Application aqueous polymer dispersions for encapsulation of granular fertilizers

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Introduction

Fertilization is an important factor influencing the growth rate and quality of plants, but also environmental pollution. There is a tendency to produce these fertilizers, which would allow improving efficiency of fertilizer while reducing the applied doses. One possibility is to use a fertilizer with a slow, controlled release of nutrients. Compound fertilizers with extended activities are produced in the form of granules. Their characteristic feature is the gradual release of nutrients by covering the granules of fertilizer coating [1÷3]. The materials used for coating fertilizer granules are, sulfur, waxes and polymers [4, 5]. The permeability of the coating is related both to the type of material used for encapsulation, and with the presence of additives, especially inorganic (silt, clay) and also received the coating process. The rate of release of ingredients can be adjusted shell thickness and porosity [6÷8]. Polymer coating much better suited to control the rate of release of fertilizer components, but the technology of polymer-coated fertilizers (PCF) are expensive compared to other encapsulation technologies fertilizers.

The aim was to obtain granular, compound fertilizer prolonged time of action, intended to trees and shrubs with the use of aqueous dispersions of polymer selected as the polymer coatings.

Experimental

To obtain a granular compound fertilizer raw materials used in Table 1 the ratio of at 7, 8:5, 2:5, 1:3,9 NPKMg.

Table 1

The components used to obtain fertilizer

No.	Component	Content, %
1	Ammonium sulfate	14.91
2	Ammonium phosphate	25.77
3	Potassium sulphate	12.27
4	Magnesium sulphate monohydrate	25.43
5	Bentonite	11.56
6	Calcium sulphate	10.06

Granulation liquid (Tab. 2) used in the granulation step was water with the addition of chelates, acting as micronutrients. In addition, the composition of the granulating liquid dye entered for defining the application of fertilizer.

Table 2

Raw materials included in the granulating liquid

No.	Component	Content, %
1	Water	93
2	A solution of chelate	6
3	Dye	1

Assuming that the polymer coating of the fertilizer should be characterized by the lowest possible environmental impact, the pellets were used for encapsulation 3 aqueous polymer dispersions:

A – acrylic-alkyd
B – aliphatic polyurethane
C – nitrocellulose

Table 3

Summary of physical properties of polymer dispersions investigated

	Dispersion A	Dispersion B	Dispersion C
Density, g/cm^3	1.22	1.03	1.02
Dry matter, %	53.61	17.22	15.18

Methodology

Granulation

Constituents of agglomerated mixed fertilizer granulation method for non-pressure in the granulator. The resulting granules were placed in containers and dried at room conditions in order to better merge the components of the granules. Then it was separated into fractions on sieves. For the coating of granules allocated to the size of 3.15 - 4.0 mm. Pellets coated with an additional surface-bentonite due to its protective properties against water and dirt.

Coating granules

Fertilizer coating process was carried out in the disc granulator. The emulsion coating metered using hand sprayer. The amount of liquid that was consumed to be administered was based on the difference in weight before and after dispensing coating. After completion of coating, granules were placed on a tray, weighed and placed in a climate cabinet for 24 hours at 50°C.

The sample was dried granulate solubility test, and the remaining amount of material subjected to the next stage of the coating. Granules coated with dispersions six times, each time taking a sample for testing dissolution rate.

Dissolution rate test

The dissolution rate of the resulting manure was determined by conductometric measuring the electrical conductivity of the resulting solution. The process of dissolution rate was studied using the conductivity type of business Elmetron CC502. Before starting to measure the dissolution rate was determined flow rate of distilled water through the system. Study the dissolution rate of fertilizer consisted of placing a sample tested at 10 fertilizer granules on a sieve mounted on a teflon column, through which flowed a constant rate of distilled water. The column was mounted in such a way that the water level in the system was at the same height as the outlet opening in the probe measurement. This represented a guarantee of the same initial conditions for each measurement. Measurement of conductivity of the filtrate was initiated when the sample placed in a sieve, while including the automatic registration of results on the computer which was connected to the conductometer. The result of the flow through a column of distilled water was dissolving fertilizer. The resulting solution flow conductivity cell connected to allow the registration of the conductivity changes in time. The filtrate was collected in a beaker placed under the probe. The trial was conducted over a period of one hour, and the coefficient of conductivity followed the reading every 30 seconds. After that time, the beaker was withdrawn from the filtrate. The remaining undissolved fertilizer was transferred to a second beaker, and rinsed with distilled water strainer. The resulting filtrate and the residue undissolved fertilizer was weighed on an analytical balance, then placed in an oven for 24 hours at 110°C and dried to constant weight. On this basis, calculate the amount of the solute and the mass loss of pellets.

Results and their treatment

When calculating the thickness *s* of the coating polymer, assumed ideal sphericity of pellets. It was also assumed that the polymer covers the entire surface of the pellets, and a sheath is composed of the polymer-free water in the drying process. The equations allowing the polymer coating thickness determined:

$$r_{n+p} = \sqrt[3]{\frac{3 \cdot V_{n+p}}{4 \pi}} \quad (1)$$

where:
r_{n+p} – radius of the granules with a polymer coating, mm
V_{n+p} – the volume of the granules and the polymer coating, mm^3

$$d_{n+p} = 2 \cdot r_{n+p} \quad (2)$$

$$d_p = d_{n+p} - d_{śr} \quad (3)$$

$$s = \frac{d_p}{2} \quad (4)$$

where:
d_p – the diameter of the polymer coating, mm
d_{n+p} – diameter of the granules with a polymer coating, mm
s – thickness of the polymer coating covering the pellet, mm.

Table 4

Shows the results of calculations of polymer content in the pellet and the thickness of the coating

Number of coating	Dispersion A		Dispersion B		Dispersion C	
	Polymer content in the pellet, %	The polymer coating thickness, μm	Polymer content in the pellet, %	The polymer coating thickness, μm	Polymer content in the pellet, %	The polymer coating thickness, μm
1	15.91	129.434	4.80	46.852	0.9961	11.384
2	19.62	164.238	11.92	121.713	1.3413	15.409
3	21.27	179.859	14.63	150.992	1.6663	19.224
4	23.06	198.512	14.77	152.494	1.9785	22.829
5	23.48	202.760	14.87	153.620	2.2576	26.067
6	23.88	206.854	14.93	154.266	2.5651	29.708

The dissolution rate of pellets

Dependence of dissolution rate of polymer-coated pellets was defined as the ratio of weight of the granules dissolved in water flowing through the column until the dissolution:

$$Q_r = \frac{m}{\tau} \quad (5)$$

Ratio as a function of slow dissolution of the polymer beads contained in the participation expressed by mass, was obtained by introducing the dissolution rate of pellets (Tab. 5):

$$z = \frac{Q_{r_0}}{Q_{r_i}} \quad (6)$$

where:
m - mass of fertilizer dissolved in the filtrate, kg
τ - dissolution time, s
Q_{r_0} - the dissolution rate of uncoated fertilizer granules, kg/s
Q_{r_i} - rate of dissolution of the granules after the coating dispersion and polymer, kg/s

Table 5

Results of determination of dissolution rate in the function of dissolution fertilizer

Number of coating	Disperion A		Disperion B		Disperion C	
	Indicator of slowing down the dissolution rate, z	The % of dissolved fertilizer	Indicator of slowing down the dissolution rate, z	The % of dissolved fertilizer	Indicator of slowing down the dissolution rate, z	The % of dissolved fertilizer
0	1.00	49.95	1.0	49.13	1.0000	49.95
1	23.00	1.82	2.6	17.42	1.3855	26.79
2	115.00	0.34	23.5	2.56	1.6084	27.98
3	230.00	0.16	77.8	0.76	5.6098	11.95
4	8.21	4.70	308.3	0.19	4.3396	11.13
5	115.00	0.34	334.0	0.18	5.1111	9.85
6	230.00	0.18	355.8	0.17	4.6000	9.84

On the basis of the results derived equations describing the functions:
- dependence on the dissolution rate of fertilizer as a function of polymer content:

$$Q_r = a \cdot e^{b x_p} \quad (7)$$

- rate slowed down depending on the dissolution of fertilizer granules as a function of polymer content:

$$z = a \cdot e^{b x_p} \quad (8)$$

- dependence on the percentage of dissolved fertilizer as a function of polymer content in the pellet:

$$Q_\tau = a \cdot e^{b x_p} \quad (9)$$

The coefficients of these equations were calculated by linear regression.

In the initial period of measurement, conductivity followed the rapid growth and after reaching the maximum value followed a mild decline. This period of decline in the value of conductivity can be described similar to the dependence of the exponential function with respect to the measurement time. Figure 1 shows an example of changes in conductivity of the filtrate from the dissolution of the granules since the dispersion process for C, depending on the polymer content.

Analysis of the curves in Figure 1 shows that after peaking can be modified to describe the relationship:

$$\frac{\kappa_V}{\tau} = a \cdot e^{b \tau} \quad (10)$$

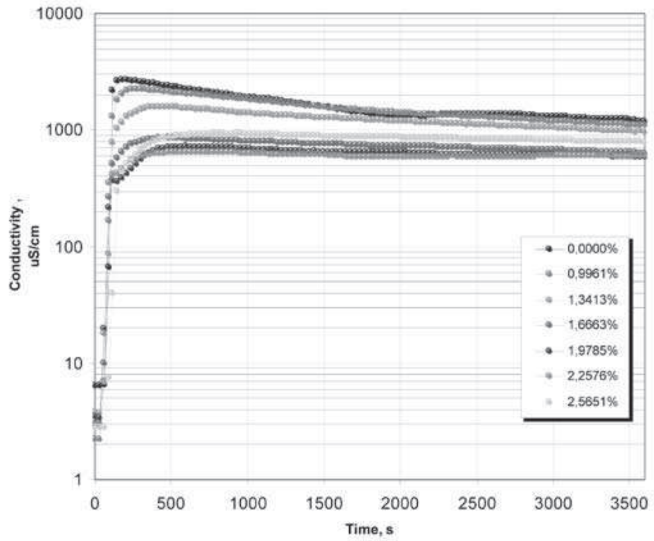

Fig. 1. Changes in the filtrate conductivity κ as a function of polymer content at the time of dissolution of pellets coated dispersion C

The coefficient *a* of equation (10) is a function of polymer content in the pellet, while some differences in the values of coefficient *b* are probably due to error indications.

Table 6

The coefficients *a* and *b* of equation (10) determined by regression

	Number of coating					
	1	2	3	4	5	6
Dispersion A						
Polymer content, %	15.91	19.62	21.27	23.06	23.48	23.88
a	420.66	368.98	145.84	5.41	8.01	7.42
b	-1.150	-1.322	-1.297	-0.957	-1.039	-1.023
R^2, %	99.81	99.43	98.66	98.87	98.96	99.37
Dispersion B						
Polymer content, %	4.80	11.92	14.63	14.77	14.87	14.93
A	$4.46 \cdot 10^{-11}$	675.82	42.36	72.73	97.04	199.72
B	3.319	-1.155	-1.277	-1.336	-1.403	-1.511
R^2, %	96.91	96.33	99.51	99.72	98.69	98.82
Dispersion C						
Polymer content, %	0.9961	1.3413	1.6663	1.9785	2.26	2.57
A	13897.78	6733.47	2837.65	1925.74	1152.41	1400.09
B	-1.319	-1.247	-1.150	-1.116	-1.047	-1.116
R^2, %	99.90	99.95	99.97	99.99	99.93	99.98

The equation changes in conductivity as a function of proper time of dissolution and polymer content in the granules, for each dispersion is shown below:

- dispersion A:

$$\frac{\kappa_V}{\tau} = \left(1419.5 - 59.428 \cdot x_p\right) \tau^{-1.131} \quad (11)$$

- dispersion B:

$$\frac{\kappa_V}{\tau} = \left(2975.2 - 193.88 \cdot x_p\right) \tau^{-1.336} \quad (12)$$

- dispersion C:

$$\frac{\kappa_V}{\tau} = 13203 \cdot x_p^{-2.7067} \; \tau^{-1.166} \quad (13)$$

Conclusions

Analyzing the results obtained and the dissolution of coating granular fertilizer can draw the following conclusions:

1. Polymer content in the pellet increases with each successive coating, which is characterized by the percentage of polymer in the pellet (x_p).
2. Cover layer of polymer pellets significantly reduces the solubility of the fertilizers. Effect of polymer coating thickness on the dissolution rate of granules can be described by the general formula $Q_r = a \cdot e^{b x_p}$
3. Dependence of conductivity changes as a function of dissolution time and polymer content in the granules can be described by the formula . $\frac{\kappa_V}{\tau} = a\ \tau^{b}$.
4. Higher dry matter content of the emulsion causes a thicker coating significantly reduces the rate of dissolution of fertilizer granules as compared to the emulsion with a lower dry matter content. It also helps to reduce the number of layers of polymer coating and shortening the time of granules.

Literature

1. Domoradzki M., Korpal W., Weiner W.: *Otoczkowanie nasion buraka ćwikłowego preparatem Chitosan i zarodnikami grzybów Trichoderma viride i Phytium oligandrum.* CHEMIK 2008, **9,** 459-460.
2. Tzika M., Alexandridou S., Kiparissides C.: *Evaluation of the morphological and release characteristics of coated fertilizer granules produced in a Wurster fluidized bed.* Powder Technology 2003, **132,** 16– 24.
3. Denis C., Hemati M., Chulia D., Lanne J.-Y., Buisson B., Daste G., Elbaz F.: *A model of surface renewal with application to the coating of pharmaceutical tablets in rotary drums.* Powder Technology 2003, **130,** 174–180.
4. Tomaszewska M., Jarosiewicz A.: *Inteligentne nawozy.* CHEMIK 2006, **6,** 328-332.
5. Tomaszewska M., Jarosiewicz A.: *Polysulfone coating with starch addition in CRF formulation.* Desalination 2004, **163,** 247-253.
6. Koshino M.: *Fertilizer Technology and Use.* Soil Science Society 1971.
7. Bluin G.M., Rindt D.W., Moore O.E.: Journal of Agriculture and Food Chemistry 1971, **19,** 801–808.
8. Rindt D.W., Bluin G.M., Getsinger J.G.: Journal of Agriculture and Food Chemistry 1968, 1**6,** 773– 778.

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