2019). Reducing agents like citrate, borohydride, etc., are used to feed electrons to metal ions that reduce metal salt to become zero-valent. A stabilizing ingredient, such as sodium citrate in the case of silver NPs production, stabilizes reduced NPs (Aashritha, 2013).

 3.2.2. Sol-gel technique: The sol-gel approach is a more chemical way of generating diverse nanostructures, particularly metal oxide NPs. In this method, the molecular precursor (usually metal alkaline compounds) is allowed to dissolve in either alcohol or water and converted into gel by warming and mixing by hydrolysis. This technique has great influence over both the surface and texture features of the materials (Parashar *et al.,* 2020). This technique involves a range of processes, comprising particle formation, hydrolysis of the precursors, agglomeration, particle formation, and condensation (Rajput, 2015).

 3.2.3. Co-precipitation: Coprecipitation is the sequential precipitation of multiple products from a solution. It is the most economical and useful way to prepare NPs. In this process, metal hydroxide is precipitated from a salt precursor in a solvent in the presence of a base.

 3.2.4. Chemical vapor deposition: Chemical vapor deposition is the chemical reaction that takes place on or near a heated substrate surface. Consequently, a vapor deposits a solid material in the shape of a single crystal, thin film, or powder (Carlsson *et al*., 2010). NPs with distinct characteristics are created by altering the temperature of the substrate, the material's composition, and the experimental setup.

 3.2.5. Flame spray pyrolysis: This could be altered via flame spray pyrolysis, which can be utilized to create nearly all elemental multicomponent nanoparticles from solvents and affordable solid and liquid precursors. Currently, functionalized cobalt nanoparticles and carbon black are produced industrially via flame spray pyrolysis (Grohn *et al.,* 2014). Since a lot of less volatile raw materials dissolve in organic solvents in addition to water, the best strategy might be to inject liquid precursors straight into the flame. This is due to the ease of handling and administering liquid precursors. One such material is zinc oxide, which can be manufactured using this method (Wallace *et al*., 2013).

 3.2.6. Spinning: Spinning is an alternative method for producing nanoparticles, mostly used for Tio² (Muhammmadi *et al.,* 2014). A spinning disc reactor with a controllable temperature system is used to synthesize NPs. A rotating disk is incorporated into the reactor's design to exclude oxygen and halt unintended chemical reactions. In order to stop undesirable reactions, this disk is frequently filled with nitrogen or inert gas. The disc rotates at various rates while the liquid— water and the precursor—is pushed in (Ealia & Saravanakumar, 2017).

3.3. Biological/green method of synthesis

 The biological synthesis of NPs begins with the mixing of precursors of noble metal salts with biomaterials. A variety of resources, such as microbes (fungus, yeast, algae, viruses, bacteria) and other plant components, can be utilized for this process (Figure 3) (Dikshit et al.*,* 2021). There are two types of this synthesis process, namely Biosorption (metal ions adhere to the living thing) and Bioreduction (chemical reduction of metal ions via biological methods), and many factors influence the choice of biological synthesis technique for nanoparticles (Zhang *et al.,* 2020). Metal nanoparticles like Ag are synthesized by the bioreduction method from the bacteria Klebsiella pneumonia (Kalimuthu et al.,2008), and Cu is synthesized from the bacteria *Bacillus sphaericus* JG-A12 by both biosorption and reduction methods (Das *et al*.,2014). Nanoparticle formation is initiated by combining biomaterials with precursors of noble metal salts (Sriramulu *et al.,*2020). Alkaloids, polyphenols, proteins, reducing sugars, and flavonoids are examples of biomaterials that serve as capping and reducing agents for forming nanoparticles (NPs) from their metal salt precursors (Kuppusamy *et al*.,2016). Metal nanoparticles from plants are synthesized by combining plant extract with metal salt, and in this case, any type of plant part, like a stem, leaf, flower, root, fruit, or even seed, can be used (Shafey,2020) (Figure 2). There are three ways in which plant-mediated synthesis of NPs may be accomplished: (i) intracellularly (inside the plant), (ii) extracellularly (using extracts from plants), and (iii) using particular phytochemicals and a number of plants possess the capacity to gather metals and then transform them into nanoparticles (NPs) within their cells (Dikshit et al.,2021). Biological applications, including biomineralization, bioremediation, bioleaching, and biocorrosion, have historically benefited from the interaction between metals and microbes (Klaus-Joerger *et al.,*2001). As a consequence of the oxidation or reduction of metallic ions by biomolecules produced by microbial cells—such as enzymes, proteins, carbohydrates, and polysaccharides—NPs are created during the process of microbial synthesis (Prabhu and Poulose,2012). Synthesis of metal nanoparticles from bacteria and fungi was done by mixing bacterial culture with metal salt solution and keeping fungal hyphae in metal ion solution, respectively (Singh *et al.,*2020) (Figure 3). Metal nanoparticles synthesized from biological sources (fungi, bacteria, plants) are shown in Table 3.

336 **Figure 3.** Green synthesis process of metal nanoparticles.

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338 **Table 3:** Metal NPs and their biological source of synthesis.

 As the sources for synthesis are easily available, the great advantage of green synthesis is that it takes less time and energy to prepare than physical or chemical methods (Bhardwaj *et al.,*2020).

4. Impacts of the MNs on plants

4.1. Supply plants with nutrients

 Metal Nanoparticles reduce nutrient loss, which improves nutrient uptake, nutrient efficiency, and crop yield through utilizing Nanoparticles as nanofertilizers in agriculture. The chemical fertilizer requirement is decreased day by day using metal nanoparticles. Nanoparticles have a long-term effect on the ecosystem and agricultural soil health (Kumar et al., 2022). Various application methods of nanofertilizer are observed, including soil application, foliar application, seed treatment, and hydroponics.

 Soil Application is a popular method, and it plays a crucial role in enhancing crop production. Physical, chemical, and biological factors like soil compaction, stability, pH, soil microbes, etc., must be considered at the time of nano fertilizer application in soil (Javed et al., 2022). In poor weather and soil conditions, foliar application may be utilized. Additionally, this method reduces nutrient loss and promotes nutrients to enter the plant system directly. It shows higher nutrient efficiency (Mahil & Kuma, 2019). ZnO nanofertilizer was reported to enhance plant growth, antioxidants, and photosynthetic pigments in maize (Azam et al., 2022). According to Salcido-Martinez et al. (2020), the highest levels of biomass and photosynthetic pigments in green beans were seen in foliar application of Mg nanoparticles (Table 4). Seed priming shows a greater improvement in germination and other growth parameter in pearl millet by using ZnO Nanoparticles (Kumar et al., 2024). Through seed priming, ZnO Nanoparticles also increased the percentage of germination in fodder maize seeds (Tondey et al., 2021). Hydroponic application using nano Si fertilizer, atonic, and nano complete fertilizer together increased the yield of Barley fodder. It is also found to be the best medium for increasing the dry matter, protein, and nutrient content (Al-Juthery et al., 2019).

 Nanoparticles can enter a plant through stomata or other above-ground parts during foliar spraying. When soil application is followed, Nanoparticles can enter through the roots (Zhu et al., 2020; Avellan et al., 2021). Plant species, growth, soil characteristics, NP types, sizes, and interactions with the root zone and soil all affect the absorption of the Nanoparticles (Singh et al., 2020; Al-Mamun et al., 2021). The diameter and concentration of the Nanoparticles play important roles (Abd-Alla et al., 2016; Pedruzzi et al., 2020). Two types of pathways, apoplastic and symplastic, are used in the absorption of Nanoparticles. The apoplast constitutes the xylem, cell walls, and intercellular space. This pathway facilitates the absorption of water and nutrients (Farvardin et al., 2020). Symplast pathway provides the movement by using plasmodesmata and neighboring cells. Several results suggested that the apoplast of the cell wall, which has a diameter of between 5 and 20 nm, represents the maximum size for absorption, translocation, and accumulation inside the plant system. The symplastic pathway is used for foliar uptake, while phloem is used to transfer the leaf to the shoot. However, there isn't sufficient evidence in favor of the Nanoparticles' following phloem transport pathway in plants. The dimension of the Nanoparticles impacts the uptake. Nanoparticles are required to overcome a lot of physiological root barriers, like the cortex, epidermis, surface cuticle, and casparian strip (Lv et al., 2019). Conversely, Nanoparticles supplied through soil application can reach the plant through the apoplast and symplast both routes (Pérez-de-Luque et al., 2017). Nanoparticles use the apoplastic pathway to move from the root to the upper portion (Lv et al., 2019).). In contrast to the symplastic process, the apoplastic pathway appears to be faster. Some examples of using Nanoparticles as nutrient delivery in agriculture are given in Table 4.

4.2. Used to control the target pest

 Metal nanoparticles (Nanoparticles) offer significant benefits throughout all agricultural stages. Additionally, the development of nanopesticide using Nanoparticles is very efficient compared to conventional fertilizers (Harish, et al., 2022). One major benefit of Nanoparticles is their minuscule size. Nanoparticles have a bigger surface area because of their small size and enable more pesticides to come into contact with insect pests (Rajna et al., 2019). In addition, they offer other benefits such as targeted distribution, less residues, regulated release of active substances, and preservation of beneficial insects (Su et al., 2022). They improve both the harvest index and the biological index. Because nanopesticides minimize loss and adverse effects, the use of nanoparticles is an environmentally friendly way (Shojaei et al. 2019).

 The features of solubility of water-insoluble compounds can be utilized by nano-pesticide formulations to overcome the challenges associated with conventional pesticide application (Kamal et al., 2022). Plant species, insecticide kind, and application method all influence how metal Nanoparticles are made. According to Namasivayam, et al. 2023, nano gel is a popular formulation type in the synthesis of silver NP formulation. One such form involves creating re- dispersible dry emulsions by combining metal and metal oxide nanoparticles (Nanoparticles) such as iron oxide, copper oxide, gold, and silver with cellulose nanocrystals. An organic solvent, an emulsifier, a pesticide, and a few other ingredients comprise the emulsifiable nano- pesticide. Nonionic and polymeric surfactants are used to create oil-in-water emulsion, which serves as an alternative to emulsifiable nanopesticide. In comparison to traditional pesticides, the particle sizes are 250 times smaller (Raj et al., 2021; Murthy et al., 2022). The most practical method for prolonging food shelf life in agriculture is encapsulation. Moreover, another kind of formulation is called nanodispersion, which consists of a blend of liquid media and nano- crystals. By offering a greater surface area, it helps the less water-soluble nanocrystals dissolve entirely in water. Less than 50 nm-sized nanocrystals dissolve more readily in water (kah et al., 2014).

 Plant pathogenic bacteria and fungi can be inhibited with metal-based nanoparticles. Pathogens and antibacterial systems interact directly (Li et al., 2023). Metal nanoparticles bind to sulfur and phosphorus in proteins and nucleic acids, decreasing membrane permeability, resulting in organelle and enzyme denaturation, and finally triggering cell death (Chaud et al. 2021). They improve the adhesion of pesticides to the insect's body, resulting in cell dehydration and a variety of histological and morphological abnormalities (Nie et al., 2023). Ag nanoparticles break through the bacterial cell wall, raising intracellular osmotic pressure and ultimately leading to cell lysis. When applied to gram-negative bacteria, this NP works better than gram-positive bacteria. The explanation for this is that gram-negative bacteria have more lipopolysaccharide and either no or little peptidoglycan layer (Zhang et al., 2016). The waxy secretion of citrus mealybugs also contributes to the adsorption of silver nanoparticles, enhancing the insecticide's anti-mealybug efficacy (Zaheer et al., 2022). Ag Nanoparticles saturated with carbons were found to cause harm to internal cellular tissues and the skin in another investigation (Sultana et al., 2018). Ag nanoparticles are also important antifungal drugs that fight a variety of fungal- caused disorders. When combined with fluconazole, biologically produced AgNP has increased antifungal efficacy against *Candida albicans* (Mussin et al., 2019).

 Zinc Nanoparticles are versatile and economically feasible for synthesis in large quantities, showcasing targeted antimicrobial properties and low phytotoxicity, making them suitable for combating various phytopathogens (Kalia et al., 2020). ZnO-nanoparticles can alter the permeability of the bacterial cell membrane by penetrating the cell membrane through the interaction of zinc oxide with the cell surface. As a result, it prevents cells from growing, resulting in oxidative stress and cell death. ZnO-nanoparticles are a great approach to protecting food from bacterial diseases in the food sector (Pavic et al., 2022; Dominic et al., 2022). Trypsin inhibitors such as gold-nanoparticles can impede the growth and reproduction of insects. There is little information available about how Nanoparticles affect insects and mites (Chaud et al., 2021). Plants respond better when Nanoparticles are used in addition to other nanoparticles or other composite materials (Table 5). However, there is much potential for employing Nanoparticles as nanopesticides, further research is still necessary to fill the knowledge gap.

Table 5: Potentiality of Nanoparticles used as nanopesticide in crops.

4.3. Effects on Improving plant growth and stress tolerance

 Nanoparticles are environmentally acceptable agricultural nutrition supplements that have benefits beyond fertilization and are easily absorbed by plants (Kaningini *et al.*, 2022). According to a report, metal-based nanoparticles show promise for managing diseases and pests that affect plants, as well as enhancing plant vigor and growth in a variety of stressful environments (Tortella *et al.*, 2023). Mainly, two categories can be applied to metallic nanoparticles. One category provides essential microelements to plants. Among them, copper (Cu), nickel (Ni), iron (Fe), and zinc (Zn) nanoparticles can be specially mentioned (Santás- Miguel *et al.,* 2023), not only for their impact on growth and development of plants (Pedruzzi *et al.*, 2020; Nazarova, 2022; Zhou *et al.*, 2023) but also for strengthening defense mechanism of plants against a range of biotic and abiotic stressors (Faizan *et al.*, 2018; Reddy Pullagurala *et al.*, 2018; Iqbal *et al.*, 2020; Salam *et al.*, 2022). The second category does not supply essential microelements (Santás-Miguel *et al.,* 2023), of which silver (Ag) and titanium (Ti) nanoparticles are noteworthy for favoring the sprouting and growth of plants (Fatima *et al.*, 2021; Mathew *et al.*, 2021) and also for some healing effects on different microbial diseases. Some other nanoparticles, such as gold (Au), selenium (Se), cerium (Ce), silicon (Si), and aluminum (Al) nanoparticles, are also utilized, but to a lesser degree. These nanoparticles have beneficial effects on specific plants and can raise the yield or safety of agricultural products (Santás-Miguel *et al.,* 2023).

 The concept of development and growth of plant is wide and inclusive, including a plant's complete life cycle, from the process of a seed beginning to grow into a plant to the point where it reaches old age and starts to deteriorate (Gutiérrez-Ruelas *et al.*, 2021). Plant growth and biological activity can both be enhanced by metal nanoparticles (Hoang *et al.*, 2019). Two varieties of metallic nanoparticles are utilized in the development and growth studies of plants:

 pure metals and metal oxides. Each metal oxide nanoparticle (NP) possesses the ability to affect the development and growth of plants (Amin *et al.*, 2021). Silver (Jhanzab *et ai.*, 2019), copper (Yasmeen *et al.*, 2018), zinc and iron oxide (Rizwan *et al.*, 2019) NPs demonstrated improved growth (Hoang *et al.*, 2019). Production of biomass, physiological and biochemical processes, development of shoots and roots, germination of seeds, enzymatic activities, nutrient elements, tolerance to stresses all these indicators of growth and also yield, yield quality, freshness and shelf life are positively affected by nanoparticles (Amin *et al.*, 2021). Additionally, NPs are capable of penetrating the chloroplasts of plants and go to the reaction center of the photosystem- II (PS-II). Once inside, NPs enhance electron transport and light absorption in chloroplasts, enhancing the efficiency of photosynthesis and stimulating plant development (Maity *et al.*, 2018).

 Some specific advancements of plant growth in recent times can be summarized as: increased biomass in corn by silver (Ag) NPs; improved antioxidant activities, proline content, leaf area and photosynthetic rate in tomato by ZnO NPs (Faizan *et al.*, 2018); increased root length, 483 lateral roots and plant height in larch by $SiO₂$ NPs; enhanced seedling growth, shoot-root length and photosynthesis efficiency in maize, watermelon and squash by Ag NPs; enhanced vegetative growth in barley and increased plant height, stem diameter, pods, seeds, sugar content in Indian mustard by Au NPs; leaf area, dry weight plant height increased in wheat by Fe and Zn NPs; tomato's yield production and chlorophyll content along with seed germination rate of chickpea are enhanced by TiO² NPs and many more (Verma *et al.*, 2021).

 Under stressful conditions, nanoparticles exert a critical influence on the molecular, physiological, and biochemical aspects of plants (Rasheed *et al.*, 2022). Their main function is to inhibit the plant's reactive oxygen species (ROS) response while promoting plant development and growth by controlling the antioxidant systems and internal plant hormones. They additionally influence how stress-related genes are regulated during transcription (Tripathi *et al.*, 2022). Recently, nanoparticles have enhanced a plant's ability to withstand both biotic and abiotic stressors. By enhancing the functions of antioxidants, they save plants from oxidative harm. (Ahmed *et al.*, 2021)

 Nanoparticles (NPs) might mitigate the detrimental effects of drought by reducing the production 498 of malondialdehyde (MDA) and hydrogen peroxide (H_2O_2) , while maintaining the effectiveness

 of the photosynthetic system (Adrees *et al.*, 2020; Ahmed *et al.*, 2021). The toxic impacts of salt stress on diverse plant species were successfully minimized through the utilization of the following nanoparticles: iron (Fe), potassium (K), copper (Cu), titanium (Ti), carbon (C), zinc (Zn), cerium (Ce), silver (Ag), manganese (Mn), and silicon dioxide (SiO2) (Zulfiqar & Ashraf, 2021). The implementation of nanoparticles in different concentrations to alleviate the consequences of thermal stress led to improved plant development and hydration (Ali *et al.*, 2021). According to Ahmed *et al.,* In plants impacted by heavy metals, nanoparticles (NPs) provide membrane stability and increase the rate of photosynthesis and chloroplast pigmentation (Ahmed *et al.,* 2021).

 NPs can influence pathogens directly or fortify defenses by decreasing fungal, viral, and bacterial infections, increasing plant nutrition, and improving crop production and nutrition quality (Kah *et al.*, 2019). Metal nanoparticles (NPs) employ various antimicrobial processes to take direct action against external organisms. They are capable of causing electron transport to be impeded, DNA destruction, and membrane rupture through the internalization and release of ions. Additionally, they have the ability to produce ROS, which can damage DNA and disrupt enzymes, as well as denaturize proteins (Tortella *et al.*, 2023).

4.4. Used as Nano-sensors and nano-priming agent

 Precision farming offers farmers a viable substitute by minimizing the use of agrochemicals and offering crop-specific solutions tailored to specific sites. This strategy reduces the need for pesticides, fertilizers, and herbicides while increasing crop yields (Yadav *et al.,* 2023). With the improvement of diagnostic methodologies and equipment, nano-biosensors have been crucial in transforming farming, and these sensors are precise, effective, and affordable when it comes to addressing an extensive array of food, environmental, and agricultural challenges (Johnson *et al*., 2021). Nano-biosensors possess the capability to identify and track a multitude of environmental and plant health-related parameters. Furthermore, these diminutive apparatuses are capable of premature detection of pathogens, pests, and diseases, which facilitates prompt intervention and mitigates crop losses (Miguel-Rojas and Pérez-de-Luque, 2023). Nano-sensors ought to possess the following characteristics: portability, affordability, non-toxicity, high target specificity, and precise, accurate, and reproducible performance. They are also used in agriculture to analyze various factors such as fertilizers, herbicides, insecticides, diseases, soil texture, and their controlled application to improve crop output (Rai et al., 2012). *Ralstonia solanacearum,* which causes bacterial wilt in tomatoes, can be targeted by nano-sensor gold nanoparticles functionalized with ssDNA through colorimetry mechanism (Khaledian et al., 2017). Uses of gold nanoparticles also includes the detection of sweet corn infection with the gram-negative bacteria *Pantoea Stewartii sbusp. Stewartia* (Zhao et al., 2014). Besides, silver and zinc oxide nanoparticles are used to target *Trichoderma harzianum* (Siddiquee *et al.,* 2014) and *Phytophthora ramorum* (Yüksel *et al.,* 2015), respectively. Monitoring and regulating the use of pesticides, fertilizers, and other chemical substances provides valuable data for precision agriculture (Duhan *et al*., 2017). For example, ZnO QDs were applied to kasugamycin to improve its photo-stabilization property along with achieving synergistic antimicrobial activity (Liang et al., 2019), and another example is targeting fenitrothion through electrochemistry mechanism which is done by nano titanium dioxide (Kumaravel et al., 2011). The nano formulation of herbicides functions as an intelligent delivery mechanism for the active component, therefore decreasing the overall concentration of the chemical compound and nanoencapsulation enhances the ability of herbicides to penetrate through the cuticle and enables a gradual and regulated release of the chemical active component (Amodeo et al., 2022).

 The process of seed germination includes bidirectional interactions between the embryo and the endosperm, with the endosperm functioning as an environmental sensor that governs the development of the embryo and the embryo regulating the destruction of the endosperm (Yan et al., 2014). Seed germination in normal conditions sometimes does not touch the expected level, and here nano priming or seed priming is a great solution. Nano-priming is a unique way of seed priming that helps to boost growth, yield, and germination of seeds by giving plants resistance to a range of stresses (Nile et al., 2022). Under both normal and stressful circumstances, nano- priming helps seeds regulate their reactive oxygen species (ROS), and it also increases the pace at which seeds germinate and produces more robust, better seedlings (Kandhol et al., 2022). In arsenic stress, seed priming with zinc oxide nanoparticles (concentrations @10, 20, 50,100, and 200 mg L− 1) enhances the seed germination rate of rice (Wu et al.,2020). Besides, they also enhance the seedling growth of fragrant rice varieties in cadmium stress (Li et al.,2021). Silver nanoparticles are very helpful for mitigating stress conditions while seeds are primed with them. Seed priming of fenugreek and lentil seeds increases seed germination during salt stress (Hojjat and Kamyab,2017) and drought stress (Hojjat and Ganjali, 2016) respectively. At the dose of 0,

 500, 1000 and 2000 mg L-1, Titanium dioxide nanoparticles enhance primed wheat seed germination in drought stress (Faraji et al.,2018) and also in cadmium stress (Faraji and Sepehri, 2019).

5. Harmful/Negative effects of using metal nanoparticles

 Agricultural practices can employ metallic nanoparticles for various purposes, primarily aiming to increase crop yield through the application of seed priming, plant protection, biosensing, nano- fertilizers, growth stimulators, and nano-pesticides. Additionally, metallic nanoparticles can be employed to address the contamination of both water and soil resulting from farming activities (Spanos *et al.*, 2021). In agriculture, nanoparticles are used 42% for fertilizer, 10% for plant breeding, 26% for animal husbandry, 4% for soil enhancement and 18% for plant protection (StatNano, 2022). Although metal nanoparticles have numerous advantages, there are still many unknowns when it comes to how these materials may have a long-term impact on the environment (da Silva Júnior *et al.*, 2022). Physical and chemical properties, manner of use, stability of nanoparticles, strength, pore size, precise dimensions, area of contact, availability for biological uptake, maturity, the improper combination, length of exposure, and type of plant are some of the variables that might cause NPs to be harmful in agriculture (Sun *et al.*, 2022; Li *et al.*, 2022; Liu *et al.*, 2022). Comprehending these variables is crucial in evaluating the possible hazards associated with the utilization of nanoparticles in agriculture (Balusamy *et al.*, 2023).

 Although the precise processes of nanoparticle toxicity remain unclear, researchers have documented that the harmful effects of nanoparticles are influenced by the following factors: (i) the NPs' tendency to bioaccumulate due to the fact that the majority of engineered NPs lack biodegradability (Yoo-Iam *et al.*, 2014); (ii) the NPs' reduced diameter, which allows for their translocation and penetration into biological structures such as cellular membranes and tissues (Ma *et al.*, 2011; Yin *et al.*, 2012) and (iii) The ability of NPs to traverse trophic levels within ecosystems facilitates biomagnification at elevated trophic levels (Judy *et al.*, 2011). Many unanswered concerns remain regarding their behavior, destiny, and effects on plants (Scherer *et al.*, 2019).

 When plants are enriched with nanoparticles, their physiological processes are typically altered by a decrease in transpiration and photosynthesis, which ultimately impacts plant development (Rajput *et al.*, 2018). The suppression of seed germination, the reduction in light synthesis, and the disturbance of plant roots are among the many negative consequences of NPs that have been documented (Singla *et al.*, 2019). Research findings indicate that NPs may shorten roots and stems by slowing down the germination process. Certain NPs not only detrimentally affect plant growth but also damage cells and subcellular organelles, impairing mitochondrial function and cell membrane integrity (Gao *et al.*, 2023). Additionally, they may affect plant growth by interfering with photochemical synthesis, altering the function of antioxidant enzymes, causing oxidative damage, and causing an imbalance in the nutritional makeup of crops intended for human consumption (Siddiqi *et al.*, 2017; Lian *et al.*, 2020).

 These nanomaterials might potentially affect vital biological functions through their interactions with living things (Burketová *et al.*, 2022). Some NPs, when transmitted to and deposited in plants, can cause phytotoxicity (Gao *et al.*, 2023). The mechanisms underlying plant toxicity caused by nanoparticles (NPs) involve three distinct processes that occur upon the interaction between NPs and plants: (i) they make it easier to produce ROS, which is harmful because of oxidative stress (Marslin *et al.*, 2017); (ii) they trigger a transcriptional response (Xun *et al.*, 2017); (iii) their genotoxic effects, resulting from their interaction with DNA or organelles (such as mitochondria) (Ghosh *et al.*, 2017). Once absorbed by plants, nanoparticles (NPs) have the ability to move through the vascular system to other tissues. Once in these tissues, they can cause oxidative stress, enhance chromosome aberration index and micronucleus, as well as genotoxic and cytotoxic effects on plants that impact root elongation and plant seed germination. (Scherer *et al.*, 2019; Khan *et al.*, 2019). Several investigations reported about NPs genotoxicity and harmful effects on a plant's DNA and other genetic components. This may result in chromosomal aberrations, mutations, or other genetic alterations in plant cells, which could have a damaging impact on the plant's general health, development, and growth. These genetic changes could affect the plant's capacity to replicate, adapt to environmental stressors, also defend against infections (Mutlu *et al.*, 2018; Sharma, 2023).

 Some specific examples of negative effects by nanoparticles can be summed up as: silver nanoparticles (Ag NPs) had a detrimental effect on the growth of cucumber plants, specifically
on the length of the roots and stems, as well as the fresh and dry weight of the plants, resulted in deduction of carotenoids in the seedlings as well as a drop in overall biomass and the levels of chlorophyll content; also inhibited photosynthesis and reduced zinc and iron nutrients (Tripathi *et al.*, 2017); toxicity of ZnO NPs on *A. thaliana* showed chlorosis, lateral roots inhibition, and leaf size reduction ultimately resulting in decreasing the level of micronutrients (Nair and Chung, 2017); root elongation of *A. thaliana* significantly reduced when exposed to carbon particles and that also kept reducing with an incremental rise in the dose (Chen *et al.*, 2018; Gao *et al.*, 2023); obstruct root pore structures and reduce transpiration and cell membrane fluidity of wheat (He *et al.*, 2021; Feregrino-Perez *et al.*, 2023); suppressed microbial symbiosis in the vicinity of plant roots of rice by TiO² NPs (Khan *et al.*, 2021); caused DNA damage, with cytotoxic and genotoxic effects on the root meristem of onion by Si NP (Liman *et al.*, 2020); reducing leaf chlorophyll content and biomass of maize and many more (Shukla *et al.*, 2024).

 Metal nanoparticles used in agriculture could upset environmental equilibrium, particularly for soil microbes (Saha *et al.*, 2022). They hold the possibility of adversely affecting a variety of microbiological functions, including the synthesis of organic matter, chemical mineralization, and nutrition cycling (da Silva Júnior *et al.*, 2022). Besides, conventional NPs are produced in ways that are both environmentally damaging and expensive (Saritha *et al.*, 2022; Jiang *et al.*, 2022). On the other hand, numerous investigations also demonstrated that plant-mediated nanoparticles have little to no ecotoxicity toward plants in general (Plachtová *et al.*, 2018).

 For the technology to be transferred from the lab to the field, NPs toxicity is a crucial standard. In an effort to reduce the toxicity of nanoparticles, scientists have coated them with various moieties; nevertheless, as of right now, no thorough study that addresses the long- and short-term impacts of nanoparticles on plants and plant-associated food chains is accessible (Balusamy *et al.*, 2023). These emphasize how crucial it is to comprehend and properly evaluate how nanoparticles and plants interact in agricultural applications (Shukla *et al.*, 2024). Despite all these reservations, nanoparticles hold immense promise as an emerging technology in agriculture (Balusamy *et al.*, 2023).

6. Future perspectives

 The significant hazards to the environment and human health have caused researchers to refocus their efforts on biologically derived metal nanoparticles (NPs) and their environmentally benign, economically viable, and sustainable synthesis. The productivity of agroecosystems may be raised by the use of NPs in a variety of ways, including as nanopesticides, nanoherbicides, nanofertilizers, nanoplant growth promoters, and nanonutrient transporters (Hossain et al.,2023). Metal nanoparticles can improve the whole process from seed germination to yield along with food quality. Including appropriate size and dose, metal nanoparticles may be engineered to target certain plant regions, delivering nutrients or pesticides directly to where they are needed maximizing nutrient uptake, and reducing runoff into waterways. So, metal nanoparticles can be used as fertilizer, which will reduce farmer's costs and also will be eco-friendly by confirming pollution-free environment. They have the ability to increase seed germination even in stressed conditions, which indicates that they can enhance seed vigor and viability and can be used in those crops that have low germination percentages and higher seed rates. After confirmation of seed germination for achieving expected yield, the physiological process of plants should be improved which can be made possible by using these metal nanoparticles without toxic effects. For better photosynthesis rate, better respiration, enhanced physiological reaction, boosted chlorophyll content and stomatal opening, facilitated redox reactions, greater stability, increased defense enzyme activity, elevated antioxidant activity, etc., metal nanoparticles can be more effective for plants and lead to sustainable agriculture. At the matured level and pre-harvest conditions, these metal nanoparticles can be more effective due to enhancing the grain's protein and lipid content, useful acid content, and weight along with forming secondary metabolites, which will smooth the biofortification process. This indicates that, in the future, these nanoparticles will be used in every agricultural sector to produce food and feed the hidden hunger all over the world. This will contribute to achieving SDG (Sustainable Development Goals). Metal nanoparticles have natural antimicrobial capabilities, which include antibacterial, antifungal, and antiviral activities and these qualities may be used to assist in the fight against pests and illnesses that affect crops. Future developments might lead to the creation of formulations based on nanomaterials that can specifically target dangerous diseases while protecting helpful bacteria in the soil. This focused approach to pest control lessens the need for chemical pesticides, lowering environmental hazards and enhancing ecosystem health. Metal nanoparticles could be engineered to confer tolerance to abiotic stresses related to drought,

 oxidative damage, heat, cold, etc. This holistic approach would provide plants with comprehensive resilience against various environmental challenges, thereby contributing to sustainable agriculture in diverse ecosystems. So, the use of metal nanoparticles in precision and sustainable agriculture has enormous potential for increasing crop resilience and maintaining food security in the face of escalating environmental concerns. Using nanotechnology, we can create bespoke solutions that maximize resource usage, reduce environmental impact, and promote agricultural sustainability.

7. Conclusion

 Despite the unexpected consequences, negative environmental impact, and toxicity sometimes, metal nanoparticles have a positive and significant impact, including growth promotion, stress mitigation, yield enhancement, etc., on the plant's life cycle. Thus, metal nanoparticles have become a promising topic that leads to precision and sustainable agriculture. Besides, the green synthesis method of metal nanoparticles is an eco-friendly method requiring less time, money and energy, is more suitable for sustainable agriculture, and can be used in the farmer stage. To feed the increasing population without doing harm to the environment, we should use these metal nanoparticles in an appropriate size and in an ethical manner. As there is much ongoing research on metal nanoparticles in agricultural sectors all over the world, the researchers should focus on the mitigation of risk factors for metal nanoparticles. They should try to ensure a better outcome in the future.

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