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# THE PRODUCTION AND INVESTIGATION OF STARCH BASED SLOW RELEASED ENCAPSULATING AGENTS

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Nowadays the protection of environmentally aware has important part in the agriculture. The growth of the plants need fill the gap of soil's nutrient. His manner included for this the fertilizing. The most developed fertilizers contain the essential microelements (B, Mn, Zn, Cu, Co, Mo), which are needed for plants, and provide their slow releasing. The native starch is a natural biopolymer that can be gained from renewable raw materials. Its good property is that the native starch able to slow the releasing of the micro components. This effect can be improved if the starch gets ionic functional groups that are able to bind cations. Different starch-phosphates were produced in solid-phase modification with changing the conditions, than we investigated the quality of these starch-phosphates (molecular weight distribution, charge density, solubility). We added copper and zinc microelements to these products using ion exchange method, and examined the dissolution of the micro components. In this paper we present our experiences about dissolution of the zinc and copper in different pH.

**Keywords:** slow release, encapsulating agent, starch derivatives

## Introduction

For many years our research group deals with the improvement of starch derivatives, which are able to slow release of micro components as fertilizers. The plants use the microelements in a minimal quantity, but their presence is essential to their growth.

Starch based encapsulating agents are organic or inorganic esters that have the capability of controlled water-repellency. With the use of them, we can reduce the speed of bioactive chemicals' release from the products. The fertilizers, which have these starch based encapsulating agents, are safe. They do not harm the health neither in the production, nor in the use phase. In addition, since active agents are better utilized, they would reduce the amount of fertilizers' production.

Native starch, in itself too, is able to decrease the speed of releasing, but if we build ionic function groups into the starch polymers, which are able to bind cations, we can improve the effect. Through the modification of starch, we replaced some of its OH groups in the anhydroglucose monomer unit by the ionic groups of phosphate with chemical reaction.

## Material and methods

### *The production of starch-phosphates*

The diammonium hydrogen phosphate (cp = 0.1 g phosphate/ 1 g starch) and the urea were dissolved in water. The pH of this solution (pH of phosphorilation = 9.6) was alkalized with sodium hydroxide, which was later sprayed to the starch. After that this mixture was heat-treated in oven (T = 145 °C; t = 1.5 h). The effect of this treatment was that phosphate groups replaced some of the starch's OH groups in the anhydroglucose monomer unit. Because of the alkalinity of the solution, two starch polymers could link through the phosphate group, and therefore we could see their polymerization. Also, because of the heat treatment, some of the molecules' degradation could be observed as well.

### *The qualification of starch-phosphates*

On the quality of starch derivates, the molecular weight distribution (Mw), solubility (Sol.), and charge density (Ch.d.) were determined. For the analysis, a dilute solution was made from starch derivates. The molecular weight distribution was determined by using size exclusion chromatography (HPSEC) and MALLS laser detector.

HPSEC uses a refractive index detector and its signal proportional with the samples' solubility (RI-area).

Charge density was determined by MÜTEK PCD 02, with a particle charge analysator, through colloid titration. This equipment neutralizes the oppositely charged polyelectrolyte solution through titrating the ionic polymer sample.

### *Binding the microelements*

Binding the microelements to the starch derivatives was performed after the heat treatment. The zinc was added in solid form, the copper in solution form to the starch-phosphate (the starch-phosphate's temperature was 70 °C).

The saturated solution of copper sulphate was sprayed to the starch derivatives during treatment. The solid/solution weight ratio was 1:1–1:0,5. When we added the $CuSO_4$'s solution and the solid $ZnSO_4*7H_2O$ together, at first we sprayed the $CuSO_4$'s solutions to the 140–145 °C starch-phosphate, than we mixed the solid $ZnSO_4*7H_2O$ with this compound.

*The investigation of the microelements' release*

The effectiveness of produced fertilizer additives were characterized by the rate of the microelements' release. The samples were put in bags made from filter cloth, and were dip them into distilled water (1:80 solid/solution). The dissolution was examined at 3 different pH values (pH1 = 5.5; pH2 = 6.5; pH3 = 7.5). It was made 2 measurement series, firstly the pH of distilled water was adjusted just before the dissolutions, than was measured day by day what happened with the pH. In the second series the 3 different pH were adjusted before dissolutions as well, but were maintained in these level every day. The pH levels were controlled with sodium hydroxide and nitric acid solution.

In given periods, after stirring the solution, samples were taken, which cubic content was not more than the solution's 1/100th part. Then the solution samples' microelements content was analyzed through the complexometric titration and atomic absorption spectrophotometer.

## Results

The parameters of the production and the quality of fertilizers additives are shown in *Tables 1* and *2*.

The micro components were added to the starch-phosphate on the strength of delineated method, than were examined their dissolution in different pH. It is important to compare the micro components dissolution in different pH, because the soil has big buffer capacity in this manner the releasing fertilizer additives affect the pH of the soils less, than the pH of the distilled water which we used in the dissolution tests. The dissolution processes are shown in *Figs. 1–8*.

*Table 1:* The parameters of the production and the quality of ready fertilizers additives

| Sample | The parameters of fertilizers production (Binding the microelements) | | | Quality of ready fertilizers additives | | | |
|---|---|---|---|---|---|---|---|
| | | | | Before binding the microelements | | | After binding the microelements |
| | T (°C) | $CuSO_4$ solution | Solid $ZnSO_4*7H_2O$ | $M_w$ ($10^6$Da) | Sol. (mV-mL) | Ch.d. (meq/g) | Ch.d. (meq/g) |
| Zn/5,5/b | 70 | | X | 11.5 | 2.84 | 0.63 | 0.48 |
| Zn/6,5/b | 70 | | X | 11.5 | 2.84 | 0.63 | 0.48 |
| Zn/7,5/b | 70 | | X | 11.5 | 2.84 | 0.63 | 0.48 |
| Cu/5,5/b | 70 | X | | 11.5 | 2.84 | 0.63 | 0.53 |
| Cu/6,5/b | 70 | X | | 11.5 | 2.84 | 0.63 | 0.53 |
| Cu/7,5/b | 70 | X | | 11.5 | 2.84 | 0.63 | 0.53 |
| CuZn/5,5/b | 70 | X | X | 11.5 | 2.84 | 0.63 | 0.45 |
| CuZn/6,5/b | 70 | X | X | 11.5 | 2.84 | 0.63 | 0.45 |
| CuZn/7,5/b | 70 | X | X | 11.5 | 2.84 | 0.63 | 0.45 |
| Zn/5,5/d | 70 | | X | 11.5 | 2.84 | 0.63 | 0.48 |
| Zn/6,5/d | 70 | | X | 11.5 | 2.84 | 0.63 | 0.48 |
| Zn/7,5/d | 70 | | X | 11.5 | 2.84 | 0.63 | 0.48 |
| Cu/5,5/d | 70 | X | | 11.5 | 2.84 | 0.63 | 0.53 |
| Cu/6,5/d | 70 | X | | 11.5 | 2.84 | 0.63 | 0.53 |
| Cu/7,5/d | 70 | X | | 11.5 | 2.84 | 0.63 | 0.53 |
| CuZn/5,5/d | 70 | X | X | 11.5 | 2.84 | 0.63 | 0.45 |
| CuZn/6,5/d | 70 | X | X | 11.5 | 2.84 | 0.63 | 0.45 |
| CuZn/7,5/d | 70 | X | X | 11.5 | 2.84 | 0.63 | 0.45 |

*Table 2:* The parameters of the dissolution of ready fertilizers additives

| Sample | Dissolution | |
|---|---|---|
| | pH | pH maintaining |
| Zn/5,5/b | 5.5 | Before dissolution(b) |
| Zn/6,5/b | 6.5 | Before dissolution(b) |
| Zn/7,5/b | 7.5 | Before dissolution(b) |
| Cu/5,5/b | 5.5 | Before dissolution(b) |
| Cu/6,5/b | 6.5 | Before dissolution(b) |
| Cu/7,5/b | 7.5 | Before dissolution(b) |
| CuZn/5,5/b | 5.5 | Before dissolution(b) |
| CuZn/6,5/b | 6.5 | Before dissolution(b) |
| CuZn/7,5/b | 7.5 | Before dissolution(b) |
| Zn/5,5/d | 5.5 | Day by day (d) |
| Zn/6,5/d | 6.5 | Day by day (d) |
| Zn/7,5/d | 7.5 | Day by day (d) |
| Cu/5,5/d | 5.5 | Day by day (d) |
| Cu/6,5/d | 6.5 | Day by day (d) |
| Cu/7,5/d | 7.5 | Day by day (d) |
| CuZn/5,5/d | 5.5 | Day by day (d) |
| CuZn/6,5/d | 6.5 | Day by day (d) |
| CuZn/7,5/d | 7.5 | Day by day (d) |

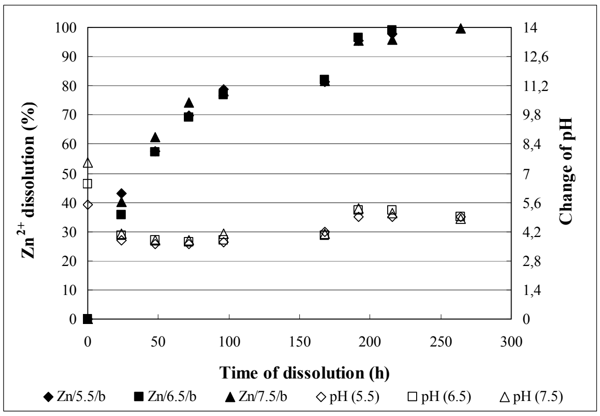


*Figure 1:* The $Zn^{2+}$ dissolution from starch-phosphate, which contain $Zn^{2+}$ micro component, in different pH and the change of pH

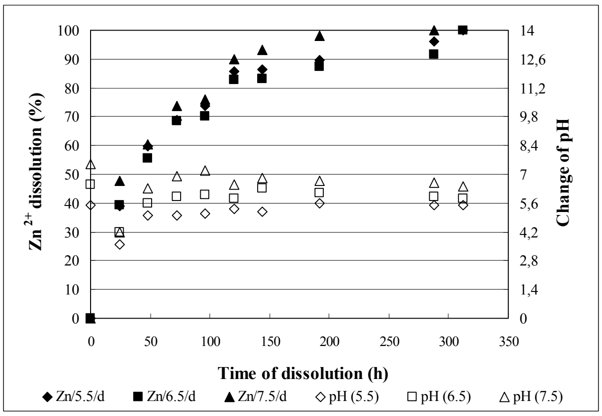


*Figure 2:* The $Zn^{2+}$ dissolution from starch-phosphate, which contain $Zn^{2+}$ micro component, in different, but maintained pH and the change of pH

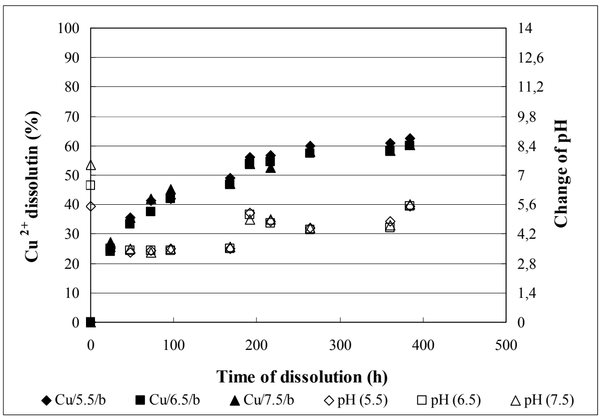


*Figure 3:* The $Cu^{2+}$ dissolution from starch-phosphate, which contain $Cu^{2+}$ micro component, in different pH and the change of pH

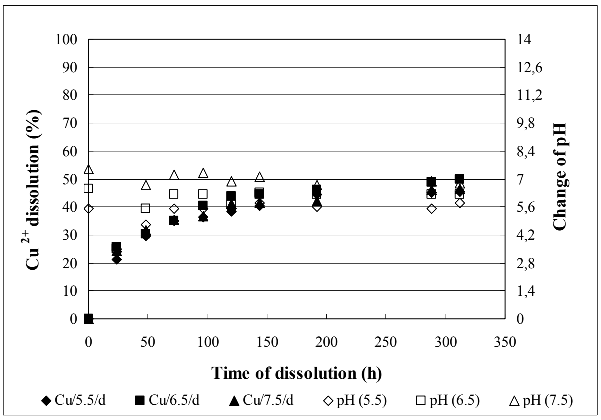


*Figure 4:* The $Cu^{2+}$ dissolution from starch-phosphate, which contain $Cu^{2+}$ micro component, in different, but maintained pH and the change of pH

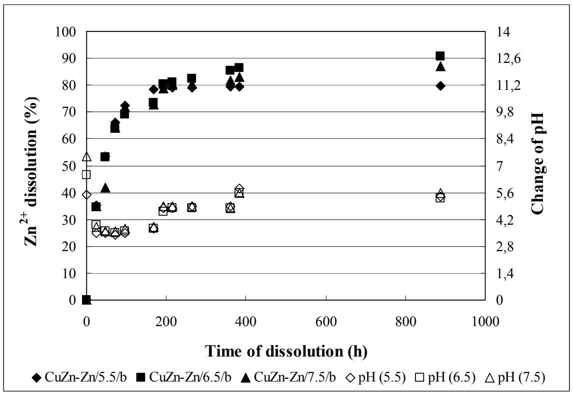


*Figure 5:* The $Zn^{2+}$ dissolution from starch-phosphate, which contain $Cu^{2+}$ and $Zn^{2+}$ micro components, in different pH and the change of pH

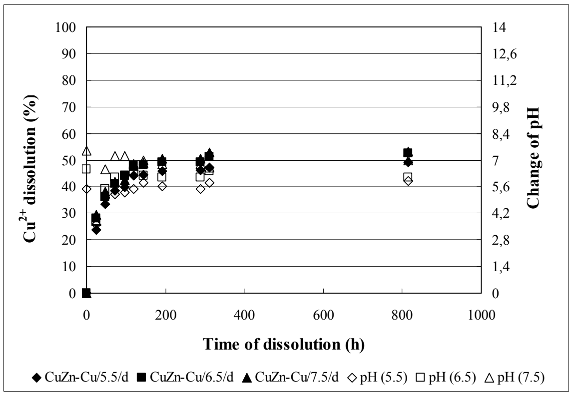


*Figure 8:* The $Cu^{2+}$ dissolution from starch-phosphate, which contain $Cu^{2+}$ and $Zn^{2+}$ micro components, in different, but maintained pH and the change of pH

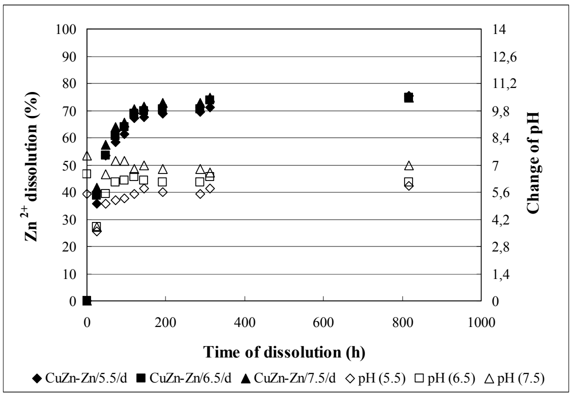


*Figure 7:* The $Zn^{2+}$ dissolution from starch-phosphate, which contain $Cu^{2+}$ and $Zn^{2+}$ micro components, in different, but maintained pH and the change of pH

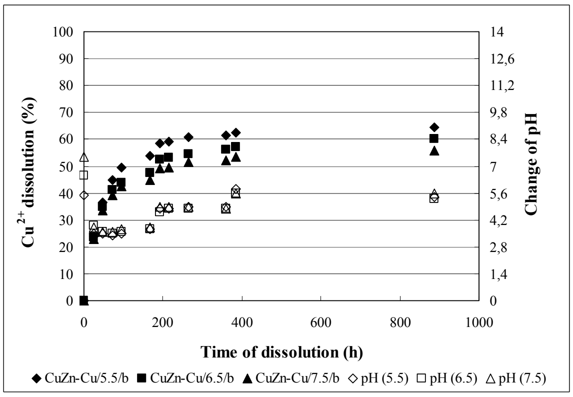


*Figure 6:* The $Cu^{2+}$ dissolution from starch-phosphate, which contain $Cu^{2+}$ and $Zn^{2+}$ micro components, in different pH and the change of pH

## Discussion

The results showed, that:

- The value of the solutions pH set in about pH = 4.5, irrespective of the solutions initial pH value.
- If we maintained the pH day by day in the original value, then we can see same phenomena by next day, but when the rate of releasing decreased, the change of pH was not significant.
- The difference of the releasing value in the three different pHs were not considerable, however the difference of the releasing value of the two different micro components was large.
- The dissolution of the zinc was faster either the micro components were separate or together.

The stable pH retarded the dissolution, therefore the chance are that the value of the dissolution is more favorable in the soil, comparing to the distillated water what we used in the laboratory tests.

## SYMBOLS

cp: g phosphate salt/ in 1g starch
T/t: temperature of heat treatment/ duration
T: temperature of the microelement's bonding
Mw: molecular weight distribution
Sol.: solubility
Ch.d.: charge density

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