# Innovative fully soluble NPK gel fertilizers based on biopolymers with controlled release of nutrients

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**Abstract.** The purpose of this work was to obtain and evaluate the properties of two innovative fertilizers based on multicomponent polymers, characterized by the controlled release of nutrients. One of the methods is based on the use of multicomponent liquid fertilizers containing different amounts of microelements NPK 15-10-50 with polyacrylamide hydrogel. The second method involves cross-linking biodegradable polyvinyl alcohol with multi-component NPK fertilizers. Keywords: macroelement, properties, fertilizers, polyvinyl alcohol, nutrient release.

## 1 Introduction

Fertilizers can be classified as single-component, multi-component or micronutrient fertilizers in solid (granular), liquid or gel states [1-4]. The uncontrolled release of nutrients over time can lead to groundwater contamination and overfertilization of soils. The pro-environmental and economic aspects of fertilization have forced the agrochemical market to produce slow-release fertilizers4. Sustained-release fertilizers include agrochemicals SRF (slow-release fertilizers) and/or interchangeably used CRF (controlled-release fertilizers). The distinction between both forms is not entirely clear, since both groups of fertilizers have similar functionalities and ultimately perform similar functions for plants.

The use of SRF/CRF has a positive effect on the uniform supply of nutrients to plants, reduces the degree of water pollution, reduces the amount of agrochemicals used and, therefore, reduces the cost of the crop due to the full use of all nutrients and substances supplied to the plants [5-8]. According to the American Plant Food Regulatory Association, CRFs are coated foods, while SRFs are nitrogenous foods that are biodegradable. However, both terms are used interchangeably in various studies.

Coated fertilizers (CRFs) are produced by coating traditional fertilizers with superabsorbents, waxes, resins, as well as polymers and hydrogels [9]. The mechanism of nutrient release by CRF fertilizers is the penetration of solvents into the layer and the dissolution of mineral salts. Due to the absorption of solvent within the coating, an increase in osmotic pressure is observed, which leads to the diffusion of organic matter into the soil

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and the supply of nutrient medium to plants. The release of nutrients from SRF occurs as a result of the decomposition of the fertilizer coating through microbiological processes in the soil.

Over the last century, we have seen the fertilizer market evolve and the emergence of innovative forms of fertilizer, particularly controlled release, which have generated a lot of interest. Gel and hydrogel fertilizers are also becoming increasingly popular and widely used [10].

To protect the environment and human health, this study attempts to create a new generation of fertilizers with optimized composition, in which nutrients will be provided in an adjusted manner depending on the rate of their absorption by plants.

## 2 Materials and methods

The following raw materials were used in the study:

– Multicomponent fertilizer NPK gel 15-10-50 with microelements from the chemical plant "YARA", Norway;

– polyacrylamide hydrogel granules with a specific surface area (S = 13.8 $mm^2$ ± 0.1) produced by Shandong Huadi Architecture Sci-Tech Company Ltd.

– Polyvinyl alcohol as a 4.5% aqueous solution was purchased from Chemicals in Gdynia, Poland.

Its molecular weight is 20,000 g/mol, and the degree of hydrolysis is 87%;

– sodium tetraborate in the form of a 4% aqueous solution from PH "STANLAB" Lublin – Borax;

– universal soil from Nature Wokas, with a pH 6.9.

Preparation of fertilizers:

Two innovative fertilizers were prepared:

– fertilizer based on polyacrylamide hydrogel beads

– fertilizer based on polyvinyl alcohol.

Preparation of fertilizer based on polyacrylamide hydrogel granules

First, liquid fertilizer NPK 12-5-6 was diluted with different 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 granules was added to each of the prepared solutions and left at room temperature until the specific surface area of the granules increased. We then determined the minimum immersion time to achieve maximum nutrient uptake by the pellets until pellet sizes became constant. Finally, the balls were removed from the solutions at intervals of 1 hour and their diameter was measured following formula (1).

The amount of phosphorus and potassium, as well as the kinetics of their release from pre-prepared hydrogel fertilizer granules, was determined. Fertilizers with the best nutrient release rates were selected. Tests were also carried out in pots with selected hydrogel fertilizer granules with the best nutrient release rates. Six measurements were taken for each data point.

## 3 Preparing fertilizer using 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 solution of PVA was prepared. Then, 10 g of the prepared polymer was placed in a 50 ml beaker and mixed with varying amounts of cross-linking agents. The resulting products were subjected to organoleptic evaluation and the amount of P and K was determined in both single-phase gel products and two-phase products. In the latter case, the gel and separated liquid were quantified and the P and K contents were determined.

The amount and type of cross-linking agent were determined to ensure the introduction of the largest amount of NPK fertilizer into the PVA. As with polyacrylamide fertilizers, fertilizer granules containing the highest amount of nutrients in the PVA hydrogel were selected for pot testing. Three measurements were carried out to determine the K2O and P2O5 content.

Absorption and desorption in fertilizers based on polyacrylamide hydrogel granules A study of the absorption and desorption of fertilizer ingredients by polyacrylamide hydrogel granules was assessed at room temperature by the degree of their swelling after application to the liquid multicomponent fertilizer NPK 12-5-6. The degree of their shrinkage after removal from the soil was also determined. Absorption and desorption were also determined by changes in the diameter of the hydrogel granules, calculated using the following formula (1):

the degree of their shrinkage.

$$S = \pi * d2$$

in which:

S – specific surface of the microcapsule, mm2;

d – microcapsule diameter, mm.

Six measurements were taken for each data point.

## 4 Determination of nitrogen, phosphorus and potassium content in fertilizers

The determination of phosphorus and potassium content is directly related to prepared fertilizers that were applied to the soil under conditions similar to growing plants. Phosphorus and potassium contents were calculated based on quantitative labelling of the occurrence of the above-mentioned elements as $K_2O$ and $P_2O_5$. The determination of phosphorus and potassium content in the soil was carried out by the Egner-Rieme method using calcium lactate14. Phosphorus and potassium were determined by colourimetric 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, and soil salinity by the conductometric method

15. Nutrient content NPK was determined using the methods included in Annex IV to Regulation (EC) No 2003/2003 of the European Parliament and of the Council of 13 October 2003.

First, soil samples were taken and analyzed. The 50-liter pot was then divided into three equal parts, separated by a polyethylene mesh, and the selected polyacrylamide or PVA fertilizer was added.

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

## 5 Results and discussion

Figure 1 shows the effect of fertilizer concentration and time of immersion of polyacrylamide hydrogel granules in water on their size. It can be noted that the introduction of polyacrylamide granules into the fertilizer concentrate (without dilution) and into its aqueous solutions led to an increase in their diameter. Moreover, a distinct change in the size of the polymer granules was associated with the solution absorption process. Polyacrylamide absorbs concentrate, aqueous solutions of fertilizers, as well as water. Regardless of the concentration of the solutions, we can observe the fastest absorption process occurring before 2 hours of the experiment, and a slightly slower absorption between 2 and 6 hours. After 6 hours, the kinetics of liquid absorption by granules did not change. From 6 to 12 hours, the diameter of the beads immersed in all absorbents increased slightly, indicating the thermodynamic equilibrium of the process.

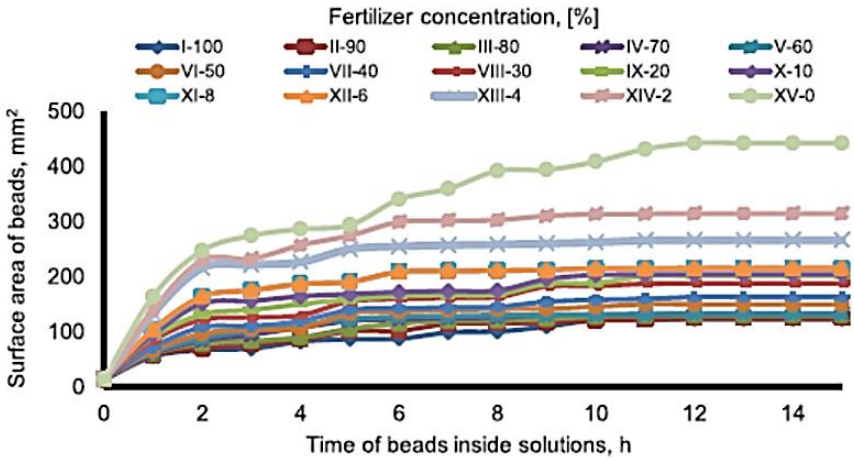


**Fig. 1**. Effect of fertilizer concentration and immersion time on the size of polyacrylamide hydrogel granules

Moreover, beads remaining in solutions for more than 12 hours did not increase the rate of liquid absorption by the polymer, as evidenced by the bead size values. The smallest changes in granule diameter were recorded for fertilizer prepared from polyacrylamide and a 40% NPK fertilizer solution (sample VII). It was also found that the lower the concentration of fertilizer in the solution, the larger the diameter of the granules. In addition, it has been found that immersing polyacrylamide granules for at least 12 hours in a solution of NPK fertilizer or an aqueous solution thereof provides maximum liquid absorption. Therefore, 12 hours was chosen for the preparation of this type of fertilizer.
The differences in the sizes of polyacrylamide granules extracted from undiluted fertilizer (concentrate) and aqueous solutions are shown in Fig. 2. The results obtained showed a noticeable decrease in the diameter of the fertilizer granules. It was also observed that regardless of the concentration of fertilizer that was absorbed by the granules, the release rate of the fertilizer/fertilizer solution remained the same. The decrease in granule size can be explained by the desorption of components included in the fertilizer (i.e. fertilizer in the form of a concentrate, its solutions or simply water), which were absorbed by the granules.

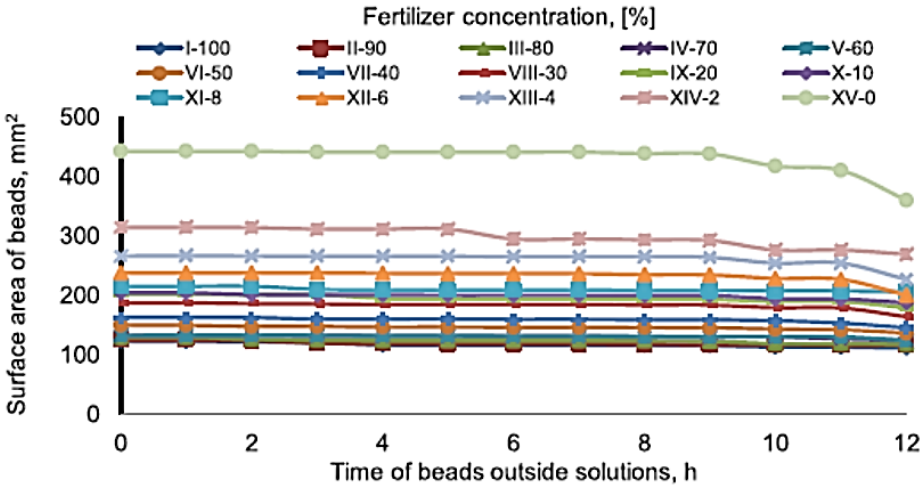


**Fig. 2.** Effect of immersion time on the area of hydrogel granules removed from NPK 12-5-6 fertilizer solutions of different granule concentrations after their application to the soil (i.e. after so-called pot tests).

We observed almost identical activity between fertilizer granules placed in the soil and fertilizers tested outdoors (Figure 2). Similar to previous results, it was found that regardless of the type of fertilizer tested, the diameter of the beads decreased slowly, mainly due to their placement in the soil. Fertilizer granules prepared from NPK concentrate (sample I), its 40% solution (sample VII) and the lowest concentration NPK salt solution of 2% (sample XIV) were selected for three-week pot trials. After their removal from the soil, an analysis of the substrate with fertilizers was carried out. The results are shown in Table 1.

**Table 1.** Characteristics of soil with polyacrylamide granules

| Sample design | pH | Soil characteristics, (mg/l) | | | |
|---|---|---|---|---|---|
| | | Salinity NaCl | $NO_3$ | P | K |
| Virgin ground | 6.8 | 400 | 32 | eleven | 128 |
| Fertilizer I | 6.8 | 1400 | 400 | 287 | 469 |
| Fertilizer VII | 6.8 | 1000 | 410 | 118 | 15 |
| Fertilizer XIV | 6.7 | 500 | 54 | 25 | |

The test results (Table 1) confirm the effect of the fertilizers used on the enrichment of the soil with elements N, P, and 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 remained unchanged before the experiment and after 3 weeks of fertilization. The greatest enrichment of soil nutrients was obtained when using undiluted NPK fertilizer, obtained from fertilizer concentrate and indicated by the symbol I.

Table 2 shows the results of single-phase and two-phase polyvinyl alcohol (PVA) products with cross-linking agents. It can be noted that it is possible to crosslink PVA with

NPK fertilizer either in the form of a concentrate or its 50% solution, or using a mixture of them with sodium tetraborate.

The results obtained showed that it is possible to crosslink a mixture of PVA with sodium tetraborate and NPK fertilizer in the form of a concentrate or its solution. It has been confirmed that the concentration of the crosslinking agent determines the form of the resulting fertilizer. The use of NPK in the form of a solution, the concentration of which in PVA does not exceed 20 pH, resulted in a homogeneous product in the form of a single-phase gel-like product. However, the use of a crosslinker at a concentration greater than 20 pH resulted in liquid separation from the initially formed fertilizer gel (gel and liquid). This may indicate that the micronutrients are not fully bound to the polymer.

It can be emphasized that it is important not only to introduce the largest amount of NPK salts into the hydrogel granules but also to the kinetics of the release of nutrients from the resulting fertilizers. Consequently, the results of determining P and K in granules allowed us to select the composition of the crosslinking agent. The amounts of P and K elements were determined as K2O and P2O5 in unreacted cross-linkers.

It was found that for all fertilizer compositions, the PVA gel contained 90-100% of the amount of salt added to 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 were bound. Based on the results of the analysis of PVA cross-linking products, the shape of the cross-linking product, therefore, should not determine the composition of the resulting fertilizers

## 6 Conclusion

Two innovative multicomponent fertilizers based on polyacrylamide and polyvinyl alcohol (PVA) with controlled release of nutrients were successfully prepared and applied.
The uptake of fertilizer solutions occurred regardless of the concentration of the fertilizer solutions and the time spent by the polyacrylamide granules in the solutions. The longer the immersion time of the balls (up to 12 hours), the higher the degree of absorption. The NPK salts bound to the gel polymer matrix regardless of the form of cross-linked PVA (single-phase: gel or biphasic form: gel in liquid). Optimal formulations were obtained using polyacrylamide fertilizers with the highest amount of NPK salts prepared by absorption of the concentrate, as well as PVA fertilizers in the form of a dense gel based on a cross-linking concentrate of 60%.

All innovative fertilizers based on polyacrylamide and PVA were characterized by a slow, controlled release of nutrients. Polyacrylamide-based fertilizers were classified as controlled-release fertilizers, while fertilizers made from environmentally friendly biodegradable polyvinyl alcohol were defined as slow-release fertilizers that enrich the substrate with nutrients.

## References

1. GOST 20851.2-75. Mineral fertilizers. Methods for the determination of phosphates. (M.: IPK Standards Publishing House, 1997)
2. Gillespie AW, Phillips CL, Dynes JJ, Chevrier D, Regier TZ, Peak D. Advances in agronomy **133**, 1-32 (2015)
3. Van Grieken R, Markowicz A, editors. Handbook of X-ray Spectrometry (CRC Press; 2001)
4. Zschornack GH. Handbook of X-ray Data (Springer Science & Business Media; 2007)

5. Białkowska, Anita, Bożena Borycka, Mohamed Bakar, and Agnieszka Rzany. Polish Journal of Chemical Technology **24**, 3, 14-18 (2022)
6. Giller I.L. Tables of interplanar distances. (M.: Nedra, 2010)
7. Nedoma I. Interpretation of X-ray powders. (Moscow: Metallurgy. 1975)
8. Downs RT, Hall-Wallace M. American Mineralogist. **88(1),** 247-50 (2003)
9. Belsky A, Hillenbrand M, Karen VL, Luksch P. Acta Crystallographica Section B: Structural Science **58(3),** 364-9 (2002)
10. Nazirova R.M., Tadjiev S.M. *Intensive technology for obtaining nitrogen, phosphorus and potassium fertilizers.* Agricultural journal of Uzbekistan. Tashkent. (2013)