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Role of Biosynthesized Copper Nanoparticles in Agriculture and Other Fields

Geeta Rautela[1,*], Rose Rizvi[2]

Abstract

In the last decades, nanotechnology has emerged as a new field of technology because of its unique qualities. The use of chemicals in medicines and agriculture such as fertilizers, pesticides, herbicides, and insecticides are very harmful to the environment so by the use of this revolutionary technology we can reduce the toxic effects on the environment. However, a biological method is very easy, simple, and free from any chemical hazards, and very eco-friendly biological entities like bacteria, fungi, algae, and plants are used in the biological synthesis of CuNPs. Different plant parts such as roots, stems, fruit, flowers, and leaves are used in the biosynthesis of NPs. CuNPs exhibited positive effects at lower concentrations but at higher concentrations exhibited toxic effects in the environment. In agriculture, CuNPs protect plants from abiotic and biotic stress conditions. CuNPs reduce the plant pathogens' growth by the generation of oxidative stress. CuNPs enhanced the plant growth and yield but at the same at higher concentrations created phytotoxicity in plants. Additionally, CuNPs taken by the plant tissue accumulated in plants which is a serious issue for human beings. Most advanced application of biosynthesized CuNPs management of plant diseases. CuNPs can be used as nano-fungicides, nematicides, and pesticides to increase agriculture production. In this paper, we focus on the biosynthesis, and positive and negative impacts of CuNPs and also provide knowledge and importance of the CuNPs in various fields like medicine and agriculture, in medicine act as anticancer and anti-diabetic agents.

Keywords: Copper nanoparticle, agriculture, insecticides, environment, nanotechnology

INTRODUCTION

In modern times, nanotechnology has emerged as a new field of science and is an extensive concern in many fields, such as medicine and agriculture. Nanoparticles have gained increasing attention because of their distinctive qualities and useful implementation in different fields. Enhancing the fabrication and approaches of nanoparticles has been applied in many fields, such as electronics, optics, textiles, medicines, catalysis, water treatments, and environmental remediation [1–5].

The most effective aspects of nanotechnology are drug delivery, targeted drug delivery, and prolonged drug delivery [6]. A new time period has appeared since the discovery of nanomedicine, in which NPs are synthesized to deliver pharmaceutical elements [7].

Researchers have synthesized various nanoparticles with significant features such as shape, pore size, and surface activity, which have various applications such as protectants, conjugation of active pesticides, encapsulation, and targeted delivery via adsorption [8].

***Author for Correspondence**
Geeta Rautela
E-mail: geetarautela1538@gmail.com

[1]Research Scholar, Department of Botany, Aligarh Muslim University, Uttar Pradesh, India
[2]Assistant Professor, Department of Botany, Aligarh Muslim University, Uttar Pradesh, India

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Many metallic nanoparticles such as silver, copper, and gold have been reported to exhibit the highest reactivity against various microorganisms. Owing to the unique features of copper nanoparticles (CuNPs), they have garnered significant attention compared with bulk metals. CuNPs have a high surface-to-volume ratio, which enables them to interact with other particles more effectively. Copper is a readily available metal that can affect the environment and human health. Despite its relatively low harmful impact, some pathologists have reported that copper can accumulate in the body, which is doubtful [9–11].

From the requirements perspective, copper oxide nanoparticles (CuONPs) are utilized in various applications, including catalysis, batteries, and gas sensors, owing to their unique properties and advantages, solar energy, and heat transfer fluids [12].

Currently, the employment of nanoparticle example-insecticides, fungicides, and nano-fertilizers has been invented [13], and the effect of nanoparticles on plants depends on different factors, such as the composition and physical and chemical properties [14].

The unique combination of expanded surface area and precise size control in CuONPs gives rise to enhanced physical and chemical properties, distinguishing them from both microscale and bulk materials [15]. Copper is widely used to distribute micronutrients, which are found in many proteins and enzymes that play important roles in plant health and nutrition.

In addition, CuNPs submerged in a polymer matrix can be used in food packaging to slow down deterioration, improve the safety of packaged food, extend life, and maintain quality. Rapid industrialization has led to a surge in environmental pollution, which poses a significant threat to ecosystems and living organisms. In response, copper nanoparticles (CuNPs) have emerged as a promising solution, offering a potential remedy to mitigate the adverse effects of pollution and restore balance in the environmental detection of pollutants [16]. One important property of metal nanoparticles is their antimicrobial activity against bacteria and fungi, and they are used as pesticidal objects which are significant agents in plant disease management [17].

ROLE OF COPPER IN PLANTS

For normal growth and development, copper is an essential element, and its activities depend upon its optimum concentration below the optimum concentration causing deficiency, and above the optimum concentration causing toxicity in plants [18]. It plays a significant role in mitochondrial respiration, protein regulation, cell wall metabolism, photosynthetic electron transport, oxidative stress response, and hormone signaling and acts as a cofactor in many enzymatic reactions, including polyphenol oxidase, amino oxidase, and superoxide. Copper efficiency has negative effects such as light chlorosis along with permanent loss of turgor pressure in young leaves, curled leaf petiole lent downwards, and light chlorosis. At higher concentrations, copper causes toxicity, oxidative stress, growth inhibition, photorespiration, and photosynthesis interference. Cu is a micronutrient present in higher concentrations in the chloroplasts. Various studies have reported that 70% of Cu is present in chloroplasts, which plays a significant role in protein and carbohydrate metabolism, synthesis of chlorophyll, and other plant pigments [19].

Synthesis of Copper Nanoparticles

Various physical, chemical, and biological methods are used for the synthesis of CuNPs. In chemical methods, microemulsion is a very common technique, and a very expensive large amount of surfactant is used, as shown in Figure 1 [20].

Among physical methods, laser ablation aerosol technique and radiolysis are very significant techniques; however, owing to the large energy consumption and employment of expensive instruments, these techniques are less popular [21].

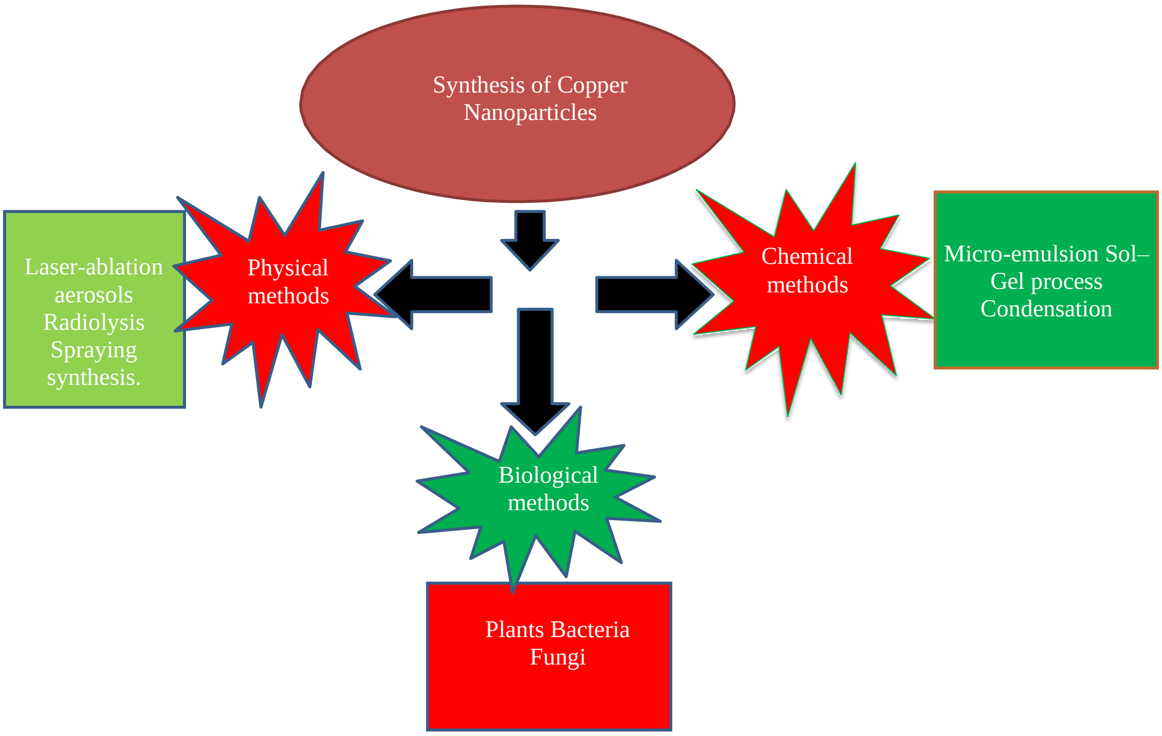

Figure 1. Methods of synthesis of CuNPs.

Different conventional methods are employed for the synthesis of CuONPs, such as precipitation [22] and gamma radiation [23]. Various studies have been carried out on the manufacture of CuONPs, which are related to the fabrication of CuONPs; among them, the involvement of chemical reactions reduced the reproducibility of CuONPs [24].

Biological Synthesis of Copper Nanoparticles

In biological synthesis, three types of biological agents are employed as follows.

Green Synthesis of Copper Nanoparticles

For the green synthesis of metallic nanoparticles, the use of plants is very cost-effective, nonhazardous, eco-friendly, and easy to handle. Plants are rich sources of biomolecules such as co-enzymes and vitamins, which can reduce metal ions to nanoparticles, making them an essential source [25]. Green biosynthesis of CuONPs is more crucial than any other method and has a very important role in several fields [26]. Plants used for the green synthesis of CuONPs contain secondary metabolites that act as capping and reducing agents [27]; thus, these biological agents function as stabilizers and reducers in the manufacturing of CuONPs [28].

Plant extracts are employed for the biosynthesis of CuNPs [29], researchers have reported that many biomolecules are present in the extracts of magnolia leaf, *Syzygium aromaticum*, *Euphorbia niruri*, *Sterculia urens*, and latex of Euphorbiaceae, which reduce Cu ions to CuNPs [30, 31]. Various medicinal plants such as *Acalypha indica* [32] and *Aloe vera* [33] have been used for the green synthesis of CuONPs.

The latex extract of *Calotropis procera* is used for the synthesis of CuNPs [34], which are very effective against tumor cells. Leaf extracts of *Capparis zeylanica* [35], *Vitis vinifera* [36], and *Nerium oleander* leaf [37] are employed for the biosynthesis of CuNPs and act as antibacterial agents. Pineapple [38], *Citrus grandis* peel [39], *Hibiscus rosa-sinensis* [40], guava [41], *Phyllanthus emblica* [41], lemon fruit [42], *Ginkgo biloba* leaf [43] are used for the synthesis of CuNPs.

Table 1. Production of CuNPs by plants.

Plants Name	**Shape of CuNPs**	**Size of CuNPs**	**References**
Syzygium aromaticum	Spherical	5-40nm	[28], [30]
Euphorbia niruri	-	-	
Sterculia urens	-	-	
Acalypha indica	-	-	[29]
Aloe vera	Spherical	40nm	[31]
Calotropis procera	Spherical	15nm	[31]
Capparis zeylanica	-	-	[32]
Vitis vinifera	Cubic	50-100nm	[33]
Nerium oleander	-	-	[34]
Pineapple	Cubic	30-50nm	[34]
Citrus grandis	Spherical	22-27nm	[35]
Hibiscus rosa-sinensis	Spherical	500nm	[35]
Guava	Flacks	15-30nm	[39]
Phyllanthus emblica	-	-	[41]
Lemon fruit	-	45nm	[42]
Ginkgo biloba leaf	Spherical	15-20nm	[43]

A study [44] reported that ripened fruit extract of *Duranta erecta* synthesized CuNPs that reduced toxic Congo red, azo dyes, and methyl orange from water [45]. Also reported that nano-coated CuNPs produced from the extract of *Tinospora cordifolia* showed antimicrobial properties.

CuNPs are synthesized from *Ocimum sanctum* which is a conventional medicinal plant in India, and contain many secondary metabolites such as alkaloids, glycosides, and tannins, which act as stabilizing and reducing agents in the synthesis of CuNPs [46]. Leaf extracts of *Lantana camara* were synthesized using CuNPs, which has been reported [47]. Extracting Citrus limon fruits is a well-ordered method for the synthesis of CuNPs and exhibits antimicrobial activity [48]. According to Singh et al. (2018) [49], CuONPs synthesized from *Centella asiatica* at room temperature exhibit antibacterial activity against *E. coli*, *P. aeruginosa*, *K pneumonia,* etc. shown in Table 1.

Biosynthesis of Copper Nanoparticles from Bacteria

Several studies have reported that microorganisms are employed for the biosynthesis of CuNPs, which are ideal for the synthesis of nanoparticles because of their short generation, mild generation conditions, and ease of culturing. Studied the isolation of CuNPs from the gram-negative bacterium *Serratia* [50]. *Morganella psychrotolerans* are used in the synthesis of 15–20 nm range CuNPs [51]. *Pseudomonas stutzeri* synthesized CuNPs with spherical shapes and sizes in the range of 8–15 nm [52]. Reported that *E. coli* is employed for the biosynthesis of CuONPs, which vary in shape and size [53]. CuNPs were fabricated from *Bacillus cereus* size range 11–33 nm which showed antibacterial activity [54].

CuO NPs (78–80 nm) are biosynthesized from *Streptomyces spp.* is performed antifungal activity against plant pathogens like *Alternaria alternata, Fusarium oxysporum, Pythium ultimum,* and *Aspergillus niger* [55]. Another spp. of *Streptomyces* like *Streptomyces capillispiralis* and *S. griseus* synthesized Cu NPs (4–59 nm) which are spherical and act as antifungal agents [56, 57] Shown in Table 2.

Biosynthesis of Copper Nanoparticles from Fungi

Various fungi are used for the synthesis of nanoparticles and are better agents than other agents. Many fungi have been employed for the synthesis of CuNPs, including *Fusarium oxysporum* (Majumdar et al., 2018) [47], *Pseudomonas* (Majumdar et al., 2018) [47], *Hypocrea lixii* [58], *Stereum hirsutum* (Cuevus et al., 2015) [27], *Rhodotorula mucilaginosa* [58]. *Penicillium aurantiogriseum, Penicillium citrinum,* and

Penicillium waksmanii have been employed for the extracellular biosynthesis of CuNPs (Honary et al., 2012) [59], as shown in Table 3.

APPLICATIONS OF COPPER NANOPARTICLES

Based on different research, CuNPs have many significant properties; one of them, anticancer properties, is the most important property because cancer is a very large and crucial disease for human beings.

Role in Medicine

Because of their qualities, significant interaction with pathogens, high biological and chemical reactivity, and large active surface area, Cu NPs are employed in medicine and dentistry [60]. Presently, public health is a worldwide challenge because bacteria are resistant to antimicrobial drugs [61]; therefore, CuNPs reduce these negative impacts, are a promising tool against pathogens, and protect the cells from adverse effects [43] and [44]. CuNPs are not only employed in medicine, but also as antibiotics to protect the circulatory, digestive, and respiratory systems. At present, it has been reported that CuNPs exhibit specific bactericidal effects against *S. aureus*, *E coli*, and *S mutants*, without changing the shear bond strength, and their adhesion properties are enhanced by addition as a nanofiller. Biosynthesized CuNPs from the tuber extract of *Dioscorea bulbifera* exhibited strong inhibitory effects, such as superior antioxidant activity against alpha-amylase and alpha-glucosidase, which act as anti-diabetic agents.

Role as Anticancer

The main mechanism of chemotherapy is to remove cancerous cells; however, chemotherapeutic agents have negative effects on normal cells and cancer cells. Biosynthesized nanoparticles are more effective against cancer and are eco-friendly. An in vitro study showed antitumor properties against human colon cancer Ccco-2 cells and human breast cancer Mcf-7 cells.

Different studies have reported that copper nanoparticles are the most effective against cancer cells owing to their colloidal properties. It has also been reported that CuNPs are synthesized from nontoxic aqueous extract of latex and can be employed in in vivo cancer therapy.

Table 2. Production of CuNPs by bacteria.

Bacteria	Shape of CuNPs	Size of CuNPs	References
Serratia spp.	Cubic	-	Hasan et al, (2008) [50]
Morganella psychrotolerans	Cubic	15–20 nm	Rajesh et al, (2011) [51]
Pseudomonas stutzeri	-	8–15 nm	Varshney et al., (2010) [52]
E. coli	Spherical	-	Singh et al, (2010) [53]
Bacillus cereus	-	11–33 nm	Tiwari et al, (2016) [54]
Streptomyces spp.	-	78–80 nm	Hassan et al., (2019) [55]
S. capillispiralis	-	4–59 nm	Hassan et al., (2018) [56]
S. griseus	-	-	Ponmurugan et al., (2016) [57]

Table 3. Production of CuNPs by fungi.

Name of fungi	Shape of CuNPs	Size of CuNPs	References
Fusarium oxysporum	-	95nm	[47]
Pseudomonas	-	84nm	[47]
Hypocrea lixii	Spherical	24nm	[58]
Rhodotorula mucilaginous	Spherical	10nm	[58]
Penicillium aurantiogriseum	Spherical	89nm	[59]
Penicillium citrinum	Spherical	85nm	[59]
Penicillium waksmanii	-	79nm	[59]

CuNPs are very effective against mouse embryonic fibroblasts, human lung carcinoma cells, Chinese hamster ovary (CHO), and human osteosarcoma (Saos), and have cytotoxic activity against MCF-7 Breast Cancer cells, and they observed that at 10µg/mL concentration, CuNPs function was not certain.

CuO NPS are synthesized from various extracts of medicinal plants and show antioxidant and cytotoxic effects against cancer cells such as human breast (MCF-7), cervical (HeLa), epithelioma (Hap-2), lung cancer (A549), and one normal human dermal fibroblast (NDHF) cell line.

Role of Copper Nanoparticles as Antimicrobial Agents

Several studies have reported that CuNPs are potential antimicrobial agents. CuNPs coated with cellulose film showed antimicrobial activity against *E. coli* and *Staphylococcus aureus*, which are the main agents of food spoilage, and also reported more antimicrobial activity against *S. aureus* than *E. coli*. CuNPs exhibited antimicrobial activity against *Micrococcus luteus*, *Staphylococcus aureus*, *Klebsiella pneumoniae* and *Pseudomonas aeruginosa*, and fungi, such as *Aspergillus niger, A flavus* and *Candida albicans*. When CuNPs and chitosan were combined with iodine, they showed the most effective activity against bacteria such as *E. coli* and *Bacillus cereus* in which iodine acts as a stabilizing agent. Similarly, nano-composite films of CuNPs and cellulose combined effect together exhibited the strongest antibacterial properties against *S. aureus* and *K. pneumoniae*. Investigator [62] studied the antibacterial properties of the biosynthesized CuONPs against both gram-negative and gram-positive bacteria.

Role of Copper Nanoparticles in Agriculture

The effect of nanoparticles in plants depends on different characteristics of plant NPs, such as composition, concentration, physical, chemical, and size [63]. Owing to their antibacterial activity, CuNPs are used in contrast to pathogenic bacteria; therefore, Cu NPs are used in manufacturing a wide range of antibacterial agent coatings for implementation in household, aerospace, and biomedical industries.

Various ancient researchers have reported that Cu showed antimicrobial activity, and according to a study [64] Cu in the nano form is a good object for controlling plant diseases. In agriculture, copper-based nanoparticles are more effective as pesticides (e.g., fungicides), fertilizers [65, 66] and antifungal agents [64].

Role of Copper Nanoparticles Increasing Growth and Yield

When CuNPs and chitosan were applied to the gather, it enhanced the number of fruits in the tomato. Nair and Chung (2014) [67] reported that due to the application of CuONPs, copper ions are dissolved, which causes lignification, enhancing the firmness of tomato fruits, which may enhance the inner cell wall and potentially increase the shelf life of the fruit. When the CuNPs were applied through foliar spraying, it increased the lycopene, vitamin C, flavonoid, and total phenol contents (López-Vargas et al., 2018) [68]. Biosynthesized CuNPs enhance plant root and shoot growth in mung beans (Siddiqi and Husen, 2020) [69].

CuNPs not only showed positive effects but also showed negative effects on plants. Various studies have reported that CuNPs applied at different concentrations induced different changes, such as shoot elongation was reduced by applying CuNPs at a concentration of 80 mg ml^{-1} [70].

Role of CuNPs in Plant Physiology and Photosynthetic System

Photosynthesis is a very specific mechanism in plants in which solar energy is converted into chemical energy, which is performed by various organs such as chloroplasts and different components of thylakoid membranes and photosynthetic pigment systems [71]. Various studies reported that when CuNPs are applied in plants it reduce the thylakoid number per granum, stomatal conductance, transpiration rate, electron transport system, and photosynthetic rate [72, 73]. A study [74] reported that CuONPs have harmful effects on the photosynthetic apparatus, such as chlorophyll, grana, and

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chlorophyll. CuNPs are aggregated when spring barley is grown in a hydroponic solution and express negative impacts creating an unordered structure of thylakoid mesophyll cells and chloroplast structures [75].

Role in Draught Protection

Plants are not only affected by biotic stress, but also by abiotic stress, such as drought, and detrimental growth affects productivity and growth, which reduces the sustainability of agriculture. For crop production, plant growth and protection from abiotic stress by nanoparticles have significant value. Van Ha et al. (2022) [76] reported that CuNPs showed positive impacts in maize protected from drought-enhanced productivity and higher water content in leaves. CuNPs protect the crop from drought stress; [77] reported that CuNPs reduced drought stress in soybeans.

Role of CuNPs in the Management of Plant Diseases

The use of CuNPs in the management of plant diseases caused by fungi, bacteria, and plant parasitic nematodes is a new revolution in agriculture (Figure 2). The use of microemulsions, liposomes, and nano-emulsions in agronomy, which reduce the transportation of pesticides, herbicides, and fungicides [78], has a great impact on plant disease management and has evolved as a new method for plant protection [79]. In comparison to the use of different fungicides and other agrochemicals, CuNPs (11–55 nm) are more effective against *Phytophthora infestans* which infects tomatoes [80]. Many studies have reported that bacterial blight in pomegranate was prevented when nanocopper was applied against *Xanthomonas* [81], and the synergistic effect of Cu with chitosan complex nanogels prevents the growth of *Fusarium graminearum* which is a very harmful plant pathogen for cereal crops [82] reported that the biosynthesized CuNPs showed the most significant effect against *F. oxysporum*, *F. culmorum*, and *F graminearum*.

According to a study [83], CuONPs showed antibacterial properties against soil-borne pathogens, such as *Ralstonia solanacearum*, and its bactericidal effect generates negative characteristics such as disturbed ATP production, decreased bacterial motility, and biofilm formation.

A study [84] reported that chitosan-coupled copper nanoparticles inhibited the growth of plant pathogens such as *Ralstonia solani* and *Pythium aphanidermatum* which cause damping disease in plants.

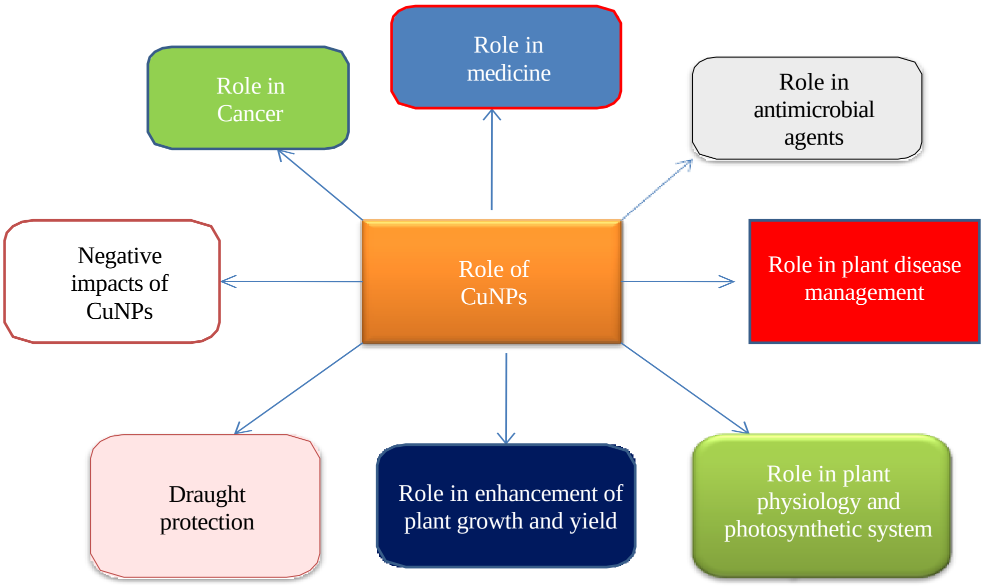

Figure 2. The role of CuNPs.

Many nanoparticles are used in plant disease management; researchers have reported that CuONPs inhibit the growth of *Botrytis cinerea* which has the highest impact than any other NPs in inhibiting gray mold disease or rose petals, a severe disease worldwide of fungal disease [85].

Various researchers reported that CuNPs showed not only fungicide and bactericide effects but also a nematocidal effect at a significant concentration, inhibited the J2 stage of *Meloidogyne incognita* and its inhibitory effect depended upon its concentration at higher concentrations, which showed a higher mortality rate [86].

INTERACTION OF CuNPs WITH MICROORGANISM

Various studies have been conducted on the antimicrobial activity of CuNPs, but the mechanism is not well understood. When nanoparticles interact with the microorganism surface, many changes occur, such as membrane damage, reactive oxygen species (ROS) protein dysfunction, and loss of enzymatic activity [87, 88]. A study [89] also reported that CuNPs come in contact with bacterial cells and that these ions engage with the cell wall, which generates ROS and causes loss of membrane integrity. Additionally, CuNPs have many negative effects, such as the formation of pits in the membrane, disruption of metabolic pathways, and oxidative stress [90–93]. This also studied [94] Cu polymers with nanoform can be significant agents due to the bactericidal effect of nano-composite release Cu ions and CuNPs and the ions come in contact with the bacterial cell membrane, interconnected with carboxyl and amine groups in the peptidoglycan layer and sulfhydryl, which causes protein denaturation. Cu ions attach to the DNA and cross nucleic acid strands, resulting in a disordered helical structure. In addition, CuNPs penetrate the cell membrane, leading to endocytosis of bacterial cells [95]. Particle size, electrostatic attraction with nanoparticles and microbial cells, and the hydrophobic or hydrophilic nature of nanoparticles are the main reasons for the enhanced susceptibility of CuNPs to micro-biocidal agents [54].

TRANSLOCATION OF CuNPs IN PLANTS

Agriculture is an important sector that attracts scientists because discharged NPs are received by the soil; therefore, it is very important to know how NPs are transported in the whole ecosystem and soil.

The shape, size, and composition are the main factors for the uptake and transportation of NPs in plants through the vascular system [96]. Before uptake, CuNPs are converted into organic complexes and copper ions [97]. Other studies have reported that NPs are attached to plant roots and NPs are translocated in plants by tissues such as cuticles, trichomes, stomata, stigma, and hydathodes aerial parts of plants and by root tissues such as root tips, rhizomes, and lateral root junctions.

According to a study [98], plants absorb NPs in the form of metal ions or their original form. NPs are also transported in various aerial parts, such as leaf stems and fruits, and settle in various locations such as vacuoles, walls, nuclei, lipid envelopes, stellar systems, and cytoplasmic matrix [99, 100, 101]. The translocation capacity of Cu NPs varies from plant to plant, in lettuce 0.5%–0.6% Cu translocated, and in alfa-alfa 3% to 5% Cu from root to shoot [102]. A study reported that [103] CuO NPs are absorbed and accumulated in tomatoes.

NEGATIVE IMPACTS OF COPPER NANOPARTICLES

Myriad studies have reported that CuNPs play an important role in epigenetic, physiological, morphological, and genetic variation, which may change the nutritional value and plant growth. Plants are closely associated with soil particles, so everything is absorbed from the soil by the roots [103, 104]. Nanoparticles generated two types of phytotoxicity in plants: (1) chemical-based phytotoxicity and (2) stress-based phytotoxicity stresses generated by the shape, size, and surface of nanoparticles. Plant-activated antioxidant defense systems against NPs stress. When NPs come into contact with plants, they induce toxicity, and plants activate their resistance against NPs stress.

NPs have negative impacts on plants, which are very harmful to plant health, one of which is the genotoxic effect that generates various toxic effects [105]. DNA damage by CuONPs has been reported in plants and crops. The toxicity of NPs is associated with their properties, such as large size and large concentration exposure duration associated with large genotoxic responses.

Many genotoxic effects are caused by CuNPs, such as abnormalities in cell cycle distributed chromosomes in metaphase, vacuolated nuclei, and laggard chromosomes [82, 106]. Nanoparticles operate at optimum concentrations because, above the optimum concentration, ROS are generated, which causes imbalances in cellular metabolism. When CuNPs are applied in low quantities (5–20 mg Cu per plant), various metabolic effects are initiated because of the accumulation of copper and the production of ROS.

CONCLUSION

Cu NPs not only work very well in the agriculture sector, but also act as antibiotics, anti-diabetic, and anticancer agents. This paper presents the biosynthesis, importance, and positive and negative effects of Cu NP in different fields. Cu NPs are biosynthesized from bacteria, fungi, and plants (roots, stems, and leaves). Cu NPs have a significant value in many fields, one of them, Cu NPs is their use as antibiotic and anti-diabetic agents. Biosynthesized Cu NPs showed the antitumor and anticancer properties against various cancer diseases. This is a very good object for such kinds of severe disease. Despite the use of Cu NPs in different fields, Cu NPs are of great importance in agricultural fields.

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