Study on the Impact of Metal Nanoparticles on Physiology and Metabolism of Plants: A Review

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A Review

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Submitted By

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Student ID: MS-180718

Session: 2017-2018

BIOTECHNOLOGY AND GENETIC ENGINEERING DISCIPLINE

LIFE SCIENCE SCHOOL, KHULNA UNIVERSITY

KHULNA-9208, BANGLADESH

MARCH, 2022

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DECLARATION

This thesis report is the original research work of the author, except as otherwise stated. The material presented has not submitted either in whole or in part for a degree for this or any other university. The findings of this review will not be published anywhere without the concurrences supervisor. Legal action would be taken in any case of infringement regarding the declaration.

Rehana Parween

Rehana Parveen

Examination Roll: MS-180718

March, 2022

Dedicated

To

My Beloved Parents

Acknowledgement

In the name of Allah, the Almighty, most Merciful, He who owns all gratitude and praises, who has given the author to pursue her education in Biotechnology and Genetic Engineering Discipline as well as for successful Completion of dissertation.

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The Author **March,2022**

ABSTRACT

Nanoparticles (NPs) have been used in plant science to improve physiology and metabolism of plant. The large surface area and small size are some of the desired attributes for NPs that can substantially ameliorate plants physiological processes, metabolism. Some metal and metal oxide nanoparticles influence the growth and development of plants. They generally enhance or reduce seed germination, shoot/root growth, biomass production and physiological and biochemical activities. This review focused on the prominent effect of Metal Nanoparticles (MNPs) on plant physiology and metabolism and to understand the prospects and problem for future research. Their uptake by plants and it's interaction with plants are also discussed for better understanding. However, Metal Nanoparticles have not always positive impact on plant in some cases; MNPs negatively affect plants due to their toxic nature. These toxic effects depend upon the size, concentration, nature and shape of nanoparticles, as well as the used plant species. MNPs also show impact on plants secondary metabolism. Alternatively, MNPs do not always exhibit positive or negative impacts on plants and no physiological influences are sometimes observed. Considering such diversity of responses after the use of MNPs on plants, this review summarizes the progress made in nanotechnology on the influence of different MNPs in plant physiology and metabolism.

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Abbreviations

Abbreviation	Elaboration
NP	Nanoparticle
MNP	Metal Nanoparticle
LSPR	Localized surface plasmon resonance
nm	nano miters
ROS	Reactive oxygen species
TDN	Titanium di oxide
µg	microgram
ml	mili liter
ppm	parts per million
MAPK	mitogen-activated protein kinase
PAL	phenylalanine ammonia lyase
PPO	polyphenol oxidase

CHAPTER 1

INTRODUCTION

Introduction

Nanotechnology is a new branch that has the implicit impact on plants. Nanotechnology has huge potential to give an opportunity for the researchers of biotechnology, biological science, plant science and other fields, to develop new tools for manifestation of nanoparticles into plants that could expand existing functions and add new ones (Cossins, 2014). Nanoparticles are present in the environment in the form of minerals, particles arising from volcanic eruptions, clays, and products of bacteria. The nanoparticles are favored over their bulk-sized substances due to their unfamiliar characteristics (Rai et al., 2009). The naturally available nanoparticles are recognized to us from historic times. Nanoparticles are assorted into many types. Among them, metal nanoparticles are being studied for their unique properties, operations and applications. Metal and metal oxides nanoparticles possess different physiochemical properties such as surface, optical, thermal, and electrical properties (Santos et al., 2014).

The metal nanoparticles are produced simply by adding reducing or oxidizing, precipitating agents during synthesis process, respectively (Sanchez-Dominguez et al., 2009). Various elements including nanoparticles form and size, core composition, purity, stability, surface composition and approach of synthesis are liable for excessive degree of reactivity of nanoparticles with biomolecules (Teske & Detweiler, 2015; Wang et al., 2016a).

Nanoparticles have unique physicochemical properties and the potential to boost the physiology and metabolism of plant (Giraldo et al., 2014). Engineered nanoparticles are able to inter into plants cells and leaves, and also can transport DNA and chemicals into plant cells (Torney et al., 2007). This area of biotechnology offers new possibilities in plant biotechnology. Many researches have raised challenge approximately feasible interplay of nanoparticles with flora and fauna withinside the surroundings (Rastogi et al., 2017). Although the use of nanoparticles has greater significance in diverse fields but it also causes adverse effects on human health and the environment (Santos et al., 2014). Plants are recognized to be one of the maximum crucial additives of the ecosystem, and their interplay with nanoparticle has been nicely studied (Yanık & Vardar, 2015; Rai et al., 2018). The nanoparticles released in environment could be taken up by plants and become the part of food chain through dietary consumption, hence affecting human health (Pittol et al., 2017). It is believed that the nanoparticles can cause both favorable as well as adverse effects in plant systems (Peralta-Videa et al., 2017).

In recent era, many scientific communities have emphasized their study on impact of nanoparticles on plant physiology and metabolism (Rastogi et al., 2017). Many researches have proven that the metal and metal oxide nanoparticles have profound impact on plant growth and improvement. Depending on their houses, nanoparticle interplay with flora has been proven to motive the morphological and physiological adjustments. Depending on their properties, nanoparticle interaction with plants has been shown to cause the morphological and physiological changes. The essential metalic oxide nanoparticles are chosen because they are essential elements for plants growth, and are nontoxic in a various range of concentrations. This group of metals included Ag, Zn, Cu, Ti and some other metal nanoparticles.

The objectives of this review are-

To clarify the information about the potential impact of metal nanoparticles on

Physiology and Metabolism of plants for scientific community.

CHAPTER 2

REVIEW OF LITERATURE

Review of Literature

2.1 Nanoparticle

Nanoparticles (NPs) are atomic or molecular summations with at least one dimension between 1 and 100nm (Laurent et al., 2010). Nanoparticles exist in this nature and can be also created as a result earthborn conditioning. Because of their submicroscopic length, they have their own specific material characteristics.

2.2 Metal Nanoparticles

Metal NPs are in introductory terms fabricated from the metal precursors. Metal nanoparticles are submicron scale entities fabricated from natural metals (e.g., silver, cerium, iron, gold, platinum, titanium, zinc, thallium etc.) or their compounds (e.g., oxides, phosphates, fluorides, hydroxides, sulfides and chlorides) (Mihranyan et al., 2012).

Metal nanoparticles comprising both of metal oxides and pure metals have presently been employed to affect the development of flora. Due to well-known localized surface plasmon resonance (LSPR) characteristics, these NPs retain own specific optoelectrical properties. The size, dimension and shape-controlled synthesis of metal NPs are important in present day cutting-edge materials (Dreaden et al., 2012). So, it will be beneficial to know about the impact of Metal nanoparticles on plant to carry out future development of plants.

2.3 Previous Research Findings Regarding Metal Nanoparticles

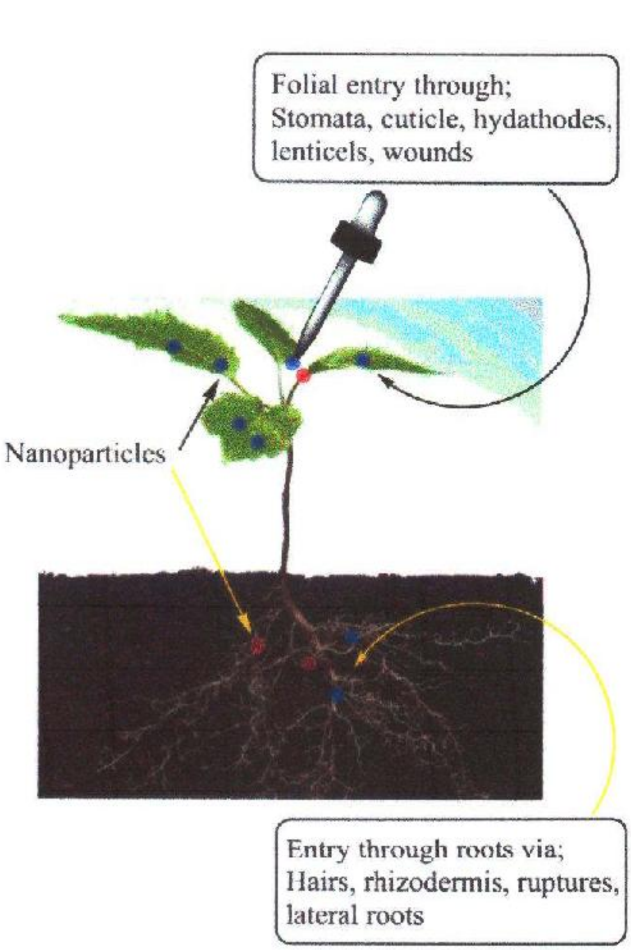
This field of research is gaining attention in this century. There are few studies displaying the useful function of metal and metal oxide nanoparticles. Some research findings regarding various metal nanoparticles are stated below-

2.3.1 Mechanism of Nanoparticle Plant Interaction

It is hypothecated that, for showing the poisonous impact the uptake of nanoparticles with the aid of using plant and their translocation into distinct tissues is necessitated. Further, primarily based totally on their transportation, houses, and reactivity, the nanoparticles might additionally intervene with distinct metabolic activity to produce an effect on plant.

2.3.1.1 Routes of Entry for NPs into the Plant Cell System

Nanoparticles are nano scale small particle like systems that are formed through reduction of certain metal salts and are competent of independent action in a process. Some of the potent nanoparticles include those attained from metals and metal oxides similar as silver nanoparticles (Ag NPs) and Zinc Oxide nanoparticles (ZnO NPs). These particles have the capacity to penetrate tiny systems and can travel to distant zones within plants to trigger different biochemical and physiological pathways. It is well understood that nanoparticles enter plant tissues either via root (root tips, rhizodermis, lateral root junctions) or the aboveground organs and tissues (cuticles, trichomes, stomata, stigma, and hydathodes) as well as through the wounds and root junctions. It has also been noticed that plants have different behavior towards redundant metal ions present in the growth medium. Metal-tolerant plants may limit nanoparticles uptake into the photosynthetic tissue by confining the transport across the root endodermis and storing them on the root cortex, whereas, hyper accumulating plants accumulate excess quantities of nanoparticles in the harvestable tissues (Manceau et al., 2008). The size, dimensions and concentration of these nanoparticles have been shown to play significant roles in governing their functions in different plants.



Ref: Khan et al., 2019

Fig. 2.1 Illustration of possible routes of entry for NPs into the plant cell system

2.3.1.2 Nanoparticle Uptake

The nanoparticles whilst found in higher concentrations are discovered to damage the plant cellular wall and plasma membrane, for this reason penetrating it and interacting with the distinct plant's strategies (Mazumdar & Ahmed, 2011; Mirzajani et al., 2013). Nanoparticles can enter plant tissue both via root or the above ground parts along with root junctions and wounds. For uptake and translocation nanoparticles has to undergo numerous chemical and physiological barriers. When nanoparticles have interaction with plant, cellular wall is the primary barrier it has to cross. Plant cellular partitions are shape which consists of cellulose which lets in the access of small particles and limiting the bigger one, consequently smaller nanoparticles can undergo this residue in a relatively smooth manner in recognize to large nanoparticles. The length exclusion restrict for the plant cellular wall is among 5 and 20 nm (Dietz & Herth, 2011). Some of the nanoparticles were stated to set off the formation of large pores in cellular wall which in addition facilitate the access of big nanoparticles (Navarro et al., 2008; Kurepa et al., 2010). From the cellular wall the nanoparticles may also pass via endocytosis (Etxeberria et al., 2006), and in addition, via the simplistic delivery, it is able to travel to distinctive plant tissues (Ma et al., 2010). (Wong et al., 2016) have proposed a mathematical model which shows lipid trade mechanism for nanoparticle delivery withinside the plant cells. The examine indicated that length, magnitude, and zeta potentials are key in figuring out the delivery of nanoparticle withinside the plant.

2.3.1.3 Nanoparticle-Plant Interaction Pathways

Nanoparticles can also additionally intervene with plant in numerous ways, which includes, through supplying micronutrients (Liu & Lal, 2015), regulation of genes (Nair & Chung, 2014), or interfering with unique oxidative approaches in plant life which leads to oxidative burst (Figure 2; Hossain et al., 2015).

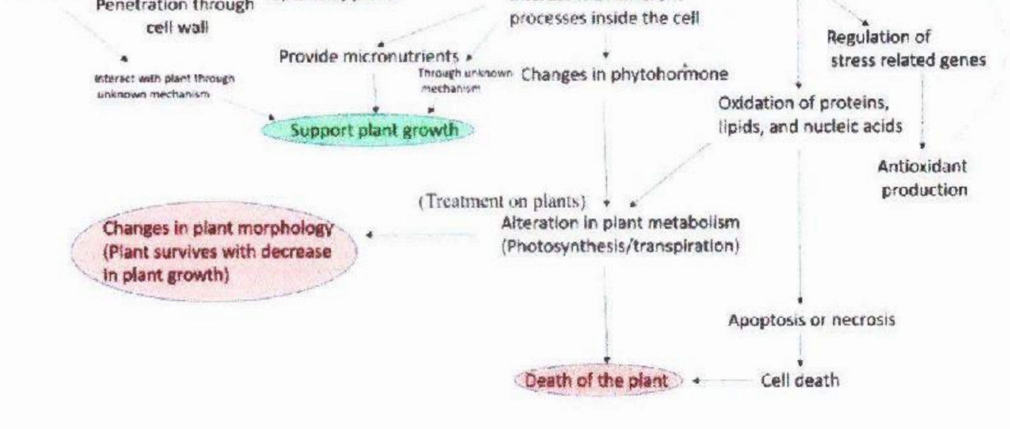


FIGURE 2.2: Mechanism of nanoparticles interaction with plant

So, it's far clear that numerous nanoparticles while found in extra outcomes into ROS manufacturing, and intervene with the oxidative mechanism, while different kinds of interactive pathways aren't deciphered and there may be nevertheless a great deal work had to apprehend the alternative pathways. Therefore, the oxidative element is elaborated in Figure 2 and similarly mentioned here. The entered nanoparticles can intervene with electron delivery chain of mitochondria and chloroplast, which can also additionally result into the oxidative burst, observed through the growth in ROS awareness (Dimkpa et al., 2013; Pakrashi et al., 2014; Faisal et al., 2013; Jiang et al., 2014; Cvjetko et al., 2017). It has been formerly mentioned that beneathneath impact of various stress factors, the rate of carbon fixation is limited, which reasons an increase in picturegraph inhibition probably steering the photosystem towards overproduction of superoxide anion radicals and H_2O (Foyer & Noctor, 2005). Once the ROS is produced because the end result of nanoparticle interaction, it's far regarded that it interacts with nearly all cell additives generating protein modifications, lipid peroxidation, and harm to DNA (Van Breusegem & Dat, 2006). Several reviews have proven an increase in lipid peroxidation and DNA damage in plants nanoparticle interplay (Atha et al., 2012; Belava et al., 2017; Cvjetko et al., 2017; Saha & Dutta Gupta, 2017), which confirms that plant interplay with nanoparticles leads into lipid peroxidation. The accelerated manufacturing of ROS can both set off apoptosis or necrosis (Van Breusegemand Dat, 2006; Rastogi & Pospíšil, 2012; Faisal et al., 2013), which leads to plant cellular death. Despite their unfavorable pastime, ROS also are regarded to have a signaling function in a lot of cell approaches such as tolerance to environmental stresses (Sharma et al., 2012). The unfavorable or signaling position of ROS relies upon at the equilibrium among ROS manufacturing and scavenging. Due to the multifunctional roles of ROS, the cells have advanced a sturdy antioxidant mechanism to exactly manipulate the extent of ROS. The antioxidant mechanism incorporates the manufacturing of enzymatic (superoxide dismutase, catalase and guaiacol peroxidase) and non-enzymatic (Ascorbate, glutathione, carotenoids, tocopherols, and phenolics) molecules (Sharma et al., 2012). To cope up with the stress plant life will increase the manufacturing of antioxidant molecules (Rastogi & Pospíšil, 2012; Sharma et al., 2012). Several reviews have proven the accelerated manufacturing of the antioxidant molecule withinside the plant below the impact of nanoparticles (Faisal et al., 2013; Jiang et al., 2014; Costa & Sharma, 2016), which confirms the regulation of antioxidant system as a reaction to nanoparticle interaction with plant. If the antioxidant produced are not able to govern the ROS, The ROS oxidized the cellular macromolecules and outcomes into the loss of life of the cellular through apoptosis or necrosis (Sharma et al., 2012), which in the end outcomes withinside the loss of life of the plant. The current reviews have additionally proven that phytohormone performs an essential function in plant stress reaction signaling (O'Brien & Benková, 2013). The hormonal manipulate of plant improvement and stress adaptation is taken into consideration to be the final results of a complicated community of synergistic and hostile interactions among diverse hormones. The ROS also are related to hormonal signaling in a complicated way and have an impact on every different activity (Kwak et al., 2006). Different hormonal pathways are recognized to be up regulated or down regulated in reaction to distinctive form of stresses (O'Brien & Benková, 2013). The determined increase in cytokinin degree in *Capsicum annuum* as a reaction to Ag NP stress and a lower in IAA and ABA in a cotton plant in reaction to CuO NP suggests that nanoparticle have an impact on the hormonal stability in flora, for that reason affecting the plant metabolism. Therefore, it may be stated that the poisonous impact of nanoparticles withinside the plant is especially mediated via ROS. The electron delivery chain in mitochondria and chloroplast operates in aerobic environment and for that reason the extra manufacturing of ROS effect the approaches (Foyer & Shigeoka, 2011). Photosynthesis is likewise taken into consideration to be a very good degree of usual overall performance of flora (Kalaji et al., 2014). It is the most effective strength enters in flora and thereby affects all elements of plant metabolism and physiology. Thus, the dimension of photosynthetic pigment and activity is a superb degree to get entry to the effect of stress factors. Different reviews have proven that the nanoparticles have an impact on the photosynthetic pigment awareness and its activity in flora (Perreault et al., 2014; Qian et al., 2013; Tripathi et al., 2017). A very excessive awareness of nanoparticles may also severely have an effect on the photosynthesis which may also bring about plant growth suppression or plant dying.

2.3.2 Silver Nanoparticles (AgNPs)

Silver nanoparticles (AgNPs) display unique physical and chemical properties as compared to their macroscale analogs. This is mainly because of their small length and, consequently, the exceptional surface region of those materials. AgNPs are attributed to pathways that encompass onsite wastewater control systems, bio solids utility, improper disposal, and the utility of AgNPs-containing natural fertilizers and pesticides (Blaser et al., 2008; Anjum et al., 2013). Soil is representative of a complicated matrix wherein NPs can interact, and for that reason constitutes an excellent conduit towards understanding NPs physio-chemical behavior (Pan & Xing, 2012). Modification of AgNP properties which includes dispersibility, stability, aggregation, dissolution rate, aging, length, and surface region can occur via the interplay of soil environments and AgNPs, for that reason affecting their availability, retention, binding affinity, delivery, or even toxicity to organisms (Bell & Kramer, 1999; Benn & Westerhoff, 2008; Geranio et al., 2009; Kim et al., 2010; Cornelis et al., 2012).

2.3.3 Copper Nanoparticles (CUNPs)

The applications of copper (Cu) and Cu-based nanoparticles, which might be based at the earth-plentiful and less expensive copper metallic, have generated a superb deal of interest in current years. The viable amendment of the chemical and physical properties of those nanoparticles the usage of exclusive artificial techniques and situations or through post synthetic chemical remedies has been in large part liable for the fast growth of interest in those nanomaterials and their programs in catalysis. In addition, the layout and improvement of novel aid and multi metallic systems (e.g., alloys, etc.) has additionally made massive contributions to the field. Copper (Cu) comes beneathneath transition metals withinside the periodic table, found in D block. Cu, as a periodic element, has atomic number 29. It is an important earth element for living beings at low concentrations and poisonous at better concentrations. Cu pollutants due to anthropic activities are a result of Cu polishing, paint, mining, plating, and printing operations (Nagajyoti et al., 2010; Ayangbenro & Babalola, 2017). Cu is a crucial micronutrient required through plants in very small quantities, playing an vital function in preserving plants' natural metabolism and increase, however its deficiency and excess are validated inhibitors of numerous physiological functions (Zhao et al., 2010), Cu excess being additionally genotoxic. Cu concentration and availability in soil rely upon pH and inorganic matter content (McCauley et al., 2009). Similar to different metallic nutrients consisting of Mn and Zn, Cu is a small element and has advantageous charges capable of strongly bind to the surface of soil particles. At high pH, the bond with soil will increase and Cu concentration in soil solution and its availability for plant uptake decreases. On the contrary, at low pH and high organic matter content, Cu solubility and availability for plants growth (McCauley et al., 2009). Deficiency of Cu in soil additionally reasons many extreme troubles in plants consisting of stunted growth, lower in productivity, not on time flowering, and sterility. Since Cu solubility is depending on the chemical physical shape of soil, it is able to be retained in soil for decades and can be taken into consideration as a prime toxicant to plant cells as it inhibits many physiological and biochemical procedures (Ahsan et al., 2007). Cu while found in excess quantities reasons toxicity; in addition copper oxide NPs (CuO NPs) have many poisonous results. CuO NPs also are utilized in biocides (Shi et al., 2011; Perreault et al., 2014). According to a mentioned study, CuO NPs of 50nm length are taken into consideration as a hard material that doesn't exhibit the equal malleability and ductility as bulk Cu (Science Daily, 2014). In particular, CuO NPs are used considerably in antimicrobial formulations and products due to their antimicrobial properties (Gabbay et al., 2006; Borkow & Gabbay, 2009; Abramova et al., 2013). Although precise information on synthesis, characterization, essential properties, and applications of CuO nanomaterials is currently present, there are numerous stones nevertheless unturned concerning metallic NP bioavailability, their uptake and translocation through plants, and their toxicity mechanism (Navarro et al., 2008; Andreotti et al., 2015). The toxicity of CuO NPs to people and environmental health has been said from preceding research (Yoon et al., 2007; Griffitt et al., 2007; Aruoja et al., 2009; Gomes et al., 2011).

2.3.4 Titanium Nanoparticles

Titanium and TiO_2 (titanium oxide) nanoparticles by growing essential metallic nutrient uptake stated to enhance plant improvement. The performance of nanoparticle is essentially justified through their chemical composition like, length of particles, surface cover area, reactive competencies with effective doses. Titanium dioxide nanoparticles play an essential function in plant growth and improvement of plant life. When nanoparticles link with plant displaying numerous modifications of their morphology and body structure that relies upon on nature and properties of nanoparticles. The exceptional studies outcomes confirmed that TDN responds to each high quality and negative approaches of plant growth and improvement. The effect of nanoparticle attention on numerous species is tremendously variable. Titanium dioxide nanoparticle improved seed germination and promoted radicle and growth of canola seedlings (Jaberzadeh et al., 2013) said that titanium dioxide nanoparticle augmented wheat plant growth and yield additives beneathneath water deficit stress conditions. Titanium dioxide nanoparticle regulates enzymes activity concerned in nitrogen metabolisms which includes nitrate reductase, glutamate dehydrogenase, glutamine synthase and glutamic-pyruvic transaminase that assist the plants to take in nitrate and additionally special treatment the conversion of inorganic nitrogen to natural nitrogen withinside the shape of protein and chlorophyll that would increase the plant biomass. It additionally acts as a photo catalyst and induces an oxidation-reduction reaction. Therefore, promote the chlorophyll formation and stimulate Ribulose 1, 5-bisphosphate carboxylase (Rubisco) activity and will increase photosynthesis, thereby increasing plant growth and improvement. Titanium dioxide nanoparticle will increase mild absorbance, hasten the delivery and conversion of the mild energy, protect chloroplasts from growing old and lengthen the photosynthetic time of the chloroplasts. It can be because of titanium dioxide nanoparticle protects the chloroplast from immoderate light through augmenting the activity of antioxidant enzymes. Overall titanium dioxide nanoparticle enhanced increase biomass and yield of crop cultivars through promoting nutrient uptake efficiency and growing photosynthesis rate of plants. Titanium (Ti) is taken into consideration a useful element for plant growth and improvement. Application of Ti through roots or leaves at low concentrations has been documented to enhance crop overall performance via stimulating the activity of certain enzymes, improving chlorophyll content material and photosynthesis, promoting nutrient mobilization, biotic and abiotic stress tolerances and enhancing crop yield and quality. There has been a growing quantity of interest withinside the literature concerning the results of titanium dioxide nanoparticle on plant overall performance. Titanium dioxide nanoparticles suspensions were used to observe the effect on seed germination of numerous crops. The end result confirmed that titanium dioxide nanoparticles improved the germination rate, root length with progressed growth rate of numerous varieties i.e., *Arabidopsis thaliana (L.)*, cabbage, corn, oilseed rape, canola, cucumber, fennel, lettuce, oat, onion, parsley, red clover, soybean, spinach, tomato and wheat.

2.3.5 Iron Nanoparticles

Nanoscale iron particles have attracted massive interest because of their particular bodily and chemical properties. Iron content material is high in soil however a huge percentage is constant on soil particles that are unavailable for flora because of its insoluble shape (Fe^{3+}) as plant take in Fe^{2+} shape from the soil. Iron performs a vital function in lots of physiological procedures inclusive of chlorophyll biosynthesis, respiration, and redox reactions (Ye et al., 2015), and an important micronutrient for plant growth. Iron is unavailable for plants in some soils, for instance, calcareous soil. Therefore, the utility of iron nanoparticles has been expanded recently. However, its long-time period effects on flora and soil ecosystems have now no longer been studied yet. A growing utility of zero valent iron nanoparticles increases critical issues for the environmental pollution. The zero-valent Fe nanoparticles have successfully been used withinside the treatment of a number of environmental contaminants which will increase the probabilities to its accumulation withinside the soil ecosystem. The research display iron nanoparticles decreased the plant chlorophyll content, root hydraulic conductivity and affected transport of dissolved nutrients, specifically Mg (Trujillo-Reyes et al., 2014; Martinez-Fernandez et al., 2016).

2.3.6 Zinc Nanoparticles

Zinc (Zn) is a crucial micronutrient however excess quantity might also additionally cause chlorosis and inhibit plant growth (Vallee & Auld, 1990; Schutzendubel and Polle, 2002). Zinc nanoparticles are round or polished metal particles with a excessive precise surface region with molecular formulation ZnO. Limited research had been accomplished thus far to decide the consequences of ZnO-NPs on plant increase and productivity (Lin and Xing, 2007; Stampoulis et al., 2009). It is nicely diagnosed that ZnO-NPs have an effect on crop improvement and yield and accumulate in plant tissue, which includes suitable for eating portions. The behavior of ZnO-NPs in flora isn't always absolutely clear; however, the optoelectrical, bodily and antimicrobial sports of ZnO-NPs provide numerous effective consequences to flora (Liu & Lal, 2015; Hussain et al., 2016). ZnO-NPs as much as a certain attention have the capability to beautify growth (Faizan et al., 2018), wherein they offer Zn^{2+} as a micronutrient (Liu & Lal, 2015).Similar inductive consequences of ZnO-NPs led to expanded stem and root growth. Pod yield per plant became 34% better with ZnO-NPs as compared to chelated bulk $ZnSO_4$ uncovered plants. ZnO-NPs improved growth and biomass manufacturing of alfalfa, tomato, and cucumber plants (de la Rosa et al., 2013; Panwar et al., 2012). Ramesh et al. (2014a, b) stated that low concentrations of ZnO-NPs imparted a useful impact on seed germination in wheat. In contrast, (Zhao et al., 2013) discovered that ZnO-NPs had no effect on growth of cucumber plants, gas exchange, or chlorophyll content. Lower concentrations of ZnO-NPs have been now no longer dangerous to cell division and early seedling growth in onion (Raskar & Laware, 2014)

2.3.7 Cerium Oxide Nanoparticles

Potential applications of CeO_2 -NPs withinside the agricultural industry consist of the control of plant diseases, promoting of plant growth, relief of plant stresses, and development of nutrient control (Adisa et al., 2019; Peralta-Videa et al., 2014; Servin et al., 2015; Rossi et al., 2016; Iftikhar et al., 2020). However, incorrect exposure to CeO_2-NPs ought to result in toxicity to each plants and soil microorganisms. Complex interactions exist among CeO_2 -NPs and plants and soil microorganisms, and each enhancive and inhibitive, in addition to no impact of CeO_2 -NPs has been documented at numerous ranges of plant improvement in distinct research (Corral-Diaz et al., 2014; Morales et al., 2013; Birbaum et al., 2010), relying upon their subcellular accumulation, physicochemical properties and ambient conditions (Asati et al., 2010). Previous research have validated that the plant-nanoparticles (NPs) interactions are ruled with the aid of using different factors which includes the dosage, size, shape, morphology of CeO_2 -NPs and soil properties (Hussain et al., 2019; Liu et al., 2019; Singh et al., 2019; Lizzi et al., 2020)

2.3.8 Effect of Some Other Nanoparticles on Plants

In addition to above-stated metallic oxide nanoparticles, there are certain different metallic oxide nanoparticles which utilized in plant increase promotion. Nickel oxide nanoparticles (NiONPs) have tremendous applications in special fields (Manna & Bandyopadhyay, 2017). The impact of NiONPs on plant increase and improvement became evaluated through various scientific communities. It has been stated that the better awareness of NiONPs exerted toxicity in plants (Pinto et al., 2019; Saleh et al., 2019). Numerous researchers have discovered that NiONPs can reason cytotoxic and genotoxic results in plants (Magaye & Zhao, 2012; Manna & Bandyopadhyay, 2017). Furthermore, NiONPs have proven to set off apoptosis in tomato root cells (Faisal et al., 2013), suppressed increase, and oxidative damage in wheat (Saleh et al., 2019). Moreover, (Chung et al., 2019b) evaluated the impact of NiONPs on increase, photosynthesis rate, and plant metabolites content. They have stated the reduction in chlorophyll, carotenoid, and sugar contents, while proline and the anthocyanins have been improved in Chinese cabbage seedlings. Recently, (Rahman et al., 2020) studied the impact of NiONPs on seed germination in Black gram and stated non-significant impact on germination percent over control. (Basker et al., 2018) stated suppressed root and shoot increase of NiO NPs on in vitro grown eggplant. However, (Chahardoli et al., 2020) stated the advanced biomass at 50 mg/L of NiO NPs remedy to hydroponically grown tissues of *Nigella arvensis L.*, whilst it changed into significantly reduced at better concentrations of those nanoparticles. Similarly, aluminum oxide nanoparticles (Al_2O_3 NPs) are used extensively in numerous sectors because of its tremendous applicability (Ghotekar, 2019). The metallic oxide nanoparticles can also additionally impose numerous worries concerning viable fitness and environmental effects (Sousa et al., 2018). Earlier researches have proven that it has unfavourable impact on plant growth and physiology. For instance, Al_2O_3 NPs was discovered to result in programmed cellular death in wheat roots (Yanık et al., 2017). The study by (Chahardoli et al., 2020) established the dose dependent results of Al_2O_3 NPs and NiO NPs on antioxidant activities and increase of *N. arvensis*. Authors similarly stated that Al_2O_3 NPs (100 mg/L) remedy ended in advanced plant increase whilst better doses-imposed toxicity. Similar findings have been recorded in *Hibiscus sabdariffa L* through (Latef et al., 2020). Besides, Al_2O_3 NPs at decrease concentration exhibited better biomass manufacturing in *Zea mays, Lepidium sativum, A. cepa L.* and *Kalanchoe daigremontiana* however lower in root dry mass through 33% at 1000 mg/kg became recorded (Asztemborska et al., 2015). An observation found out that there may be dose-established reduction withinside the mitotic index and rise in chromosomal aberrations (Rajeshwari et al., 2015; Debnath et al., 2020). The cellular stress, damages to cellular membrane, and higher quantity deactivation of the cellular protection structures have been stated upon exposure to metallic oxides nanoparticles like Al_2O_3 NPs, ZnO NPs, and TiO_2 NPs (Czyżowska & Barbasz, 2019). Few different metallic oxide nanoparticles additionally have proven outstanding effect on increase and body structure of plant. A study indicated that stannous oxide nanoparticles (SnO_2 NPs) and Ag doped SnO_2 NPs caused cytotoxicity in tobacco cellular cultures accordingly suppressing the cellular proliferation and viability in concentration based manner (Mahjouri et al., 2020).

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CHAPTER 3

REVIEW METHODS

Review Methods

For this review, at first many scientific journals and research papers were selected related to the topic- the impact of metal nanoparticles on physiology and metabolism of plant. In this regard, published research article and authentic web-based information were considered. I read those articles focused on the positive and negative impact of metal nanoparticles on plant physiology and metabolism.

So, the information were collected from the following sources-

Books

To understand those articles few books related to plant physiology, biochemistry were studied.

Journals and Thesis Papers

Scientific journals on plant physiology and metabolism are very important sources for the fulfillment of this review.

Websites Visited

Some of the websites which were visited for this review are given below-

https://scialert.net/

https://www.britannica.com/science/nanoparticle

https://www.frontiersin.org/

CHAPTER 4

DISCUSSION

Discussion

4.1 Metal Nanoparticles on Plant Physiology and Metabolism

Plant physiology and improvement is broader term which incorporates stages from seed germination to senescence of plant (Kanwar et al., 2019). Nanoparticles were mentioned to reveal useful or poisonous impact on the plant growth and developmental procedures viz. in seed germination, plant growth and physiology (Verma et al., 2018; Khan et al., 2019a). Several research groups studied impact of metallic and metallic oxide nanoparticles on plant physiology observed to be positive, negative, and neutral, it can be due to certain elements like size, concentration, physicochemical properties of nanoparticles, and plant species type (Rizwan et al., 2019a; Zhao et al., 2020). The metal oxide nanoparticles display more impact mostly through raising or reducing the plant growth and improvement procedures which includes germination, shoot and root development, biomass productivity, biochemical, and physiological activities (Siddiqi & Husen, 2017). Nanoparticles were additionally discovered to have application as nano fertilizer and nano pesticides, for promotion of plant growth, genetic improvement, plant disease treatment, and nutrient management (De la Rosa et al., 2017). For plant growth, many metals serve as the micronutrients, and hence, the metallic nanoparticles are demonstrated to be the effective plant growth promoting entities. Among metallic nanoparticles, metal oxides nanoparticles are being favored as plant growth promoting agents. This is due to the fact they could easily release the metals as micronutrients withinside the region of plant roots, and hence, they may be effortlessly taken up through plants for carrying out further metabolism. Therefore, there's a need to study the impact of various nanoparticle on plant physiology and metabolism.

4.2 Impact of Metal Nanoparticles on Plant Physiology

There is both positive and negative impact of metal nanoparticles on plant physiology. Impact of some metal nanoparticles are discussed below-

4.2.1 Impact of Silver Nanoparticles (AgNPs)

Among distinct nanoparticles, AgNPs have greater utility due to they are utilized in diverse products (Boxall et al., 2008; Rai et al., 2009; Wijnhoven et al., 2009). Through sludge and surface water the AgNP can also additionally without difficulty reach to the plants. The AgNPs of 25 nm at high concentration was discovered to interrupt the mobileular wall and harm the vacuoles of root cells of *Oryza sativa,* for that reason inflicting a poisonous impact (Mazumdar and Ahmed, 2011). It is likewise found that the AgNP became not able to penetrate the root cells of *O. sativa* while found in low concentration (as much as 30μg/mL), while the better concentration became able to break the mobileular shape and cause the poisonous impact (Mirzajani et al., 2013). The authors additionally mentioned that, the 30μg/mL hastens root increase, while 60μg/mL restricts the capacity of root to grow. The observations suggest that the penetration of AgNP is essential to cause a poisonous impact, while when found in surrounding, it can have a advantageous effect on plants. (Krishnaraj et al., 2012) found a slight or no impact of biologically synthesized AgNP on *Bacopa monnieri.* The synthesized nanoparticle precipitated the protein and carbohydrate synthesis and reduced the entire phenol contents, which may be taken into consideration as an advantageous impact, it can be because of the presence of various length (2–50 nm) of nanoparticle with distinct penetration ability withinside the maximum carried out concentration (100 ppm), or the distinct chemical property of biologically synthesized NP. The AgNP of 200–800 nm length became determined to enhance the plant growth (Jasim et al., 2016), while 35–40 nm of AgNP became found to definitely affect the root and shoot growth of various plant (Pallavi et al., 2016), which can be because of the incapability of the penetration of big nanoparticles studied in low concentration (Mirzajani et al., 2013). Different length of AgNP used withinside the diverse research suggests a clear correlation among the dimensions and poisonous relation of NP to the plant, the NP with lower size became usually found to have higher toxicity to the plant in comparison to large NP (Yin et al., 2012; Jiang et al., 2014; Cvjetko et al., 2017). AgNPs (of relatively small length i.e., <30 nm) whilst implemented in high concentration had been observed to inhibit the root and shoot growth in different plant studied (Dimkpa et al., 2013; Qian et al., 2013; Tripathi et al., 2017; Vinkovi'c et al., 2017). Physiological influences of AgNP had been observed withinside the form of a decrease in transpiration (Hawthorne et al., 2012), chlorophyll concentration (Mirzajani et al., 2013; Qian et al., 2013; Tripathi et al., 2017); and chlorophyll fluorescence (Tripathi et al., 2017). Recent researches have proven that once AgNP became mixed with different treatment/compounds, it could have a distinct effect on plants (Berahmand et al., 2012; Belava et al., 2017; Tripathi et al., 2017). This may be defined through the impact of different compound on AgNP. Whereas the nitric oxide became observed to relieve the effect of AgNP through regulating Ag uptake, an antioxidant system, oxidative stress, and anatomical structure (Tripathi et al., 2017). The look at actually suggests AgNP exhibit an effect on different aspect of plant physiology, and metabolism which relies upon on the size, properties, and concentration of the NP in use. On the basis of the indicated research, it may be hypothesized that for showing poisonous consequences AgNP need to penetrate the plant tissue and intervene with different metabolic activities. For better understanding, the impact of various AgNP on a plant is summarized in Table 1.

TABLE 1: Impact of AgNP on plants

Size (nm)	Plant studied	Impact	References
25	*Oryza sativa*	Nanoparticles broke the cell wall and damaged the vacuoles of root cells.	Mazumdar & Ahmed, 2011
<100	*Cucurbita pepo*	Reduction in plant biomass and transpiration.	Hawthorne et al., 2012
18.34	*Oryza sativa*	-Up to 30µg/mL accelerates root growth whereas 60µg/mL restrict the root ability to grow. -Branched root systems were enhanced through the treatment of 30µg/mL	Mirzajani et al., 2013

10	*Triticum aestivum*	-The Ag NPs reduced the length of shoots and roots of wheat in a dose-dependent manner. -Furthermore, 2.5 mg/kg of the NPs increased branching in the roots of wheat, thereby affecting plant biomass. -Accumulation of Ag was detected in the shoots, indicating an uptake and transport of the metal from the Ag NPs in the sand.	Dimkpa et al., 2013
200–800	*Trigonella foenum-graecum*	-Enhancement in plant growth and diosgenin synthesis was observed.	Jasim et al., 2016
35–40	*Triticum aestivum, Vigna sinensis, Brassica juncea*	-Relatively unaffected (wheat) -The optimum growth promotion and increased root nodulation was observed at 50 ppm treatment (cowpea). -Improved shoot parameters were recorded at 75 ppm (brassica).	Pallavi et al., 2016

4.2.2 Impact of Copper and Copper Oxide Nanoparticles

Copper is a crucial micronutrient, that's included in lots of proteins and enzymes, therefore, playing a enormous function in plant health and nutrition. Copper nanoparticles (Cu NP) are extensively utilized in distinct industrial applications such as, an antimicrobial agent, catalysts, gas sensors, electronics, batteries, heat transfer fluids, etc. (Kasana et al., 2017). Due to its oxidative property, copper oxide nanoparticles (CuO NP) are assumed to have a higher poisonous impact than Cu NP. CuO NP became discovered to have a positive effect on Elodea densa (waterweed) and stimulate photosynthesis at low concentration (<0.25 mg/L), however the effect scenario absolutely changes with better doses and at 1 mg/L concentration a clear suppression in photosynthesis was determined (Nekrasova et al., 2011). The root morphology was mentioned to be adversely affected with Cu and CuO NP, with almost entire inhibition with a high dose of NP (Lee et al., 2008; Adhikari et al., 2012; Perreault et al., 2014; Shaw et al., 2014; Song et al., 2016; Adams et al., 2017). CuO NP was determined to enhance the manufacturing of ROS in flora (Nair and Chung, 2014; Shaw et al., 2014). Different antioxidant compounds had been determined to be considerably multiplied in plants dealt with with NP indicating the activation of the protecting mechanism by plants (Shaw et al., 2014; Song et al., 2016). CuO NP was also determined to negatively have an effect on the photosynthetic activity through inactivating PS II reaction centers, and inflicting a decrease in electron transport, thylakoid quantity per grana, photosynthetic rate, photosynthetic pigments, transpiration rate, stomatal conductance (Perreault et al., 2014; Costa and Sharma, 2016). Phytohormones had been additionally determined to be altered as a response to CuO NP (Nair and Chung, 2014; Van et al., 2016). When distinct sorts or plants had been studied together, the impact of CuO NP was discovered to be different in genetically diverse flora (Lee et al., 2008; Adhikari et al., 2012; Atha et al., 2012; Van et al., 2016; Wang Z. et al., 2016). The study shows that the Cu and CuO NPs are poisonous to flora while found in concentrations higher than 0.2 mg/L and it impact the growth, physiology, and biochemistry of plants. For better understanding, the impact of various Cu NP on a plant is summarized in Table 2

TABLE 2: Impact of Cu and CuO NP on plants

Size (nm)	Plant studied	Impact	References
Around 20 (Cu nanoparticle)	*Phaseolus radiates* *Triticum aestivum*	-Decrease in seedling and shoot growth with an increase in nanoparticle concentration. -In *P. radiates* no adverse effect on shoot growth was observed till 800mg/L concentration whereas in *T. aestivum* shoot growth was affected even at 200mg/L concentration. -Roots were more effected by the nanoparticles than the shoot.	Lee et al., 2008
30 (CuO)	*Elodea densan*	Stimulated photosynthesis up to 0.25mg/L level whereas suppress it above 1 mg/L concentration	Nekrasova et al., 2011
<50 (CuO)	*Glycine max* *Cicer arietinum*	-A decline in root and shoot growth on above 100mg/L concentration. -A decline in root and shoot growth on above 45 mg/L concentration.	Adhikari et al., 2012

30–40 (CuO)	*Lemna gibba*	-Dose-dependent decrease in plant growth, and PS II activity. -Inactivation of PSII reaction centers, a decrease in electron transport, and an increase in thermal energy dissipation.	Perreault et al., 2014
43 ± 9 (CuO)	*Elsholtzia splendens*	-Dose-dependent decrease in root length. -Dose-dependent decrease in chlorophyll a, b and total chlorophyll was observed.	Shi et al., 2014
40 (CuO)	*Lemna minor*	-Increase in peroxidase, catalase, and superoxide dismutase activity. -Increase in lipid peroxidation. -Inhibition of plant growth.	Song et al., 2016
<50 (CuO)	Wheat	-Inhibition of root elongation by CuO NP (>10 mg/kg). -exposure resulted in root hair proliferation and shortening of the zones of division and elongation.	Adams et al., 2017

20–40 (CuO)	*Arabidopsis thaliana*	-Inhibit seedling growth of different ecotypes -CuO NP was observed from root till seeds.	Wang Z. et al., 2016

4.2.3 Impact of Titanium Dioxide Nanoparticles (TiO_2 NP)

TiO_2 NP belong to the maximum used nanoparticles, which can be utilized in cosmetic and skin care products, antibacterial and cleansing air products, paints, and for decomposing natural matter in wastewater (Castiglione et al., 2011; Clément et al., 2013). Few researches were carried out to signify the impact of TiO_2 NP indicates that the TiO_2 NP may also have an effect on plant life in positive and negative approaches (Table 3). Due to photo catalytic properties of titanium nanoparticles, maximum of the research wherein TiO_2 NP was used at foliar stage has proven a positive effect on plant (Table 3); Gao et al., 2008; Jaberzadeh et al., 2013; Raliya et al., 2015). Spinach was found to have greater than 60% increases withinside the fresh weight and dry weight beneathneath the influence of TiO_2 NPs (Gao et al., 2008). The foliar treatment of TiO_2 NP additionally confirmed a higher growth of the plant, increase in fruit yield, and chlorophyll concentration in *Solanum lycopersicum* (Raliya et al., 2015). Jaberzadeh et al. (2013) stated that TiO_2 NP counteracts the water stress in *Triticum aestivum* through enhancing agronomic traits. The smaller TiO_2 NP was additionally discovered to be transported through roots, it was recommended that above diameter 140 nm, TiO_2 NPs are now no longer gathered in roots. TiO_2 NPs with a diameter above 36 nm was discovered to be accrued in wheat root parenchyma however did not attain the stele and therefore, do not translocate to the shoot (Larue et al., 2012). A plant reaction to hydroponics exposure to TiO_2 NPs may also range from the reaction to TiO_2 NP-infected soil exposure. Colloidal suspensions of nanoparticles had been discovered to inhibit the leaf growth and transpiration through physical outcomes on root-water transport system (Asli &

Neumann, 2009). At high concentration, TiO_2 NP was discovered to be poisonous to plant life, even in soil system (Rafique et al., 2014). The study shows that the effect of TiO_2 NP on distinctive plant life depends at the concentration, approaches of treatments, and length of NP. The study additionally indicated that availability of TiO_2 NP for a plant is unique whilst supplied through foliar treatment than through soil or water solution. The positive impact of TiO_2 NP was correlated with the photo catalytic activity of Ti, however the mechanism at the back of this interaction is to this point now no longer understood. For higher understanding, the impact of various Ti NP on a plant is summarized in Table 3

TABLE 3: Impact of TiO_2 NP on plants

Size (nm)	Plant studied	Impact	References
5	*Spinacia oleraces*	-More than 60% increase in plant fresh and dry weight. -The amount of Rubisco activase increased by 42%.	Gao et al., 2008
25	*Zea mays*	-Leaf growth inhibition and transpiration via physical effects on root water transport.	Asli & Neumann, 2009
14 25 140	*Brassica napus* *Triticum aestivum*	-Absorbed by plants, with Brassica having higher capacity to absorbed nanoparticle. (14 nm particle was absorbed more than 25 nm) - Moderate or no effect on plant growth. -Accumulation in roots TiO_2 -NPs with a primary diameter lower than 140 nm	Larue et al., 2012

15	*Linum usitatissimm*	-Reduction in root biomass, and root length. -Reduction in seed germination after 24 h.	Clément et al., 2013
11.93–18.67	*Triticum aestivum*	-Increase in root and shoot length with the treatment of 60 mg/Kg or less. -Decrease in root and shoot length above 60 mg/Kg concentration	Rafique et al., 2014.
25 ± 0.64	*Solanum lycopersicum*	-Up to a 250 mg/Kg promoted the plant height, root length, and biomass. -Lycopene content and fruit yield were maximum for 100 mg/Kg. -Chlorophyll concentration increases up to 750 mg/Kg of nanoparticle.	Raliya et al., 2015
<25	*Hydrilla verticillata*	-Increase in catalase and glutathione reductase activity. -10 mg/L concentration has shown increase in hydrogen peroxide level.	Okupnik & Pflugmacher, 2016

4.2.4 Impact of Iron Nanoparticles

Currently, iron nanoparticles have attracted a great deal interest worldwide from the scientists due to their sturdy magnetic properties. Considering those facts, (Rui et al., 2016) evaluated the effectiveness of Fe NPs as fertilizer to replace conventional Fe fertilizers that have diverse shortcomings. It turned into observed that addition of Fe_2O_3

NPs to the soil improved the biomass, chlorophyll content, and overall Fe content of peanut plants, a crop which could be very sensitive to Fe deficiency (Sarwar et al., 2020). The Fe_2O_3 NPs promoted the growth of peanut through regulating phytohormone contents and antioxidant enzyme activity. A study by (Suresh et al., 2016) recommended that there may be widespread impact on peanut plant leaves grown after the application of nano and bulk Fe_2O_3 suspension to seeds earlier than sowing. Since the increase in plant growth with Fe_2O_3 NPs was observed for plenty seed types, this study claims to reliably predict the extremely good capacity of Fe_2O_3 NPs as nano fertilizers. The consequences of positive and negative charged Fe NPs at the physiology and reproductive potential of *A. thaliana* had been studied at low and high concentration by (Bombin et al., 2015). The plants handled with low concentration did not display any enormous outcomes on seeding and root length. Remarkably, the treated plants did not display any observable phenotypic modifications in ordinary size or general plant structure, indicating that environmental infection by nanoparticles could cross dangerously overlooked which is a reason for concern. (Boutchuen et al., 2019) mentioned a new changed seed presoak approach using a drop of Fe-enriching hematite (α- Fe_2O_3) nanoparticles dispersion to enhance growth and manufacturing in four specific legume species, i.e., chickpea, green gram, black bean, and red bean. Consequently, this treatment mentioned to enhance the plant growth by approximately 230–830% in green gram displaying the best growth. In addition, an increase withinside the survival span of plants, a twofold increase in fruit manufacturing per plant, nearly times quicker fruit manufacturing, and wholesome second-generation plants was recorded after treatment with those nanoparticles; however, there had been mild species-specific variations. For higher understanding, the impact of various Fe NP on a plant is summarized in Table 4

TABLE 4: Impact of Iron NP on plants

Name/Size(nm)	Plant studied	**Impact**	**References**
Fe_3O_4 (10)	*Triticum aestivum*	-NP exposure did not alter germination, plant growth and	Iannone et al., 2016

		chlorophyll content. -Plant exposed to NP showed a favorable response to prevent oxidative damage	
Fe_3O_4 (17.7 ± 3.9)	*Zea mays*	Germination index was observed to be higher with 20 and 50 mg/L NP treatment whereas decreases with 100 mg/L treatment.	Li et al., 2016
Iron pyrite (FeS_2)	*Spinacia oleracea*	Significantly better growth.	Farooqui et al., 2016
Iron oxide	*Arabidopsis thaliana*	Inhibitory effects on development.	Bombin et al., (2015)
Fe_2O_3	peanut plant	increased the biomass, chlorophyll content, and total Fe content	Sarwar et al. 2020
Hematite(α- Fe_2O_3)	chickpea, green gram, black bean, and red bean	plant growth by about 230–830% in green gram showing the highest increase	Boutchuen et al., (2019)

4.2.5 Impact of Zinc Nanoparticles

Zn is crucial micronutrient for the growth and improvement of plant liable for modulating function, structure, and activity of many enzymes (Brown et al., 1993). (Umar et al., 2020) evaluated the impact of foliar and soil utility of ZnO NPs on growth and improvement of maize plant and mentioned advanced growth, better yield, and improved Zn contents in grains. The better photosynthesis rate, plant growth, and greater biomass manufacturing were stated with the seed priming of ZnO NPs than control. A massive enhancement in plant height (16%), shoot dry weight (58%), root dry weight (36%), wide variety of tillers per plant (69%), spike length (87%), and grain yield (185%) of wheat was mentioned with ZnONPs (100 mg/L) over control. Moreover, wheat plants with ZnONPs showed notably better Zn concentration in distinct plant components including roots, shoot, and grains compared to control, hence, ZnONPs can be used as a supply of Zn for leveraging the Zn deficiency in cereal crop plants. ZnONPs also can be used for powerful seed treatment to enhance both Zn nutrients and plant growth (Elhaj Baddar & Unrine., 2018). However, (Dhoke et al., 2013) studied the impact of ZnONPs at the growth and improvement of hydroponically grown *Vigna radiata* seedlings. It was determined that foliar utility of ZnONPs accelerated the accumulation of root and shoot biomass. Likewise, an increase in shoot and root length, shoot and root dry mass, leaf area, and photosynthetic parameters of *Solanum lycopersicum* was additionally recorded after treatment with ZnONPs (Faizan et al., 2017). However, ZnONPs additionally preclude arsenic toxicity by raising seed germination, biomass production, and reducing uptake of arsenics in rice (Wu et al., 2020). Moreover, numerous researches discovered the bad effect of the ZnONPs at the plant improvement. In general, the phytotoxicity of nanoparticles may be evaluated through the parameters like physiological indexes, phytohormones concentrations, crop yield, and few more (Fincheira et al., 2020). Besides, researches have mentioned that ZnONPs have an effect on biomass accumulation and photosynthesis in *Arabidopsis* (Wang et al. 2016b). germination, root growth, and leaf development in *Arabidopsis* was drastically inhibited upon treatment with ZnONPs (Lee et al., 2010). A study confirmed bad impact of ZnONPs on wheat with reduced photosynthetic performance and decrease antioxidant activity (Tripathi et al., 2017). The latest reviews have proven that there may be reduction in biomass accumulation, lack of root mobileular viability, decrease content of photosynthetic pigment, and greater zinc accumulation in ZnONPs challenged maize seedlings (Adhikari et al., 2020). Besides, few reviews have established the restricted shoot and root growth, altered chlorophyll content and decrease photosynthetic performance in tomato because of ZnONPs treatment (Wang et al., 2018). For higher understanding, the impact of various Zn NP on a plant is summarized in Table 5

TABLE 5: Impact of Zinc NP on Plants

Size(nm)	Plant Studied	Impact	References
ZnO (20 ±5)	*Lolium perenne*	-Dose-dependent inhibition of root elongation. -Above 20 mg/L concentration, a decrease in seedling biomass was observed.	Lin & Xing, 2008
ZnO (25)	*Arachis hypogaea*	-Zn as a micronutrient can be delivered to plant through NP. -Up to 1,000 mg/L the NP promoted seed germination and growth vigor, whereas 2,000 mg/L was observed to be toxic for plant	Prasad et al., 2012
ZnO (15.37)	*Triticum aestivum*	-Reduced photosynthetic efficiency. -improved growth, higher yield -Inhibition of antioxidant activity. -Nitric oxide ameliorates the nanoparticle toxic effect.	Tripathi et al., 2017; Umar et al., 2020
ZnO	*Brassica nigra*	Significantly inhibited germination, stimulatory effect on shoot growth but inhibited root length.	Zafar et al., 2016
ZnO	*Vigna radiata*	growth and	Dhoke et al.,

		development	2013
ZnO	*Solanum lycopersicum*	increase in shoot and root length, shoot and root dry mass, leaf area, and photosynthetic parameters	Faizan et al. 2017
ZnO	*Arabidopsis*	germination, root growth, and leaf development inhibited	Lee et al., 2010

4.2.6 Impact of Cerium oxide (CeO_2) NP on plants

Much interest is paid in the direction of the extensive unfold applications of cerium based compounds like cerium oxide nanoparticles (CeO_2 NPs) in agriculture (Ebbs et al., 2016). These nanoparticles had been proven to have notable interactions in plants. The impact CeO_2 NPs on plant growth and body structure had been recorded by many researchers (Rico et al., 2020a). However, the progressed plant physiology in hydroponically grown soybean was stated withinside the presence of CeO_2 NPs (Rossi et al., 2018). Furthermore, (Skiba & Wolf, 2019) studied physiological modifications in *P. sativum* upon exposure with the CeO_2 NPs and in addition uptake and translocation technique for copper, zinc, manganese, and iron was investigated. In the plant, it was found that CeO_2 NPs performs promising function beneathneath stressful conditions. Recent study found out that seed primed with poly (acrylic acid)-coated CeO_2 NPs enhances plant physiological parameters. It was discovered that the seedling root length, anatomical structure, fresh weight and dry weight, and root vitality have been advanced through many folds below salt stress as in comparison with controls (An et al., 2020). Additionally, it was discovered that when treatment with CeO_2 NPs, wheat growth and shoot biomass improved through 9 and 12%, respectively, in comparison to control (Rico et al., 2017), Many research defined the function of CeO_2 NPs in decline of concentration of heavy metals that are being translocated from the roots of plants (Rossi et al., 2017, 2018). Moreover, (Abbas et al., 2020) concluded that CeO_2 NPs as much as 500 mg/L concentration improves the rate of photosynthesis, transpiration and stomatal conductance therefore promote the plant growth however CeO_2 NPs (2000 mg/L) has negative impact on plant growth. It was discovered that there's impartial impact on plant biomass, photosynthetic pigment contents, membrane permeability, and lipid peroxidation, while CeO_2 NPs mediated metabolites modifications in leaves and roots have been recorded (Zhang et al., 2019b). The impact of the CeO_2 NPs on plant increase and body structure, antioxidant defense systems, and dietary profiling was evaluated through numerous scientific groups. Several researches proven the negative influences of those nanoparticles on various plant species. For example, CeO_2 NPs-treated tomato offspring confirmed diminished growth and accumulation of greater quantity of Ce (Wang et al., 2013). Similar effects have been recorded in *B. rapa,* wherein multigenerational exposure to CeO_2 NPs ended in to retarded increase and decrease productiveness withinside the succeeding generations (Ma et al., 2016). In some other study, it was found out that first-generation exposure of wheat to CeO_2 NPs causes modifications in plant body structure and nutrient profile withinside the second-generation plants (Rico et al., 2017). Another study confirmed that when exposure to CeO_2 NPs, alteration withinside the antioxidant protection system was recorded in case of *Phaseolus* vulgaris (Majumdar, 2015). In addition, the CeO_2 NPs at better concentration additionally stated to modify the growth of *Hordeum vulgare* (Mattiello et al., 2016). Meanwhile, the impact of CeO_2 NPs at the nutritional capability of tomato fruit grown on *Fusarium* infested soil became examined and minimum decrease in nutritional value was recorded (Adisa et al., 2020). The reviews advised that commonly plant roots uptake the CeO_2 NPs, and in addition, they're transported to the aerial parts and additionally show inhibitory impact on increase and productiveness of plant (Zhao et al., 2013; Wojcieszek et al., 2019). With respect to CeO_2 NPs. A study cited that the lower doses of CeO2NPs, showed progressed plant growth however higher doses resulted phytotoxicity in *A. thaliana* (Yang et al., 2017b). However, wheat plant exposed to CeO_2 NPs at a completely high concentration 400 mg/kg drastically reduced the photosynthetic pigment content than control (Du et al., 2015). Recently, it was discovered that CeO_2 NPs efficaciously translocated and gathered in crop plants there through affecting nutritional value of plant products (Hussain et al., 2019). For higher understanding, the impact of various Ce NP on a plant is summarized in Table 6

TABLE 6: Impact of CeO_2 NP on plants

Size(nm)/ Name	Plants Studied	Impact	References
CeO_2 (8)	*Oryza sativa*	-Under NP influence, rice grain contain less Fe, S, prolamin, glutelin, lauric acid, valeric acid, and starch in comparison to control	Rico et al., 2013
CeO_2 (10 ± 3.2)	Transgenic cotton (Bt-29317) Conventional cotton (Jihe321)	-Destruction of vascular bundles. -Conventional cotton was more sustainable to CeO_2 nanoparticle stress in comparison to transgenic cotton.	Nhan et al., 2015
CeO_2 (8)	*Triticum aestivum*	-400 mg/Kg of NP decreased the chlorophyll content. -Exposure to 200 mg/Kg resulted in embryos with larger vacuoles, whereas 400 mg/Kg resulted in reduced number of vacuoles.	Du et al., 2015
CeO_2 -citric acid coated (8+2) CeO_2 (8)	*Solanum lycopersicm*	-At 250 mg/kg, coated NP increased total Chlorophyll, chl-a, and chl-b. -At 500 mg/kg, coated and bare NP	Barrios et al., 2016

		increased stem length by 13 and 9%, respectively.	
CeO_2	wheat	growth and shoot biomass increased by 9 and 12%	Rico et al., 2017

4.2.7 Impact of few important Metal and Metal Oxide NPs on Plants

Beside the above-mentioned nanoparticles there are few other metals which have impact on plant physiology. Those are mentioned below-

TABLE 7: Impact of few important Metal and Metal Oxide NPs on Plants

Name (size in nm)	Plants Studied	Impact	References
Al_2O_3 (not mentioned)	*Nicotiana tabacum*	Dose-dependent decrease in the average root length, the average biomass, and the leaf count of the seedlings.	Burklew et al., 2012
NiO (< 100)	*Hordeum vulgare*	Decrease in leaf surface area, chlorophyll and Carotenoids.	Soares et al., 2016
CdO (7–60)	*Hordeum vulgare*	No change in total chlorophyll concentration	Vecerova et al., 2016
NiO (< 100	*Hordeum vulgare*	Decrease in leaf surface area, chlorophyll and carotenoids.	Soares et al., 2016
SnO_2	Tobacco	suppressing the cellular proliferation and viability	Mahjouri et al., 2020

4.3 Impact of Metal Nanoparticles on Plant Metabolism

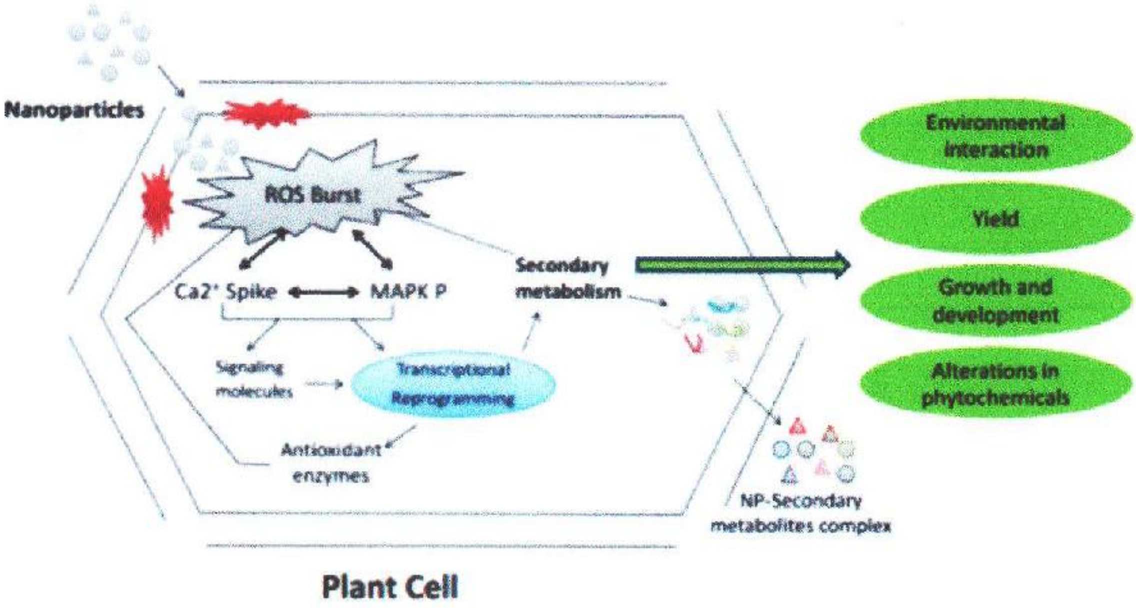
Plants produce numerous essential secondary metabolites that are often used as their defense compounds. Nanoparticles (NPs) are known to significantly alter plant metabolism in a dose-dependent manner, with effects ranging from stimulation to toxicity. The medicinal value of those metabolites has known as for the need for their greater manufacturing in plants. Some of the techniques used for enhancing the content of secondary compounds via plant cell and organ cultures consist of changing the culture medium composition, supplying precursors and elicitors and changing the environmental condition. Nano materials amongst different techniques also can be employed for the extended production of those compounds. It has been recommended via numerous researches that the utility of nanoparticles to plants and their cultures in vitro can elicit the production of essential secondary metabolites. For instance, the addition of aluminium oxide (Al_2O_3) nanoparticles notably enhanced the phenolic content in cell suspension cultures of tobacco. Various sorts of nanoparticles had been proven to enhance the amount of secondary metabolites. In a study through Al-Oubaidi and Mohammed-Ameen the portions of essential oils increased withinside the callus cultures of *Calendula officinalis* whilst exposed to Ag NPs. Similarly, the addition of titanium oxide (TiO_2) nanoparticles enhanced the amount of chlorogenic acid, cinnamic acid, gallic acid, o-coumaric acid, and tannic acid withinside the callus cultures of *Cicer arietinum*. Furthermore, blended utility of various nanoparticles has additionally been demonstrated to be powerful in improving the metabolite content in plants. For instance, maximum accumulation of overall phenolic compounds was found in *Prunella vulgaris* calli set up in reaction to the addition of Au-Ag NPs (1:3). The numerous sorts of nanoparticles employed for the enhancement of secondary metabolites manufacturing in plants consist of Ag NPs, ZnO NPs, $CuSO_4$ NPs, Fe NPs and TiO_2 NPs. Specific secondary metabolites enhancement via application of those nanoparticles encompass anthocyanins in *Arabidopsis thaliana* seedlings, steviol glycosides in shoot cultures of *Stevia rebaudiana*, rosmarinic acid and caffeic acid in *Satureja khuzestanica* shoot cultures, artemisinin in hairy root cultures of *Artemisia annua*, taxol in *Corylus avellana* mobileular suspension culture, atropine in hairy root cultures of *Datura metel*, aloin in Aloe vera suspension cells, hyoscyamine and scopolamine in hairy root cultures of *Hyoscyamus reticulatus*, and capsaicin in *Capsicum frutescens* cell suspension cultures. The actual mechanism of rushing up the secondary metabolism through nanoparticles is yet to be set up. One feasible mechanism consists of the technology of reactive oxygen species (ROS) through the nanoparticles which in the long run cause the secondary metabolism to deal with the stress caused through ROS. Conclusively, nanoparticles had been proven to noticeably have an effect on the manufacturing of bioactive compounds in distinct plants and plant cell cultures and therefore may be employed as general elicitors in plant cell, tissue and organ cultures to produce precious metabolites.

4.3.1 Metal Nanoparticles as Signals in Plants Secondary Metabolism

So far, a few researches have confirmed that NPs could have an effect on plant secondary metabolism. For example, the concentration of phenolic compounds secreted to an extracellular medium was improved 127.5 and 22.1%, respectively, in *Haematococcus pluvialis* (microalga) after treating with 100 mg/L TiO_2 NPs (Comotto et al., 2014). Artemisinin content was expanded 3.9-fold in *Artemisia annua L.* hairy root cultures after 900 mg/L AgNPs treatment for 20 days (Zhang et al., 2013). This growth was related to oxidative stress (H_2O_2 manufacturing), lipid peroxidation and CAT activity. A significant increase in diosgenin concentration was found in fenugreek after 2 mg/kg AgNP treatment (Jasim et al., 2017). Ferulic acid and isovitexin had been increased in barley plants exposed to CdO (cadmium oxide) NPs in air for three weeks at a concentration of 2.03×0.45× 105 particles cm^3 (Veˇceˇrová et al., 2016). In *A. thaliana*, anthocyanin and flavonoid biosynthetic genes were upregulated in response to AgNPs (Garcia-Sanchez et al., 2015). Although all of the studies mentioned above provide proof for NP-mediated modulation of plant secondary metabolism, the subsequent studies offer an indirect link among ROS and secondary metabolism. When A. thaliana was exposed to 250 and 1000 mg/L CeO_2 and indium oxide (In_2O_3) NPs, further to excessive ROS manufacturing, the activities of phenylalanine ammonia lyase (PAL) and polyphenol oxidase (PPO) had been substantially induced (Ma et al., 2016) revealed a likely role of secondary metabolism in protection against oxidative stress. Furthermore, phenylalanine ammonia lyase is the primary enzyme of the general phenylpropanoid pathway that catalyses the deamination of phenylalanine to cinnamic acid and play a key position in diverting aromatic amino acids from primary metabolism to phenylpropanoid pathway. ZnO NP treatment induced salicylic acid (SA), while it suppressed jasmonic acid (JA) in *A. thaliana* (Vankova et al., 2017. In *A. thaliana* plants treated with AgNPs expression of ET biosynthetic additives 1-aminocyclopropane-1-carboxylate synthase ACC and ACC oxidase 2 was reduced (Syu et al., 2014), suggesting that those NPs could inhibit ET perception and have an effect on its biosynthesis. BRs, the steroidal phytohormones that play crucial position in secondary metabolite accumulation, stress responses and adaptation (Çoban & Göktürk Baydar, 2016) could ameliorate ZnO NP-triggered oxidative stress through enhancing antioxidant capacity and redox homeostasis in tomato seedlings (Li et al., 2016). NO, another well-known signaling molecule that performs a central role in secondary metabolite production in plant cells (Zhang et al., 2012; Zeng et al., 2014), is likewise involved in plant–NP interactions. For instance, Ag NP-induced phytotoxicity might be alleviated by NO in *P. sativum* seedlings (Tripathi et al., 2017). There are numerous traces of evidence available in few literature implicating ROS-mediated signaling events as inductive cues for plant secondary metabolism. ROS themselves are signaling molecules, capable of inducing plant secondary metabolism (Simon et al., 2010). This might be determined during the wound induced activation of secondary metabolism in which ROS plays a key function as signaling molecule (Jacobo-Velazquez et al., 2015). In addition, ROS also can serve as signals for different messengers like jasmonic acid (JA) (Wuand Ge, 2004), salicylic acid (SA) (Maruta et al., 2012; Noshi et al., 2012; Wrzaczek et al., 2013; Baxter et al., 2014), ethylene (ET) (Zhang et al., 2016a,b), NO (Wang et al., 2013; Lindermayr & Durner, 2015), brassino steroids (BRs) (Xia et al., 2009), etc., that are capable of modulating secondary metabolisms directly or indirectly. To assist the perception that ROS induced by NPs acts as signals for secondary metabolism.

4.3.2 Mechanism of Modulation of Plant Secondary Metabolism by NPs

Although the aforementioned reviews suggest that NPs are interfering with numerous signaling pathways and capable of modulating plant secondary metabolism, the ideal mechanism through which this modulation ought to arise is not understood. We agree with that the initial responses of plants to NPs can also additionally encompass accelerated levels of ROS, cytoplasmic Ca^{2+} and upregulation of mitogen-activated protein kinase (MAPK) cascades similar to other abiotic stresses (Figure 4.1) because of the subsequent reasons. Recognition of AgNPs via plasma membrane certain receptors prompted a Ca^{2+} burst and ROS induction in *A. thaliana* (Sosan et al., 2016). Ca^{2+} levels and associated signaling pathway proteins have been determined to be upregulated withinside the proteomic evaluation of AgNP treated *O. sativa* roots (Mirzajani et al., 2014). AgNPs, or ions released thereof, restrict cell metabolism through binding to Ca^{2+} receptors, Ca^{2+} channels, and Ca^{2+}/Na^{+} ATPases. As sensed via calcium binding proteins (CaBPs) or different NP-specific proteins, NPs either mimic Ca^{2+} or signaling molecules withinside the cytosol (Khan et al., 2017). MAPK phosphorylation and activation of downstream transcription factors generally result in the transcriptional reprogramming of secondary metabolism in plants (Vasconsuelo & Boland, 2007; Schluttenhofer & Yuan, 2015; Phukan et al., 2016). Although no direct proof for the involvement of MAPK pathways in plant-NP interactions is available, animal and human cell line studies found that analogous pathways are involved in AgNP-induced signaling (Eom & Choi, 2010; Lim et al., 2012), and it is been postulated that plants may also make use of MAPK cascade upon exposure to Ag NPs (Kohan-Baghkheirati & Geisler-Lee, 2015).



Ref: Fazal et al., 2019

Figure 4.1: The possible mechanisms involved in nanoparticle (NP)-mediated modulation of plant secondary metabolism.

NPs could enter plant cells (fig 4.1) via plasmodesmata causing physical damage to the plasma membrane. NPs can result in reactive oxygen species (ROS) production, calcium spikes, antioxidant machinery activation, mitogen-activated protein kinase (MAPK) cascades, etc., that can cause transcriptional reprogramming of secondary metabolism. Activation of enzymatic antioxidant and non-enzymatic machineries including secondary metabolism would possibly scavenge the ROS and protect the cells from oxidative damage. However, the precise results of modifications in plant secondary metabolism on plant's performance, environmental interaction, growth, development and yield are still unknown. On the other hand, the capacity of NPs to enter plant cells and exit as NP-secondary metabolite complexes should probably be exploited for molecular pharming (dotted arrows).

CHAPTER 5

SUMMARY & CONCLUSION

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Summary and Conclusion

In current age, nanoparticles are used intensively and turning into a part of the human life. This review indicates the impact of NPs on plant physiology and metabolism. It is clear from compiled information that impact of NPs varies from plant to plant and relies upon on their mode of application, size, and concentrations. This review exhibits that the research on NPs, essentiality for plants, is in the beginning; more rigorous works are needed to understand physiological, biochemical, and molecular mechanisms of plants in terms of NPs. Also, more research is needed to discover the mode of action of NPs. It is clear from the studies that metal and metal oxides nanoparticles in excess are dangerous to flora, whereas, whilst present in traces it could be useful for plants. Therefore, the increasing concentration of nanoparticles in the environment may cause a serious impact on agriculture in future. This review took out clear information from known literature to shows an influence of metal and metal oxide nanoparticle on the plant, but there are needs of research to understand the molecular mechanism of plant nanoparticle interaction. There are few researches showing the beneficial role of metal and metal oxide nanoparticles in agriculture, but the mechanism at large extant are not understood, and the studies are in its primitive stage. Therefore, a lot of study is needed before bringing the nanoparticles to the field. Most of the study performed shows morphological variation caused to plants due to metal and metal oxide nanoparticles. The study also shows a clear lack of standardization for nanoparticles phytotoxic assay. Therefore, research is needed to be done in the area to understand the impact of metal and metal oxides nanoparticle on plant physiology and molecular biology. Because by Understanding the intimate dynamics of nanoparticle in plants can prove to be fruitful for the development of areas like agronomy, horticulture, plant pathology, plant physiology, etc. in future. That, in return, can assist to ensure agricultural sustainability. Similarly, this may also help to pave the way to combat the drastic climate change and satisfy growing food demands for the ever-increasing world population.

Nanotechnology is an emerging technology working in all fields of science. The field of nanotechnology has shown fascinating applications among wide areas. However, the applications of nanotechnology in agriculture sector are an integral part of sustainable development. Many types of nanoparticles have been shown to be useful for such purpose. There are some metals and metal oxides which are used as micronutrients for the plant growth. When mixed with soil they can be absorbed by the plants. On the similar path, the respective nanoparticles of metals and metal oxides can also be useful for plant growth. The advantage of using nanoparticles of corresponding metals and metal oxide lies in their larger effect with minimum amount. These nanoparticles can promote the plant growth. On the contrary, if they are being used beyond certain concentrations, they can affect the soil ecosystem and thus restrict the growth of soil microorganisms and the plants itself. Hence, there is a need to consider the harmful effects of nanoparticles before applying them for any purpose. For optimal use of metal oxide nanoparticles for plant growth, there is a need for collaborative study among the scientific community from material science, plant biology, and toxicology. The study should focus on the optimal use of nanoparticles with minimum side effects on the human health and environment. Such approach will compel the fruitful use of nanotechnology for the sustainable agriculture for the betterment of human and environment. So it is required to commercialize metal nanoparticles for sustainable agriculture.

CHAPTER 6

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