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Agnieszka LIS-KRZYŚCIN[1], Zbigniew J. BURGIEŁ[2]
and Irena WACŁAWSKA[3]

STUDIES OF FUNGISTATIC ACTIVITY OF COPPER-MODIFIED GLASSY FERTILISERS

BADANIA FUNGISTATYCZNEJ AKTYWNOŚCI SZKIEŁ NAWOZOWYCH MODYFIKOWANYCH DODATKIEM MIEDZI

Abstract: The subject of the present work was to study the possibilities of using glassy fertilisers both as mineral slow-release fertilisers and as material showing fungistatic activity. Apart from P, K, Ca, Mg and Si, the chemical composition of glassy fertilisers could contain a combination of microelements (0–10 % mas.). Thanks to the fungistatic activity of copper, glassy fertilisers modified with 2, 5 and 10 % of copper addition could become the subject of the study. Fungistatic activity of copper introduced into glassy fertilisers was studied with the aim of checking its effect on vegetative growth of the mycelium of *Fusarium culmorum*. The experiments covered the behaviour of copper-modified glassy fertilisers in hydroponic and soil cultivation. The results show very low fungistatic activity of glassy fertilisers.

Keywords: glassy fertilisers, copper, fungistatic activity

One of the main factors that pollute the environment, especially soils and waters, is agriculture. With the use of mineral fertilisers and pesticides, unfavourable substances are introduced into the environment. In order to reduce the influence of agriculture on the environment, research aimed to search for new materials which perform fertilising or protective functions has been carried out. In AGH – University of Science and Technology, Krakow, PL, a new type of mineral fertilisers, glassy fertilisers which can perform such a function, has been developed [1].

Glassy fertilisers are silicon-phosphorus-potassium fertilisers providing a plant with basic macroelements, such as phosphorus, potassium, calcium and magnesium, as

[1] Department of Soil Cultivation and Fertilization in Horticulture, University of Agriculture in Krakow, Al. 29 Listopada 54, 31-425 Kraków, Poland, email: alis@ogr.ar.krakow.pl

[2] Department of Plant Protection of the University, email: zjburgiel@ogr.ar.krakow.pl

[3] Department of Advanced Ceramics, AGH – University of Science and Technology, Al. A. Mickiewicza 30, 30-059 Kraków, Poland, email: iwac@interia.pl

well as with microelements (Cu, Fe, Mn, Zn, B and Co). Their chemical composition can be regulated in many ways depending on plants' nutritive requirements, and can be grouped as follows: SiO_2 > 27 % mas., P_2O_5 0–15 % mas., CaO 15–30 % mas., MgO 15–30 % mas., K_2O 0–20 % mas. and microelements 0–10 % mas. The internal structure of glass is similar to the structure of silicon minerals, and has a form of a net composed of silicon and oxygen atoms, where other components remain in free spaces. Mineral glassy fertilisers are produced with the traditional method of melting (1300–1400 °C) the mixture of such materials as: apatite, phosphorite, serpentine marble, potash (anhydrous potassium carbonate), and oxides incorporating appropriate microelements. The glassy mass obtained is calcined and then crushed. Due to vitrification and the appropriate chemical composition, glasses are difficult to dissolve in water, whereas their dissolubility increases with the extent of disintegration [2, 3]. The mechanism of releasing the components of glassy fertilisers resembles natural processes of erosion based on a phenomenon described as incongruent dissolving. In the process, the components of the dissolving solid substance get into the solution in proportions different from those in which they occur [4]. In the soil environment, the crystallization of secondary minerals, such as calcium and potassium silicates, takes place on the glass surface. They gradually decompose, and the cations contained in them are released. The cycle of these changes depends on the environmental conditions (pH, concentration of nutritive components, temperature, soil biological activity) [1, 5–7]. As a result, mineral glassy fertilisers show considerable flexibility of behaviour in the soil environment, depending on the physico-chemical conditions and the resultant nutritive needs. The usefulness of the glasses as a fertilisers in the cultivation of garden plants was examined during pot and field experiments [5, 8].

Inorganic copper compounds are characterised by high fungistatic activity [9]. Taking the above into account, glassy fertilisers with an increased amount of this component were developed.

The aim of the research was to check the fungistatic activity of copper-modified glassy fertilisers, as studies are being made into the possibility of their usage in cultivation mats, which in turn could be applied to hydroponics.

Material and methods

The examined glassy fertilisers were characterised by the unchanging content of SiO_2, P_2O_5 and K_2O. The copper content amounted to: 2 % (object 1), 5 % (obj. 2) and 10 % (obj. 3) of the mass of CuO. In relation to copper, the part of CaO and MgO changed, though the proportion of the MgO/CaO content remained unchanged, and equalled to 1 (Table 1). The glassy fertiliser fraction 0.1–0.3 mm in diameter was used for the research.

The effect of copper released from glassy fertilisers on the growth of *Fusarium culmorum* (W. G. Sm) Sacc. fungus, on a culture medium and in the soil environment was studied in laboratory conditions.

In the first stage of the research, 1 g of glassy fertiliser was shaken out from 100 cm^3 of the 0.1 % solution of Superba Red (N : P_2O_5 : K_2O = 7 : 9 : 25 + micro) for 3 hours on a rotatory shaking machine with the speed of 30 rotations per minute. The reaction of the culture medium was brought to pH 6.5–6.6. The obtained solutions were agar solidified (2 g · 100 cm^{-3}), poured into a Petri scale pan, and instilled with an agar disc (5 mm in diameter) overgrown with a *Fusarium culmorum* (W. G. Sm) Sacc mycelium [10].

Table 1

Chemical content of glassy fertilisers

Glassy fertilisers/objects	CuO	SiO_2	P_2O_5	K_2O	MgO	CaO
	[%]					
1	2.00	49.50	5.00	10.00	16.75	16.45
2	5.00	49.50	5.00	10.00	15.25	15.25
3	10.00	49.50	5.00	10.00	12.75	12.75

For the comparison of fungistatic activity of copper contained in the solution, the experiment also comprised a combination (object 4) with copper fungicide Miedzian 50 P (50 % copper oxychloride), concentrated in the culture medium to 100 mg · dm^{-3}. Scale pans filled with the culture medium with no copper content in it made the control object. After five days of cultivation, the diameter of the fungus colony in two perpendicular directions was measured. On the basis of the measurement, the percentage of the colony's growth inhibition was calculated by means of Abbott's formula [10].

The experiment was conducted in five replications. The results were statistically elaborated with the variance analysis method. The significance of differences among combinations was assessed on the basis of the repeated Duncan test ($p = 0.05$).

At the same time, an experiment in which a test fungus was cultivated on aqueous agar made of water (pH 6.5–6.6) where glasses with a certain copper content were shaken out, was conducted. The pattern of the experiment was analogous to the one described above.

The second stage of the research concerned the effect of a copper-modified glassy fertiliser added to the substrate on the settling of *Fusarium culmorum* fungus on the soil. To study that effect, the incubation of a soil mixture consisting of clay loam and compost acquired from a biological compost supplier was conducted in a ratio of 2 : 1. The compost was introduced in order to increase the mixture's biological activity. A glassy fertiliser containing 2, 5 and 10 % CuO in a dose of 4 g · dm^{-3} was inserted to the prepared substrate. The control object was the substrate with no glassy fertiliser content. The soil incubation was performed for 10 weeks in the temperature of 22–24 °C at the optimum humidity (60 %). The substrate samples were sterilised twice for 30 minutes in an autoclave (1.5 Pa, 110 °C), and next infected with a test fungus cultivated for 4 weeks on a sand-maize culture medium (quartz sand + 3 % maize meal). 10 g of inoculum was added to 100 g of the substrate, and in sterile conditions the components were mixed and ground in a mortar. Such material was incubated in room temperature for two weeks.

The assessment of the ground homing by the test fungus was carried out with Warcup's tabular-sandy method in Mańka's modification [11].

Two parallel series of the experiment were conducted in 10 repetitions each. The results were elaborated statistically with the variance analysis method, assessing the importance of the differences among combinations on the basis of Duncan test ($p = 0.05$).

Results and discussion

In each of the experiment combinations with the hydroponic culture medium, the *Fusarium culmorum* fungus created a delicate netlike aerial mycelium without the pigmentation typical of this species.

In the mediums containing copper, a slight but significant inhibition of the colonies' growth was observed. The degree of inhibition depended on the copper content in the glassy fertiliser (Table 2). The strongest inhibition of the fungus growth was identified in mediums with 10 % CuO. The colonies' diameter was smaller by 13.9 % than in the control object. A slightly stronger inhibition of the fungus' growth (18.8 %) was observed in the mediums containing Miedzian 50 WP [a.i. copper oxychloride].

Table 2

Evaluation of the effect of copper released from glassy fertilisers on the growth of *Fusarium culmorum* fungus

Combination	Diameter of the colony [mm]	Growth inhibition [%]
1	56.7 c*)	4.9
2	55.2 c	7.4
3	51.3 b	13.9
Miedzian 50 WP	48.4 a	18.8
Control	59.6 d	–

* Means indicated by the same letter do not differ significantly at $p = 0.5$.

The introduction of glassy fertilisers with various content of CuO into the substrate did not significantly affect the settling of the *F. culmorum* fungus. The number of units that formed the colonies on 1 g of the substrate in particular combinations is presented in Table 3.

Table 3

Evaluation of the effect of copper released from glassy fertilisers on the settling of *Fusarium culmorum* fungus on the substrate

Combination	Series I	Series II
Control	2575 a	2615 a
1	2515 a	2590 a
2	2485 a	2573 a
3	2494 a	2570 a

Inorganic copper compounds are known to be characterised by high activity and a wide spectrum of fungicidal activity. Many years ago some of them (alkaline copper carbonate) were used to lace seeds, and together with the seed material were introduced into the soil. Due to their phytotoxical activity and poor effectiveness in protection against pathogens causing seedling canker, their application into the soil was abandoned [9].

The research that had been performed showed low fungistatic activity both of the copper introduced with the glassy fertiliser and the Miedzian 50 WP preparation in relation to the *F. culmorum* fungus. In laboratory experiments on fungicides, the effectiveness lower than 49 % is considered insufficient [10]. However, the results achieved in an in vitro observation cannot be directly compared to natural conditions. The root excretions have been noticed to exhibit the ability of modifying both the amount and the pace of releasing mineral components from glassy fertilisers [3, 6]. Thus, supposedly, the plants' presence in such an arrangement could additionally influence mutual interactions of the ions present, and increase the efficiency of the glasses used with the addition of copper.

Conclusions

The achieved results show that using copper-modified glassy fertilisers will not affect the phytosanitary state of substrates and soils. Nevertheless, it may improve plants' provision with this microelement.

References

[1] Stoch L., Stoch Z. and Wacławska I.: Patent, PL 185229131 2003
[2] Stoch L. and Wacławska I.: Zesz. Probl. Post. Nauk Roln., 1996, **429**, 293–299.
[3] Stoch L., Wacławska I. and Lis-Krzyścin A.: Chem. Agricult., 2000, ***2***, 74–80.
[4] Korapetjanc M.C.: Wstęp do teorii procesów chemicznych. PWN, Warszawa 1983.
[5] Ostrowska J, Lis-Krzyścin A. and Wacławska I.: Folia Univ. Agric. Stetin. 190, Agricultura, 1998, **72**, 253–269.
[6] Ostrowska J., Lis-Krzyścin A. and Wacławska I.: Rocz. AR w Poznaniu CCCXLI, Ogrodnictwo, 2000, (35), 133–140.
[7] Wacławska I. and Ostrowska J.: Proc. Int. Congr. Glass 2. Ext., Edinburgh, 990–991, 2001.
[8] Ostrowska J., Lis-Krzyścin A. and Wacławska I.: Chem. Agricult., 2000, **2**, 67–73.
[9] Borecki Z.: Fungicydy stosowane w ochronie roślin. PWN, Warszawa 1984.
[10] Kowalik R. and Krechniak E.: Materiały do metodyki badań biologicznych ocen środków ochrony roślin. IOR, Poznań 1961.
[11] Mańka K.: Zesz. Probl. Post. Nauk Roln., 1964, **160**, 9–23.

BADANIA FUNGISTATYCZNEJ AKTYWNOŚCI SZKIEŁ NAWOZOWYCH MODYFIKOWANYCH DODATKIEM MIEDZI

Katedra Uprawy Roli i Nawożenia Roślin Ogrodniczych, Uniwersytet Rolniczy
Katedra Ochrony Roślin, Uniwersytet Rolniczy
Katedra Ceramiki Specjalnej, Akademia Górniczo-Hutnicza

Abstrakt: Przedmiotem prezentowanej pracy było zbadanie możliwości wykorzystania szkieł nawozowych nie tylko jako nawozów mineralnych o wydłużonym działaniu, lecz także materiałów odznaczających się fungistatyczną aktywnością. Do składu chemicznego szkieł nawozowych można wprowadzić oprócz P, K, Ca, Mg i Si, zestaw mikroelementów w przedziale 0–10 % mas. Znając fungistatyczną aktywność miedzi, za przedmiot badań obrano szkła nawozowe, do których składu wprowadzono 2, 5, 10 % mas. tego mikroelementu. Oddziaływanie miedzi sprawdzano, badając jej wpływ na wzrost wegetatywny grzybni *Fusarium culmorum*. Badania dotyczyły zachowań szkieł nawozowych modyfikowanych miedzią w uprawach hydroponicznych i glebowych. Badane szkła nawozowe wykazują bardzo słabe działanie fungistatyczne.

Słowa kluczowe: szkła nawozowe, miedź, fungistatyczna aktywność