Synthesis Optimization and Characterization of Microencapsulated N-P-K Slow-Release Fertilizers

Abstract: Slow-release microencapsulated N, P, and K fertilizer synthesis was optimized and the products exhaustively characterized. Four NPK formulations with nutrient mass ratios of 1:0:0, 1:1:0, 1:1:1, and 2:1:1 were characterized following European Council Regulation 2003/2003 for fertilizers as well as ICP-AES, \(^1\)H-NMR, FT-IR, HPLC, elemental analysis, XPS, SEM, dynamic light scattering, thermogravimetry, differential thermogravimetry, activity index, and leaching rate. These fertilizers have good slow-release properties and decrease waste and crop contaminants, improving environmental protection. Compared to classic granulated fertilizers, plant nutrient availability was improved allowing reduced application. Nutrient leaching parameters describing four different kinetic models were evaluated.

Keywords: slow release, fertilizer, urea-formaldehyde, environment protection

1 Introduction

Chemical fertilizers have been crucial to the growth of world agricultural production by approximately 50% over the last 40 years [1-3]. According to the UN Food and Agriculture Organization, 1 kg of nutrient (N, P, K) yields an average harvest of 8.8 kg corn, 7.3 kg wheat, 8.5 kg rice, 5.5 kg soy, etc. Moreover, according to American specialists, the harvest is 41% controlled by chemical fertilizers and less by herbicides (15–20%), soil quality (15%), hybrid seed (8%), or irrigation (5%). However, about 20–70% of the applied nitrogen is lost to the environment, causing serious pollution and increasing costs [4-7]. The nitrogen effectively used is 50–70% in the first year, for potassium it is 50–60%, while for phosphorus it is around 15% [8]. A further 1–2% per year may be used over the following decades. An important quantity is lost by immobilization, denitrification, volatilization, or leaching. These losses are most important for nitrogen, and cause ground water and soil pollution with nitrates, nitrosamines, or other harmful compounds [9,10]. These appear in foods, affecting health [11,12].

Improved fertilizer utilization can reduce the amounts used. Fertilizer design considers two parameters: solubility over time, influenced by interaction with the soil, and plant uptake. Slow/controlled release allows the nutrients to be completely absorbed. These fertilizers contain at least one nutrient that either delays its availability after application or is available for significantly longer than a standard “quickly available fertilizer” [13]. According to standard SR EN 13266/2001, a slow-release fertilizer must release no more than 15% after 24 h, no more than 75% in 28 days and at least 75% overall.

Slow/controlled release fertilizers have been based on urea-aldehyde resins, polyvinylidene chloride [14-16], hydrogel nanocomposites [17,18], kaolin-chitosan systems [19,20], polysulfones [21,22], polyamides [23], polyesters [24], polyvinyl alcohol [25], polyurethanes [26,27], and other hybrid systems [28]. Current trends focus on biopolymers [29]. Crosslinking/copolymerization with aldehydes has many applications in host-guest chemistry [30], with applications in application or transport forms [31,32]. Other authors describe slow release nitrogen fertilizers based on a urea-formaldehyde polymer [33], or using alkylbenzenesulfonic acid cross linked urea-formaldehyde resin [34]. Although controlled release fertilizer use has almost doubled over the last decades, it still comprises only a small percentage of total fertilizer use [35].

An ideal fertilizer: i) gives optimal development with a single application for the season; ii) gives maximum nutrient absorption; iii) has minimal side effects on soil, water, and air [36-38].
The present study examines urea-formaldehyde as a nitrogen fertilizer. Environmental decomposition of urea-formaldehyde resin is due to microbial action. Thus, N release depends strongly on biological activity, controlled by soil clay content, pH, moisture, wetting and drying, and temperature.

The main objective of this work is the preparation and characterization of a slow-release fertilizer with microstructures that release nutrients when plants need them, and with minimal environmental effects. An urea-formaldehyde polycondensate was prepared by interfacial condensation in a microemulsion.

2 Experimental Procedure

Comparative studies were conducted on four samples with N : P₂O₅ : K₂O mass ratios of 1:0:0, 1:1:0, 1:1:1, and 2:1:1, denoted NPK 100, NPK 110, NPK 111, and NPK 211.

2.1 Materials

Urea prills (46% N) were supplied by SC Donau Chem SRL, Romania. The formaldehyde source was UF80 pre-condensate, (57 ± 1% formaldehyde, 23 ± 0.5% urea), supplied by SC VIROMET SA, Romania. Poly(vinyl alcohol) agglomerant (mean molecular weight 95,000 g mol⁻¹, 90% hydrolysed) was supplied by Sigma Aldrich. DILUANT C6000 (tech., 99.6%) supplied by SC UTCHIM SRL, Romania was the solvent instead of toluene; linear alkylbenzenesulfonic surfactants LABS-H and SPAN 80 were from STERA CHEMICALS SRL, Romania; monoammonium phosphate for P determination was supplied by SC UTCHIM SRL, Romania; potassium chloride, 40% KOH, and 85% phosphoric acid for pH adjustment after polycondensation were supplied by SC Chimreactiv SRL, Romania. All were used as received.

2.2 Synthesis method

Urea-formaldehyde resins form by reaction of formaldehyde with excess urea at controlled pH, temperature, mole ratio and reaction time, yielding polymethylene urea polymers with different molecular weights [39]. Fertilizer preparation was by an initial pre-polymerization followed by a polycondensation. In the pre-polymerization, urea reacts with basic formaldehyde forming mono-, di-, and trimethylolureas. This is a water miscible liquid, stable in weak base. This pre-polymer solution was brought to a pH around 5 and monoammonium phosphate and potassium chloride were subsequently added. The pre-polymerization product underwent polycondensation-crosslinking in acidic medium using linear alkylbenzenesulfonic acid (LABS-H) catalyst in organic solvent. Polycondensation for 2 hours at 50–70°C yielded products with medium molecular weights. Water was removed by azeotropic distillation, followed by drying at 70–80°C to remove residual solvent. The fertilizers were treated with polymeric agglomerants and extruded to 3 mm diameter extrudates.

The NPK slow-release fertilizers were differentiated into three fractions. F1: the cold water soluble fraction (CWSF – soluble in water at 25°C) is mainly urea, dimers, and short U-F chains and is immediately available. F2: the hot water soluble fraction (HWSF – insoluble in water at 25°C, but soluble at 100°C) contains methylene ureas with medium-length U-F chains, and represents slow-release nutrients. F3: the hot water insoluble fraction (HWIF – components insoluble in cold or hot water) is mainly long U-F chains containing the extremely slow release and unavailable components.

2.3 Equipment and characterization methods

The fertilizer N, P₂O₅, and K₂O contents were determined according to European Council Regulation 2003/2003 for fertilizers [40]. Nitrogen was determined by the Kjeldahl method with acid catalysis on a Kjeldahl Behrotest system and a K 350 distillation unit. After Kjeldahl digestion, the ammonia released by base addition was absorbed in 2% boric acid and titrated with standard 0.1 M H₂SO₄ to a bromocresol endpoint.

Phosphorus was determined by extraction as monobasic ammonium phosphate followed by acidic precipitation of quinoline phosphomolybdate. Potassium was determined by precipitation with sodium tetraphenylborate in weakly alkaline solution. Because tetraphenylborate precipitates both potassium and ammonium, the ammonium interference was removed by converting it to the unreactive hexamethylenetetramine with formaldehyde.

Fertilizer samples were mineralized with a Berghof microwave digester in nitric acid and hydrogen peroxide. The resulting solution was analysed using inductively coupled plasma atomic emission spectrometry (ICP-AES) on a Varian Liberty 110 instrument with V-groove nebulizer, Fassel torch, and Czerny-Turner monochromator. Phosphorus was identified at 214.914 nm and potassium at 769.896 nm. The LOD was greater than 0.4 mg kg⁻¹.
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$^1$H-NMR spectra were acquired with a Varian Gemini 300 BB operated at 300 MHz. The samples were dissolved in dimethyl sulfoxide (DMSO) and analysed at room temperature with a 12.9° pulse and 32 scans. Fourier transform infrared analyses were performed on a Perkin Elmer GX FT-IR spectrophotometer from (10,000 – 20) cm$^{-1}$. Liquid chromatograms were recorded on a HPLC with a diode array detector at $\lambda = 200$ nm, on a Metacarb 67 H column. The mobile phase was 0.05 M aqueous $\text{H}_2\text{SO}_4$ at 0.6 mL min$^{-1}$ and 86 atm. Carbon, hydrogen, nitrogen, sulphur, and oxygen were determined by elemental analysis using a Perkin-Elmer 2400 Series II with thermal conductivity detector, at 975°C combustion temperature and 500°C reduction temperature. A Thermo Scientific K-Alpha instrument gave X-ray photoelectron spectra with a Al Kα (1486.6 eV) source, working at 200 eV and $2 \times 10^{-9}$ mbar. Product morphology was determined using a FEI Quanta 200 SEM.

**Activity index (AI)**

The activity index (AI) characterizes the slow-release performance:

$$AI = \frac{HWSF}{HWSF + HWIF} \times 100$$

The effects of temperature, U/F ratio, and pH on the AI were studied.

### 2.4 Slow release experiments

Slow release tests of NPK 111 fertilizer were performed in a glass column ($L = 600$ mm, $D = 200$ mm) filled with 1–2 mm sand. NPK 111 (20 g) was incorporated 20 cm from the top. The column was washed with 50 mL distilled water at 8 day intervals and the leachate (P1-P8) analysed for N, P, and K. The degree of leaching was determined for each sample P1-P8.

### 3 Results and Discussion

Synthesis of urea-formaldehyde resins to specified degrees of polycondensation is difficult and the resulting mixture of three methylolureas increases the difficulty of analysis. Morphologically, the products are almost spherical with monolithic compact structures, as observed from the SEM images. However, the sphericity is altered by local heating during scanning. The particle dimensions measured by SEM are confirmed by DLS analyses; mean diameters are 2.1–2.7 µm for all samples, with no variation correlated with synthesis parameters. Both SEM and DLS showed particle agglomeration.

The elemental analyses are in Table 1. The results obtained by classic methods are confirmed by faster and easier modern XPS and ICP-AES. The correlations between classic and modern methods are good; their complementary nature contributes to a fuller characterization.

XPS showed intense signals for carbon (C1s) at ~285 eV, nitrogen (N1s) at ~400 eV, and oxygen (O1s) at ~531 eV. Lower intensity signals appeared for phosphorous (P2p) at ~134 eV and potassium (K2p) at ~292 eV. To determine the nitrogen surface and internal distributions these results were compared with the EA results and expressed as the N/C ratio. EA gave a higher N/C ratio than XPS. The highest N/C ratios were observed for NPK 100 and NPK 211, suggesting that N is concentrated inside the particle.

![Figure 1: SEM images of NPK 100 fertilizer (d$_m$ = 2.5 µm by DLS).](image)
Figure 2: SEM image of NPK 110 fertilizer ($d_m = 2.1 \, \mu m$ by DLS).

Figure 3: SEM image of NPK 111 fertilizer ($d_m = 2.3 \, \mu m$ by DLS).

Figure 4: SEM image of NPK 211 fertilizer ($d_m = 2.6 \, \mu m$ by DLS).
rather than at the surface. The presence of C inside the particles suggests that polymerization occurs throughout the particle, forming a network that incorporates the fertilizer elements.

Table 1: Elemental composition.

| Method          | Elements | NPK 100 | NPK 110 | NPK 111 | NPK 211 |
|-----------------|----------|---------|---------|---------|---------|
| EC Directive    | N        | 36.77   | 21.24   | 16.01   | 11.08   |
|                 | P        | 0       | 21.87   | 16.93   | 5.11    |
|                 | K        | 0       | 0       | 17.30   | 5.97    |
| XPS             | N        | 24.72   | 23.73   | 18.75   | 29.03   |
|                 | P        | 0       | 1.39    | 1.47    | 1.15    |
|                 | K        | 0       | 0       | 0.32    | 0       |
|                 | C        | 49.64   | 63.18   | 47.01   | 44.04   |
|                 | N/C ratio| 0.498   | 0.059   | 0.398   | 0.659   |
| ICP-AES         | P        | 0       | 23.10   | 15.96   | 5.10    |
|                 | K        | 0       | 0       | 16.00   | 6.00    |
| EA              | N        | 37.76   | 20.56   | 17.12   | 11.40   |
|                 | C        | 26.27   | 32.29   | 20.11   | 16.00   |
|                 | H        | 6.67    | 8.19    | 5.61    | 4.90    |
|                 | S        | 0.84    | 0.97    | 0.78    | 0.73    |
|                 | N/C ratio| 1.437   | 0.574   | 0.851   | 0.712   |

P and K, which are not part of the polymer, are concentrated mainly inside the particles. K is not even detected at the NPK 211 surface. Very low concentrations of Ca (in NPK 100) and Si (in NPK 100, NPK 110, and NPK 111) are detected. CaO is added for pH correction in the last synthesis step, while Si may originate from small amounts of Mg₃Si₄O₁₀(OH)₂ (talc).

In agreement with earlier work [38], ¹H-NMR spectra for NPK 211 gave signals at ~2.5 ppm for DMSO, ~3.15 ppm for OH; ~4 ppm for NH and H₂O; ~4.5 ppm for CH₂; and ~5.6 ppm for NH₂. These signals also appear in the other systems as shown in Figs. 6a, b and c.

Increasing formaldehyde increases the CH₂ amplitude and decreases that of NH₂, confirming the synthesis reaction proposed. Thus, for a 1:1 U/F ratio the CH₂ amplitude is highest and the NH₂ lowest. A high U/F ratio leads to highly cross linked products with high molecular weight. The resulting low solubility diminishes the activity index and the slow-release properties. Since the aldehyde signal (~9–10 ppm) is absent and the amine signal is strong, mono-methyl urea and dimethyl urea preponderantly form, without residual formaldehyde.

HPLC chromatograms show that all the products elute simultaneously after 6 minutes, with a maximum at...
Figure 6: a) $^1$H-NMR spectra of urea-formaldehyde precondensate for U/F 1/1. b) $^1$H-NMR spectra of urea-formaldehyde precondensate for U/F 1.5/1. c) $^1$H-NMR spectra of urea-formaldehyde precondensate for U/F 2.4/1.
Figure 7: HPLC chromatograms of the methylolurea products a) before dilution; b) after 1:1 dilution with water.

Figure 8: FT-IR spectra of urea-formaldehyde precondensate for U/F a) 1/1; b) 1.5/1; c) 2.4/1.
6.4 min, suggesting a high reactivity and association tendency among components.

If the concentrated solution is diluted 1:1 with water the chromatogram shows at least three components with elution times of 6.0, 6.4, and 8.2 min, corresponding to mono-, di-, and trimethylolurea. Since MetaCarb 67 H is a metal sulfonated polystyrene resin which separates the compounds by ion-exchange, ligand-exchange, size- and ion-exclusion mechanisms, the order of elution is monomethylolurea (6.0 min), dimethylolurea (6.4 min), and trimethylolurea (8.2 min). This order is strongly correlated with both the molecular weights and the available hydroxyls which may interact with the stationary phase metal ion, a strong interaction increasing the retention time. Based on the peak areas a semi-quantitative estimate shows a decrease from mono- to trimethylolurea.

FT-IR shows a broad peak at 3344‒3336 cm⁻¹, shifting to lower frequency with increasing urea content, characteristic of polymeric hydroxyl [38] as well as NH and NH₂ stretching in urea. Other characteristic peaks were the C=O stretch at (1651 ± 2) cm⁻¹, the (1545 ± 3) cm⁻¹ amide NH₂ deformation combined with the C—N stretch, and the (1004 ± 1) cm⁻¹ C—O stretch in aliphatic chains, as
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in methylolurreas. The 1H-NMR result showing the absence of residual formaldehyde is confirmed by the absence of a 2650‒2745 cm⁻¹ aldehyde peak.

Thermal analysis characterises the thermal stability and thermal behavior. The first thermal event occurs at 150‒250°C, with a maximum at 220.4°C for NPK 100, 238.9°C for NPK 110 and NPK 111, and 210.2°C for NPK 211. In this temperature range the polymer urea residues decompose to ammonia, CO₂, and nitrogen oxides. The decomposition is gradual and depends on the degree of polycondensation. The next thermal event occurs at 250‒400°C, with different maxima for each system.

Carbonization of the polymer remnant takes place above 400°C, representing 10-15% of the initial mass. The residue at 700°C is lowest for NPK 100 (4.152%), followed by NPK 110 (17.42%), NPK 111 (29.78%) and NPK 211 (32.34%). Thermal stability beyond 50°C guarantees stability during transport, manipulation, and application.

Fig. 10 shows the effect of synthesis temperature, U/F ratio and pH on the activity index. Optimum values are shown. A temperature of around 60°C gives a good polycondensation and slow-release fertilizers. Below this temperature reaction initiation is delayed, while above 60°C fast polycondensation forms large blocks with low workability. The optimum U/F ratio of around 1.8 leads to almost spherical aggregates, easily separated by filtration. At lower ratios when formaldehyde predominates, the product is sticky and viscous, almost liquid at U/F equal to 0.3. At U/F ratios higher than 1.8, the product agglomerates in blocks due to rapid polycondensation. The highest AI occurs around pH 5. In more acidic conditions the polycondensation reaction is very fast, exothermic, and uncontrollable, which leads to block products; an almost neutral environment gives a very low reaction rate, an increased reaction time, and a low yield.

NPK 111 fertilizer leaching was compared with standard fertilizers. Nitrogen leaching was 44.6% for ammonium nitrate and 42.2% for urea. NPK 111 nitrogen leaching (37.56%) is reduced in comparison with these classic fertilizers. Nitrogen release in 64 days of intensive irrigation is comparable to that of commercially available slow-release fertilizers like Osmoform. P₂O₅ and K₂O also showed release rates substantially lower than the classic granular fertilizers ammonium phosphate and potassium chloride, as shown in Table 2.

Nutrient release kinetics (Fig. 11) were fitted to linear, power, and exponential equations [41-43], and also with a new type, the sigmoidal model (Table 3). The R² values show that the results are best fitted by different kinetic models. Nitrogen leaching is best described by an asymptotic exponential, potassium leaching seems to follow a linear model, while phosphorus leaching is best described by a sigmoidal model. Further studies will be conducted to determine the NPK nutrient leaching mechanisms.
Table 3: Kinetic equations, parameters and coefficients of determination.

| Model     | N                          | P                          | K                          |
|-----------|----------------------------|-----------------------------|----------------------------|
| Linear    | $q = 278.44 + 16.646 \cdot t$ | $q = -24.213 + 6.8202 \cdot t$ | $q = -10.433 + 8.4042 \cdot t$ |
|           | $R^2 = 0.9327$             | $R^2 = 0.9648$              | $R^2 = 0.9984$              |
| Power     | $q = 157.36 \cdot 0.0553^t$ | $q = 40.973 \cdot 0.7208^t$ | $q = 53.713 \cdot 0.7856^t$ |
| (Higuchi model) | $R^2 = 0.9741$             | $R^2 = 0.9921$              | $R^2 = 0.9975$              |
| Asymptotic exponential | $q = 1234.1 - 1212.2 \cdot 0.0553^t$ | -                           | -                           |
| Sigmoidal | $q = \frac{390.33}{1 + e^{-32.165 \cdot t}}$ | -                           | -                           |

4 Conclusions

Synthesis of encapsulated fertilizer in urea-formaldehyde matrices was optimized based on maximizing the activity index. Optimum temperature, pH, and urea/formaldehyde mass ratio were 60°C, pH = 5 and U/F = 1.8. All the products obtained had an AI greater than 40%, the minimum required for slow or controlled release fertilizers. These ensure more efficient nutrient uptake and allow decreased application without productivity loss as well as reducing pollution.

Leaching tests of NPK 111 suggest that this product can compete with commercially available fertilizers in providing longer nutrient availability than urea or ammonium nitrate. The activity index meets the specifications for “slow-release” fertilizers.

The parameters for nutrients’ leaching were determined by regression for four different kinetic models.

Acknowledgements: The authors gratefully acknowledge financial support provided by the grant “Fertilizers with slow/controlled release of active compounds, prepared by microencapsulation in environmental friendly polymeric structures (SLOREFERT)”, ERA NET-MANUNET Project co-financed by the Romanian Government through UEFISCDI, CF 7-057/2012 and Nucleus project P.N. 09.09.01.06/2014.

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