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Use of a colloidal solution of metal and metal oxide-containing nanoparticles as fertilizer for increasing soybean productivity

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ABSTRACT

Since the availability of micronutrients in agricultural soil are strongly depended on changes in soil characteristics, microfertilizers are one of the most effective means of influencing crop productivity and product quality. The use of nanoparticles of metals compensates for the loss of microelements, increases the stress tolerance of plants, both of which improve the quality of the final product. The aim of the research was to study the characteristics of a colloidal solution of metal nanoparticles (Mn, Cu, Zn, Ag, Fe) using X-ray diffraction to estimate the prospects of using them in agrotechnology. The objectives of the study included optimizing the method for treating plants and determining effective concentrations of metal nanoparticles and their composition, combined with traditional fertilizers (NPK), for enhancing soybean productivity. The objects of the study were varieties of soybean recommended for the forest-steppe ecoregion of Ukraine: ultra-early and early maturing Annushka and Ustya, respectively. The results obtained indicate the feasibility of using of a colloidal solution of metal nanoparticles as fertilizer due to its properties (phase composition, size) in agricultural technologies for soybean, which improves the productivity of this crop.

Keywords: nanoparticles, X-ray diffraction, soybean (*Glycine max* (L.) Merr.), pre-sowing seed treatment, foliar treatment, yield

INTRODUCTION

Nowadays, due to global challenges, agriculture is adopting modern technologies and materials for sustainable development (Chen and Yada, 2011). Nanotechnology provides innovative means and products such as carbonaceous nanoparticles, metal oxides, quantum dots, zero-valent metals and nanopolymers, which can modify conventional agricultural practices, namely by reducing the number of applications of plant protection products, minimizing nutrient losses in fertilization, and increasing yields through optimized nutrient management (Chaudhry et al., 2008; Peters et al., 2016).

Nanoparticles, depending on their physical and chemical properties, interact with a plant's organism, causing alterations in the metabolism of the organism as well as on a cellular level (Garcia-Gomez and Fernandez, 2019). The efficiency of nanoparticles is determined by their chemical composition, concentration, size, surface covering, reactivity, and, most importantly, the effective dose and mode of their application, and the plant species (Brunner et al., 2006; Ma et al., 2010; Khodakovskaya et al., 2012; Tian et at., 2019). The results of technological research show that a solution of metal nanoparticles is compatible with all types of fertilizers and pesticides.

The use of metal nanoparticles compensates for the loss of the microelements in soil or their inaccessibility for plants and increases plant resistance, optimizes the metabolic processes of plants according to the climatic conditions occurring during the growing season while improving the quality of the final product. Moreover, the use of metal nanoparticles increases the effectiveness of the main macronutrients – nitrogen, phosphorus and potassium. It is also an efficient way to apply pesticides and fertilizers in a controlled manner (Duhan et al., 2017). The application of nanofertilizers provides environmentally safe products due to improving the efficiency and sustainability of agricultural practices by having to use less input and by generating less waste that connected with conventional products and approaches (Scrinis and Lyons, 2007). However, some researchers speculate that there is a risk connected with releasing nanomaterials into the soil and their accumulation in the edible parts of crops that could hide some toxicity to consumers (Pérez-de-Luque, 2017; Elemike et al., 2019).

Soybean (*Glycine max* (L.) Merr.) is the world's most widespread legume which provides an important source of protein and oil. According to Ainsworth et al. (2012), global soybean production and yield per hectare has been increasing steadily over the past century owing to improved agronomy and breeding. However, in order to meet the needs of a growing world population given the unsustainable expansion of the land area devoted to this crop, yields must increase at a faster rate than at present. That is why the present research mainly focused on the nutrient base of crop development and recent approaches that can be implemented for soybean agrotechnology (Coman et al., 2019; Shang et al., 2019). The present research was warranted to elucidate the effect of a colloidal solution of nanoparticles of metals, based on their properties biogenic metals (Mn, Cu, Zn, Fe) and metals, which are used as plant protection agents against microbial activity and bacterial diseases (Cu and Ag), on soybean productivity. The objectives of the study included the optimization of methods for treating and determining effective concentrations of metal nanoparticles and the composition of the most successful application to be used with traditional fertilizers (NPK) in soybean cultivation technologies in the northern forest-steppe eco-region of Ukraine.

MATERIALS AND METHODS

The patented stock complex of a colloidal solution of metal nanoparticles (Mn, Cu, Zn, Ag, Fe) was used in the present study. The process of obtaining of the colloidal solution of nanoparticles is based on the electrical treatment of granules of iron, manganese, copper, zinc and other metals. The main components underlying generating the metal nanoparticles are granules, cathodes and anodes (made from the same material as the granules), a working chamber, and bidistilled water (dielectric) (Lopatko et al., 2009).

The X-ray analysis of water specimens, subsequently evaporated at 60°C, was performed using an Ultima IV (Rigaku) diffractometer with monochromatic Cu K α-radiation. A graphite single crystal monochromator installed on a diffraction beam was used. The diffraction patterns were registered by step scanning in the angle range of $2\vartheta$of 6 – 90°, scan step – $2\theta=0.04°$ and the exposure time of 2 s. A full-profile analysis of the diffraction patterns and the phase composition was done using PowderCell 2.4 software. The full-profile analysis was carried out by fitting an experimental diffraction pattern from a sample to a theoretically calculated diffraction pattern from the mixture of polycrystalline phases present in the sample. The parameters that describe the background, the profiles of the diffraction peaks, the texture factors, and the volume fraction of the phases were refined by minimizing the factor of divergence (R-factor) of the theoretical and experimental patterns by the least square method (Karpets et al., 2003).

Field research on the effects of the multicomponent colloidal solution of metal nanoparticles on soybean yield formation was conducted over 3 seasons in the fields of the Department of Crop Growing of the National University of Life and Environmental Sciences of Ukraine's Agronomic Research Station. Since there were no significant differences between the yields over 3 seasons, the diagrams in present paper show average values.

Typical agricultural technologies for cultivating soybean in the northern forest-steppe eco-region of Ukraine were used. Analysis of soil samples was performed according to the State standard of Ukraine (DSSU, 2006). The soil of the experimental plots is characterized as typical low-humus coarse-grained black soil. The humus content in the arable layer is 4.4% (by Turin's method), a pH of 6.8- 8.3; and with an absorption capacity of 30.7-32.5 mg eq per 100 g of soil. The composition of the mineral solid phase of the soil is made up of 37% physic clay and 63% sand. The density of the soil in the equilibrium state is 1.16-1.25 g/cm^3. The humidity of resistant wilting is 10.8%. The groundwater level is 5-6 m.

The soil is also characterized by a high content of nutrients. In the 0-20 cm layer: the total nitrogen content is 0.27-0.31% (by Kjeldahl method), phosphorus – 0.15-0.25% and potassium 2.3-2.5% (according to Kirsanov). The amount of mobile phosphorus according to Chirikov was 4.5-5.5 mg per 100 g of soil.

Soybean seeds were sown in the soil at a temperature of 10-12 °C at the seeding depth. The total unit area was 84 m^2, the accounting area 52.8 m^2. All of the treatments were performed in four repetitions. The seeding rate of the soybean seeds was 700 thousand seeds per 1 ha. Harrowing before germination as well as a herbicide mixture of Aram (1.0 L per ha) and Basagran (2.0 L per ha) were applied as plant protection.

Two experiments were conducted to determine the effectiveness of the solution of metal nanoparticles. The first experiment focused on using the colloidal solution of metal nanoparticles in a soybean growing technology. Mineral fertilizers at a rate of $N_{30}P_{30}K_{30}$ were applied during pre-sowing cultivation. Ultra-early and early maturing cultivars of soybean recommended for the forest-steppe eco-region of Ukraine Annushka (PE Scientific Breeding and Seed-growing company ”Soy age”) and Ustya (NSC “Institute of Agriculture of UAAS”) respectively were used. The structure of the experiment included 2 types of treatments – a pre-sowing seed treatment with the complex solution of metal nanoparticles and a pre-sowing seed treatment with further foliar spraying also with a complex solution of metal nanoparticles in the budding phase. The given complex solution of metal nanoparticles was tested in concentrations of 120 and 240 mg/L, which was recommended because of long-term research by the staff of the Department of Crop Growing of the National University of Life and Environmental Sciences of Ukraine.

The complex solution of metal nanoparticles for the pre-sowing seed treatment was used based upon a mixture rate of 0.1 L per ton (100 ml of solution per 10 L of water and 10 tons of seeds). The working solution of the metal nanoparticles for foliar spraying in the budding and flowering phase of soybean growth was prepared based upon the mixture rate of 1 L of product per 100-300 L of water/ha.

The second experiment was designed to compare the use efficiency of a seed and foliar treatment of soybeans containing a solution of metal nanoparticles (120 and 240 mg/L) with the effect of conventional mineral fertilizers on soybean productivity and then to recommend the best composition of this solution for agriculture practice used in the northern forest-steppe eco-region of Ukraine.

Ammonium nitrate (N – 30%), granular superphosphate (P_2O_5 – 19%) and potassium salt (K_2O – 40%) in rates of $N_{30}P_{60}K_{60}$, $N_{60}P_{60}K_{60}$ and $N_{90}P_{60}K_{60}$ were applied during primary tillage. Each type of treatment was compared to the relevant untreated control (distilled water).

All biological and analytical determinations were performed in triplicate. The data were subjected to a variance analysis (ANOVA) with a subsequent Duncan’s multiply range test at $P<0.05$. The data were expressed as the means of replicates ± a standard deviation.

RESULTS AND DISCUSSION

The properties of the nanoparticles in the experimental colloidal solution obtained by X-ray diffraction and the diffraction patterns of the specimens (Ag, Cu, Mn, Zn, Fe) are presented in Table 1 and Figures 1-4, respectively. According to the diffraction pattern peak intensities, the given colloidal solution consists of metal and metal oxide

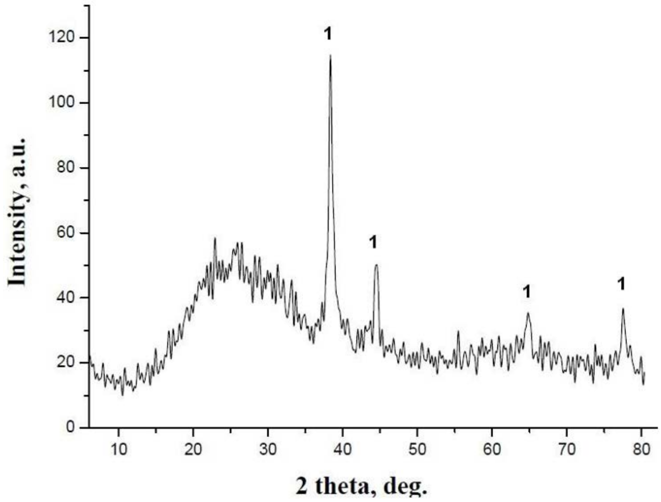

Figure 1. The results of the full-profile analysis of the diffraction pattern for the Ag sample: 1 – Ag

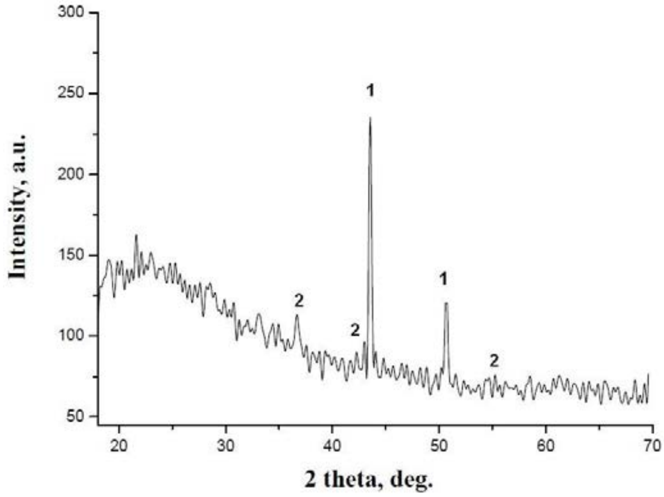

Figure 2. The results of the full-profile analysis of the diffraction pattern for the Cu sample: 1 – Cu; 2 – Cu_2O

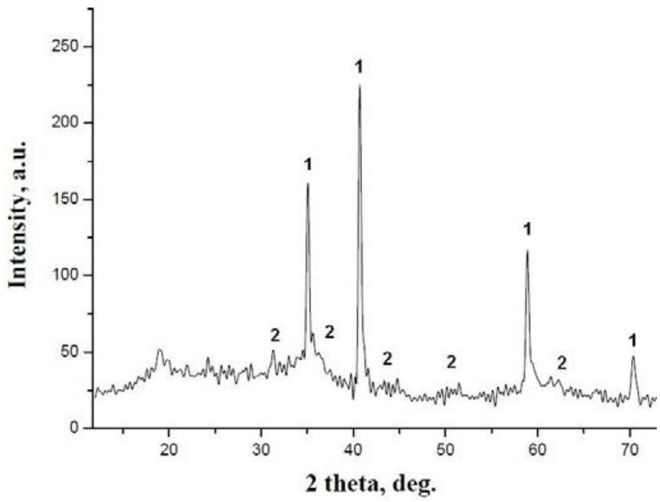

Figure 3. The results of the full-profile analysis of the diffraction pattern for the Mn sample: 1 – MnO; 2 – $MnCO_3$

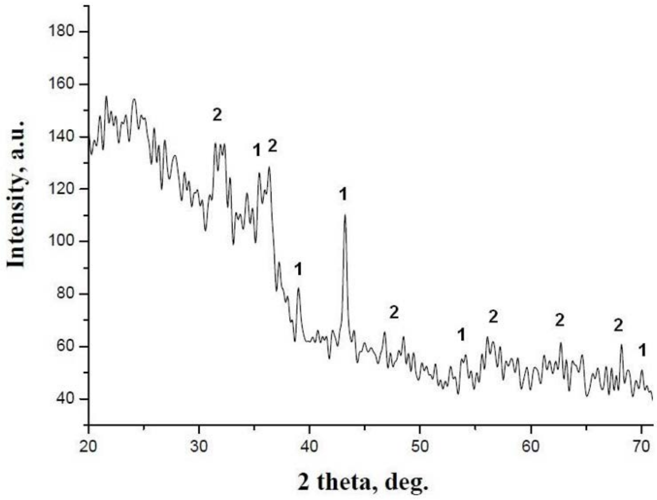

Figure 4. The results of the full-profile analysis of the diffraction pattern for the Zn sample: 1 – Zn; 2 – ZnO

Table 1. Materials characterizations of colloidal solutions of metal-based nanoparticles

Sample	Phase content		Size, nm
	Phase	Mass fraction, %	
Ag	Ag	100	20
Cu	Cu	91,55	78
	Cu_2O	8,45	–
Fe	Fe	16,78	–
	Fe_3O_4	25,91	30
	FeO	57,31	25
Mn	MnO	97,84	53
	$MnCO_3$	2,16	–
Zn	Zn	13,73	45
	ZnO	86,27	

“-” not identified

nanoparticles with a mass fraction of up to 98%, and sizes of nanoparticles from 11 (ZnO) to 78 (Cu) nm. However, the Fe component failed to describe due to an insufficient amount of it in the colloidal solution. The study of Wong et al. (2016) indicated that size, magnitude, and zeta potentials are key to determining the transport of nanoparticles inside the plant.

The determined characteristics of the nanoparticles allow us to suggest their availability to the plants under experimental conditions during pre-sowing and foliar treatments. Mahakham et al. (2017) proposed the mechanism underlying nanopriming-induced seed germination. The beneficial role in this process belongs to silver nanoparticles, which includes: the creation of the seed coat nanopores through the expression of aquaporin genes in germinating seeds, thus enhancing water uptake into seeds; mild stress-induced agents or reactive oxygen species-generating agent, and as a nanocatalyst for intensifying starch-degrading enzyme activity. When nanoparticles interact with plants under root or foliar applications, they have to cross the cell wall first. The size exclusion limit for a plant cell wall is between 5 and 20 nm, however, it has been reported that some nanoparticles could induce the formation of larger pores in cell walls that facilitate the uptake of larger nanoparticles. Then nanoparticles move through endocytosis with further symplastic transport to and storage in various plant tissues (Rastogi et al., 2017; Siddiqi and Husen, 2017). However Wang et al. (2013) provided evidence that particles that did not exceed the diameter of 100 nm penetrated the foliar stomata after spray treatment and were translocated from leaves to stems and roots through the sieve elements.

Indicators of individual plant productivity and the yields of the soybeans are believed to be the criteria for assessing the efficiency of photosynthesis, biological nitrogen fixation and the formation of plant productivity (Hungria et al., 2005; Long et al., 2006; Ainsworth et al., 2012). Research on methods for applying multi-component solutions of metal nanoparticles for fertilizing soybeans revealed the most effective one (Figures 5a, 5b).

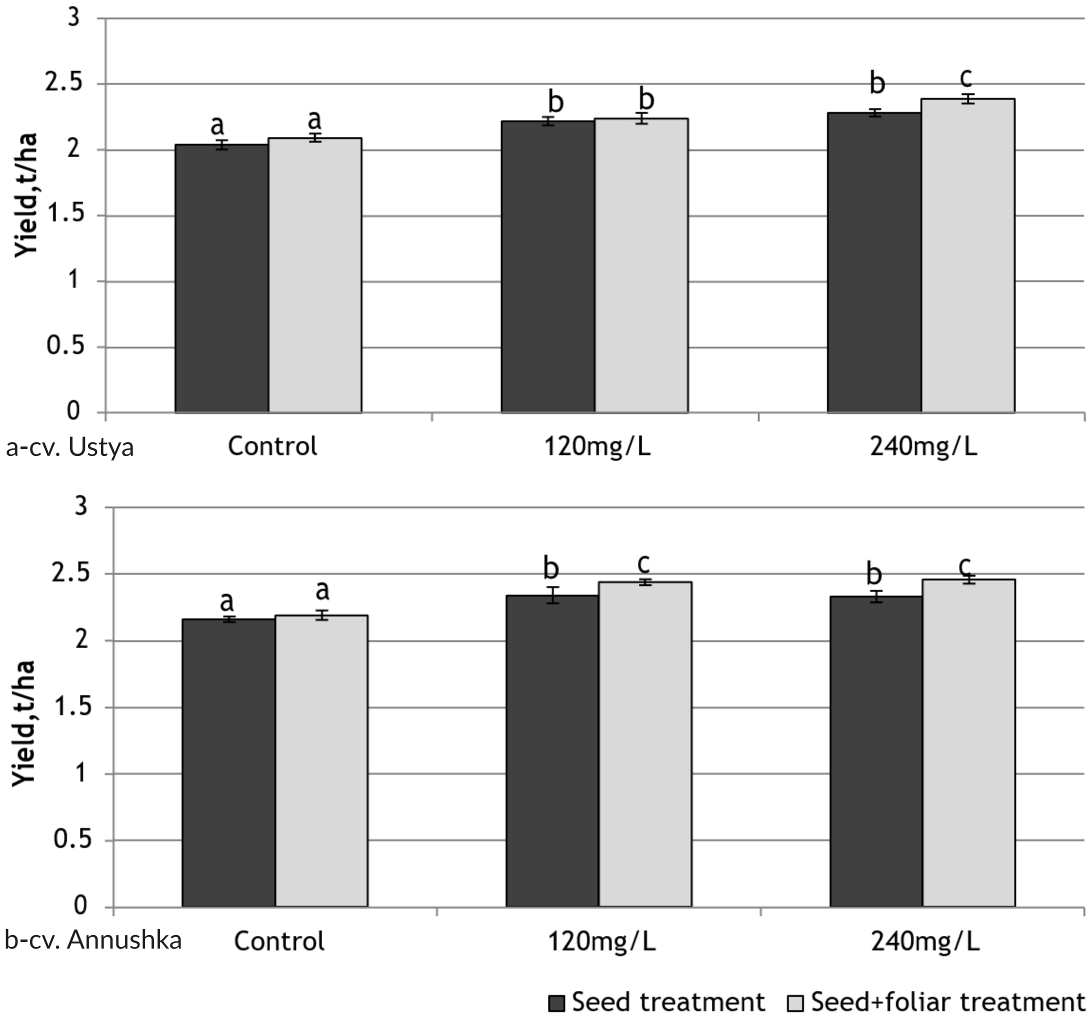

Figure 5. The yields of soybean cvs. Ustya (a) and Annushka (b) depending on the method of application (seed and combined seed and foliar treatments) and concentrations (120 and 240 mg/L) of the colloidal solution of metal nanoparticles, 1st experiment (The values labelled with different letters were significantly different at P<0.05 according to Duncan's multiply range criterion)

Thus, pre-sowing seed and combined seed and foliar treatments with multicomponent solutions of metal nanoparticles with a background of $N_{30}P_{30}K_{30}$ provided significant increases in crop yields in both cultivars as compared to the control options in the amounts of 1.5-3.0 tons per hectare. Presented data indicate that the 1st experiment, with the use of a solution of metal nanoparticles in a 240 mg/L concentration for a combined treatment of soybeans, provided significantly higher yields of cv. Ustya (Figure 5a). It is known that the influence of nanoparticles on plants can be dose dependent, namely an inverse dependence was observed (Prasad et al., 2012; Mirzajani et al., 2013). For example, a crop treatment with nanoparticles in high concentrations (2000 ppm) revealed an inhibitory effect on the germination, growth and yields of peanuts (Prasad et al., 2012).

On the contrary, increasing the productivity of cv. Annushka depended only on the method of application of the metal nanoparticles solution (Figure 5b). Similarly, several studies have shown that the application of nanoparticles, including seed treatments, promotes the growth and development of seedlings; moreover, foliar nutrition is a beneficial option when nutrient deficiency cannot be corrected by applying fertilizer to the soil (Sarkar et al., 2007; Sheykhbaglou et al., 2010; Janmohammadi and Sabaghnia, 2015). For example, foliar spraying of peanuts with ZnO nanoparticles promoted an almost 30% increase in pod yields as compared to the use of chelated $ZnSO_4$ (Prasad et al., 2012). Although earlier achievements show some prospects for using metal nanoparticles in agrotechnology, there is a shortage of information about the efficiency of different methods for treating plants with metal nanoparticles and the choice of the dose to apply on plants, not only at seed germination, but also during the crop's development.

The use of numerous nanoparticle applications in agrotechnology is predetermined by their ability to enter plant tissues for further transportation up- and down through the vascular system of the plants. However, their uptake and translocation (through the apoplast or symplast pathway, endocytosis) in plant organisms are limited by chemical and physiological barriers (cell walls, Casparian strips) (Schwab et al., 2016; Wang et al., 2016). One of the advantages of using nanoparticles as fertilizers is their very small effective concentrations; nevertheless, the positive effect of their application is obvious. Previous studies showed the potential of metal nanoparticles in increasing plant growth and in improving crop development. It was determined, that silver nanoparticles increased the length of roots in maize and cabbage plants in comparison with $AgNO_3$ (Pokhrel and Dubey, 2013). Gold nanoparticles influenced the number of leaves, the leaf area, plant height, and the sugar and chlorophyll content that resulted in better crop yields (Arora et al., 2012). In addition, an up to 25% increase in winter wheat yields was observed due to a pre-sowing treatment of winter wheat seeds with metal nanoparticles (Batsmanova et al., 2013). Despite numerous studies on nanomaterials-induced plant growth promotion and stress tolerance, the underlying mechanisms still remain uncovered. The influential effects of nanomaterials on crop growth under unfavourable conditions at least partly can be explained by the increased activity of enzymatic system of plant (Shang et al., 2019).

When compared to the effect of conventional mineral fertilizers, the colloidal solution of metal nanoparticles stands out owing to its high use efficiency on soybean productivity. As expected, the soybean yield depended on the dose of the mineral fertilizer applied – the most effective was applying $N_{60}P_{60}K_{60}$ (Figure 6). Beyond this, the productivity of soybeans on that nutritional background increased by 18% after a pre-sowing seed and foliar treatment of the soybean crop with 240 mg/L of a complex solution of metal nanoparticles.

A considerable amount of literature demonstrates that nanostructured fertilizers can increase the nutrient use efficiency of plants through mechanisms such as the targeted delivery and the slow or controlled release of agrochemicals. They could precisely release their active ingredients in response to environmental triggers and biological demands. It has been reported recently that nanofertilizers can improve crop productivity

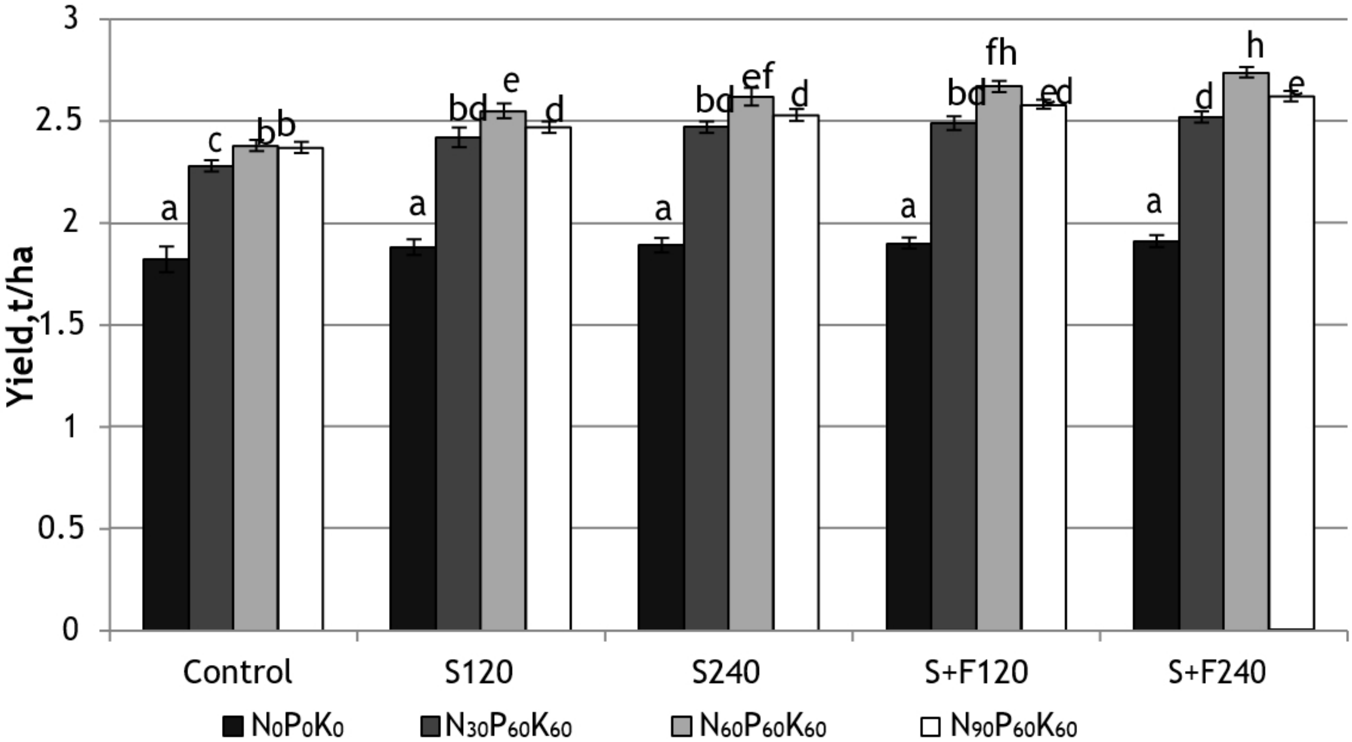

Figure 6. Yields of soybean (cv. Annushka) depending on the method of treatment (seed (S) and combined seed and foliar (S+F) treatment), the concentration of the complex solution of metal nanoparticles (120 and 240 mg/L) and the application of mineral fertilizers (NPK), 2nd experiment (The values labelled with different letters were significantly different at $P<0.05$ according to Duncan's multiply range criterion)

by enhancing the rate of seed germination, seedling growth, photosynthetic activity, nitrogen metabolism, carbohydrate, protein and oil synthesis (Solanki et al., 2015; Cao et al., 2018; Sheykhbaglou et al., 2018; Garcia-Gomez and Fernandez, 2019). In light of these facts, presented data allow to suggest that the application of metal nanoparticles also assists in augmenting the activity of conventional fertilizers.

CONCLUSIONS

A multi-component colloidal solution of metal and metal oxide-containing nanoparticles was analysed. The determined characteristics of the nanoparticles (size and phase content) allows to suggest their availability to the plants under experimental conditions, and to recommend researched colloidal solution for pre-sowing seed treatment and foliar spraying in the budding phase of cultivating early maturing soybean cultivars on the low-humus containing black soils of the forest-steppe eco-region of Ukraine. However, some peculiarities of applying a colloidal solution of metal nanoparticles between cultivars were observed. Thus, the most effective way to apply them for obtaining high yields of soybean of cv. Ustya is a combined seed and foliar treatment with a colloidal solution of metal nanoparticles in the concentration of 240 mg/L. On the other hand, only the means of treatment were more essential to the Annushka variety, regardless of dose, since the combined seed and foliar application improved soybean yield. Also treating soybeans (cv. Annushka) with metal nanoparticles assists in augmenting the impact of conventional fertilizers (NPK) that resulted in promoting yields on the background of $N_{60}P_{60}K_{60}$.

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