Effect of iron, copper and molybdenum nanoparticles on morphometric parameters of Solanum tuberosum L. plants

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Over the past decade, nanotechnology caused the need for rigorous research on ultrafine nanomaterials which enhance productivity and quality of agricultural products. However, most studies are controversial; it is difficult to compare doses of nanoparticles and types of plants. In the experiment, nanoparticles of Fe (90–110 nm), Cu (50–110 nm) and Mo (100–120 nm) at four concentrations with a geometric progression were used to treat potato tubers. Germination energy was determined according to GOST 12038-84; the content of photosynthetic pigments was determined according to the method by N. D. Smashevsky (2011), phytotoxicity was determined according to the method by Kazev K. (2013). Thus, the data indicate that treatment of Solanum tuberosum L. tubers with iron nanoparticles stimulated the growth of the length of sprouts (55.1% and 21.4%), roots (34.4% and 12.5%) and chlorophyll a (57-98%) at a concentration of 0.0125 ... 0.025 M. At the same time, copper and molybdenum nanoparticles are ineffective by the significance of their effects on plants.

1. Introduction

Nowadays, the development and implementation of nanotechnology in industries, medicine, and agriculture have been affected by technogenic nanoparticles [1]. Due to their unique properties, nanoparticles are widely used in areas, in catalysts, cosmetics, medicines [2]. Researchers deal with the issues of their impact on the environment [3,4]. The potential impact of nanoparticles on the environment should be carefully analyzed; falling into the soil during atmospheric deposition and raining, nanomaterials accumulate in the soil, due to their poor migration ability [5]. Plant organisms as primary sources are diverse and accessible objects [6] whose use makes it possible to evaluate both the specificity of the effect of nanoparticles and their dose-dependent effects. Sensitivity of plants is an indicator of ecotoxicity of nanomaterials [7]. In addition, plant organisms serve as a bioaccumulant for transporting nanoparticles; as a result, plant agrocenoses can suffer from oxidative stress caused by nanoparticles [8].

There are experimental materials which show how unique and diverse nanoparticles are in their manifestations. Their properties depend on the physical nature, methods of preparation, sizes, structures of nanoparticles and the biological model on which tests are carried out. Main physiological indicators of toxic effects of NPs are germination energy, elongation of roots, biomass of leaves. A number of researchers [9, 10] indicate that some NPs can have significant negative consequences: reduction in seed germination and inhibition of sprout and root length.

There are no experimental data on the effect of nanoparticles on biochemical and physiological processes in the sprouts of Solanum tuberosum L. plants. The concentration of photosynthetic pigments...
determines the activity of the photosynthetic apparatus, the rate of accumulation of assimilant, which affects productivity and growth of plants. Thus, these studies are relevant in modern science and environmental management, since the pros and cons of nanoparticles require a comprehensive assessment.

2. Materials and methods
The studies were carried out in the Center for Collective Use of the FSBI FSC BST RAS. Biological activity of Fe (90-110 Nm), Cu (50-110 Nm) and Mo (100-120 Nm) nanoparticles was tested at 4 concentrations with a geometric progression (0.0125; 0.025; 0.05 and 0.1 M) and in 3 replications. Before the experiment, potato tubers were disinfected in a 0.01% KMnO4 solution for 5 minutes, washed with distilled water and dried for 15-20 minutes. Then the tuber was laid out in plastic containers (5-7 cm) in 10 pcs. Suspensions of nanoparticles were prepared according to TU 931800-4270760-96, the drug was dissolved in distilled water and processed in an ultrasonic disperser (UZDN, f-35 kHz, N-300 W, Russia) for 30 minutes. The tuber samples were poured with 100 ml of fresh suspensions of NPs of Fe, Cu, and Mo shaken the container for 5 minutes; the suspension was discharged. Untreated tubers (0 g/kg) were used as control ones. Containers with tubers were germinated in a climatic chamber (“POL-EKO-APARATURA Sp.J.”, Typ: KK 1200 TOP + FIT) for the first week without illumination at a temperature of 23 ± 1°C and humidity of 83 ± 2%. For the subsequent three weeks, they were germinated at a temperature of 25 ± 2°C, and for 8 hours - at a temperature of 18 ± 2°C and humidity of 83 ± 2% (GOST 20290-74). Germination was determined in accordance with GOST 12038-84. The content of photosynthetic pigments was determined in the ethanol extract by the method by N.D. Smashevsky [11]. The content of chlorophyll and carotenoids was determined by the weight of raw green mass; calculations were carried out according to the Smith and Benitez formulas (Wintermans, de Mots, 1965). To assess the toxicity, the phytoeffect (effect of inhibition) [12] was determined by formula:

\[ Et = \left( \frac{Lc}{Lk} \right) \times 100\% \]

where Et is the effect of inhibition, %; Lc is the average length of roots, cm; Lk is the average length of roots in the control option, mm.

3. Discussion
Analysis of publications devoted to the effect of metal NPs on plant organisms showed that the most common indicators are germination and sprout and root lengths. Calculation of the germination energy of tubers showed that during treatment with Fe nanoparticles at a concentration of 0.0125 and 0.25 M, there was a significant increase in the length of sprouts by 55.1% and 21.4% (P≤0.05) and roots by 34.4% and 12.5% relative to the control option. At a concentration of 0.1 M, the metal had a negative effect on the germination of tubers and the length of sprouts (55-70%). In the presence of Cu and Mo NPs in doses from 0.0125 to 0.1 M, the germination energy value was lower than the control one by 1.7 and 1.2 times, respectively (P <0.05). At the same time, the length of sprouts at the same concentrations was lower than the control one by 22.0% and 36% (Fig. 1, 2).

![Figure 1](image-url) **Figure 1.** Potato biometrics after the action of nanoparticles: the average length of sprouts. Note: * the variant is significantly different from the control one (P≤0.05)
Treatment of tubers with iron nanoparticles improves growth parameters at a concentration of 0.0125 and 0.025 M which is not true for copper and molybdenum nanoparticles (Fig. 1, 2). This corresponds to the literature data, since potatoes can filter out nanoparticles avoiding their effects, unlike other crops (wheat, cucumber, soybean) [13].

As shown by the measurement results, on the 21st day, when exposed to suspensions of copper and molybdenum nanoparticles at concentrations of 0.05 and 0.1 M, a slowdown in the growth of roots and sprouts was observed in comparison with the control option up to 65.0%. The “growth inhibition effect” of the length of roots and sprouts was manifested both on the 14th and 21st days after the treatment of tubers with copper and molybdenum NPs (Table 1).

Physiological capabilities of plants are determined by the structural and biochemical organization of the pigment apparatus. It is known that chlorophylls a, b and carotenoids play a key role in photosynthetic processes; changes in their concentration and ratio in the pigment complex is an indicator of environmental distress. Therefore, studies of the effect of iron, copper, and molybdenum nanoparticles on the pigment content in plant leaves were carried out.

Analysis of chlorophyll content in the leaves of Solanum tuberosum sprouts showed some differences due to the presence of nanoform metals.

Table 1. Evaluation of the effect of Fe, Cu and Mo NPs on Solanum tuberosum growth inhibition

| Options   | Inhibition effect, % | Sprout length | Root length |
|-----------|----------------------|---------------|-------------|
|           |                      | 14 days       | 21 days     | 14 days     | 21 days     |
| Fe 0.0125 | -                    | -             | -           | -           | -           |
| Fe 0.025  | -                    | -             | -           | -           | -           |
| Fe 0.05   | 7.1                 | 12.8          | 9.3         | 18.8        |
| Fe 0.1    | 50                  | 31.6          | 25          | 36.2        |
| Cu 0.0125 | 21.4                | 12.0          | 34.4        | 39.8        |
| Cu 0.025  | 42.8                | 28.0          | 40.6        | 50.0        |
| Cu 0.05   | 54.0                | 46.6          | 50.0        | 57.0        |
| Cu 0.1    | 57.0                | 64.0          | 63.6        | 65.0        |
| Mo 0.0125 | 28.0                | 4.0           | 35          | 30.4        |
| Mo 0.025  | 40.0                | 20.0          | 28          | 40.0        |
| Mo 0.05   | 52.0                | 37.0          | 50          | 56.0        |
| Mo 0.1    | 62.0                | 59.0          | 57          | 59.0        |
The positive effect of Fe nanoparticles at doses of 0.0125-0.1 M on the level of chlorophyll a and b in sprouts was established; its content increased by more than 57%-98% (Fig. 3). An increase in chlorophyll was caused by iron ions isolated from their composition.

Figure 3. The content of photosynthetic pigments in of Solánum tuberósum L. sprouts treated with suspensions of iron nanoparticles.

However, the lack of changes in chlorophyll content under the influence of copper nanoparticles was reliable, although insignificant (by 4.7%), and chlorophyll b increased at all concentrations, but the maximum 2.5-fold increase was observed at a concentration of 0.05 M (Fig. 4). The similar pattern was observed in germs when exposed to molybdenum NPs. Dark color of sprouts was accompanied by a decrease in chlorophyll content at a concentration above 0.025 M (by 6.9%). At the same time, the level of chlorophyll b changed by 2.5-3 times (Fig. 5). There are contradictory data regarding the effect of NPs on chlorophyll content: some researchers speak about an increase in the content of pigments [14], others - about a decrease in chlorophylls [15].

Parallel to chlorophylls a and b, carotenoids are part of the pigment-protein system. Analysis of carotenoid content in Solanum tuberosum sprouts showed that this group of photosynthetic pigments was not sensitive to metal NPs. Therefore, after the treatment with Cu and Mo, an increase in carotenoids was observed in (by 45%) (P> 0.05) which indicates an increase in oxidative processes or a primary nonspecific reaction to stress.

Figure 4. The content of photosynthetic pigments in Solánum tuberósum L. sprouts treated with suspensions of copper nanoparticles.
Figure 5. The content of photosynthetic pigments in Solánum tuberósum L. s sprouts treated with suspensions of molybdenum nanoparticles.

It is important to note that when treating with Fe NPs at a concentration above 0.05 M, significant deviation of the level of carotenoids from the control one was observed (from 4.2% to 20.3%). A sharp increase in the concentration of green pigments is a factor limiting photosynthesis. The synthesis of chlorophylls is very sensitive to all sorts of influences that disrupt metabolic processes in the cell. An increase in the concentration of Fe nanoparticles increases the content of carotenoids in the sprouts; this is due to the mobilization of compensatory mechanisms of the plant in order to preserve its level of assimilation process.

4. Conclusion
Summarizing the results of biological activity of Fe, Cu, and Mo NPs for the Solánum tuberósum model plant, we can conclude that nanometals contributed to both inhibition and increase in plant growth depending on their sensitivity, as well as physicochemical features of the nanomaterials under study. If we compare copper and molybdenum nanoparticles by the significance of their effects on Solánum tuberósum L. plants, they are ineffective, and iron nanoparticles have a stimulating effect on the length of sprouts, roots and chlorophyll content at a concentration of 0.025…0.025 M.

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