ISSN 1993-6842 (on-line); ISSN 0233-7657 (print)
Biopolymers and Cell. 2024. Vol. 40. N 2. P 83–95
http://dx.doi.org/10.7124/bc.000AAF

UDC 606.61:579.864: [579.2/6+612.392.98] + 676.22.017

The influence of metal nanoparticles on plants

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The use of metal nanoparticles in agriculture opens the prospects for increasing the efficiency and sustainability of agricultural production. This technology makes it possible to apply miniature metal particles, such as nanosilver, nanomanganese, nanocopper, nanozinc, *etc.*, with maximum precision and targeting. The prospects of using metal nanoparticles include such aspects as increasing soil fertility, protecting plants from pests and diseases, effective water management, enhancement of the nutritional quality of plants, improvement of seed and germination, sensor technologies for monitoring, and reducing negative environmental impact. With the need to ensure safety and take into account the environmental impact, the use of metal nanoparticles has the potential to transform agriculture, ensuring sustainable production growth and reducing its environmental footprint.

Keywords: agriculture, nanotechnology, nanoparticles, nanometals, microorganisms, green biosynthesis.

Introduction

At present, the rapid development and use of nanotechnology in agriculture, medicine, biology and other fields, the topic of studying metal nanoparticles for their practical use becomes increasingly relevant and promising.

Nanotechnology is a branch of science that deals with nanomaterials, helps overcome size limitations and can change the view of science world. The interaction of nanomaterials with plants has not been fully elucidated. There are various and often conflicting reports on the uptake, translocation, accumulation, biotransformation, and toxicity of nanoparticles in various plant species. One of the nanomaterials most frequently studied as an antibacterial agent is silver nanoparticles (AgNPs) [1]. The use of such metals as zinc, copper, iron, and manganese is important for the agricultural

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industry. They are transition metals involved in important biological processes in plants. These metals are the cofactors of metalloproteins acting as regulatory elements. Excess or deficiency of these metals can have a strong impact on the photosynthetic functions of the plant. Therefore, the use of nanoparticles of these metals is of great importance for the plant development [2, 3].

There are two main methods of nanoparticle synthesis (i.e., top-down and bottom-up methods), which are used to produce nanomaterials of appropriate size, shape, and functionality [4]. However, traditional physicochemical methods create environmental and biological hazards due to the toxic reducing agents used during the process. Thus, to meet the increasing demand for an environmentally sustainable technology for the production of metal nanoparticles, the biomimetic or "green" synthesis methods using biological molecules or whole organisms have been utilized as an environmentally friendly approach [5, 6].

The use of plant cell cultures for biological synthesis of metal nanoparticles is a rapidly developing area of research in bionanotechnology. Frequent attempts to use nanoparticles in agriculture are explained by a number of problems with traditional methods of seed treatment, such as chemical sterilization of seeds [7]. Traditionally used organic sterilants have such significant disadvantages as high consumption, toxicity and the ability of pathogens to adapt to and withstand sterilants. It is believed that the use of protectors based on metal nanoparticles may be promising for the application of nanotechnology in the field of presowing seed treatment. Furthermore, nanoparticles can be used as components of new fertilisers in the agricultural industry, plant protection products, and herbicides [8–10].

Today, nanoparticles are widely used all over the world. They are famous for their unique physico-chemical and biological properties. They also have a number of advantages compared to the traditional preparations: can provide a complete wetting of the surface of plants, are completely absorbed by plants, do not delaminate under the influence of heat and light, are not washed away in the rain, their working solution can be stored for years, remaining active [11].

Various studies show that nanoparticles can affect plants at the biochemical, physiological and molecular levels [3]. Iron, zinc, copper, manganese and other elements in a nanosized state can contribute to the growth and development of plants. Nanosized metals show a high bactericidal activity, low toxicity and do not accumulate in the human body [12].

Silver nanoparticles

Silver nanoparticles (AgNPs) are the particles ranging in size from 2 to 100 nm containing about 20–15,000 silver atoms. They are used in medicine to treat wounds and burns and in agriculture. Studies of the antimicrobial properties of silver nanoparticles against various pathogens, such as viruses, fungi, and some types of bacteria, confirmed their effectiveness [13–15]. The mechanism of action of silver nanoparticles is associated with their accumulation on the membrane of microorganisms and the formation of pores, causing the changes in the permeability of a cell wall and suppression of cellular respiration. They have been shown not only to have antibacterial effects, but also to inhibit the growth of fungi such as *Candida* (*C. albicans,* *C. glabrata, C. parapsilosis, C. tropicalis*, *etc.*) [13, 14]. It was also shown that colloidal solutions containing silver nanoparticles can inhibit the growth of *Aspergillus*, *Penicillium* and *Trichoderma* sp. [15].

Nanosilver is characterized by a high efficiency in eliminating bacterial infections [16]. Silver ions get involved in many processes at the molecular level in bacterial cells, which leads to the inhibition of their growth and even death [16]. The use of $AgNO_3$ as a source of silver for the disinfection of plant tissues is quite common, but the use of nAg is a new method. It was shown [17] that nAg has the same efficiency as $AgNO_3$. Namely, it can suppress the development of more than 600 different microorganisms. Nano Ag is characterized not only by antibacterial, but also by antiviral and antifungal effects [18, 19]. In addition, the application of AgNPs in properly selected concentration does not have a negative effect on the growth or reproduction of plants in cultures *in vitro*. It was found that AgNPs have a good effect on barley germination and growth. The seeds treated with AgNPs at concentrations of 6 and 8 mg/dm3 had fewer infected grains, which led to larger sprouts and roots and increased the content of chlorophyll and β-carotene in the plant [20, 21].

Silver nanoparticles (AgNPs) are among the most well-known nanoparticles whose effects have been investigated. Obviously, the effect of AgNPs on higher plants depends on the species and age of the plants, the size and concentration of the nanoparticles, the experimental conditions such as temperature, and the duration and method of exposure. Because of the above-mentioned properties, nanosilver is of particular interest. In the nanoscale state, silver shows a sharp increase in catalytic and biological activity [22]. Thus, the use of nanosilver allows researchers to reduce its concentration by several orders of magnitude, while maintaining the level of bactericidal properties. AgNPs with a size of 9–15 nm are the most effective in eliminating pathogenic microorganisms [23].

There are also literature sources concerning the effect of 10–100 nm AgNPs, which were synthesized by the green method using *Berberis lycium* Royle extract, to increase the yield of *Pisum sativum* L. Pea seeds were soaked, and seedlings were sprayed on the leaves with AgNPs of 0, 30, 60 and 90 μM. The positive effect of silver nanoparticles applied to P. sativum was found. High yields of pea cultivars were reported for the plants treated with AgNPs of 60 μM, indicating that this concentration of silver nanoparticles is optimal for maximum yield [24].

Carica papaya callus extract was also used for the synthesis of silver nanoparticles [25]. Later, the bioactive AgNPs were produced using the callus extracts of *Solanum incanum* L., *Taxus yunnanensis, Citrullus colocynthis* and *Pyrenacantha grandiflora* [26–29]. In general, the plant cell cultures are a promising source of reducing agents, as they are characterized by simpler and faster biomass growth compared to plants. The green synthesized silver nanoparticles have excellent bactericidal effect as compared to those produced by traditional chemical and physical methods [30].

Manganese nanoparticles

Manganese (Mn) is an essential trace element that plays many functional roles in plant metabolism. Manganese acts as an activator and cofactor of numerous metalloenzymes in plants. Due to its ability to easily change its oxidation state in biological systems, Mn plays an important role in a wide range of enzyme-catalyzed reactions, including redox reactions, phosphorylation, decarboxylation, and hydrolysis [31].

The main function of Mn in plants is attributed to its role as a central substituent of the water-splitting complex in the photosystem II reaction center. In addition, MnSOD (superoxide dismutase (SOD)), which detoxifies reactive oxygen species (ROS), is present in mitochondria. Mn is also bound by germine and germine-like proteins, which are located in cell walls and catalyze the production of hydrogen peroxide (H_2O_2) from oxalate. H_2O_2 contributes to the defense against pathogens as a signal, as an antimicrobial agent, and as a lignification inducer. There are several enzymes (for example, decarboxylases and dehydrogenases inthe tricarboxylic acid cycle; phenylalanine-ammonia-lyase in the synthesis process of the secondary metabolite of shikimic acid) that do not bind Mn, but are activated in its presence [32].

MnO has attracted the interest of many researchers due to its action and electromagnetic characteristics [33]. Various methods for the synthesis of MnO have been developed, such as the self-reactive microemulsion, deposition and solid reaction [34–36]. However, the use of natural products for the recovery and stabilization of metallic Mn in nanoparticles is more environmentally friendly, inexpensive and easier compared to the above methods [37–39].

MnO nanoparticles were successfully synthesized by the biosynthesis method using a green tea extract as a stabilizer and a reducing agent [35]. The MnONPs synthesized from tea were characterized by several methods, proving that they had bioactive groups. MnONPs synthesized from green tea inhibited the development of *Escherichia coli*, *Klebsiella pneumoniae*, and *Pseudomonas aeruginosa*. The combination of MnONPs with antibiotics increases the effectiveness of antibiotics against gram-negative bacteria. The biosynthesis of MnO can be considered as promising for the development of recent antimicrobial agents [35].

MnO nanoparticles are mainly produced by bacteria in the environment [40]. In recent studies, phytoextracts have been used in the production of Mn nanoparticles [38, 41]. However, the physiological and toxicological effects of various Mn nanoparticles on agricultural crops are relatively less known. The studies were carried out on the synthesis of manganese oxide nanoparticles (MnONPs) using an onion extract. This extract was shown to be effectively used for production of the oval crystalline Mn_2O_3 nanoparticles (MnONPs) with a size of 22–39 nm

MnONPs were found significantly affect chlorophyll and antioxidant profiles at the concentration of 20 mg×l^{-1}. And conversely, at the concentration of $\leq$40 mg×l^{-1}, the priming had a significant effect on a phenolic acid profile of leaves and a phytohormone profile in seedling of watermelon. However, the observed physiological results of the watermelon seed treatment by MnONPs were specific to the genotype and concentration-dependent. The results of this study in total demonstrated that the green synthesized MnO nanoparticles can be a safer seed treatment agent compared to widespread analogues $KMnO_4$ and Mn_2O_3 for increasing watermelon yield at the optimal effective concentration. However, further research is needed on the precise influence of seed treatment by MnONPs on the total agricultural production, including its role in providing resistance to the various abiotic and biotic stresses for other horticultural crops [42]. The effect of NPs as nanofertilizers on the plant may also differ depending on the method of application.

One of the few studies that researched MnNPs found that shoots and grain spraying resulted in a higher Mn content in shoots and grain, and a lower content of nitrate nitrogen in a soil, and a higher P content in a soil and shoots compared with the application of MnNPs to a soil for wheat. These results indicate that the application of MnNPs through leaves may have a more intense effect on nutrient composition in wheat. In addition, the influence of Mn nanoform through the soil can affect plants, unlike the influence of mass or ionic Mn [32].

Copper nanoparticles

Recently, copper (Cu), nickel (Ni), zinc (Zn), *etc.* have been used to synthesize NPs instead of noble metals such as gold and silver which are rare and expensive. NPs of copper oxide (CuO) have a wide range of applications in various fields and are used in the catalytic, optical, superconducting and magnetoresistive materials and solar energy conversion [43–50]. CuONPs also have antimicrobial, antidiabetic, anticancer and biocidal properties. CuONPs are non-toxic and have an antimicrobial efficacy in combating plant diseases, a photocatalytic activity for a dye waste treatment, and many other environmental applications [48].

Copper deficiency and toxicity in the soil can affect plant physiology by altering photochemical and biochemical processes within the plant. Copper sulphate is widely used in crop production despite its toxic effects. To reduce the impact of toxicity on the plant, it is advisable to use copper nanoparticles (CuNPs). CuNPs in the recommended dose improved the pigment content and antioxidant activity in the plant and have no toxic effects, including morphological and/or physiological changes [41, 51].

A lack of copper negatively affects the plant reproduction. Pollen grains are formed in smaller quantities, while cereals are characterized by empty grain spikelets. In appearance, the lack of copper can also be noticed on the leaves, namely, white spots appear on the edges, and the leaves curl into a “tube”. In general, the growth and development of the plant slow down [52]. Copper in excess has a toxic effect on plants, and oversaturation of copper also causes an iron deficiency. A growth slows down, and the leaves are covered with brown spots from below. Such areas become vulnerable to diseases [53].

In the literature [53], there are the studies in which a biologically oriented process of a green synthesis of copper oxide nanoparticles (CuONPs) was considered using *Morus alba* leaves extract as a reducing agent. Seedlings of *Brassica oleracea* var. *botrytis* and *Solanum lycopersicum* were exposed to CuONPs in a sandy environment. The exposure of 100 and 500 mg/l of CuONPs to the plant resulted in a significant decrease in the total content of chlorophyll and sugar in the two plants studied, while 10 mg/l ofNPs slightly increased the content of pigment and sugar only in tomato plants. The enhancement of lipid peroxidation, electrolyte leakage, and antioxidant enzyme activity was observed depending on the dose when plants were exposed to CuONPs. The lignin deposition was observed in the roots of both plants treated with the highest concentration of CuONPs [53, 54].

Perhaps, more active accumulation of NPs by tomato plants compared to cauliflower was associated with the difference in root morphology. The first study of Cu nanoparticles (CuNPs) action against fungi was reported by Giannousi *et al* [55]. Ever since in various studies the antifungal effect of Cu was observed and CuNPs began to be considered a sustainable treatment option for fungal diseases [56, 57]. In addition, CuNPs have several advantages, for example, they are cheap and highly available, and their production in the form of nanoparticles is economical. Therefore, there are many studies on the use of CuNPs for the effects on phytopathogenic fungi [58–61].

The methods of chemical synthesis include the chemical reduction [62–65], whereas the biological synthesis with various plant extracts is widely used due to its naturalness and non-toxicity to the environment [55, 62, 66]. Finally, the commercial nanoparticles that are effective and readily available have also been analyzed regarding the inhibition of phytopathogenic fungi: *Aspergillus* (*A. flavus*, *A. fumigates, A. niger*, *A. terreus*) and *Fusarium oxysporum, Cladosporium musae, etc.* [65, 67, 68].

In general, small nanoparticles are between 10 and 30 nm in size and more easily penetrate through the cell membrane, causing a rupture and a leakage of cell contents [69, 70]. Something similar happens with Cu nanoparticles of medium size (from 40 to 70 nm). However, when their size increases, their penetration into the cell membrane becomes more difficult and inhibition of the growth and development of pathogen colonies decreases [60, 66]. Meanwhile, large Cu nanoparticles (from 80 to > 100 nm) inhibit the growth of mycelium and spores, thus demonstrating their antifungal ability [65, 71].

Another decisive factor in inhibiting the growth of phytopathogenic fungi is the concentration of Cu nanoparticles. Up to date, various concentrations (e.g., low, medium, and high ones) have been analyzed on phytopathogenic fungi. For example, low concentrations of Cu nanoparticles were analyzed against *F. oxysporum* at 0.1, 0.25 and 0.5 ppm. Although the lowest concentration (0.1 μM) promoted a severe oxidative stress in mycelia, the highest concentration (0.5 μM) showed an antifungal activity against *F. oxysporum* [66].

In addition, Cu nanoparticles have antifungal activity at medium concentrations (for example, 5, 10 and 20 ppm). They showed a significant antifungal activity against *F. oxysporum* and *Phytophthora cactorum,* which were inhibited by increasing the incubation time for different concentrations. To give another example, the doses of 5–35 μM were used against *Rhizoctonia solani, F. oxysporum, F. redolens, P. cactorum, Fasciola hepatica, Grifola frondosa* and *Sparassis crispa,* showing antifungal ability of Cu nanoparticles at the concentration of 35 ppm. In this case, there was neither the growth of mycelia nor the development of the studied pathogens [72]. The highest concentration of CuNPs (450 μM) was used against *Fusarium* sp. showing excellent antifungal activity [73]. Another study was conducted with four different high doses (i.e., 50, 100, 500 and 1000 μM) against *Botrytis cinerea, Alternaria alternata, Monilinia fructicola, Colletotrichum gloeosporioides, Fusarium solani, F. oxysporum*. In this study, CuNPs showed a toxic activity at all concentrations, and at the highest concentration of 1000 μM, they inhibited all phytopathogens [69]. In general, Cu nanoparticles exhibit the antifungal ability by affecting the phytopathogen intracellularly and extracellularly. Therefore, copper nanoparticles are the excellent option for the control and treatment of various diseases of agronomic importance.

Zinc nanoparticles

Zinc (Zn) is an important micronutrient required for the normal metabolic functioning of living organisms [74]. Zinc plays an important role in plant metabolism, as it is a component of more than 300 enzymes. Without zinc, the synthesis of nucleic acids does not occur, as it activates RNA and DNA polymerases, and the general synthesis of proteins is also disrupted. Zinc increases plant resistance to drought, heat, and cold. A lack of zinc in various parts of plants leads to the accumulation of phenolic compounds, which have a negative effect on the plant and reduce its resistance to disease [75]. In addition, Zn deficiency leads to a decrease in various metabolic processes, such as the growth and, ultimately, the yield [76, 77].

Fertilizers in the nanoscale (1–100 nm) significantly enhance the effect points due to their reduced volume, which, as a result of rotation, can improve the contact and absorption of trace elements when fertilizing crops [78]. The exogenous application of nanofertilizers has proven its effectiveness, as they provide nutrition of crops in a stable and established mode instead of conservative fertilizations [79, 80].

NPs can be absorbed by leaves and transferred to all plant tissues through aerial organs and cellular structures [81]. The application of ZnONPs is one of the most effective options for significantly increasing agricultural yields worldwide under the stressful conditions. ZnONPs can change the agricultural and food industries with several innovative tools to resolve the oxidative stress symptoms caused by abiotic stress. In addition, the effects of ZnONPs on physiological, biochemical and antioxidant activities in various plants have been properly researched [82].

Researches have shown that the environmentally compatible synthesis of ZnO nanoparticles using *Senna occidentalis* leaf extract functioned as a natural reducing agent and stabilizer. The use of phytosynthesized nanoparticles as the nanopriming to enhance a germination and metabolic activity of germinating Pusa basmati (*Oryza sativa* L.) rice seeds is an alternative to the traditional hydropriming. The nanopriming can be further used as a technique to improve zinc content in rice seeds, which increases its nutritional value and also supports a rapid germination [83].

The researches demonstrate that zinc oxide nanoparticles (ZnONPs) positively regulate the plant resistance to various environmental stresses. However, up to date, the limited in-formation has been obtained regarding the role of ZnONPs in the regulation of salinity stress in plants [77, 84]. In these studies, a role of ZnONPs in the regulation of tomato salt endurance was investigated (*Lycopersicon esculentum* Mill.). The tomato plants were subjected to the salinity stress with NaCl (150 mM) during transplantation 15 days after sowing. The foliar application of ZnONPs at different levels, namely, at 10, 50 and 100 mg/l in the presence/absence of NaCl (150 mM) was carried out 25 days after sowing and the sampling was carried out 35 days after sowing. The results of the study showed that a foliar spraying of ZnONPs significantly increased a shoot length and a root length, a biomass, a leaf area, chlorophyll content and photosynthetic properties of tomato plants in the presence/absence of salinity stress. In addition, the application of ZnONPs mitigates the negative effects of salinity stress on a tomato growth, and also increases the protein content and an activity of antioxidant enzymes such as peroxidase (POX), superoxide dismutase (SOD), and catalase (CAT) under the salt stress conditions. Besides, ZnONPs play an important role in reducing NaCl toxicity in tomato plants. Therefore, ZnONPs can be used to improve the growth performance and the mitigation of NaCl-induced adverse effects in tomato [85].

Conclusion

The use of metal nanoparticles such as silver, copper, iron, manganese and zinc in agriculture will open up new opportunities to improve yields, production efficiency, resource conservation and environmental friendliness. A unique feature of metal nanoparticles, namely low toxicity, plays a key role in their use in the agricultural sector. The biogenic metals, due to their extremely high activity and the size corresponding to the size of living cells, are more effectively and safely perceived by plants as micronutrients. As a result, the rates of application of vital trace elements are significantly reduced and the risk of possible negative environmental consequences from overdosing fertilizers is reduced.

The prospects of the metal nanoparticles use include such aspects as:

– increase of soil fertility: the addition of metal nanoparticles helps to increase the soil fertility by improving chemical processes and mineral metabolism, contributing to yields;

– protection of plants from pests and diseases: metal nanoparticles can create antimicrobial coatings that help to control pests and diseases;

– efficient water management: the use of nanoparticles helps to optimize water storage and use, especially in conditions of moisture deficit;

– improvement of the nutritional quality of plants: metal nanoparticles can serve as a source of trace elements and fertilizers, providing plants with essential nutrients;

– improved seed and germination: treating seeds with nanoparticles helps to increase their viability and germination, contributing to higher yields;

– reduced environmental impact: the use of nanoparticles can help to reduce the need for chemical pesticides and fertilizers, contributing to sustainable agriculture.

Given the growing need for sustainable and efficient agriculture, the use of metal nanoparticles can be a key innovation strategy to achieve these goals.

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Вплив наночасток металів на рослини

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Використання наночасток металів в сільському господарстві відкриває перспективи для збільшення ефективності та стійкості сільськогосподарського виробництва. Ця технологія дозволяє застосовувати мініатюрні частинки металів, такі як наносрібло, наномарганець, наномідь, наноцинк тощо, з максимальною точністю та спрямованістю. Перспективи використання наночасток металів включають такі аспекти як: збільшення родючості ґрунту, захист рослин від шкідників та хвороб, ефективне управління водним режимом, підвищення поживності рослин, покращене насіння та проростання, сенсорні технології для моніторингу, зменшення негативного впливу на навколишнє середовище. З необхідністю забезпечення безпеки та урахуванням впливу на навколишнє середовище, використання наночасток металів має потенціал перетворити сільське господарство, забезпечуючи стійкий ріст виробництва та зниження його екологічного відбитку.

Ключові слова: сільське господарство, нанотехнології, наночастки, нанометали, мікроорганізми, зелений біосинтез.

Received 15.09.2023