

Ion exchange with copper-tetraamine on NaA (LTA) type synthesised zeolite

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Abstract

A crop growing in the right quantity and quality can only be secured if nutrients are provided in an adequate quantity and available form. Copper (Cu) has primary importance among microelements in growing winter wheat. Lack of Cu hinders nitrogen uptake by plants. Therefore, increasing bioavailability is important in crop production. It has been conducted successful foliar fertilisation experiments with Tetraamminecopper(II) sulphate for several years. The efficiency of the applied compound was enhanced by the application of a retarded nutrient-supply. To secure retardation, ion exchange was carried out in NaA type synthesised zeolite with Tetraamminecopper(II) sulphate. Structure of Tetraamminecopper(II) sulphate, and zeolite ion-exchanged by copper-tetraamine was analysed with a derivatogram and X-ray diffraction. Derivatogram analyses revealed heat stability. X-ray diffraction analyses revealed that copper-tetraamine ions exchanged a significant part of the sodium ions of zeolite in ion exchange.

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Introduction

Essential microelements have a unique role in living organisms and play a crucial role in governing biochemical processes in the cells. Metal ions are capable of interacting with the negative or with the electron-rich parts of the protein molecules through their positive charges (Messerschmidt 2010). According to Yamashita *et al.* (1990), metal ions can easily interact with hydrophilic groups (oxygen, nitrogen, sulphur). These metal ions can bind four or more ligands (Berg 1987).

Copper is one of the most critical essential microelements in living organisms, bound mainly to proteins, act as metalloenzyme (Graham and Welch 2000; Nicolici *et al.* 2016). Copper typically

plays an essential role in redox processes in the cell (Körös 1980). The organic matter part of Cu is found in the chloroplasts of plants involved in the electron transport of photosynthesis. Copper-containing enzymes (polyphenol oxidase, ascorbic acid oxidase) in chloroplasts act as electron suppliers of copper ($\text{Cu}^{2+} - \text{Cu}^+$). Copper is also crucial in the metabolic processes of proteins and carbohydrates, and it promotes the synthesis of proteins and carbohydrates. Acting on the carbohydrate metabolism, copper accelerates the oxidation of glucose. Its effect can be explained by the change in valence (Judel 1962; Pais 1999; Giczi *et al.* 2018).

Copper is an essential microelement not only for plants, but it is inevitable for animal and human

organisms. Therefore, it is imperative to supply living organisms with copper in the form of metalloenzyme through the food chain. The most important food sources for human nutrition have plant origin. Replenishing the worldwide copper-deficiency became the main task of research.

Oats, barley, and wheat are the most sensitive to copper deficiency. Copper deficiency in cereals begins with the whitening of leaf tips and narrow, twisted leaves are formed. In poorly supplied plants, incomplete tuber or ear formation, and reduced eyes formation can be observed. In some cases the ears are empty. Soil copper loss is mainly caused by extraction by plants and leaching (Tölgyesi 1969).

Mining of the world's copper-bearing minerals is declining due to depleting reserves. Rising prices are placing an increasing burden on farmers. The salt of the metal complex is used to replace micronutrients in soils in order to save costs. Copper replacement can take place in the soil or through the foliage of the plant. The possibility of compensating for the copper deficiency in soils is reduced by the fact that a larger amount of copper is required. So, the higher price of copper compounds limits such replacement. Therefore, the replacement of copper through foliage has become more and more critical.

The copper demand of winter wheat has been replaced for a long time by a copper-tetraamine compound produced from microelectronic waste (Szakál *et al.* 2014). In this work, Cu in the form of copper-complexes was presented on the foliage to improve winter wheat yield and quality. The selected form of copper-complex was Tetraamminecopper(II) sulphate. The suitable copper replacement criteria through foliage are that it needs to have high stability. The ligand has to be a valuable substance for the plant and needs to have a retarded effect. This compound meets the first two criteria, but Tetraamminecopper(II) sulphate cannot provide the retarded effect for the plant. Thus, ion exchange of copper-tetraamine cations with synthesised zeolite anions was applied. Application of such Cu-complexes during the time of the experiment resulted in the improvement of the quality parameters of winter wheat. The achievements are discussed in light of critical

physico-chemical parameters of applied forms of copper complexes.

Research has shown that zeolites are excellent adsorbents, catalysts, ion exchangers, and molecular sieves. Natural zeolites are widely used in agriculture, but the synthesised zeolites are not widespread; their use as a foliar fertiliser is unknown. The production of synthetic zeolite is inexpensive and has the advantage that, unlike natural, it manufactures in high purity. As a new possibility, the ion-exchanged-synthesised zeolite was used as a foliage fertiliser in this research.

Zeolites are porous materials with a high specific surface area, the pores of which can vary between 0.3 and 2.0 nm. Zeolites are three-dimensional, microporous, crystalline solids with a well-defined structure, containing aluminium, silicon, and oxygen as builders. Zeolites are found in natural or artificially produced (synthesis) form. There are more than 60 types of zeolites in nature in volcanic or sedimentary media. The most common and most mined zeolites are chabazite, clinoptilolite, and mordenite. The number of synthesised zeolites artificially produced for different purposes is approximately 150.

Zeolites are the primary components of crystalline aluminium silicates TO_4 ($T = Si^{4+}, Al^{3+}$). They are built from SiO_4 and AlO_4 tetrahedrons (Flanigen *et al.* 2010). Tetrahedrons bind on edges sharing oxygen atoms, and as a result, they can create 16 larger units assigned as secondary components. The crystal structure of zeolite is made up of secondary building blocks, while in one, two or all three directions of space, caves extend in uni-, bi- or tri-dimensions of space (Nagy *et al.* 1998). Zeolites are formed from structural units, components, and cages (Fig. 1), e.g. sodalite, zeolite A, faujasite and EMT zeolite are formed from sodalite cage (Schwanke *et al.* 2018).

When building their tri-dimensional framework, SiO_4 tetrahedrons can be exchanged with AlO_4 tetrahedrons by isomorphic substitution. Trivalent aluminium in AlO_4 tetrahedrons has a negative charge neutralised by cations, mainly alkali metals and alkali earth metals (Fig. 2). The negative charge is often neutralised by Na^+ cation (Ward 1976; Armbruster and Gunter 2001).

Zeolites have a specific surface area of 800 – 1,000 $m^2.g^{-1}$. In caves and channels of zeolites, different

molecules can be stored (Ramsay and Kallus 2000). In the channels, water, and cations can be found mostly. Most of the water in the channels of zeolite is stored in the grid structure channels through absorption. A smaller amount of water forms a hydration shell that coordinates with cations. If subjected to heat, water can be removed continuously and irreversibly. With the desorption of water, the molecular-sized pores become free, thus allowing the uptake of foreign molecules and the formation of selective adsorption. Most of the water can be removed at 100 – 200 °C. Total dehydration occurs at 400 °C.

The widespread use of zeolites is enhanced by its ion exchange capacity, variable size channels, high stability, high melting point (above 1,000 °C) insoluble in water and inorganic solvents (Breck 1974; Moshoeshoe *et al.* 2017).

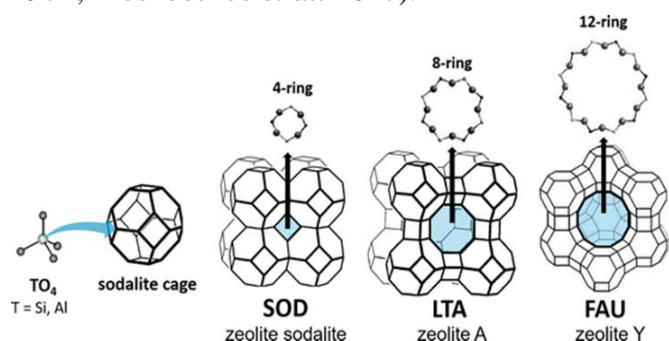


Fig. 1. Construction of A type of zeolite from a sodalite unit (Schwanke *et al.* 2018).

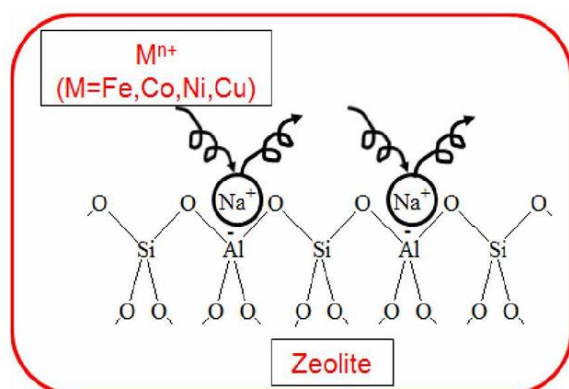


Fig. 2. Negative charge is neutralised by Na⁺ ion, Si/Al = 1, Na-A zeolite (Zhao *et al.* 2012).

The International Zeolite Association (IZA-SC) has created a database of zeolite structures (atlas, three-letter code); accordingly, NaA-type zeolite is a member of the LTA group (Baerlocher *et al.* 2007).

In this work, synthesised NaA (LTA) zeolite was studied and applied. The basic unit of the structure of LTA is the sodalite framework. Cubic octahedron is the component of A-type zeolite with a pore size of 0.4 nm that enables ion exchange and binding gases (Ramsay and Kallus 2000). The NaA type zeolite is widely used and can be described with the molecular formula $\text{Na}_{12}\text{Al}_{12}\text{Si}_{12}\text{O}_{48}\cdot 27\text{H}_2\text{O}$. LTA type zeolites exert high ion exchange capacity due to low ratio of Si/Al (~ 1), while ion exchange can be described by isotherm most clearly (Nagy *et al.* 1998; Bujnová and Lesný 2004; Remenárová *et al.* 2014). Such ion exchange features appear promising for application in Cu delivery to plants.

Copper-amine-complex

Copper (II) forms complexes with nitrogen-containing ligands such as $\text{CuX}_2\text{n NH}_3$, where n in general 2, 4, 5 or 6, X anion forms a bridge across the metal ions. Addition of alcohol to the ammonia solution of copper sulphate (II) results in slow crystallisation of $[\text{Cu}(\text{NH}_3)_4]\text{SO}_2\cdot\text{H}_2\text{O}$ complex, where the four nitrogen atoms form a quadratic plane's structure around copper (II), and there is water in the fifth position. X-ray diffraction analyses have shown that copper (II)-tetraamine complex in solutions containing copper-amine complexes possess a distorted octahedron structure.

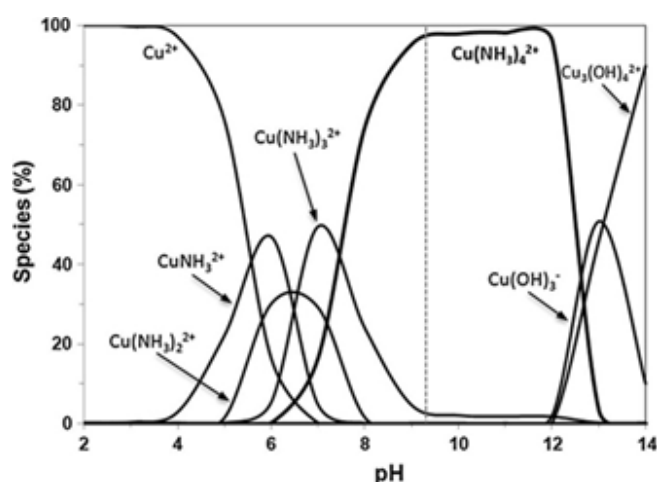


Fig. 3. Species distribution of copper-amine complex as a function of pH (Triki *et al.* 2017).

The two water molecules also coordinate with the central copper ion under and above the plane determined by the four N atoms. The Cu-O bond

distance is 2.33 Å, while Cu-N (equatorial) is 2.03 Å. This latter bond is much longer than the Cu-O_(eq) (1.94 Å) in copper (II)-hexa-aqua-complex (Morosin 1969; Szakál 1993). In copper-tetramine complex products have been measured $\beta_1=4.14$, $\beta_2=7.66$, $\beta_3=10.53$, $\beta_4=12.68$ (Bjerrum 1941). The species distribution curve of the copper-tetramine complex is in Fig. 3. The solution contained Cu(NH₃)₄²⁺ ions in the highest quantity at pH 9.3.

Experimental

All the analysis of this research was carried out at the University of Pannonia, Institute of Materials Science (Veszprém, Hungary).

Copper-containing substances

Tetraamminecopper(II) sulphate was used for ion exchange. NaA type synthesised zeolite (Trade name: Zeolon P4A) was used to modify zeolite ion-exchanged with copper-tetraamine for analyses with a derivatograph and X-Ray diffraction.

Tetraamminecopper(II) sulphate

The reaction of copper-sulphate 18 wt % solution and undiluted ammonium hydroxide 26 wt % was used to produce Tetraamminecopper(II) sulphate copper content of 12 wt % and pH 9.3 (referring to Fig. 3). Tetraamminecopper(II) sulphate was crystallised by adding 100 % ethyl alcohol with cooling. Crystalline Tetraamminecopper(II) sulphate was examined by X-ray diffraction and analysed with a Q-1500 D MOM derivatograph.

Ion exchange on Zeolon P4A (NaA) type synthesised zeolite

Zeolon P4A synthesised zeolite was used for the ion exchange process in the water-diluted solution of Tetraamminecopper(II) sulphate complex (pH 9.3). The structure of ion-exchanged zeolite was analysed using the X-Ray diffractometer (Philips PW3710). The morphology and composition of the materials' elements were studied with a scanning electron microscope (Philips XL 30-ESEM).

Producing synthesised zeolite ion-exchanged by copper-tetraamine

For ion exchange in Zeolon P4 zeolite with Tetraamminecopper(II) sulphate, a 10 wt % suspension of synthesised zeolite in distilled water was added to the 12 wt % suspension of Tetraamminecopper(II) sulphate while stirring. Based on the preliminary analyses, it was used 100 % surplus of Tetraamminecopper(II) sulphate to achieve the ion exchange. After stirring for two hours, the suspension was let to settle, and the surplus copper complex with distilled water was removed by decantation. Decantation was continued until the amount of detectable copper in the aqueous phase became constant. The formed suspension was dried at 30 °C (in open space). Content of Cu was determined by Inductively Coupled Plasma Mass Spectrometry (ICP-MS), and organic nitrogen content was determined by Kjeldahl- method (O'Sullivan 2011).

Results and Discussion

Analysis of Tetraamminecopper(II) sulphate with derivatograph

Analysis of the crystalline Tetraamminecopper(II) sulphate was carried out with a derivatograph in the Institution of Material Science University of Pannonia. Fig. 4 shows the derivatogram of Tetraamminecopper(II) sulphate.

The figure clearly shows that during the heating process at temperature peaks of 176.0 °C, 210.5 °C, 319.5 °C and 389.5 °C mass reduction and endotherm processes occurred (DTA – Differential Thermal Analysis). Mass reduction at these peaks (TGA curve) (TGA - Thermogravimetric Analysis) presumably can be related to the removal of 4 ammonia content of copper-tetraamine complex through chemical decomposition. Up to 632.1 °C, the four ammonia molecules could be removed entirely during the decomposition of the complex. The calculated ammonia content of the weighed 400 mg Tetraamminecopper(II) sulphate was 119.53 mg (29.88 %). The derivatograph showed data of higher values by 151.79 mg (37.95 %). Besides ammonia, the water preserved in the zeolite is likely responsible for higher values. At

higher temperatures, at TG (799.9 °C and 859.9 °C, result from the decomposition of sulphate respectively), the measured weight reduction could (decomposition products: SO₂, SO₃, and O₂).

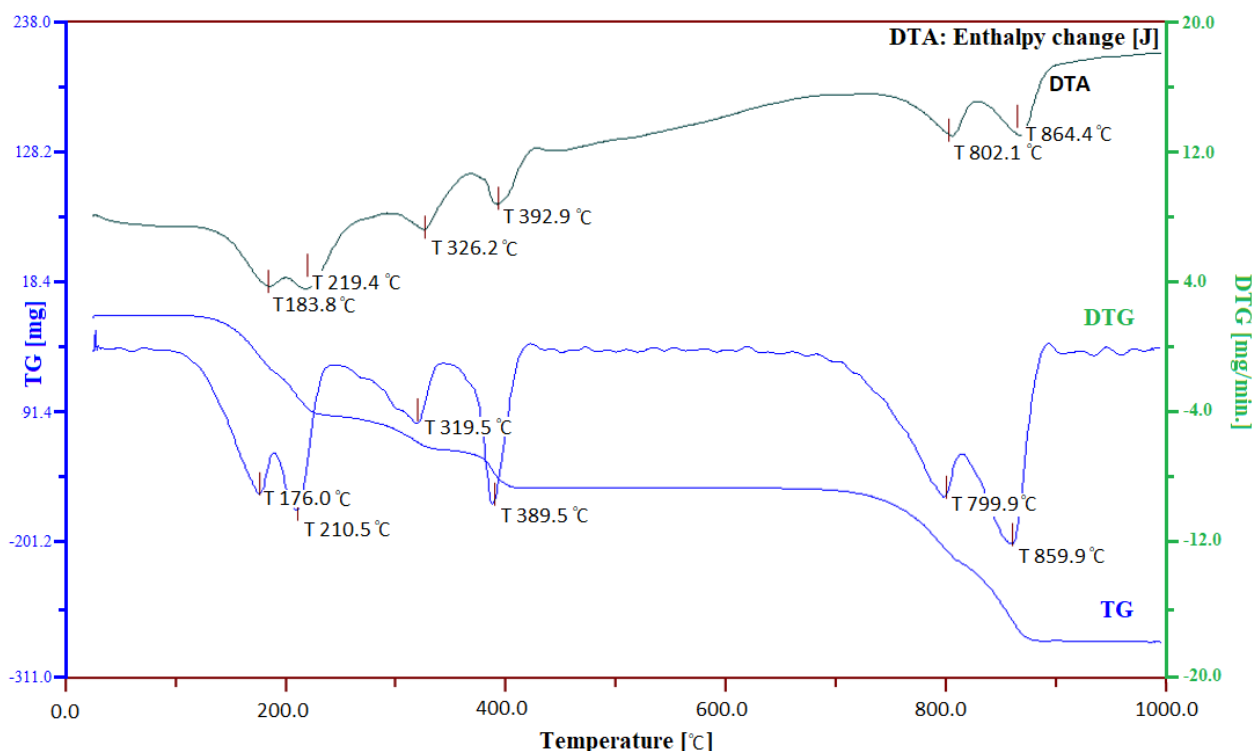


Fig. 4. Thermal stability of Tetraamminecopper(II) sulphate (Tamás Korim, 2020).

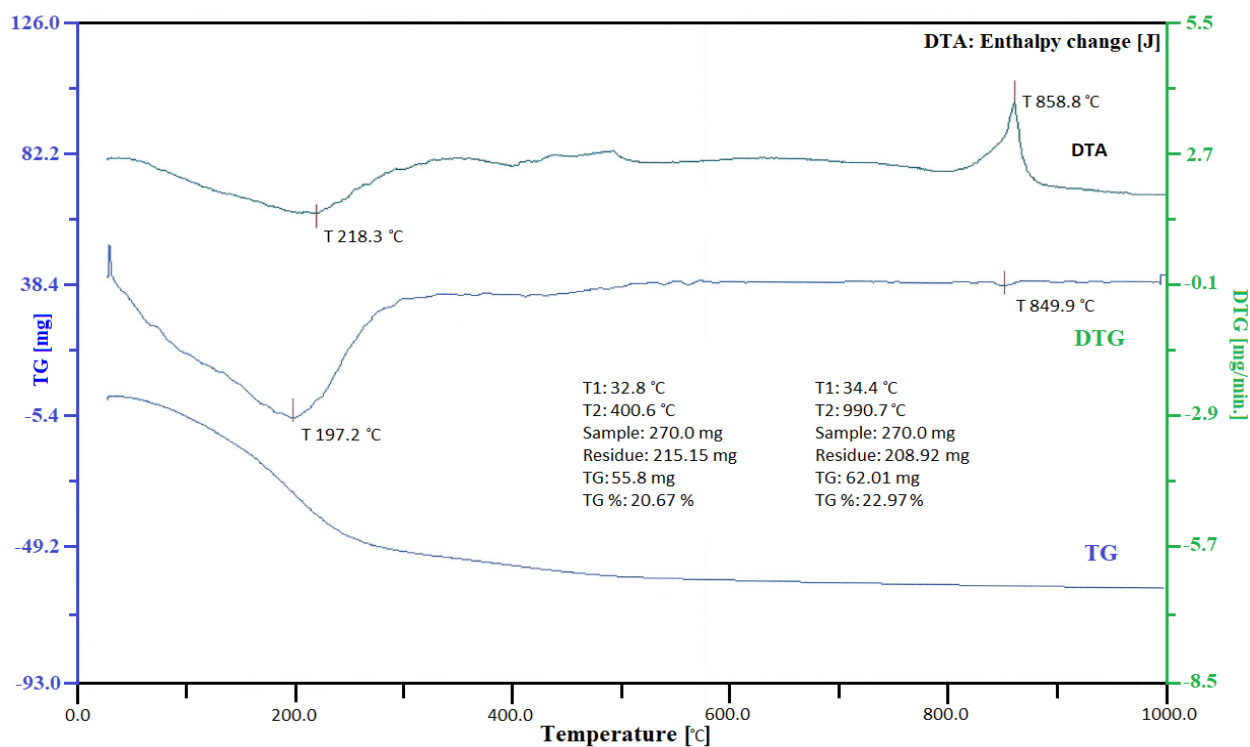


Fig. 5. Derivatogram of Zeolone P4A type synthesised zeolite (Tamás Korim, 2020).

Analysing Zeolon P4A type synthesised zeolite and ion-exchanged zeolite with a derivatograph

It was considered necessary to study whether the ion exchange does induce any changes in the zeolite. Therefore, the corresponding derivatogram was compared with that of the initial zeolite. Na⁺ cations bind the negative positions of the studied Zeolon P4A type zeolite. The Fig. 5 shows TG, DTG and DTA curves of the changes in Zeolon P4A zeolite due to rising temperatures. The TG curve shows that water binds in the channels and surface of zeolite with high adsorption capacity. Water desorption occurs until reaching the temperature ~ 400 °C, with a measured volume of 20.3 wt %. The maximum of the endothermic prolonged water release was 197.2 °C based on the DTG curve.

Due to rising temperatures, the DTA curve showed an exothermic reaction at 858.8 °C, resulting in a reduction in mass of 2.3 wt %.

Derivatograph analysis of zeolite ion-exchanged with copper-amine

The Fig. 6 shows the derivatogram of Zeolon P4A type zeolite treated with Tetraamminecopper(II) sulphate. Following the ion exchange, the zeolite's Cu content was 4.98 wt %, determined with ICP-MS. The nitrogen content was 3.76 % (equivalent to 4.56 wt % NH₃), corresponding to copper-tetraamine's ammonia content in the zeolite of 85.5 %. Based on these data, the presence of di- and triamine forms was also hypothesized.

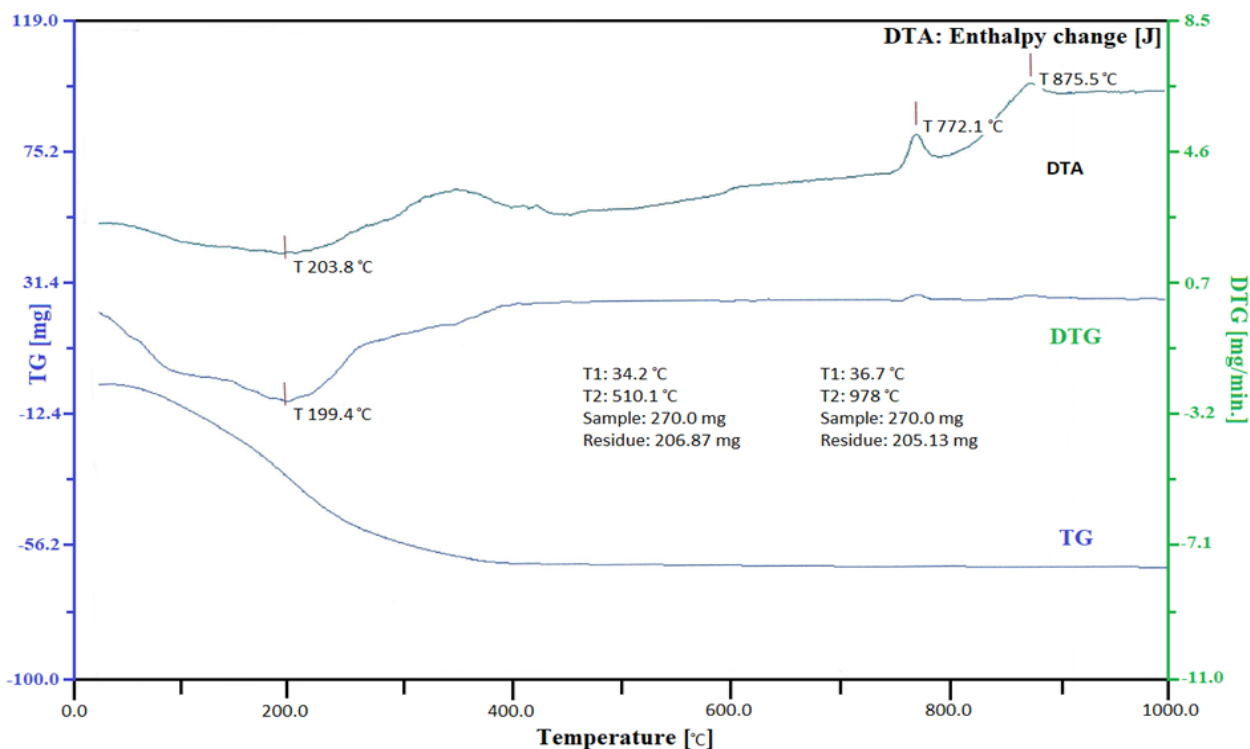


Fig. 6. Derivatogram of Zeolite ion-exchanged with copper-tetraamine-sulphate (Tamás Korim, 2020)

The DTA curve of the Tetraamminecopper(II) sulphate shows the gradual transmission of ammonia molecules at four definite endotherm peaks. In the case of ion exchange with the copper-tetraamine complex compound, the gradual release of ammonium molecules with the water remaining in the zeolite can be monitored through a single peak. A new peak providing exothermic reaction

formed at the DTA curve of the ion-exchanged zeolite at 772.1 °C and resulted in a slight increase in mass compared to the DTA curve of zeolite. The mass of ion-exchanged zeolite was 270 mg weighed into the derivatograph. The mass of ammonia put through ion exchange was 12.35 mg. During the analysis, the temperature was increased to 510.1 °C and measured a mass loss of 64.53 mg

(corresponds to 23.9 % of the ion-exchanged zeolite mass). Subtracting the weight of ammonia (12.35 mg) from 64.53 mg, 52.18 mg remains, what most likely gives the weight of residual water (this water mass form 19.32 % of the measured mass of ion-exchanged zeolite).

Energy Dispersive X-ray EDX analysis of Zeolon P4A zeolite

The Fig. 7 shows the EDX spectrum of Zeolon P4A type of synthesized zeolite. EDX records clearly show that the Si : Al ratio in the zeolite is close to 1 : 1 (10.16 % of Si, 11.81 % of Al). Sodium (replaceable) content represents 16.52 %, and that present in anion sites makes out 14.05 % of atoms participating in the zeolite.

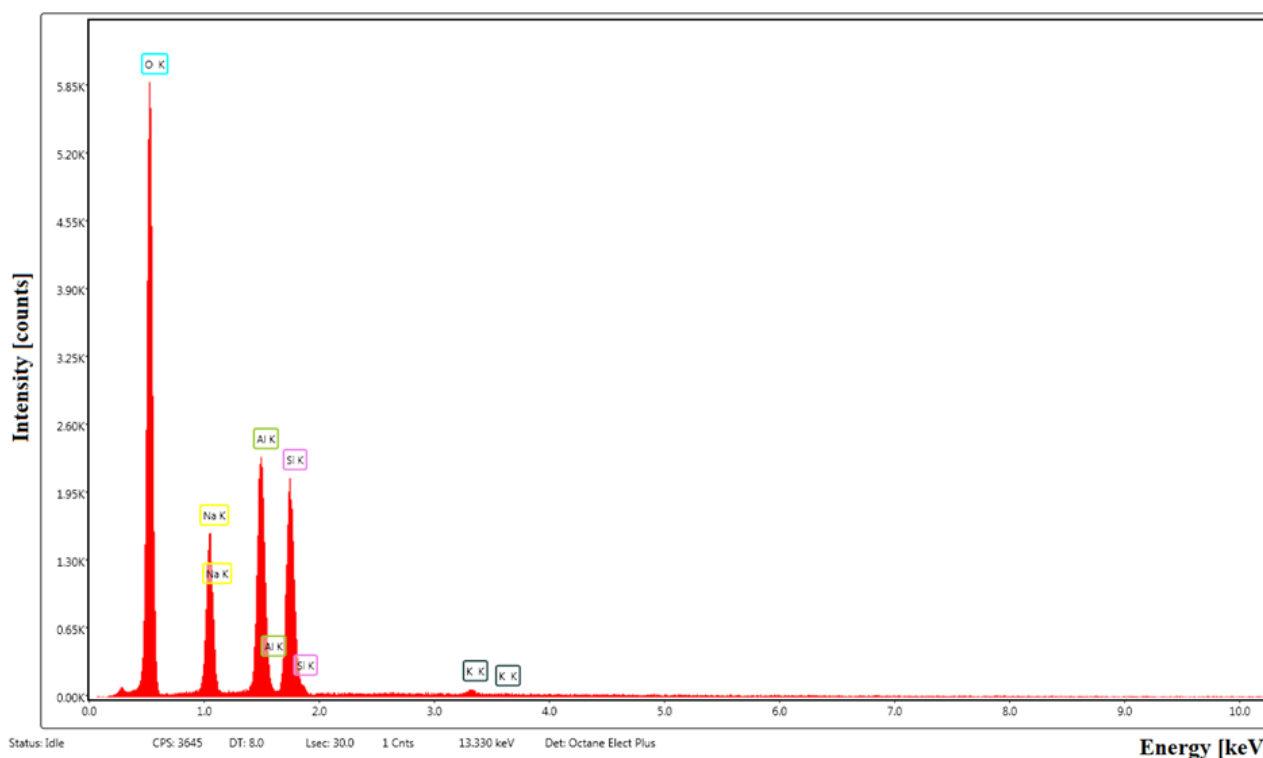


Fig. 7. EDX spectrum of synthesised zeolite of Zeolon P4A (Tamás Korim, 2020)

EDX analysis of copper ion-exchanged synthesised zeolite

EDX records provide reliable evidence of the progress and size of ion exchange (Fig. 8). Based on the recording, the EDX spectrum of the ion-exchanged zeolite shows that the ratio of Si : Al in the zeolite was approximately 1. No change in the lattice structure likely occurred due to ion exchange. This was supported by the X-ray diffraction phase analysis.

X-Ray Diffraction analyses

Quality phase analyses tested Cu-tetraamine, zeolite and Cu-zeolite samples. The Fig. 9 shows the XRD records of the three samples. The figure clearly shows that the diffractogram of zeolite and Cu-ion-exchanged zeolite are identical, referring to either the diffraction peaks or their intensity ratio. This is important because if a solid solution formed due to the Cu-infiltration, grid destruction would develop, followed by a change in the distance values of d-plane-network, which again would change the peak positions according to the Bragg-equation. Therefore, it can definitely be said that Cu did not incorporate build into the zeolite's crystal grid structure.

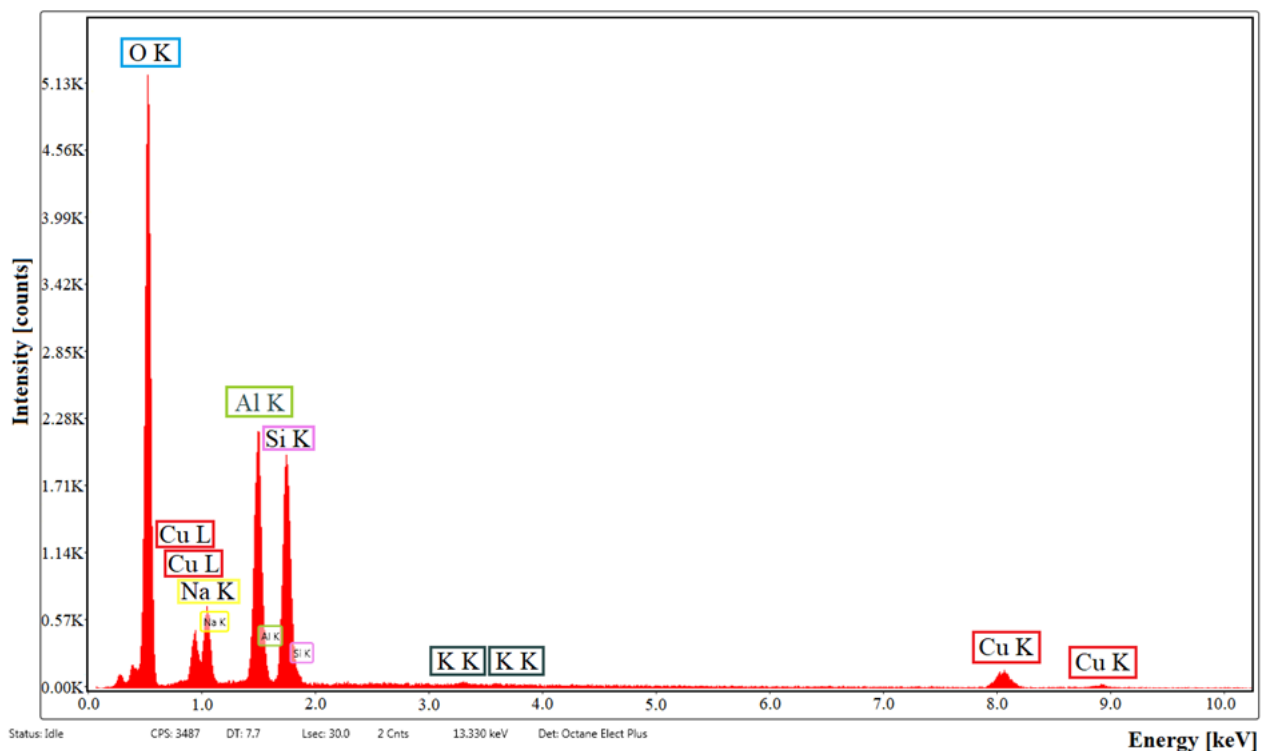


Fig. 8. EDX spectrum of zeolite ion-exchanged with copper-tetramine-sulphate (Tamás Korim, 2020)

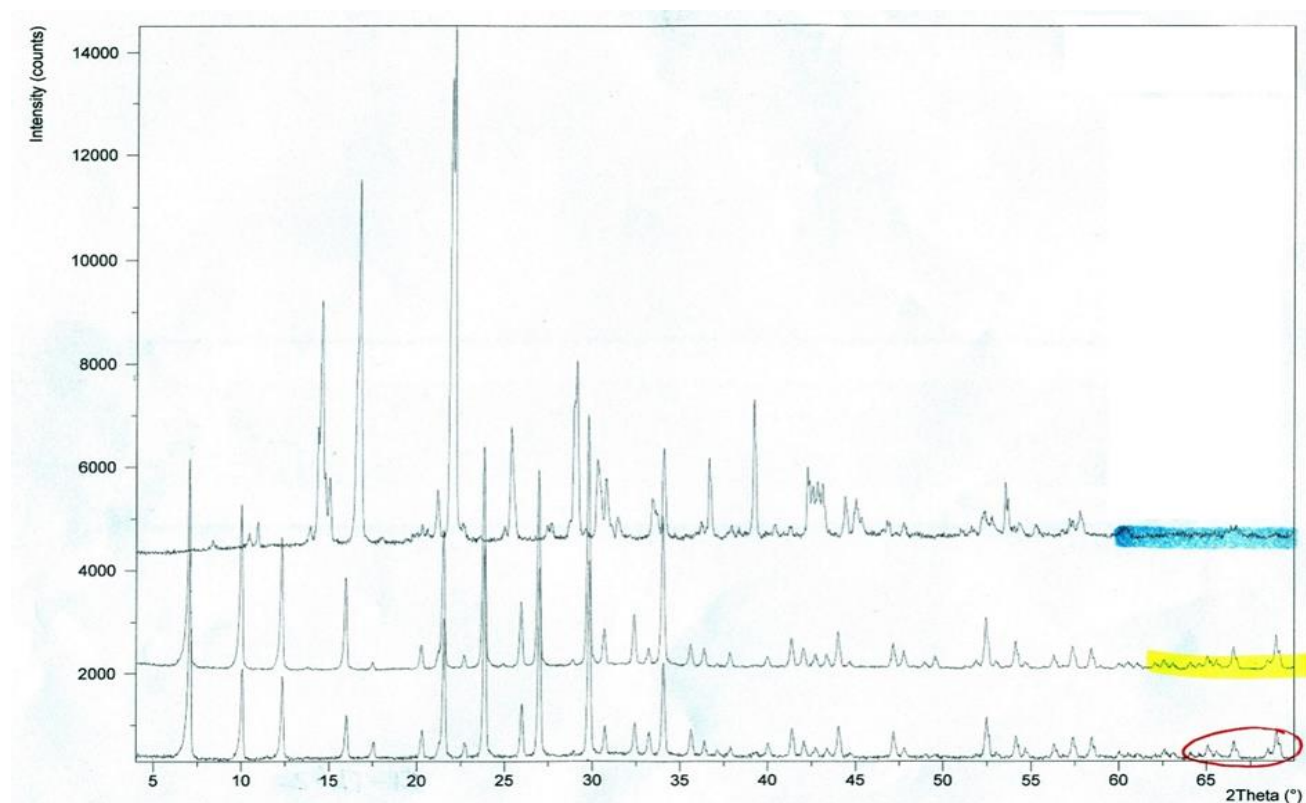


Fig. 9. XRD records of Cu-tetraamine, zeolite and Cu-zeolite samples (Tamás Korim, 2020).
 Note: During the test, different materials were marked with colours (20729 Cu-tetraamine: blue; 20723 Zeolit: yellow; 20721 Cu Zeolit: red circle).

Conclusion

Safe and quality crop production assumes to provide the crop with nutrients. Copper has a primary role among the essential microelements. The efficiency of foliar application of complex compounds can be increased if their retard-effect is ensured. The sodium ion was changed with copper-tetraamine ion in NaA type synthesised zeolite with the high ion-exchange capacity to ensure retardation. It was possible to immobilise the Cu-complex on the zeolite. Derivatograph analysis confirmed heat stability of the complex ion introduced through ion exchange, the decomposition of the complex did not start on the plant surface.

Energy dispersive X-Ray analyses (EDX) revealed that Si:Al ratio approached 1 : 1 (Si atom % = 10.16 and Al atom % = 11.81) in the synthesised zeolite. This ratio did not change even after ion exchange, which ensures high ion exchange capacity. X-ray diffraction (XRD) analyses show clearly that the diffractograms of zeolite and Cu-ion-exchanged zeolite were identical, referring to either the diffraction peaks or their intensity ratio. As a result, it can be stated that Cu did not build into the zeolite's crystal grid structure. The usefulness of copper ion-exchanged zeolite as a foliar fertiliser was proved by the fact, that according to its thermoderivatogram, the release of ammonia (decomposition of copper tetramine ion) takes place above 100 °C, so there is no intraday decomposition in the foliage. After ion exchange, the measured copper content of the zeolite is 4.98 wt % (ICP measurement) and the nitrogen content is 3.76 % (corresponding to 4.56 wt % NH₃). Based on the calculations that provided 85.5 % of the ammonia content of copper tetramine in the synthesised zeolite, it can be assumed that the triamine form is also present in the ion-exchanged zeolite.

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Conflict of Interest

Authors declare that there is no conflict of interest.

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