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Role of Biosynthesized Copper Nanoparticles in Agriculture and Other Fields

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ABSTRACT

In the last decades, nanotechnology has emerged as a new technology field because of its unique qualities. Usage of chemicals in medicines and agriculture, such as fertilizers, pesticides, herbicides, and insecticides is very harmful to the environment. Hence by the use of this revolutionary technology, it can be possible to reduce the toxic effects in the environment. Copper is one of the key micronutrients which play a great role in growth and development. CuNPs have distinctive chemical and physical qualities that make them applicable in different fields. Physical and chemical synthesis of CuNPs is very expensive, time-consuming, and harmful to the environment. However, the biological synthesis of CuNPs from bacteria, fungi, and plant extract is very eco-friendly free from any chemical hazards. Biosynthesized CuNPs are characterized by the UV-visible spectroscopy, FTIR, TEM, and SEM with EDX. In agriculture, CuNPs protect the plant from abiotic and biotic stress conditions. Due to the small size of CuNPs easily absorbed by the plants and protects the plants from abiotic and biotic stress. Different biotic factors such as predators, parasites, insects, pests, and soil-born phytopathogens are responsible for crop losses. Most advanced application of biosynthesized CuNPs management of plant diseases. CuNPs not only exhibit positive impacts but also show negative impacts in plants at higher concentrations. This review focus on the biosynthesis, and positive and negative impacts of copper nanoparticles (CuNPs), and also provide knowledge and importance of the CuNPs in various fields like medicine and agriculture, in medicine act as anticancer and antidiabetic agents.

1. Introduction

In modern days the nanotechnology is emerging as a new field of science that is extensively concern in many fields like medicine and agricultural fields. Nanoparticles (NPs) gained more attentiveness because of their distinctive qualities and useful implementation in different fields. By enhancing the fabrication and approaches of NPs are applied in many fields like electronics, optics, textiles, medicines, catalysis, water treatments, and environmental remediation [1]. The most effective impression of nanotechnology is found in drug delivery, target drug delivery, and prolonged delivery of a drug [2]. A new period has appeared after finding out the nanomedicines, in which NPs are synthesized to delivered pharmaceutical elements.

Researchers synthesized various nanoparticles which have significant features such as shape; pores size and surface activities and these nanoparticles have various applications such as protectant, conjugation of active pesticides, encapsulation, and targeted delivery via adsorption [3]. There are many metallic nanoparticles like as silver, copper, and gold expressed the highest reaction against various microorganism reported by many research.

Because the presence of a special type of feature in CuNPs increases the awareness in comparison to bulk metals, CuNPs have a high surface volume ratio interact with other particles, one important thing about CuNPs it is simply obtainable metal NPs so that this cooper (Cu) metal affect the environment and health in the population and due to low harmful impact on, some pathologist reported that Cu deposited in the body and this is now doubtful [4].

In the current time employment of NPs example-insecticides, fungicides & nano-fertilizers are invented and the effect of NPs on plants depends on different things like as composition, physical and chemical properties. Due to enlarge surfaces areas & possible size express higher physical and chemical qualities so that CuO NPs are different in comparison to other micro and bulk component [5]. Cu is widely used distributed micronutrient which is found in many proteins and enzymes has an important role in health and nutrition of the plant. In addition CuNPs

submerged in polymer matrix can be used in food packaging for slowdown of deterioration, safety of packaged food, life extension and maintain quality.

Due to huge development of industry, large amount of pollutants introduced in environment which creates big problem in environment as well as living organism so that CuNPs are used detection of pollutants [6]. One important property of metal nanoparticles are showed the antimicrobial activity against bacteria and fungi and used as a pesticidal object which is significant agents in plant disease management.

2. Role of Copper (Cu) in Plants

For normal growth and development Cu is an essential element and its activities depends upon its optimum concentration below optimum concentration cause deficiency and above optimum concentration causes toxicity in plants [7].

It has a significant importance and participate in mitochondrial respiration, protein regulation, cell wall metabolism, photosynthetic electron transport, oxidative stress response, hormone signaling and act as a cofactor many enzymatic reaction for examples - polyphenol oxidase, amino oxidase and super oxide. Copper efficiency creates negative impacts like as light chlorosis along with permanent loss of turgor pressure in young leaves, curled leaves petiole lent downwards and light chlorosis. At higher concentration copper caused toxicity, oxidative stress, growth inhibition and photo-respiration and photosynthesis interferences. The requirement of Cu as a micronutrient yet present in higher concentration in chloroplast. Various study reported that reported that 70% of Cu is present in chloroplast which play significant role in protein and carbohydrate metabolism, synthesis of chlorophyll and other plant pigments.

3. Synthesis of Copper Nanoparticles (CuNPs)

Various methods are used for the synthesis of CuNPs like physical, chemical and biological (Fig. 1). Chemical methods contains following techniques like microemulsion, sol-gel process and condensation is very common technique and which is very expensive huge amount of surfactant

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which are very harmful for the environment [8]. In physical methods have following techniques such as laser ablation, aerosol technique and radiolysis are very significant techniques but due large energy consumption and employment of expensive instrument these techniques are less popular [9]. There are different conventional methods employed for the synthesis of CuONPs like as precipitation gamma radiation. Various specific research are carried out for the manufactured of CuONPs, which is relate to fabrication of CuONPs, among them involvement of chemical reaction reduced the reproducibility of CuONPs.

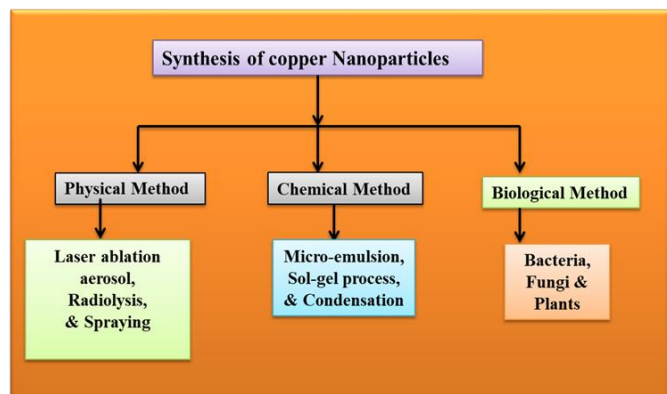


Fig. 1 Different methods of CuNPs synthesis

3.1 Biological Synthesis of Copper Nanoparticles

3.1.1 Green Synthesis of Copper Nanoparticles

For the green synthesis of metallic nanoparticles employments of plants are very cost effective, nonhazardous, eco-friendly and easy to handle. Plants are rich sources of biomolecules like as co-enzyme and vitamins which have capacity to reduced metal ions to nanoparticles makes plants as essential sources (Table 1). Green biosynthesis of CuONPs are very crucial than any other method which is have very important role in several fields [10]. Utilization of plants for the green synthesis of CuONPs, plants contains secondary metabolites which act as a capping and reducing agents so that this is clear biological agent functions as stabilizers and reducers and both in manufacturing of CuONPs [11]. Latex extract of *Calotropis procera* are used for the synthesis of CuNPs [12] which is very effective against tumor cells. Leaf extract of *Capparis zeylanica* [13] *Vitis vinifera*, *Nerium oleander* leaf [14] are employed for biosynthesis of CuNPs and act as antibacterial agents. Pineapple [15], *Citrus grandis* peel [16], *Hibiscus rosa sinensis* [17], guava and *Phyllanthus emblica* [18], Lemon fruit [19], *Ginkgo biloba* leaf [20] etc. leaf extract are used for the synthesis of CuNPs. Ripened fruit extract of *Duranta erecta* is synthesized CuNPs which reduced toxic congo red, azo dyes, and methyle orange from water [21]. Nano-coated CuNPs are produced from extract of *Tinospora cardiafolia*, which showed the antimicrobial properties [22]. Leaf extract of *Lantana camara* were synthesized CuNPs reported by Majumder et al. [23]. Extract of extract of citrus lemon fruits are very well ordered method for the synthesis of CuNPs and expressed antimicrobial activity [24]. CuONPs are synthesized from *Centella asiatica* at room temperature, exhibited antibacterial activity against *E. coli*, *P. aeruginosa*, *K pneumonia* etc., [25].

Table 1 Production of CuNPs by plants

Name of Plant	Shape of CuNPs	Size of CuNPs	References
<i>Calotropis procera</i>	Spherical	15 nm	[12]
<i>Capparis zeylanica</i>	-	-	[13]
<i>Nerium oleander</i>	-	-	[14]
Pineapple	Cubic	30-50 nm	[15]
<i>Citrus grandis</i>	Spherical	22-27 nm	[16]
<i>Hibiscus rosa sinensis</i>	Spherical	500 nm	[17]
Guava and <i>Phyllanthus emblica</i>	-	15-30 nm	[18]
Lemon fruit	-	45 nm	[19]
<i>Ginkgo biloba</i> leaf	Spherical	15-20 nm	[20]
<i>Duranta erecta</i>	-	-	[21]
<i>Tinospora cardiafolia</i>	-	-	[22]
<i>Lantana camara</i>	-	-	[23]
Citrus limon fruits	-	-	[24]
<i>Centella asiatica</i>	-	-	[25]

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3.1.2 Biosynthesis of Copper Nanoparticles using Bacteria

Several studies reported that microorganism are employed for the biosynthesis of CuNPs (Table 2), bacteria are ideal object for the synthesis of nanoparticles, because of short generation, mild generation condition and ease of culturing [26]. CuNPs are isolated from gram negative bacteria *Serratia*. *Morgenells psychrotolerens* are used in synthesis of 15-20 nm range CuNPs [27]. *Pseudomonas stuezeri* are synthesized CuNPs spherical in shape, size in 8-15 nm [28]. *E. coli* is employed for the biosynthesis of CuONPs which is variable in shape and size [29]. CuNPs were fabricated from *Bacillus cereus* size range 11-33 nm which showed the antibacterial activity [30]. CuO NPs (78-80 nm) are biosynthesized from *Streptomyces spp.* is performed antifungal activity against plant pathogens like as *Aletrnaria alternata*, *Fusarium oxysporum*, *Pythium ultimum* and *Aspergillus niger* [31]. Another spp. of *Sterptomyces* like as *S. capillspiralis* and *S. griseus* synthesized Cu NPs (4-59 nm) which spherical in shape act as antifungal agents [32,33].

Table 2 Production of CuNPs by bacteria

Name of Bacteria	Shape of CuNPs	Size of CuNPs	References
<i>Serratia spp.</i>	Cubic	-	[26]
<i>Morgenells psychrotolerens</i>	Cubic	15-20 nm	[27]
<i>Pseudomonas stuezeri</i>	-	8-15 nm	[28]
<i>E. coli</i>	Spherical	-	[29]
<i>Bacillus cereus</i>	-	11-33 nm	[30]
<i>Streptomyces spp</i>	-	78-80 nm	[31]
<i>S. capillspiralis</i>	-	4-59 nm	[32]
<i>S. griseus</i>	-	-	[33]

3.1.3 Biosynthesis of Copper Nanoparticles using Fungi

Various fungi are used for the synthesis of nanoparticles (Table 3) and are the better agents than the any other agents. Lots of fungi are employed for the synthesis of CuNPs such as *Fusarium oxysporum* [34], *Hypocera lixii* and *Rhodotorula mucilaginosa* [35], *Penicillium aurantiogriseum*, *Penicillium citrinum* and *Penicillium waksmanii* was employed for the extracellular biosynthesis of CuNPs [36].

Table 3 Production of CuNPs by fungi

Name of fungi	Shape of CuNPS	Size of CuNPs	References
<i>Fusarium oxysporum</i>	-	95 nm	[34]
<i>Hypocera lixii</i>	Spherical	24 nm	[35]
<i>Rhodotorula mucilaginosa</i>	Spherical	10 nm	[36]
<i>Penicillium aurantiogriseum</i>	Spherical	89 nm	[36]
<i>Penicillium citrinum</i>	Spherical	85 nm	[36]
<i>Penicillium waksmanii</i>	-	79 nm	[36]

4. Applications of Copper Nanoparticles

4.1 Role in Medicine

Because of their qualities and significant interaction with pathogen, their high biological and chemical reactivity and their large active surface area Cu NPs are employed in medicine and dentistry, and many other fields (Fig. 2). In present time public health is a worldwide challenge due to bacteria are resistance against antimicrobial drugs [37], so that CuNPs reduced these negative impact and a promising tool against pathogens and protect the cell from adverse effect [38]. CuNPs not only employed as medicine but also as antibiotic prevent circulatory, digestive and respiratory system. Biosynthesized CuNPs from tuber extract of *Dioscorea bulbifera* exhibited strong inhibitory effect such as superior antioxidant and against alpha amylase and alpha glucosidase act as antidiabetic agents [39].

4.2 Role as Anticancer

The main motto of chemotherapy is remove cancerous cells but chemotherapeutic agent creates negative impacts in normal cells and cancer cells. Biosynthesized nanoparticles are more effective against cancer and eco-friendly treatment [40]. *In-vitro* study exhibited antitumor property against human colon cancer cell Ccco-2 cell and human breast cancer MCF-7 cell [41]. Different studies reported that due to colloidal properties copper nanoparticles are most significant object against cancer cells. This is also reported that CuNPs are synthesized from nontoxic aqueous extract of latex can be employed in vivo cancer therapy and also reported that CuNPs are very effective against mouse embryonic fibroblast, human lung carcinoma cell, chinese hamster ovary (CHO) and human osteosarcoma (Saos). CuNPs have cytotoxic activity against MCF-7 Breast Cancer cell and they observed that at 10µg/mL concentration

CuNPs function was not sure. CuO NPS are synthesized from various plant extract of medicinal plant showed antioxidant and cytotoxic effect against cancer cells like as human breast (MCF-7) cervical (Hela), epithelioma (Hap-2) and lung cancer (A549) and one normal human dermal fibroblast (NDHF) cell line [42].

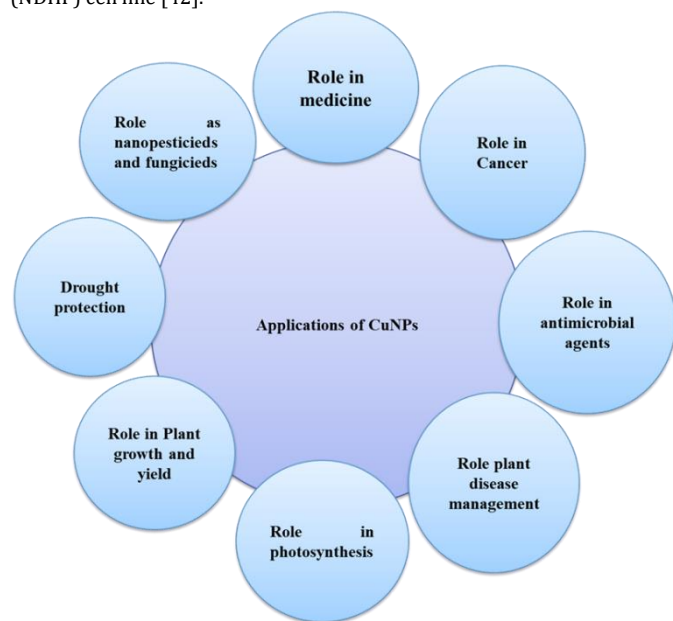


Fig. 2 Applications of CuNPs

4.3 Role of Copper Nanoparticles as Antimicrobial Agents

Many studies reported that CuNPs is a potential antimicrobial agent. Jia et al., [43] reported that CuNPs coated with cellulose film was showed antimicrobial activity against *E.coli* and *Staphylococcus aureus*, which is the main agents of food spoilage and also reported showed more antimicrobial activity against *S. aureus* than *E. coli*. CuNPs was expressed antimicrobial activity against *Micrococcus luteus*, *S. aureus*, *Klebsiella pneumoniae* and *Pseudomonas aeruginosa* and fungi like as *Aspergillus niger*, *A. flavus* and *Candida albicans* [44]. When CuNPs and chitosan are combined with iodine was showed most effective activity against bacteria like as *E. coli* and *Bacillus cereus* in which iodine act as a stabilizing agent [45]. Likewise nanocomposite film of CuNPs and cellulose combined effect together exhibit strongest antibacterial property against *S. aureus* and *K. pneumoniae* [46]. Biosynthesized CuONPs showed the antibacterial property against both gram negative and gram positive bacteria.

4.4 Role of Copper Nanoparticles in Agriculture

The effect of nanoparticles in on plants is depended on different characteristics on plants NPs for examples- composition, concentration, physical, chemical and size [47]. Due to antibacterial activity CuNPs are used opposite to pathogenic bacteria so that CuNPs are used in manufacture wide range of antibacterial agents coating for implementation in household, aerospace industries and biomedical. Various ancient researchers are reported that Cu showed antimicrobial activity. According to Elmer et al., [48] Cu in nano form is good object for controlling plant diseases. In agriculture copper based nanoparticles are more effective as pesticides (e.g. fungicides), fertilizers [49] and antifungal agents [50].

4.5 Role of Copper Nanoparticles Increase in Growth and Yield

Due to application of CuONPs copper ions are dissolved which caused the lignification so that this property enhanced the firmness of tomato fruits which may be result enhance in pericarp cell wall and it potentially increased the fruit shelf-life. When the CuNPs are applied through the foliar spary it increased the lycopene, vitamin C, flavanoids and total phenol contents [51]. Biosynthesized CuNPs enhanced plant root growth and shoot growth in mung bean [52]. CuNPs not only showed positive impacts but also showed negative impacts in plants. Various studies reported that CuNPs applied at different concentrations expressed different changes, such as shoot elongation was reduced by applying CuNPs at 80 mg mL⁻¹ concentration [53].

4.6 Role of CuNPs in Plant Physiology and Photosynthetic System

Photosynthetic is very specific mechanism in plants in which solar energy changed into chemical energy, which is done by various organs like <https://doi.org/10.30799/jnst.351.25100102>

as chloroplast and different components thailakoids membranes and photosynthetic pigments systems [54]. Various studies reported that when CuNPs are applied in plants it reduced the thailakoid number per granum, stomatal conductance, transpiration rate, electron transport system and photosynthetic rate [55]. According to CuONPs is showed harmful effect against photosynthetic apparatus such as chlorophyll, grana and chlorophyll [56]. CuNPs are aggregated, when spring barley grown in hydroponic solution and expressed negative impacts creates unordered structure of thylakoid mesophyll cell and chloroplast structure [57].

4.7 Role in Drought Protection

Plants are not only affected by biotic stress but also affected by abiotic stress like as drought and detrimentally growth affect the productivity and growth which reduced the sustainability of agriculture. For crop production, plant growth and protection from abiotic stress nanoparticles have significant value [58]. CuNPs showed positive impacts in maize protected from draught enhanced productivity and higher water content in leaf. CuNPs are protected the crop from draught stress, CuNPs reduced draught stress in soybean.

4.8 Role of CuNPs in the Management of Plant Diseases

The employment of CuNPs in management of plant diseases which is caused by fungi, bacteria and plant parasitic nematodes is new revolution in agriculture. Used of micro-emulsion, liposomes and nanoemulsion in agronomy which is reduces the transportation of pesticides, herbicides and fungicides so that nanotechnology have great impact in plant diseases management and evolved as a new methods in plant protection in comparison to employment different fungicides and other agrochemicals CuNPs (11-55 nm) are most effective against *Phytophthora infestans* which infected tomato [59]. Many research reported that bacterial blight in pomegranate was prevented when nanocopper applied against *Xanthomonas* [60] and because of synergistic effect Cu with chitosan complex nanogels prevents the growth of *F. graminearum* which is very harmful plant pathogen for cereal crops. Shende et al., [61] reoprted that biosynthesized CuNPs is showed most significant effect against *F. oxysporum*, *F. culmonrum* and *F. graminearum*. CuONPs showed antibacterial property against soil born pathogen like as *Ralstonia solanacearum*, it's bactericidal effect are most effects generates negative characteristic as such as disturbed the ATP production, decrease bacterial motility and formation of biofilm [62]. Chitosan coupled copper nanoparticles inhibited the growth of plant pathogens like as *Ralstonia solani* and *Pythium aphanidermatum* which is caused the damping disease in plants [63]. Many nanoparticles are used in plant disease management; researchers are reported that CuONPs inhibits the growth of *Botrytis cinerea* which is highest impact than any other NPs in inhibiting gray mold disease or rose petals, a severe disease worldwide of fungal disease [64]. Various researchers reported that CuNPs showed not only fungicides and bacetricides effects but showed the nematocidal effect at significant concentration, CuNPs exhibited inhibitory effected against the J2 stage of *Meloidogyne incognita* and its inhibitory effect depends upon it's concentration at higher concentration showed higher mortality rate [65].

4.9 Intraction of CuNPs with Microorganism

Various studies carried out against the antimicrobial activity of CuNPs but mechanism is not proper understood. When nanoparticles are interacted with microorganism surface creates many changes like as membrane damage, reactive oxygen species (ROS) protein dysfunction and loss of enzymatic activity [66]. CuNPs come in contact of bacterial cell and these ions engaged with cell wall which generates ROS and loss of membrane integrity [67]. Additionally, CuNPs are showed many negative effects like as formation of pit in the membrane, disruption of metabolic pathways and oxidative stress [68]. Cu polymer with nanoform can be significant agents due to bactericidal effect of nano-composite release Cu ions and CuNPs and these ions come in contact of bacterial cell membrane, interconnected with carboxyl and amines group in peptidoglycan layer and sulphahydral which caused the denaturation of protein. Cu ions attach with DNA and cross nucleic acid strands, caused disordered the helical structure. In addition to when CuNPs are attached and penetrate the cell membrane which leads endocytosis of bacterial cell [69]. Particles size, electrostatic attraction with nanoparticles and microbial cell, hydrophobic or hydrophilic nature of nanoparticles these characteristic are main reason enhanced the susceptibility of CuNPs as a micro-biocidal agents [70].

4.10 Translocation of CuNPs in Plants

Agriculture is an important sector which attract the scientist. Because discharged NPs are received by soil, so that is very important to know how

NPs are transported in whole ecosystem and soil. Shape, size and composition are the main factor for uptake and transportation of NPs in plants through vascular system. CuNPs are before uptake in plants changed into organic complex and copper ions [71]. Other studies reported that NPs are stucked with plant root and NPs are translocated in plants by tissue of like as cuticles, trichomes, stomata, stigma and hydathodes aerial parts of plants and by root tissue like as root tip, rhizomes and lateral root junction. Plants absorbed NPs in the metal ions or original form. NPs are also transported in various aerial parts for example leaves stems and fruits and setteled down various locations such as vacuols, walls, nucleus, lipid envelops, stellar system and cytoplasmic matrix [72]. Translocation capacity of CuNPs varies from plant to plant, in lettuce 0.5 to 0.6% Cu translocated and in alfa-alfa 3% to 5% Cu from root to shoot [73]. CuO NPs are absorbed and accumulated in tomato.

5. Negative Impacts of Copper Nanoparticles

Various studies reported that CuNPs played important role in epigenetic, physiological, morphological and genetic variations which may be changes the nutritional value and plant growth. Plants have close associations with soil particles so that everything absorbed from the soil by root [74]. Nanoparticles generated two types phytotoxicity in plants (1) Chemical based phytotoxicity and (2) Stressed based phytotoxicity. Strees is generated by shape, size and surface of nanoparticles. Plant activated antioxidant defense system against NPs stress. When NPs come in contact of plants it creats toxicity, plant activate their resistancy against NPs stress. Sometimes NPs generated negative impacts in plants which are very harmful for plants health one of them is genotoxic effect which generates various toxic effects. DNA was damaged by CuONPs in plants and crops. Toxicity of NPs is associated with its properties such as large size and large concentration exposure duration of NPs associated with large genotoxic responses. Lots of genotoxic effects are created by CuNPs like as abnormality in cell cycle distributed chromosome in metaphase, vacuolated nucleus and laagered chromosome [75]. Basically nanoparticles are worked on optimum concentration because above the optimum concentration of nanoparticles are generated reactive oxygen species (ROS) which cause imbalances in cellular metabolism. When CuNPs is applied at low quantity (5-20 mg Cu per plant) initiate metabolic various effect because of accumulation of copper and production of ROS [75].

6. Conclusion

CuNPs is not only working very well in agriculture sector but also CuNPs act as antibiotic, antidiabetic and anticancer agents. This paper represented the biosynthesis, importance, positive and negative impacts of CuNP in different fields. CuNPs are biosynthesized from bacteria, fungi and plants parts (root, stem and leaf). CuNPs have a significant value in many fields role in medicinal field one of them, CuNPs is used as an antibiotic agents and antidiabetic objects. Biosynthesized CuNPs showed the antitumor and anticancer property against the various cancer diseases this is very good object for such kinds of severe disease. Despite employments of CuNPs in different fields, CuNPs have a valuable importance in agricultural fields. Cu is the one the most important essential element which required for the by the plants. CuNPs exhibited strong antimicrobial activity against the insect-pest of crop plants and fungi so that can be used as novel nanofertilizers, nanopesticides and nanoherbicides at lower concentrations. Ultimately different research reported that CuNPs could be harmful when used at higher concentrations. Implementation of CuNPs at higher concentrations can be affect the plant metabolism and also affected the yield.

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