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POLYMER CONDITIONED FERTILIZERS

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S-au obținut şi caracterizat două tipuri de fertilizanți condiționați cu polimeri, pentru eliberare lentă a principiilor active. Produsele au fost obținute în stare solidă, printr-o metodă de impregnare prin reticulare. Pentru optimizarea procesului de obținere s-au influența pH-ului şi temperaturii asupra indicelui de activitate. De asemenea, s-a studiat capacitatea polimerilor de a forma structuri de tip "core-shell" în condițiile de reacție monitorizate. Produşii au fost analizați utilizând tehnici moderne, ca FT-IR, ^{1}H-RMN sau microscopie electronică de baleiaj.

Two types of polymer conditioned fertilizers, with slow release of active compounds, were synthesized and characterized. The products have been obtained in solid form, through a crosslinking impregnation method. The influence of pH and temperature on the activity index was investigated in order to reach an optimization of the process. Also, the capacity of said polymers to form core-shell structures in the monitored conditions was investigated. The products were characterized using modern techniques, as Fourier transform infrared microscopy, ^{1}H-NMR or scanning electron microscopy.

Keywords: Slow release, fertilizers, polymers, conditioning

1. Introduction

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

The advantage of polymer formulated fertilizers is the releasing of active ingredients through solubilization in a much longer period of time, as compared to simple, non-conditioned fertilizers. Thus, the plants benefit of an enhanced nutrition for a longer period in the vegetal cycle and larger productions are ensured because of a superior use of the nutrients. On the other hand, the nutrients are levigated in reduced amounts, thus the dosages of fertilizers can be reduced

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without diminution of plants productivity. Also the chemical pollution of soil is reduced by these polymer formulations.

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 latest 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 emulsion, polyvinyliden 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 that 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]

We obtained solid fertilizer microstructures, which allow a slow release of the fertilizing compositions, in periods of time comparable to those required for total sorption of active components by plants, thus having a much higher activity as compared to similar products. In order to obtain the said fertilizers, we choosed a process of formulation with urea - formaldehyde resins. The composites were obtained in form of microspheres containing the fertilizing compositions.

The estimation of slow-release activity is performed through the Activity Index (AI). Initially, the UF resins had an AI of 40-45. After studies and researches, an AI of 55-60 has to be reached [14].

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 [15]:

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

(II) 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.

(III) 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 [16], is expressed as activity index (AI), which is calculated [17] from the mass ratio of the three fractions above:

$$\mathrm{AI} = \frac{II}{II + III} x100 \qquad (1)$$

or

$$\mathrm{AI} = \frac{CWI - HWI}{CWI} x100 \qquad (2)$$

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 [18].

2. Experimental procedure

2.1. 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 hydroxyde, aqueous standard solution, concentration 40%±1; *n*-hexane, supplier Vega Ploieşti
- Sodium tetraphenylborate, supplier Fluka.

All the materials were used as received, with no further purification operations.

2.2. Working mode

Stage I (prepolymerization)

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

In the synthesis flask, under stirring, we introduced 150 grams 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 25 grams of technical urea. 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 were condensed in a total reflux condenser and returned in system. After 30 minutes, a new amount of 155 grams urea was introduced, and stirring continued other 90 minutes 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 on the entire period of reaction.

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. The product was characterized through HPLC, FT-IR and ^{1}H-NMR methods.

Stage II (polycondensation)

The amounts refer to a macronutrient ratio of $N:P_2O_5:K_2O = 2:1:1$, with the mention that for other compositions, with other nutrient ratios, the same working mode may be employed, changing only the mass ratio between the raw materials. Also, parameters as pH or temperature were monitored during the experiments in order to achieve an optimization of the process.

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, forming complex, three-dimensional structures, as viewed on Fig. 2.

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 (30 grams), in order to reach the established U/F ratio. It was established the mass ratio $N: P_2O_5: K_2O$, according to which was calculated the amount of mineral salts of monoammonium phosphate (MAP) and potassium chloride (KCl) necessary. The amount of the abovementioned 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 C_{12-14} ethoxylated with 3 moles of ethylene oxide, having a hydrophilic-lipophilic balance of nearly 8), (solution 2), which has to realize 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 realized, 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. The product was characterized through analyses of nutrients (nitrogen, phosphorus and potassium) and by measuring the activity index.

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.

2.3. Characterization

The physical and chemical characterization of the fertilizing formulations was made according to the Appendix IV of the Directive 2003/2003 of EC [16] 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.

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.

3. Results and Discussions

We elaborated two fertilizing compositions with slow release, consisting in urea-aldehyde conditioned fertilizers. One composition was conditioned NPK fertilizer, with a macronutrient ratio of $N:P_2O_5:K_2O = 2:1:1$. The macronutrient ratios are expressed as follows: nitrogen is expressed as molecular nitrogen (N_2), phosphorus as phosphorus pentaoxide (P_2O_5), and potassium as potassium oxide (K_2O). Beside that, for conditioning was also selected urea, in order to make a simple "slow-release" fertilizer, which to ensure large amounts of nitrogen. The products were characterized from physical and chemical point of view, as well as regarding the activity index.

The synthesis process of the said composites has two stages: a first stage (I), called prepolymerization, and a second stage (II), called polycondensation. 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 Fig. 1.

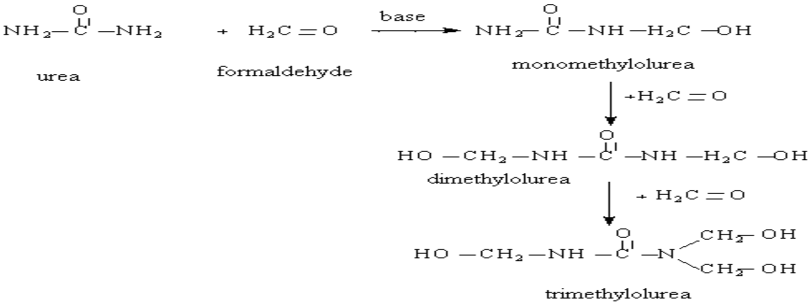


Fig. 1. Reaction between urea and formaldehyde

In stage II, the products obtained 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, forming complex, three-dimensional structures, as viewed on Fig. 2.

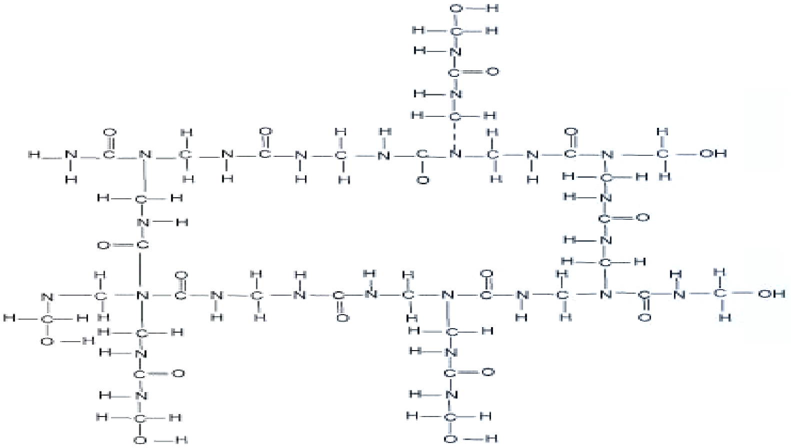


Fig. 2. Crosslinked product

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.

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 the interference and association of the functional groups.

In the ^{1}H-NMR spectra, in Fig. 3, can be observed the following signals: ~2.5 ppm and ~3.15 ppm for proton in CH_2 groups; ~4 ppm for proton in NH group; ~4.5 ppm for proton in OH group; ~5.6 ppm for proton in NH_2 group [19].

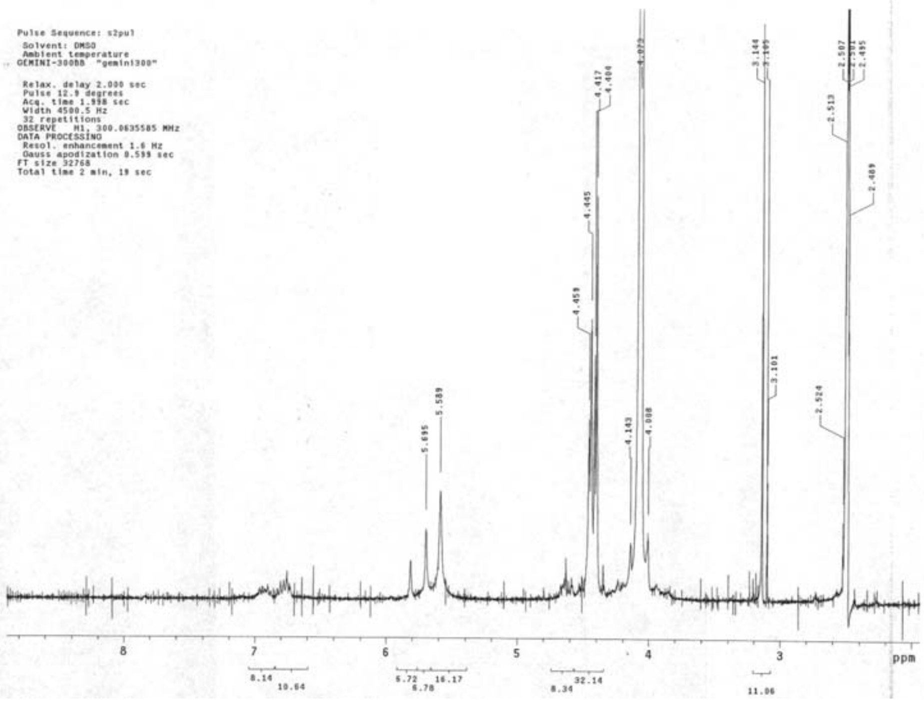


Fig. 3. ^{1}H-NMR spectra of the urea/formaldehyde prepolymer

In the FT-IR spectra, in Fig. 4, can be observed the following signals:

1003,49 cm^{-1}, characteristic for CH_2OH groups, 1547,77 cm^{-1}, for CO-NHR groups, 1651,33 cm^{-1}, for $CO(NHR)_2$ and the wide band at 3343,99 cm^{-1}, characteristic for polymeric hydroxyl (intermolecular OH bonds) [19].

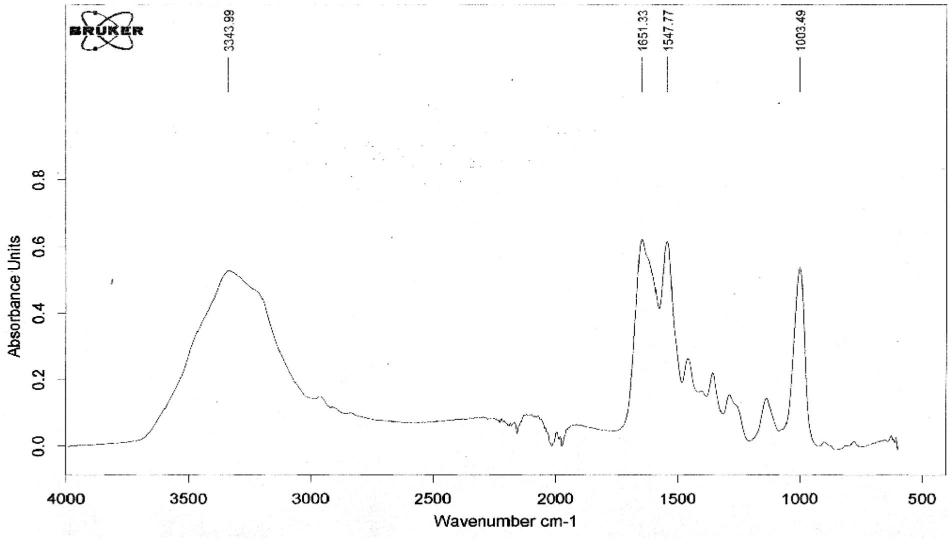
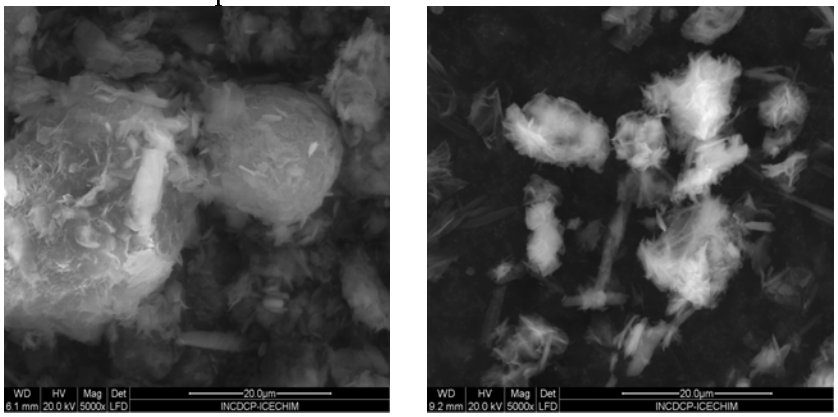


Fig. 4. FT-IR spectra of the urea/formaldehyde prepolymer

The results from scanning electron microscopy are presented in Fig. 5 and show a monolithic structure of the obtained products. The urea conditioned product seems more compact than the NPK formulated fertilizer.



(a) (b)

Fig. 5. SEM micrographs of the conditioned fertilizers. Conditioned urea (a); Conditioned NPK fertilizer (b)

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 influence these parameters have on the activity index of the finished product. The monitored parameters with influences on the quality of the finished product were pH and temperature.

A representation of the influence of the pH in the second stage of obtaining the conditioned fertilizers is shown in Fig. 6. The influence of the pH is significant in the polycondensation process. 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 exothermic process leading to an autoacceleration of the polycondensation stage. The crosslinking degree becomes uncontrollable, the finished product being in form of a powder of hard microcrystals, affecting also the values of the activity index. Other conditions were:

- Molar ratio U/F = 2:1;
- Initial temperature = 17° C;
- Maximum temperature = 70° C;
- Duration of stage II= 2 hours;
- solvent = toluene;
- quantity of Neopal MA 3 = 3 g;

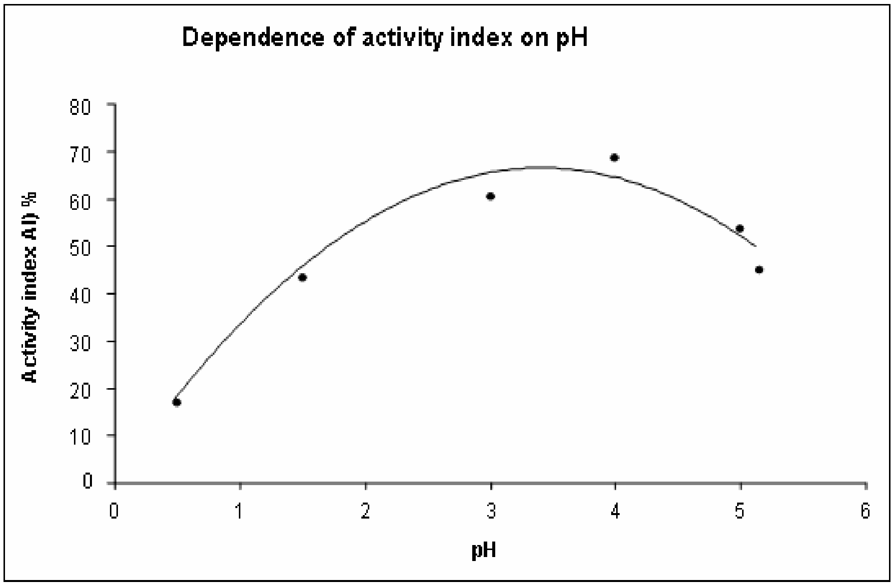


Fig. 6. Influence of pH in the polycondensation stage on the activity index of the finished product

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 Fig. 7. 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 start even after two hours, the product remaining 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. Other conditions were:

- duration of Stage I= 2 hours;
- Molar ratio U/F = 2:1;
- Initial temperature = 17° C;
- Maximum temperature = 80° C;
- Duration of stage II= 2 hours;
- pH in Stage II = 4.5-5
- solvent = toluene;
- quantity of Neopal MA 3 = 3 g;

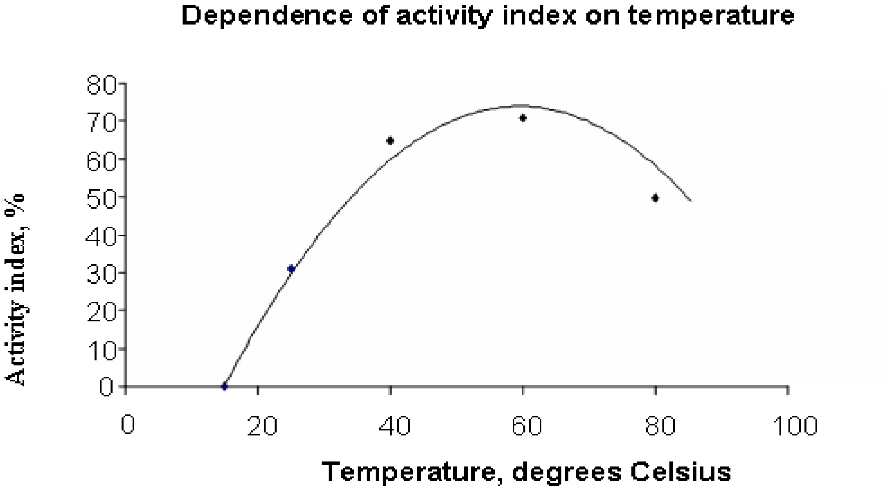


Fig. 7. Influence of temperature in the polycondensation stage on the activity index of the finished product

4. Conclusions

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

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 the said compositions we obtained activity indexes over 40%, the minimal imposed value for a product to be considered as a "slow-release fertilizer". These values for the activity index are obtained if the parameters that we monitored have, simultaneously, the following values: a temperature of ~60°C and a pH value of 4, in the polycondensation stage.

The urea-formaldehyde resins do not develop, in the given conditions, core-shell structures. The products obtained show a monolithic structure, with the conditioned urea being more compact than the NPK conditioned fertilizer.

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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