*Polish Journal of Chemical Technology, 24, **3**, 14—18, 10.2478/pjct-2022-0017*

Innovative NPK Fertilizers based on Polyacrylamide and Polyvinyl Alcohol with Controlled Release of Nutrients

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The aim of the present work was the preparation and properties evaluation of two innovative fertilizers based on multicomponent polymers characterized by a controlled release of nutrients. One method was based on a multicomponent liquid containing different amounts of microelements NPK 12-5-6 fertilizers with polyacrylamide hydrogel beads. The second method concerned the cross-linking of biodegradable polyvinyl alcohol with multicomponent NPK fertilizers. Polyacrylamide-based compositions with the highest amount of NPK salts as well as polyvinyl alcohol-based fertilizers in dense gel form, based on 60 phr crosslinking concentrate have shown optimal properties. Regardless of the type of fertilizers used, their components were released slowly. The obtained fertilizers were classified according to the kinetics of nutrient release. Fertilizers made from polyacrylamide based fertilizers have been classified into a group of controlled release fertilizers (CRF), while those made from biodegradable environmentally friendly polyvinyl alcohol have been defined as slow released fertilizers (SRF).

Keywords: polyacrylamide, fertilizers, polyvinyl alcohol, nutrients release

INTRODUCTION

Fertilizers can be classified as single-component, multi-component or microelement fertilizers[1] in solid (granulated) or liquid states. Uncontrolled release of nutrients over time can lead to groundwater pollution and over-fertilization of soils[2, 3]. The pro-ecological and economic aspects of fertilization have forced the agrochemicals market to produce slow-acting fertilizers[4]. Slow action fertilizers include agrochemicals SRF (Slow Release Fertilizers) and/or interchangeably used CRF (Controlled Release Fertilizers). The distinction between both forms is not entirely unambiguous because both groups of fertilizers have similar functionalities and ultimately have analogous functions for plants[4].

The use of SRF/CRF positively influences the equal supply of nutrients to plants, decreases the degree of water pollution, reduces the amount of applied agrochemicals and consequently reduces the cost of the crops by complete use of all nutrients and substances supplied to plants[5, 6]. According to the Association of American Plant Food Control Officials, the CRFs are coated products, whereas the SRFs are nitrous products decomposed by microorganisms. However, both terms are used interchangeably in various studies[7, 8].

Coated fertilizers (CRF) are produced by coating traditional fertilizers with super-absorbents, waxes, resins, as well as polymers and hydrogels[9]. The nutrients release mechanism of CRF fertilizers is to infiltrate the solvents into the coat and dissolve the mineral salts. Due to the solvent absorption, an increase in osmotic pressure is observed inside the coat, leading to the diffusion of organic matter in the soil and the supply of medium to the plants[10, 11]. The release of nutrients from SRF occurs place as a result of decomposition of fertilizer coating due to microbiological processes in the soil.

During the last century, we observed the development of the fertilizers market and the appearance of innovative forms of fertilizers, in particular those with controlled release, which aroused great interest. Gel and hydrogel fertilizers are also becoming increasingly popular and widely used[8, 12, 13].

With the aim of protecting the natural environment and human health, this study attempts to produce a new generation of fertilizers with an optimized composition and whose nutrients will be provided in an adjusted manner at the rate of their absorption by the plants.

MATERIALS

The following raw materials were used in the study:
– Liquid NPK 12-5-6 multi-component fertilizer with microelements from Chemical Plant „Siarkopol", Poland;
– polyacrylamide hydrogel beads with a specific surface of (S = 13,8 mm^2 ± 0,1) produced by Shandong Huadi Architechture Sci-Tech Company Ltd.
– polyvinyl alcohol as 4,5% water solution was purchased from Kemikals Gdynia, Poland.
Its molecular weight is 20000 g/mole and degree of hydrolysis 87%;
– sodium tetraborate in the form of 4% water solution from P.H. "STANLAB" Lublin – Boraks;
– universal soil from Nature Wokas, with a pH of 6,9.

PREPARATION OF FERTILIZERS

Two innovative fertilizers were prepared:
- polyacrylamide hydrogel beads based fertilizer
- fertilizer based on polyvinyl alcohol.

Preparation of polyacrylamide hydrogel beads based fertilizer

First, the NPK 12-5-6 liquid fertilizer was diluted with various amounts of water to obtain different aqueous solutions (I – 100%, II – 90%, III – 80%, IV – 70%, V – 60%, VI – 50%, VII – 40%, VIII – 30%, IX – 20%, X – 10%, XI – 8%, XII – 6%, XIII–XIV – 2%, XV – 0%). Then, 1 g of hydrogel beads was introduced into each of the prepared solutions and were left at room temperature until the specific surface area of the beads increased. Next, we determined the minimum immersion time of the beads in a solution with the fertilizer ensuring the highest degree of nutrients uptake by the beads until the dimensions of the beads are constant. Finally, the beads were removed from the solutions with 1 hour intervals and their diameter was measured according to formula (1). The amount of phosphorus and potassium was determined as well as the kinetics of their release from previously prepared hydrogel fertilizer beads. Fertilizers with the best nutrient release rate were selected. Pot tests were also carried out on selected hydrogel fertilizer beads with the best nutrient release rate. Six measurements were made for each data point.

Preparation of fertilizer with the use of polyvinyl alcohol

Three types of polyvinyl alcohol (PVA) crosslinkers were used in the study: a 4% aqueous solution of sodium tetraborate, NPK fertilizer (as a concentrate - without dilution with water or as a 50% aqueous solution) and a mixture of sodium tetraborate and NPK fertilizer (concentrate or its 50% solution).

First, a 4.5% aqueous PVA solution was prepared. Then, 10 g of the prepared polymer was placed in 50 ml beaker and mixed with various amounts of crosslinking agents. Obtained products were subjected to organoleptic evaluation and the amount of P and K was determined in both the single-phase gel products and the two-phase products. In the latter case, the gel and the separated liquid were quantified and the content of P and K determined. The amount and type of crosslinking agent were determined, which ensured the highest amount of NPK fertilizer introduced into the PVA. As with the polyacrylamide fertilizers, fertilizer beads containing the highest amount of nutrients in the PVA hydrogel were selected for the pot tests. Three measurements were carried out for the determination of K_2O and P_2O_5 content.

CHARACTERIZATION

Absorption and desorption in fertilizers based on polyacrylamide hydrogel beads

The study of the absorption and desorption of the fertilizer ingredients by the polyacrylamide hydrogel beads was evaluated at room temperature by the degree of their swelling after introduction into the liquid multi-component NPK 12-5-6 fertilizer. The degree of their shrinkage after removal from the soil was also determined. Absorption and desorption were also specified by the change of the hydrogel beads diameter calculated according to the following formula (1):
the degree of their shrinkage.

$$S = \pi \cdot d^2 \quad (1),$$

in which:
S – microcapsule specific surface, mm^2;
d – microcapsule diameter, mm.
six measurements were carried out for each data point.

Determinations of nitrogen, phosphorus and potassium in the fertilizers

The determination of phosphorus and potassium concerned directly the prepared fertilizers which were placed in the soil under conditions analogous to plant cultivation. The content of phosphorus and potassium was calculated on the basis of quantitative marking of the appearance of the above-mentioned elements in the form of K_2O and P_2O_5. The determination of phosphorus and potassium in the soil was carried out by the Egner-Riehm method by using calcium lactate[14]. Phosphorus and potassium were determined by colorimetric and atomic absorption methods, respectively. Nitrate was determined by the potentiometric method. Soil acidity determined by its pH value was determined by the potentiometric method, while soil salinity by the conductometric method[15]. The NPK nutrients were determined with the methods included in Annex IV of the Regulation (EC) No. 2003/2003 of the European Parliament and of the Council of October 13, 2003.

Pot tests

First, soil samples were taken and analyzed. Then a 50-liter pot was divided into three equal parts, separated by a polyethylene net and the selected fertilizers based on polyacrylamide or PVA were introduced.

The experiment was carried out for 3 weeks at a temperature of 20 ± 1 °C with soil moisture of 55% ± 5. During the tests, the fertilizer was removed from the pot sector every two days. The samples were then analyzed and K and P content were determined.

RESULTS AND DISCUSSION

Figure 1 shows the effect of fertilizer concentration and immersion time of polyacrylamide hydrogel beads on their dimensions. It can be noted that the introduction of polyacrylamide beads into the fertilizer concentrate (without dilution) and into its aqueous solutions led to an increase in their diameter. Moreover, the distinct change of the dimensions of polymer beads was related to the solution absorption process. Polyacrylamide absorbs the concentrate, the aqueous fertilizer solutions as well as water. Regardless of the concentration of the solutions, we can observe the fastest absorption process occurred up to 2 hours of experiment and slightly slower absorption between 2 and 6 hours. After 6 hours, the kinetics of liquid absorption by the beads was unchanged. From 6 to 12 hours, the diameter of the beads immersed in all the absorbents slightly increased, thus suggesting the thermodynamic equilibrium of the process.

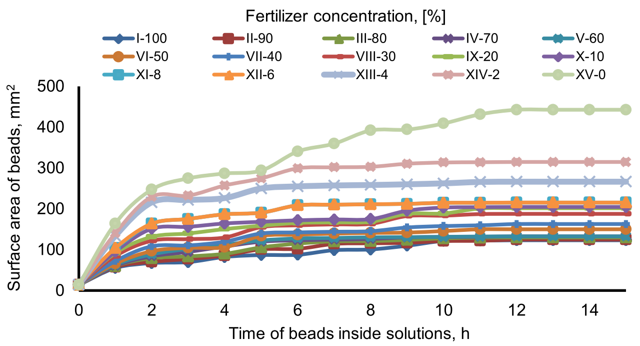

Figure 1. Effect of fertilizer concentration and immersion time on the dimensions of polyacrylamide hydrogel beads

Moreover, the beads remaining for more than 12 hours in the solutions did not affect the increase in the rate of liquid uptake by the polymer, as evidenced by the bead size values. The smallest changes in the diameter of the beads were recorded for the fertilizer obtained from polyacrylamide and 40% solution of NPK fertilizer (sample VII). It has been also found that the lower the concentration of fertilizer in the solution, the larger the diameter of the beads. Additionally, it was found that the immersion of polyacrylamide beads for at least 12 hours in an NPK fertilizer solution or its aqueous solution provides the maximum degree of absorption of the liquids. Hence, 12 hours were selected for the preparation of this type of fertilizer.

The variations in the dimensions of polyacrylamide beads removed from undiluted fertilizer (concentrate) and aqueous solutions are shown in Fig. 2. Obtained results revealed a notable decrease of the diameter of fertilizer beads. It was also noted that regardless of the concentration of fertilizers that was absorbed by the beads, the release rate of the fertilizer/fertilizer solution was unchanged. The reduction of the dimensions of the beads could be explained by the desorption of the integral fertilizer ingredients (i.e the fertilizers in the form of concentrate, its solutions or simply water) which were absorbed by the beads.

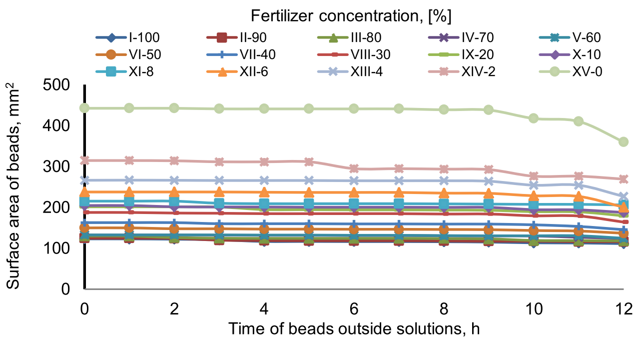

Figure 2. Effect of immersion time on the area of hydrogel beads removed from fertilizer NPK 12-5-6 solutions having different concentrations

A study was also carried out on the activity of fertilizer beads after their introduction into the soil (i.e after carrying out the so-called pot tests). We noticed almost identical activity from the fertilizer beads placed in soil and fertilizers tested outdoors (Fig. 2). Similarly to the previous results, it was found that regardless of the type of fertilizers tested, the diameter of the beads slowly decreased mainly due their placement in the soil.

The fertilizer beads obtained from NPK concentrate (sample I), its 40% solution (sample VII) and the NPK salt solution with the lowest concentration of 2% (sample XIV) were selected for three week pot tests. After their removal from the soil, an analysis was performed on the substrate with the fertilizers. The results are shown in Table 1.

Table 1. Soil characteristics with polyacrylamide beads

Sample designation	pH	Soil characteristics, [mg/l]				
		salinity NaCl	NO_3	P	K
Virgin ground	6,8	400	32	11	128
Fertilizer I	6,8	1400	400	287	1301
Fertilizer VII	6,8	1000	410	118	469
Fertilizer XIV	6,7	500	54	25	152

The results of the tests (Table 1) confirm the effect of the fertilizers used on the enrichment of the soil with elements N, P, K. The higher the salt concentration in the fertilizers, the more salt was desorbed into the soil. However, no effect of fertilizer application on soil acidity was noted. The soil pH before the experiment and after 3 weeks of fertilization remained unchanged.

The greatest soil enrichment with nutrients was obtained by using undiluted NPK fertilizer obtained from the fertilizer concentrate and designated by the symbol I. It was found that the lower the concentration of the NPK solution to prepare the fertilizer, the lower the increase in soil nutrients.

Due to the best effect of soil enrichment during the slow and steady release of nutrients from the fertilizer, it was established that the best obtained fertilizer is the new generation fertilizer obtained with a 12-hour absorption of NPK concentrate by the hydrogel polyacrylamide beads although its lack of biodegradability.

Table 2 shows the results of single phase and two phase polyvinyl alcohol (PVA) products with crosslinking agents. It can be noted that it is possible to crosslink PVA with NPK fertilizer both in the form of a concentrate or its 50% solution or by using their mixture with sodium tetraborate.

Obtained results showed that it is possible to crosslink the PVA mixture with sodium tetraborate and NPK fertilizer as a concentrate or its solution. It was confirmed that the concentration of the crosslinking agent determinates the form of the produced fertilizer. The use of NPK in the form of a solution whose concentration does not exceed 20 phr in PVA led to a homogeneous product in the form of a single phase gel product. However, the use of a crosslinking agent at a concentration greater than 20 phr resulted in the separation of the liquid from the initially formed gel of the fertilizer (gel and liquid). This

Table 2. Characterization of PVA cross-linking products with: fertilizer concentrate (K). 50% aqueous solution of fertilizer concentrate (50 K). sodium tetraborate (B) and average K_2O and P_2O_5 content in the resulting cross-linked samples

Sample symbol	PVA of cross-linking product	Cross-linking agent	Amount of crosslinking agent, [phr in PVA]			The content of elements, [%]			
						Liquid		Gel fertilizer bead	
			K	50K	B	K_2O	P_2O_5	K_2O	P_2O_5
1.	Gel	Mixture of 50% NPK solution with sodium tetraborate	0	10	20	0.50	0.60	92.19	87.75
2.	Gel in liquid	Mixture of NPK concentrate with sodium tetraborate	25	0	5	0.60	0.80	90.62	83.68
3.		Concentrate	30	0	0	0.80	0.80	87.50	83.68
4.			40	0	0	0.63	0.68	90.16	86.12
5.			60	0	0	0.62	0.58	90.31	88.16
6.			80	0	0	0.10	0.12	98.44	97.55
7.			100	0	0	0.00	0.08	100.00	98.37
8.			200	0	0	0.00	0.08	100.00	98.37
9.			300	0	0	0.00	0.08	100.00	98.37

may indicate that the micronutrients are not completely bound to the polymer.

It can be emphasized out that not only the introduction of the greatest amount of NPK salts into the hydrogel beads is important, but also the kinetics of the release of nutrients from the obtained fertilizers. Therefore, the results of the determination of P and K in the beads allowed the selection of the composition of the crosslinking agent. The amount of P and K elements was determined as K_2O and P_2O_5 in unreacted crosslinking agents.

It was found that for all fertilizers compositions, the PVA gel contained 90–100% of the amount of salt introduced in the NPK fertilizer. In the single phase product (sample 1, Table 2) and two phase products (samples 2–9, Table 2), almost 100% of K and P was bound. Based on the results of the analysis of PVA crosslinking products, the form of the crosslinking product should therefore not determine the composition of the fertilizer produced.

As shown in Fig. 3, in two phase PVA products crosslinked with fertilizer concentrate (samples 3–9, Table 2), the amount of nutrients increased with the amount of NPK salt used for crosslinking. The most advantageous solution seems to be gel fertilizer beads prepared with the use of the highest amounts of NPK concentrate used in the amount of 80, 100, 200, 300 phr (samples 6–9). The values of K and P amounts close to zero in the liquid separated from the gel and about 100% binding of nutrients could be used for the selection of samples for further research.

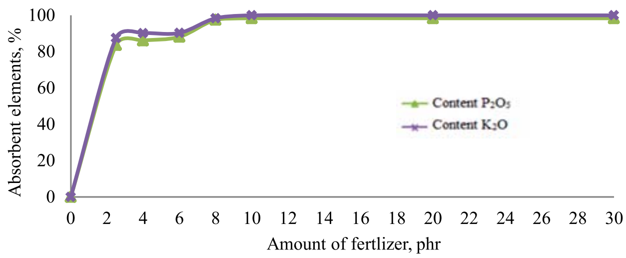

Figure 3. Effect of the fertilizer content on the amount of nutrients in the fertilizer beads

However, due to the consistency of the gel beads and the greatest amount of elements, the best fertilizers seem to be those with 60, 80 and 100 phr of concentrate (samples 5, 6 and 7). Therefore, these latter fertilizers were selected for pot tests. These tests made it possible to determine the kinetics of nutrient release, which is very important from the point of view of the fertilizer industry.

As mentioned above, biodegradable polyvinyl alcohol has a gel structure and hydrophilic nature, which may lead to the release of NPK fertilizers into water from crosslinked PVA. The release of fertilizer must be preceded by the absorption of water from the reaction system and the slow desorption of the solutions produced during the biodegradation of the PVA until the concentrations inside the fertilizer and soil are equal. Such phenomenon could lead to an increase in the weight of fertilizer weight in the soil. Therefore, fertilizer samples 5, 6 and 7 (Table 2) were selected and placed in the soil and the changes in the weight of the beads were determined.

As confirmed by various investigations, the water solubility of poly(vinyl alcohol) (PVA) is dependent on its molecular weight, the degree of crosslinking as well as the degree of hydrolysis[16–18]. It has been shown that the higher the molecular weight of the polymer, its degree of hydrolysis and crosslinking, the lower its solubility. Hassan et al.[19] demonstrated that the higher the solubility, the faster the biodegradation in the soil. For these reasons, the PVA with a relatively high molecular weight (20,000 g/mole) and a degree of hydrolysis of 87% connected with a large amount of hydroxyl groups was selected in this study.

It was also demonstrated that the rate of nutrient release is affected by the roughness of the surface of the fertilizer beads[10, 20, 21] as well as the eventual presence of micropores[20]. An increased surface roughness connected with reduced surface energy leads to efficient controlled release of fertilizers. However, obtained gel fertilizer beads had a smooth surface with imperceptible roughness, and consequently negligible effect on the efficiency of prepared fertilizers.

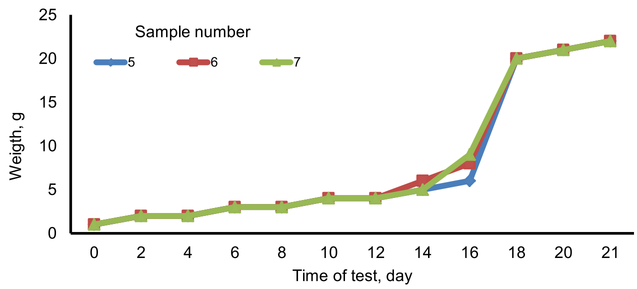

Figure 4. Variations of fertilizer weight during pot tests

From Figure 4, a slow increase in weight for all fertilizers was observed during the first 16 days of testing. However, the increase was more pronounced for the next 2 days, followed by stabilization. This suggests the correctness of the previously proposed mechanism for the release of nutrients, which should be confirmed by pot tests. It was also demonstrated that all tested hydrogel fertilizer beads underwent complete disintegration after 3 weeks in the ground. The results of the tests are presented in Table 3.

Table 3. Soil analysis after three weeks of fertilization with PVA based gel bead

Sample name	pH	Soil characteristics, [mg/l]			
		salinity NaCl	NO_3	P	K
Starting ground	6.9	300	4	28	97
5	6.5	1000	540	81	400
6	6.4	1100	540	89	360
7	6.3	1300	900	126	560

The results in Table 3 showed a distinct effect of fertilizer concentration on the amount of elements in the soil. The salinity increased and the content of N, P and K increased significantly in the soil, while soil pH decreased slightly with increasing amount of NPK concentrate in the fertilizer. Moreover, we can suggest that the absorption process of a polyvinyl alcohol based a fertilizer took place gradually until the complete disintegration of the polymer, enriching the soil with nutrients. The subsequent potential biodegradation of PVA is beneficial to the environment. In addition to the slow release of nutrients important for plants, it acts as the soil conditioner by improving its structure.

CONCLUSION

Two innovative multi-component fertilizers based on polyacrylamide and polyvinyl alcohol (PVA) with controlled release of nutrients have been successfully prepared and applied.

Absorption of the fertilizer solutions occurred regardless of the concentration of fertilizer solutions and the time spent by the polyacrylamide beads in the solutions. The longer the immersion time (up to 12 h) of the beads, the higher the degree of absorption. The NPK salts were bound with the gel polymer matrix whatever the form of crosslinked PVA (single phase: gel or two phase forms: gel in liquid). The optimal compositions were obtained with polyacrylamide fertilizers with the highest amount of NPK salts, prepared by the absorption of concentrate as well as PVA fertilizers in the form of dense gel, based on 60 phr crosslinking concentrate.

All innovative fertilizers based on polyacrylamide and PVA were characterized by slow, controlled release of nutrients. The polyacrylamide based fertilizers have been classified as controlled release fertilizers, whereas those prepared from environmentally friendly biodegradable polyvinyl alcohol have been defined as slow release fertilizers that enrich the substrate with nutrients.

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