THE APPLICATION OF COPPER AND ZINC CONTAINING ION-EXCHANGED SYNTHESISED ZEOLITE IN AGRICULTURAL PLANT GROWING

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Abstract: Foliar application of copper and zinc containing ion exchanged synthesised „zeolon-P4A" type zeolite was used in experiments. Foliar application in winter wheat experiments proved that plants had a better uptake and utilisation of copper and zinc bound on zeolite. As a result of the treatments yields and four quality parameters increased.

Key words: Zeolite, copper, zinc, retard, protein, gluten, baking quality index

1. Introduction

Winter wheat (*Triticum aestivum* L.) is grown on most of the arable land of Hungary. Quality loss causes an even greater problem in maintaining export competitiveness. This problem is due to weather conditions but mainly to nutrient supply deficiency (KÁDÁR, 1992).

Qualitative and quantitative plant growing can only be achieved if it is combined with proper plant nutrition. Besides the three macro elements (N, P, K) essential micro elements are inevitable. Because of their function in the enzyme activity we have to give priority to the essential microelements copper and zinc in the nutrient supply of soil and plants. Their lack greatly influences both the quantity and the quality of plant growing. Winter wheat gives an especially sensitive response to these microelements. 30% of Hungary's soils show copper deficiency, and 60-70% of zinc.

The lack of these microelements can be restored through the soil or the foliage (SZAKÁL *et. al*.; 2000, 2003). In order to deliver microelements copper salts are mainly used for soil treatment and different microelement complexes are used for foliar treatments for the sake of better utilisation and better uptake. In our experiments we studied the influence of copper and zinc ion exchanged synthesised zeolite on winter wheat.

Plants leaves ensure nutrient uptake for the development of plants. Photosynthesis and the regulation of transpiration are the primary tasks of foliage. Because of their structure leaves can uptake nutrients under certain conditions and to a certain extent only. Foliar nutrient supply can only be successful if we find the proper compounds and conditions. The plant controls ions reaching the cell walls by the turgor pressure in the skin tissues. Nutrient ions passing through the cell walls are adsorbed and get into the protoplasm. The movements of ions taken up through the leaves differ from each other greatly. The advantage of nutrient uptake through the leaves is that it gets very quickly and directly to the leaf cells, where they are utilised.

1.1. Microelements copper and zinc

The average zinc content of the earth' crust is about 70 mg/kg, and its copper content about 55 mg/kg. Only a very small part of them is in a form that is absorbable by plants. The copper and zinc content of Hungary's arable land is very limited: the upper cultivated layer contains 90-450 kg of zinc and 12-10kg of copper per hectare. About 1 %- of them is in an available form (GYŐRI, 1962). Copper has a stronger complex forming capacity than zinc, and because of its higher adsorption energy a small part of it is in an available form.

Primary function of copper and zinc is that through its positive charge it can contact electron rich parts of small and large molecules, mainly proteins being present in living organisms. Metal ions can be bound to proteins in different ways:

- Metallo-enzymes: if metal ions are strongly bound to side chains of amino-acids,
- Enzyme-activating: if metal ions are not a part of the structure but their presence is inevitable to induce enzyme activity.

The role of essential microelements copper and zinc was proved in forming of enzymes by more than 200 enzymes (SPIRO, 1983). Copper can be found in high amounts in the granum and chloroplast. Its lack hinders nitrogen uptake and protein synthesis. It plays an important role in transpiration metabolism and electron transport. Copper plays a role in the redox processes in cells, and zinc in H-transportation reactions (KŐRÖS, 1980). As a result of acid rains metal ions leach out and hinder enzyme activity, which directly influences plant development (DESSLER and BÖRLITZ, 1986).

The relationship between auxin and zinc is known since 1940. Zinc directly influences plant growth, enhances the activity of RNA polymerase and glutamine-acid dehydrogenase in nitrifying micro-organisms and improves the ammonia-N metabolism. An abundant supply of zinc contributes to triptophan synthesis in plants.

1.2. Influence of copper and zinc compounds on flour quality

Hungarian and foreign researchers have tested the influence of copper and zinc on flour quality for a long time. Publications on the application of chelates and other complexes are already available. FLYN *et al.* (1987) observed an increased protein content and yield in their experiments. The same results achieved PETERSON *et al.* (1986), HAN and SHEPHERD (1991). Higher copper and zinc content resulted in higher protein content. The Department of Soil Management and the Department of Chemistry at the Faculty of Agriculture and Food Sciences of the University of West Hungary carried out experiments with copper and zinc complexes of different ligands and applied them in soil or foliar treatments for more than 20 years (SCHMIDT *et al.*, 1999, BARKÓCZI *et al.*, 2000, SZAKÁL *et al.,* 2003). These experiments delivered especially good results with the application of copper-tetramine and zinc-carbohydrate complexes in foliar treatments. The best results were achieved when the experiments were carried out in the phenological phase of flowering. We produced and used synthesised ion-exchanged copper-zeolite in our experiments, which is not commonly used in agriculture. With the use of ion-exchanged zeolite we proved that a slow-release process was taking place and the compound had a positive effect on raw protein content and baking quality index.

Zeolites are crystal alkali- or alkali-earth metal-aluminium-hydro-silicates. The trivalent Al containing tetrahedrons have one negative charge, therefore the positive charged metal ions neutralise it. The smallest units of zeolites are the cells, which can be explained by the following formula:

$$M_{x/n}\ [(AlO_2)_x(SiO_2)_y]\ wH_2O,$$

where *M* cation is of *n* valent, *w* is the number of water molecules, (*y*+*x*) is the number of tetrahedrons in the elemental cell. *y/x* i.e. rate of Si/Al important feature of zeolites can range from one to infinity, e.g. the zeolite structured silicates practically do not contain any Al. The rate of 1:1 is theoretically the lowest limit, as in zeolites AlO_4 tetrahedrons cannot connect with each other directly but through SiO_4 tetrahedrons. In zeolite structured metal silicates the rate of Si/M can be very low otherwise it will damage the structure. We call second generation zeolites those which are synthesised with the use of ionic or neutral organic compounds, mostly amines or quaternary ammonium salts, which have a leading role in structure-forming owing to their structure controlling effect.

1.3. Ion exchange of zeolites

From physically and chemically point of view ion exchange is balancing process, which can be described by ion exchanging isotherms. The balance of ion exchange can be described by the following formula:

$$Z_B A^{ZA}{}_S + Z_A B^{ZB}{}_Z = Z_B A^{ZA}{}_Z + Z_A B^{ZB}{}_S$$

where Z_B, Z_A means the cation charge, sub-index S means concentrations of balance in the solution, Z on the zeolite. Synthesised zeolites generally contain Na ions. Through ion exchange of Na-ions by other ions the pore size of zeolite changes. Through exchange of ions of larger pore size it will decrease (e.g. the pore diameter of Na-LTA decreases from 0.4 nm to 0.3 nm). If the pore diameter of the entering ion is smaller the phenomenon will turn round (e.g. in case of calcium ions the pore entry is 0.5 nm).

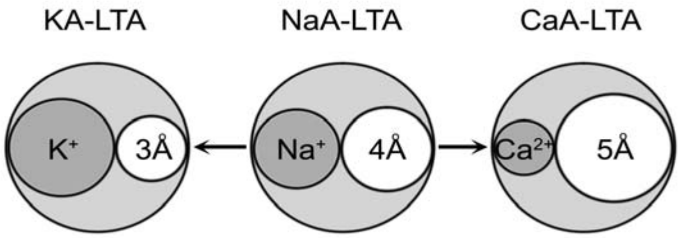

Fig. 1. Change of zeolite pore sizes affected by cations (KIRICSI and HANNUS, 2007.)

Exchange of ions is size selective. Ion exchange is carried out in water medium. Ions are there in hydrated form. Hydrated forms are bigger in size, therefore they cannot always penetrate into the structure of zeolite; in dehydrated form ion exchange is easy. Ion exchange is carried out at a temperature of 80 °C, hydrate membrane is smaller.

2. Material and Methods

Experiments on winter wheat were launched in four repetitions randomized blocks design on plots of $10m^2$. Foliar treatments were introduced at the end of tillering on Danube alluvial soil. Treatments were done with high pressure hand sprayers. We took samples and measured yield and chemical composition. The zinc content of the applied zinc-zeolite was 2.8 m%, and copper content of copper-zeolite was 4.4 m%. Zeolites were mixed and applied in the form of water-suspension. Plots were harvested with plot-combine harvester.

2.1 Effect of copper and zinc on the yield

As a result of copper ion exchanged synthesised zeolite and zinc ion-exchanged synthesised zeolite treatments yields increased in both cases. The most considerable yield increase was produced by copper-zeolite treatments. Based on the copper-zeolite experiments we can state that as a result of copper-zeolite treatments yields increased significantly, but zinc-zeolite treatments produced only a little rise in yield.

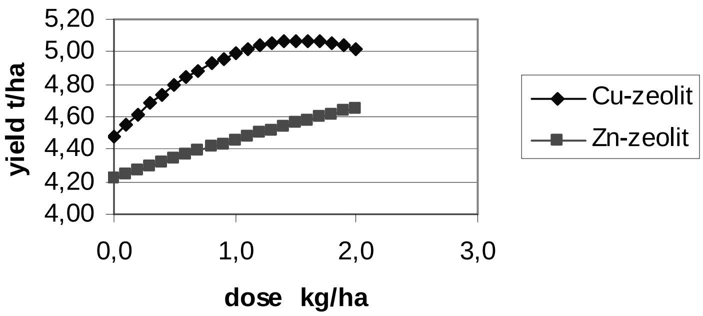

Fig. 2. Effect of Zn zeolite and Cu-zeolite on the yield

2.2 Effect of copper-zeolite, zinc-zeolite on raw protein content

As a result of copper-zeolite the raw protein content increased significantly but at a lower rate, than due to zinc-treatment. As an effect of zinc-treatment the raw protein content increased continuously. No toxic effect could be shown even at a dose of 2 kg/ha.

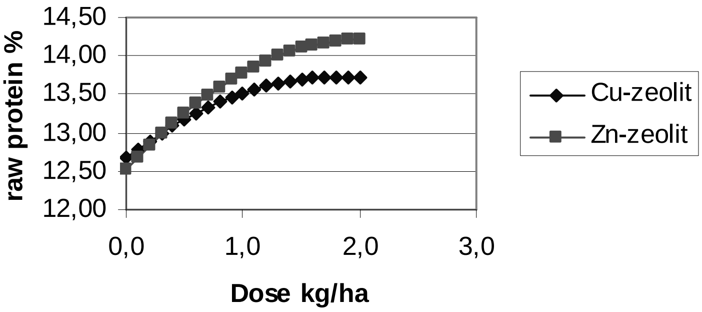

Fig. 3. Effect of Zn-zeolite and Cu-zeolite on raw protein

3. Conclusions

Experiments of foliar treatments were carried out with ion-exchanged zeolite on winter wheat for three years. The experiments were launched on small plots of calcareous Danube alluvial soil. On average of three years copper treatments were effective, if yield increase was set as a goal. As a result of zinc-zeolite the increase of raw protein was more favourable than that of copper-zeolite treatment.

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