

Use of Polysulfone in Controlled-Release NPK Fertilizer Formulations

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Encapsulation of fertilizers in polymeric coatings is a method used to reduce fertilizer losses and to minimize environmental pollution. Polysulfone was used for a coating preparation for soluble NPK granular fertilizer in controlled-release fertilizer formulations. The coatings were formed by the phase inversion technique (wet method). The influence of the polymer concentration in the film-forming solution on the physical properties of the coatings was examined. The coating structure controls the diffusion of the elements from the interior of the fertilizer granule. It was experimentally confirmed that the use of polysulfone as a coating for a soluble fertilizer decreases the release rate of components. Moreover, the release rate of nutrients from coated granules decreases with the decrease of the coating porosity. In the case of coating with 38.5% porosity, prepared from 13.5% polymer solution after 5 h of test, 100% of NH_4^+ was released, whereas only 19.0% of NH_4^+ was released after 5 h for the coating with 11% porosity. In addition, coating of fertilizers leads to improvement of handling properties, and the crushing strength of all coated fertilizers was an average 40% higher than that for uncoated NPK fertilizer.

KEYWORDS: Polysulfone; coated fertilizer; controlled-release fertilizer; slow-release fertilizer

INTRODUCTION

Fertilizers are one of the most important products of the agrochemical industry. They are added to soil to release nutrients necessary for plant growth (1). However, the potential hazards of fertilizers to the environment have resulted in stringent limitations on their use. About half of the applied fertilizers, depending on the method of application and soil condition, is lost to the environment, which results in the contamination of water (2, 3). Use of conventional fertilizers may lead to concentration levels that are too high for effective action. A high concentration may produce undesirable side effects either in the target area, which could lead to crop damage, or in the surrounding environment (1).

One method to effectively reduce losses of nutrient components is the use of slow-release fertilizers. These fertilizers may be produced as chemically or physically prepared slow-release fertilizers (4).

The types of fertilizers and the factors affecting nutrient release in slow-release fertilizers are summarized in **Table 1** (4, 5).

In general, controlled-release fertilizers demonstrate many advantages over the conventional type, such as decreased rate of removal of the fertilizer from the soil by rain or irrigation water, sustained supply of minerals for a prolonged time,

increased efficiency of the fertilizer, lower frequency of application in accordance with normal crop requirement, minimized potential negative effects associated with overdosage, and reduced toxicity (1–3, 6–9).

The method of production of physically prepared slow-release fertilizers has been described in many papers (4, 6–9). A general idea is to provide granules of water-soluble fertilizers with an insoluble coating (4). Various materials were found to be suitable for coating purposes. The most important of these include wax and sulfur and organic polymers such as polyolefins (10), polyethylene (2, 3, 11), polystyrene (12), kraft pine lignin (5), and polyacrylamide (13).

In the case of controlled-release fertilizer (CRF) it is essential that the release rate be determined. To obtain the desired increase in plant growth, ~80% of active components should be released to the soil over a period of between 5 and 30 days. Typically, the time for the release of 100% of the fertilizer should not exceed ~60 days (14).

In the present work, polysulfone was used as a coating for soluble NPK granular fertilizer in CRF formulations. The main objective of our research was to obtain a very compact and minimally porous coating to prepare a slow-release fertilizer. The effects of the polymer concentrations in the film-forming solution on the coating structure were investigated. The results of dynamic tests, performed for the determination of the release rate of active components through single or double polymer coatings, are presented.

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Table 1. Types of Slow-Release Fertilizers

fertilizer type	examples	main factors affecting nutrients release	preparation
Low-Solubility Slow-Release Fertilizers			
magnesium ammonium phosphate isobutylidene-diurea (IBDU)	MagAmp	particle size, moisture	chemically chemically
	Woodace 20-4-11	particle size, hardness, moisture	
Organic Slow-Release Fertilizers			
urea formaldehyde	ureaform, nitroform	bacterial activity	chemically
Controlled-Release Fertilizers (Coated Fertilizers)			
sulfur-coated urea resin- and polymer-coated materials	SCU, Scotts 17-3-8	coating thickness, temperature, moisture	physically physically
	Osmocote 18-6-12, Nutricote 18-6-8	coating thickness, temperature	

MATERIALS AND METHODS

Preparation of Encapsulated Fertilizer. A series of fertilizers with different coatings were prepared at laboratory scale. The base fertilizer used was a water-soluble granular fertilizer NPK 6-20-30, produced by Chemical Plant "Police" S.A. X-ray diffraction analysis showed that the fertilizer contains NH_4Cl , KCl , and $\text{NH}_4\text{H}_2\text{PO}_4$. The diameter of the granules used was in the range from 2 to 5 mm.

Polysulfone (PSF 1700) was employed for the preparation of polymer coating. *N,N*-Dimethylformamide (DMF) was used as the polymer solvent. The concentrations of polymer in solutions were in the range from 10 to 20%. Coating solutions were prepared by dissolution of the solid polymer in DMF. The coatings were formed by the phase inversion technique using water as a precipitation bath (15, 16). The temperature of the precipitation bath was 293 K.

Before the coating process, the base NPK fertilizer was subjected to screening. Granules with a diameter of 3.15 mm were used for the coating. The granular fertilizer was successively added to polymer solution at 318 K. Granules covered with a polymer solution layer were subsequently dropped into a precipitation bath, where the gelation process takes place. The container with the precipitation bath was 0.4 m high. The falling time of the granules in the liquid was long enough to achieve the precipitation of the polymer solution. The time of the gelation was ~ 5 s. The coated granules were separated from the water after a maximum of 1 min and then dried in a dryer (377 K) to a constant mass. The double coating was achieved by immersion of the single-coated fertilizer into an adequate polymer solution followed by the precipitation in water and drying.

Physical Properties. The granules of coated fertilizer were cut, and mineral fertilizer was removed. Measurements of thickness and porosity of the prepared coating were performed, and scanning electron microscopy (SEM) images of the coatings were evaluated. Crushing strength of encapsulated fertilizers was also determined. The polymer coatings of granules were wetted before porosity measurements. The coating porosity (ϵ) was determined by using a gravimetric method, based on the differences in weight between the wet coating (surface drying with blotting paper) (w_w) and dry coating (dried in 377 K to a constant mass) (w_d) (17):

$$\epsilon = \frac{\frac{w_w - w_d}{\rho_w}}{\frac{w_w - w_d}{\rho_w} + \frac{w_d}{\rho_p}} \times 100\% \quad (1)$$

In eq 1 ρ_w and ρ_p are the densities of water and polymer, respectively.

Thickness was estimated using the micrometer screw. The morphology of coatings was examined using SEM. Coatings were frozen in liquid nitrogen, broken to obtain cross sections, and coated with gold for SEM observation. The mechanical properties of prepared coated fertilizers were determined by the measurements of crushing strength using an Automated Materials Testing System (INSTRON 4206). The crosshead speed was 1.00 mm/min.

Release Rate of Active Components in Water. The release rate of nutrients as a function of time for each of the products obtained was examined at room temperature. The dynamic tests were conducted for 5 h. One gram of each encapsulated fertilizer was placed in a beaker containing 50 mL of water. For five measurements five beakers were

Table 2. Description of the Composition of the Coating Forming Solution

fertilizer	composition of coating solution		viscosity (cP)	density (g/cm ³)
	polymer (%)	solvent (%)		
NPK-PSF10	10	90	53	0.936
NPK-PSF12.5	12.5	87.5	115	0.94
NPK-PSF13	13	87	132	0.941
NPK-PSF13.5	13.5	86.5	150	0.950
NPK-PSF14	14	86	167	0.952
NPK-PSF15	15	85	184	0.954
NPK-PSF16	16	84	352	0.957
NPK-PSF17	17	83	466	0.972
NPK-PSF18	18	82	675	0.992
NPK-PSF20	20	80	779	1.005

prepared at the same time. The mixtures were mechanically mixed. At regular intervals, every hour, samples of solution were taken in turn from the beakers, and the concentrations of particular ingredients were determined. Sample from which the solution was sampled was not used in further investigations. Therefore, the amount of sample for analysis does not influence the subsequent release process.

The static tests were conducted for 10 days, in aqueous medium. The fertilizer with polymeric coating was distributed in 10 beakers containing 50 mL of water each. The beakers were stored at room temperature. During experiments the samples of solution were taken from subsequent containers for measurements of concentrations of N, P, and K every 24 h.

The release rate was estimated as the amount of macroelement (in percent) released after time t in relation to the initial concentration of this component in the fertilizer. The phosphates content in a sample, calculated as P_2O_5 , was determined by using the colorimetric vanadate-molybdenum method. The intensity of color of the yellow complex formed was proportional to the phosphorus concentration. The NH_4^+ and K^+ contents were determined by using the potentiometric method (ORION 920A) using adequate ion selective electrodes.

The influence of temperature on the release rate of macroelements through the polymer coating was also determined. The tests were performed at temperatures of 285, 295, and 308 K in aqueous medium.

RESULTS AND DISCUSSION

Table 2 shows the composition of the coating-forming solutions and their densities and viscosities. The latter parameters of coating-forming solutions were estimated at 293 K. The density determined experimentally was in the range from 0.936 to 1.005 g/cm³. As expected, the density increases with an increase of polysulfone concentration in the film-forming solution. The viscosity of solutions was determined using the Hoesppler viscosimeter. The viscosity ranged from 53 cP for the solution with the lowest polymer concentration to 779 cP for the solution with the highest concentration. The viscosity of polymer solutions has an influence on the coating preparation. When the solution viscosities were either too low or too high (10 and 20% solution), the films that coated the granules were

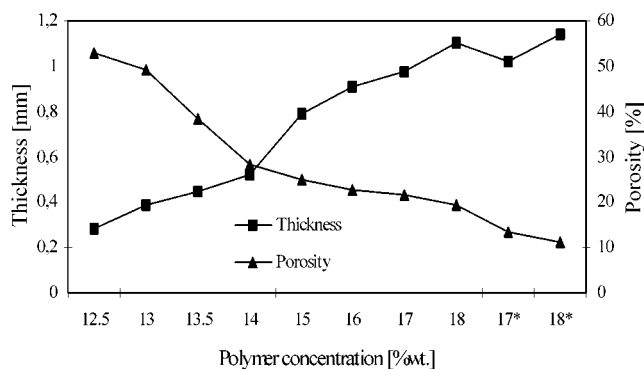


Figure 1. Coating thickness and porosity of single and double coatings (designated *), prepared from PSF solutions of different polymer concentrations.

incomplete or damaged. These defects can affect the physical properties of the fertilizers and the rate of release of the active elements. Thus, the fertilizers NPK-PSF10 and NPK-PSF20 coated by a 10 or 20% polymer solution were rejected as being defective. Moreover, the viscosity of the polymer solution influences the thickness of the polymer solution layer deposited on a fertilizer granule and, as a result, the structure of the prepared coating.

The porosity is a crucial parameter of the polymer coatings. This feature limits the diffusion of both water toward the fertilizer granule and nutrient flow outside the granule. The porosity was determined by a comparison of the weights of dry and wet coatings. The difference of weight corresponds to the amount of water, which can penetrate the coating. The influence of polymer concentrations in the film-forming solutions on the porosity of prepared coatings is shown in **Figure 1**. The porosity was in the range from 53.0 to 19.4% for a single coating. The coatings formed from a solution with a higher PSF concentration exhibited a lower porosity. This reduction in porosity is associated with the precipitation rate of the polymer from a casting solution upon immersion in the precipitation bath. In the first step a dense skin layer is formed that acts as a barrier for diffusion of the coagulation medium inward and of the solvent out from the casting solution. The rate of solvent–water exchange is slower in the case of solutions with a higher polymer concentration. This resulted in a denser and minimally porous coating structure. During the subsequent coating of previously coated granules of fertilizer, the first layer was slightly dissolved. The SEM images reveal that for double coating there is no border between the first and second layers. Moreover, the subsequent coating repairs any defects of the first polymer layer. As a consequence, the porosity of the double coating was significantly lower than that for the single coating. The porosity of double coatings (fertilizers denoted *) prepared from 17 and 18% solutions decreased ~8%; thus, the double coatings have porosities of 13.4 and 11.0%, respectively (**Figure 1**).

The average thickness of fertilizer coatings measured by the micrometer screw is presented in **Figure 1**. This is an average from 10 measurements. The results demonstrate that the thickness of coatings is influenced by the polymer concentration in casting solutions. However, the thickness varies insignificantly in the case of double coating. The thickness of double coatings increased only ~4%, although its weight was nearly 2 times higher. This is associated with the fact that during the subsequent coating, the first layer is slightly dissolved. The double coating is compact and has a low porosity.

Crushing strength is a measure of the resistance of granules to deformation or fracture under pressure. This is a very

Table 3. Crushing Strength of Prepared Fertilizers

fertilizer	crushing strength (kg/grain)	standard deviation
NPK	4.3	0.77
NPK-PSF13.5	5.9	0.63
NPK-PSF16	6.2	0.92
NPK-PSF18	6.3	1.05
NPK-PSF18*	9.4	1.31

important feature for handling and bag storage. Low crushing strength causes the fertilizer to be mechanically unstable. The crushing strength was measured by applying pressure to individual prills. The magnitude of pressure exerted on the fertilizer granule was continuously increased until the destruction of the granule was observed. This maximum load value was considered to be the crushing strength. As presented in **Table 3** (average from 10 measurements), the crushing strength of all coated fertilizers was higher than that of uncoated NPK fertilizer. The crushing strength insignificantly increased with the concentration of polymer in the film-forming solution. A significant difference was observed when the single- and double-coated fertilizers were compared. For single-coated fertilizer NPK-PSF18 the crushing strength was 6.3 kg/grain, and for double-coated NPK-PSF18* the crushing strength was 9.4 kg/grain. The difference was caused by the more compact structure of the double coating.

The microphotographs of the fertilizer coatings were made to determine their structure. As can be seen in **Figure 2**, the prepared coatings are asymmetric with a thin top skin layer, which is ~2 μm thick. Its structure has a lower porosity and is more compact in comparison with the porous structure below. The skin layer acts as a barrier for mass transfer and hence reduces the rate of water diffusion into the granules and the diffusion of ingredients outside the granule. Under the skin layer is a spongy base layer, comprising 99% of all the coating thickness. The bottom spongy layer has the macroporous structure of a honeycomb with a small amount of large pores. The skin determines the transport role, due to its structure. The sublayer imparts a mechanical resistance to the coating, but the thicker the sublayer, the longer the diffusion length of nutrients. As a consequence, the release rate of macronutrients from coated fertilizer is decreased.

We assumed that the mechanism of nutrient release from coated granules of fertilizer is the same as presented in **Figure 3** (18). In the first stage (A), water penetrates the porous coating. Then the nutrients are successively dissolved in the solution (B) and thereafter diffuse through the coating (C). The coating consists a barrier for transport of encapsulated nutrients. The release rate of the nutrients through polymer coating is also limited by a rate of the base fertilizer solubility.

The dynamic tests were performed for assessment of the release rates of the active components through polymer coating. The release rate is a function of the coating structure, and it can be controlled by the thickness and porosity of the coating. **Figure 4** shows the percentages of N, P, and K released in the tests. The release rates of macroelements from fertilizers NPK-PSF12.5 and NPK-PSF13 are not presented in the diagram because they were rapidly released. A high rate of components release in the case of these fertilizers suggests the presence of large pinholes and imperfections in the coating film.

The water initially diffuses into the coated granule during the lag phase. Very soon a saturated solution of the fertilizer is created within the granule. Thus, at sink conditions the driving force for the mass transfer of nutrients from the core to the

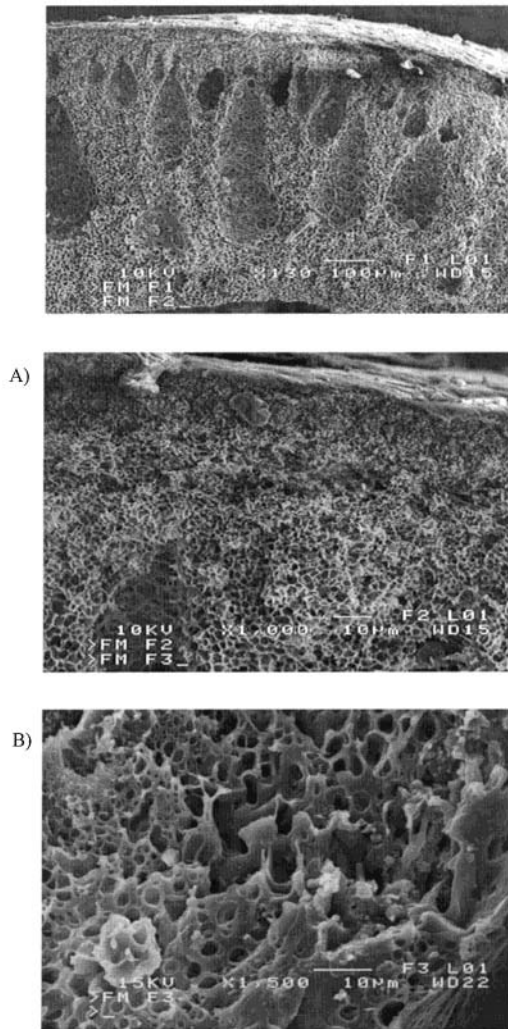


Figure 2. SEM of cross section of double coating prepared from 18 wt % of PSF solution: (A) top layer; (B) bottom layer.

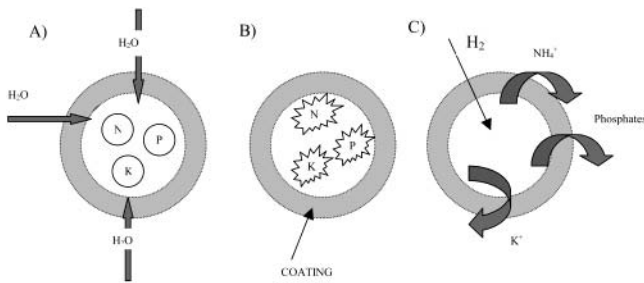


Figure 3. Mechanism of nutrient release from coated granule of fertilizer. surroundings will be a constant concentration difference: the saturation concentration minus the surrounding concentration. This results in a constant zero-order release that can be observed in **Figure 4**. When the core is starting to be depleted of nutrients, the concentration in the core decreases and subsequently the release rate will be slower, which is shown by the declining curve for the preparations with the lowest mass transfer resistance. However, the presented results are valid only for the water system used, and the dynamic test of nutrient release from coated granules is designed for a comparison of the efficiency of different CRFs. The structure of the prepared coating will be crucial to the release of the nutrients from a coated granule.

As can be seen (**Figure 4**), the release rate of nutrients from coated granules decreases when the polymer concentration in

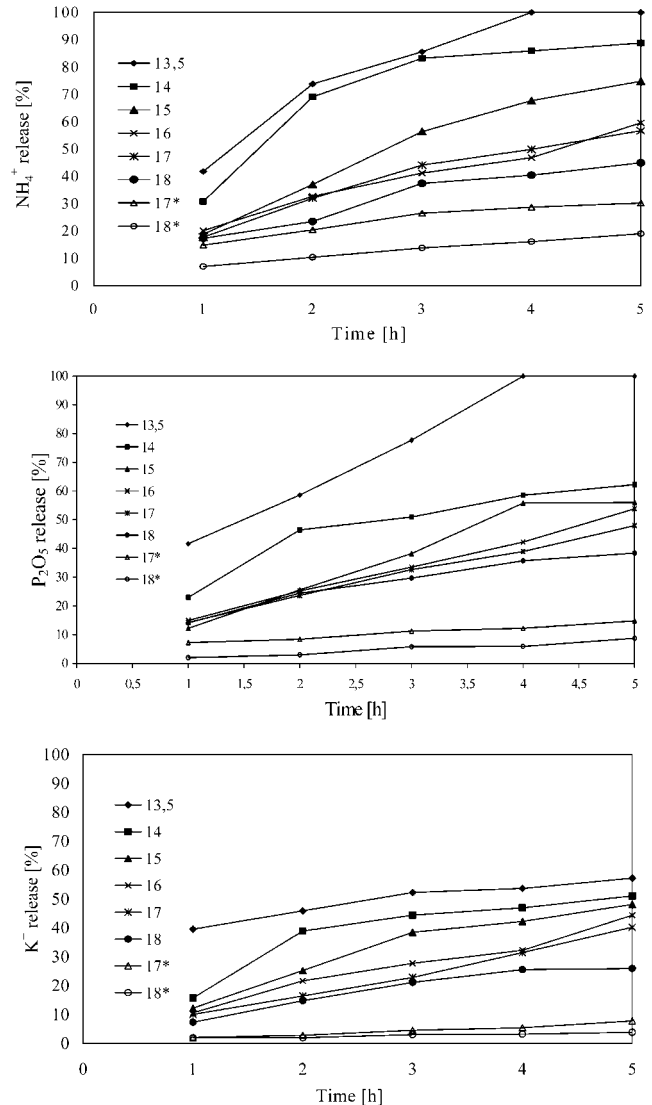


Figure 4. Nutrient release in water as a function of time at room temperature for NPK fertilizers with different coatings (dynamic tests).

the coat-forming solution is higher. The ingredients from fertilizer NPK-PSF13.5 were released most rapidly: 100% of P_2O_5 , 100% of NH_4^+ , and 56.3% of K^+ were released after 4 h of test. It was influenced by the high porosity of the coating (**Figure 1**) and the thin skin layer. The ingredients from sample NPK-PSF18 were released significantly more slowly. The coating of this fertilizer was prepared from a solution of polymer, where the polymer concentration was higher by 4.5% in comparison to that used for NPK-PSF13.5. In this case after 5 h of test 44.9% of NH_4^+ , 38.4% of P_2O_5 , and 25.9% of K^+ were released (**Figure 4**). Thus, an increase of the polymer concentration in the film-forming solution up to 18% causes the decrease of the release rate of components by ~50–60%. The coatings formed from solution with a higher polysulfone concentration exhibit a lower porosity. Lower porosity of the coating and denser skin layer decreases the rate of their release. **Figure 5** shows the comparison of the amounts of NH_4^+ released after 5 h from corresponding fertilizers and their coating porosities.

Moreover, the coatings prepared from PSF act as selective barriers, and the components from the granule were released with at different rates. The results shown in **Figure 4** demonstrate that the NH_4^+ ions were released most rapidly, whereas the release of K^+ ions was the slowest. A comparison of the

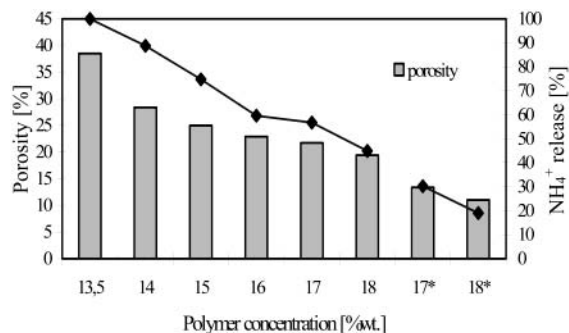


Figure 5. Composition of NH₄⁺ released after 5 h from the fertilizers and their coatings porosity.

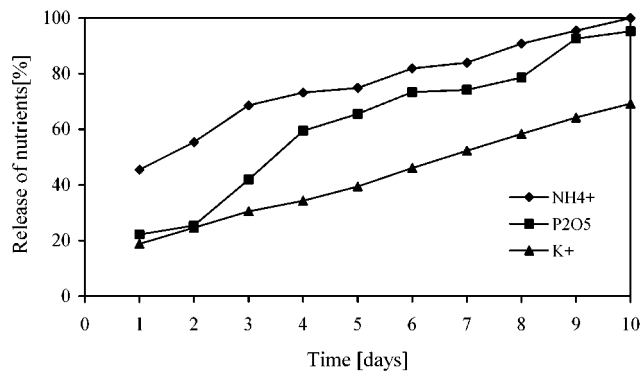


Figure 6. Nutrient release in water from granules of fertilizer twice coated with 18% polymer solution as a function of time (static tests).

diffusion coefficients, calculated from the Stokes equation (19) (diffusion coefficient of NH₄⁺ was 9.77×10^{-10} m²/s, that of K⁺ was 8.14×10^{-10} m²/s, and that of H₂PO₄⁻ was 5.43×10^{-10} m²/s), indicates that the release rate of ions should be in the following order: NH₄⁺ > K⁺ > H₂PO₄⁻. The obtained results demonstrate that ions are released in a quite different order, that is, NH₄⁺ > H₂PO₄⁻ > K⁺. These differences can be caused by the interactions between ions, which was not taken into account in the calculation of diffusion coefficients (diffusion coefficients were calculated for single ions and for infinitely diluted solution). It is also possible that the ions are hindered in different ways by the polymer coating.

The double coating of granules caused the slowest release of ingredients. In the case of sample NPK-PSF18* (double coating prepared from 18% polymer solution) after 5 h, 19.0% of NH₄⁺, 8.7% of P₂O₅, and 3.8% of K⁺ were released. A decline of the release rate was caused by the more compact structure of this coating and 2 times lower porosity of the double coating in comparison with that for the single coating (Figures 1 and 4).

The static tests were performed for sample NPK-PSF18*, because in this case the release of macroelements (in dynamic tests) was the slowest. Figure 6 shows the relationship between the time of the test and the released amount of nutrients. As can be seen after 10 days of test, 100% of NH₄⁺, 95% of P₂O₅, and 69% of K⁺ were released. The time of NPK release is within the recommended time (14), although the static tests were made in water. It can be suspected that the time of component release in soil will be much longer.

The influence of temperature on the release rate of macroelements through the polymer coating is presented in Figure 7. The tests were performed using NPK-PSF17*. This is a double-coated fertilizer, the coatings of which were prepared from 17% polymer solution. The process temperatures were 285, 295, and 308 K. The results indicate that the temperature has a

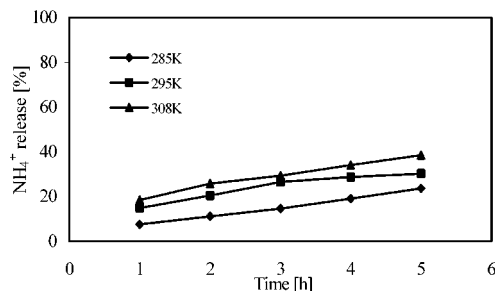


Figure 7. Influence of temperature on the release of NH₄⁺ through double coating prepared from 17% polymer solution.

significant influence on the release of N, P, and K ions. The dependence of the dissolution rate of the encapsulated material on the temperature is mainly due to the increased solubility of the base fertilizer and a higher diffusion rate as the temperature increases. When the test was finished (after 5 h), 23.7% of NH₄⁺, 8.3% of P₂O₅, and 3.51% of K⁺ at 285 K were released. In the case of the test performed at the temperature of 308 K, after 5 h, 38.5% NH₄⁺, 18.4% P₂O₅, and 14.6% K⁺ were released (Figure 7).

It was observed that the use of polysulfone as a coating for soluble NPK granular fertilizer significantly decreases the release rate of components. The dynamic tests, performed in the same conditions but for uncoated fertilizer, showed that this fertilizer was dissolved after 11 min (at 285 K), 9 min (at 295 K), and 5 min (at 308 K) of test. For comparison, in the case of fertilizer NPK-PSF18* after 5 h of test, only 7% of components had been released.

CONCLUSIONS

- (1) The use of polysulfone as a coating for soluble NPK granular fertilizer significantly decreases the release rate of components.
- (2) The concentration of polysulfone in the film-forming solution influences the coating structure.
- (3) The release rate of NPK from coated granules decreases with a decrease of the coating porosity.
- (4) The increase of the number of polymer layers forming the coating causes a decrease of the release rate of macroelements, due to a denser structure.
- (5) The coated fertilizers have a higher crushing strength in comparison with uncoated fertilizer.
- (6) The temperature affected the release rate of ingredients from encapsulated fertilizer. The increase of temperature caused an increase in the release rate of NPK.

LITERATURE CITED

- (1) Akelah, A. Novel utilizations of conventional agrochemicals by controlled release formulations. *Mater. Sci. Eng.* **1996**, *C4*, 83–98.
- (2) Salman Omar, A. Polyethylene-coated urea. 1. Improved storage and handling properties. *Ind. Eng. Chem. Res.* **1989**, *28*, 630–632.
- (3) Salman Omar, A.; Hovakeemian, J.; Khraishi, N. Polyethylene-coated urea. 2. Urea release as affected by coating material, soil type and temperature. *Ind. Eng. Chem. Res.* **1989**, *28*, 633–638.
- (4) Pipko, G. Method for manufacture of slow-release fertilizers. EP 0276179, 1988.
- (5) Cabrera, R. I. Let the nutrients flow slowly. *Am. Nurseryman* **1997**, *3*, 32–37.

- (6) El-Refaie, K.; Sakran, Al. A. Controlled release formulations of agrochemicals from calcium alginate. *Ind. Eng. Chem. Res.* **1996**, *35*, 3726–3729.
- (7) Byung-Su, K.; Young-Sang, C.; Hyun-Ku, H. Controlled release of urea from rosin-coated fertilizer particles. *Ind. Eng. Chem. Res.* **1996**, *35*, 250–257.
- (8) Heulaly, F. M.; Abdel-Bary, E. M.; Sarhan, A. A.; Abdel-Razik, H. H. Minimalization of water pollution and environmental problems via controlled release styrene butadiene rubber formulations containing ammonium nitrate. *Plast., Rubber Compos. Process. Appl.* **1993**, *19*, 111–115.
- (9) Al-Zahrani, S. M. Utilization of polyethylene and paraffin waxes as controlled delivery systems for different fertilizers. *Ind. Eng. Chem. Res.* **2000**, *39*, 367–371.
- (10) Kosuge, N.; Tobataku, K. Coated granular fertilizers. EP 030331, 1989.
- (11) Posey, T.; Hester, R. D. Developing a biodegradable film for controlled release of fertilizer. *Plastics Engineering* **1994**, *1*, 19–21.
- (12) Garcia, M. C.; Diez, J. A.; Vallejo, A.; Garcia, L.; Cartagena, M. C. Use of kraft pine lignin in controlled-release fertilizer formulations. *Ind. Eng. Chem. Res.* **1996**, *35*, 245–249.
- (13) Rajsekharan, A. J.; Pillai, V. N. Membrane-encapsulated controlled-release urea fertilizers based on acrylamide copolymers. *J. Appl. Polym. Sci.* **1996**, *60*, 2347–2351.
- (14) Pauly, D.; Nyborg, M.; Solberg, E. High efficiency controlled release phosphate-based fertilizer. EP 0731067, 1996.
- (15) Strathmann, H.; Kock, K.; Amar, P. The formation mechanism of asymmetric membranes. *Desalination* **1975**, *16*, 179–203.
- (16) Mulder, M. *Basic Principles of Membrane Technology*; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1991.
- (17) Tomaszewska, M. *Membrane Distillation*; Monography; Prace Naukowe Politechniki Szczecińskiej: Szczecin, Poland, 1996 (in Polish).
- (18) Thomaschewski, D. Fertilizers for future. *Fert. Int.* **1998**, *366*, 73–75.
- (19) Koryta, J. *Electrochemistry*; PWN: Warszawa, Poland, 1980 (in Polish).

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