

## Ethylcellulose as a coating material in controlled-release fertilizers

Krzysztof Lubkowski\*, Aleksandra Smorowska, Marta Sawicka, Elwira Wróblewska, Alicja Dzienisz, Małgorzata Kowalska, Marcin Sadłowski

West Pomeranian University of Technology, Szczecin, Faculty of Chemical Technology and Engineering, Department of Organic and Physical Chemistry, Piastów Ave. 42, 71-065 Szczecin, Poland

\*Corresponding author: e-mail: krzysztof.lubkowski@zut.edu.pl

Ethylcellulose polymer was used as a coating material in the preparation of controlled release fertilizers. The materials have been prepared with the use of an immersion method. The mass ratio of polymer to fertilizer was in the range of 0.165–0.285 and the layer thickness was in the range of 204–244  $\mu\text{m}$ . Mechanical properties of the prepared materials were significantly better in comparison with the initial fertilizer. Measurements of time and the degree of release of mineral components from the obtained materials were determined with a standard method. Ethylcellulose-coated materials have met the requirements of controlled release fertilizers.

**Keywords:** mineral fertilizers, controlled release, ethylcellulose.

### INTRODUCTION

Mineral fertilizers belong to the group of essential products of agricultural industry. They provide nutrients to crops, increase their growth and at the same time they play an important role in regulating both pH and fertility of the soil. Global population growth and the subsequent need for increased food production continues to drive mineral fertilizer consumption<sup>1, 2</sup>. The human population doubled from 3.1 mld to almost 6.2 mld between 1961 and 2001. At the same time grain and meat production and fertilizer consumption increased by a factor of 1.4, 2.3 and 6.0<sup>1</sup>, respectively. The global population is expected to reach 9.6 mld by 2050<sup>3</sup>, so further increases in the production of mineral fertilizers are seen as inevitable.

Apart from a slight decrease in consumption in 2008/2009 due to the crisis in the banking system, consumption of mineral fertilizers has systematically increased in recent years from 135 Mt (81 Mt N, 32 Mt P<sub>2</sub>O<sub>5</sub>, 22 Mt K<sub>2</sub>O) in 2000/2001 to 186 Mt (113 Mt N, 41 Mt P<sub>2</sub>O<sub>5</sub>, 32 Mt K<sub>2</sub>O) in 2016/2017, while worldwide demand is forecast to reach 199 Mt in 2020/2021<sup>4</sup>.

An increased production of fertilizers contrasts with a relatively low nutrient use efficiency (NUE). Assimilation of fertilizer nitrogen by plants is approximately 50% on average<sup>1, 5–7</sup>, whereas an uptake of phosphorous and potassium reaches 10–25% and 50–60%, respectively<sup>8–11</sup>. Low effectiveness of nutrients assimilation may cause serious problems in view of environmental protection<sup>5, 12–15</sup> and human and animal health<sup>1, 5, 14, 16</sup>. The economic aspect of the issue is no less important<sup>17, 18</sup>: annual losses of nutrients can be estimated at 60–80 Mt, corresponding to the financial losses of 18–24 mld USD. During the production of 1 kg of fertilizer about 1 kg of oil is used<sup>19</sup>, which means irreversible loss of the natural resources. In view of current and possible future energy problems fertilizer losses must be minimized.

An improvement in the effectiveness of nutrients assimilation can be achieved, among others, through development, production and application of the so-called “intelligent fertilizers”, which release mineral components according to the nutrient requirements of the plants<sup>10, 20, 21</sup>. The examples of such materials are slow-release fertilizers (SRF) and controlled-release fer-

tilizers (CRF). According to the *Association of American Plant Food Control Officials (AAPFCO)*<sup>22</sup> slow-release fertilizers (SRF) are chemically or biologically decomposed materials with a high molecular weight, complex structure and low solubility in water, whereas controlled-release fertilizers (CRF) are materials in case of which the release of mineral components takes place through a polymer layer or a membrane.

CRF materials have many advantages like decreased nutrient losses and enhanced nutrient-use efficiency, minimization of fertilizer-associated risks such as leaf burning, water contamination, and eutrophication and reduced application and labour costs<sup>23</sup>. One of the drawbacks of CRF is, that after nutrient consumption a considerable amount of non-functional polymer remains in the soil, amounting to approximately 50 kg/ha per year<sup>10</sup>. Good and possible way is to produce CRF using biodegradable materials, either natural materials or biosynthetic materials manufactured from renewable raw materials<sup>24</sup>.

An extensive group of materials tested for their suitability in the preparation of controlled release fertilizers are polysaccharides like starch and its derivatives<sup>24–25</sup>, cellulose and its derivatives<sup>26–29</sup> and chitin and its derivatives<sup>30–32</sup>. Ethylcellulose is a multifunctional, water-insoluble cellulose ether approved for many pharmaceutical applications like release multiparticulate coating, microencapsulation of active substances, taste-masking of bitter active substances, release binder in inert matrix systems or solvent and extrusion granulation<sup>33–35</sup>. The properties of ethylcellulose may be also useful in a control release of nutrients from mineral fertilizers. So far, this solution has not yet been commercialized, nevertheless there are scientific studies aimed at application of ethylcellulose in agrochemistry. Attempts were made to coat granulated ammonium nitrate with ethylcellulose<sup>26–27</sup>, which showed that the process of nitrogen release can be controlled by the thickness of the coating film and by the addition of various plasticizers to ethylcellulose. Ethylcellulose was also used to coat the granules of urea, although together with other coating substances, such as aluminosilicates (montmorillonite, diatomite and palygorskite)<sup>28</sup> or superabsorbents based on acrylic acid copolymers<sup>29</sup> – as a result, double-coated CRF materials were obtained, mainly with improved water retention. However, there

has been no research so far on the coating of NPK fertilizers with the use of ethylcellulose, at least in the light of the available literature data.

Therefore, the aim of presented work was to obtain materials with controlled release properties by covering granules of a commercial multicomponent (NPK) fertilizer with ethylcellulose (EC) as an example of biopolymer material, with the use of an immersion method. The objective of the work was the characterization of the prepared materials and evaluation of the nutrient release kinetics.

## EXPERIMENTAL

### Material

As a source of active mineral, macronutrient components (nitrogen, phosphorous, potassium) the commercial, granulated, multicomponent fertilizer NPK(S) 6-20-30-(7) (POLIFOSKA®6, GA Chemical Plant "Police" S.A.) was used in the experiment. The fertilizer contains at least 92% of grain class within the range 2–5 mm. Its bulk density is about 0.9–1.0 kg/dm<sup>3</sup>. For the experiment the fraction of granules with a diameter of 4–5 mm was selected.

Ethylcellulose with excellent thermoplastic properties (ETHOCEL™, Dow Chemical Company, Michigan, USA) was used as a coating material in the preparation of controlled release fertilizers. According to the producer information ETHOCEL™ polymers have an ethoxyl content of 48–49.5% and viscosities ranging from 3 mPa·s to 385 mPa·s. Preliminary experiments have shown that ethylcellulose with the viscosity of 10 mPa·s is an optimum coating material in view of the best application properties. To obtain a 10 wt% solution, 10 ± 0.1 g of ethylcellulose were dissolved, gradually and with the use of a magnetic stirrer, in 90 ± 0.1 g of ethanol.

### Preparation

Initially weighed fertilizer granules (4–5 mm), were covered with ethylcellulose by the immersion method. Granules of fertilizer were placed separately as a monolayer on the stainless steel wire cloth (dimensions of 20 cm × 20 cm, opening size = 1.6 mm × 1.6 mm), dipped into the solution (with a contact time of 2–3 s), gravity filtered and then dried at 60°C to evaporate the solvent residue. Multiple dipping/drying procedure controlled and determined the amount of covering polymer layer. After the preparation process the obtained fertilizer materials have been weighed again. As a result of the preparation, materials with the various mass ratio of biopolymer to fertilizer (P/F) have been obtained.

### Methods

The content of three main components of the fertilizer, namely nitrogen (5.7 wt% N-NH<sub>4</sub><sup>+</sup>), phosphorous (19.8 wt% P<sub>2</sub>O<sub>5</sub>), and potassium (29.5 wt% K<sub>2</sub>O) were determined with potentiometry (ammonium ion selective electrode, Orion), spectrophotometry (Spekol 11, Carl Zeiss) and emission flame photometry (BWB-1), respectively. The measured contents of mineral components were consistent with the data declared by the fertilizer producer.

The morphology of the ethylcellulose-coated granules and the thickness of the covering layers were examined with the use of the scanning electron microscope with a cold field emission (HITACHI SU8020, resolving power 1.3 nm), coupled with the energy dispersive X-ray analyzer (EDX – Thermo Scientific). Granules were mechanically polished to achieve a flat cross section and coated with a thin conductive film of chromium (turbo-pumped sputter coater Quorum Q150T ES system). Microscopic observations were performed at an accelerating voltage of 138 eV. The thickness of the polymer layers was measured at a magnification range of X50. EDX mapping of the samples were also performed.

The mechanical strength of the prepared materials was measured with a commercial table-top strength testing machine Zwick/Roell Z2.5 with the TestExpert II ver. 2.2 software. The granules were compressed individually in a radial direction between two rigid plates with the maximum testing force  $F_{max}$  of 2.5 kN and at a constant crosshead test speed of 10 mm/s. The load at which fracture of the granule occurred was recorded as the crushing strength. For each sample, a total of 25 parallel measurements were carried out. Crushing strength was normalized with the granule diameter and compared with the mechanical properties of a commercial fertilizer.

Measurements of time and the degree of release of phosphates from the prepared fertilizer materials were performed in water, according to the standard method<sup>36</sup>. Five granules of the prepared material (weighed with the accuracy of 0.0001 g) were placed in a plastic cap beaker with 50 ± 0.5 mL of distilled water. The release experiments were performed in static conditions, without stirring. After 1 h of incubation at a constant temperature of 25°C, the solution was decanted and the beaker was filled again with 50 ± 0.5 mL of distilled water. This procedure was repeated after 3, 6, and 24 h and after 3, 5, 7, 14, 21, and 28 days.

To determine the amount of released phosphates spectrophotometry method was used. In this method orthophosphate ions react with an acidic solution of molybdate and vanadate ions to form a vanadate phosphomolibdate complex of yellow-orange colour. All solutions were prepared in double-distilled water with reagent grade salts. A standard solution of orthophosphates (PO<sub>4</sub><sup>3-</sup>, 1000 mg/dm<sup>3</sup>) was prepared by dissolving 0.4792 g of KH<sub>2</sub>PO<sub>4</sub> (POCh S.A., Poland) in water and making the solution up to 250.0 cm<sup>3</sup>. Ammonium molybdate solution was prepared by dissolving 20.0 g of (NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub>·4H<sub>2</sub>O (POCh S.A., Poland) in 250 cm<sup>3</sup> water. Ammonium metavanadate was prepared by dissolving 1.0 g of NH<sub>4</sub>VO<sub>3</sub> (POCh S.A., Poland) in hot water, addition of 5 cm<sup>3</sup> of nitric acid and making the solution up to 100 cm<sup>3</sup>. The signals were measured with the use of Spekol 11 UV/Vis spectrometer (Carl Zeiss, Germany) equipped with a 10 mm length flow cell. The measurements were taken in the extinction mode at wavelength of 460 nm.

The release of all water-soluble mineral components of the fertilizer was also measured with the use of a CPC 505 pH/conductivity meter with temperature compensation (Elmetron, Zabrze, Poland). Polymer-coated granules with a given polymer to fertilizer ratio (P/F) were placed in a glass beaker with 50 ± 0.5 mL of distilled water.

The sample was kept at a constant temperature of 25°C, and the conductivity was measured automatically every hour for 6 days (144 h). At the end of the experiment, the granules were mechanically crushed to determine the final conductivity value.

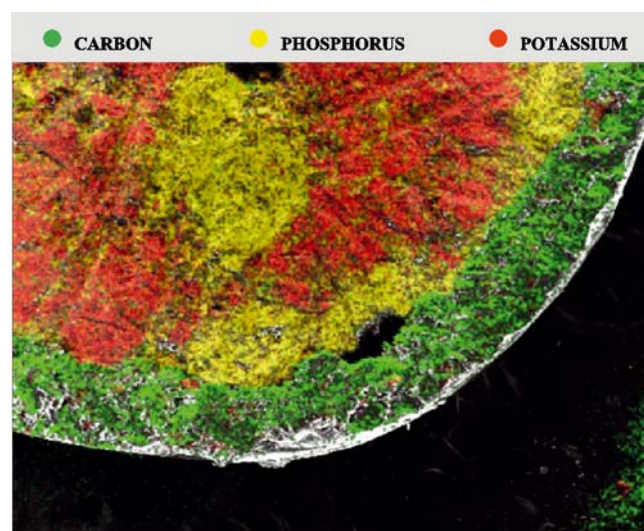
## RESULTS AND DISCUSSION

Granules of the starting NPK fertilizer were of regular, spherical shape and uniform light-grey to dark-grey colour. They were hard, although subjected to adequate crushing force they may be easily crumbled to small pieces and then milled to powder. Previously performed XRD measurements<sup>32, 37</sup> have shown that the NPK fertilizer includes nitrogen and phosphorus mainly in the form of mono- and diammonium phosphates and potassium in the form of potassium chloride and there are no essential differences in the position and intensity of the peaks between the spectra of the prepared materials and the starting fertilizer.

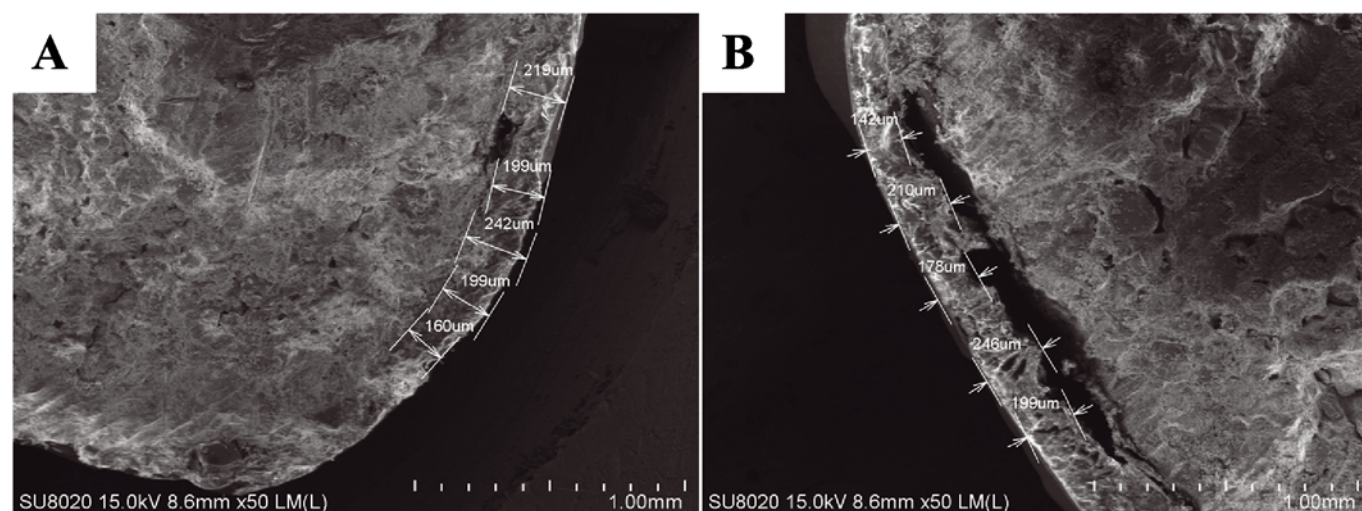
Fourteen samples of materials with a different mass ratio of ethylcellulose to fertilizer (P/F in the range from 0.16 to 0.29) have been obtained in the experiment. The mass ratio of polymer to fertilizer P/F was determined based on the mass balance of the process. The fertilizer granules are covered completely with ethylcellulose. The core of the prepared materials, consisting of the fertilizer components, is surrounded by an inert ethylcellulose layer. The surface of the prepared materials is uniform, dense and compact. There are no visible cracks and fractures on their surfaces.

The cross section SEM images of the NPK fertilizer granules, covered with the layer of ethylcellulose with two different, extreme mass ratio of polymer to fertilizer (0.165 and 0.285), are presented in Fig. 1. The thickness of the layer varies around the granule, hence to evaluate it properly twenty measurements have been carried out (with five measurements for every quarter of the cross-sectioned granule). On the basis of these measurements, the mean value of the polymer coating thickness was determined, which is 204  $\mu\text{m}$  in the case of the material with the mass ratio of polymer to fertilizer P/F = 0.165 (Fig. 1A) and 244  $\mu\text{m}$  in the case of the material with the mass ratio P/F = 0.285 (Fig. 1B).

Distribution of elements in the prepared materials has been resolved with the use of the scanning electron microscope coupled with the energy dispersive X-ray analyzer. The EDX mapping of the cross-sectioned granule of the material with the mass ratio of ethylcellulose to fertilizer P/F = 0.165 is presented in Fig. 2. The EDX analysis has proved that only carbon occur in the layer of polymer coating. The structure of the formed layer is homogeneous, with carbon atoms spread regularly in the layer. It means that the polymer do not penetrate into the granule core. The EDX mapping shows also the areas with higher concentration of potassium (red dots) and phosphorus (yellow dots), which are the components of potassium chloride and ammonium phosphate salts. It can be stated, that the components of the granule core do not pass into the ethylcellulose layer as well. To confirm that observation, a granule covered with the polymer layer was cut in half and mineral components of the fertilizer were rinsed off with water. A thorough inspection of the ethylcellulose layer has not revealed any differences in the appearance of inside and outside surface of the layer.

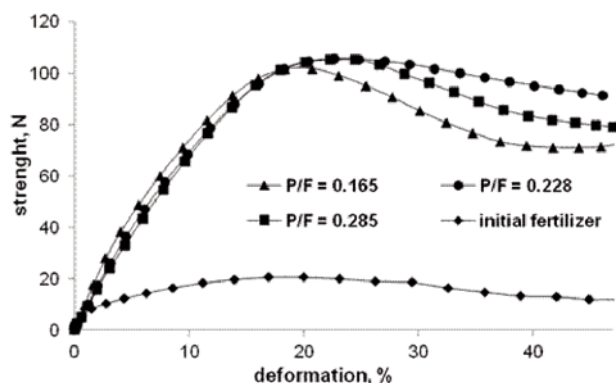


**Figure 2.** EDX mapping for the material with the mass ratio of ethylcellulose to fertilizer P/F = 0.165 (green dots – carbon, yellow dots – phosphorus, red dots – potassium)



**Figure 1.** SEM images of the fertilizer granules covered with ethylcellulose with the extreme mass ratio of polymer to fertilizer (A – P/F = 0.165; B – P/F = 0.285).

The crushing strength measurements have been carried out for the samples of prepared materials with different mass ratios of ethylcellulose to fertilizer – 0.165, 0.228 and 0.285 respectively and for the starting NPK fertilizer. For each sample 10 parallel measurements have been performed and the mean value of the crushing strength have been calculated. Dependences of the crushing strength upon deformation for the ethylcellulose covered materials and for the starting NPK fertilizer are presented in Fig. 3.



**Figure 3.** Crushing strength as a function of deformation for the materials with a different mass ratio of ethylcellulose to fertilizer and for the initial fertilizer

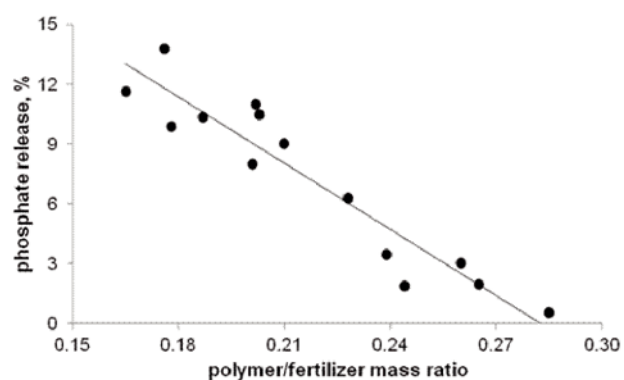
Fertilizers may be considered as typical materials with a brittle failure mode. Fertilizer granules are porous, they are built up of various mineral compounds with lots of flaws, dislocation and crystal edges<sup>38, 39</sup>. Any discontinuation in the fertilizer granule bulk should be treated as a defect and the reason of the stress concentration. The mechanical damage of the fertilizer granule ensues from brittle failure being the result of an abrupt disastrous increase of a decisive defect under tensile stress induced in the material bulk. In the case of the starting NPK fertilizer, fracture or rather cracking of the granule occurred at the crushing strength of 21 N, with the mean deformation of 17%. Obtained value of the crushing strength (21 N) corresponds to pressure of 2.1 kg/granule and is comparable with the literature data for various granulated fertilizer compounds: urea (1.5 ÷ 3.5 kg/granule), TSP – triple superphosphate (1.5 ÷ 3 kg/granule), MAP – mono ammonium phosphate (2 ÷ 3 kg/granule) or ammonium sulfate (1.5 ÷ 2.5 kg/granule)<sup>40</sup>. Contrary to the starting NPK fertilizer, ethylcellulose-coated granules exhibited significantly higher resistance towards the crushing force. For all prepared and examined materials, the crushing force was incessantly increasing along with deformation up to the value of 20%, where maximum crushing strength occurred. Maximum crushing force achieved the value in the range of 100–110 N in the case of all examined materials.

The final assessment, especially environmental evaluation, of the prepared fertilizer materials requires thorough and detailed field experiments. However, it has been shown<sup>26</sup> that the release of mineral components from controlled release fertilizers in soil might be easily predicted from the release experiments performed in water. Taking into account numerous publications<sup>26, 41–45</sup>, this approach (nutrient release in water) seems to be fully justified and acceptable in the research area

related to the controlled-release fertilizers evaluation. In the presented manuscript we focused only on issues related to the nutrient release in water, whereas the experiments related to the nutrient release in soil will be addressed in another paper. As a consequence, all prepared ethylcellulose-coated fertilizer materials were submitted to water release experiments, according to the standard method<sup>36</sup>. Obviously, it should be kept in mind that nutrient release rate is different in different medium, the fastest release rate is in water, then water-saturated sand, and the slowest in sand<sup>46</sup>.

The results of the investigation on phosphates release from the prepared ethylcellulose-coated materials, within the period of 24 h, are presented in Fig. 4. It was reported in the series of papers<sup>13, 37, 46–48</sup> that release rate of P (as orthophosphates) is significantly lower as compared to K,  $N-NH_4^+$  and  $N-NO_3^-$ . As a reason of that dependency, some strong interactions among nutrients in the fertilizer granule and differences in nutrients solubility are pointed out<sup>47</sup>. The release rate of phosphates may be treated as a “bottleneck” of all nutrients release. When release rate of phosphates is determined and then release rate of all other nutrients is surely faster.

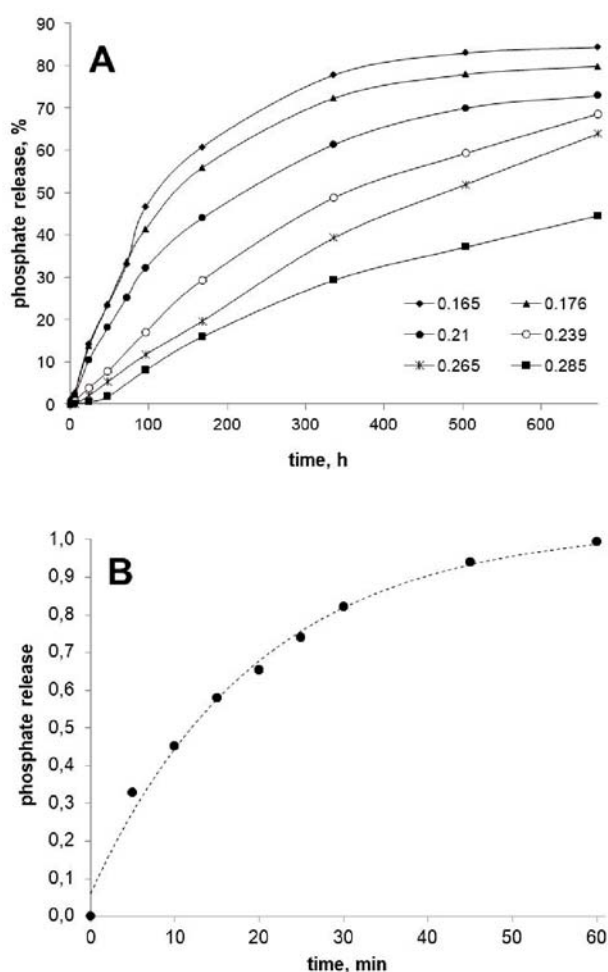
A fertilizer may be denominated as a slow or controlled release fertilizer, provided that no more than 15% of nutrients is released from it within 24 hours, no more than 75% of nutrients is released from it within 28 days, and at least 75% of nutrients is released from it at declared release time<sup>10, 36</sup>. It can be seen from the data presented in Figure 4 that for all prepared ethylcellulose-coated materials, with the mass ratio of polymer to fertilizer in the range from 0.16 to 0.29, the release of phosphate is lower than 15% within 24 hours. It means that these materials meet the first aforementioned criterion of controlled release fertilizers.



**Figure 4.** Release of phosphates vs. the mass ratio of ethylcellulose to fertilizer after 24 hours of measurement

The results of release experiments within the period of 28 days for all the materials coated with ethylcellulose, with the mass ratio of polymer to fertilizer from 0.16 up to 0.285 are shown in Fig. 5A. During the experiments amounts of released phosphates were determined as a function of time, at constant temperature of 25°C. The long-lasting release experiments has demonstrated that for the group of materials, with the mass ratio of ethylcellulose to fertilizer at least 0.21, the release of phosphates is less than 75% within 28 days, which means that these materials fulfil also the second criterion of controlled release fertilizers. For the group of materials

with the mass ratio of ethylcellulose to fertilizer less than 0.21, the release of phosphates after 28 days is slightly higher than 75%. The results of studies on the release of phosphates from ethylcellulose-coated materials can be compared with the results of studies on the phosphate release from the uncoated fertilizer, which are presented in Fig. 5B. The total release of phosphates from the uncoated fertilizer, which means complete dissolution of fertilizer in water, occurs after about 60 minutes. The use of a suitable coating material, in this case the use of ethylcellulose, significantly extends the release time of phosphates and, in general, all mineral components of the fertilizer.



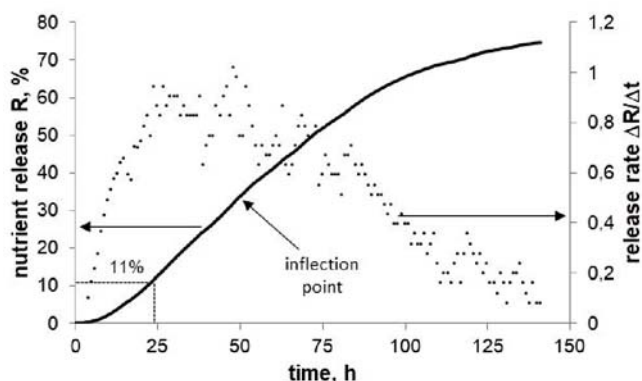
**Figure 5.** Phosphate release from ethylcellulose-coated materials with different mass ratio of ethylcellulose to fertilizer (A) and phosphate release from uncoated NPK fertilizer (B)

Phosphates and generally nutrient release from the prepared polymer-coated materials depend upon the mass ratio of polymer to fertilizer. Decrease of phosphate release takes place with the grow of the mass ratio of polymer to fertilizer and with the increase of the layer thickness. Diffusion mechanism of the release might be pointed out as a reason of that correlation<sup>47</sup>. Along with the grow of the layer thickness, the value of diffusion coefficient decreases and the release process is more and more hindered. However, one have to keep in mind that all presented here release experiments were performed in water. As it was earlier mentioned,

nutrients release from polymer-coated controlled release fertilizers is mainly controlled by diffusion mechanism. When the material coated with biodegradable polymer is investigated in those conditions (water release experiments) then probably an impact of diffusion coefficient on the release patterns is of crucial importance. But if the release experiments from the materials covered with biodegradable polymer were performed in soil then some other factors and parameters, especially microorganism biodegradation of the polymer layer, would be important.

Considering the fact that the release of phosphates does not fully reflect and describes the release process from ethylcellulose-coated NPK fertilizers, conductivity tests were also carried out. The use of the conductivity measurements makes it possible to determine the release of all mineral components of the fertilizer that dissolve in the aqueous solution. Figure 6 presents the results of nutrient release measured by conductivity for the sample of prepared material with the mass ratio of ethylcellulose to fertilizer P/F = 0.202. The release of the nutrients of the fertilizer  $R(\%)$ , was calculated according to the equation  $R = \sigma_t \cdot 100/\sigma_F$ , where  $\sigma_t$  represents the measured conductivity at time  $t$  and  $\sigma_F$  represents the final conductivity value.

Release of nutrient from polymer-coated CRF can be described in three stages<sup>10, 47</sup>: lag period, linear stage, and decay period. In the experiment presented in Figure 6, the lag period is quite long. Placing the tangent line onto the experimental curve at the inflection point (54th hour) enables a rough estimate of the lag time, which is between 7 and 18 h. The linear stage of the release profile cannot be identified because the release rate constantly increases until the maximum release rate is reached at the 54th hour of the process. From that point, the release rate slowly decreases, and the release  $R$  reaches 70% after 125 h. Furthermore after 24 h, the release of all water-soluble fertilizer components is approximately 11%, significantly below the limit of the first requirement of slow/controlled-release fertilizers (15% within 24 hours).



**Figure 6.** Release of phosphates within the period of 150 h from ethylcellulose-coated material with the mass ratio of polymer to fertilizer P/F = 0.202

## CONCLUSIONS

Materials with controlled release properties can be obtained as a result of coating the multicomponent fertilizer granules with ethylcellulose, with the immersion method. The obtained materials differ from each other with the layer thickness and the mass ratio of polymer

to fertilizer. The mass ratio of polymer to fertilizer was in the range of 0.165–0.285 and the layer thickness was in the range of 204–244  $\mu\text{m}$ . Mechanical properties of the prepared materials were significantly better in comparison with the initial fertilizer. Ethylcellulose-coated materials meet the requirements of controlled release fertilizers. The use of ethylcellulose in the preparation of controlled-release fertilizers may bring many benefits, especially in the context of environmental protection, as it was proved in the presented paper. Ethylcellulose is not a cost-effective material, although its price is comparable with other biodegradable polymers. The high price of ethylcellulose seems to be the main obstacle of its possible acceptance as a fertilizer component. Nonetheless, it is to be hoped that this price will decrease in the future with the widespread use of biodegradable materials in chemical technology, especially in agrochemistry.

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