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## AN EFFECT OF THE COPPER'S NANOPARTICLES APPLICATION ON THE DEGREE OF COVERING THE SPRAYED OBJECTS

Summary

The main purpose of the study was to compare the average and total degree of covering the sprayed plants with the foliar fertilizer with copper and the nanocopper. The measurement of covering degree was performed in "Aporo" sprayed chamber at a constant speed of (11.16 m·s<sup>-1</sup>) and at two pressures values 0.2 and 0.28 MPa for two nozzles standard: one-stream XR110-02, and a dual-stream DF120-02. Tests were conducted at a constant speed for different pressures and two conventional nozzles. The samplers in the form of water sensitive paper were used. The degree of covering was calculated using a computer image analysis method. Statistical tests were carried out based on an analysis of the average group and homogeneity of variance (ANOVA). It was found that, when the nanocopper was applied, the average degree of covering and the total degree of covering were higher than while using the foliar fertilizer (Mikrovit) with copper, regardless of the pressure and the nozzle used in tests.

Key words: foliar fertilizer, water sensitive paper; average degree of covering, nanocopper; spraying plants, nozzles

# WPŁYW ZASTOSOWANIA NANOMIEDZI NA STOPIEŃ POKRYCIA OPRYSKIWANYCH OBIEKTÓW

Streszczenie

Celem badań było porównanie średniego oraz całkowitego stopnia pokrycia roślin opryskiwanych nawozem dolistnym miedzi i nanomiedzią Badania stopnia pokrycia wykonano w komorze opryskowej "Aporo". Doświadczenie przeprowadzono ze stałą prędkością opryskiwania (11.16 m·s<sup>-1</sup>), przy dwóch ciśnieniach roboczych 0.2 i 0.28 MPa dla dwóch rozpyłaczy standardowych: XR 110-02 i DF 120-02. Użyto próbników w postaci papierków wodoczułych, które umieszczano na powierzchniach poziomych i pionowych sztucznych roślin. Stopień pokrycia obliczono dzięki wykorzystaniu komputerowej metody analizy obrazu. Przeprowadzono testy statystyczne oparte na analizie średnich w grupach oraz analizę jednorodności wariancji (ANOVA). Stwierdzono, że przy zastosowaniu do oprysku pierwiastka nanomiedzi średni stopień pokrycia oraz całkowity stopień pokrycia był wyższy niż przy zastosowaniu nawozu dolistnego Mikrovit, niezależnie od ciśnienie oraz rozpyłacza wykorzystanego w badaniach.

Słowa kluczowe: nawóz dolistny, nanomiedź, stopień pokrycia, opryskiwanie roślin, rozpylacz

#### 1. Introduction

The nanotechnology is currently used in many areas of human life, especially- in medicine, in food and textile industry, as well as in agriculture [10, 15, 16]. Its use allows the introduction of more effective plant protection products as well as the growth regulators and fertilizers in cultivation process. [7, 17]. For a few years, the use of nanoparticles copper, silver and carbon has increased, what has been confirmed by numerous studies [11, 12, 23]. In such areas as technology, industry, medicine and agriculture, various possibilities to implement the nanomaterial are observed. Due to the permanent increase in production of nanomaterials, it is required to reduce their emission to the environment. Increasingly, the researchers have recognized the negative impacts of the nanoproducts residues on living organisms, e.g. on bacterial, algae, fungus, plants, small invertebrates and fishes. The nano impurities used in various ways can cause a pollution of water and all its elements. It is especially dangerous when there is the lack of chances to

reduce the nano-fractions in the existing wastewater treatment because of its poor quality [1, 14].

The main problem of modern cultivation is posed by an intensive field crops production. It involves the use of large doses of mineral fertilizers and pesticides, when their residues are dispersed in soil and water. The occurrence of plant protection products was found in all types of water circulating in the ecosystem - in atmospheric precipitation, surface waters and groundwater [8, 18]. Plant protection products have become commonly used in agricultural production, despite the creation of threats in the chain soilplant-human. Some of the active substances, part of the plant protection product and its metabolites may enter the trophic chain of humans and animals, along with the yield of the crop. Then, they become harmful residues. Already a many years ago, researchers found that synthetic pesticides have become a fast, convenient and universal element in protecting crops against pathogens - despite the large public awareness of the consequences that entail excessive use of pesticides [3, 13].

An analysis of the papers showed the real scale of the problem of the chemical crop protection and its consequences. For this reason, the process of plant protection should be conducted with high efficiency and friendly to the environment, especially during food consumption and fertilization process. The authors of many studies emphasized that an increase in crop yields and improvement of plant health are possible due to the foliar fertilizers. These formulations provide macro- and micronutrients, and may even reduce the infestation of plants by pests and diseases [2, 19]. The foliar feeding is a very effective method in completing nutrients, because the pace and extent of fertilizers, which are applied directly to the plant, are more effective than fertilizing the soil, but is limited by the ability to use larger amounts of these ingredients and their absorption by plants. The residues in the environment arising from traditional chemical compounds derived from the plant protection products and residual compounds in the nano form, can cause a problem and a threat to the entire ecosystem. Therefore, the main purpose at which the study should be aimed concerns determining the method that allows the reduction of a harmful effect of pesticides in the environment, including living organisms.

The degree of covering is one of the most important indicators of the quality assessment procedure of spraying, therefore, the aim of the study was to compare the average and total degree of covering plants sprayed with nanocopper and copper foliar fertilizer.

#### 2. Material and Methods

The test included two phases. The first one was conducted in the laboratory, at the Institute of Soil Science and Plant Cultivation, National Research Institute, Department of Weed Science and Tillage Systems in Wroclaw. The tested objects were sprayed with foliar fertilizer Mikrovit Copper 80, Company Intermag and Copper (II) oxide, nanopowder, <50 nm (Sigma-Aldrich). Both preparations were applied at a dose of 160 g Cu/ha. The degree of coverage was performed in the spraying chamber "Aporo". The tests were accompanied by two operating pressures (0.2 and 0.28 MPa) and the speed of 0.86 m/s. The temperature in the laboratory was 20° C and the humidity was 60%. During the study, two conventional nozzles: flat fan XR 110 02 and a dual flat fan DF 120 02 were used. Three artificial plants were located in the measured chamber, (Fig. 1), which was used as repetitions. On the artificial plants few samples in the form of papers WSP (Water Sensitive Paper) produced by Albuz company and measuring 2.5x7.5 cm<sup>2</sup> were located. Samples were attached to the horizontal (upper and lower) and vertical (transverse approach (Anj) surfaces, transverse leaving (Aod), longitudinal left (Apl) and right (App)).

In the second phase, based on the computer analysis, the degree of covering on the tested objects was determined. For this purpose, the samples were converted to the digital form with the use of scanner, and then processed with Adobe Photoshop 7.0 CE. On the surface of each placed paper, three randomly selected fragments, measuring 10x10 mm, were marked, and then a size of the sprayed surface was analyzed. The degree of covering was calculated on the basis of the ratio of liquid-coated surface probes to the selected surface part, which amounted to 1cm<sup>2</sup>. Total covering degree was determined by multiplying the degree of cover-

ing (each of horizontal and vertical surfaces) and surface sprayed around the probe, which was 18.75 cm<sup>2</sup>.



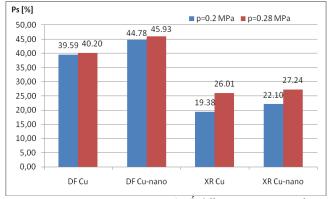
Source: own work / Źródło: opracowanie własne

Fig. 1. Artificial plants with samplers *Rys. 1. Sztuczne rośliny z próbnikami* 

For verification of the significance of differences in the results referring to the degree of covering, the statistical tests were performed, which were based on the analysis of a mean group (*LSD* test post-hoc) and the analysis of homogeneity of variance (Leven's test). It showed the interactions between the degrees of covering of the plants according to the preparation used for spraying. The Statistica 12.5 program was used to perform a statistical analysis.

#### 3. Results

The results of the mean covering degree (Ps) when sprayed as fertilizer with copper and nanocopper for the tested nozzles (XR 110-02 and DF 120-02) at a pressure of 0.2 MPa and 0.28 are shown in Fig. 2. It should be noted that the method used in the measurement of the covering degree, showed a few trace quantities on the bottom surface of the horizontal part of the probe. Figure 2 clearly shows that the average covering degree is higher when a spray with the nanocopper element was applied, irrespective of the pressure applied during spraying and the type of nozzle used for test.



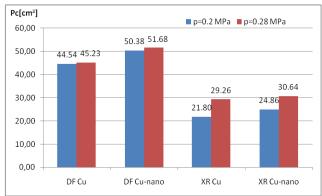
Source: own work / Źródło: opracowanie własne

Fig. 2. The average degree of covering (Ps) of sprayed plants for the tested nozzles at a pressure of 0.2 MPa and 028 MPa

Rys. 2. Średni stopień pokrycia (Ps) opryskiwanych roślin dla badanych rozpylaczy przy ciśnieniu 0,2 i 0,28 MPa

The highest average covering (45.93%) was recorded for the dual flat fan nozzle DF 120-02 when the nanocopper and pressure of 0.28 MPa were used. The lowest value of the average degree of covering (19.38%) was observed for the probe covering foliar fertilizer Microvit Copper 80 at a pressure of 0.2 MPa and applied with a flat fan nozzle XR 110-02.

Fig. 3 shows the results of the total degree of covering (Pc) for flat fan nozzle XR 110-02 and dual flat fan nozzle DF 120-02 at working pressure of 0.2 MPa and 0.28 MPa. Higher quality of total covering (Pc) was observed when the plants were sprayed with the nanocopper element. The dual flat fan nozzle DF 120-02 was characterized by a higher degree of total covering than flat fan nozzle XR 110-02 (e.g. at pressure level of 0.2 MPa, the total covering of probes by the nanocopper nozzle for DF 120-02 was higher by about 25.52 cm² than nozzle XR 110-02). The lowest value of the total degree of covering (21.80 cm²) was determined while the XR 110-02 was tested and accompanied by the foliar fertilizer Mikrovit Copper 80 at pressure 0.2 MPa.



Source: own work / Źródło: opracowanie własne

Fig. 3. The total covering degree (Pc) of the sprayed probes for the test nozzles at a pressure of 0.2 MPa and 0.28 MPa Rys. 3. Calkowity stopień pokrycia (Pc) opryskiwanych próbników dla badanych rozpylaczy pracujących przy ciśnieniu 0.2 MPa i 0.28 MPa

The further analysis showed that the dual flat fan DF 120-02 used at pressure of 0.2 MPa resulted in a higher degree of total covering, while the nanocopper element was applied and amounted to 5.84 cm<sup>2</sup>. Moreover, it was greater than the Mikrovit Copper 80 fertilizer (while a pressure increased to 0.28 MPa, the difference was 6.45 cm<sup>2</sup>).

Table 1 shows the results of statistical analysis of the variance homogeneity (Leven's test). From Tab. 1 and figure 4 it results that there are significant differences between the values of total degree of covering, which was confirmed by the homogeneity of variance (test Leven's). At the significance level of 0.05, a magnitude probability was very low (0.000001), and indicated the diversity of results (Tab. 1).

Tab. 2. showed a result of the total degree of covering for each type of liquid. From the analysis it follows, that a significant difference of probe covering was observed in cases of XR and DF (two types of tested nozzles) because the difference was significant for the probability of 0.018. The lower difference was observed for groups 5 and 6 – for one stream nozzle, while the nanocooper was applied.

#### 4. Discussion

It was noted that while using the flat fan nozzle XR 110-02 at pressure of 0.2 MPa the average degree of covering probe with nanocopper element was higher by about 2.7% than when it was used the foliar fertilizer Mikrovit Copper 80 (pressure increased to 0.28 MPa, difference increased to 1.23%) (fig. 2).

The studies aimed at determining the degree of covering on various vertical and horizontal surfaces Szewczyk et al. [20] and Szewczyk et al. [21] also conducted and concluded that the degree of covering significantly depends on the size of traces and speed, as well as on the type of nozzle used during the spray treatment. From the conducted analysis it follows that one-stream nozzles cover the vertical surfaces less and the dual-stream nozzles cover the horizontal surfaces less. Foque and Nuyttens [4, 5] conducted a study using the sprayers with air assistance, on the basis of which they stated: coverage of the lower surface of the leaves and increase in the degree of coverage of the sprayed surface.

An increase in pressure of the sprayed liquid, at constant speed, resulted in the increase of a liquid dose on the sprayed surface. The Figs. 2 and 3 confirm that the use of the dual flat fan nozzle DF 110-02 caused a few increases in the average degree of covering, as well as in the total degree of covering while the pressure increased to 0.28 MPa.

Table 1. The homogeneity test of variance (Levena's test) for total and mean coverage Tab. 1. Test jednorodności wariancji (test Levene'a) dla całkowitego i średniego stopnia porycia

	Differences are significant at p-value < ,05000							
Variable	SS Effect	df Effect	MS Effect	SS Error	df Error	MS Error	F	p-value
Total covering		5	1.869247	0.000000	2	0	5.923882E+29	0.0000001
Mean covering	0.0000001	5	0.000000	0.000000	2	0.000000		

Source: own work / Źródło: opracowanie własne

Table 2. The least significant difference (LSD) test for analyzed variables (for nozzles and liquid types) *Tab. 2. Test najmniejszej istotnej różnicy (NIR) dla badanych rozpylaczy oraz cieczy roboczych* 

	LSD test; p-v	alue < ,05000				
Type of liquid	{1} M=42.185	{2} M=20.740	{3} M=40.200	{4} M=45.930	{5} M=26.010	{6} M=27.240
DF {1}		0.018158	0.635710	0.406198	0.045854	0.053097
XR {2}	0.018158		0.032359	0.019694	0.279660	0.211764
DF Cu {3}	0.635710	0.032359		0.300842	0.075704	0.088805
DF Cu-nano {4}	0.406198	0.019694	0.300842		0.040644	0.045796
XR Cu {5}	0.045854	0.279660	0.075704	0.040644		0.794564
XR Cu-nano {6}	0.053097	0.211764	0.088805	0.045796	0.794564	

Source: own work / Źródło: opracowanie własne

During the covering analysis, the greater dose of sprayed liquid should result in a better degree of the sprayed surface. The study showed that when the dual stream nozzle was used, it was unnecessary to increase a pressure and the dose of sprayed liquid. A similar conclusion has been defined by Szewczyk et al. [22]. Many other studies were devoted to determining the impact of changes in pressure and operating speed of the sprayer, changing the angle of the spray in the longitudinal plane and perpendicular to the ground, and the use of adjuvant as a rate of the degree of coverage [6, 9]. The majority of the experiments were performed using different nozzles. It was noted that the appropriate choice of the nozzle causes the proper course of treatment and the desired degree of coverage on the intended surface.

The described method allows the improvement of the quality of spraying process and can improve an economic situation of farmers, who buy expensive plant protection products.

It can be concluded that the application of nanoelements during the spraying process will result in a decrease in pesticide use in agricultural practices. The obtained result of coverage degree will be verified through the determination of the liquid properties during spraying on selected real crops and determination of the surfaces of tested plants. If innovative elements as well as the morphological features of cultivated plants used in the author's studies of nanospraying contribute to the reduction in performed pesticides, it will be possible to limit their remains throughout the ecosystem and improve environmental conditions.

#### 5. Conclusions

- 1. The average degree of covering and the total degree of covering was higher when the nanocopper element was applied, regardless of type of nozzles for the treatment and pressure.
- 2. The dual flat fan nozzle DF 120-02 was characterized by a higher mean and a total degree of covering than the flat fan nozzle XR 110-02.
- 3. The statistical analysis of the interaction between analysed elements indicated that the use of the nanocopper spray formulation accompanied by dual flat fan nozzle DF increased the quality of spraying, but use only nanocooper element did not change its effectiveness significantly.

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