Theses of doctoral (PhD) dissertation

APPLICATION OF COPPER TETRAMINE COMPLEX AND SYNTHETIC ZEOLITE ION EXCHANGED WITH COPPER-TETRAMINE AS FOLIAR FERTILISER IN WINTER WHEAT (*TRITICUM AESTIVUM L.*), AND THEIR EFFECT ON THE CONTENT VALUES

written by

Tamás Szakál

Mosonmagyaróvár

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THESES OF DOCTORAL (PhD) DISSERTATION

SZÉCHENYI ISTVÁN EGYETEM
MEZŐGAZDASÁG- ÉS ÉLELMISZERTUDOMÁNYI KAR
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WITTMANN ANTAL NÖVÉNY-, ÁLLAT- ÉS ÉLELMISZER-
TUDOMÁNYI MULTIDISZCIPLINÁRIS
DOCTORAL SCHOOL
HABERLANDT GOTTLIEB NÖVÉNYTUDOMÁNYI
DOKTORI PROGRAM

Doctoral School and Program Manager:
Prof. Dr. Ördög Vince DSc

Supervisors:
Dr. Kalocsai Renátó Associate Professor
Dr. Plutzer Judit Senior Research Fellow

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1. INTRODUCTION AND OBJECTIVES

1.1 Introduction

To supply the human population with sufficient quantity and quality food causes ever growing problems. Winter wheat has a special role in human nutrition. Researchers focus on reaching higher and higher yields on a certain area. They intend to achieve continuous yield increases first of all by the selection of varieties and often exceeded fertilizer-applications, which very often cause soil deterioration. Unfavourable impacts of high scale fertilization can soon be detected, e.g. deterioration of soil structure, soil acidification, more rapid loss of nutrients through leaching.

It is known and approved that nutrient stock of soils has reduced greatly. Besides the one-sided and progressive replenishment of macro-elements micro-element deficiencies also got into the focus of research in the past period of time. Winter wheat, which has a high rank in nourishment, reacts very sensitively on the deficiency of the micro-element copper. Main parts of soils in Hungary show copper deficiency. Due to the reasons mentioned before we have to pay attention to the replacement of this micro-element. Micro-elements can be replenished through the soil or in foliar application. Replenishing them through the soil can be limited, as we have to apply them in higher quantities. Further the high costs of copper-compounds can mean a restricting factor as well.

A further problem is that different plant cultures have different optimal nutrient requirements. Based on soil tests we may try to replenish micro-elements through the soil, but the changing requirements of the plants can only be followed by foliar applications. Different metal salts are used in soil applications to replenish micro-elements mostly. Metal salts or different metal complex compounds can be used to replenish nutrients in foliar applications. Many of the adequate metal salts can only be applied in small quantities and on few plants, because of their severe burning effects. To overcome this adverse effect and to ensure a better nutrient uptake manufacturers produce different complexes of metals. Nutrient uptake is determined by the stability of the complex-compound (compounds of low stability can quickly fall apart and those of high stability cannot release the micro-elements), their ligand, size and heat stability. Further important criteria of compounds used in foliar application are the adhesiveness and retardation effect.

Copper as a micro-element has its role in plant nourishment and it is also an excellent fungicide and so it protects the plants against pathogens. It has an important role in controlling *Fusarium* species. Applying appropriate copper compounds the quantity of the dangerous toxins of the fungus *Fusarium graminearum* (DON levels) can be controlled.

The quantity of mined copper-compound diminished because of the high rate of industrial use. The high prize of them imposes a growing burden on their use in agriculture. That is why I chose the recycling of high purity **copper containing** microelectronic **wastes** in my research work.

1.2. Research Objectives

The objectives of my research work can be summarised as follows:

- Production of copper-tetramine-sulphate from copper containing microelectronic wastes.
- Using a new method, not known by us before, we transfer copper-tetramine cation into NaA-type synthesised zeolite to produce copper-tetramine ion-exchanged synthesised-zeolite.
- As a control method of the new product we examined the synthesised zeolite ion-exchanged by copper-tetramine with thermo-gravimetric (heat stability) and X-Ray-diffraction (structure) examination methods.

- Agar-diffusion method is used to examine the fungicide effect of synthesised zeolite ion-exchanged by copper tetramine, a product that has not been used in plant control yet. The efficiency of synthesised zeolite that was ion-exchanged by copper tetramine was examined and compared to that of copper-oxy-chloride (control agent).
- Foliar application of copper-tetramine and copper-tetramine-sulphate ion-exchanged in zeolite in doses of 0.1; 0.3; 0.5; 1.0; and 2.0 kg/ha copper on winter wheat to improve yield quantity and quality (raw protein-, gluten and protein content).

2. MATERIAL AND METHOD

2.1. Production of copper-tetramine-sulphate

Reacting copper-sulphate suspension and concentrated ammonium-hydroxide we produced copper-tetramine-sulphate that contained 12.0 m% copper and had a pH-value of 9.3. The species distribution of copper-amine-complexes examined on the pH values prove that mainly tetramine-forms can be observed at this pH-value. We added ethyl-alcohol and crystallised copper-tetramine-sulphate by cooling the suspension.

2.2. Production of synthesised zeolite ion-exchanged by copper tetramine

For the ion-exchange I used NaA (LTA) type synthesised zeolite of sodalite framework. The applied A-type zeolite is composed of cuboctahedron with 6 square faces and 8 hexagonal faces. In A-type zeolites binding happens with a cube and square faces forming a pore size of 0.4 nm that ensures ion exchange. As a commercial product A-type zeolite is one of the most important synthesised zeolites. NaA zeolite contains the most exchangeable sodium cations, because a Si/Al=1, which is positive for the copper ion exchange. A unique property of the NaA zeolites is that the exchangeable cations can be removed without the break of the structure and then new cations can be transported into the cavities and channels. The first synthesised zeolite is an NaA type one which was mostly researched and widely used and which can be described with the molecular formula $Na_{12}Al_{12}Si_{12}O_{48}$x $27H_2O$. I selected NaA synthesised zeolite for my experiments because of their positive ion exchange properties. I exchanged sodium ion for copper tetramine ion.

For the ion-exchange of copper-tetramine cation I used the Zeolon P4 zeolite produced by MAL Ajkai Timföldgyár. We prepared 10 m%- distilled water suspension of synthesised zeolite. We added copper-tetramine-sulphate (12 m%-copper) to the suspension under constant stirring. Based on the preliminary examinations we used the excess of 100% copper-tetramine-sulphate. After 2 hours of stirring we let the suspension consolidate and removed the excess of copper-complex with distilled water. The received suspension was dried at 30 °C (open air) and we examined its nitrogen content from the powdered samples with Kjeldahl method. X-Ray diffraction method was used to determine the quality of the crystalline phases in the zeolite induced by the ion-exchange with copper-amine-complex.

2.3. Instruments used to examine the compounds

- Derivatograph

A derivatograph can be used to carry out thermo-analytical examinations to analyse the physical and chemical changes in the material if the sample is exposed to heat. We can measure the change in enthalpy (TA; DTA) or the weight change (TG; DTG) depending on what properties of the material to be examined are influenced by the changes. As thermic analysis is an indirect method it is reasonable to complete it with a direct method e.g. XRD. We used the Q-1500 D MOM system derivatograph to carry out measurements in Pannon University Materials Engineering Department.

We analysed the heat stability of copper-tetramine-sulphate and copper-tetramine-ion-exchange-zeolite with derivatograph.

- Scanning Electron Microscope, SEM

A scanning electron microscope can be used to examine the surface of the sample material. SEM records and evaluates the secondary electrons from the sample during the analysis. The recorded signals give information about the topographical properties, the morphology, chemical composition of the sample surface and crystal structure of the sample materials.

We examined zeolite and synthesised zeolite ion-exchanged with copper-amine with PHILIPS XL 30 ESEM scanning electron microscope. Morphological analyses were done in vacuum with the detection of secondary and backscattered electrons in Pannon University Materials Engineering Department.

- X-Ray Diffraction (XRD)

One of the most important non-destructive structure-analysis is the X-Ray diffraction test (XRD). X-Ray diffraction tests offer us information about the building elements of crystals and the structures of the elemental cells. In the analysis we expose a small part of the powder-like material to monochromatic X-rays while rotated. X-rays scatter on it flexibly. X-Ray scattering gives information about the atoms and their structure. If the X-Ray beam suffers diffraction and interference on the crystal structure we can call it X-Ray diffraction. X-Ray diffraction tests were carried out in a powder-diffractometer Philips PW 3710, with Cu Kα radiation and parameters 50kV, 40mA in a graphite monochrometer producing monochromatic X-Rays in Pannon University Materials Engineering Department.

2.4. Large Scale Experiments

Experiments were launched on cancerous chernozem soil in winter wheat (*Triticumaestivum L.*) in Regöly in Tolna County, in the years 2011, 2012 and 2014. The aim of my research work was to analyse the large-scale foliar application of synthesised zeolite that was ion-exchanged with copper-tetramine and that has not been used in the agricultural practice so-far. In my experiments we carried out foliar treatments with ion-exchanged zeolite to replenish copper in soils with copper deficiency or soils with medium copper supply.

Foliar treatments were carried out in two phenological phases at shooting and flowering with a product of 0.1; 0.3; 0.5; 1.0; and 2.0 kg/ha copper content. We produced copper-tetramine-sulphate for the treatments. We carried out the ion-exchange with zeolite-sulphate on the NaA type Zeolon P4 zeolite manufactured in Hungary. Harvest was done with a harvester equipped with yield-monitor. We analysed the samples for raw-protein, gluten and starch content with a Perten Inframatic 9 200 type rapid analyser in a non-destructive way. The applied analyser (NIR) operates in infra-red close spectrum of 1100-1400 nm using the theory of transmission.

2.5. Soil composition of the experimental fields

The Mosonmagyaróvár laboratory of Synlab Umweltinstitut Ungarn Ltd. carried out the extended soil analyses according to the Hungarian standard MSZ-08-0202:1977. It was necessary to complete the soil analyses results measured at depths of 0-30cm, because nutrient uptake is more advantageous at depths of 30-60cm. Results of analyses show that in deeper layers $CaCO_3$ content increases and humus and available quantity of copper and zinc decrease. Phosphorous content influencing micro element uptake show low values and their quantity also decreases in the deeper layers. Copper-supply of the soils involved into the experiment show low values on plot 12/1 and moderately good values on plot R 3-4. Zinc values are approximately the same and low on both plots. We managed to select a plot that met our aims as we planned to carry out our experiments on soils with low and higher content of copper. There we could examine the efficiency of copper replacement.

2.6. Fungicide efficiency tests

It is well known that cooper compounds have an important role in controlling fungus diseases. Therefore I concerned it very important to analyse the fungicide effect of copper-compounds applied in the foliar experiments. We analysed the *Fusarium graminearum* NCAIM F.00730 strain of fungi that cause mycosis of cereals with in vitro agar diffusion method.

The aim of our field experiments was to analyse the effect of applied copper doses (0; 0.1; 0.3; 0.5; 1.0; 2.0; 4.0 kg/ha). To calculate the concentrations I counted with 300 litre spray liquid commonly used in large scale practice. As a result we calculated the concentrations of the applied suspensions this way, which was equivalent to copper concentrations of 0; 0.17; 0.50; 0.83; 1.67; 3.33; 6.67 g/dm^3 in the experiments. As a control agent we selected 50m% copper-oxy-chloride 50 WP among the copper containing plant protection agents. We prepared 3000 mg/dm^3; 2000 mg/dm^3; and 1000 mg/dm^3 copper suspensions from the water-suspension of copper-oxy-chloride and applied as control agent. The fungicide efficiency was analysed on potato-dextrose agar with agar-diffusion hole-test method.

3. RESULTS AND EVALUATION

3.1. Analysing copper-tetramine-sulphate with derivatograph

Derivatograph analysis of crystalline copper-tetramine-sulphate was carried out in the Materials Engineering Department of Pannon University. During heating the four peaks at temperatures 176.0°C, 210.5°C, 319.5°C and 389.5°C showed loss in mass and endotherm processes (DTA). Loss in mass at theses peaks (TG curve) can be combined with the remove of four ammonia molecules of copper-tetramine-complex through decomposition. Reaching the temperature of 532.1°C, the four ammonia molecules could totally be removed during the decomposition process of the complex. The calculated ammonia content of the weighed 400 mg copper-tetramine-sulphate amounted 119.53 mg (29.882%). Measurements with the derivatograph produced higher values, the loss was 151.79 mg (37.947%). The higher value derived from ammonia and water encapsulated in zeolite.   At higher temperatures (799.9°C and 859.9°C) weight loss measured at TG can be combined with the decomposition of sulphate (decomposition products: $S0_2$, $S0_3$, 0_2).

3.2. Analysis of Zeolon P4A type synthesised zeolite and ion-exchanged zeolite with derivatograph

We think it necessary to examine if ion-exchange induce any changes in zeolite. To trace that we need to compare it with the derivatogram of the initial zeolite. On TG curve we found water in different bindings in the channels and on the high adsorption capacity surface of zeolite. Water release happened until reaching app. 400°C. Its measured quantity amounted 20.3 m%. Endotherm process of water release reached its maximum on the DTG curve at 197.2°C. As a result of further heating DTA curve showed exothermic reaction at 858.8°C and this process (DTG curve) showed 2.3 m% loss in mass.

DTA curve of copper-tetramine-sulphate shows the gradual release of ammonia molecules at four explicit peaks. If we carried out the ion-exchange with copper-tetramine-complex compounds these peaks did not appear. We can follow the gradual release of ammonia molecules through one peak, which happens together with the water retained in zeolite. Compared to DTA curve of zeolite a new peak appears on the ion-exchanged zeolite DTA curve at a temperature of 772.1°C, which was created by an exothermic reaction and resulted in a minimal weight increase. We weighed into the derivatograph 270mg ion-exchanged zeolite, which got 12.35mg ammonia content through ion-exchange. The analysis showed that reaching the temperature of 510.1°C produced 64.53 mg loss in mass (23.9% of the mass of ion-exchanged zeolite). If we deduct the mass of ammonia we get 12.35 mg, i.e. we get 52.18 mg, which represent the mass of residual water in all probability (this water quantity amounts 19.32% of the measured ion-exchanged-zeolite).

3.3. Energy-Dispersive-X-Ray-spectroscopy (EDX) and X-Ray Diffraction (XRD) Analyses

EDX analysis of synthesised zeolite (Zeolon P4A)

Based on EDX spectroscopy of Zeolon P4A synthesised zeolite we can determine that the Si: Al rate approaches 1:1 (Si atom %= 10.16 and Al atom%= 11.81) in the zeolite. Sodium in the anions position (exchangeable) amounts 16.52% giving 14.05% of the atoms participating in zeolite.

EDX analysis of copper-ion-exchanged synthesised zeolite

EDX spectroscopy gives us a reliable picture about the process and extent of ion-exchange. With the help of the scan of the EDX spectrum we can determine that the rate of Si: Al in zeolite approaches one, i.e. we can presume that ion-exchange did not induce any changes in the grid-structure. This was supported by the X-Ray diffraction phase-analysis. The quantity of copper-ions in zeolite after ion-exchange amounted 6.69 m %.

X-Ray diffraction (XRD) tests

We subjected all Cu-tetramine, zeolite and Cu-zeolite samples to a quality phase-analyses. We could well observe that zeolite and Cu-ion-exchanged zeolite produced totally the same diffractogram, as for both the positions of diffraction peaks and the intensity rates. This is important. If through the insertion of Cu a solid suspension would be created it would cause a change in the values of d-spacing due to the destruction of grids. According to the Bragg's Law this would result the change in the peaks' position. Therefore it is obvious that Cu did not insert into the crystal-grid of zeolite.

3.4. Results and evaluation of field experiments with foliar applications

At harvest we analysed the yield, the raw-protein, the gluten and the starch content. To determine the efficiency of the treatments we carried out statistical evaluations every year and made an average statistical assessment of the three experimental years.

Evaluation of the data received by yield assessment:

We achieved significant yield increase as a result of treatments with **copper-ion-exchanged zeolite** in copper doses of 0.5 kg/ha and higher in 2011 and 0.3kg/ha and higher in 2012 and 2014 as well as in average of the three years.

Foliar treatments with **copper-tetramine-sulphate** did not show any significant differences in average yields in 2011. But in 2012 copper doses higher than 0.3 kg/ha produced significant yield increase. In 2014 average yields differed at a significance level of 0.5%, if we applied copper in doses 0.5 kg/ha and higher.

We received significant increase in the yields in average of three years if we applied copper 0.5 kg/ha or higher doses (Table 11). Comparison of the effects of copper-ion-exchanged zeolite and copper-tetramine-sulphate treatments: both materials showed efficiency in the treatments – they produced yield increase compared to the control. Both treating materials (in average of the three years) reached their maximum with doses of 1.34-1.51 kg/ha. Copper-tetramine-sulphate had a better yield increasing effect in treatments with lower doses.

Evaluating the data of raw-protein analysis:

Treatments with **copper-ion-exchanged zeolite** increased raw-protein content significantly in the years 2011, 2012 and 2014 with copper doses of 0.3 kg/ha and higher, as well as in average of the three years with copper doses of 1.0kg/ha and higher.

Significant differences in raw-protein content were shown by foliar treatments with **copper-tetramine-sulphate** in the years 2011, 2012 and 2014 at doses of 0.5 kg/ha and higher. Raw-protein content measured in average of the three years did not show any significant differences. Copper doses of 2.0 kg/ha produced significant differences in raw-protein content in average of the three years.

Comparison of the efficacy of treatments with copper-ion-exchanged zeolite and copper-tetramine-sulphate. Both materials were effective in the treatments: compared to the control they produced protein increase measured in percentage. Treatments with copper-ion-exchanged zeolite proved to be more effective than treatments with copper-tetramine-sulphate at both doses.

Evaluation of gluten analysis data:

Treatments with **copper-ion-exchanged zeolite** with doses of 0.3kg/ha or higher produced significant increases in gluten content in the years 2011, 2012 and 2014. In average of the three years gluten contents increased significantly if we applied doses higher than 0.5 kg/ha.

When we applied **copper-tetramine-sulphate** in foliar treatments gluten content increased significantly with doses of 0.1kg/ha or higher in the years 2011 and 2012. In 2014 0.3kg/ha and higher copper doses produced significant increases, which could be explained by more rainfall in the season. In average of the three years gluten content increased significantly if we applied copper doses of 0.5 kg/ha and higher.

Comparing the effects of foliar treatments with copper-ion-exchanged zeolite and copper-tetramine-sulphate we can conclude that both materials were efficient in the applications and compared to the control the gluten contents increased. In treatments with copper-tetramine-sulphate gluten content reached its maximum at doses of 1.51kg/ha and this maximum could be reached in treatments with copper-ion-exchanged zeolite at doses of 1.86 kg/ha.

3.5. Results of agar-diffusion tests

In the agar-diffusion tests copper-zeolite containing products always showed more significant inhibiting effects compared to the control. In our tests we realized that the diameter of the zones of inhibition increased due to the gradually increasing copper concentrations.

4. CONCLUSIONS AND SUGGESTIONS

Supported by the results of experiments with two compounds (prepared by myself) i.e. copper-tetramine-sulphate and copper-ion-exchanged zeolite, applied on the folium of winter wheat in two phenological phases, I suggest their agricultural application as follows:

1. If our aim is to increase **yield**, then it is reasonable to apply copper-tetramine-sulphate. Copper-tetramine-complexes produce higher measurable yield at lower copper doses compared to the copper-ion-exchanged zeolite. If we apply copper-ion-exchanged zeolite we can reach higher efficiency at higher copper doses only.

2. If we aim to grow winter wheat with higher **protein** content we suggest to apply copper-ion-exchanged zeolite. The demand on winter wheat with high protein content has increased recently. If there is more rainfall copper-ion-exchanged zeolite is more effective on protein content because of the retardation effect.

3. If our aim is to increase the **gluten** content of winter wheat, copper-tetramine-complexes increase the gluten content to some extent at low copper dosage (Cu= 0.5 kg/ha) compared to copper-ion-exchanged zeolite. Ion-exchanged zeolite with higher copper dosage produce higher increase in gluten content than copper-tetramine-complexes.

4. It is recommended to apply copper-ion-exchanged zeolite to ensure retardation and because of its excellent fungicide effect.

As a summary, if we intend to grow winter wheat of good yield and good quality the application of copper-ion-exchanged zeolite is recommended.

5. **NEW SCIENTIFIC RESULTS**

1. In large scale practice through the ion-exchange in Zeolon P4A (NaA) type synthesised zeolite a part of the Na^+ cations can be exchanged by $[Cu(NH_3)_4]^{2+}$ cations. The energy dispersive EDX spectra of zeolite shows that the rate of Si: Al approximately 1/1 did not change due to the ion-exchange (Si atom %= 10.16, Al atom%= 11.81).

X-ray diffraction tests (XRD) also prove that the diffractogram of zeolite and Cu-ion-exchanged zeolite are practically the same referring both to the position of diffraction peaks or the rate of their intensity. So it is obvious that Cu did not insert into the crystal-grid of zeolite.

2. It is proven that copper-ion-exchanged zeolite can be used as foliar fertilizer because the release of ammonia (decomposition of copper-tetramine-ion) happens at a temperature higher than 100ºC as described by the thermo-derivatogram, so it will not decompose on the leaves during the day. As a result the ion-exchange zeolite contained 4.98 m% copper (ICP measure), 3.76 % nitrogen (equivalent to 4.56 m% NH_3), which, based on the calculations, ensure the ammonium content of copper-tetramine in synthesised zeolite at 85.5%. Therefore it can be assumed that the triamine form was also present in the ion-exchanged zeolite.

3. Analyses on *Fusarium graminearum* NCAIM F.00730, a fungus infecting cereals, carried out with in vitro agar diffusion method proved that copper-ion-exchanged zeolite offers a better fungicide effect than the traditional copper-oxy-chloride.

4. Using copper-tetramine-ion-exchanged synthesised NaA type zeolite of 4nm pore size, we can manufacture a foliar fertilizer product, which is suitable for efficient nutrient replacement and which has not been utilized in large scale farming for foliar fertilization so far. Applying zeolite, ion-exchanged by copper-

tetramine as a foliar fertilizer I managed to prove that it contributed to the increase of yield, raw-protein and gluten content of winter wheat.

6. LIST OF PUBLICATIONS

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