

# Polymeric Microstructures for Slow Release of Fertilizers

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*A number of four polymer conditioned fertilizers, with slow release of active compounds, were synthesized and characterized. The new fertilizers have been obtained in solid form, through a crosslinking impregnation method. The influence of pH, temperature and molar ratio between raw materials on the activity index was investigated in order to reach an optimization of the process. The products were investigated using modern techniques, as Fourier transform infrared microscopy, HPLC, <sup>1</sup>H-RMN or scanning electron microscopy.*

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A modern and sustainable agriculture implies the use in appreciable amounts of fertilization products. It is well-known that from these used amounts, only a part is absorbed by plants in an useful way, significant amounts of fertilizers being washed in unusable areas or degraded by environmental factors, before being absorbed by plants, thus having a limited capacity of instant sorption for mineral nutrients. On the other hand, use of exaggerated amounts of mineral fertilizers leads inevitably to the appearance in culture plants of chemical compounds derived from these fertilizers (nitrates, nitrosamines etc), that can be found inherently in the foods, affecting the health of population, so having an extremely powerful impact over environment.

Taking into account the necessity of reducing the impact of the use of chemical fertilizers on the alimentary quality of vegetal production, we realized modern formulations of fertilizers, with slow/controlled release of active substance, so that will be totally metabolized by plants.

According to an accepted definition on international plan, the slow/controlled release fertilizers are those fertilizers which contain at least one nutrient that either delays its availability in the uptaking and utilization processes for plants after application, or is available to the plant for a significantly longer period than a standard considered to be a "quickly available fertilizer".

Development of processes and slow-release methods for active compounds represents a great concern for the specialists and research groups from prestigious institutions. Taking into account its many advantages, the domain of formulation components, additives, enhancers, synergists, encapsulation or managed release materials has been exponentially developed in the last years. The classes of compounds regarded by this technique are extremely various, from drugs, enzymatic systems and food ingredients to encapsulation of very toxic wastes, for their denoxioning.

Formulation materials could be urea-aldehyde resins but also materials like latex, polyvinylidene chloride [1] or polyurea, polyamides, polyesters, polycarbonates or polyurethanes [2,3]. Aldehydes are known reagents in crosslinking/copolymerization processes, leading to products with many application in host-guest chemistry [4], a domain of great interest with application in dosage or transport forms of many products [5]. Other references [6,7] describe nitrogen fertilizers, with slow release, obtained in an urea-formaldehyde polymer. The

compounds with slow release encapsulated in urea-formaldehyde matrixes have also other applications than the industry of fertilizers [8]. Melamine – formaldehyde resins, polystyrene, polyurethane and phenolic resins are also used as shell materials for encapsulation of different chemicals [9-13].

Decomposition of urea-formaldehyde resins is mainly due to microbial action. The release of N from these compounds thus depends strongly on soil properties such as biological activity, clay content, pH, and external conditions such as moisture content, wetting and drying, and temperature [14, 18, and 19].

We obtained solid fertilizer microstructures, which permit a slow release of fertilizing compositions, in such periods of time were a total sorption of active components by plants will occur and have a much higher activity compared to similar products. In order to obtain the said fertilizers, we chose a process of formulation with urea - formaldehyde resins. The composites were obtained in form of microspheres containing the fertilizing compositions.

## Experimental part

### Materials

The raw materials used in the experiments for fertilizers formulation are presented below:

- urea: granules, supplied by SC Donau Chem SRL Turnu Măgurele;
- formaldehyde aqueous solution, 37%, supplier SC Chimreactiv SRL Bucharest;
- paraformaldehyde, solid, containing minimum 98% formaldehyde, supplier BDH Chemicals Ltd, England;
- monoammonium phosphate, supplier SC UTCHIM SRL Rm. Vâlcea;
- potassium chloride, supplier SC Chimreactiv SRL Bucharest;
- phosphoric acid aqueous solution, 85% supplier SC Chimreactiv SRL Bucharest;
- potassium hydroxide aqueous standard solution, concentration 40%±1;
- *n*-hexane, supplier Vega Ploiești sodium tetraphenylborate, supplier Fluka.

### Instruments

- Kjeldahl system for nitrogen determination
- <sup>1</sup>H-RMN Varian Gemini 300 BB, operated at 300 MHz

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Composition no.	macronutrient ratio
1	N:P:K=2:1:1
2	N:P:K=1:1:1
3	N:P:K=1:1:0
4	conditioned urea – simple slow-release fertilizer

**Table 1**  
MACRONUTRIENT RATIOS IN THE  
FORMULATED COMPOSITIONS

- Spectrophotometer FT-IR GX, Perkin Elmer domain 10.000 – 20 cm<sup>-1</sup>
- Scanning electron microscope FEI Quanta 200
- HPLC with UV detection (Diode Array) λ=200nm, column: Metacarb 67 H, mobile phase: water/ H<sub>2</sub>SO<sub>4</sub> 0.05 M, mobile phase flow rate: 0.6mL/min, pressure 86 atm

In the synthesis flask, under stirring, we introduced 100 g aq. sol. of formaldehyde 37% and 0.5 mL KOH sol 40% in order to reach a pH of 8.5-9. When the temperature inside the flask reached 40°C, we added 36 g of technical urea. The installation scheme is presented in figure 2.

### Methods

The physical and chemical characterization of the fertilizing formulations was made according to the Annex IV of the Directive 2003/2003 of EC [15] for EC fertilizers. Thus, the nitrogen was determined by Kjeldahl method, phosphorus by extraction as monobasic ammonium phosphate followed by acid precipitation as quinoline phosphomolybdate and the potassium by precipitation with sodium tetraphenylborate in weak alkaline medium. Because sodium tetraphenylborate is a selective reagent for potassium and ammonium, the interference of the latter is removed by addition of formaldehyde, to form hexamethylenetetramine, which does not interfere in analysis.

### Experiment setup

We elaborated four fertilizing compositions with slow release, consisting in urea-aldehyde conditioned fertilizers, which were characterized from physical and chemical point of view, as well as regarding the activity index. The four compositions prepared are presented in table 1.

In table 1, the macronutrient ratios are expressed as follows: nitrogen is expressed as molecular nitrogen (N<sub>2</sub>), phosphorus as phosphorus pentoxide (P<sub>2</sub>O<sub>5</sub>), and potassium as potassium oxide (K<sub>2</sub>O). Besides that, for conditioning was also selected urea, in order to make a simple "slow-release" fertilizer, which will ensure large amounts of nitrogen.

#### Stage I (prepolymerization)

The total amount of urea introduced was chosen so that we have a molar ratio U/F between 1.4/1....2/1.

In stage I, urea reacts with formaldehyde, in alkaline medium, and according to the molar ratio of reactants, can generate mono-, di- or trimethylolureas, according to figure 1.

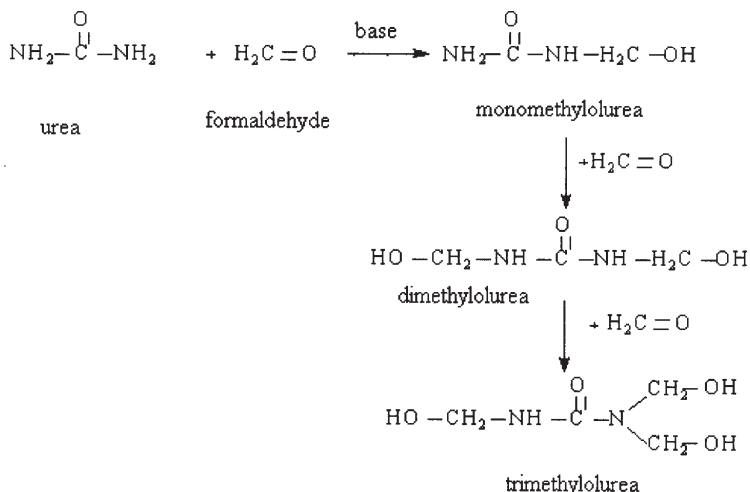


Fig. 1. Reaction scheme for obtaining the prepolymer from urea and formaldehyde

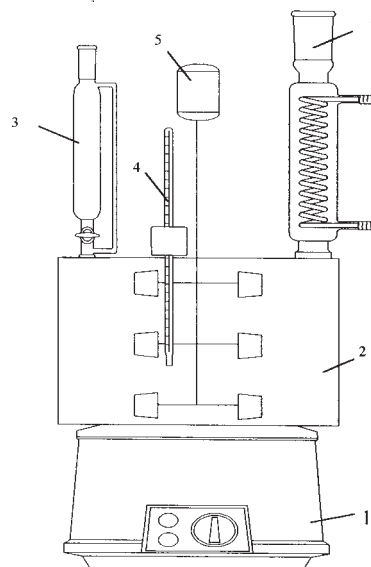
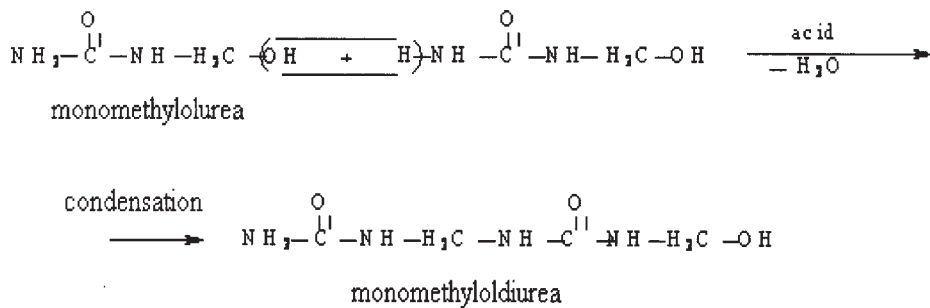


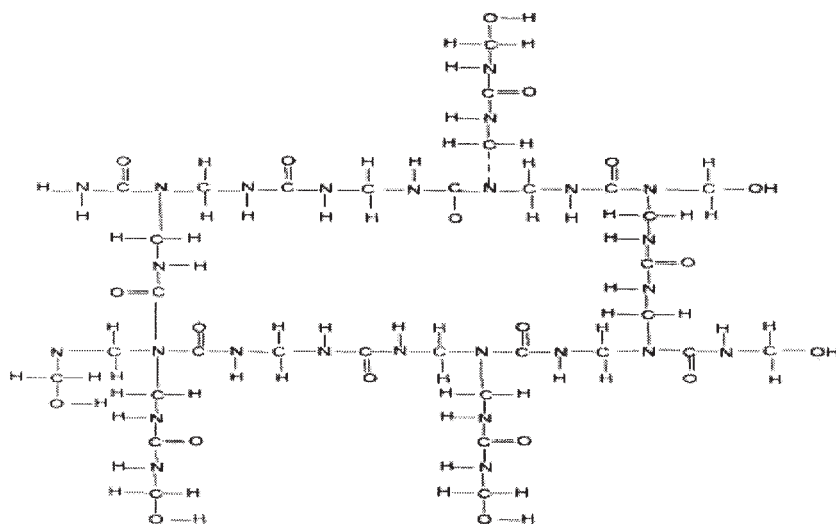
Fig. 2. Installation used in synthesis:  
1-electrical heater; 2-reaction vessel with four necks; 3-dropping funnel; 4-thermometer; 5-stirring system; 6-condenser

The temperature was raised gradually to 65-70° C, maintaining the pH of 8.5-9 through periodic addition of KOH 40%. The volatile compounds are condensed in a total reflux condenser and returned in system.

After 30 min, a new amount of 55 g urea is introduced, and stirring is still continued for another 90 min at 85-90° C, maintaining the pH. With the advance of the process, we observed a growth of viscosity, with formation of methylolureas. The reaction product remained, nonetheless, in liquid form for the entire period of reaction.



(a)



(b)

Fig. 3. (a) Condensation product; (b) fully crosslinked product

After two hours, the product was cooled to room temperature and we followed the next stage of the process. The product was liquid, water soluble and stable for short time in weak alkaline medium.

### Stage II (polycondensation)

The experiments refers to a macronutrient ratio of  $\text{N}:\text{P}_2\text{O}_5:\text{K}_2\text{O} = 2:1:1$ , with the mention that for other compositions, with other nutrient ratios, the same working mode was employed, changing only the mass ratio between the raw materials. Also, other parameters, as pH or temperature were monitored during the experiments in order to achieve the process optimization.

The products generated in the stage I, undergo, through modification of pH in acid domain (2-5), a complex process of polycondensation-crosslinking, with elimination of water molecules, according figure 3a. Subsequently, the polycondensation process advances, forming complex, three-dimensional structures, as viewed on figure 3b.

Under continuous stirring, we added cca 10 mL of aqueous solution of phosphoric acid 20%, till reaching a pH of 4.5-5. Subsequently, we added the remainder urea (55 g), in order to reach the established U/F ratio. It was established the mass ratio  $\text{N}:\text{P}_2\text{O}_5:\text{K}_2\text{O}$ , according to which was calculated the necessary amount of mineral salts of monoammonium phosphate (MAP) and potassium chloride (KCl). The amount of the above mentioned salts was added on the prepolymer solution, previously brought to a pH of 4.5-5, under continuous stirring and ambient temperature.

Separately, we prepared an organic solution of 200 mL organic solvent (*n*-hexane) + 3 grams non-ionic surfactant Neopal MA 3 (alcohols  $\text{C}_{12-14}$  ethoxylated with 3 moles of ethylene oxide, having a hydrophilic-lipophilic balance of nearly 8), (solution 2), which has to achieve a dispersion of the aqueous phase that contains the macronutrients. We prepared also an organic solution of 50 mL *n*-hexane and

10 grams linear-alkyl-benzenesulfonic acid (LABS-H), which is the polycondensation catalyst (solution 3).

At ambient temperature, under continuous and vigorous stirring, we added solution 2 over solution 1 (the prepolymer and other salts necessary for the fertilizer). A very fine dispersion was achieved, in which the small droplets of aqueous phase were surrounded by the solvent. We observed also a big growth of the mass viscosity. Subsequently, we added the solution 3 in the reaction. After 5 minutes of vigorous stirring and reaching a pH of 3.5-4.5, we started the heating, till we reached a temperature of 40-45°C. The rate of reaction is proportional with the temperature, but in order to obtain products of relatively large dimensions, a temperature of 50-70°C is required.

After two hours, we added an ammonia solution (25%) for reaching a pH of 6-6.5 and started the azeotropic distillation. After distillation of water, the fertilizer was dried in an oven at 70-80°C, till constant weight, in order to eliminate the traces of solvent from the product.

### Stage III (extruding)

In order to perform the tests for activity index, it has been imposed an agglomeration of the microspheres obtained in stage II, in larger entities, with a diameter of 2.5-4 mm. For this, the batches designated to enter the tests were conditioned with a series of agents of polymeric nature (polyvinyl acetate in latex form, polyethylene glycol, polyvinyl alcohol, stearin), ingredients that were introduced in a proportion of 10% related to the fertilizer, and extruded in a manual extruder, with 3 mm holes.

The urea-formaldehyde-fertilizers composites are separated in the following three fractions, according to their water solubility, in order to determine criteria for assessing the expected rate of release [14]:

Cold Water Soluble- CWS (25°C), consisting mainly of urea, dimers and short (soluble) UF chains. The nutrients in this fraction are readily available.

Hot Water Soluble – HWS (100°C), containing methylene ureas and chains of intermediate length. The nutrients in this fraction are slowly released into the soil.

Hot Water Insoluble – HWI, containing intermediate and long chains and consisting of extremely slow decomposing and/or practically unavailable nitrogen.

By subtracting CWS from HWS, the amount of cold water insoluble product, CWI, is obtained.

The mode, in which the various proportions of methyleneureas affect the release and efficiency of the nutrients, for use in domain of fertilizers [15], is expressed as activity index (AI), which is calculated [16] from the mass ratio of the three fractions above:

$$a. AI = \frac{II}{II + III} \times 100, \text{ or}$$

$$b. AI = \frac{CWI - HWI}{CWI} \times 100$$

AI provides an estimate of the fraction of relatively long-lasting release. Initially, the UF resins had an AI of 40-45. After studies and researches, an AI of 55-60 has to be reached [17].

As working mode, we took 1 gram of product, introduced it in 250 mL water at 25°C and kept under stirring for 30 min. The product was subsequently filtered, dried and weighed. The amount of dried product that remained on the filter was noted as Cold Water Insoluble (CWI). The difference between the initial amount (1 g) and CWI was noted as Cold Water Soluble (CWS). The amount of CWI was introduced in hot water, maintaining the dilution and stirring. The water was heated to 100°C and maintained at this temperature for 30 min. The filtration and drying procedure was repeated and the amount of product that remained on filter was noted as Hot Water Insoluble (HWI).

The difference between the amount of CWI introduced and HWI resulted was noted as Hot Water Soluble (HWS).

For the morphological analysis we used a scanning electron microscope model FEI Quanta 200, with low vacuum working mode. The sample was disposed on a metallic support, using a double adhesive carbon band.

## Results and discussions

Urea-formaldehyde resins are materials with a reactivity that makes very difficult the preparation of compounds with specific intermediary degrees of polycondensation. Usually a mixture of the three methylolureas is formed. The said mixture is very difficult to break into components during analysis because of the interference and association of the functional groups.

In the <sup>1</sup>H-NMR spectra, in figure 4, can be observed the following signals: ~2.5 ppm and ~3.15 ppm for proton in CH<sub>2</sub> groups; ~4 ppm for proton in NH group; ~4.5 ppm for proton in OH group; ~5.6 ppm for proton in NH<sub>2</sub> group [20].

In the FT-IR spectra, in figure 5, can be observed the following signals: 1003.49 cm<sup>-1</sup>, characteristic for CH<sub>2</sub>OH groups, 1547.77 cm<sup>-1</sup>, for CO-NHR groups, 1651.33 cm<sup>-1</sup>, for CO(NHR)<sub>2</sub> and the wide band at 3343.99 cm<sup>-1</sup>, characteristic for polymeric hydroxyl (intermolecular OH bonds) [20].

From the HPLC spectra, in figure 6, it can be observed that the separation of the methylolureas is difficult because of reactivity and association of functional groups. For a non-diluted sample, as well as for an extremely diluted one, the signal is unique and no separation is possible (fig. 4a). The only tendency of separation is observed at a 1/2 dilution and λ=200 nm (fig. 4b).

The results from scanning electron microscopy are presented in figure 7 and show a monolithic structure of the obtained products. The urea conditioned product seems more compact than the NPK formulated fertilizers.

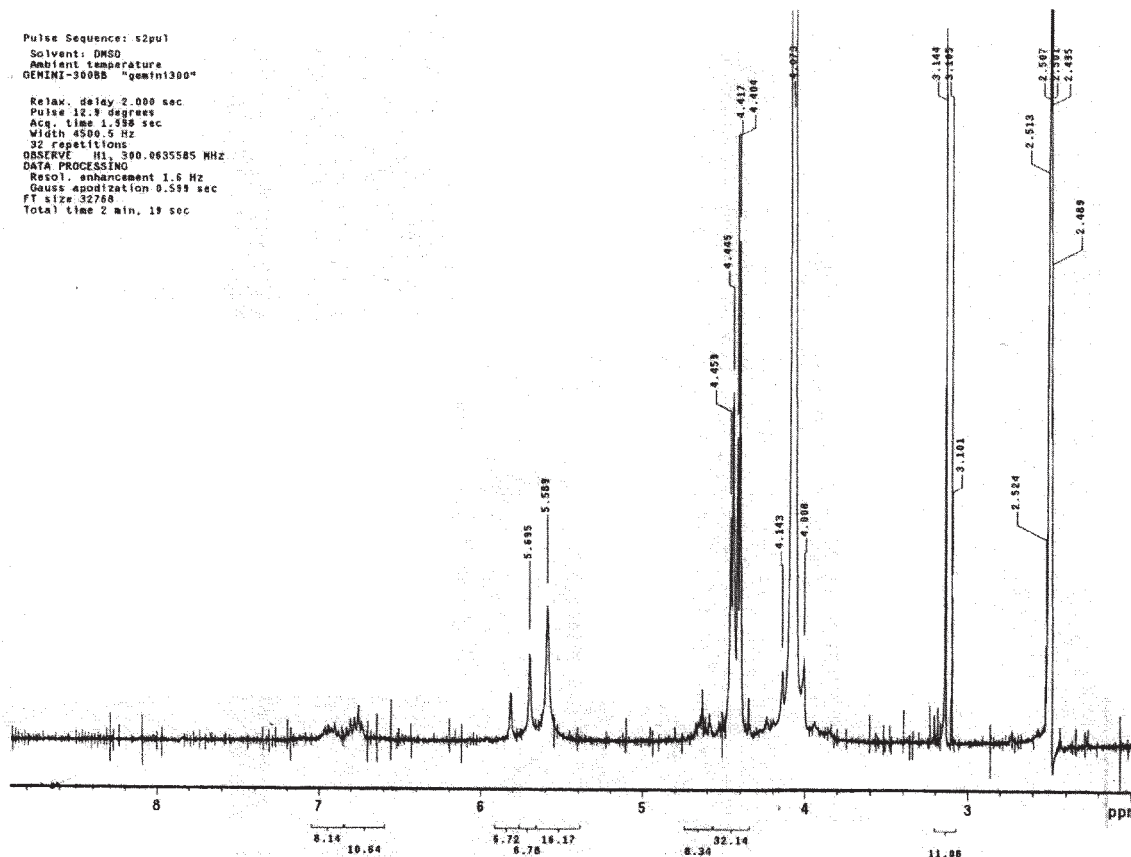


Fig. 4. <sup>1</sup>H-NMR spectra of the urea/formaldehyde prepolymer

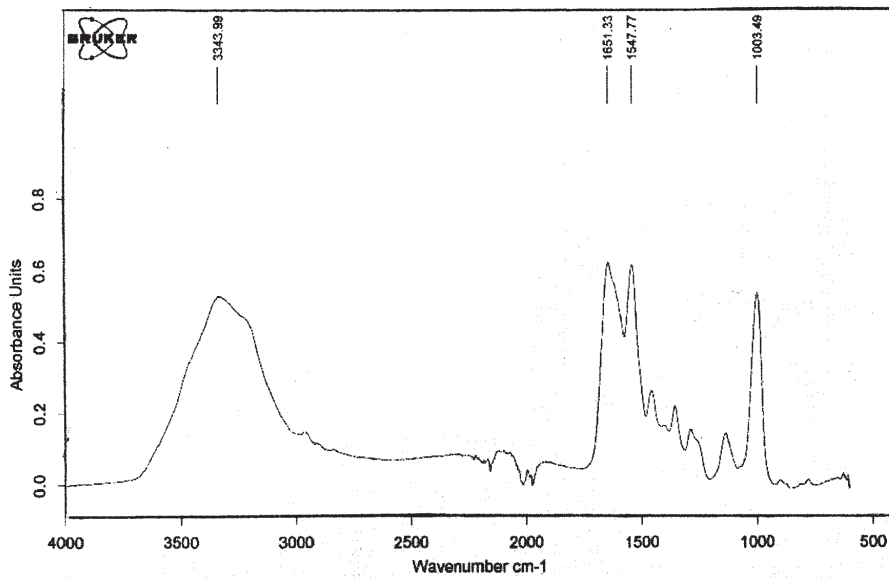


Fig. 5. FT-IR spectra of the urea/formaldehyde prepolymer

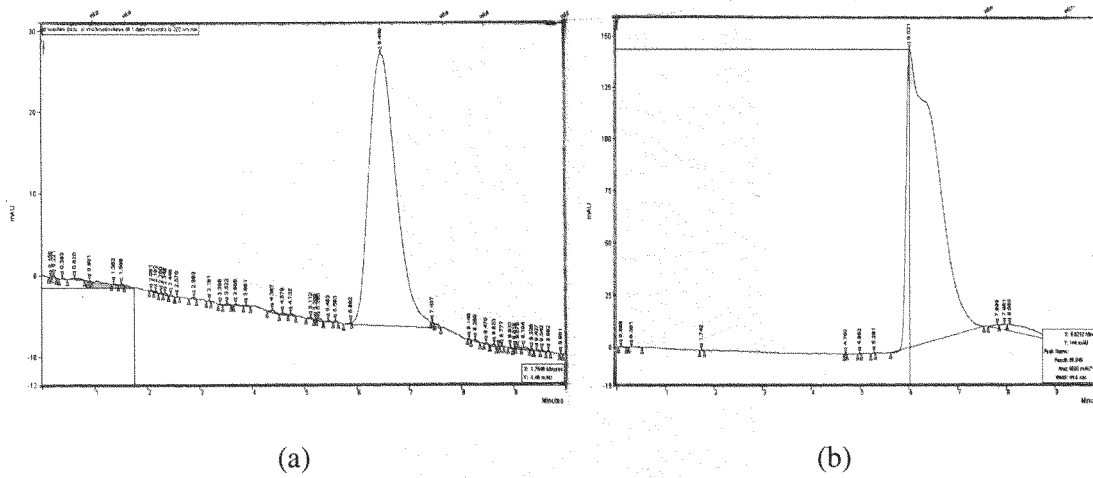


Fig. 6. HPLC chromatogram for methylolureas. (a) non-diluted sample; (b) sample diluted at 1/2 with water

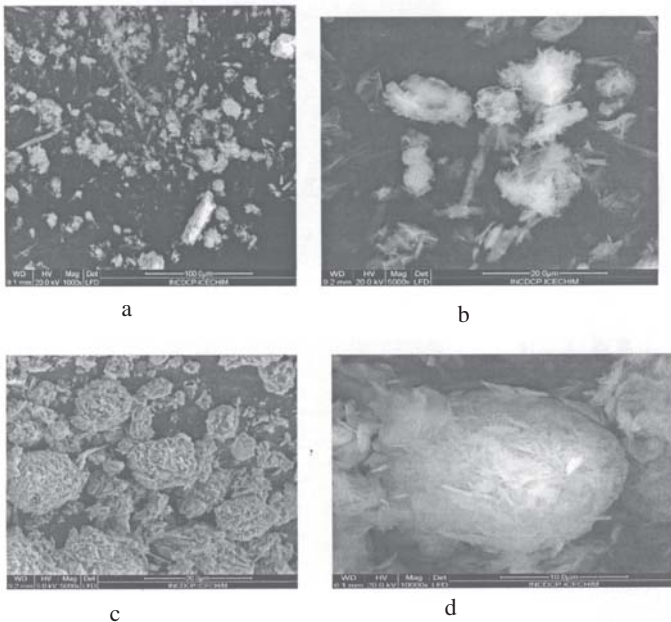


Fig. 7. SEM micrographs of the conditioned fertilizers. conditioned NPK fertilizer (a and b); Conditioned urea (c and d)

The experiments performed had as purpose, on one hand, the establishment of necessary parameters for formulation of agrochemical products and, on the other hand, verification of the influences these parameters have on the activity index of the finished product. The parameters with influences on the quality of the finished product were determined as being pH, temperature and urea-formaldehyde molar ratio.

A representation of the influence of the pH in the second stage of obtaining the conditioned fertilizers is shown in figure 8. The influence of the pH is significant in the polycondensation process. The crosslinking (polycondensation) of methylolureas prepared in the prepolymerization stage take place only in acid media. If the pH is too high (>5.5), the polycondensation rate is very small, even at temperatures over 70-80° C, leading to a pasty, agglomerated product. On the other hand, a very low pH leads to a very high rate of polycondensation, this

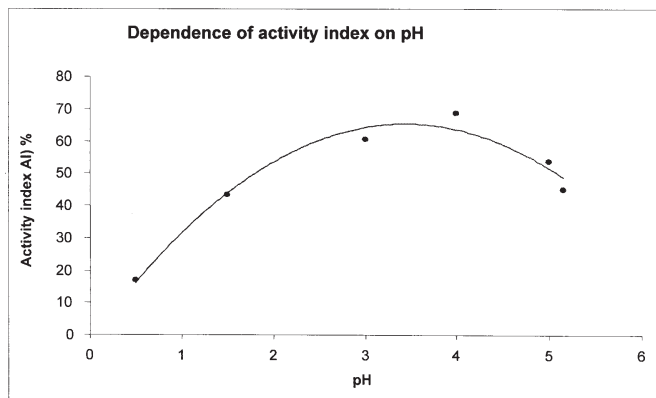


Fig. 8. Influence of pH in the polycondensation stage on the activity index of the finished product

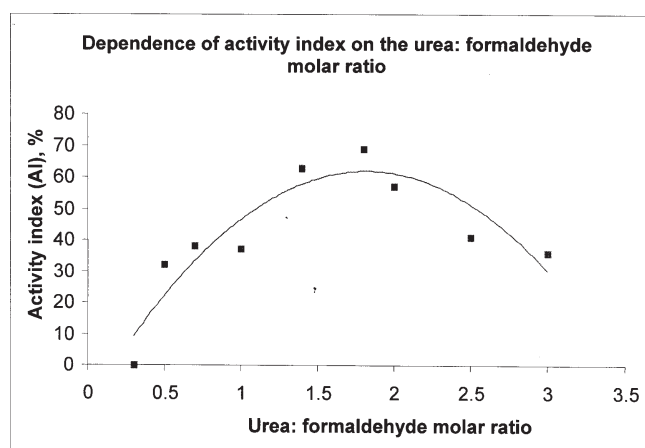


Fig. 9. Influence of initial urea: formaldehyde molar ratio on the activity index of the finished product

exothermic process leading to an autoacceleration of the polycondensation stage. The crosslinking degree becomes uncontrollable, the finished product being a powder of hard microcrystals, affecting also the values of activity index.

Because the urea-formaldehyde molar ratio is an important parameter in the process, we performed a series of experiments at different values of these molar ratios to observe the influence of this parameter on the physical and chemical characteristics (including activity index) of the finished product. The results are presented in figure 9.

We performed a series of experiments in order to test the influence of the temperature in the polycondensation stage on the activity index, the results being presented in figure 10. Regarding the influence of the temperature on the characteristics of the finished product and its activity index, can be mentioned the following: at low temperatures (15 – 20°C), the polycondensation does not initiate even after two hours, the product maintaining itself liquid. On the other hand, a too high temperature (>80°C) leads to an instantaneous polycondensation the finished product being in form of crystals that agglomerate in large blocks and are hard to process through filtration, granulation, extrusion or other processing methods.

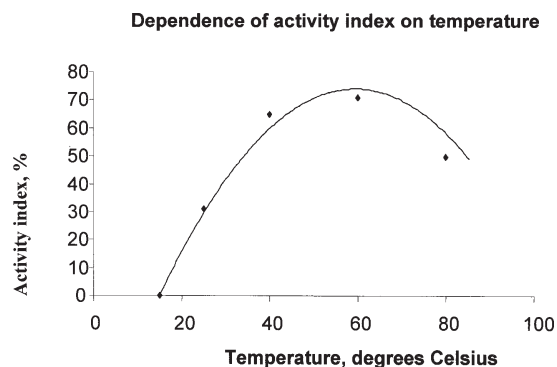


Fig. 10. Influence of temperature in the polycondensation stage on the activity index of the finished product

## Conclusions

We performed a series of studies and experiments concretized in elaboration of four fertilizing compositions with slow release, consisting in fertilizers formulated in urea-aldehyde structures, which were characterized from physical and chemical point of view, but also for slow-release activity.

All the fertilizing compositions that respected the optimal parameters had superior physical and chemical characteristics that facilitate deposition, handling and differential fertilization according to their content of active ingredients.

For all the types of solid formulations we obtained activity indexes over 40%, the minimal imposed value for a product to be considered as a “slow-release fertilizer”. These values for activity index are obtained if the parameters that we monitored have, simultaneously, the following values: a temperature of ~60°C, a pH value of 4 and the initial molar ratio between urea and formaldehyde is ~1.8.

Through their qualities, these products can generate a superior fertilization regarding the use of nutrients, diminution of dosages, together with the protection of plant productivity. Because urea-aldehyde resins are degraded under microbial activity in soil, these formulated fertilizers also reduce the chemical pollution of soil.

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