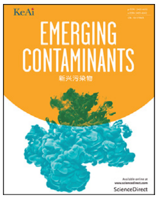
Emerging Contaminants 10 (2024) 100352

Contents lists available at ScienceDirect

Emerging Contaminants

journal homepage: www.keaipublishing.com/en/journals/emerging-contaminants



Copper nanoparticles as a potential emerging pollutant: Divergent effects in the agriculture, risk-benefit balance and integrated strategies for its use

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ARTICLE INFO

Article history:
Received 15 January 2024
Received in revised form
29 March 2024
Accepted 30 April 2024

Keywords:
Cu-based NPs
Agriculture
Plant growth
Pest control
Soil interaction

ABSTRACT

At the forefront of agricultural innovation, copper-based nanoparticles (Cu-based NPs) have seized global attention in recent years, revolutionizing fields as diverse as electronics, medicine, and, notably, agriculture. Their prowess in combating phytopathogenic microorganisms, boosting plant yield and defenses, and their dual role as pesticides or fertilizers - depending on the dosage - positions them at the epicenter of exciting scientific advancements. However, this is a two-edged sword: the environmental impact of Cu-based NPs is an escalating concern. The release of these particles post-use raises serious questions about the accumulation of toxic copper levels in soil and, consequently, in crops. In a market with rising metal nanoparticles, a deeper exploration is essential to balance the benefits and risks associated with Cu-based NPs in agriculture. This review synthesizes the state-of-the-art Cu-based NP synthesis, their application as antimicrobial agents, pesticides, and fertilizers, and their interactions with soil, highlighting its advantages and disadvantages. Finally, we delve into future perspectives, spotlighting the research gaps in Cu-based NP studies that beckon for attention in the coming years.

1. Introduction

Nanotechnology has swiftly risen to prominence, playing an indispensable role in many fields, encompassing industry, medicine, agriculture, chemistry, food science, and electronics [1,2]. This ascent is mainly due to the unique reactivity of nanoparticles (NPs), which stems from their diminutive size (within the 1–100 nm range) and a substantially increased surface-area-to-volume ratio. These attributes have propelled the application of NPs to the forefront of burgeoning scientific inquiry [3]. In particular, the development of metal and metal oxide nanoparticles (MNPs) has seen an exponential rise, credited to their superior physicochemical properties that notably enhance biological activities in agricultural systems. Prominent MNPs, such as Au, Ag, Fe, Cu, and Zn, have undergone extensive testing in model organisms to ascertain their efficacy in fostering plant growth and pest control, underscoring their potential to revolutionize agricultural practices [4,5].

Despite their promise, MNPs undergo chemical transformations,

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Peer review under responsibility of KeAi Communications Co., Ltd.

https://doi.org/10.1016/j.emcon.2024.100352

transport, aggregation, and dissolution within agricultural systems, posing potential environmental risks [6]. The dose-dependent effects of MNPs have been demonstrated in various studies involving living model organisms. Notably, MNPs can exhibit toxic effects on diverse organisms and microorganisms within ecosystems at higher concentrations, mainly due to bioaccumulation, biomagnification, and translocation processes [7]. Considering these concerns, many research efforts have been directed towards assessing the environmental impact of MNPs, aiming to comprehensively understand their effects on plant-soil ecosystems and human health [8]. Specifically, copper and copper oxide nanoparticles (Cu-based NPs) have garnered significant interest in agriculture due to their crucial roles in the biological processes of animals, plants, and microorganisms [9–11]. A range of Cu-related products, including copper salts, metallic copper, copper sheets, bimetallic (Ag-Cu) compositions, and more recently, Cu-based NPs or copper-polymer composites, have been extensively researched for their antimicrobial properties against bacteria, yeasts, fungi, nematodes, and viruses [12–14]. In this context, copper nanoparticles, encompassing various copper forms, are emerging as a vital tool in agriculture. Their use not only enhances agricultural yield but also plays a key role in minimizing the impacts of pests, thereby contributing to more sustainable and efficient agricultural practices.

Emerging contaminants refer to all chemical compounds or substances identified with potential or actual hazards to human health or the environment or those not yet regulated by existing health standards [15–17]. Nanomaterials and nanoparticles, including Cu-based nanoparticles, are considered emerging contaminants [17] due to the identification of new direct or indirect pathways through which Cu-based nanoparticles can be spread in the environment, highlighting their status as a significant concern worldwide. In recent years, a growing body of research has endorsed using Cu-based nanoparticles (NPs) in agriculture, highlighting their potential to address challenges related to global food demand and scarcity [18–21]. On one front, Cu-based NPs have been recognized as a viable alternative to traditional pesticides, showcasing remarkable antifungal efficacy against a variety of plant pathogens, including *Fusarium kuroshium*, *Colletotrichum gloeosporioides, Rhizoctonia solani, Pythium aphanidermatum, Botrytis cinerea, Sclerotinia sclerotiorum*, and *Phytophthora infestants* [22–26]. Notably, nanocomposites containing Cu-based NPs have proven effective in combating copper-resistant *Xantomonas perforans*, a significant cause of tomato bacterial spots [27]. On another front, Cu-based NPs have gained attention as potential fertilizers at lower concentrations, demonstrating an ability to enhance plant growth and yield [19,20,28,29]. Thus, Cu-based NPs emerge as a multifaceted tool, offering a sustainable solution to mitigate the adverse effects of excessive chemical pesticide and fertilizer use. However, it's crucial to recognize Cu-based NPs as potential emerging pollutants, especially in water and soil at specific concentrations. Several studies have revealed that Cu-based NPs can disturb various ecological compartments, posing environmental risks at doses exceeding 0.5 mg kg^{-1} of Cu-based NPs in soil [30–33].

This underscores the need for a balanced approach in their application, ensuring agricultural efficacy while safeguarding environmental health. Toxicological studies of different Cu-based NPs have been carried out to determine their ecological and human impact. It is essential to mention that Cu-based NPs behavior has depended on their physicochemical properties and environmental chemistry (i.e., salinity, pH, total organic carbon, ionic strength, temperature, and redox potential, among others), being relevant parameters to evaluate their toxicity [34]. For instance, Cu-based NPs at doses from 5 to 20 mg per plant trigger the generation of reactive oxygen species (ROS) [35]. In the same study, the authors unveiled that Cu-based NPs can be rapidly dissolved in water, oxidized, and transformed into the soil, promoting their persistence at toxic levels (>50–500 μg L^{-1}). Furthermore, the toxic dose of Cu-based NPs has been 10 times lower than their ionic form in different organisms such as rodents, plants, aquatics, and cell cultures, showing their cytotoxic [36]. Therefore, knowing the risks of using Cu-based NPs is essential to determine their environmental implications. This review presents comprehensive literature about the advantages and disadvantages of Cu-based NPs for agriculture, with particular emphasis on plants.

2. Synthesis of copper-based nanoparticles (Cu-based NPs)

The synthesis of Cu-based NPs is pivotal in advancing nanotechnology and its myriad applications. While this topic is not the central focus of our review, in-depth explorations regarding applications in various fields can be found in the works of Bhagat et al. [37]. Various methods have been employed in synthesizing Cu-based NPs, from physical and chemical to biological approaches. Chemical methods, for instance, often involve the reduction of copper using agents like sodium borohydride [38], aqueous hydrazine solution [39], or ascorbic acid [40]. Other notable techniques include hydrothermal synthesis [41], the sol-gel process [42], laser ablation [43], photochemical reactions [44], and electrochemical methods [45], each offering unique advantages in terms of particle size control, distribution, and morphology.

A critical challenge in synthesizing Cu-based NPs is the rapid oxidation of copper ions upon exposure to oxygen, which can lead to unwanted nanoparticle aggregation. This oxidation not only complicates the synthesis process but also affects the stability and quality of the nanoparticles. To mitigate this issue, researchers have developed strategies to protect the nanoparticles. One practical approach involves coating the nanoparticles with protective polymers such as poly (allylamine) or allylamine, which can prevent oxidation for extended periods, ranging from 30 to 60 months [46]. Additionally, the use of thiolate capping ligands, particularly those with short alkyl chains like $-(CH2)_2-$ and a hydrophilic carboxylic acid end group, has been proposed as an effective means to retard copper oxidation [47]. These innovations in synthesis techniques enhance Cu-based NPs' stability and expand their potential applications across various domains, including agriculture, medicine, and environmental remediation.

Chemical synthesis has been one of the most used methods for obtaining Cu-based NPs since it is possible to obtain small and homogeneous nanoparticles by controlling reaction parameters such as pH, temperature, and reaction time, among others. In this context, the main disadvantage is the production of toxic wastes because of the use of solvents, which can negatively impact the environment. As an alternative, nanobiotechnology proposes using environmentally friendly and safe methods. Herein, the biogenic synthesis of nanostructures fulfills these requirements [48]. Generally, various microorganisms, algae, and plants have been satisfactory in synthesizing Cu-based NPs. Some examples of Cu-based NPs synthesized through biogenic routes are shown in Table 1. In plants, extracts of different parts, such as stems, flowers, or leaves, have been helpful for biogenic synthesis. An important aspect is that controlling the nanoparticle size is more complicated in biogenic synthesis. In this sense, the concentration or type of compounds participating in nanoparticle formation is entirely different at intraspecific or interspecific levels. For this reason, as shown in Table 1, sizes are varied but always on a nanometric scale and efficient in terms of antimicrobial capacity.

Table 1
Copper-based nanoparticles synthesized through biogenic route and their antimicrobial activity.

Biological Source	Size (nm)	Shape	Antimicrobial Activity	Dose	Reference
Pseudomonas fluorescens **and** ***Trichoderma viride*** **(cell-free extract)**	40–100 20–80	Irregular-shaped and spherical	*Phytophthora parasitica*	100–150 mg L^{-1}	[169]
Cynodon dactylon **(leaf extract)**	120–129	Spherical	*Escherichia coli* *Bacillus subtilis Staphylococcus aureus* *Klebsiella pneumoniae*	50–200 μg mL^{-1}	[170]
Delonix regia **(leaf extract)**	69–108	Marginally spherical	Not reported	Not reported	[171]
Celastrus paniculatus **(leaf extract)**	2 ± 10 nm	Spherical	*Fusarium oxysporum*	0.12–0.24 % w/w	[172]
Aspergillus terreus **(cell free filtrate)**	50	Spherical	*Staphylococcus aereus Bacillus subtilis* *Candida albicans* *Aspergillus niger* *Aspergiullus terreus* *Penicillium expansum* *Fusarium oxysporum*	Not reported	[173]
Aspergillus flavus **(fungal supernatants)**	5–12	Spherical	*Aspergillus niger* *Fusarium oxysporum Alternaria alternata*	Not reported	[174]
Antartic bacterial strains: ***Marinomona*** **ef1,** ***Rhodococcus*** **ef1,** ***Pseudomonas*** **ef1,** ***Brevundimonas*** **ef1, and** ***Bacillus*** **ef1**	40	Spherical/ovoidal	*Escherichia coli* *Staphylococcus aureus Candida albicans*	3.12–25 μg mL^{-1}	[175]
Cassia auriculata **(flowers extract)**	200	Spherical	*Staphylococcus aureus Escherichia coli* *Serratia sp* *Aspergillus niger Aspergillus fumigatus*	250–1000 μg mL^{-1}	[176]
Macrocystis pyrifera **(aqueous extract of brown algae)**	2–50	Spherical	Not reported	Not reported	[177]
Sargassum longifolium **(aqueous extract of brown algae)**	40–60	Spherical	*Vibrio parahemolyticus Aeromonas hydrophila* *Serratia marcescens* *Vibrio harvey*	25–100 μg mL^{-1}	[178]
Hyptis suaveolens **(leaf extract)**	7.2	Spherical	*Bacillus cereus* *Pseudomonas fluorescens* *Saccharomyces cerevisiae*	12.5–200 mg mL^{-1}	[179]
Annona squamosa **L (stem barks aqueous extract)**	13.7 ± 3.3	Spherical	*Staphylococcus aureus Eschericia coli* *Candida albicans*	1–20% w/v	[180]
Averrhoa carambola **(leaf extract)**	24.8	Spherical, oval and irregular shaped	*Bacillus megaterium Staphylococcus aureus* *Escherichia coli* *Salmonella typhi* *Pseudomonas aeruginosa*	6.25–100 μg mL^{-1}	[181]
Azadirachta indica **(leaf extract)**	20–80 nm	Spherical	*Escherichia coli* *Rhizopus oryzae*	25–100 mg L^{-1}	[182]
Spinacia oleracea **(leaf extract)**	134.8	Oval, spherical, hexagonal and cubical	*Staphylococcus aureus* *Escherichia coli* *Aspergillus flavus* *Rhizopus* *Aspergillus fumigatus*	Not reported	[183]

3. Cu-based NPs as modulating agents of plant growth

Recent advances in nanotechnology have revealed that Cu-based NPs exhibit enhanced physicochemical properties compared to bulk materials, thereby markedly improving their biological impact on plants [49]. In this sense, copper (Cu) is an essential microelement that plays a vital role as a cofactor of plant proteins, having great relevance for the main biochemical functions in cells and, consequently, in normal plant growth and development [50,51]. Cu has a similar role to iron (Fe) at the physiological level of plants, which can explain why Cu-proteins have Fe cofactors as a counterpart [51]. However, the conditions for Cu toxicity are linked to a decreased Fe content at the shoot and root level. Thus, Cu is associated with homeostasis in the photosynthetic machinery and the electron transport chain in the mitochondria and chloroplast [52,53]. For this reason, conventional agrochemicals containing Cu sources have been widely applied in agriculture to improve crop yield [54].

On the other hand, conventional Cu-based fertilizers tend to accumulate in the environment, producing detrimental effects on non-target organisms. The excess of Cu in plants adversely affects their development, leading to their withering and death. In this sense, Cu-based NPs have emerged as an essential tool to decrease the Cu concentration in the agricultural environment with better plant action efficiency. The slow release of Cu ions from nanoparticles constitutes an important alternative to reduce the application of conventional fertilizers (bulk material) and their negative impacts [55]. An appropriate concentration of Cu-based NPs can positively affect plants at biochemical, morphological, and physiological levels, enhancing crop productivity (Fig. 1) [6].

Diverse plant species have been evaluated to determine the impact of Cu-based NPs (Table 2). For instance, the exposure of *Lycopersicum esculentum* to 20 mg L^{-1} of Cu-based NPs improved the seed germination percentage to 95% [57]. However, germination was reduced at higher concentrations (40–160 mg L^{-1}) of Cu-based NPs, indicating seed stress. Root length, shoot length, biomass, and seedling vigor index were increased up to 20 mg L^{-1} of Cu-based NPs. These results suggest that the decrease of the parameters at concentrations above 20 mg L^{-1} can be produced by the aggregation of Cu-based NPs aggregation, the stopping up of the root pores, and the uptake of nutrients. Leaf pigments of *L. esculentum* as chlorophyll and carotenoids were also increased at the same concentration, highlighting their importance in improving photosynthesis. The same study showed increased antioxidant enzymes (superoxide dismutase and glutathione peroxidase) as the Cu-based NPs concentration increased. Another study focused on the Cu-based NPs impact on nutrient modulation of *Medicago sativa* [58]. The results showed that macronutrients

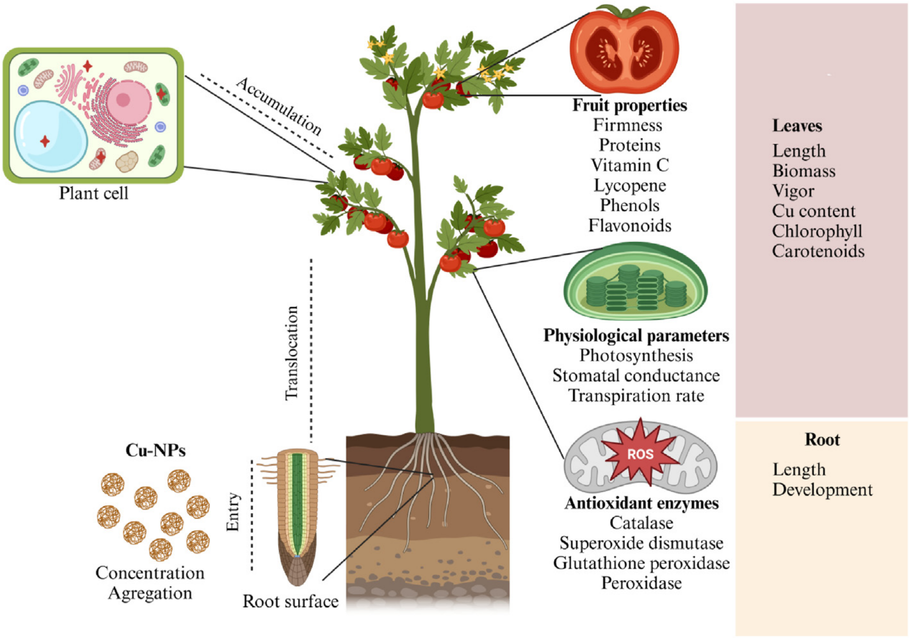

Fig. 1. Main pathways and effects of Cu-based NPs foliar application on plant growth modulation.

(Ca, Mg, P, and S) maintained their concentration after exposure to Cu-based NPs at the root and shoot levels. Fe increased at the root and leaf levels. As expected, Cu content increased in roots, shoots, and leaves after applying 80 and 280 mg L^{-1} of Cu-based NPs. The same study showed that the root and shoot length increased compared to the control, with 80 mg L^{-1} of Cu-based NPs being the most efficient concentration. Additionally, this study compared the effect of Cu-based NPs, the bulk, and ionic forms of Cu, presenting significant evidence that Cu-based NPs alter most poorly the homeostasis of nutrients at the shoot, leaves, and root levels.

The foliar application of Cu-based NPs on *Solanum lycopersicum* has been studied by various authors due to its importance to both a healthy diet and the economy. The beneficial effect of Cu-based NPs on *S. lycopersicum* was demonstrated due to the increase of K-content in the fruit, which is fundamental for its quality [28]. The firmness, pH, and electrical conductivity increased in the fruit after exposition to 250 mg L^{-1} Cu-based NPs, thus enhancing the cell wall hardening and, consequently, the *S. lycopersicum* shelf-life. Furthermore, total proteins, vitamin C, lycopene, glutathione, phenols, and flavonoids increased. Likewise, catalase and superoxide dismutase activity increased after exposure to Cu-based NPs, suggesting their essential role in eliminating reactive oxygen species (ROS) [28]. However, the same authors reported high concentrations of Cu-based NPs (500 mg L^{-1}) induced negative effects on *S. Licopersicum*. It notes that *S. lycopersicum* is a crop adversely affected by saline stress. Thus, a study prospected the impact of foliar application of Cu-based NPs to mitigate it. The results demonstrated that 250 mg L^{-1} of Cu-based NPs mitigated the saline stress by improving the ratio of Na^+/K^+. Besides, it increased the phenol content in leaves and fruits, vitamin C, flavonoids, and glutathione [59]. The Cu-based NPs application enhanced the antioxidant enzymatic activities of ascorbate peroxidase, glutathione peroxidase, phenylalanine ammonia-lyase, and superoxide dismutase. These findings suggest that the foliar application of Cu-based NPs is a critical tool to mitigate the negative impact of salt stress on *S. lycopersicum* production through the activation of enzymatic and non-enzymatic pathways [59]. Hernández-Hernández et al. tested the joint application of Cu-based NPs with selenium nanoparticles (SeNPs). The authors reported that applying 10 mg L^{-1} of Cu-based NPs together with 20 mg L^{-1} of SeNPs increased the average weight of plants. On the other hand, a concentration of 1 mg L^{-1} SeNPs combined with 10, 50, and 250 mg L^{-1} of Cu-based NPs triggers an increase in chlorophyll content, glutathione, superoxide dismutase, glutathione peroxidase, and phenylalanine ammonia-lyase on *S. lycopersicum* [60]. These results show an increased capacity to maintain ROS balance in plant cellular reactions. The application of both NPs also improved the fruit quality by increasing vitamin C, flavonoids, total soluble solids, firmness, and titratable acidity. Specifically, vitamin C (ascorbate) is one of the most important antioxidants that participate as a cofactor of redox enzymes in photosynthesis due to its participation in eliminating free radicals. Lopez-Lima et al. evidenced that Cu-based NPs increased the chlorophyll content index and Cu leave content after the application from 0.5 to 1 mg mL^{-1} [61]. Moreover, 0.5 mg mL^{-1} increased stem and root length, and the leaves number at 0.5 and 0.75 mg mL^{-1}.

Additionally, other plant species of commercial interest have been studied in recent years. A study by Shende et al. indicated that Cu-based NPs at 20 mg L^{-1} promoted the *Cajanus cajan* growth, stimulating the increase of root length, fresh and dry weight, and performance index [62]. The study highlights the transport and accumulation of Cu in plant cells, specifically in chloroplast, cytosol, mitochondria, and vacuole. Rawat et al. reported that Cu-based NPs, their bulk and anionic forms at 125, 250, and 500 mg kg^{-1}, did not affect the foliar area, chlorophyll content, biomass, and productivity of *Capsicum annum* [63]. Likewise, physiological parameters such as evapotranspiration, stomatal conductance, and photosynthesis were not affected by Cu-based NPs but decreased with the application of bulk and ionic Cu, mainly at 250 and 500 mg kg^{-1}

On the other hand, Wang et al. showed that the Cu-based NPs application in *Lactuca sativa* promoted its growth by increasing the shoot biomass [29]. At a physiological level, 200 mg L^{-1} of Cu-based NPs increased the transpiration rate and stomatal conductance without affecting the photosynthetic rate and intercellular CO_2 concentration. More recently, it was reported that wheat seedlings respond to Cu-based NPs in a dose-response manner, where

Table 2
Experimental conditions to test plant growth modulated by Cu-based NPs.

Cu-based NPs	Plant species	Doses	Best dose	Bioassays	Growth parameter	Reference
Cu-based NPs	*Medicago sativa*	80 mg L^{-1} 280 mg L^{-1}	80 mg L^{-1}	Soil potting	- Cu content - Root and shoot fresh weight. -Root and shoot length.	[58]
Cu-based NPs	*Zea mays*	69.4 μM	69.4 μM	Soil potting Controlled conditions	- Shoot biomass - Shoot dry weight - Leaf water control - Anthocyanin content - Antioxidant activity.	[66]
Cu_2ONPs	*Lycopersicum esculentum*	20 mg L^{-1} 40 mg L^{-1} 60 mg L^{-1} 80 mg L^{-1} 100 mg L^{-1} 120 mg L^{-1} 140 mg L^{-1} 160 mg L^{-1}	20 mg L^{-1}	In vitro	-Germination percentage - Root length - Shoot length - Biomass - leaf pigments	[57]
Cu-based NPs	*Lactuca sativa*	200 mg L^{-1} 400 mg L^{-1}	200 mg L^{-1}	Soil potting	- Shoot biomass -Stomatal conductance - Transpiration rate	[29]
Cu-based NPs	*Zea mays*	3 mg L^{-1} 4 mg L^{-1} 5 mg L^{-1}		Controlled and field conditions	- Mass - Productivity - Antioxidant enzymes - Chlorophyll concentration - Anthocyanin - Germination rate	[56]
Cu-based NPs (Size: 50 nm) + **Salt conditions**	*Solanum lycopersicum*	250 mg L^{-1}	250 mg L^{-1}	Nutrient solution Greenhouse conditions	- Fruit quality -Antioxidants accumulation	[59]
Cu-based NPs + **SeNPs**	*Solanum lycopersicum*	10 mg L^{-1} 50 mg L^{-1} 250 mg L^{-1}	Depend on parameter	Soil potting Greenhosue conditions	- Fruit weight - Yield of fruit - Chlorophyll content - Antioxidant activity.	[60]
Cu-based NPs	*Lactuca sativa* *Daucus carota*	0.1 mg L^{-1} 0.5 mg L^{-1} 4.7 mg L^{-1} 23.6 mg L^{-1} 47.3 mg L^{-1}		Hydroponic system	- Root diameter	[70]
Cu-based NPs	*Solanum lycopersicum*	50 mg L^{-1} 125 mg L^{-1} 250 mg L^{-1} 500 mg L^{-1}	250 mg L^{-1}	Soil potting		
Cu-based NPs	*Oryza sativa*	2.5 mg L^{-1} 10 mg L^{-1} 50 mg L^{-1} 100 mg L^{-1} 1000 mg L^{-1}	Depend on parameter	Petri dishes Hydroponic system	- Uptake of Cu - Shoot dry weight - Root fresh mass	[68]
Cu-based NPs	*Cajanus cajan*	20 mg L^{-1}	20 mg L^{-1}	Soil potting	- Height - Root length - Fresh and dry weight - Performance on index of seedlings	[62]

0.06 mg mL^{-1} increased shoot and root at 172 and 215 %, respectively, while Chlorophyll A and B enhanced at the same concentration [64]. Other studies have conducted experiments on plant species subjected to abiotic stress. For instance, the Cu-based NPs application to *Zea mays* improved its productivity after exposure to 4 mg L^{-1} [56]. The same study showed that using Cu-based NPs with Fe and Co-NPs increased the germination rate and growth as well as the superoxide dismutase and peroxidase, leading to the best tolerance to drought stress in *Z. mays*. Additionally, Cu-based NPs stimulated the *Z. mays* growth under drought conditions, increasing the leaf water content and biomass [65]. The Obtained data showed that, compared with the control, Cu-based NPs enhanced the anthocyanin, chlorophyll, and carotenoid content of *Z. mays*. A decrease in ROS in primed plants with Cu-based NPs is also worth mentioning. Therefore, this study showed the vital role of Cu-based NPs in favoring the growth of *Z. mays* by an increase in the water balance, photosynthesis pigments, and stress tolerance through the activation of ROS-scavenging system and anthocyanin biosynthesis. Otherwise, Nechitailo et al. reported that 0.004, 0.0008, and 0.00016 mg L^{-1} of Cu-based NPs improved the radical activity and root length on *Capsicum annuum* [66]. It notes that Cu-based NPs can be crucial in enhancing the plant tolerance to abiotic stress.

Other studies have demonstrated adverse or contradictory effects despite the positive results found in plants after Cu or Cu-based NPs exposure. For example, Da Costa and Sharma [67] reported that the exposition of *Oryza sativa* to 2.5, 10, 50, 100, and 1000 mg L^{-1} (<30 nm) of Cu-based NPs induced stress impact, which was reflected by the low number of thylakoids per granum, and the declined photosynthetic rate, transpiration rate, photosynthetic pigments, and stomatal conductance [67]. This study showed that Cu accumulated in the chloroplast, causing photosynthetic alterations. Thus, the stress was evidenced at the oxidative and osmotic levels [67]. Previously, Cu-based NPs exhibited a toxic effect on *Phaseolus radiatus* and *Triticum aestivum* under in vitro conditions, demonstrating bioaccumulation and particle agglomeration at higher concentrations of 200–1000 mg L^{-1} [68]. Afterward, Margenot et al. reported that Cu-based NPs increased the root diameter of *Lactuca sativa* and *Daucus carota* in all concentrations tested (0.8–798.9 mg L^{-1}) but decreased the root length and germination rate as the applied Cu-based NPs increased [69]. Another study evidenced that Cu-based NPs (50–200 mg L^{-1}) produced a phytotoxic effect in *Cucumis sativus* grown in a hydroponic medium for 4 days. In particular, phenotypic changes, such as decreased biomass and photosynthetic pigments, were observed [70]. The same study reported adverse effects on the root plasma membrane and increased hydrogen peroxide and malondialdehyde in *C. sativus*.

In general, the studies concerning the impact of Cu-based nanoparticles (NPs) on plant growth and development, as mentioned above, demonstrate a differential effect contingent upon the applied concentration. Thus, there is a pressing need for additional research to ascertain their true impact on plants through dose-response bioassays. Moreover, it is crucial to elucidate the mechanisms of action to gain a more comprehensive understanding of the physiological, morphological, and biochemical effects on plant development. Such insights will enhance our knowledge of nanoparticle-plant interactions and pave the way for safer and more effective applications of nanotechnology in agriculture, ensuring the sustainability of ecosystems and the protection of biodiversity.

4. Cu-based NPs as potential pest control management in crops

4.1. Antimicrobial

Fungi are considered to be one of the most problematic microorganisms. Consequently, different fungal diseases have negatively impacted farming production. Fungi present a more significant challenge than bacteria in agriculture for numerous reasons, and their resilience to conventional pesticides is an important concern worldwide [71]. Unlike bacteria, which can often be targeted and eliminated with specific antibiotics or pesticides, fungi possess complex life cycles and robust cellular structures, making them inherently more resistant to chemical control [72]. Their spores can survive in harsh conditions and lie dormant in the soil for a prolonged time, springing back to life when conditions become favorable. Furthermore, fungi attack mode is more hostile, often invading plant tissues deeply and causing systemic infections that are hard to control [73]. Their robust survival mechanisms, ability to quickly evolve resistance, and limited chemical fungicidal options make these microorganisms a formidable enemy in agriculture, posing a persistent threat to crop health and yield. In this regard, some fungi, such as *Botrytis cinerea*, *Colletotrichum* spp., *Fusarium* spp., and *Phytophthora* spp., among others, have caused significant crop losses [74]. Nowadays, synthetic fungicides are the main controllers against different fungal species. However, the need for organic foods or food free of chemicals (i.e., pesticides, antibiotics, or hormones) is increasing. This relies on the fact that a strong resistance toward conventional antifungals has been reported, leading to the search for friendly alternatives [18]. In this perspective, Cu-based NPs have been considered a friendly antifungal to apply to crops, mitigating the negative impact of conventional fungicides. It has been shown that the fungicidal activity of Cu-based NPs depends on the sensibility of the fungus species. Research studies have been performed in the last years to test their effectiveness. Ghasemian et al. presented significant evidence that Cu-based NPs (10 nm) at concentrations from 20 to 100 mg L^{-1} inhibited the growth of *Penicillium chrysogenum*, *Alternaria alternata*, *Fusarium solani*, and *Aspergillus flavus* [75]. As the concentration of Cu-based NPs applied increased, the antifungal action increased, indicating its important activity on filamentous fungi despite the different susceptibility. Furthermore, Cu-based NPs of 3–10 nm have inhibited the growth of *Phomadestructiva* (DBT-66), *Curvularialunata* (MTCC no. 2030), *Alternaria alternata* (MTCC no 6572), and *Fusarium oxysporium* (MTCC no. 1755) [76]. Later, a study performed by Viet et al. presented significant evidence of Cu-based NPs at 450 mg L^{-1} causing the inhibition of 93.98% of *F. oxysporium* [77].

The antifungal activity of Cu-based NPs was tested against *B. cinerea*. In this study, a dose of 50 mg L^{-1} was adequate to protect rose petals [78]. Eslami Chalandar et al. formulated Cu and Cu-based NPs that inhibited the growth of *Penicillium italicum* and *P. digitatum* on orange fruits at concentrations from 5 to 15% [79]. In the same year, Sidhu et al. reported the efficient activity of copper sulfide nano-aquaformulations (8–12 nm) to suppress the growth of *A. alternata*, *Drechslera oryzae,* and *Curvularia lunata* [80]. Doses from 3 to 15 μg mL^{-1} reached 100 % radial growth inhibition of the tested fungi, which is more efficient than a commercial fungicide (Captan). Afterward, Haghighi and Ghorbani showed that Cu-based NPs (~50 nm) with a 5%–20% concentration suppressed the *Penicillium* sp growth [81]. In the same year, it was reported that Cu-based NPs (5–35 mg L^{-1}) inhibited the growth of Oomycetes such as *Meripilus giganteus*, *Rhizoctonia solani*, *Fusarium redolens*, *F. oxysporium* and wood-decay fungi as *Fistulina hepatica*, *Meripilus giganteus*, and *Sparassiscrispa* under controlled conditions [82]. This study suggested the important role of Cu-based NPs in protecting seedlings and safeguarding trees and woods against pathogenic fungi. Other species of fungi can be suppressed by $Cu_3(PO_4)_2 \cdot 3H_2O$ nanosheets at 10 mg L^{-1} and Cu-based NPs at 1000 mg L^{-1}, which inhibited the growth of *F. oxysporium* f sp. niveum on *Citrullus lanatus* after foliar application [83].

Du et al. synthesized Cu_2O-Cu NPs (5.4 nm) stabilized by alginate to control *Neoscytalidium dimidiatum*, fungus-producing brown spot disease on dragon fruit plants [84]. The study showed that 30 mg L^{-1} of Cu_2O-Cu NPs inhibited fungus growth by 100 %. In the same year, Pariona et al. presented important evidence of Cu-based NPs (0.1–1 mg L^{-1}) as antifungal against *Fusarium solani*, *Neofusicoccum* sp., and *F. oxysporium* through morphological changes in mycelium and damage in cell membranes [85]. ROS at the cellular level was found in all the evaluated fungi. Another study affirmed that colloidal Cu-based NPs (5–20 mg L^{-1}) with sizes from 53 to 174 nm inhibited *F. oxysporium* and *Phytophthora capsici* after 3 days of exposure [86]. Oussou-Azo et al. reported that Cu-based NPs (40–60 nm) and Cu-based NPs (<50 nm) suppressed the *Colletotrichum gloeosporioides* growth, where the colony diameter decreased after exposure to 100–1000 mg L^{-1} of NPs [24]. The results indicated ~90–100 % mycelium inhibition after applying 50–100 mg L^{-1}. Microscopic observations showed that hyphae have a swollen appearance and the loss of filamentous structure, suggesting a destruction of the hyphal cell wall. Furthermore, Cu-based NPs (26 nm, 100 μgmL^{-1}) synthesized by the biological route had antifungal activity against *Aspergillus niger* and *Candida albicans*.

Phytopathogenic bacteria also adversely affect crops worldwide, producing economic losses in global food production [87]. In this context, few reports have described the antimicrobial activity of Cu-based NPs against soilborne bacterial pathogens. Cu-based NPs (<17 nm) can have a great impact on soil bacterial species such as Bacilli, Flavobacteria, and Gamma proteobacteria, of which 11 species were highly sensitive, according to the described by Concha-Guerrero et al. [88]. In this study, Cu-based NPs had a toxic effect at 25 mg L^{-1}, and cell membrane damage on bacterial species was induced above 160 mg L^{-1}. Cu-based NPs also produced the killing of *Chryseobacterium indoltheticum* strain CSA28, *Pantoeaananatis* strains CSA34 and CSA35, and *Brevibacillus laterosporus* strain CSS8. Other studies have reported antibacterial activity on specific species. For example, the research by Kala et al. showed that Cu-based NPs had action against *Xanthomonas oryzae* pv. *oryzae*, responsible for the leaf blight of paddy [89]. Another study reported that *Pseudomonas syringae* was inhibited after exposure to 200 mg L^{-1} of Cu-based NPs. It should be noted that no negative effect on *Rhizobium etli*, Rhizobium *meliloti,* and *Rhizobium tropici* was found, indicating its selective effect [18].

Ralstonia solanacearum is a pathogen bacterium adversely affecting diverse fruit families (i.e., banana, peanuts, and cucumber, among others). It was reported that 250 mg L^{-1} of Cu-based NPs (size: 40–80 nm) kill *R. solanacearum* by inhibiting the biofilm formation and decreasing the ATP production and swarming motility. Photographs captured by transmission electron microscopy (TEM) evidenced the ultrastructural damage at the cellular level. Molecular techniques showed the downregulation of genes associated with pathogenesis and motility [90]. *Xanthomonas* is also a relevant bacterial disease affecting tomato production. *Xanthomonas perforans* is one of the main pathogens belonging to this genre. It was evidenced that Cu-based NPs from 100 to 1000 μg mL^{-1} had strong inhibition on the *X. perforans* population, and its combination through the synthesis of a hybrid of Cu/Zn NPs improved the efficiency. The authors observed a significant reduction in the leaves damage twenty days after exposure to Cu/Zn hybrid NPs (50–500 μg mL^{-1}) [91]. Later, El-Batal et al. presented an innovative study showing the effect of Cu-based NPs and streptomycin on bacterial diseases in potato plants [92]. The results showed a film inhibition of *Clavibactern michiganensis* sub sp. *sepedonicus*, *R. solanacearum*, and *Dickeyasolani,* ranging between 83 and 90 % inhibition. Although the inhibition was less than 95%, it is interesting to mention that antibiotic penetration is slowed or ineffective in the presence of exopolysaccharides (EPS) in the biofilms [93]. Therefore, the results obtained by the authors with CuO NPs-streptomycin nano-drug are highly encouraging, mainly because it was used at a low dosage (10.0 μg mL^{-1}).

4.2. Insecticidal activity

The development of nanotechnology has been demonstrated to be efficient for controlling microorganisms. Nevertheless, few studies have been carried out on the management of insects [94]. Applying Cu-based NPs and Cu-based NPs for insect pest management has emerged as an economical, efficient, and eco-friendly strategy [12]. A study on *Spodoptera littoralis* (Lepidoptera: Noctuidae) showed that CuO nanostructures incorporated through an artificial diet produce larval mortality. Specifically, 50–300 mg concentrations for 150 mL of artificial diet produced larval mortality from 40 % on day 1–~100% on day 4 [95]. It was observed that mouth pupae and adult insects deform. Insects of *Spodoptera littoralis* (2nd instar larvae) were exposed to doses from 150 to 600 mg L^{-1} of CuO nanostructures (200–300 nm), which were dispersed on the surface of *Ricinus communis* L leaves. The results showed that as the concentration of nanostructures increased, the mortality of *S. littoralis* also increased after three days of applying the treatments ($LC_{50} = 232$ mg L^{-1}). A biochemical characterization indicated that carbohydrates, proteins, and lipids decreased while phenol oxidase and chitinase activities increased [96]. In the same year, Dorri et al. reported a significant reduction of Tetranychus urticae. Koch. (Acari: Tetranychidae) After applying the CuO nanocapsule was tested by spraying different concentrations (1–5.5 g L^{-1}) on the leaves of *Phaseolus vulgaris* [97]. Moreover, important effects of Cu-based NPs were observed on *Phenacoccus solenopsis* Tinsley (Hemiptera: Pseudococcidae), where the data indicated toxicity after 96 h of treatment applied: 40 % of mortality rate and a significant cell viability reduction (30–38 %) [98]. *Tribolium castaneum* (Coleoptera: Tenebrionidae), characterized for being an important stored grain pest, has also been controlled for Cu-based NPs. In this sense, El-Saadony et al. performed a bioassay using 2 mL containing 50–300 μg mL^{-1} of Cu-based NPs (48.07 nm), which were applied to insects cultured in 20 kg of cereal [99]. In this study, the mortality was dose-dependent on the Cu-based NPs applied, obtaining 30, 67 and 100 % mortality on days 1, 3, and 5 after the application of 300 μg mL^{-1} of Cu-based NPs ($LC_{50} = 36.89$ μg mL^{-1} after 5 days).

4.3. Antinematode

Copper NPs have been useful in pest control; however, scarce studies exist on their activity in nematodes. Kucharska et al. reported that Cu-based NPs at 2 and 5 mg L^{-1} induced 50 % mortality in *Steinernema feltiae* (Filipjev, 1934) on day 5 [100]. Furthermore, Cu-based NPs at concentrations from 1.8 to 15.9 mg L^{-1} produced significant changes in *Caenorhabditis elegans:* a reduction in body length, changes in feeding behavior, and a reduction in reproduction. It was also observed neuronal deformation, which contributes to the stress response. Similarly, Mashock et al. evidenced a higher sensibility of *C. elegans* to Cu-based NPs than $CuSO_4$, which was demonstrated by a reduction in body length, reproduction capacity, and feeding behavior [101]. Mohamed et al. presented substantial evidence about the nematocidal effect of Cu-based NPs (100 nm) against *Meloidogyne incognita* at a concentration of 0.2 g L^{-1}, which produced 100% of its mortality [102].

4.4. Antiviral activity

Copper-based nanoparticles have also emerged as potent against viruses, showcasing remarkable virucidal activities [103–105]. Their efficacy has been demonstrated in the fight against various human and animal viruses [103,104]. These nanoparticles exhibit a dual mode of action; not only do they disrupt the structural integrity of viral particles, preventing them from infecting host cells, but they also induce the production of reactive oxygen species (ROS) or activation of metabolite production in plants, further degrading viral components [106,107].

As mentioned above, Cu-based NPs have been extensively researched and proven effective against various human and animal viruses, highlighting their potential as a potent antiviral agent. Despite their success in these areas, there remains a significant gap in our understanding of their effectiveness against plant viruses. The application of copper nanoparticles for controlling diseases caused by viruses in plants is still in its early stages, with limited information on their potential and efficacy. This presents a unique challenge for researchers and agriculturalists alike. Bridging this knowledge gap is essential for unlocking the full potential of copper nanoparticles in agriculture, offering a promising avenue for developing sustainable and environmentally friendly solutions for plant disease management.

5. Toxicity of Cu-based NPs on plants

Cu-based NPs have been widely reported for their positive effects on inducing plant growth and controlling phytopathogens. However, some adverse effects of Cu-based NPs have been reported on plants [108]. Although copper is an important micronutrient, some concentrations have a toxic effect on plant tissue, depending on the species. For instance, Xiong et al. indicated that Cu-based NPs could harm the production of leafy vegetables due to their ability to be translocated through plant tissue, where a high uptake was evidenced in lettuce and cabbage at 10 and 250 mg per plant, decreasing the photosynthesis, plant weight, and water content [109]. Furthermore, Olchowik et al. evidenced that 50 ppm of Cu-based NPs produced disturbance in plastids, starch content, and plastoglobules of *Quercus robur* L [110]. Concentrations from 10 to 80 mg L^{-1} of Cu-based NPs produced tissue damage of *Allium cepa* by altering the root apical meristem, the nucleus of meristematic cells, and disrupting the cell and nuclear membrane [111]. It was demonstrated that applying Cu-based NPs modulates some nutrients' concentration, decreasing the Fe and P content in the shoots of *Medicago sativa* [112]. Moreover, Cu-based NPs (100–500 mg L^{-1}) harm the growth of *Glycine* max L by altering physiological mechanisms such as the expression of genes related to the generation of reactive oxygen species and oxidative stress [113]. Cu-based NPs reduce the seed germination of *Coriandrum sativum* at concentrations of 20 and 80 mg kg^{-1} soil [114]. Similarly, Cu-based NPs inhibit the germination rate of *Oryza sativa*, and even decrease photosynthetic parameters, transpiration rate, and stomatal conductance at 1000 mg L^{-1} [67].

6. Cu-based NPs interacting with soil

6.1. Entry routes

Recent reports have forecasted the MNPs production for the following years, including Cu-based NPs. For instance, Reports and Data (2023) informed a MNP market size of USD 2.40 Billion just in 2021 [115]. This value is expected to grow with a compound annual growth rate (CAGR) of 11.5% between 2022 and 2030, being the most demanded of platinum, gold, silver, and copper nanoparticles. The rise in demand for Cu-based NPs can be associated with their growing use in electronics, semiconductors, catalyst applications, and agriculture to a lesser extent. A report by Allied Market Research in 2022 estimated a global nano copper oxide market of $39.09 million in 2021, expected to grow at a CAGR of 8.1% to reach $84.81 million in 2031 [116]. These data demonstrate that the concentration of metals in wastewater treatment plants (WTTPs), such as copper from Cu-based NPs, is also expected to increase after using and disposing of MNPs. Fig. 2 shows the main entry routes and fate of Cu-based NPs in soil. In WTPs, more than 70% of the MNPs from the influents can be removed, while the remaining can persist in sewage sludges, commonly used as a soil amendment [117]. In this context, a more recent study evidenced a dose-dependent effect of the sludge concentration for the attachment of different MNPs, where the ionic strength can influence their sorption. Also, more saline concentrations in sludges could decrease the metal sorption. The authors also observed that the sorption effect in the sewage sludge was specific for different metals [118]. This fact denotes the importance of considering environmental conditions when sludges are used in agriculture because metals' bioavailability will depend on the sorption/desorption capacity of MNPs in sludges (see Fig. 3).

Different studies have already estimated the impact of MNPs once released into the environment in the last few years. For instance, by 2010, Keller et al. estimated that 63–91% of the global nanoparticle production (260,000–309,000 metric tons) finished in landfills [119]. From this total, 200 metric tons would have corresponded to Cu-based NPs, having as predominant environmental fates soil and water. Kaegi et al. estimated that MNPs were around <10 mg kg^{-1} in the sewage sludge, where Cu-based NPs were also detected [120]. As mentioned above, the MNPs, including Cu-based NPs, can reach soil through sewage sludge as an agricultural nutritional additive. Herein, the copper content in Union Europe countries varies between 27.2 and 578.1.mg kg^{-1} [121]. Specifically in Germany, 1.9 million tons of sewage sludges were produced in 2010, and 30% were used for agriculture, containing 300–350 mg kg^{-1} of copper [122]. In the case of Chile, it is around 15% [123]. This relatively common agricultural practice links the transport of MNPs to valuable lands, and a continuous application can elevate the metal presence in soil, reaching toxic levels for benefic microorganisms (those participating in biogeochemical cycles) or for human health. In this regard, a study evidenced that at a determined concentration, Cu-based NPs contained in composted sewage sludge enhance rice's biomass production and increase soil's N and K levels. However, adding Cu-based NPs at pollutant levels in the sludge (>1500 mg kg^{-1} of Cu according to the respective country legislation) increased the Arsenic in rice grain to a toxic level, thus endangering human health [124].

According to these findings, it is evident that the input of Cu-based NPs will unavoidably increase. This can be aggravated by the constant use of sewage sludges as an amendment in agriculture and the expected increase in Cu-based nano pesticide production for the following years. The main issue in this sense is the need for an appropriate evaluation of adverse effects on non-target organisms and the lack of techniques to quantify MNPs in complex media like sewage sludge [32]. It has to be highlighted that regulations and limits for MNPs in sewage sludges are limited, which concerns the scientific community.

6.2. Behavior in soil and impact on its microorganisms

Currently, Cu-based NPs and Cu-based NPs are being applied in many consumer products and studied to find new applications (e.g., high thermal and electrical conductivity products, catalysts, lubrication, dental supplies, and agronomic products) [125–128]. In this sense, soil is considered the primary environmental endpoint of MNPs, and it has been demonstrated that they could interact in different forms depending on the physicochemical characteristics of both nanoparticles and soil. Some parameters, mainly pH, have influenced the stability of Cu-based NPs and other MNPs in soil. For instance, it has been estimated that the dissolution of Cu ions (Cu^{2+}) from mineral CuO increases one magnitude order due to 0.5 unit decreased pH [129]. Julich and Gäth found a positive correlation between the Cu-based NPs sorption in soil with organic matter content, iron oxides, and the pH of soil solution [130]. In this study, the nanoparticle sorption was higher compared to Cu ions (Cu^{2+}), which can be associated with different agglomeration/aggregation processes of nanoparticles, according to the authors.

On the other hand, it has been generally assumed that metal oxide dissolution in calcareous soils can be negligible. Nevertheless, even in alkaline soils, the dissolved natural organic matter and aqueous carbonates can dissolve Cu ions from Cu-based NPs through complexation, similar to those at more acidic conditions [131]. Additionally, the aging of Cu-based NPs in soil is an important parameter. Sekine et al. discussed the easy process of CuNP dissolution in soil in 3 days [132]. The nanoparticle behavior rapidly aligned to the copper ions dissolved from copper chloride, where the effect also depended on the soil solution pH. Thus, the higher the pH, the slower copper dissolution.

Other parameters influencing the MNPs behavior in soil are intrinsic to their chemical characteristics, such as their surface coating and aggregation or disaggregation abilities, which affect their water transport and, consequently, their adsorption or desorption to soil particles [133,134]. In this sense, capping agents (such as chitosan, polyethylene glycol, and polyvinyl pyrrolidone) have been used to stabilize Cu-based NPs and avoid copper oxidation [135,136]. These compounds alter the physicochemical properties of nanoparticles and, consequently, their biological activities and environmental impact.

The concern regarding the environmental impact of Cu-based NPs is increasing since some studies have evidenced their effect

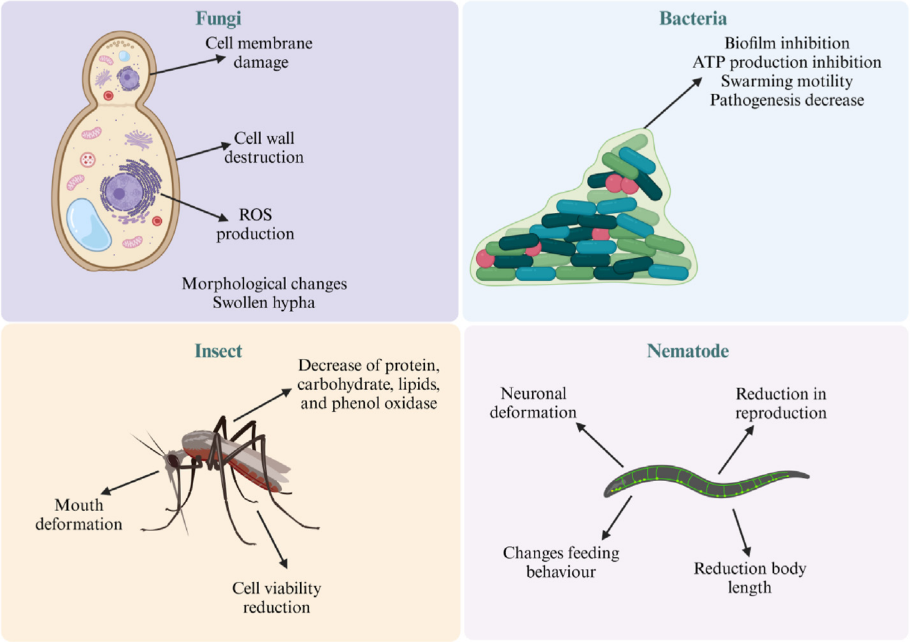

Fig. 2. Physiological impacts of copper nanoparticles to pest control on fungi, bacteria, insects, and nematode.

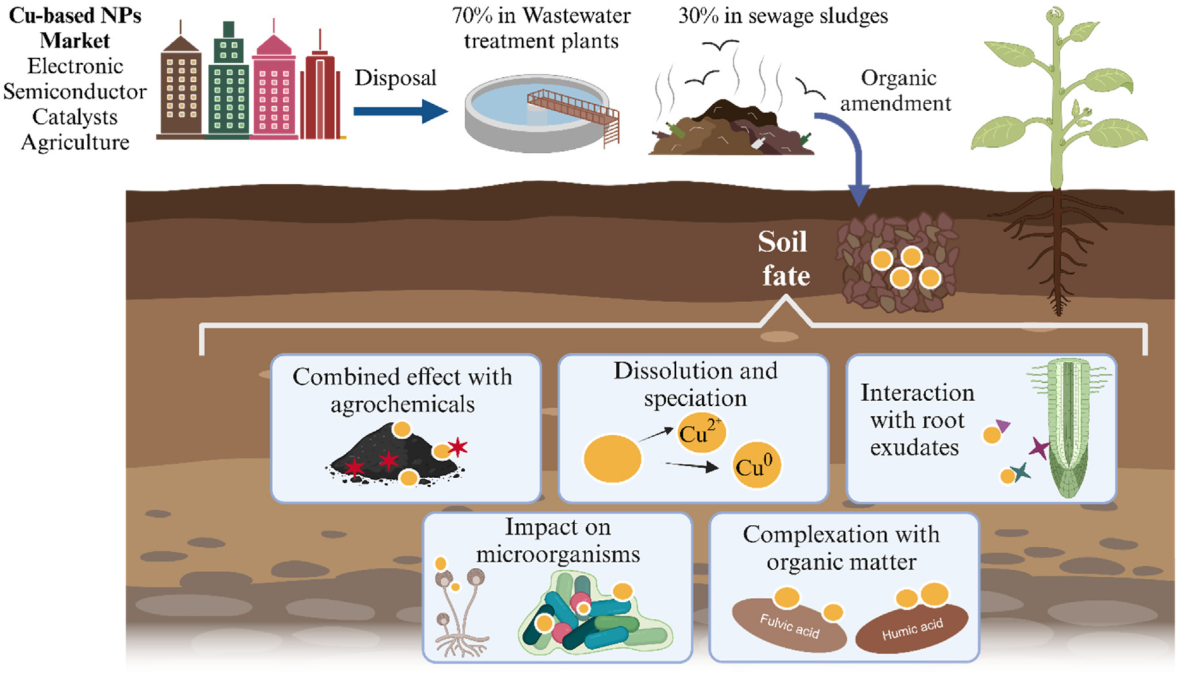

Fig. 3. The main entry routes and interactions of Cu-based NPs in soils.

on soil microorganisms. For instance, Frenk et al. evaluated the harmful effect of different Cu-based NPs concentrations on two soil biotas: a sandy clay loam (SCL) and a sandy loam (SL) [137]. The fullness of bacteria (e.g., Bacilli class) was reduced after the exposure to 0.1% Cu-based NPs in the SL soil, while in the SCL, this occurred at 1%. Rhizobiales or Sphingobacteriaceae were also negatively affected. These effects were related to the clay and organic matter content interacting with Cu-based NPs, which can be a potential mechanism to reduce their toxicity in soil microorganisms. Cu-based NPs and copper ions have also provoked significant changes in the *Phragmites australis* and *Halimione portulacoides* rhizosphere (salt marsh plants) and their associated communities [138]. Consequently, this indicates that Cu-based NPs might cause perturbation in ecosystem activities. Findings from Shah et al. demonstrated that Cu-based NPs (50 mg) significantly impact microbial communities of acidic soils, which is influenced by the high organic carbon content that prolongs the Cu-based NP retention in soil [133].

Some studies have evaluated the influence of different contexts in soil. For instance, Cu-based NPs between 100 and 1000 mg kg^{-1}

have negatively impacted flooded paddy soil. Herein, a decline in soil microbial biomass and enzyme activities (including urease, phosphatase, and dehydrogenase) was observed, consistent with the increased copper bioavailability in soil solution and microbial cells [139]. The authors also observed that the elevated stress ratio values exerted by Cu-based NPs might also affect the soil microorganisms, impacting by modifying their nutrient bioavailability. Differences between a rhizospheric and a bulk soil have also been found. In detail, Gao et al. observed a higher influence of the rhizospheric soil on the dissolution and toxicity of 500 mg kg^{-1} Cu-based NPs, compared with bulk, which was associated with the influence of the root exudates affecting the copper ions dissolution [140]. Therefore, distinct effects on soil microbial communities could be anticipated. Parada et al. observed that Cu-based NPs (at 0.05 and 0.15% w/w) coexisting with atrazine (at a field dose of 3 mg kg^{-1}) caused a significant impact on the abundance of nitrifying bacteria and archaea communities of a soil-plant system, thus, imposing a negative effect on the nitrification capacity of a soil-plant system [32]. However, over 30 days, these communities were gradually adapted, and nitrification was recovered. This study also evidenced a dose-dependent assimilation of copper in plants, which could have influenced the microbial impact of Cu-based NPs.

Other studies focused on the influence of the shape or size of nanoparticles. Zhai et al. found that spherical Cu-based NPs at 100 mg L^{-1} were more toxic to soil microbial communities than rod-shaped ones, suggesting that their morphology influenced their dissolution capacity (copper ions released from nanoparticles) [141]. Qiu et al. observed that different sizes of Cu-based NPs (50 nm and 80 nm) showed a different aggregation behavior in eight different soils [142]]. The 80 nm Cu-based NPs formed hetero/homo-aggregates when their zeta potential was near zero in the soil. The aggregation size for 50 nm Cu-based NPs rapidly decreased to reach stability via forming hetero agglomerates with natural colloids in soil. Thus, they exhibited a higher sedimentation rate. In this process, pH affected zeta potential, consequently affecting CuONP stability, and the dissolved organic matter increased the CuONP suspension in the soil solution.

6.3. *Co-existence with other pollutants*

The clay and organic matter contents are critical factors controlling the pollutant's adsorption in soil, particularly agrochemicals such as pesticides [143]. However, the metal presence in the soil also significantly impacts pesticide behavior [144–146]. Previous knowledge has demonstrated the formation of metal/pesticide complexes or the competition between metal and pesticide for adsorption sites in soil [147,148]. For instance, Morillo et al. observed that copper could adsorb to soil directly or form bonds with glyphosate previously adsorbed [149]. Yu et al. demonstrated that glyphosate had a major influence on copper sorption/desorption in soil compared to methamidophos, which occurred due to a stronger complexation capacity with Cu^{2+} ions [150]. Similarly, an increase in the lead amount provoked higher adsorption of glyphosate, acting as a bridge between the herbicide and soil [151]. In the case of carbendazim, its capacity has been demonstrated to suppress cadmium adsorption to soil [152]. It has to be mentioned that different contexts of soil parameters were considered in these studies, such as pH and organic matter content, which had an important influence. Only a few studies have related the pesticide adsorption in soil with titanium, zinc, or silver. Instead, they were evaluated in pesticide removal from water [153,154].

Scarce information exists about the interaction between MNPs and other pollutants. However, the physicochemical properties of nanoparticles are known to be different from their respective bulk (i.e., non-nano materials). Thus, their adsorption to soil components can also differ [130,155]. Some studies have evidenced that MNPs, including Cu-based NPs, exhibit a higher affinity for soil components (e.g., organic matter, humic acid) than metals' bulk form [120,156,157]. In this sense, a study focused on the atrazine (ATZ) adsorption in the presence of Cu-based NPs in soil and the microbial community's change. The results showed that after 30 days, ATZ adsorption increased by the presence of Cu-based NPs (0.05–0.15% w/w). However, Cu-based NPs at 0.15 % w/w significantly decreased the ATZ removal, enhancing 10-fold its half-life. In the case of $CuSO_4$ at the same dose, the half-life increased 7-fold, supporting the idea that nanoparticles can increase the negative impact. The microbial community profiles (fungi, bacteria, and nitrifying bacteria) remained unaltered, which suggests that Cu-based NPs could enhance the ATZ persistence in soil, probably due to physicochemical interaction over soil particles instead of a microbial impact [31]. This was consistent with a previous study that examined the effects of Cu-based NPs on the microbial community composition and enzyme activity of agricultural soil amended with biosolids over 30 days, where no significant effect on soil or enhanced enzyme activity was found [158].

Identifying the effects of MNPs on pesticide adsorption in soil might be a priority for an adequate environmental risk assessment in agriculture. It can be generalized that studies involving more realistic field conditions are still necessary. Specifically, short, and long-term studies must address possible interferences of MNPs on the adsorption processes and bioavailability of pesticides.

6.4. *Importance of copper speciation in the environment*

In our comprehensive assessment of the environmental and biological impacts of copper-based nanomaterials, we must highlight the significance of chemical speciation and the distinct toxicity profiles of various copper compounds [159]. The differential toxicity observed, for example, between copper sulfate ($CuSO_4$), which poses a heightened risk to soil microbial biomass [160,161] and other copper forms (Cu^0, Cu_2O, $Cu(OH)_2$, Cu_2S and CuO), underscores the complexity of ecological risks associated with these nanomaterials. Particularly notable is the comparison between the toxicity levels of copper oxide (CuO) and copper hydroxide ($Cu(OH)_2$) [162], which illustrates the critical importance of chemical form in determining environmental impact. The transformation and affinity of Cu-based NPs for soil components varied between soils depending on their speciation [163]. Applying Cu-based nanoparticles to 21 different soils demonstrated differences in the relative abundance of Cu species (Cu^0, Cu_2O, and CuO) depending on the soil type and pH, also influencing microbial community change index (MCC_{50}) [163]. Similar results were reported by [164], demonstrating that Cu-based nanoparticle speciation and microbial properties were influenced mainly by land management, where labile Cu fraction significantly affected soil microbial properties.

On the other hand, the ecological interaction of copper with sulfur or sulfates leads to copper sulfide (Cu_2S) formation. This process significantly alters the bioavailability of copper in the soil, thereby modulating its toxicity and highlighting the intricate dynamics of Cu environmental behavior [165]. In this regard [120], reported that sulfidation is crucial in altering various metals and metal oxide nanoparticles during wastewater treatment, effectively diminishing their potential harmfulness to environmental organisms. The binding of copper to sulfur, reducing its mobility and uptake by organisms, acts as a natural control mechanism, potentially mitigating the adverse effects of copper-based nanomaterials on both target and non-target organisms [165]. Nonetheless, studies have shown that when Cu-based nanoparticles undergo sulfidation in water-based solutions, they have a more significant negative impact on *Oryzias latipes* embryos than CuO nanoparticles. The authors reported that this increased harmful effect is likely due to the higher levels of free copper ions released from the Cu_2S nanoparticles, leading to a substantial rise in oxidative stress and toxicity in embryos [166]. Understanding these interactions is essential for accurately evaluating the risks and managing the applications of copper-based nanomaterials in environmental contexts.

7. Future directions

As nanotechnology tools continue to overlap with modern agricultural science, the potential of Cu-based NPs in modulating plant growth has become a matter of keen relevance. In the subsequent years, more research is expected to focus on delineating the specific physiological or molecular mechanisms that Cu-based NPs activate and influence plant cellular processes, such as nutrient uptake, photosynthesis, and/or hormonal regulation. Moreover, it is necessary for advanced research that aims at fine-tuning the size, concentration, and application method to optimize the positive effects on crops while minimizing any adverse impacts on plants or the environment. Furthermore, as global food security becomes more pressing, the researchers might explore the synergistic effects of combining Cu-based NPs with other growth-promoting agents or techniques. Ultimately, a holistic approach, integrating genomics, nanotechnology, and plant physiology, will be pivotal in harnessing the full potential of Cu-based NPs for sustainable and enhanced crop production.

As the quest for sustainable and eco-friendly crop pest control solutions increases, the potential of Cu-based NPs in agricultural pest management is quickly gaining more attention worldwide. Future research needs to focus on the specific action modes of Cu-based NPs against crop pests and pathogens, understanding their impact on insect, fungal, or bacterial physiology, behavior, and reproduction. Moreover, due to increased concerns about antibiotic resistance in pests, research into the synergistic use of Cu-based NPs with other bio-control agents might become prevalent. Comprehensive field trials and long-term ecological impact studies will be crucial in establishing the safety, feasibility, and economic viability of integrating Cu-based NPs into mainstream agricultural pest control strategies.

Finally, the long-term environmental impacts of Cu-based NPs on soil ecosystems and non-target organisms are not fully understood. Continuous use might lead to accumulation in soil, affecting its quality. In addition, more studies are required to understand the potential effects of Cu-based NPs in the presence of other contaminants or combined with environmental abiotic stressors. Understanding the environmental impact of materials such as copper nanoparticles becomes paramount as our global reliance on nanotechnology grows. In upcoming years, studies on the effects of copper nanoparticles in soil ecosystems are expected to delve deeper into their sub-microscopic interactions with soil microbes, plants, and invertebrates. We anticipate a surge in research exploring the long-term accumulation effects and potential biomagnification up the food chain. Advanced molecular biology and imaging techniques will likely shed light on the nanoparticle's influence on microbial community structures, enzymatic activities, and genetic expressions within the soil. Given the potential widespread use of copper nanoparticles in various industries, a multidisciplinary approach that integrates toxicology, ecology, and nanotechnology will be critical in guiding regulations and ensuring the sustainable use of these materials without jeopardizing the health and balance of our soil ecosystems. As with any emerging nanotechnology, there will be a need for clear policies and regulations for the safe use of Cu-based NPs in agricultural lands. However, this might vary from country to country, complicating international trade.

CRediT authorship contribution statement

Gonzalo Tortella: Writing – review & editing, Writing – original draft, Resources, Project administration, Conceptualization. **Olga Rubilar:** Writing – review & editing, Writing – original draft, Funding acquisition, Conceptualization. **Paola Fincheira:** Writing – review & editing, Writing – original draft, Conceptualization. **Javiera Parada:** Writing – review & editing, Writing – original draft, Conceptualization. **Halley Caixeta de Oliveira:** Writing – review & editing, Writing – original draft, Conceptualization. **Adalberto Benavides-Mendoza:** Writing – review & editing, Writing – original draft, Conceptualization. **Sebastian Leiva:** Writing – review & editing, Writing – original draft. **Martín Fernandez-Baldo:** Writing – review & editing, Writing – original draft, Conceptualization. **Amedea B. Seabra:** Writing – review & editing, Writing – original draft, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

This review was financed by ANID/FONDECYT 1230529 and in part by ANID/FOVI220003, Universidad de La Frontera DI23-3002, PP23-0046, DI23-10002, ANID/FONDAP/15130015 and 1523A0001 and the Coordination for the Improvement of Higher Education Personnel (Capes, Brazil) – Finance Code 001. ABS acknowledges the fellowship granted by the National Council for Scientific and Technological Development (CNPq, Brazil, grant no. 313117/2019–5). ABS appreciates the support from Sao Paulo Research Foundation (FAPESP, Brazil, grant no. 2022/00321–0).

References

[1] D. Mittal, G. Kaur, P. Singh, K. Yadav, S.A. Ali, Nanoparticle-based sustainable agriculture and food science: recent advances and future Outlook, Frontiers in Nanotechnology 2 (2020), https://doi.org/10.3389/fnano.2020.579954.

[2] S. Sahani, Y.C. Sharma, Advancements in applications of nanotechnology in global food industry, Food Chem. 342 (2021) 128318, https://doi.org/10.1016/j.foodchem.2020.128318.

[3] D. Letchumanan, S.P.M. Sok, S. Ibrahim, N.H. Nagoor, N.M. Arshad, Plant-based biosynthesis of copper/copper oxide nanoparticles: an Update on their applications in biomedicine, mechanisms, and toxicity, Biomolecules 11 (2021), https://doi.org/10.3390/biom11040564.

[4] M. Chaud, E.B. Souto, A. Zielinska, P. Severino, F. Batain, J. Oliveira-Junior, T. Alves, Nanopesticides in agriculture: benefits and challenge in agricultural productivity, toxicological risks to human health and environment, Toxics (2021), https://doi.org/10.3390/toxics9060131.

[5] P. Fincheira, G. Tortella, N. Duran, A.B. Seabra, O. Rubilar, Current applications of nanotechnology to develop plant growth inducer agents as an innovation strategy, Crit. Rev. Biotechnol. 40 (2020) 15–30, https://doi.org/10.1080/07388551.2019.1681931.

[6] H. Chen, Metal based nanoparticles in agricultural system: behavior, transport, and interaction with plants, Chem. Speciat. Bioavailab. 30 (2018) 123–134, https://doi.org/10.1080/09542299.2018.1520050.

[7] G.R. Tortella, O. Rubilar, N. Durán, M.C. Diez, M. Martínez, J. Parada, A.B. Seabra, Silver nanoparticles: toxicity in model organisms as an overview of its hazard for human health and the environment, J. Hazard Mater. 390 (2020) 121974, https://doi.org/10.1016/j.jhazmat.2019.121974.

[8] V. Rajput, T. Minkina, M. Mazarji, S. Shende, S. Sushkova, S. Mandzhieva, M. Burachevskaya, V. Chaplygin, A. Singh, H. Jatav, Accumulation of nanoparticles in the soil-plant systems and their effects on human health, Ann. Agric. Sci. (Cairo) 65 (2020) 137–143, https://doi.org/10.1016/j.aoas.2020.08.001.

[9] H. Ahmad, K. Venugopal, A.H. Bhat, K. Kavitha, A. Ramanan, K. Rajagopal, R. Srinivasan, E. Manikandan, Enhanced biosynthesis synthesis of copper

oxide nanoparticles (CuO-NPs) for their antifungal activity toxicity against major phyto-pathogens of apple orchards, Pharmaceut. Res. 37 (2020) 246, https://doi.org/10.1007/s11095-020-02966-x.

[10] F. Mondaca, A.I. Mtz-Enriquez, N. Pariona, in: K.A.B.T.-C.N.N.-G. of A. Abd-Elsalam, S.A. for (Eds.), Chapter 8 - Copper-Based Nanostructures for Plant Disease Management, Nanobiotechnology for Plant Protection, Elsevier, 2022, pp. 185–201, https://doi.org/10.1016/B978-0-12-823833-2.00025-8.

[11] S. Taifa, A. Muhee, R.A. Bhat, S.U.I. Nabi, A. Roy, G.A. Rather, A.A. Khan, S.M. Bashir, M. Patwekar, S. Wahab, S. Alghamdi, A.S. Dablool, A. Kabrah, U. Hani, A.M. Bannunah, F. Patwekar, J. Mallick, Evaluation of therapeutic efficacy of copper nanoparticles in *Staphylococcus aureus*-induced rat mastitis model, J. Nanomater. 2022 (2022) 7124114, https://doi.org/10.1155/2022/7124114.

[12] M. Rai, A.P. Ingle, R. Pandit, P. Paralikar, S. Shende, I. Gupta, J.K. Biswas, S.S. da Silva, Copper and copper nanoparticles: role in management of insect-pests and pathogenic microbes, Nanotechnology Reviews, Nanotechnology Reviews 7 (2018) 303–315, https://doi.org/10.1515/ntrev-2018-0031.

[13] I. Salah, I.P. Parkin, E. Allan, Copper as an antimicrobial agent: recent advances, RSC Adv. 11 (2021) 18179–18186, https://doi.org/10.1039/D1RA02149D.

[14] M. Vincent, R.E. Duval, P. Hartemann, M. Engels-Deutsch, Contact killing and antimicrobial properties of copper, J. Appl. Microbiol. 124 (2018) 1032–1046, https://doi.org/10.1111/jam.13681.

[15] A.S. El-Kalliny, M.S. Abdel-Wahed, A.A. El-Zahhar, et al., Nanomaterials: a review of emerging contaminants with potential health or environmental impact, Discover Nano 18 (2023) 68, https://doi.org/10.1186/s11671-023-03787-8.

[16] EPA, U.S.E.P.A, Emerging contaminants nanomaterials. https://archive.epa.gov/region9/mediacenter/web/pdf/emerging_contaminant_nanomaterials.pdf, 2010.

[17] S.D. Richardson, S.Y. Kimura, Emerging environmental contaminants: challenges facing our next generation and potential engineering solutions, Environmental Technology & Innovation 8 (2017) 40–56, https://doi.org/10.1016/j.eti.2017.04.002.

[18] S. Banik, A. Pérez-de-Luque, In vitro effects of copper nanoparticles on plant pathogens, beneficial microbes and crop plants, Spanish J. Agric. Res. 15 (2017) e1005, https://doi.org/10.5424/sjar/2017152-10305.

[19] M.Y. Kohatsu, C.N. Lange, M.T. Pelegrino, J.C. Pieretti, G. Tortella, O. Rubilar, B.L. Batista, A.B. Seabra, T.A. de Jesus, Foliar spraying of biogenic CuO nanoparticles protects the defence system and photosynthetic pigments of lettuce (*Lactuca sativa*), J. Clean. Prod. 324 (2021) 129264, https://doi.org/10.1016/j.jclepro.2021.129264.

[20] M.Y. Kohatsu, M.T. Pelegrino, L.R. Monteiro, B.M. Freire, R.M. Pereira, P. Fincheira, O. Rubilar, G. Tortella, B.L. Batista, T.A. de Jesus, A.B. Seabra, C.N. Lange, Comparison of foliar spray and soil irrigation of biogenic CuO nanoparticles (NPs) on elemental uptake and accumulation in lettuce, Environ. Sci. Pollut. Control Ser. 28 (2021) 16350–16367, https://doi.org/10.1007/s11356-020-12169-x.

[21] T.A. Shalaby, S.M. El-Bialy, M.E. El-Mahrouk, A.E. Omara, H.S. El-Beltagi, H. El-Ramady, Acclimatization of in vitro banana seedlings using root-applied bionanofertilizer of copper and selenium, Agronomy (2022), https://doi.org/10.3390/agronomy12020539.

[22] E. Ibarra-Laclette, J. Blaz, C.A. Pérez-Torres, E. Villafán, A. Lamelas, G. Rosas-Saito, L.A. Ibarra-Juárez, C. de J. García-ávila, A.I. Martínez-Enriquez, N. Pariona, Antifungal effect of copper nanoparticles against *Fusarium kuroshium*, an obligate symbiont of *Euwallacea kuroshio* ambrosia beetle, Journal of Fungi 8 (2022), https://doi.org/10.3390/jof8040347.

[23] P. Ntasiou, E. Vellis, A. Giannopoulos, G.S. Karaoglanidis, in: Novel Copper Nanoparticles for the Control of Tomato Foliar and Fruit Diseases, IECPS 2021, MDPI, Basel Switzerland, 2021, p. 4, https://doi.org/10.3390/IECPS2021-11987.

[24] A.F. Oussou-Azo, T. Nakama, M. Nakamura, T. Futagami, M.C.M. Vestergaard, Antifungal potential of nanostructured crystalline copper and its oxide forms, Nanomaterials (2020), https://doi.org/10.3390/nano10051003.

[25] M.E. Sadek, Y.M. Shabana, K. Sayed-Ahmed, A.H. Abou Tabl, Antifungal activities of sulfur and copper nanoparticles against cucumber postharvest diseases caused by Botrytis cinerea and Sclerotinia sclerotiorum, Journal of Fungi 8 (2022), https://doi.org/10.3390/jof8040412.

[26] G.L. Vanti, S. Masaphy, M. Kurjogi, S. Chakrasali, V.B. Nargund, Synthesis and application of chitosan-copper nanoparticles on damping off causing plant pathogenic fungi, Int. J. Biol. Macromol. 156 (2020) 1387–1395, https://doi.org/10.1016/j.ijbiomac.2019.11.179.

[27] A. Strayer-Scherer, Y.Y. Liao, M. Young, L. Ritchie, G.E. Vallad, S. Santra, J.H. Freeman, D. Clark, J.B. Jones, M.L. Paret, Advanced copper composites against copper-tolerant *Xanthomonas perforans* and tomato bacterial spot, Phytopathology 108 (2018) 196–205, https://doi.org/10.1094/PHYTO-06-17-0221-R.

[28] E. López-Vargas, H. Ortega-Ortíz, G. Cadenas-Pliego, K. de Alba Romenus, M. Cabrera de la Fuente, A. Benavides-Mendoza, A. Juárez-Maldonado, Foliar application of copper nanoparticles increases the fruit quality and the content of bioactive compounds in tomatoes, Appl. Sci. 8 (2018) 1020, https://doi.org/10.3390/app8071020.

[29] Y. Wang, Y. Lin, Y. Xu, Y. Yin, H. Guo, W. Du, Divergence in response of lettuce (var. ramosa Hort.) to copper oxide nanoparticles/microparticles as potential agricultural fertilizer, Environmental Pollutants and Bioavailability 31 (2019) 80–84, https://doi.org/10.1080/26395940.2019.1578187.

[30] E.G. Canli, Alterations on the activities of ion ATPases in the gill and muscle of freshwater mussel (*Unio tigridis*) exposed to copper, Commagene Journal of Biology 5 (2021) 150–154, https://doi.org/10.31594/commagene.1020323.

[31] J. Parada, O. Rubilar, M.C. Diez, M. Cea, A. Sant'Ana da Silva, C.E. Rodríguez-Rodríguez, G.R. Tortella, Combined pollution of copper nanoparticles and atrazine in soil: effects on dissipation of the pesticide and on microbiological community profiles, J. Hazard Mater. 361 (2019) 228–236, https://doi.org/10.1016/j.jhazmat.2018.08.042.

[32] J. Parada, O. Rubilar, D.Z. Sousa, M. Martínez, M.A. Fernández-Baldo, G.R. Tortella, Short term changes in the abundance of nitrifying microorganisms in a soil-plant system simultaneously exposed to copper nanoparticles and atrazine, Sci. Total Environ. 670 (2019) 1068–1074, https://doi.org/10.1016/j.scitotenv.2019.03.221.

[33] G.R. Tortella, O. Rubilar, M. Cea, C. Rodríguez-Rodríguez, A. Seguel, J. Parada, Sorption parameters of carbendazim and iprodione in the presence of copper nanoparticles in two different soils, J. Soil Sci. Plant Nutr. (2019), https://doi.org/10.1007/s42729-019-00037-8.

[34] J. Liu, M. Simms, S. Song, R.S. King, G.P. Cobb, Physiological effects of copper oxide nanoparticles and arsenic on the growth and life cycle of rice (Oryza sativa japonica 'koshihikari'), Environmental Science & Technology 52 (2018) 13728–13737, https://doi.org/10.1021/acs.est.8b03731.

[35] A.A. Keller, A.S. Adeleye, J.R. Conway, K.L. Garner, L. Zhao, G.N. Cherr, J. Hong, J.L. Gardea-Torresdey, H.A. Godwin, S. Hanna, Z. Ji, C. Kaweeteerawat, S. Lin, H.S. Lenihan, R.J. Miller, A.E. Nel, J.R. Peralta-Videa, S.L. Walker, A.A. Taylor, C. Torres-Duarte, J.I. Zink, N. Zuverza-Mena, Comparative environmental fate and toxicity of copper nanomaterials, NanoImpact 7 (2017) 28–40, https://doi.org/10.1016/j.impact.2017.05.003.

[36] T. Ameh, C.M. Sayes, The potential exposure and hazards of copper nanoparticles: a review, Environ. Toxicol. Pharmacol. 71 (2019) 103220, https://doi.org/10.1016/j.etap.2019.103220.

[37] M. Bhagat, R. Anand, P. Sharma, P. Rajput, N. Sharma, K. Singh, Review—multifunctional copper nanoparticles: synthesis and applications, ECS Journal of Solid State Science and Technology 10 (2021) 63011, https://doi.org/10.1149/2162-8777/ac07f8.

[38] M.S. Aguilar, G. Rosas, A new synthesis of Cu_2O spherical particles for the degradation of methylene blue dye, Environ. Nanotechnol. Monit. Manag. 11 (2019) 100195, https://doi.org/10.1016/j.enmm.2018.100195.

[39] Y. Kamikoriyama, H. Imamura, A. Muramatsu, K. Kanie, Ambient aqueous-phase synthesis of copper nanoparticles and nanopastes with low-temperature sintering and ultra-high bonding abilities, Sci. Rep. 9 (2019) 899, https://doi.org/10.1038/s41598-018-38422-5.

[40] P. Chawla, N. Kumar, A. Bains, S.B. Dhull, M. Kumar, R. Kaushik, S. Punia, Gum Arabic capped copper nanoparticles: synthesis, characterization, and applications, Int. J. Biol. Macromol. 146 (2020) 232–242, https://doi.org/10.1016/j.ijbiomac.2019.12.260.

[41] B. Ashok, N. Hariram, S. Siengchin, A.V. Rajulu, Modification of tamarind fruit shell powder with in situ generated copper nanoparticles by single step hydrothermal method, Journal of Bioresources and Bioproducts 5 (2020) 180–185, https://doi.org/10.1016/j.jobab.2020.07.003.

[42] J. Calvo-de la Rosa, M. Segarra, Optimization of the synthesis of copper ferrite nanoparticles by a polymer-assisted sol-gel method, ACS Omega 4 (2019) 18289–18298, https://doi.org/10.1021/acsomega.9b02295.

[43] A.A. Antipov, A.G. Putilov, A.V. Osipov, A.E. Shepelev, V.N. Glebov, A.M. Maliutin, Synthesis of copper nanoparticles by laser ablation, J. Phys. Conf. 2316 (2022) 12004, https://doi.org/10.1088/1742-6596/2316/1/012004.

[44] S. Giuffrida, L.L. Costanzo, G. Ventimiglia, C. Bongiorno, Photochemical synthesis of copper nanoparticles incorporated in poly(vinyl pyrrolidone), J. Nanoparticle Res. 10 (2008) 1183–1192, https://doi.org/10.1007/s11051-007-9343-2.

[45] N.K. Jain, S. Pathak, M. Alam, Synthesis of copper nanoparticles by pulsed electrochemical dissolution process, Ind. Eng. Chem. Res. 58 (2019) 602–608, https://doi.org/10.1021/acs.iecr.8b03146.

[46] N. Jardón-Maximino, G. Cadenas-Pliego, C.A. Ávila-Orta, V.E. Comparán-Padilla, L.E. Lugo-Uribe, M. Pérez-Alvarez, S.F. Tavizón, G. Santillán, J.S. de, Antimicrobial property of polypropylene composites and functionalized copper nanoparticles, Polymers 13 (2021), https://doi.org/10.3390/polym13111694.

[47] G.D.M.R. Dabera, M. Walker, A.M. Sanchez, H.J. Pereira, R. Beanland, R.A. Hatton, Retarding oxidation of copper nanoparticles without electrical isolation and the size dependence of work function, Nat. Commun. 8 (2017) 1894, https://doi.org/10.1038/s41467-017-01735-6.

[48] D. Sharma, S. Kanchi, K. Bisetty, Biogenic synthesis of nanoparticles: a review, Arab. J. Chem. 12 (2019) 3576–3600, https://doi.org/10.1016/j.arabjc.2015.11.002.

[49] Y. Shang, M.K. Hasan, G.J. Ahammed, M. Li, H. Yin, J. Zhou, Applications of nanotechnology in plant growth and crop protection: a review, Molecules 24 (2019) 2558, https://doi.org/10.3390/molecules24142558.

[50] R.A. Festa, D.J. Thiele, Copper: an essential metal in biology, Curr. Biol. 21 (2011) R877–R883, https://doi.org/10.1016/j.cub.2011.09.040.

[51] B. Printz, S. Lutts, J.-F. Hausman, K. Sergeant, Copper trafficking in plants and its implication on cell wall dynamics, Front. Plant Sci. 7 (2016), https://doi.org/10.3389/fpls.2016.00601.

[52] C.M. Cohu, M. Pilon, in: R. Hell, R.-R. Mendel (Eds.), Cell Biology of Copper BT - Cell Biology of Metals and Nutrients, Springer Berlin Heidelberg, Berlin, Heidelberg, 2010, pp. 55–74, https://doi.org/10.1007/978-3-642-10613-2_3.

[53] K. Ravet, M. Pilon, Copper and iron homeostasis in plants: the challenges of oxidative stress, Antioxidants Redox Signal. 19 (2013) 919–932, https://doi.org/10.1089/ars.2012.5084.

[54] A. Obrador, D. Gonzalez, J.M. Alvarez, Effect of inorganic and organic copper fertilizers on copper nutrition in *Spinacia oleracea* and on labile copper in soil, J. Agric. Food Chem. 61 (2013) 4692–4701, https://doi.org/10.1021/jf305473f.

[55] A. Rastogi, M. Zivcak, O. Sytar, H.M. Kalaji, X. He, S. Mbarki, M. Brestic, Impact of metal and metal oxide nanoparticles on plant: a critical review, Front. Chem. 5 (2017), https://doi.org/10.3389/fchem.2017.00078.

[56] S.A. Hoang, L.Q. Nguyen, N.H. Nguyen, C.Q. Tran, D.V. Nguyen, N.T. Le, C.V. Ha, Q.N. Vu, C.M. Phan, Metal nanoparticles as effective promotors for Maize production, Sci. Rep. 9 (2019) 13925, https://doi.org/10.1038/s41598-019-50265-2.

[57] S. Ananda, G. Shobha, K. Shashidhara, M. Vishwaprakash, Nano-cuprous oxide enhances seed germination and seedling growth in *Lycopersicum esculentum* plants, J. Drug Deliv. Therapeut. 9 (2019) 296–302, https://doi.org/10.22270/jddt.v9i2.2554.

[58] K. Cota-Ruiz, Y. Ye, C. Valdes, C. Deng, Y. Wang, J.A. Hernández-Viezcas, M. Duarte-Gardea, J.L. Gardea-Torresdey, Copper nanowires as nanofertilizers for alfalfa plants: understanding nano-bio systems interactions from microbial genomics, plant molecular responses and spectroscopic studies, Sci. Total Environ. 742 (2020) 140572, https://doi.org/10.1016/j.scitotenv.2020.140572.

[59] F. Pérez-Labrada, E.R. López-Vargas, H. Ortega-Ortiz, G. Cadenas-Pliego, A. Benavides-Mendoza, A. Juárez-Maldonado, Responses of tomato plants under saline stress to foliar application of copper nanoparticles, Plants 8 (2019), https://doi.org/10.3390/plants8060151.

[60] Hernández-Hernández, Quiterio-Gutiérrez, Cadenas-Pliego, Ortega-Ortiz, Hernández-Fuentes, Cabrera de la Fuente, Valdés-Reyna, Juárez-Maldonado, Impact of selenium and copper nanoparticles on yield, antioxidant system, and fruit quality of tomato plants, Plants 8 (2019) 355, https://doi.org/10.3390/plants8100355.

[61] D. Lopez-Lima, A.I. Mtz-Enriquez, G. Carrión, S. Basurto-Cereceda, N. Pariona, The bifunctional role of copper nanoparticles in tomato: effective treatment for Fusarium wilt and plant growth promoter, Sci. Hortic. 277 (2021) 109810, https://doi.org/10.1016/j.scienta.2020.109810.

[62] S. Shende, D. Rathod, A. Gade, M. Rai, Biogenic copper nanoparticles promote the growth of pigeon pea (*Cajanus cajan* L.), IET Nanobiotechnol. 11 (2017) 773–781, https://doi.org/10.1049/iet-nbt.2016.0179.

[63] S. Rawat, V.L.R. Pullagurala, M. Hernandez-Molina, Y. Sun, G. Niu, J.A. Hernandez-Viezcas, J.R. Peralta-Videa, J.L. Gardea-Torresdey, Impacts of copper oxide nanoparticles on bell pepper (*Capsicum annum* L.) plants: a full life cycle study, Environ. Sci.: Nano 5 (2018) 83–95, https://doi.org/10.1039/C7EN00697G.

[64] H.L. Essa, M.S. Abdelfattah, A.S. Marzouk, Z. Shedeed, H.A. Guirguis, M.M.H. El-Sayed, Biogenic copper nanoparticles from *Avicennia marina* leaves: impact on seed germination, detoxification enzymes, chlorophyll content and uptake by wheat seedlings, PLoS One 16 (4) (2021) e0249764. https://doi:10.1371/journal.pone.0249764.

[65] D. Van Nguyen, H.M. Nguyen, N.T. Le, K.H. Nguyen, H.T. Nguyen, H.M. Le, A.T. Nguyen, N.T.T. Dinh, S.A. Hoang, C. Van Ha, Copper nanoparticle application enhances plant growth and grain yield in maize under drought stress conditions, J. Plant Growth Regul. 41 (2022) 364–375, https://doi.org/10.1007/s00344-021-10301-w.

[66] G.S. Nechitailo, O.A. Bogoslovskaya, I.P. Ol'khovskaya, N.N. Glushchenko, Influence of iron, zinc, and copper nanoparticles on some growth indices of pepper plants, Nanotechnologies in Russia 13 (2018) 161–167, https://doi.org/10.1134/S1995078018020052.

[67] M.V.J. Da Costa, P.K. Sharma, Effect of copper oxide nanoparticles on growth, morphology, photosynthesis, and antioxidant response in *Oryza sativa*, Photosynthetica 54 (2016) 110–119, https://doi.org/10.1007/s11099-015-0167-5.

[68] W.-M. Lee, Y.-J. An, H. Yoon, H.-S. Kweon, Toxicity and bioavailability of copper nanoparticles to the terrestrial plants mung bean (*Phaseolus radiatus*) and wheat (Triticum aestivum): plant agar test for water-insoluble nanoparticles, Environ. Toxicol. Chem. 27 (1) (2008) 1915, https://doi.org/10.1897/07-481.

[69] A.J. Margenot, D.A. Rippner, M.R. Dumlao, S. Nezami, P.G. Green, S.J. Parikh, A.J. McElrone, Copper oxide nanoparticle effects on root growth and hydraulic conductivity of two vegetable crops, Plant Soil 431 (2018) 333–345, https://doi.org/10.1007/s11104-018-3741-3.

[70] K.A. Mosa, M. El-Naggar, K. Ramamoorthy, H. Alawadhi, A. Elnaggar, S. Wartanian, E. Ibrahim, H. Hani, Copper nanoparticles induced genotoxicty, oxidative stress, and changes in superoxide dismutase (SOD) gene expression in cucumber (*Cucumis sativus*) plants, Front. Plant Sci. 9 (2018), https://doi.org/10.3389/fpls.2018.00872.

[71] F. Almeida, M.L. Rodrigues, C. Coelho, The still underestimated problem of fungal diseases worldwide, Front. Microbiol. 10 (2019) 214. http://doi:10.3389/fmicb.2019.00214.

[72] G. Anand, K.C. Rajeshkumar, in: V.R. Rajpal, I. Singh, S.S. Navi (Eds.), Challenges and Threats Posed by Plant Pathogenic Fungi on Agricultural Productivity and Economy, Fungal Diversity, Ecology and Control Management. Fungal Biology, Springer, Singapore, 2022, https://doi.org/10.1007/978-981-16-8877-5_23.

[73] J. Mapuranga, N. Zhang, L. Zhang, J. Chang, W. Yang, Infection strategies and pathogenicity of biotrophic plant fungal pathogens, Front. Microbiol. 13 (2022) 799396. http://doi:10.3389/fmicb.2022.799396.

[74] V.S. Brauer, C.P. Rezende, A.M. Pessoni, R.G. De Paula, K.S. Rangappa, S.C. Nayaka, V.K. Gupta, F. Almeida, Antifungal agents in agriculture: friends and foes of public health, Biomolecules 9 (2019), https://doi.org/10.3390/biom9100521.

[75] E. Ghasemian, A. Naghoni, B. Tabaraie, T. Tabaraie, In vitro susceptibility of filamentous fungi to copper nanoparticles assessed by rapid XTT colorimetry and agar dilution method, J. Mycolog. Med. 22 (2012) 322–328, https://doi.org/10.1016/j.mycmed.2012.09.006.

[76] P. Kanhed, S. Birla, S. Gaikwad, A. Gade, A.B. Seabra, O. Rubilar, N. Duran, M. Rai, In vitro antifungal efficacy of copper nanoparticles against selected crop pathogenic fungi, Mater. Lett. 115 (2014) 13–17, https://doi.org/10.1016/j.matlet.2013.10.011.

[77] P. Van Viet, H.T. Nguyen, T.M. Cao, L. Van Hieu, Fusarium antifungal activities of copper nanoparticles synthesized by a chemical reduction method, J. Nanomater. (2016) 1957612, https://doi.org/10.1155/2016/1957612.

[78] Y. Hao, X. Cao, C. Ma, Zetian Zhang, N. Zhao, A. Ali, T. Hou, Z. Xiang, J. Zhuang, S. Wu, B. Xing, Zhao Zhang, Y. Rui, Potential applications and antifungal activities of engineered nanomaterials against gray mold disease agent *Botrytis cinerea* on rose petals, Front. Plant Sci. 8 (2017), https://doi.org/10.3389/fpls.2017.01332.

[79] H. Eslami Chalandar, H. Reza Ghorbani, H. Attar, S. Abolhasan Alavi, Antifungal effect of copper and copper oxide nanoparticles against Penicillium on orange fruit. Biosciences, Biotechnology Research Asia 14 (2017) 279–284, https://doi.org/10.13005/bbra/2445.

[80] A. Sidhu, H. Barmota, A. Bala, Antifungal evaluation studies of copper sulfide nano-aquaformulations and its impact on seed quality of rice (*Oryzae sativa*), Appl. Nanosci. 7 (2017) 681–689, https://doi.org/10.1007/s13204-017-0606-7.

[81] M. Haghighi, H.R. Ghorbani, Optimization of copper nanoparticles synthesis using E. coli and the study of its antifungal activity, Nanomed. J 5 (2018) 90–95, https://doi.org/10.22038/nmj.2018.005.005.

[82] M. Aleksandrowicz-Trzcińska, A. Szaniawski, J. Olchowik, S. Drozdowski, Effects of copper and silver nanoparticles on growth of selected species of pathogenic and wood-decay fungi in vitro, For. Chron. 94 (2018) 109–116, https://doi.org/10.5558/tfc2018-017.

[83] J. Borgatta, C. Ma, N. Hudson-Smith, W. Elmer, C.D. Plaza Pérez, R. De La Torre-Roche, N. Zuverza-Mena, C.L. Haynes, J.C. White, R.J. Hamers, Copper based nanomaterials suppress root fungal disease in watermelon (*Citrullus lanatus*): role of particle morphology, composition and dissolution behavior, ACS Sustain. Chem. Eng. 6 (2018) 14847–14856, https://doi.org/10.1021/acssuschemeng.8b03379.

[84] B.D. Du, D.T.B. Ngoc, N.D. Thang, L.N.A. Tuan, B.D. Thach, N.Q. Hien, Synthesis and in vitro antifungal efficiency of alginate-stabilized Cu2O-Cu nanoparticles against Neoscytalidium dimidiatum causing brown spot disease on dragon fruit plants (*Hylocereus undatus*), Vietnam Journal of Chemistry 57 (2019) 318–323, https://doi.org/10.1002/vjch.201900022.

[85] N. Pariona, A.I. Mtz-Enriquez, D. Sánchez-Rangel, G. Carrión, F. Paraguay-Delgado, G. Rosas-Saito, Green-synthesized copper nanoparticles as a potential antifungal against plant pathogens, RSC Adv. 9 (2019) 18835–18843, https://doi.org/10.1039/c9ra03110c.

[86] N.-D. Pham, M.-M. Duong, M.-V. Le, H.A. Hoang, L.-K.-O. Pham, Preparation and characterization of antifungal colloidal copper nanoparticles and their antifungal activity against *Fusarium oxysporum* and *Phytophthora capsici*, Compt. Rendus Chem. 22 (2019) 786–793, https://doi.org/10.1016/j.crci.2019.10.007.

[87] P.M.M. Martins, M.V. Merfa, M.A. Takita, A.A. De Souza, Persistence in phytopathogenic bacteria: do we know enough? Front. Microbiol. 9 (2018) https://doi.org/10.3389/fmicb.2018.01099.

[88] S.I. Concha-Guerrero, E.M.S. Brito, H.A. Piñón-Castillo, S.H. Tarango-Rivero, C.A. Caretta, A. Luna-Velasco, R. Duran, E. Orrantia-Borunda, Effect of CuO nanoparticles over isolated bacterial strains from agricultural soil, J. Nanomater. (2014) 1–13, https://doi.org/10.1155/2014/148743.

[89] A. Kala, S. Soosairaj, S. Mathiyazhagan, P. Raja, Green synthesis of copper bionanoparticles to control the bacterial leaf blight disease of rice, Curr. Sci. 110 (2016) 2011, https://doi.org/10.18520/cs/v110/i10/2011-2014.

[90] J. Chen, S. Mao, Z. Xu, W. Ding, Various antibacterial mechanisms of biosynthesized copper oxide nanoparticles against soilborne *Ralstonia solanacearum*, RSC Adv. 9 (2019) 3788–3799, https://doi.org/10.1039/c8ra09186b.

[91] R. Carvalho, K. Duman, J.B. Jones, M.L. Paret, Bactericidal activity of copper-zinc hybrid nanoparticles on copper-tolerant *Xanthomonas perforans*, Sci. Rep. 9 (2019) 20124, https://doi.org/10.1038/s41598-019-56419-6.

[92] A.I. El-Batal, N.M. Balabel, M.S. Attia, G.S. El-Sayyad, Antibacterial and antibiofilm potential of mono-dispersed stable copper oxide nanoparticles-streptomycin nano-drug: implications for some potato plant bacterial pathogen treatment, J. Cluster Sci. 31 (2020) 1021–1040, https://doi.org/10.1007/s10876-019-01707-4.

[93] R. Srinivasan, S. Santhakumari, P. Poonguzhali, M. Geetha, M. Dyavaiah, L. Xiangmin, Bacterial biofilm inhibition: a focused review on recent

therapeutic strategies for combating the biofilm mediated infections, Front. Microbiol. 12 (2021) 676458. http://doi:10.3389/fmicb.2021.676458.

[94] C.G. Athanassiou, N.G. Kavallieratos, G. Benelli, D. Losic, P. Usha Rani, N. Desneux, Nanoparticles for pest control: current status and future perspectives, J. Pest. Sci. 91 (2018) 1–15, https://doi.org/10.1007/s10340-017-0898-0.

[95] A.A. Atwa, N.A. Salah, W.E. Khafagi, A.A. Al-Ghamdi, Insecticidal effects of pure and silver-doped copper oxide nanosheets on *Spodoptera littoralis* (Lepidoptera: Noctuidae), Can. Entomol. 149 (2017) 677–690, https://doi.org/10.4039/tce.2017.36.

[96] H.A. Ayoub, M. Khairy, S. Elsaid, F.A. Rashwan, H.F. Abdel-Hafez, Pesticidal activity of nanostructured metal oxides for generation of alternative pesticide formulations, J. Agric. Food Chem. 66 (2018) 5491–5498, https://doi.org/10.1021/acs.jafc.8b01600.

[97] H.R. Dorri, S. Khaghani, A. Moghadam, D. Ghanbari, M.R. Bihamta, The effect of copper nano-capsules on the control of two spotted spider mite (tetranychusurticae), Journal of Nanostructures 8 (2018) 316–324, https://doi.org/10.22052/JNS.2018.03.012.

[98] E. León-Jimenez, B. Valdéz-Salas, D. González-Mendoza, O. Tzintzun-Camacho, Synthesis and insecticide activity of Cu-nanoparticles from *Prosopis juliflora* (sw) DC and *pluchea seric*ea (Nutt.) on *Phenacoccus solenopsis* Tinsley (Hemiptera: Pseudococcidae), Rev. Soc. Entomol. Argent. 78 (2019) 12–21, https://doi.org/10.25085/rsea.780202.

[99] M.T. El-Saadony, M.E. Abd El-Hack, A.E. Taha, M.M.G. Fouda, J.S. Ajarem, S. N. Maodaa, A.A. Allam, N. Elshaer, Ecofriendly synthesis and insecticidal application of copper nanoparticles against the storage pest *Tribolium castaneum*, Nanomaterials 10 (2020) 587, https://doi.org/10.3390/nano10030587.

[100] K. Kucharska, E. Pezowicz, D. Tumialis, D. Kucharski, B. Zajdel, Nanoparticles of copper and entomopathogenic nematodes *Steinernema feltiae* (Filipjev, 1934) in reducing the number of the lesser mealworm beetle *Alphitobius diaperinus* (Panzer, 1797), Annals of Warsaw University of Life Sciences-SGGW Animal Science 53 (2014) 29–35.

[101] M.J. Mashock, T. Zanon, A.D. Kappell, L.N. Petrella, E.C. Andersen, K.R. Hristova, Copper oxide nanoparticles impact several toxicological endpoints and cause neurodegeneration in *Caenorhabditis elegans*, PLoS One 11 (2016) e0167613, https://doi.org/10.1371/journal.pone.0167613.

[102] E.A. Mohamed, S.F. Elsharabasy, D. Abdulsamad, Evaluation of in vitro nematicidal efficiency of copper nanoparticles against root-knot nematode *Meloidogyne incognita*, South Asian Journal of Parasitology 2 (2019) 13–18.

[103] P. Yugandhar, T. Vasavi, Y. Jayavardhana Rao, P. Uma Maheswari Devi, G. Narasimha, N. Savithramma, Cost effective, green synthesis of copper oxide nanoparticles using fruit extract of *Syzygium alternifolium* (Wt.) Walp., characterization and evaluation of antiviral activity, J. Cluster Sci. 29 (2018) 743–755.

[104] G. Tortella, O. Rubilar, P. Fincheira, J.C. Pieretti, P. Duran, I.M. Lourenço, A.B. Seabra, Bactericidal and virucidal activities of biogenic metal-based nanoparticles: advances and perspectives, Antibiotics 10 (2021) 783.

[105] T. Farooq, M. Adeel, Z. He, M. Umar, N. Shakoor, W. da Silva, Y. Rui, Nanotechnology and plant viruses: an emerging disease management approach for resistant pathogens, ACS Nano 15 (4) (2021) 6030–6037, https://doi.org/10.1021/acsnano.0c10910.

[106] Y. Rajani, P. Mishra, S. Kumari, P. Saini, R.K. Meena, Role of nanotechnology in management of plant viral diseases, Mater. Today: Proc. 69 (2022) 1–10.

[107] A. Warghane, R. Saini, M. Shri, I. Andankar, D. Kumar Ghosh, B. Ananda Chopade, Application of nanoparticles for management of plant viral pathogen: current status and future prospects, Virology 592 (2024) 109998, https://doi.org/10.1016/j.virol.2024.109998.

[108] V. Rajput, T. Minkina, A. Fedorenko, S. Sushkova, S. Mandzhieva, V. Lysenko, N. Duplii, G. Fedorenko, K. Dvadnenko, K. Ghazaryan, Toxicity of copper oxide nanoparticles on spring barley (*Hordeum sativum* distichum), Sci. Total Environ. 645 (2018) 1103–1113, https://doi.org/10.1016/j.scitotenv.2018.07.211.

[109] T. Xiong, C. Dumat, V. Dappe, H. Vezin, E. Schreck, M. Shahid, A. Pierart, S. Sobanska, Copper oxide nanoparticle foliar uptake, phytotoxicity, and consequences for sustainable urban agriculture, Environmental Science & Technology 51 (2017) 5242–5251, https://doi.org/10.1021/acs.est.6b05546.

[110] J. Olchowik, R. Bzdyk, M. Studnicki, M. Bederska-Błaszczyk, A. Urban, M. Aleksandrowicz-Trzcińska, The effect of silver and copper nanoparticles on the condition of English oak (*Quercus robur* L.) seedlings in a container nursery experiment, Forests 8 (2017) 310, https://doi.org/10.3390/f8090310.

[111] F. Deng, S. Wang, H. Xin, Toxicity of CuO nanoparticles to structure and metabolic activity of *Allium cepa* root tips, Bull. Environ. Contam. Toxicol. 97 (2016) 702–708, https://doi.org/10.1007/s00128-016-1934-0.

[112] J. Hong, C.M. Rico, L. Zhao, A.S. Adeleye, A.A. Keller, J.R. Peralta-Videa, J.L. Gardea-Torresdey, Toxic effects of copper-based nanoparticles or compounds to lettuce (*Lactuca sativa*) and alfalfa (*Medicago sativa*), Environ. Sci. J. Integr. Environ. Res.: Process. Impacts 17 (2015) 177–185, https://doi.org/10.1039/C4EM00551A.

[113] P.M.G. Nair, I.M. Chung, A mechanistic study on the toxic effect of copper oxide nanoparticles in soybean (*Glycine max* L.) root development and lignification of root cells, Biol. Trace Elem. Res. 162 (2014) 342–352, https://doi.org/10.1007/s12011-014-0106-5.

[114] N. Zuverza-Mena, I.A. Medina-Velo, A.C. Barrios, W. Tan, J.R. Peralta-Videa, J.L. Gardea-Torresdey, Copper nanoparticles/compounds impact agronomic and physiological parameters in cilantro (*Coriandrum sativum*), Environ. Sci. J. Integr. Environ. Res.: Process. Impacts 17 (2015) 1783–1793, https://doi.org/10.1039/C5EM00329F.

[115] Reports and data, Metal Nanoparticles Market Size, Share, Trends, by Metal (Platinum, Gold, and Silver), by Synthesis Process (Chemical and Physical), by End-Use Industry (Pharmaceutical & Healthcare and Catalyst), and by Region Forecast to 2030 [Internet], 2023. Accessed on August, 2023. Available from: https://www.reportsanddata.com/report-detail/metal-nanoparticles-market.

[116] Allied Market Research, Nano Copper Oxide Market by End User (Electricals and Electronics, Energy Storage, Paints & Coatings, Catalysts, Others), in: Global Opportunity Analysis and Industry Forecast, 2021-2031 [Internet], 2022. Accessed on August, 2023. Available from: https://www.alliedmarketresearch.com/nano-copper-oxide-market.

[117] P. Cervantes-Avilés, A.A. Keller, Incidence of metal-based nanoparticles in the conventional wastewater treatment process, Water Res. 189 (2021) 116603, https://doi.org/10.1016/j.watres.2020.116603.

[118] S. Choi, M. Johnston, G.-S. Wang, C.-P. Huang, The uptake of engineered nanoparticles by sludge particulates, Water (2023), https://doi.org/10.3390/w15162872.

[119] A.A. Keller, A. Ehrens, Y. Zheng, B. Nowack, Developing trends in nanomaterials and their environmental implications, Nat. Nanotechnol. 18 (8) (2023 Aug) 834–837, https://doi.org/10.1038/s41565-023-01409-z. PMID: 37280284.

[120] R. Kaegi, A. Voegelin, B. Sinnet, S. Zuleeg, H. Hagendorfer, M. Burkhardt, H. Siegrist, Behavior of metallic silver nanoparticles in a pilot wastewater treatment plant, Environ. Sci. Technol. 45 (2011) 3902–3908, https://doi.org/10.1021/es1041892.

[121] K. Fijalkowski, A. Rorat, A. Grobelak, M.J. Kacprzak, The presence of contaminations in sewage sludge – the current situation, J. Environ. Manag. 203 (2017) 1126–1136, https://doi.org/10.1016/j.jenvman.2017.05.068.

[122] B. Wiechmann, C. Dienemann, C. Kabbe, S. Brandt, I. Vogel, A. Roskosch, Klärschlammentsorgung in der Bundesrepublik Deutschland, Umweltbundesamt c/o GVP, Bonn, Germany, 2012.

[123] J. Cartes, P. Neumann, A. Hospido, G. Vidal, Life cycle assessment of management alternatives for sludge from sewage treatment plants in Chile: does advanced anaerobic digestion improve environmental performance compared to current practices? J. Mater. Cycles Waste Manag. 20 (2018) 1530–1540, https://doi.org/10.1007/s10163-018-0714-9.

[124] L. Duc Phung, S. Dhewi Afriani, P. Aditya Padma Pertiwi, H. Ito, A. Kumar, T. Watanabe, Effects of CuO nanoparticles in composted sewage sludge on rice-soil systems and their potential human health risks, Chemosphere 338 (2023) 139555, https://doi.org/10.1016/j.chemosphere.2023.139555.

[125] T. Begildayeva, S.J. Lee, Y. Yu, J. Park, T.H. Kim, J. Theerthagiri, A. Ahn, H.J. Jung, M.Y. Choi, Production of copper nanoparticles exhibiting various morphologies via pulsed laser ablation in different solvents and their catalytic activity for reduction of toxic nitroaromatic compounds, J. Hazard Mater. 409 (2021) 124412, https://doi.org/10.1016/j.jhazmat.2020.124412.

[126] M. Escribà-Gelonch, G.D. Butler, A. Goswami, N.N. Tran, V. Hessel, Definition of agronomic circular economy metrics and use for assessment for a nanofertilizer case study, Plant Physiol. Biochem. 196 (2023) 917–924, https://doi.org/10.1016/j.plaphy.2023.02.042.

[127] V.W. Xu, M.Z. Nizami, I.X. Yin, O.Y. Yu, C.Y. Lung, C.H. Chu, Application of copper nanoparticles in dentistry, Nanomaterials (2022), https://doi.org/10.3390/nano12050805.

[128] Z.-B. Zhao, J.-D. Liu, X.-Y. Du, Z.-Y. Wang, C. Zhang, S.-F. Ming, Fabrication of silver nanoparticles/copper nanoparticles jointly decorated nitride flakes to improve the thermal conductivity of polymer composites, Colloids Surf. A Physicochem. Eng. Asp. 635 (2022) 128104, https://doi.org/10.1016/j.colsurfa.2021.128104.

[129] D.A. Palmer, The solubility of crystalline cupric oxide in aqueous solution from 25°C to 400 °C, J. Chem. Therm. 114 (2017) 122–134, https://doi.org/10.1016/j.jct.2017.03.012.

[130] D. Julich, S. Gäth, Geoderma Sorption behavior of copper nanoparticles in soils compared to copper ions, Geoderma 235–236 (2014) 127–132, https://doi.org/10.1016/j.geoderma.2014.07.003.

[131] J.M. Hortin, A.J. Anderson, D.W. Britt, A.R. Jacobson, J.E. McLean, Copper oxide nanoparticle dissolution at alkaline pH is controlled by dissolved organic matter: influence of soil-derived organic matter, wheat, bacteria, and nanoparticle coating, Environ. Sci.: Nano 7 (2020) 2618–2631, https://doi.org/10.1039/D0EN00574F.

[132] R. Sekine, E.R. Marzouk, M. Khaksar, K.G. Scheckel, J.P. Stegemeier, G.V. Lowry, E. Donner, E. Lombi, Aging of dissolved copper and copper-based nanoparticles in five different soils: short-term kinetics vs. Long-term fate, J. Environ. Qual. 46 (2017) 1198–1205, https://doi.org/10.2134/jeq2016.12.0485.

[133] V. Shah, T.P. Luxton, V.K. Walker, T. Brumfield, J. Yost, S. Shah, J.E. Wilkinson, M. Kambhampati, Fate and impact of zero-valent copper nanoparticles on geographically-distinct soils, Sci. Total Environ. 573 (2016) 661–670, https://doi.org/10.1016/j.scitotenv.2016.08.114.

[134] M. Bundschuh, J. Filser, S. Lüderwald, M.S. McKee, G. Metreveli, G.E. Schaumann, R. Schulz, S. Wagner, Nanoparticles in the environment: where do we come from, where do we go to? Environ. Sci. Eur. 30 (2018) 6, https://doi.org/10.1186/s12302-018-0132-6.

[135] R. Javed, F. Rais, M. Kaleem, B. Jamil, M.A. Ahmad, T. Yu, S.W. Qureshi, Q. Ao,

Chitosan capping of CuO nanoparticles: facile chemical preparation, biological analysis, and applications in dentistry, Int. J. Biol. Macromol. 167 (2021) 1452–1467, https://doi.org/10.1016/j.ijbiomac.2020.11.099.

[136] R. Javed, M. Ahmed, I. ul Haq, S. Nisa, M. Zia, PVP and PEG doped CuO nanoparticles are more biologically active: antibacterial, antioxidant, antidiabetic and cytotoxic perspective, Mater. Sci. Eng. C 79 (2017) 108–115, https://doi.org/10.1016/j.msec.2017.05.006.

[137] S. Frenk, T. Ben-Moshe, I. Dror, B. Berkowitz, D. Minz, Effect of metal oxide nanoparticles on microbial community structure and function in two different soil types, PLoS One 8 (2013) e84441, https://doi.org/10.1371/journal.pone.0084441.

[138] J.P. Fernandes, C.M.R. Almeida, F. Andreotti, L. Barros, T. Almeida, A.P. Mucha, Response of microbial communities colonizing salt marsh plants rhizosphere to copper oxide nanoparticles contamination and its implications for phytoremediation processes, Sci. Total Environ. 581–582 (2017) 801–810, https://doi.org/10.1016/j.scitotenv.2017.01.015.

[139] C. Xu, C. Peng, L. Sun, S. Zhang, H. Huang, Y. Chen, J. Shi, Distinctive effects of TiO_2 and CuO nanoparticles on soil microbes and their community structures in flooded paddy soil, Soil Biol. Biochem. 86 (2015) 24–33, https://doi.org/10.1016/j.soilbio.2015.03.011.

[140] X. Gao, A. Avellan, S. Laughton, R. Vaidya, S.M. Rodrigues, E.A. Casman, G.V. Lowry, CuO nanoparticle dissolution and toxicity to wheat (Triticum aestivum) in rhizosphere soil, Environ. Sci. Technol. 52 (2018) 2888–2897, https://doi.org/10.1021/acs.est.7b05816.

[141] Y. Zhai, E.R. Hunting, M. Wouterse, W.J.G.M. Peijnenburg, M.G. Vijver, Importance of exposure dynamics of metal-based nano-ZnO, -Cu and -Pb governing the metabolic potential of soil bacterial communities, Ecotoxicol. Environ. Saf. 145 (2017) 349–358, https://doi.org/10.1016/j.ecoenv.2017.07.031.

[142] Y. Qiu, Z. Mu, N. Wang, X. Wang, M. Xu, H. Li, The aggregation and sedimentation of two different sized copper oxide nanoparticles in soil solutions: dependence on pH and dissolved organic matter, Sci. Total Environ. 731 (2020) 139215, https://doi.org/10.1016/j.scitotenv.2020.139215.

[143] M. Cazanga, M. Gutierrez, M. Escudey, G. Galindo, A. Reyes, A.C. Chang, Adsorption isotherms of copper, lead, nickel, and zinc in two Chilean soils in single- and multi-component systems: sewage sludge impact on the adsorption isotherms of Diguillin soil, Soil Res. 46 (2008) 53–61.

[144] B. Ruttkay-Nedecky, O. Krystofova, L. Nejdl, V. Adam, Nanoparticles based on essential metals and their phytotoxicity, J. Nanobiotechnol. 15 (2017) 33, https://doi.org/10.1186/s12951-017-0268-3.

[145] T. Taghizade Firozjaee, N. Mehrdadi, M. Baghdadi, G.R. Nabi Bidhendi, Application of nanotechnology in pesticides removal from aqueous solutions - a review, Int. J. Nanosci. Nanotechnol. 14 (2018) 43–56.

[146] T. Undabeytia, E. Morillo, C. Maqueda, Simultaneous adsorption of cadmium and a cationic pesticide on montmorillonite, Toxicol. Environ. Chem. 43 (1994) 77–84, https://doi.org/10.1080/02772249409358019.

[147] Z. Pei, X. Shan, B. Wen, S. Zhang, L. Yan, S.U. Khan, Effect of copper on the adsorption of p-nitrophenol onto soils, Environmental Pollution 139 (2006) 541–549, https://doi.org/10.1016/j.envpol.2005.05.025.

[148] Q.-H. Tao, H.-X. Tang, Sorption behaviour of atrazine onto natural sediments under various solution conditions, Adsorpt. Sci. Technol. 22 (2004) 639–652, https://doi.org/10.1260/0263617042844210.

[149] E. Morillo, T. Undabeytia, C. Maqueda, A. Ramos, The effect of dissolved glyphosate upon the sorption of copper by three selected soils, Chemosphere 47 (2002) 747–752, https://doi.org/10.1016/S0045-6535(01)00338-1.

[150] Y. Yu, Q. Zhou, Z. He, Effects of methamidophos and glyphosate on copper sorption-desorption behavior in soils, Science in China Series C: Life Sciences 48 (2005) 67–75, https://doi.org/10.1007/BF02889803.

[151] Y.-B. Si, Y. Xiang, C. Tian, X.-Y. Si, J. Zhou, D.-M. Zhou, Complex interaction and adsorption of glyphosate and lead in soil, Soil Sediment Contam.: Int. J. 22 (2013) 72–84, https://doi.org/10.1080/15320383.2012.714421.

[152] X. Li, Q. Zhou, S. Wei, W. Ren, X. Sun, Adsorption and desorption of carbendazim and cadmium in typical soils in northeastern China as affected by temperature, Geoderma 160 (2011) 347–354, https://doi.org/10.1016/j.geoderma.2010.10.003.

[153] V. Lizano-Fallas, M. Masís-Mora, D. Espinoza-Villalobos, M. Lizano-Brenes, C.E. Rodríguez-Rodríguez, Removal of pesticides and ecotoxicological changes during the simultaneous treatment of triazines and chlorpyrifos in biomixtures, Chemosphere 182 (2017) 106–113, https://doi.org/10.1016/j.chemosphere.2017.04.147.

[154] S. MiarAlipour, D. Friedmann, J. Scott, R. Amal, TiO2/porous adsorbents: recent advances and novel applications, J. Hazard Mater. 341 (2018) 404–423, https://doi.org/10.1016/j.jhazmat.2017.07.070.

[155] M.J.B. Amorim, J.J. Scott-Fordsmand, Toxicity of copper nanoparticles and $CuCl_2$ salt to *Enchytraeus albidus* worms: survival, reproduction and avoidance responses, Environmental Pollution 164 (2012) 164–168, https://doi.org/10.1016/j.envpol.2012.01.015.

[156] P.R. Cáceres-Vélez, M.L. Fascineli, M.H. Sousa, C.K. Grisolia, L. Yate, P.E.N. de Souza, I. Estrela-Lopis, S. Moya, R.B. Azevedo, Humic acid attenuation of silver nanoparticle toxicity by ion complexation and the formation of a Ag3+ coating, J. Hazard Mater. 353 (2018) 173–181, https://doi.org/10.1016/j.jhazmat.2018.04.019.

[157] H. El Hadri, S.M. Louie, V.A. Hackley, Assessing the interactions of metal nanoparticles in soil and sediment matrices - a quantitative analytical multi-technique approach, Environ. Sci.: Nano 5 (2018) 203–214, https://doi.org/10.1039/C7EN00868F.

[158] B. Asadishad, S. Chahal, A. Akbari, V. Cianciarelli, M. Azodi, S. Ghoshal, N. Tufenkji, Amendment of agricultural soil with metal nanoparticles: effects on soil enzyme activity and microbial community composition, Environmental Science & Technology 52 (2018) 1908–1918, https://doi.org/10.1021/acs.est.7b05389.

[159] J. Shi, L. Sun, C. Peng, C. Xu, Y. Wang, X. Chen, H. Lin, J. Yang, T. Liu, Y. Chen, Copper Speciation and Transformation in Soil-Plant System, in: Twenty Years of Research and Development on Soil Pollution and Remediation in China, 2018, pp. 151–164. http://doi:10.1007/978-981-10-6029-8_10.

[160] A. El-Ghamry, Abid Subhani, Wael Mohd, Changyong Huang, Xie Zhengmiao, Effects of copper toxicity on soil microbial biomass, Pakistan J. Biol. Sci. 3 (2000) 907–910.

[161] J.L.A. Shaw, J.G. Ernakovich, J.D. Judy, M. Farrell, M. Whatmuff, J. Kirby, Long-term effects of copper exposure to agricultural soil function and microbial community structure at a controlled and experimental field site, Environmental Pollution 263 (2020) 114411. http://doi:10.1016/j.envpol.2020.114411.

[162] S.P. Shahane, A. Kumar, Estimation of health risks due to copper-based nanoagrochemicals, Environ. Sci. Pollut. Res. Int. 29 (17) (2022) 25046–25059. http://doi:10.1007/s11356-021-17308-6.

[163] V. Shah, T.P. Luxton, V.K. Walker, T. Brumfield, J. Yost, S. Shah, M. Kambhampati, Fate and impact of zero-valent copper nanoparticles on geographically-distinct soils, Sci. Total Environ. 573 (2016) 661–670. http://doi:10.1016/j.scitotenv.2016.08.1.

[164] J.U. Osafo Eduah, A. Arthur, J. Agbesi Dogbatse, I. Amoako-Attah, E. Acheampong Afful, Ecological effects of soil physicochemical properties and copper speciation on the microbial properties associated with land use management in cacao production, Environmental Technology & Innovation 33 (103538) (2024), https://doi.org/10.1016/j.eti.2024.103538.

[165] H. Xu, P. Zhang, E. He, W. Peijnenburg, X. Cao, L. Zhao, X. Xu, H. Qiu, Natural formation of copper sulfide nanoparticles via microbially mediated organic sulfur mineralization in soil: processes and mechanisms, Geoderma 430 (2023) 116300, https://doi.org/10.1016/j.geoderma.2022.116300.

[166] L. Li, L. Hu, Q. Zhou, C. Huang, Y. Wang, C. Sun, G. Jiang, Sulfidation as a natural antidote to metallic nanoparticles is overestimated: CuO sulfidation yields CuS nanoparticles with increased toxicity in medaka (*Oryzias latipes*) embryos, Environmental Science & Technology 49 (4) (2015) 2486–2495, https://doi.org/10.1021/es505878f.