CHAPTER

Plant-mediated copper nanoparticles for agri-ecosystem applications

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1 Introduction

Cu-NPs are being developed in the last years to be used in agriculture as fertilizers and pesticides due to their excellent reactivity and antipathogenic properties (Keller et al., 2017; Raliya et al., 2017). Cu-NPs production up to 200 tons/year based on recent estimates (Keller et al., 2013). These huge amounts deposited in the soil and atmosphere increased the risk of bioavailability and toxicity in the environment (Kah and Hofmann, 2014). The effect of such metal-based nanomaterials ranged between positive, neutral and negative effects. According to Zuverza-Mena et al. (2017), the variation in Cu-NPs effects could be related to growing media, method of nano-copper application and the targeted species. The form of the Cu-NPs was validated to be a controlling agent for nano-copper toxicity; spherical particles followed by rod and polygonal-shaped particles are gradually the most toxic forms (Zhai et al., 2016). The shape of the NP which defines the surface area or the surface of contact is a better estimator of phytotoxicity than the applied concentration (Ma et al., 2010). In all cases, Cu-NPs affected plant growth directly or indirectly. The former impact is related to plant toxicity, nutrition or hormone-like effects while the latter impact is due to antifungal, antibacterial and antiviral properties of Cu-NPs used for the suppression of pathogens (Husen and Siddiqi, 2014). As mentioned previously, the method of application plays a key role in Cu-NPs impact. Foliar spraying and fertigation improved bioactive compounds (phenols, β-carotene, lycopene and vitamins) of tomato and jalapeño peppers (Hernández et al., 2017; Hernández-Fuentes et al.,

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2017; Juarez-Maldonado et al., 2016; Pinedo-Guerrero et al., 2017), fruit weight in cucumber (Hong et al., 2016), chlorophyll content and N assimilation in mung beans (Pradhan et al., 2015a), proline content in wheat (Zhang et al., 2018). In parallel, these stimulatory effects were coupled with an increase in enzymatic and antioxidant activity (Fu et al., 2014; Hernández-Hernández et al., 2018). Similarly, studies evidenced the antimicrobial potentials of Cu-NPs against pathogens such as *phytophtora infestans* and others (Giannousi et al., 2013; Kanhed et al., 2014; Saharan et al., 2015). Inhibitory effects following Cu-NPs were also reported by many authors on lettuce, alfalfa (Hong et al., 2015), ryegrass (Atha et al., 2012), brown mustard (Rao and Shekhawat, 2016), cilantro (Zuverza-Mena et al., 2015), radish (Atha et al., 2012), carrot (Ebbs et al., 2016) and corn (Zhao et al., 2017b). These particles could alter the normal plant metabolic functions through a strong binding capacity with proteins, carboxyl, sulfhydryl, or imidazole groups. Thus, to cause oxidant stress in plants (ROS generation and OH-radical formation) (Rao and Shekhawat, 2016). In comparison, fewer studies reported the effect of Cu-NPs on soil properties and bacterial community. The impact of such particles was validated to be related to soil texture; clay particles reduce the toxicity of nanoparticles more than sand and loam (Schlich and Hund-Rinke, 2015). Frenk et al. (2013) indicated an adverse effect of CuO-NPs especially on the community composition of Rhizobiales and Sphingobacteriaceae taxa. This effect was evidenced in sandy loam soil and less in sandy clay soil.

The current chapter will emphasize all the aspects of the Cu-NPs application in the agri-ecosystems.

2 Synthesis of copper nanoparticles

Many approaches were used to synthesize CuNPs, including methods for hydrothermal, sol-gel, sonochemical, micro-emulsion, thermal decomposition, and chemical reduction (Dang et al., 2011). Among all, the chemical reduction method for the synthesis of CuNPs is widely selected because it is quick, robust, effective in yield, needs limited equipment and inexpensive technique. While the process of chemical synthesis is found to be simple and cost-effective, some use hazardous raw materials and are not environmentally friendly. The biosynthesis of nanoparticles has drawn the attention of many researchers due to the expensive and extreme reaction conditions of their physical and chemical processes. On the other hand, biological approaches do not require the use of poisonous solvents or the synthesis of dangerous by-products. Several researchers have indicated that because the nanoparticles are biosynthesized free of toxic chemicals, it is more appropriate for the biological application of nanoparticles (Gericke and Pinches, 2006). As a result, researchers used microorganisms, plant and seed extracts to look for new, cheap routes for the synthesis of nanoparticles (Subhankari and Nayak, 2013). Nanoparticles preparation biosynthetic process theoretically reduces toxicity and makes the nanoparticles more biocompatible. The utilization of seed extracts has benefits across the different biosynthetic methods, like easily accessible and safe to treat, for the large-scale synthesis of nanoparticles using biosynthesis and easily scalable (Song and Kim, 2009). The seed extracts can provide a safer way to synthesize nanoparticles, since they are free of toxic chemicals and are normal reducers and cappers (Kudle et al., 2012).

2.1 Synthesis from plants

Copper nanoparticles were synthesized from various copper salts, such as copper acetate, copper chloride, copper sulfate and copper nitrate, using extracts derived from different plants belonging to different classes (Table 1). Copper nanoparticles were synthesized thus for quite some time now using physical and chemical methods, the biological nanoparticle synthesis has recently begun.

Plant parts (leaf, root, bark, etc.) are thoroughly washed with tap water to remove particles from the soil, sun-dried for 1–2 h to eliminate the residual moisture, cut into small pieces and removed. The extract is extracted by centrifugation and filtration (Fig. 1). Various concentrations of plant extract and metal salts (e.g., cupric sulfate,

Table 1 Plants and their parts used for the biosynthesis of CuO NPs.

Copper nanoparticles	Plant	References
CuO NPS	*Azadirachta indica*, *Pongamia pinnata*, *Lantana camara* (Leaves)	Shiny et al. (2019)
	Citrus reticulata (Orange peel)	
	black bean extract	Nagajyothi et al. (2017)
	Alternanthera sessilis (leaf)	Niraimathi et al. (2016)
	Aloe vera (leaf)	Kerour et al. (2018)
	Calotropis procera (leaf)	Reddy (2017)
	Ferulago angulate (aerial part)	Mehr et al. (2018)
	Garcinia mangostana (leaf extract)	Prabhu et al. (2017)
	Galeopsidis herba (Plant extract)	Dobrucka (2018)
	Plantago asiatica (leaf extract)	Nasrollahzadeh et al. (2017)
	Matricaria chamomilla (flower)	Duman et al. (2016)
	Syzygium aromaticum (bud)	Rajesh et al. (2018)
	Rubus glaucus (leaf and fruit)	Kumar et al. (2017)
	Thymus vulgaris L. leaves	Nasrollahzadeh et al. (2016)
	Stachys lavandulifolia (flowers)	Khatami et al. (2017)
	Azadirachta indica (leaves)	Nagar and Devra (2018a, b)
	Rosa canina (fruit)	Hemmati et al. (2018)
	Allium saralicum (leaves)	Tahvilian et al. (2019)
	Lantana camara (flower)	Chowdhury et al. (2020)
	Hagenia abyssinica (Brace) JF. Gmel. (Leaf)	Ananda Murthy et al. (2020)
	Adiantum lunulatum (whole plant)	Sarkar et al. (2020)
	Annona muricate (leaf)	Sukumar et al. (2020)

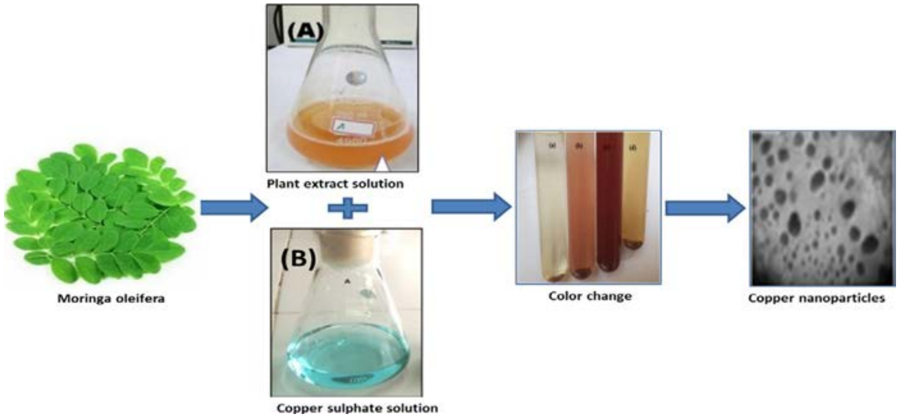

FIG. 1

Diagram illustrated plant-mediated synthesis of copper nanoparticles.

cupric chloride, copper nitrate, cupric acetate) are incubated for NP synthesis in a shaker at various time intervals, at varying pH and temperature. NP formation is controlled by color change in the reaction mixture. In the end, the reaction mixture is centrifuged at low velocity to eliminate any media or large particles. Eventually, the NPs can be centrifuged at high velocity or with a gradient of pressure, washed thoroughly in water/solvent (ethanol/methanol) and collected as a bottom pellet (Subhankari and Nayak, 2013; Joshi et al., 2019).

The addition of *Calotropis procera* latex extract to copper acetate solution with constant shaking at room temperature leads to the synthesis of copper nanoparticles with an average size of 15 nm (Harne et al., 2012). Copper nanoparticles ranging from 5 to 40 nm were synthesized using a 1:1 ratio of *Syzygium aromaticum* aqueous extract and 0.001 M copper sulfate (Subhankari and Nayak, 2013). Copper oxide nanoparticles of 46 nm were synthesized with *Tabernaemontana divaricate* leaf extract and mixed with copper sulphate under continuous stirring (Sivaraj et al., 2014). Copper nanoparticles have been synthesized by applying the *Vitis vinifera* leaf extract to the test tube with copper sulfate and placed in the darkroom for incubation at room temperature (Angrasan and Subbaiya, 2014). In another analysis, the addition of *Aloe vera* flowers extracts to copper acetate aqueous solution in the dark and the reaction was carried out at 50°C in a steam bath for 30 min, resulting in synthesized of copper nanoparticles with 40 nm spherical average size (Karimi and Mohsenzadeh, 2015). Fresh Andean blackberry fruit and leaves were heated in deionized water at 65–70°C for 60 min and the filtrate was combined with copper nitrate solution and stirred at 75–80°C for the synthesis of copper oxide nanoparticles with a mean diameter of 43.3 nm and 52.5 nm using fruit and leaf extract respectively (Kumar et al., 2017). The synthesis of CuO NPs using leaf extracts of different plants (*Azadirachta indica,* *Hibiscus sinensis, Murraya koenigii, Moringa oleifera*, and *Tamarindus indica*). UV visual spectroscopy showed a band centered between 220 and 235 nm (Rehana et al., 2017). Vishveshvar et al. (2018) synthesized CuO NPs using an aqueous solution of copper (II) sulfate and *Ixora coccinea* leaf extract.

Using the *Enicostemma axillare* (Lam.) leaf extract, CuONPs were synthesized using a simple and environmentally friendly green path. CuONPs characteristic absorption peak was in UV-Vis spectrum at around 264 nm. The morphological and structural character of green NPs is revealed by scanning electron microscopy (SEM) and transmission electron microscopy (TEM) studies. The mean particle size had been estimated at 30 nm (Mali et al., 2019). In addition, the synthesis of Cu/CuO-NPs from $CuSO_4$ solution using aqueous lemongrass leaf extract as the reduction and capping agent. Results suggested the rapid production of stable Cu/CuO-NPs. Upon adding aqueous lemongrass leaf extract $CuSO_4$ solution converted from light blue to yellowish-green. The Cu/CuO-NPs obtained were spherical, with a size of between 5.67 and 9.10 nm (Tu, 2019). Sugarcane (*Saccharum officinarum*) is an abundant source of sugar in the fruit. SCJ includes reducing sugar and nonsugar reducing (glucose & sucrose). This contains ions such as potassium, calcium and sodium. The juice is also well known for producing food additives such as malic acid, oxalic acid, D-gluconic citric acid and the synthesis of copper oxide (CuO NPs) (Angeline Mary et al., 2019).

Cu NPs synthesis using *Curcuma longa* extract. The size of the particles is in the range of 5–20 nm. Additionally, both gram-positive and gram-negative microorganisms are examined for antibacterial activity of the collected Cu NPs. The region where Cu NPs inhibit gram-positive bacteria is like gram-negative bacteria (Jayarambabu et al., 2020). A green process for synthesizing nanoparticles of copper/copper oxide using seedless dates extract. Because of its high phenolic and flavonoid content, Cu/Cu_2O NPs were synthesized according to the chemical reduction method using the extract of seedless dates as a reducing agent. Transmission Electron microscopy showed the synthesis of approximately spherical particles (Mohamed, 2020). Additionally, CuNPs synthesis using aqueous sumaq (*Rhuscoriaria* L.) fruits is extracted as a stabilizing agent. The Rhuscoriaria fruit extract was combined with the solution of copper sulfate and hydrazine hydrate as a reduction agent and sodium hydroxide as catalysts. TEM photograph shows synthesized CuNPs having semi-sphere forms with a diameter of 22–27 nm. The XRD data showed the average size of crystallite was 18 nm (Ismail, 2020). Also, CuO nanoparticles were synthesized using leaf extract of *citrus aurantifolia* which is a cost-effective and nontoxic process. The nanoparticles with biosynthesized CuO have been used as a photocatalyst and as an antibacterial agent for wastewater purification from the factories and living spaces (Rafique et al., 2020). CuO/C nanocomposites were prepared by adding the copper sulfate pentahydrate solution with the *Adhatoda vasica* plant extract under certain conditions. The SEM images showed the average thickness of the CuO/C nanoflakes was 7–11 nm (Bhavyasree and Xavier, 2020).

2.2 Synthesis from agriculture waste and other wastes

Agro Waste is a term used to describe the waste material produced during farming practices that can be any chemical, pesticide or fertilizer. These materials are typically hazardous and must be reduced in usage, but they are needed in greater quantities to obtain optimum crop products (Zamare et al., 2016). Agro waste contains even pieces of plants that are not used as food. Once crops are grown, there are other similar problems, such as farm waste, which accounts for about 80% of agricultural biomass. This waste that causes the release of gasses into the atmosphere in bulk amounts is often burned by farmers. Now a day, it's the biggest source of smog (fog + smoke) and it poses a significant threat to common man's safety. It is therefore important to take the time to handle the waste strategically to save, recycle and reuse the waste (Krishnaswamy et al., 2014).

Agro wastes have various forms. These can primarily be divided into two major groups, i.e., crop residues and residues from the agricultural industry. There are two more categories of agricultural residues, namely field residues (stem, seeds, stalks, etc.) and process residues (Husk, Bagasse, Molasses). Waste from the agricultural industry can contain any commercially processed agricultural waste such as orange peel, potato peel, groundnut oil cake, and soybean oil cake (Sadh et al., 2018). The extracts of cauliflower (*Brassica oleracea*), potato (*Solanum tuberosum*) and pea (*Pisum sativum*) peel were used to synthesis CuO-NPs from $CuCl_2$. $2H_2O$. This reaction was very slow, as the yield of NPs took 24 h at 60°C. Both NPs obtained from the above sources ranged from 22.2 to 31.60 nm in monoclinic form (Ranjbar-Karimi et al., 2010).

Residues of agricultural goods that are dumped as waste are rich in bioactive compounds (Omar et al., 2012). Such contaminants may be used as raw material for various investigations and industries. This can help to minimize production costs and reduce pollution loads for the environment. *B. oleracea* sub sp. *Botrytis* (L.) (Common name: Cauliflower) is one of the most popular and widely used vegetables (Gupta et al., 2018). It is therefore included in the group of waste products with a higher waste index and can therefore be included in value-added goods (Shivani and Deepak, 2018). Besides, the cauliflower leaves show the existence of phytochemicals such as alkaloids, flavonoids, hormones, terpenoids, anthraquinone, proteins, phenols, quinone and carbohydrates (Gowri and Manimegalai, 2017). These phytoconstituents can play an important role in reducing metal ions such as copper and zinc nanoparticles to their nanoform (Gupta and Chandra, 2020).

The green and simple method by which CuO NPs are biosynthesized using banana peel extract as a reduction and stabilizing agent. XRD, EDX, FE-SEM, FTIR were used to characterize CuO NPs that were biosynthesized. The findings indicate the high purity of the CuO NPs synthesized by the banana peel extract and the average particle size is 60 nm. Due to the smaller size and high purity, the biosynthesized CuO NPs showed an excellent photocatalytic activity (Aminuzzaman et al., 2017). Also, the CuO NPs were synthesized using vegetable waste extracts such as Cauliflower waste, Potatoes and Peas peels. The extracts were aimed at acting as capping agents to get control over the resulting CuO NPs' microstructure and morphology. The CuO NPs generated with cauliflower extract have demonstrated a high degradation of MB (96.28%) compared to obtained with Potatoes peels (87.37%) and Peas peels (79.11%) (Ullah et al., 2017). Copper oxide nanoparticles were biosynthesized with *Zea mays* L. dry husk extract. Red Colored Cubic Nanoparticles Cu2O was first obtained via this simple, eco-friendly, green synthesis path. The Cu_2O nanoparticles have been thermally oxidized at 600°C to pure monoclinic CuO nanoparticles (Nwanya et al., 2019).

Biosynthesis of CuO-NPs from gum karaya has been reported (Padil and Černík, 2013). A mixture of $CuCl_2$ and gum was rendered alkaline in aqueous solution and heated at 75°C with continuous stirring. After 1 h, the blue copper chloride was black and was isolated as a black powder. Furthermore, under laboratory conditions, CuO-NPs from *Eichhornia crassipes* weed were successfully synthesized in aqueous media (Vanathi et al., 2016). Also, biosynthesis of the CuO-NPs from *Punica granatum* aqueous peel extract at room temperature was investigated. Extract of peel was observed containing amino acids and phenols that convert copper ions to CuO-NPs (Ghidan et al., 2016).

The green synthesis was achieved using an aqueous solution of the *P. granatum* peel extract and the monohydrate of copper acetate. The Debye-Scherrer formula measured an average crystalline size of about 35.80 nm. Also, the disc diffusion approach tested the fabricated CuO NPs for antibacterial activity. The CuO NPs demonstrated excellent antibacterial activity against the *Escherichia coli* pathogenic bacterial strain (Siddiqui et al., 2020). Copper nanoparticles were made from old computers with powdered waste printed circuit boards (WPCBs) by reduction using L-Copper nanoparticles were prepared using L-ascorbic acid-reducing agent (L-ascorbic acid reductant) and (CTAB) as an additive at room temperature from powdered old computers. Characterization tests for the copper nanoparticles produced revealed its spherical shape with particle size in the 5–32 nm range. The method studied is considered to be merely efficient and environmentally friendly for the preparation of copper nanoparticles from WPCBs with the goal of recycling e-waste to obtain a higher value product (Tatariants et al., 2018; El-Nasr et al., 2020).

2.3 Mechanism of copper nanoparticle formation

Plant extracts have a broad variety of metabolites (enzymes, proteins, amino acids, vitamins, polysaccharides, and organic acids such as citrates) and phytochemicals respective functions (Nasirian, 2012) that can act both as reducing and stabilizing agents in the metal NP synthesis. Bioreduction is a fairly complicated process. Biomolecules such as water-soluble phytochemicals are flavones, organic acids and quinones in the extract were used as a reducing agent (Al-Samarrai, 2012). Provide electrons for metal ions, which can be reduced to elementary metal. The forming atom serves after reduction as the nucleation center, followed immediately by the creation time when the smaller neighboring particles fusion into a bigger NP. In the final stage of synthesis, the capacity of plant extracts to stabilize the NP ultimately determines its energy-foster, stable morphology. Material is applied, known as a capping agent, to prevent further growth and keep the particles in the nano-range. Plant extract biomolecules can serve as a reducing agent, or the same molecules can act as both a reducing agent and a capping agent such as natural (gum) hydrocolloids isolated from trees (Padil and Černík, 2013). During various plant extracts, the mechanisms for the formation of NP differ from species to species and, thus, their basic characteristics still need to be thoroughly clarified.

Secondary metabolites, such as terpenoids, polyphenols, flavonoids, alkaloids, phenolic acids, etc., reduce metal ion to nullifying metals or stabilize MNPs. Flavonoids comprise a broad group of polyphenolic compounds, the transformation of flavonoids from the enol to the keto will lead to metal reductions. Flavonoids are well known in their capacity to chelate metal ions. Some flavonoids, such as quercetin are considered to have heavy chelating activity because of the presence of hydroxyls and functional carbonyl groups (Anjum et al., 2015). Except for the crude extract, single pure secondary metabolites will synthesize metal NPs (Sahu et al. 2016). It has been documented that the amino acids, sugars, and fatty acids in gum karaya can act as a reduction and capping agent for metal oxide NPs (Padil and Černík, 2013).

3 Implementation of Cu-NPs in agriculture

The use of Cu-NPs in agriculture as a potential fertilizer or pesticide started 12–15 years ago. Although its implementation was not always coupled with stimulatory effect, however, it seems that the demand for such materials is increasingly expected and occurring. By 2022, this market is expected to reach 120.67 million $ (Nano Copper Oxide Market Size and Industry Forecast—2022, 2016). The evolution of the market reflects an increase in the amount of Cu-NPs deposited in the environment (Wang et al., 2020). In the last two decades, many trials reported the interaction of Cu-NPs with plants. Noteworthy, despite the type of interaction (stimulatory or inhibitory), the effect of Cu-NPs on plant appeared to be related to many factors such as particle characteristics, targeted crops and exposure conditions (dose, period, method, and experimental conditions) (Zuverza-Mena et al., 2017) (Table 2). Plant age is also a critical factor in determining the type of interaction with Cu-NPs; crops at early stages of growth are more sensitive to Cu-NPS than at later stages (Keller et al., 2017).

It is well known that nano-sized copper particles are absorbed easily and released in various parts (Dapkekar et al., 2018; Raliya et al., 2017). It was observed that Cu-NPs where accumulated in roots intercellular spaces of sweet potato, sugarcane and pepper (Bonilla-Bird et al., 2018; Rawat et al., 2018; Tamez et al., 2019). Afterwards, translocation to stems, leaves and fruit occur (Zhao et al., 2016a, 2016c). On the contrary, the findings reported by Tamez et al. (2019) revealed a Cu-accumulation restricted to the roots of sugarcane with no translocation to the above-ground parts and tissues. In all cases, contradictory observations are related to doses of Cu-NPs

Table 2 Impacts on Cu-NPs implementation on crops.

Concentration of Cu-NPs	Size (nm)	Crop	Observed effects	References
CuO: 75–600 mg/kg	10–100	*Allium fistulosum*	Increase in Ca in roots and bulb, in Ca and Fe in roots, in allicin in leaves	Wang et al. (2020)
CuO: 20, 40, and 60 mg/kg	10–100	*Saccharum officinarum*	Increase in Cu and Zn content in roots, decrease in P, B, Mn, Fe, Zn and Mo content in roots, reduction in APX and SOD activity	Tamez et al. (2020)
CuO: 50 and 200 mg/kg	10–100	*Cucurbita pepo*	Increase in Cu content in all plant parts, decrease in Zn and B contents in roots, decrease in CAT and SOD activity in roots	Tamez et al. (2019)
CuO: 50 and 500 mg/kg	14.85	*Triticum aestivum*	Reduction in Fe and Zn in grains, reduction in the level of isoleucine (Ile), leucine (Leu), threonine (Thr) and histidine (His) grains	Wang et al. (2019)
CuO: 0.025 mg/mL	1.5–20	*Lens culinaris*	Increase in lipid peroxidation and proline content, defense enzymes, total phenols, ROS and H_2O_2	Sarkar et al. (2020)
CuO: 125, 250, 500, and 1000 mg/kg	25	*Vigna unguiculata*	Toxicity at 250–500 mg nCu/kg, accumulation and biotransformation of Cu in roots and shoots, reduction in photosynthetic pigments	Ogunkunle et al. (2019)
CuO: 200, 400 and 800 mg/L	20	*Coriandrum sativum*	Reduction in biomass, root length and photosynthetic pigments, damage to the root plasma membrane, increase in the level of H_2O_2 and MDA and in cell electrolyte leakage	AlQuraidi et al. (2019)
CuO: 10, 30, 100, 200, and 300 mg	<50	*Triticum aestivum*	Reduction in root elongation, reduction in Fe, Ca, Mg, Mn, and K in roots and shoots (dose-dependent effect)	McManus et al. (2018)
CuO: 50 and 500 mg/kg	40	*Arachis hypogaea*	Reduction in amino acids, increase in resveratrol content (stress signal)	Rui et al. (2018)
nCuO: 34.4 g/m^2	20–100	*Brassica oleracea, Lactuca sativa, Brassica oleracea*	Accumulation of nCuO in leaf tissues of lettuce followed by collard green and then kale	Keller et al. (2018)

Continued

Table 2 Impacts on Cu-NPs implementation on crops—cont'd

Concentration of Cu-NPs	Size (nm)	Crop	Observed effects	References
CuO: 50, 100, and 200 mg/L	10–30	*Cucumis sativus*	A decrease in biomass and photosynthetic pigments, increase in cell electrolyte leakage (damage in the root plasma membrane), H_2O_2 and MDA, induction of Cu-Zn SOD gene expression	Mosa et al. (2018)
CuO: 50, 125, 250, 500 mg/L	50 nm	*Solanum lycopersicum*	Improve in firmness, lycopene, vitamin C and ABTS antioxidant, increase in SOD and CAT, decrease in APX and GPX	López-Vargas et al. (2018)
CuO: 25 and 100 mg/L	48.3	*Moringa oleifera Lam*	Accumulation in bioactive compounds, antioxidant capacity and photosynthetic pigments in leaves, reduction in bioactive compounds in fruits	Juárez-Maldonado et al. (2018)
CuO: 50 and 100mg/kg	10–100 nm	*Phaseolus vulgaris*	Reduction in Fe and Mg content in seeds, no significant effect on sugar and starch	Apodaca et al. (2018)
CuO: 125, 500, and 1000 mg/kg	< 25 and 60–80	*Vigna unguiculata*	Dose and particle size-dependent effects: increase in CAT (in roots), MDA (in leaves), APX and GR (in both parts) activity, reduction in SOD activity in roots and leaves	Ogunkunle et al. (2018)
500 and 4000 ppm	28.45	*Arachis hypogaea*	Variation in biochemical constituents, increase in total protein in leaves (with 500 ppm), decrease in β-sheet of secondary structure of protein	Suresh et al. (2016)
200, 400, and 800 mg/kg	40	*Cucumis sativus*	13 amino acids were upregulated (increase in tyrosine), decrease in the photosynthetic rate and water use efficiency, increase in the transpiration and stomatal conductance rates	Huang et al. (2018)
1, 10, 50, 100, 500, and 1000 mg/L	16 and 45	*Lactuca sativa, Daucus carota*	increase in root diameter of lettuce and carrot (dose-dependent effect), reduction in hydraulic conductivity in lettuce roots	Margenot et al. (2018)
50, 100 and 200 mg/kg	10–100	*Origanum vulgare*	Increase in water content, reduction in shoot biomass, starch, total sugar, reducing sugar, reduction in Ca, Fe, Mg, and Mn contents in root and shoot	Du et al. (2018)
15.6 mM	50	*Triticum aestivum*	Stimulation in lateral shoot formation, induction of oxidative stress, accumulation of proline	Zhang et al. (2018)

20, 200, and 2000 μg/mL	18	*Solanum lycopersicon*	Inhibition in root/shoot length, decrease in fresh and dry biomass (dose-dependent effect). Improvement in plant growth (minimal dose), increase in SOD, CAT, GPX activities and LPO in roots and shoots (high dose), ROS generation	Ahmed et al. (2018)
5, 25, and 50 mg/L	40–60 nm	*Glycine max*	Improve in germination and primary root formation	Hoe et al. (2018)
20 ppm	33 nm	*Cajanus cajan*	Increase in height, root length, fresh and dry weights and performance index of seedlings	Shende et al. (2017)
10, 100, 200, 300, 400, 500, 600, 700, and 800 mg/L	50 nm	*Triticum aestivum*	Increase in the content of pectin (dose-dependent), amide I, amide II and lignin. Increase in lipid peroxidation	Sharma and Uttam (2017)
0.3, 0.15, 0.06, 0.03, and 0.015 g/L	14 nm	*Solanum lycopersicon*	The optimal effect observed following the application of 0.06 g/L, differences in catalase activity in the leaves and lycopene concentration in the fruit	Juárez-Maldonado et al. (2018)
0.02, 0.2, 2, and 10 mg	25 nm	*Solanum lycopersicon*	Increase in dry weight of roots and yield (high dose), less effect observed for the remaining traits	Hernández-Hernández et al. (2018)
50 and 100 mg/kg	10–100 nm	*Phaseolus vulgaris*	Increase in Cu content in the plant parts. No effect on growth traits	Apodaca et al. (2017)
50 and 100 mg/kg	10–100 nm	*Pisum sativum*	Increase in Fe and Ni content, and Cu content in the plant parts. Negligible effect (when applied alone)	Ochoa et al. (2017)
50, 100, 500, and 1000 mg/kg	34–52 nm	*Oryza sativa*	Decrease in redox potential, fresh weight of grain (1000 mg/kg), increase in soil EC, accumulation of Cu in the aleurone layer of rice	Peng et al. (2017)
125, 500, and 1000 mg/kg	25 nm	*Kleine rheinlanderin*	Promotion of seed emergency, chlorophyll contents (chlorophyll a and b), reduction in soluble protein content (1000 mg/kg)	Ogunkunle et al. (2017)
10 or 250 mg per plant	40–60 nm	*Lettuce and cabbage*	Decrease in plant weight, net photosynthesis level, and water content, translocation of Cu from leaves to roots potential health risk associated with consumption of vegetables contaminated with CuO-NPs	Xiong et al. (2017)

Continued

Table 2 Impacts on Cu-NPs implementation on crops—cont'd

Concentration of Cu-NPs	Size (nm)	Crop	Observed effects	References
100, 500, or 1000 mg/kg	25–55 nm	*Ipomoea batatas*	Adverse effect on tuber biomass (high dose), accumulation of Cu in the peel and flesh	Bradfield et al. (2017)
0.01, 0.02, and 8 ppm	< 50 nm	*Zea mays*	Bioaccumulation of Cu in plant cells, enhancement of growth, influence on the activity of glucose-6-phosphate dehydrogenase and the pentose phosphate pathway	Adhikari et al. (2016)
200, 400, and 800 mg/kg	40 nm	*Cucumis sativus*	Perturbation of Fe uptake, and in C and N metabolism, increase in Ca, K, S, P, Zn, and Mg contents in fruits (dose-dependent), alteration of metabolite profile in fruits, up-regulation of proline, glycine, valine, pelargonic acid, arachidic acid, xylose, benzoic acid and down-regulation of citric acid, myo-inositol, ornithine, 1-kestose	Zhao et al. (2016a, b, c)
1, 10, 100, and 1000 mg/L	25–55 nm	*Daucus carota*	Accumulation of Cu in taproots. No significant effect on growth	Ebbs et al. (2016)
200, 400, and 800 mg/kg	40 nm	*Cucumis sativus*	Perturbation of fruit metabolite profile (sugars, organic acids, amino acids, and fatty acids)	Zhao et al. (2016a, b, c)
10, 200, and 1000 mg/L	20–40 nm	*Oryza sativa*	Reduction in root length, root hairs vigor and shoot biomass, inhibition in the production of phytohormones, promotion of Fe and Na content in roots, increase in isopentenyl adenine in shoots	Le Van et al. (2016)

applied; a threshold of Cu below which no toxicity nor translocation would occur (5-15 mg/kg) (Yruela, 2013). According to Tamez et al. (2020), although it was found that although Cu accumulated in internal plant tissues in the same form, however, the translocation of Cu between parts is directly related to the initial Cu-form (Kocide 3000, Cu-NPs, micro-sized CuO and $CuCl_2$) and the applied dose. The presence of Cu-NPs in root matrix caused inhibition in nutrient uptake (Ca, Mg, K, etc.) in short to moderate Cu-NPs-exposed crops (Adams et al., 2017; Du et al., 2018; Hong et al., 2015; Ochoa et al., 2017; Rawat et al., 2018; Wang et al., 2017). Contradictory findings were reported regarding Sulfur content in plants exposed to Cu-NPs; while it reduced in kidney plants (Apodaca et al., 2017), it was increased in bell pepper roots and leaves (Rawat et al., 2018). The possible reason of the inhibition in S accumulation could be due to an up-regulating effect of Cu ions on sulfate transporters through a bonding ability with sulfate in soil, leading to the formation and translocation of calcium sulfate to plant parts (Hong et al., 2015; Rawat et al., 2018). Inconsistent effects were similarly observed for Mn accumulation under Cu-NPs (Apodaca et al., 2017; Zuverza-Mena et al., 2015).

Exposure of crops to Cu-NPs caused alteration of amino acids reflecting an active defense mechanism. Numerous studies reported in the last 4 years the up-regulation of amino acids in roots (Zhao et al., 2016a, c, 2017a, c, d). Huang et al. (2017), the translocation of Cu in plant parts could be prevented. Instead, such ions will bind firmly with amino acids forming complexes. Short term exposure to Cu-NPs has widely experimented, on the contrary, the interaction crop-Cu-NPs on a long-term basis is highly required. A 200 days exposure of sugarcane to Cu-NPs was recently tested by Tamez et al. (2020) and reflected a reduction in APX and SOD activity, and in nutrient content in roots except for Cu and Zn. Additionally, Tamez et al. (2019), observed on the same crop an induction of oxidative stress. Stress signal was occasionally coupled with a dose-dependent depression in plant growth (biomass, root system), photosynthetic pigments (chlorophyll and carotenoids), physiological traits and yielding capacity (Atha et al., 2012; Mosa et al., 2018; Nair and Chung, 2015; Shi et al., 2014) (Table 2). Atha et al. (2012), the inhibition in the performance of Cu-NPs-exposed crops is due to a mutagenic DNA caused by DNA destruction or alteration. The basis of such a phenomenon is the activation of an antioxidant system through the generation of ROS and alteration of lipid peroxidation (Du et al., 2017; García-Gómez et al., 2017). The toxic effect caused by Cu-NPs was intensively reported in previous studies and stated in this chapter in the previous section. Such toxicity is strongly due to the induction of oxidative stress in exposed plants. The accumulation of copper element in nanoscale form induced ROS production coupled with the accumulation of antioxidant enzymes such as catalase (CAT), peroxidase (POD), and superoxide dismutase (SOD) (Ahmed et al., 2019; Kim et al., 2012).

The table above includes recent experiments done in the last five years. As mentioned previously, the implementation of Cu-NPs in horticulture started 15 years ago. Accordingly, studies before 2016 also pointed out, general and specific aspects of such implementation on crop performance. The exposure of rice to Cu-NPs experimented through a foliar spray, hydroponic system or soil amendment. In all systems, the presence of Cu-NPs caused inhibition in vegetative performance through reduction in germination rate and root morphology and ultrastructure aberration. Additionally, rice-exposed plants showed a decline in photosynthetic pigments and oxidative stress evidenced by an increase in MDA and proline content (Peng et al., 2015b; Shaw and Hossain, 2013). According to Peng et al. (2015a), Cu-NPs moved easily in root membrane starting in the epidermis, exodermis, cortex, and epidermis to arrive in the shoots of rice plants. Moreover, inhibition in nutrient uptake as a result of Cu accumulation was intensively reported following the Cu-NPs exposure of various crops. As a result of Cu accumulation in plant tissues, reactive oxygen species could be formed (Anjum et al., 2015) reflecting the induction of oxidative stress. Fifteen days of exposure of lettuce to Cu-NPs caused a reduction in P and Fe content in shoots (Hong et al., 2015). Similar inhibitory effects on B, Zn, Mn, Ca, Mg, P, and S uptake in shoots were also reported on [cilantro (Coriandrum sativum) (Zuverza-Mena et al., 2015]. Noteworthy, the inhibitory effect of Cu-NPs was occasionally dose-dependent (Shaw et al., 2014); on Syrian barley, only high doses of Cu-NPs reduced shoot and root growth. In all cases, numerous studies described the performance of crops following their exposure to Cu-NPs, the common between almost all these studies is the alteration in plant physiology and performance. These studies included crops such as mung bean, brown mustard, cucumber, lettuce, thale cress, radish, perennial ryegrass, annual ryegrass, wheat, maize, duckweeds, squash etc (Atha et al., 2012; Dimkpa et al., 2012a; Musante and White, 2012; Nair et al., 2014; Nair and Chung, 2015; Pradhan et al., 2015b; Shi et al., 2011; Trujillo-Reyes et al., 2014; Wang et al., 2012).

4 Phytotoxicity and interaction with soil community

In the previous part of this chapter, studies revealed phytotoxicity of Cu-NPs on crops. Phytotoxicity of these particles seemed to be related to their nano-size, duration of exposure and doses. In general, toxicity starts from the soil through the accumulation of nano-copper. This latter complexes with soil organic matter and other metal components or plant exudates making it more stable (Gao et al., 2018; Peng et al., 2017; Servin et al., 2017). Accordingly, the fate and transformation of Cu-NPs and consequently the potential toxicity is highly related to soil characteristics, structure and texture (including aeration, soil pH and temperature) (Anjum et al., 2015; Yu et al., 2018). For instance, sulfidation -a process that increases availability of solubility of Cu-NPs (Ma et al., 2014)—occurs under various environmental conditions related to pH and ions species. Similar conditions also affect aggregation and dissolution of Cu-NPS (Gogos et al., 2017). Shah et al. (2016), an increased rate of Cu-NPs transformation is coupled with low soil pH (acid soils) due to its complexation with H^+ ions leading to the release of copper ions. Nonetheless, the low mobility of Cu element promotes its adsorption in the soil (Ben-Moshe et al., 2013).

The stability of Cu-NPs in the soil makes it toxic for microorganisms considered beneficial for the soil and plants such as nitrifying bacteria, nitrogen-fixing bacteria, Arbuscular mycorrhiza (Kasana et al., 2016). Previous studies reported the inhibitory effects of Cu-NPs on ecosystems microorganisms such as Saccharomyces cerevisiae, cyanobacteria, diatoms and others (Anyaogu et al., 2008; Kasemets et al., 2009). Additionally, the inhibitory role of Cu-NPs on bacterial metabolic activity in the soil which is related to carbon utilization (Echavarri-Bravo et al., 2015; Sillen et al., 2015). Collins et al. (2012) observed a susceptibility of rhizosphere microorganisms belonging to Flavibacteriales and Sphingomonadales to NPs. Similarly, susceptibility to Cu-NPs was observed in the strains *Brevibacillus laterosporus*, *Chryseobacterium indoltheticum*, and *Pantoea ananatis* isolated from soils (Concha-Guerrero et al., 2014). Mohanty et al. (2014), inhibition of CH_4 oxidation could occur as a result of Cu-NPs. On the contrary, Dimkpa et al. (2012a), siderophores- or ion carrier which are compounds with strong soluble iron-binding ability secreted by soil bacteria, fungi and others- were not affected by the exposure to a concentration of Cu ions equivalent to that released by Cu-NPs (Dimkpa et al., 2012b, 2013). Furthermore, *E. coli* and *S. aureus* showed low susceptibility to such particles (Baek and An, 2011). Contradictory findings on the microbes-Cu-NPs interaction have been reported (Anjum et al., 2015). It seems that these metal-NPs have the ability due to their size to penetrate the membrane of microorganisms leading to toxicity as a result of copper accumulation in their cells (Karlsson et al., 2008). The complexation of Cu with intracellular enzymes could also lead to alteration in microorganism metabolic activity and cell death. Mahapatra et al. (2008), this was the case of strains of *Klebsiella pneumoniae, Pseudomonas aeruginosa*, and *Salmonella paratyphi*. Additionally, generation of ROS and disruption of DNA replication were observed to occur in bacteria such as *E. coli* or others exposed to Cu-NPs (Applerot et al., 2012; Deryabin et al., 2013; Lu et al., 2013).

5 Application of copper nanoparticles

Over the past few years, there has been a detonation of interest in the synthesis and applications of various metal nanoparticles due to their outstanding optical and electronic properties, especially gold, copper and silver nanoparticles. Copper nanoparticles (CuNPs) have gradually become an active area of research due to their unique physical, chemical, electrical and optical properties, low cost, availability and exhibit good antibacterial properties (Phillips et al., 2011). The prime advantage of CuNPs is their low cost and its availability compared to gold and silver nanoparticles, resulting in the ample synthesis and various applications of CuNPs.

5.1 Biotic stress

Bacteria, fungi, viruses, nematodes and pests are the principal causative agents of plant diseases (Table 3). Such phytopathogens are responsible for losses of about 10%–40% in the production and efficiency of food crops (Mohamed and Abd-El Hameed, 2014; Helmi and Mohamed, 2016; Mohamed et al., 2016; Sofy et al.,

Table 3 Impacts on Cu-NPs implementation on stressed crops (Part 1: biotic stress).

	Pathogen	Effects	References
CuNP	Red root-rot Disease *Poria hypolateritia*	Maximum control over *P. hypolateritia* infection where the disease incidence was 17.5%	Ponmurugan et al. (2016)
Copper nanoparticles: Cu_2O and CuO	*Pseudomonas aeruginosa Escherichia coli* *Klebsiella pneumoniae Staphylococcus aureus* *Fusarium oxysporum*	These biosynthesized nanoparticles were found to be highly toxic against two Gram-negative, Gram-positive bacterial strains and fungus	Arya et al. (2018)
CuNP	Pink disease *Corticium salmonicolor*	Powerful antifungal activity	Cao et al. (2014)
CuNP	White-rot fungus (*Trametes versicolor*) *Poria placenta*	The highest antifungal effect [under 5% of mass loss (ML)]	Pařil et al. (2017)
CuNP	*Alternaria alternata*, *Botrytis cinerea*	Higher inhibition of both fungi	Ouda (2014)
CuNP 3–10 nm	*F. oxysporum, C. lunata, A. alternata, and P. destructiva*	Antifungal activity	Kanhed et al. (2014)
Cu2O, CuO Cu/ Cu_2O (11–14 nm)	*Phytophthora infestans*	All the tested copper-based nanoparticles were effective against the fungi	Kasana et al. (2016)
CuNP	*Fusarium* sp.	The diameter of the fungal colony almost does not increase and could inhibit 93.98% of the fungal growth of fusarium after 9 days of incubation	Viet et al. (2016)
(CuChNp)	Blast disease *Pyricularia grisea*	In vitro: A typical inhibition of fungal spore germination (up to 80%) of *P. grisea* was found in CuChNp amended medium when compared to control In vivo: CuChNp application delayed the blast symptom appearance in finger millet plants	Sathiyabama and Manikandan (2018)
CuNPs (50–100 nm)	*Alternaria alternate*	In vitro: Largest inhibition zone of A. alternate in response to 90µg/mL of Cu NPs compared to 60 µg/mL, 30 µg/mL and control In vivo: 90 µg/mL CuNPs showed highest antifungal activity and lowest lesion diameter of tomato rot after treatment compared to control and other treatments	Al-Dhabaan et al. (2017)

Copper-chitosan nanocomposition (CuCs)	The Fungus, *Fusarium oxysporum*	In vitro: 100% fungal inhibition	Mohamed et al. (2018)
CuNP	*Alternaria carthami, Aspergillus niger, Fusarium oxysporum Colletotrichum gloeosporioides, Colletotrichum lindemuthianum, Drechslera sorghicola, Macrophomina phaseolina, Rhizoctonia bataticola* *Rhizopus stolonifer*	Strong antimicrobial activity against plant fungal pathogen The maximum activity of copper nanoparticles was found against fungal pathogen *Alternaria carthami* (zone of inhibition 18.5 $\pm$ 1.7) while the minimum activity was found against *Rhizopus stolonifer* (zone of inhibition 10.5 $\pm$ 0.5)	Shende et al. (2016)
CuNP	*Rhizoctonia solani, Xanthomonas axonopodis* pv. *punicae Xanthomonas axonopodis* pv. *citri*	Strong antimicrobial activity against plant bacterial pathogen The maximum activity of copper nanoparticles was found against bacterial pathogen *Xanthomonas axonopodis* pv. punicae (zone of inhibition 17.25 $\pm$ 0.95) while the minimum activity was found against *Rhizoctonia solani* (zone of inhibition 10 $\pm$ 0.81)	Shende et al. (2016)
CuNP	*Puccinia. cinnamomi* *Pseudomonas syringae*	60% growth inhibition compared to 46% with a commercial formulation of CoC completely inhibited the bacterial growth	Banik and Luque (2017)
Cu@TWEEN20 and Cu@TEG NPs	*Erwinia amylovora Pseudomonas syringae Xanthomonas campestris*	Inhibition of bacterial growth	Gkanatsiou et al. (2019)
Cu@TWEEN20 NPs	*Pseudomonas syringae*	Bacterial growth was totally inhibited after 48 h	Gkanatsiou et al. (2019)
CuNP	*Xanthomonas axonopodis* pv. Punicae pomegranate bacterial blight	Reduced number or no watersoaked areas developing on leaves infiltrated with Xap treated with nanocopper compared to the control.	Mondal and Mani (2012)
CuNP	Storage Pest *Tribolium castaneum*	*T. castaneum* was suppressed after 5 days of exposure	El-Saadony et al. (2020)

Continued

Table 3 Impacts on Cu-NPs implementation on stressed crops (Part 1: biotic stress)—cont'd

	Pathogen	Effects	References
Copper oxide nanosheets (CuO)	*Spodoptera littoralis* (Lepidoptera: Noctuidae)	The third-instar and fifth-instar groups' cumulative larval mortality reached 48.3% ± 0.43% and 46.6% ± 1.0% when fed for 1 day, and it increased to 97.6% ± 1.3% and 100% when fed for more than 4 days Mortality in the control groups did not exceed this percentage 5.8% ± 0.2%	Atwa et al. (2017)
Cu/ Zn-nanoparticles Size is 74.33–59.46 nm	Cotton Mealybug, *Phenacoccus solenopsis* (Hemiptera: Pseudococcidae)	More than 30% mortality of *P. solenopsis* was observed with Cu/Zn-nanoparticles after 96 h of treatment. A significant reduction of the cell viability by 50% in insect exposed to Cu/Zn-nanoparticles	Mendez-Trujillo et al. (2019)
CuO NP Size is 40 nm	Green peach Aphid *Myzus persicae*	Percentage mortality of first, second, third and fourth Nymphal instars is 86%	Ghidan et al. (2016)
Copper oxide nano-capsules Size is 50nm	Two Spotted Spider Mite (*Tetranych usurticae*)	The population of the mite after 72 h of treatment was 1 mite while that of the control was 26.7	Dorri et al. (2018)
CuNP Size is 100 nm diameter	Root-knot Nematode *Meloidogyne Incognita*	100% mortality of J2 after 3 days of incubation.	Mohamed et al. (2019)
CuNP	*Escherichia coli* *Staphylococcus aureus*	Antibacterial activity	Awwad and Amer (2020)
CuNP	*Escherichia coli, Pseudomonas aeruginosa, Klebsiella pneumoniae, Staphylococcus aureus* *Aspergillus niger* and *Candida albicans*	Antifungal and antibacterial activity	Bhavyasree and Xavier (2020)
Cu-chitosan NCs	*Rhizoctonia. solani*	Antifungal activity	Rubina et al. (2017)
Cu-chitosan NCs	*Rhizoctonia solani*	Antifungal activity	Abd-Elsalam et al. (2018)

2020a, b; Mansour et al., 2020). While it is not possible to eliminate diseases and pests, its management was an area of continuous improvement. Traditional control of pests relies heavily on pesticides, such as insecticides, fungicides, and herbicides. Given many benefits, such as high quality, quick action and efficacy, pesticides have harmful side effects on nontarget species, the revival of the pest population and resistance (Mohamed and Akladious, 2017; Mohamed et al., 2018a). Another way to control pathogens is used of hormones and natural compounds like Jasmonates, essential oils, benzothiadiazole, and Trichoderma are the examples of natural compounds that help to minimize plant infections (Aly et al., 2012, 2013, 2017; Abd El-Rahman and Mohamed, 2014; Ashry et al., 2018). However, the resistance of plant pathogens and pests to pesticides, the formation of resistant isolates and accumulation of high quantities of agrochemical contaminants in the ecosystem. All these factors have researchers urged them to look for fresh and reliable materials that do not cause resistance and are less costly (Lamsal et al., 2011). Currently, the metallic nanoparticles are thoroughly being explored and extensively investigated as a potential for the control of plant diseases and pests, early-stage detection of pathogen, and eliciting an immune response in the host plants. Several types of metallic nanoparticles such as silver, copper and gold have been documented to demonstrate high activity against some microbes, microorganisms and pests. Moreover, copper nanoparticles are more cheaper than silver or gold nanoparticles so that the use of copper nanoparticles as antimicrobial agents have recently been given more attention than the other nanoparticles (Cao et al., 2014). The biocidal activity of CuNPs and/or the copper ions discharged from CuNPs could be due to its strongly adsorbed on the surface of the microbial cells due to the large surface area of the nanoparticles which caused (i) disruption of the permeability of cells and release of essential elements (Raffi et al., 2010), (ii) denaturation of integrated biomolecules (Wei et al., 2010), and (iii) stimulation of microbial cell oxidizing damage (Delgado et al., 2011). At the same time, the copper ions discharged may be moved within microbial cells or attached to its external surfaces leading to cell apoptosis via protein denaturation and cell membrane disruption (Palza, 2015). The capability of copper nanoparticles to control plant pests can reflect the ability of nanoparticles to transcend epithelial cells lining the gut and endothelial cells via transcytosis (Yamanaka and Leong, 2008). Furthermore, nanoparticles can proceed easily along the dendrites, axons, blood, and lymphatic vessels, causing oxidative stress and other effects (Oberdörster et al., 2005). This section deals with the antimicrobial and pest activity studies carried out with the copper nanoparticles.

5.1.1 Fungicidal effect

The biologically synthesized copper nano-fungicide could be a possible alternative control measure for tea root disease, which in turn have a very high surface area with a tremendous driving force for diffusion in rhizosphere that ultimately reduces the dependency on commercially available bulk copper fungicide (Ponmurugan et al. 2016). Furthermore, copper nanoparticles showed the highest antifungal activity in rubber trees infected with *Corticium salmonicolor* (Cao et al. 2014). Another study deals with the antifungal effects of copper nanoparticles on beech wood specimens against white-rot fungus (*Trametes versicolor*) and pine wood against brown-rot fungus (*Poria placenta*). This research has shown that copper nanoparticles at the concentration of 3 g/L are effective against both tested fungi (under 5% of ML) (Pařil et al. 2017). Also, higher fungal growth inhibition of *Alternaria alternata* and *Botrytis cinerea* was observed at a concentration of 15 mg/L of three nanoparticles tested (AgNPs, CuNPs, and Ag/Cu NPs) and the two fungi showed growth inhibition with increased incubation time. (Ouda, 2014). In addition, there is an antifungal activity of CuNPs against plant pathogenic fungi *F. oxysporum*, *C. lunata*, *A. alternata*, and *P. destructive*. CuNPs was more effective than fungicide bavistin against all pathogenic fungi (Kanhed et al., 2014). Another study showed a typical inhibition of spore germination (up to 80%) of *Pyricularia grisea* responsible for blast. Antifungal activity of CuNPs (50–100 nm) on tomato fruits rot caused by *A. alternate* increased gradually three weeks after treatment. Injecting tomato fruits with 90 μg/mL CuNPs before infecting the fruits with the suspension of *A. alternate* displayed very little development of the fungus after one week of incubation accompanied by very mild symptoms (Al-Dhabaan et al. 2017).

In vivo and in vitro experiments were conducted to study the effect of copper-chitosan nano-composition (CuCs) on the fungus, *Fusarium oxysporum* of a date palm. The results showed 100% fungal inhibition in vitro. While in vivo, disease severity of the inoculated date palm seedlings treated with nano-composition was significantly lower than that of the inoculated date palm seedlings which were treated with RizolexTM (+ ve Control) and water (− ve Control) (Mohamed et al., 2018). Also, Shende et al. (2016) study the antifungal activity of CuNP on various phytopathogenic fungi showed maximum activity of copper nanoparticles on fungal pathogen *Alternaria carthami* (18.5 ± 1.7) while the minimum activity against *Rhizopus stolonifer* (10.5 ± 0.5).

5.1.2 Bactericidal effect

The antimicrobial effect of biologically synthesized copper nanoparticles from tulsi leaf extract was analyzed based on the zone of inhibition. Copper nanoparticles exhibited strong antimicrobial activity against plant bacterial pathogen such as *Rhizoctonia solani*, *Xanthomonas axonopodis* pv. *citri*, *X. axonopodis* pv. *punicae*. Copper nanoparticles have been found to have the maximum activity against bacterial pathogen *X. axonopodis* pv. *punicae* (17.25 ± 0.95), though marginal activity against *R. solani* was found (10 ± 0.81). For *R. solani*, the MIC of copper nanoparticles against bacteria was found to be 0.01 mg/mL and 0.03 mg/mL for *X. axonopodis* pv. Punicae and *Axonopodis Xanthomonas* pv. *citri* (Shende et al. 2016).

Another study showed inhibition of *oomycete P. cinnamomi* against CuNPs, which is the most devastating plant pathogens causing substantial economic losses in agriculture, forestry and horticulture. CuNPs recorded near 60% growth inhibition compared to 46% with a commercial formulation of CoC at a dose of 100 mg/L. In addition, the growth of *Pseudomonas syringae* bacteria which can infect a wide range of species was completely inhibited in vitro with CuNPs at 200 mg/L (Banik and Luque, 2017).

5.1.3 Insecticidal effect

In this study, CuNPs are biosynthesized by *Pseudomonas fluorescens*. They were tested for Insecticidal activity against the storage pest *Tribolium castaneum.* The mortality rates of *T. Castaneum* adults increased their exposure time with increased concentration of Bio CuNPs. More precisely, LC50 of adults *T. castaneum* treated for 24 h exposure to Bio CuNP's were 693.7 ppm. This value decreased dramatically to 130.5 and 36.89 ppm after three and 5 days, respectively. Besides, *T. castaneum* was suppressed at the higher concentration of Bio CuNPs (300 ppm) after 5 days of exposure (El-Saadony et al., 2020). The insecticidal effect of pure and silver-doped copper oxide nanosheets on *Spodoptera littoralis* (Lepidoptera: Noctuidae) was studied. There was a significantly higher effect when the CuO in the diet was increased to 300 mg. Cumulative larval mortality in the third-instar and fifth-instar groups reached 48.3% ± 0.43% and 46.6% ± 1.0% when fed for 1 day, and it increased to 97.6% ± 1.3% and 100% when fed for more than 4 days. Mortality in the control groups did not exceed 5.8% ± 0.2%. Thus, a longer feeding duration with the treated diet resulted in higher larval mortality (Atwa et al., 2017). Another study was conducted to investigate the effect of green synthesized Cu/Zn-nanoparticles using an aqueous leaf extract of *Prosopis juliflora* (mezquite) against *Phenacoccus solenopsis*. The results of the viability test for Cu/Zn-nanoparticles of *P. juliflora* showed a significant reduction of the cell viability by 50% in insect exposed to Cu/Zn-nanoparticles *P. juliflora* (Mendez-Trujillo et al., 2019). In this in vitro experiment, Copper oxide nanoparticles were synthesized using *P. granatum* peel extract and its effect on green peach aphid was investigated. The results revealed that CuONPs (8000 μg/mL) can cause 86% mortality of first, second, third and fourth Nymphal instars of green peach aphid, *Myzus persicae* (Ghidan et al., 2016). Also, Dorri et al. (2018) studied the effect of Copper Nano-capsules on regulating Two Spotted Spider Mite (*Tetranych usurticae*). After 72 h of treatment, the mite population revealed that the highest number of mites was linked to the control treatment (26.7), and the lowest was 5 (5.5 g/L nanocapsule) with 1 mite.

5.1.4 Nematicidal effect

In vitro nematicidal efficiency of copper Nanoparticles against Root-knot Nematode *Meloidogyne incognita* was evaluated. Juveniles (J2) of M. incognita were incubated in soil saturated with CuNPs (spherical shape; 100 nm diameter) for 3 days, it was found that J2 mortality is directly proportional to the concentration of CuNPs and 0.2 g/L was sufficient to cause 100% mortality (Mohamed et al., 2019).

5.1.5 Mechanism of antimicrobial activity of CuNPs

CuNPs antimicrobial activity relates to ions emitted from nanoparticles. The behavior is further intensified by its small size and high surface area to volume, which helps them to communicate closely with microbial membranes (Dizaj et al., 2014). The antimicrobial activity is caused by its tendency to switch between the oxidation states of its cuprous-Cu [I] and cupric-Cu [II] (Fig. 2). NPs cause further damage to the bacterial cells since Cu ions can form ROS on the surface in the presence of

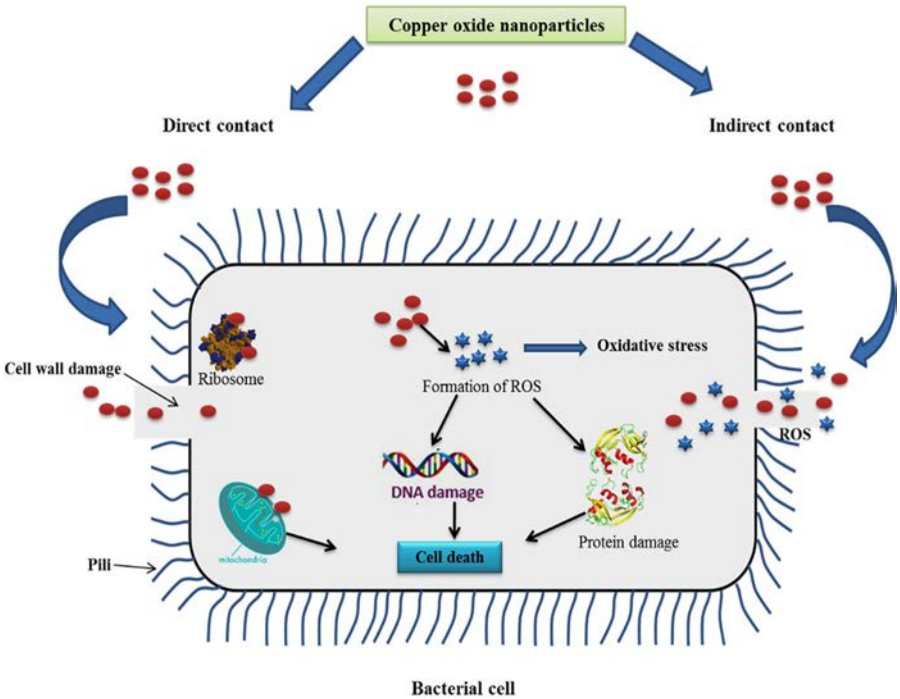

FIG. 2

The diagrammatic representation of copper nanoparticles antibacterial mechanism.

different functional amine groups from biological molecules (Pramanik et al., 2012). NPs can bind with DNA molecules after entering the cell and damage the helical structure by cross-linking the nucleic acid strands within and between them. Copper ions also disrupt biochemical processes inside bacterial cells. Also, copper ions can form chelates with biomolecules which can cause functional protein inactivation. Some studies thought NPs could spread directly across the membrane when the size was small enough. Meanwhile, NPs travel through the ion channels and the transporter proteins to cross the plasma membrane. Many NPs join cells by "endocytosis": they are surrounded by the membrane, and vesicles carry NPs to cells (Chang et al., 2012). The effect of the intracellular ROS mediated by CuNPs occurs. NPs can interact directly with oxidative organelles such as mitochondria, redox-active proteins can stimulate the development of ROS in cells, and NP-produced ions can induce ROS through various chemical reactions. ROS can induce breakage of DNA strands and affect gene expression. CuNPs activity originates primarily from the Cu^{2+} species' direct contact with the cell components. Cu^{2+} reduces the cell components to Cu^{+} and is primarily responsible for the inactivation of bacteria (Meghana et al., 2015). In another studies, copper nanoparticles have been identified as an effective antibacterial agent against the broad range of bacterial species due to interactions with phosphorous and −SH groups resulting in DNA and protein denaturation (Schrand et al., 2010). In general, the smaller particle size results in greater antimicrobial action (Zain et al., 2014).

5.2 Abiotic stress

Since their emergence, plants have inherently lived in harsh environments. Various physical or chemical factors are detrimental to them, including low or high temperature, insufficient or excessive moisture (drought or flood), high salinity, heavy metals, and ultraviolet (UV) radiation (Table 4). These stresses (collectively referred to as abiotic stresses) are posing a serious threat to agriculture and ecosystems, leading to a decline in crop yields (Mohamed and Abdel-Hamid, 2013; Wani et al., 2016; Mohamed et al., 2019).

Due to their sessile nature, plants must face pressure and develop effective adaptation strategies to avoid or endure their adverse effects to survive and reproduce. Many cellular, physiological and morphological defenses have been established. The most obvious is the cuticle, a universal outermost shield Yeats and Rose, 2013).

Therefore, what is emerging is the desaturation of membrane lipids, the activation of reactive species (RS) scavengers, the induction of molecular chaperones, and the accumulation of compatible solutes are more general and conservative of cell defense responses. This is consistent with the fact that membrane damage, RS damage, protein denaturation and osmotic pressure (mainly dehydration) can be caused by a variety of abiotic stresses. In the stress response, these defense mechanisms are carefully designed by a complex regulatory network involving upstream signalling molecules, including stress hormones [such as abscisic acid (ABA), reactive oxygen species (ROS), and hydrogen sulfide (H_2S), nitric oxide (NO), polyamines] (PAs), plant pigments and calcium (Ca^{2+}), and downstream gene regulators, especially transcription factors (TFs).

In the field, plants often endure unpredictable combinations of stress, rather than a single (Slama et al., 2015; Wani et al., 2016). In the case of climate change, soil salinization and environmental pollution, the situation is even worse. Under the demand of population growth, crops must be equipped with multistress tolerance.

Abiotic stress leads to a series of morphological, physiological, biochemical, and molecular changes that adversely affect plant growth and productivity. Drought and salinization are the most common abiotic pressures, threatening global food security. The development of stress-resistant plants may be a valuable strategy to solve the problem of declining global food production. Traditional breeding methods have achieved limited success in improving the stress resistance of crops. To this end, there is an urgent need to explore new strategies and develop them to complement existing traditional and advanced breeding tools (Scrinis and Lyons, 2007). Among the latest technologies, nanotechnology is the most promising technology in the era of agriculture and plant biotechnology. The application of nanoparticles or nanodevices will affect all stages of plant development, whether positive or negative. Nanotechnology has the novel characteristics of nanomaterials, which can easily carry out agricultural

Table 4 Impacts on Cu-NPs implementation on stressed crops (Part 2: abiotic stress).

Abiotic stresses	Optimum concentration/ Treatment duration	Plant species	Stress response	References
Salinity stress	250 mg/L of Cu NP	Tomato (*Solanum licopersicum*)	Increase and maintain the content of bioactive compounds caused by saline stress	Hernández-Fuentes et al. (2017)
	250 mg/L of Cu NP	Tomato (*Solanum licopersicum*)	Foliar spraying of copper nanoparticles on tomatoes under salinity appears to induce stress tolerance to salinity by stimulating the plant's antioxidant mechanisms	Pérez-Labrada et al. (2019)
Drought stress	CuO, 300 mg/kg 7 days	*Triticum aestivum* L	CuO and ZnO NPs interacted with root-colonizing microbes and altered plant growth and function under drought	Yang et al. (2018)
	Seed pretreatment with colloidal solution of Cu and Zn nanoparticles	*Triticum aestivum* seedlings	Cu, Zn-nanoparticles decreased the negative effect of drought action upon plants	Taran et al. (2017)
Mineral toxicity	CuO, 200, 400, and 800 mg/L	*Coriandrum sativum*	Root length and biomass where both decreased significantly in accordance with increasing CuNP concentration, along with a significant decrease in total chlorophyll content	AlQuraidi et al. (2019)
	50, 100, and 200 mg/L of CuNP	*Cucumis sativus*	Adverse phenotypical changes along with decreased biomass and decreased levels of the photosynthetic pigments (Chlorophyll a and b) in a concentration-dependent manner. Moreover, CuNP induced damage to the root plasma membrane as determined by the increased electrolyte leakage. A significant increase in H2O2 and MDA contents were detected in C. sativus CuNP treated plants	Mosa et al. (2018)

research and relieve stress in crop improvement programs. The main significant effect of plant abiotic stress is usually caused by oxidative stress (Servin and White, 2016). Under this oxidative stress, nanomaterials can help stressed plants to strengthen their defense systems, including antioxidant enzymes, mainly peroxidase, superoxide dismutase and catalase (Patra et al., 2016). On the other hand, these nanomaterials may also cause oxidative stress in plants at higher concentrations (Li et al., 2015; Saharan and Pal, 2016; Zaytseva and Neumann, 2016) due to the accumulation of reactive species (oxygen and nitrogen) leading to damage in proteins, nucleic acids and cell membrane (Khan et al., 2017).

Copper is an important element of plant nutrition (Yruela, 2005). On average, 1 kg of dry plant tissue contains 10 mg of copper. Extensive research has been conducted on the deficiency or excess of copper in plants (Yruela, 2005). However, there is limited information about the role of copper-based nanomaterials in plants. Research on plant exposure to Cu based nanomaterials includes metallic nano copper (nCu), nano-CuO (nCuO), and composite nanoparticles of a Cu core coated with CuO. To this end, in this chapter, we try to outline the effects of nano-copper on plant abiotic stress.

5.2.1 Salinity

Salt stress is the stubbornest kind of global increase in the salinity of cultivated land (Yuan et al., 2015; Mohamed et al., 2018b; Ghonaim et al., 2020). When the NaCl concentration exceeds 200 mM, most plants will not survive (Zhou et al., 2016), because high salinity will widely affect its life cycle, including seed germination, seedling growth, vegetative growth and flowering (Guo et al., 2018) are caused by ion toxicity, osmotic pressure, oxidative damage and nutritional deficiencies (Feng et al., 2014; Zhao et al., 2010). More seriously, it is interlinked with drought, another global issue, which can be aggravated by extreme temperatures (Slama et al., 2015).

Soil salinity reduces crop yields and ultimately reduces crop productivity in salt-affected areas, posing a global threat to global agriculture. Salt stress reduces crop growth and yield in many ways. Salt stress has two main effects on crops. Osmotic pressure and ionic toxicity. Due to the increase in salinity, the osmotic pressure in soil solution under salt stress exceeds the osmotic pressure in plant cells, thus limiting the ability of plants to absorb water and minerals such as K^+ and Ca^{2+}. These primary effects of salt stress cause some secondary effects, such as the production of assimilate, the reduction of cell swelling and membrane function, and the reduction of cytoplasmic metabolism.

5.2.2 Drought

Nowadays, due to the continuous increase in temperature and carbon dioxide levels in the atmosphere, the climate around the world has changed (El-Beltagi et al., 2020a). Due to climate change and uneven rainfall distribution, drought is important to stress for plants Due to severe drought conditions, the soil water available for plants has steadily increased and caused premature plant death. The stagnation of crop growth caused by drought is the first response to plants. Plants under drought conditions will reduce the growth of buds and reduce their metabolic requirements. Afterwards, plants under drought conditions synthesize protective compounds by mobilizing the metabolites required for their osmotic adjustment (Mohamed et al., 2018b, 2018c).

Nanoparticles improve drought resistance by enhancing antioxidant systems, nutrient absorption, photosynthesis, reducing reactive oxygen species, and regulating protein and signal transduction pathways. From the compiled information, the role of nanoparticles varies from plant to plant and depends on its application, size, and concentration. Besides, more research is needed to explore the mode of action of nanoparticles, their interaction with biomolecules, and their effect on plant gene regulation and expression under drought stress.

5.2.3 Mineral toxicity

The increasing dependence of agriculture on fertilizer and sewage irrigation and rapid industrialization have added toxic metals to agricultural soils, which have had a detrimental effect on the soil-plant environmental system (Akladious and Mohamed, 2017; El-Beltagi et al., 2020b; Moustafa-Farag et al., 2020; Sofy et al., 2020a, b).

Nanotechnology promises a significant effort to mitigate the drought stresses. Several recent studies (Table 4) have evaluated nanoparticle-mediated in different stresses.

6 Conclusion and prospects

The implementation of Cu-NPs in agro-ecosystems seems to have phytotoxic to neutral effects except when applied on biotic stress. These effects varied based on plant species, exposure duration and dose and method of application. In this chapter, numerous studies reported the bioaccumulation of copper in nanoscale in plant parts (roots, stems, and leaves). Green synthesis of copper and copper oxide nanoparticles has gained great significance in the recent past due to its simplicity, cost-effectiveness and environment-friendly nature. Synthesis of metal/metal oxide NPs by the green method is more environmentally friendly than chemical synthesis methods. A large number of plant extracts have been successfully applied for the biogenic synthesis of Cu and CuO NPs. The bioactive compounds in the plant extracts were found to play a dual role of reduction of the copper ions and stabilization of copper NPs. Thus, affecting plant metabolism and inducing oxidative stress. Additionally, soil properties and bacterial community also were affected by Cu-NPs accumulation. The effect of Cu-NPs is highly related to soil texture and properties; toxicity was more evidenced more in sandy and loamy soil and less in clay soil. Regardless of these effects, statistics reflect an increase in Cu-NPs production and demand. Accordingly, additional studies and researches should focus on the fate, biotransformation and accumulation of Cu-NPs in ecosystems aiming to reduce the toxicity of such particles in soils and plants.

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