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Research Article

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Properties of potassium dihydrogen phosphate and its effects on plants and soil

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Abstract: One of the challenges of the modern world is to improve human nutrition and to safely increase the yield of agricultural production using existing agricultural land. It is clear that sufficient agricultural efficiency cannot be achieved without fertilizers, but fertilizers must cause minimal damage to the soil. Microorganisms, such as spore-forming bacteria, actinomycetes, fungi, algae, and protozoa play an important role in the soil and keep soil healthy. One of the soil substances involved in reactions that take place in plants is cellulose. This study investigated the effect of potassium dihydrogen phosphate (PDP), synthesized (via conversion between potassium chloride and ammonium dihydrophosphate) and granulated with the addition of microcrystalline cellulose (MC), on plants (winter wheat *Toras,* Lithuania) and soil microorganisms. The data of plants fertilized with pure KH_2PO_4, ones fertilized with PDP granulated with MC, and grown without fertilizers were compared in this study. Scanning electron microscopy and differential scanning calorimetry analysis were used to characterize the obtained product. One-way analysis of variance was used to evaluate the differences of the mean values between groups. In all cases, the significance level was $p \leq 0.05$. The effect of pure KH_2PO_4 on plant indicators was found to be lower than that of granular PDP with MC. The length of the leaves was 29.63 and 31.20 cm, green mass was 0.471 and 0.763 g, ash mass was 0.015 and 0.019 g, respectively. In addition, granular PDP with MC did not adversely affect the soil microorganisms because the number of any species of bacteria (Spore b., mineral nitrogen assimilating bacteria, cellulose degrading bacteria) did not decrease and a slight increase in the number of Actinomycetes (from 8.5×10^5 to 2.9×10^6 KSV/g) and molds (from 3.0×10^4 to 1.4×10^5 KSV/g) was observed. The granular PDP with MC that we developed and used have better physical properties, higher agrochemical efficiency and cause less harm to soil microorganisms compared to pure PDP.

Keywords: bacteria, cellulose, fertilizers, potassium dihydrogen phosphate, soil, winter wheat

1 Introduction

Agriculture and production will need to improve faster than the population growth in order to improve people's nutrition and reduce food insecurity and malnutrition. Achieving this purpose will be required in the existing agricultural land. Improvements will therefore need to be made through sustainable practices that make good use of land and water resources without damaging the environment [1].

The cost of agricultural production is becoming increasingly important for the viability of farms in the short and long term. Fertilizer prices are a major problem for farmers, as fertilization costs have recently become an important part of the total cost of agricultural production. Fertilizer prices are affected based on their physical properties and logistics costs. Certain costs, such as higher natural gas prices, have a direct impact on production by creating economies of scale. As the price of natural gas rises rapidly and production costs rise, so do the costs of producing nitrogen fertilizers, as ammonia synthesis depends on natural gas. The conversion of phosphate rocks from raw material to fertilizer use is a slightly different process involving surface mining. Phosphate-coated soils and rocks must be removed using draglines. These draglines are very large and expensive pieces of equipment running on electricity that has become more expensive. As a result, phosphate fertilizers find themselves in situation similar to that of ammonia conversion plants, and companies are starting to look elsewhere for lower prices. Regarding potassium fertilizers,

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although potash is produced in potassium mines, it is also exposed to electricity. Everywhere, mines are up to a mile underground. Roughly ten countries produce potassium and even fewer countries export the product, making supplies even more limited [2,3]. One of the ways to increase the efficiency and availability of fertilizers even in poorer countries is the production of concentrated fertilizers using the cheapest available raw materials such as potassium chloride [4] by the simplest method of manufacturing. Highly concentrated fertilizers from potassium phosphates (potassium hydrogen phosphate and potassium dihydrogen phosphate (PDP)) are widely known and used. Unfortunately, they are usually expensive (KH_2PO_4 – 968–1,162 €/t, $KHPO_4$ – 871–1,065 €/t) [5] due to excessive manufacturing costs or limited phosphate rock resources. As a result of high prices, PDP is usually used for highly chlorine-sensitive plants (e.g., tobacco, potato, a few fruits, berry, vegetables, some tree crops, and some soybean varieties) in greenhouses or hydroponics. Nevertheless, this sensitivity varies depending on the growing conditions [6].

Potassium is the major cation in the cytoplasm of plants essential for the activity of various enzymes that are involved in primary metabolism. Potassium is involved in the regulation of turgor, protein synthesis, sugar transport, and photosynthesis [7–14]. Based on the above literature, it can be stated that potassium has a significant influence on the uptake and use of other nutrients in plants. When a plant is deficient in potassium, it is likely that it will activate a signaling mechanism that moves motile potassium ions from old leaves to new ones to support modulation of stomata diaphragm osmosis in the latter [15,16]. Most of the potassium in the soil is insoluble. Therefore, potassium-dissolving microorganisms, a component of the soil microbial community, can colonize the rhizosphere, promote crop yields, and enhance plant responses to stress in adverse climates. Microorganisms play an important role in providing plants with an available form of potassium and ecologically improving soil fertility. Most scientists agree that it is important to study the effects of mineral potassium fertilizers on natural soil microorganisms, but this problem is still given little attention, as most studies focus on nitrogen and phosphorus fertilizers [17–20]. It should be noted that assimilation of mineral fertilizers depends on the activity of the microorganisms living in the soil as well as their solubility in the soil solution. Coatings of various films are used in production of fertilizers which plants can absorb over a longer period of time. Physical methods can be applied for coating fertilizers with a variety of coatings with additives. Inorganic substances (phosphates, sulfur, oxides, clay, or gypsum), thermosetting or thermoplastic resins, synthetic organic polymers (alkyd), natural organic polymers (lignin and latex), mixed sulfur-polymer, and chitosan are used as coatings. Thus, dissolution of such fertilizers in the soil is prolonged, plants absorb them, and thereby, environmental pollution is reduced. Soluble nitrogen and phosphorus fertilizers are among the ones for which these statements can be applied [21,22].

Phosphorus performs various physiological and biochemical functions in plants. It is used for energy transfer and storage through adenosine triphosphate in biological systems and contributes to the synthesis and stability of deoxyribonucleic acid and ribonucleic acid. Phosphorus is required for the structural and functional integrity of cell membranes and is a source of energy that promotes many chemical reactions in the plant. In the presence of phosphorus deficiency, structural disorders of cell membranes can be expected to adversely affect the transport of nutrients across root cell membranes. It enters the plant through root hair, root tips, and the outermost layers of root cells. Phosphorus uptake is also facilitated by mycorrhizal fungi, which grow along with the roots of many crops. Phosphorus is mainly absorbed as a primary orthophosphate ion ($H_2PO_4^-$), but some are also absorbed as a secondary orthophosphate (HPO_4^{2-}), the latter form of which increases with the increase in the soil ph. Once in the root of the plant, phosphorus can be stored in the root or transported to the upper parts of the plant. It is incorporated into organic compounds through various chemical reactions. These organic compounds are formed in the plant and, together with the inorganic phosphate ions derived from the soil, transfer phosphorus throughout the plant where it is available for further reactions. In terms of plant energy reactions, phosphorus plays a vital role in almost all the plant processes where energy is transferred [23–25].

Cellulose microfibrils are a major component of the cell walls surrounding each cell. In the primary cell walls of plants, cellulose accumulates in microfibrils having a diameter of few nanometers. The stiffness and orientation of these microfibrils control cell expansion; therefore, cellulose synthesis is a major factor in plant growth and morphogenesis. In order to expand, the primary cell walls are nanocomposite materials in which long nanometer-sized cellulose microfibrils flow through a hydrated matrix of xyloglucan, pectin, and other polymers [26–28]. Natural cellulose microfibrils are partially crystalline, which are insoluble cable-like structures typically consisting of approximately 36 hydrogen-bonded chains containing 500–14,000 β-1,4-linked glucose molecules. About one-third of the mass of most plants is cellulose [29–33].

The effectiveness of many of the substances necessary for the plant, which are present in the soil or added with fertilizers, depends on the number of microorganisms and their effects. The issue of microorganisms' distribution in soil is not sufficiently analyzed and evaluated. Conventional microbiological studies of soil indicate that the composition of bacterial group in different soils is not the same. Forms of bacteria that do not form spores predominate in the soil. Spore-forming bacteria make up about 10–20% of total bacterial count. Actinomycetes, fungi, algae, and protozoa also live in large quantities in soil. 1 g of soil contains tens and hundreds of thousands, often millions, of fungi and actinomycetes. Ammonifying bacteria, actinomycetes, microscopic fungi, and other microorganisms cause mineralization of organic matter in the soil and the release of ammonium nitrogen from plants. Soil's microflora has varied composition and content because it is responsible for conversion of mineral nitrogen to organic forms (immobilization process), to increase the uptake of phosphorus, potassium, and other nutrients into plants. Formation processes of actinomycetes or radial fungi, which are transient forms between bacteria and fungi, also play a significant role in the soil. They are actively involved in decomposition of nitrogen and nitrogen-free organic matter, including the most persistent compounds that make up the soil humus, or humus. Thus, the activity of soil's microflora is crucial for soil's health and proper development of plants [34–37].

From the review of the literature, it can be seen that it is difficult to maintain a healthy soil and not harm the microorganisms in the soil when using concentrated fertilizers. Therefore, it is a challenge to select materials that are friendly to the soil and the environment, are effective for plants, but do not reduce the effectiveness of fertilizers.

The aim off this work is to evaluate the effect of PDP, synthesized in a simple way and then granulated with microcrystalline cellulose (MC), on plants and soil.

2 Material and methods

2.1 Materials

Materials used in this work were chemically pure substances of potassium chloride (KCl, 99–100.5% Sigma–Aldrich), ammonium dihydrogen phosphate ($NH_4H_2PO_4$, 99.0% Fluka Analytical), pure PDP (KH_2PO_4, 99–100.5% Sigma–Aldrich), ammonium chloride (NH_4Cl, 99.0% Sigma–Aldrich), MC, manufactured by JRS Pharma GmbH & Co, Emcocel 90 M, and purified, partially depolymerized cellulose was used as a binder, which best suited for dry or wet granulation, with a particle size of 90–60 μm, density of 0.25–0.37 g/cm^3, and pH of 6.65 [38].

2.2 Granulation methodology of PDP

Fertilizers were granulated in the laboratory drum-type granulator-dryer at a 5° tilt angle and constant (27 rpm) rotation speed (Figure 1) [39].

Raw materials were supplied to the granulator preheated up to 55–65°C, hot air for drying the granules was supplied into the drum-type granulator by an air fan. For irrigation, tap water was used, which was injected into the raw material mixture in a separate mixture before the mixture was placed into the drum-type granulator-dryer. By using the PDP (fraction <1 mm), 21 samples were granulated in the laboratory granulator repeating the procedure two or three times. To aid granulation, MC was used. The resultant granules were dried in an oven from 8 to 16 h at 60°C, and then their physical and chemical properties were assessed.

2.3 Analysis of the granular product

The chemical composition of liquid and crystallized solid phases after synthesis between KCl and $NH_4H_2PO_4$ was analyzed by employing methods of chemical analysis: concentration of ammonium nitrogen (NH_4^+) was established by the Kjeldahl method (Vapodest 45s, C. Gerhardt GmbH & Co. KG, Konigswinter, Germany). The concentration of phosphorus (P_2O_5) was determined by using the photo colorimetric method (T70/T80 UV-VIS, PG Instruments Limited, Lutterworth, UK). The concentration of chlorine (Cl^-) was determined by employing the potentiometric method with the use of silver nitrate (TitroLine alpha plus, SI Analytics GmbH, Mainz, Germany). The concentration of potassium (K_2O) was discovered by employing the marginal solutions method by flame photometric method (PFP–7, Cole-Parmer Ltd, Staffordshire, UK) [40].

Differential scanning calorimetry analysis was performed by using Netzsch DSC 214 Polyma thermal analyzer (Mettler-Toledo, Greifensee, Schweiz) and setting the following parameters: 10°C/min temperature-raising speed, 25–300°C temperature range, with weights of standard–blank Al crucible furnace atmosphere air samples equaling 13 mg.

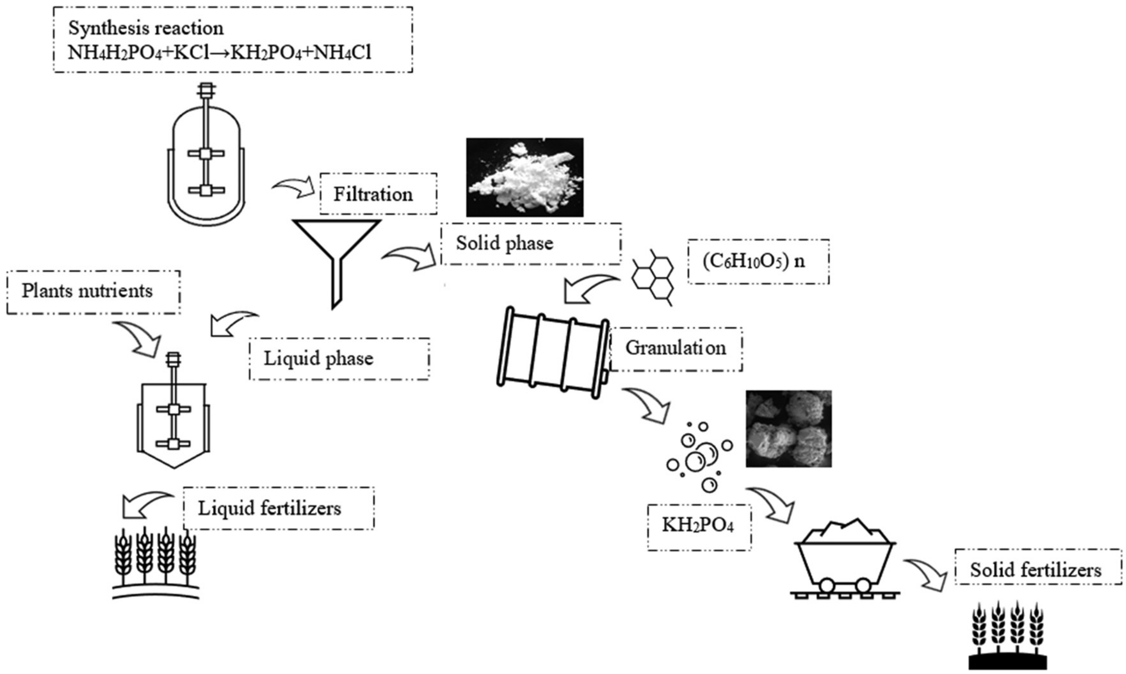

Figure 1: PDP synthesis and obtaining final granulated product.

For scanning electron microscopy (SEM), the FEI Quanta 200 FEG electronic microscope (FEI Company) was used at magnification rates of 10–500,000.

pH measurement was performed with a pH meter HANNA pH 211 (HANNA Instruments, Woonsocket, RI, USA) with a glass electrode HI1131B (Hanna Instruments Woonsocket, RI, USA). Granulated PDP was fractioned by using RETSCH (Retsch GmbH, Haan, Vokietija) woven sieves, and the distribution of fractions (%) was determined by weighing with electronic scales (KERN & SOHN GmbH, Balingen, Germany) with weighing precision of 0.001 g [41].

The amount of moisture in granules was measured with the electronic moisture analyzer HG53 (KERN & SOHN GmbH, Balingen, Germany). It utilizes the thermogravimetric principle, i.e., its activity is based on the decrease in weight during heating until the sample reaches the final stable weight.

The static strength of granules was determined by using the IPG-2 device (AO "УНИХИМ с ОЗ", Yekaterinburg, Russia). The measurement range of 5–200 N was used, whereas the margin of error was ± 2.0% from the upper limit of measurement (when the temperature is 20 ± 5°C). Calculations were made by using standard methodology [42].

The hygroscopicity study of raw materials and granulated PDP was performed by placing the samples in a desiccator of two different environments: vapor of saturated sodium nitrite solution and water vapor. During the experiment, the temperature in the desiccators filled with saturated sodium nitrite solution was 20.5 ± 1.6°C, with humidity of 73.4 ± 0.8%. The temperature in the desiccator filled with water was 19.6 ± 0.4°C, and the relative humidity was 97.5 ± 1.1%. To determine the amount of moisture absorbed, the analyzed samples were weighed daily until constant weight was reached but no longer than 24 days. Every test sample was performed in triplicate.

The TA.XTplus Texture Analyzer from Stable Micro Systems (Stable Micro Systems Ltd, Godalming, UK) was used to characterize the stiffness and strength of the granules. Individual granules were loaded at a constant test speed of 0.01 mm/s into a cylindrical stainless-steel tool (5 mm in diameter) up to the deformation extent of 0.3 mm. The step motor used for the positioning of the tool had a distance resolution of 0.001 mm. The force necessary to drive the tool into the sample at a constant speed was recorded by a load cell (capacity: 50 N, accuracy: 5 mN). Once the threshold force (0.05 N) was exceeded, the data from the load cell was recorded at a frequency of 10 Hz to obtain the force–displacement curve [43].

2.4 Method for evaluation of agrochemical efficiency of fertilizers

The agrochemical assessment of the complex fertilizer was conducted by employing the method of modified micro-vegetative experiments *in vitro*. The experiment was conducted in plastic plant pots 4 cm × 4 cm× 4 cm in size, filled with the same amount (32 g) of mildly alkaline sandy loam. Four pre-sprouted seeds of winter wheat (*Toras*, Lithuania) were planted into each plant pot (16 small pots, for each sample). Artificial 1,000 lx light of daylight lamps was used. Pure PDP and granulated PDP were used for fertilization. The seedlings were fertilized every 4 days, six times, using 10 mL of 0.043 g/100 mL (K – 0.14%; P – 0.093%) concentration fertilizer solution for each plant pot. Wheat was grown until the sprouts started turning yellow because of almost exhaustive consumption of the nutrients (24 days).

2.5 Isolation and enumeration of microorganisms

To recover bacterial community, 10 g soil samples were suspended in 90 mL of sterile water. The number of soil microorganisms of main groups were isolated and enumerated for the serial dilution technique by applying 1 mL of soil suspension dilution on the surface of nutrient media for different microorganism groups with fourfold repetition. Meat-peptone agar (10.0 g/L peptone, 2.0 g/L Na_2HPO_4, 0.1 g/L KH_2PO_4, 0.5 g/L $MgSO_4$, 0.1 g/L $CaCO_3$, 0.005 g/L $FeCl_3$, 10.0 g/L starch, and 15.0 g/L agar) was used for ammonifying bacteria. Starch-ammonia agar (2.0 g/L $(NH_4)_2SO_4$, 1.0 g/L K_2HPO_4, 1.0 g/L $MgSO_4$, 1.0 g/L NaCl, 3.0 g/L $CaCO_3$, 10.0 g/L starch, and 15.0 g/L agar) was used for bacteria assimilating mineral nitrogen. The modified Han's (MH) medium (1.88 g/L carboxymethyl cellulose, 0.5 g/L sodium citrate, 2.0 g/L KH_2PO_4, 7.0 g/L K_2HPO_4, 0.1 g/L $MgSO_4 \cdot 7H_2O$, 1.0 g/L $(NH_4)_2SO_4$, 10.0 g/L agar, and 0.2 g/L Congo red) was used for cellulose degrading bacteria. Potato-dextrose agar (*Liofilhem*, Italy) was used for molds [44].

The number of microorganisms in the soil samples was expressed as a number of colony-forming units (CFU) per gram of soil samples.

2.6 Statistical analysis

The results were expressed as the arithmetic mean value of no less than two measurements ± standard deviation (SD). The results were calculated with 95% probability. In all cases, the significance level was $p \leq 0.05$. One-way analysis of variance was used to evaluate the differences of the mean values between groups. Depending on the accuracy of the method, the investigation of the properties of the same sample was performed 3–20 times; the arithmetic mean value of the determined values is presented in this study.

3 Results and discussion

Production of PDP commonly involves highly expensive raw materials, which are hard to obtain, for example, phosphoric acid is neutralized with potassium hydroxide or potassium carbonate. Replacing these costly substances with cheaper substituents would consequently make the final product cheaper thus increasing its availability. Using specific conditions of conversion reaction of potassium chloride and ammonium dihydrogen phosphate, PDP was obtained. This way of production does not require the use of expensive raw materials such as potassium hydroxide (KOH: from 1,100 €/t) and thermal phosphoric acid (H_3PO_4: 800–1,100 €/t), and replaces them with cheaper ones (KCl: 325–414 €/t and $NH_4H_2PO_4$: 500–700 €/t) [45].

Crystalline PDP was obtained by carrying out a conversion reaction between potassium chloride and ammonium dihydrophosphate. The obtained product was in the form of white crystals of various sizes and the chemical composition was highly similar to pure KH_2PO_4 [46]. The chemical composition of PDP contains not only potassium and phosphorus but also 1.89% nitrogen and 1.87% chlorine. In order to ensure that the synthesized product is stable and suitable for use, physical properties such as pH, humidity, and hygroscopicity were determined and compared with analogous properties of pure KH_2PO_4. pH of 10% solution of PDP was 3.8, humidity (after filtering) was 17–20%, and humidity (after drying) was 3.3%, while the pH value of 10% solution of pure KH_2PO_4 was 4.5 and humidity was 1.3%.

The purity of the PDP was assessed by measurements of heat capacity dependence on temperature (Figure 2). The data obtained show that the curve (Figure 2b) showing the change in heat capacity of the PDP corresponds to the temperature dependence of the heat capacity of the reagent pure PDP (Figure 2a). Identical peaks are seen in both curves from 220 to 240°C and from 260 to 290°C. Comparing the heat capacity of these two materials (PDP and pure KH_2PO_4), numerical values of the measured heat capacity are almost coinciding. Heat capacity is 0.88 J/(g K) and 0.93 J/(g K) at 25°C, and 0.96 J/(g K) and 1.03 J/(g K) at 60°C of PDP and pure KH_2PO_4, respectively. The other temperature dependences of the heat capacity measured

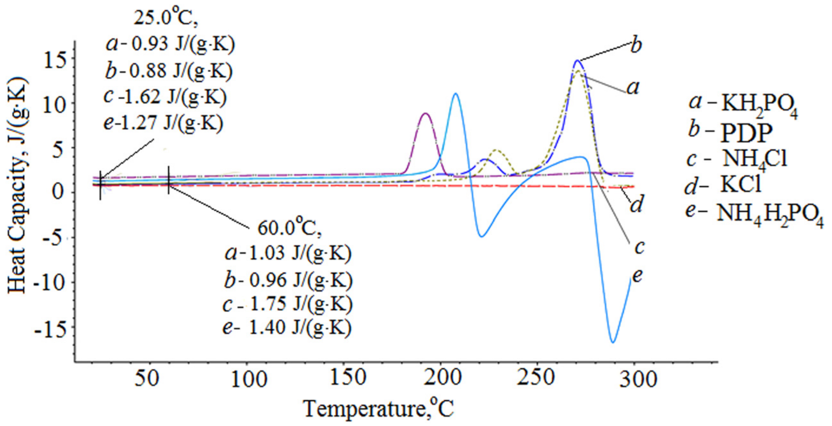

Figure 2: Heat capacity dependence on temperature.

for the reagents (NH_4Cl, KCl, and $NH_4H_2PO_4$) (Figure 2c–e) are fundamentally different. Therefore, it can be concluded that the synthesized substance is PDP.

In most cases, granular products are superior to powders because they stay loose for longer, do not dust, are easier to sift, do not leach surface water for longer, do not alter soil for a longer time due to the smaller surface area which is in contact with soil components. This way, granular products fertilize more efficiently [47]. This crystallized product may be used directly as potassium and phosphorus fertilizer. Alternatively, it could be used in the production of NPK fertilizers.

The published results [48] indicate that to produce granulated PDP with optimal properties, the use of water does not suffice. It is also necessary to use other additives in order to improve the physical and mechanical properties of the granules. Analysis of scientific publications on the binding materials used in the granulation technology suggests that if the aim is to obtain maximally pure PDP, cellulose should be chosen as the binder because it contains no additional nutrients used by plants. In addition, cellulose was chosen for its cohesion properties [49]. SEM photos show the structure of pure MC (Figure 3a) and its distribution among PDP crystals after granulation and crushing (Figure 3b). Element distribution in Figure 3 corresponds to the chemical composition of the substances. Carbon and oxygen were determined in the MC, while carbon, oxygen, potassium, phosphorus, a little nitrogen, and chlorine were found in the PDP spectrum, which agrees with the results of the chemical analysis [50].

In order to explore the distribution of physical and mechanical properties in the sample of granulated PDP (Figure 4), Texture Analyzer with Exponent software was employed (25 granules of either size category were used).

Analysis of the distribution of granulated PDP in terms of size (Figure 4a) shows that ~2.3 mm granules account for 40% of the total 1.5–3.5 mm fraction. The weight of the granules (Figure 4b) depending on their size in the total 1.5–3.5 mm fraction ranges from 5.7 to 28 mg. In this fraction, predominant granules weigh ~11 mg and

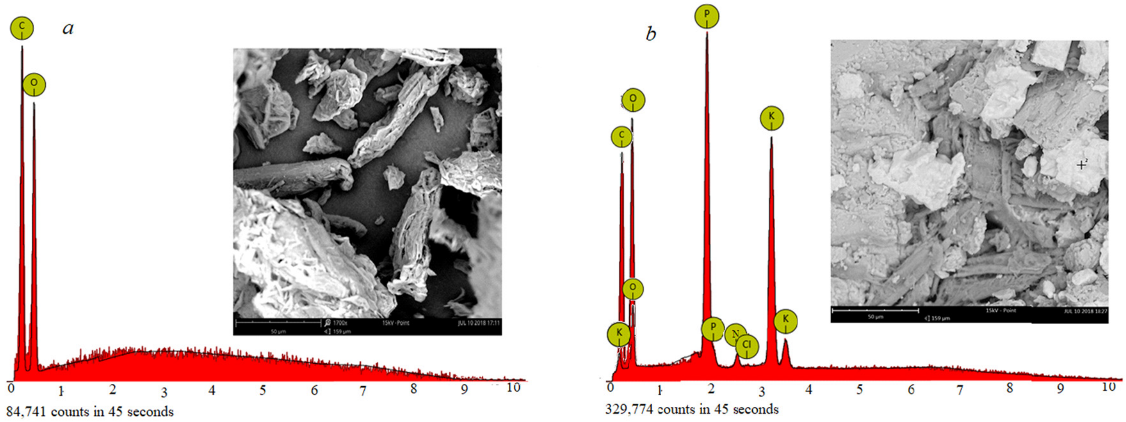

Figure 3: SEM photos and element distribution spectra of: (a) pure MC and (b) PDP granulated with MC and water and crushed.

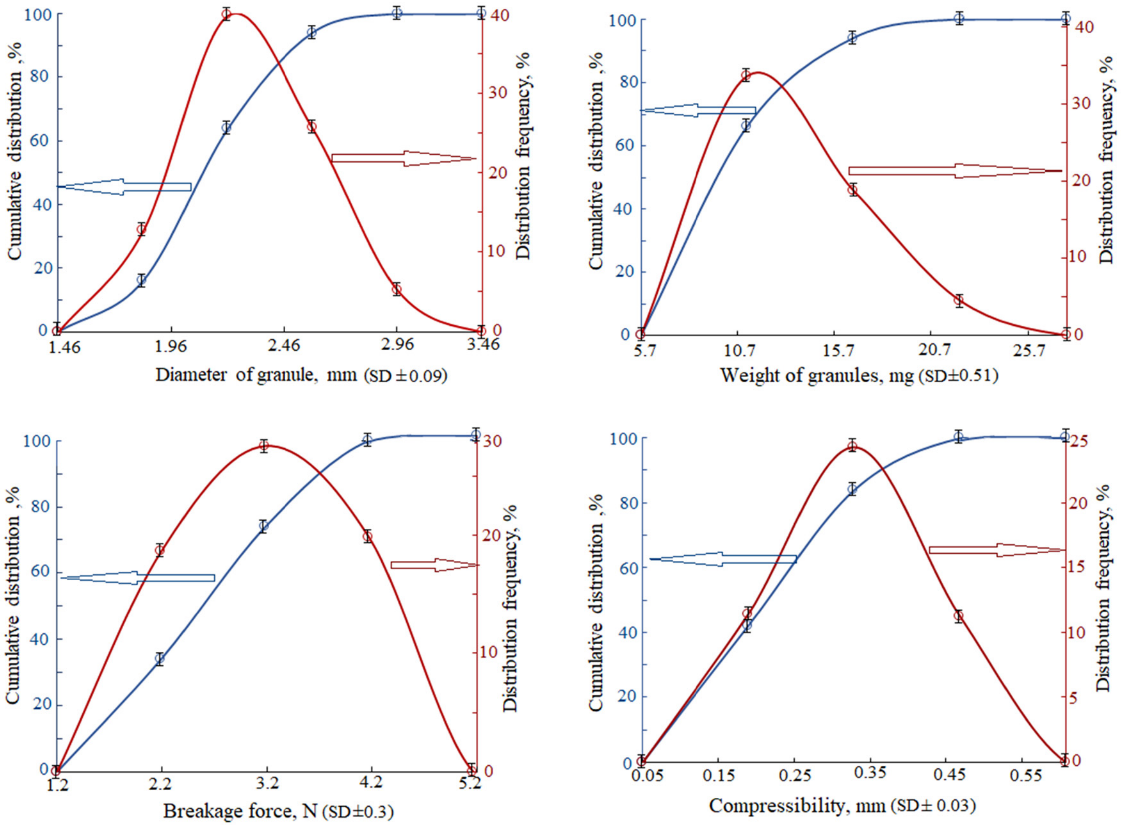

Figure 4: Physical and mechanical properties of the granulated PDP, produced by wetting with water and adding 5% MC.

make up 33% of the total batch. Breakage force (Figure 4c), which shows the strength of granules, was investigated to be in the range of 1.2–5.2 N. A force of 3.2 N was required to break 30% of the granules tested, about 20% of the granules were broken with a force of 2.2 N or 4.2 N, and the remaining (30%) did not fall within the study range. Figure 4d shows that granules were of low plasticity because 25% of the granules had the compressibility of 0.35 mm and more than 50% did not fall within the range studied. In summary, such a granular product can be used as a granular PK fertilizer.

Hygroscopicity of pure substances KH_2PO_4, MC, and granulated PDP was measured by observing the alterations of the weight of the fertilizer sample when water vapor absorption was taking place (Table 1). The experiment was performed by storing the test substances in desiccators and weighing the samples daily until constant weight or until approximately 100% humidity absorption (24 days) was achieved in two different conditions: (1) in the desiccator with saturated sodium nitrite solution at the temperature of 20.5 ± 1.6°C and the relative humidity of 73.4 ± 0.8% and (2) in the desiccator with water vapor at the temperature of 19.6 ± 0.4°C and the relative humidity of 97.5 ± 1.1%.

The obtained results showed that the maximum humidity of the PDP granules with MC (0.94 ± 0.15 wt%) and of pure MC (0.33 ± 0.04 wt%) was reached within 20 days, and that of the crystalline KH_2PO_4 (2.42 ± 0.31 wt%) was reached within 22 days, by storing the samples in a saturated sodium nitrite environment. It is clear that the addition of MC has a positive effect on the granular product as it becomes less hygroscopic.

To simulate stressful conditions, the hygroscopicity of the test samples was also determined by storing substances in the saturated water vapor environment. As it can be seen from the results, the amount of moisture absorbed was significantly higher than in a sodium nitrite solution vapor environment, and it resulted in 99.89 ± 0.27 wt% of the PDP granules with MC, 15.45 ± 0.31 wt% of the pure MC, and 99.99 ± 0.16 wt% of the crystalline KH_2PO_4. The results show that under these conditions, moisture absorption lasted for all 24 days until it reached almost 100%. It can be stated that under these conditions, the addition of MC did not have a positive effect on hygroscopicity of the granular product.

Agrochemical assessment of the produced PDP fertilizer was performed by conducting micro-vegetation tests, which yielded conclusions on the absorption of the nutrients

Table 1: Hygroscopicity of pure KH_2PO_4, MC, and PDP with MC

Sample	Absorbed moisture content (wt%)											
	Duration (days)											
	2	**4**	**6**	**8**	**10**	**12**	**14**	**16**	**18**	**20**	**22**	**24**
In saturated $NaNO_2$ solution environment												
KH_2PO_4	0.13 ± 0.15	0.16 ± 0.04	0.29 ± 0.19	0.45 ± 0.26	0.71 ± 0.17	0.87 ± 0.23	1.09 ± 0.11	1.45 ± 0.41	1.62 ± 0.08	2.05 ± 0.29	2.42 ± 0.14	2.42 ± 0.31
MC	0.05 ± 0.01	0.07 ± 0.01	0.11 ± 0.01	0.17 ± 0.06	0.21 ± 0.08	0.27 ± 0.01	0.28 ± 0.04	0.31 ± 0.02	0.32 ± 0.01	0.33 ± 0.04	0.34 ± 0.01	0.34 ± 0.03
PDP with MC	0.11 ± 0.05	0.12 ± 0.12	0.24 ± 0.14	0.39 ± 0.21	0.47 ± 0.18	0.53 ± 0.09	0.72 ± 0.17	0.86 ± 0.11	0.92 ± 0.22	0.94 ± 0.15	0.95 ± 0.14	0.96 ± 0.06
In H_2O environment												
KH_2PO_4	6.68 ± 0.09	17.54 ± 0.31	23.11 ± 0.11	31.89 ± 0.16	48.79 ± 0.14	53.12 ± 0.23	68.25 ± 0.08	72.26 ± 0.12	84.29 ± 0.25	92.45 ± 0.31	98.51 ± 0.05	99.99 ± 0.16
MC	0.39 ± 0.11	1.19 ± 0.23	3.59 ± 0.08	6.97 ± 0.15	9.33 ± 0.18	10.63 ± 0.21	12.81 ± 0.14	13.31 ± 0.16	14.49 ± 0.04	15.12 ± 0.18	15.21 ± 0.25	15.45 ± 0.31
PDP with MC	0.39 ± 0.09	1.40 ± 0.16	5.29 ± 0.17	10.16 ± 0.21	16.14 ± 0.19	28.59 ± 0.32	40.95 ± 0.09	63.53 ± 0.04	70.14 ± 0.05	80.38 ± 0.59	91.33 ± 0.19	99.89 ± 0.27

contained in the fertilizer and their impact on the plants. Before conducting agrochemical tests, clean soil tests were performed and corresponding results were obtained: P – 0.018% and K – 0.025%. In order to evaluate objectively the effect of the produced PDP with MC, pure KH_2PO_4 was used for fertilization and no fertilizer was used for control fertilization. Different plant parameters (length of leaves, green mass, ash mass) were investigated and the results are presented in Figures 5–7.

As it can be seen from Figure 5, fertilization had some influence on the leaf length of the crop. In both cases, when pure KH_2PO_4 and PDP were used, a similar average of leaves length was determined: 29.63 and 31.20 cm, respectively. This leaf length average is higher compared to control samples sprinkled with water only, which produced an average of 27.69 cm.

The results presented in Figure 6 show that the largest share of the green mass of wheat leaves was obtained when the PDP granulated with MC was used. In many cases, the lowest green mass of the wheat was obtained when it was not fertilized at all (i.e., treated with water only). Fertilization with pure KH_2PO_4 yielded almost the same green mass (average value of 0.471 g) as when treatment with water alone (average value of 0.441 g), but less than fertilizing PDP with MC (average value of 0.763 g). This suggests that plants have better absorbed nutrients from granular PDP.

Analyzing the amount of ash formed by plants burning process at 900°C temperature (Figure 7), it can be noted that in many cases, mass of the ash correlates with the green mass. Ash mass, which corresponds to the mineral part of the plant, was larger when green mass was larger, and leaves were longer. The largest mass of ash (average value of 0.019 g) was obtained when the PDP granulated with MC was used. The least mass of the ash was obtained when wheat was not fertilized at all. The pure KH_2PO_4 did not have any significant impact on the ash mass of the crop leaves, because the difference between the average value of ash when pure KP was used and ash of untreated samples was only 0.003 g.

Summarizing the influence of pure KH_2PO_4 and PDP, granulated with MC, on the growth of winter wheat seedlings, it can be stated that the effect of PDP is higher because the seedlings were longer, accumulated more green mass and more mineral substances. It can be assumed that this was due to the chemical composition of the PDP obtained by conversion. In this case PDP contains not only phosphorus and potassium but also a small amount (about 2%) of nitrogen, which is also a very important macronutrient. During the study period, 5% addition of MC had a positive effect on the growth of winter wheat.

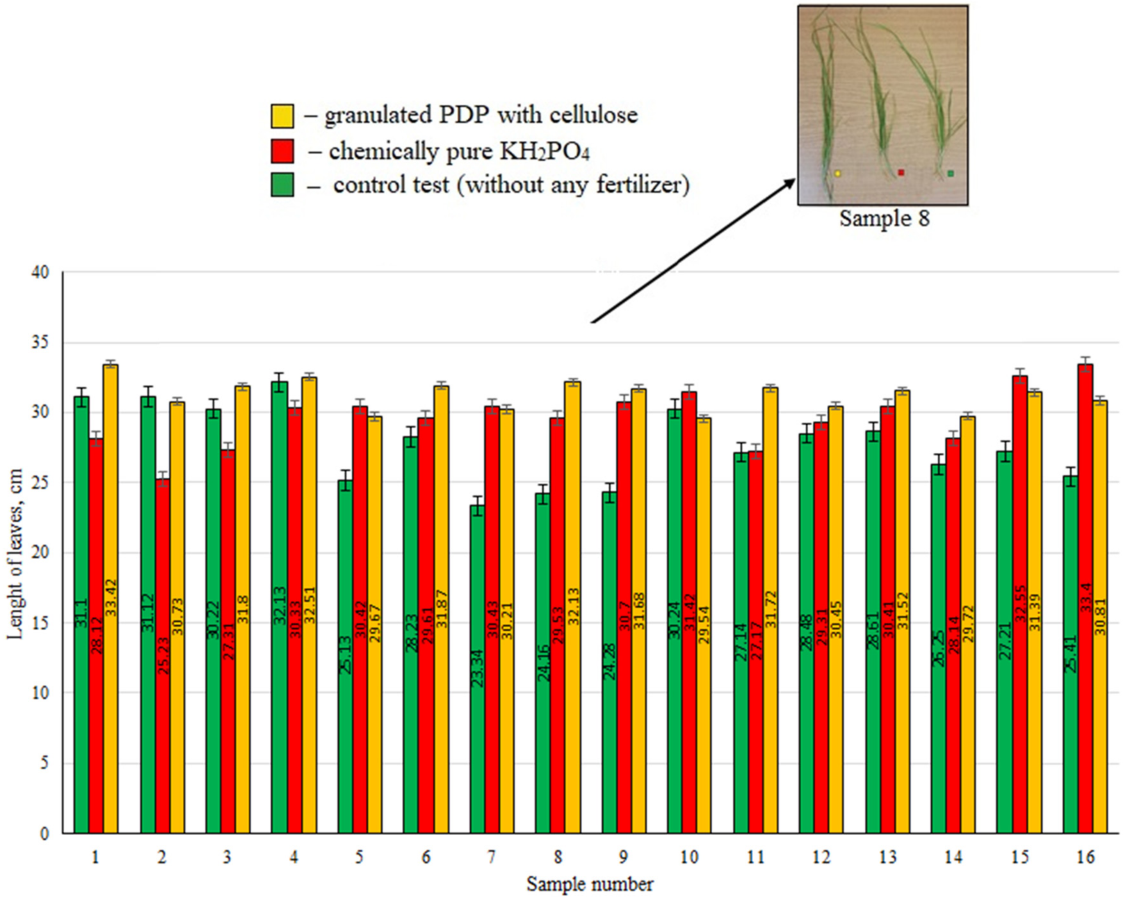

Figure 5: Length of leaves dependency on the type of fertilizers.

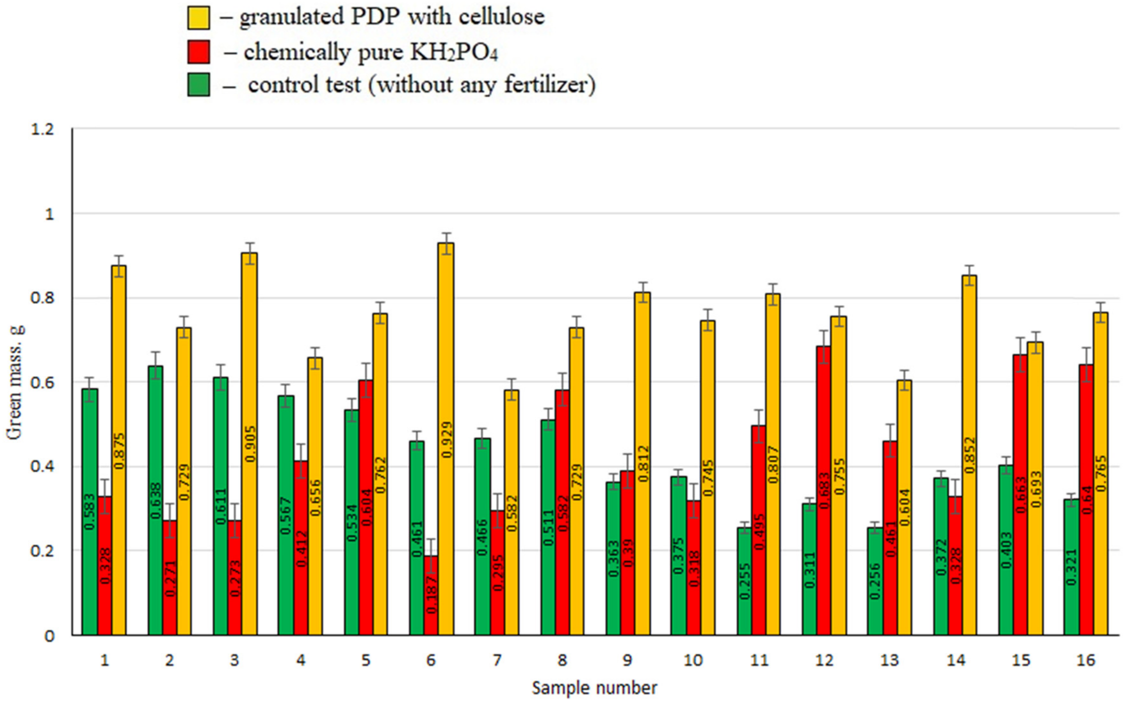

Figure 6: Leaf green mass dependence on the type of fertilizer.

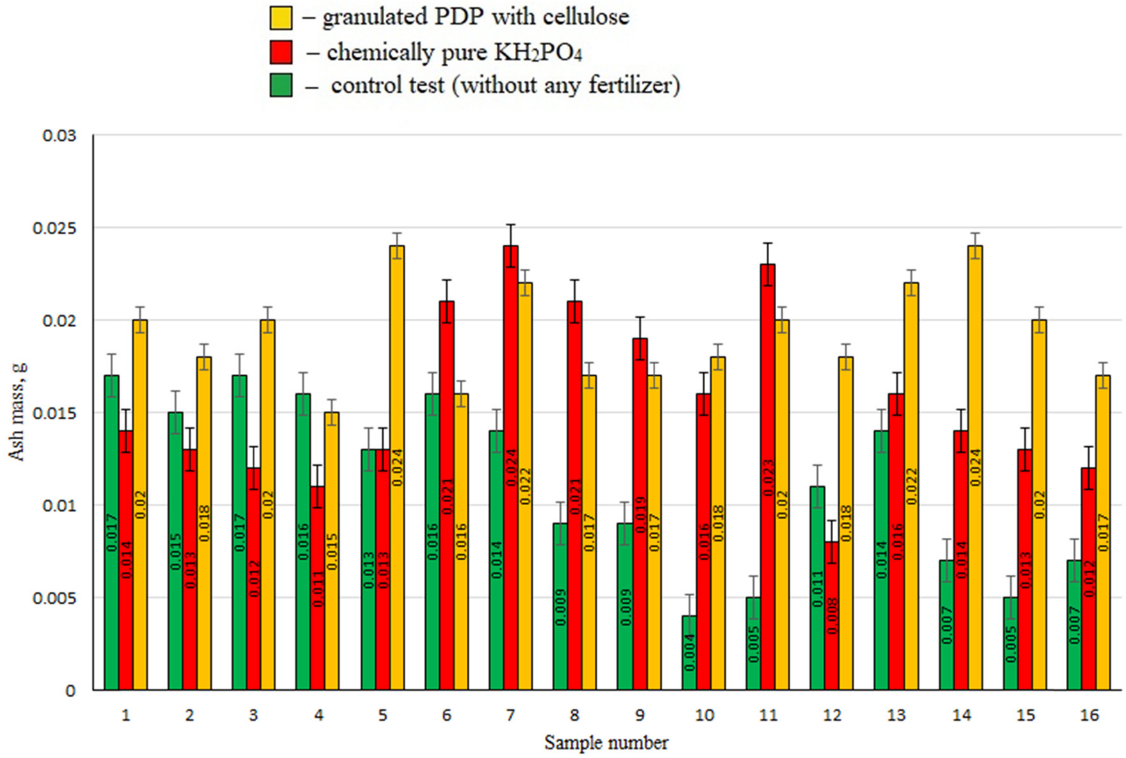

Figure 7: Leaf ash mass dependence on the type of fertilizer.

In accordance with Tan et al. [51], unbalanced fertilization and the use of concentrated fertilizers significantly deplete the soil and induce soil fertility problems, the change in various bacteria in the soil before and after fertilization was studied. Soil samples were taken from six plant pots (three from Sample 3 and three from Sample 7) in which wheat was grown in parallel under analogous conditions (control test, PDP granulated with cellulose, and chemically pure KH_2PO_4) and each sample was analyzed in triplicate. The result (Table 2) of the microbiological analysis of each sample is given as an approximate average of the three measurements. Comparing the presented data, it can be observed that the use of pure KH_2PO_4 slightly reduced the number of Spore b. bacteria (from 1.3×10^5 to 1.5×10^4 KSV/g), mineral nitrogen assimilating bacteria (from 1.2×10^5 to 1.6×10^4 KSV/g), and cellulose degrading bacteria (from 1.9×10^6 to 1.3×10^5 KSV/g). The number of actinomycetes remained practically unchanged (8.5×10^5 KSV/g control and 3.7×10^5 KSV/g after fertilization with pure KH_2PO_4) and there was a slight increase in molds (from 3.0×10^4 to 2.5×10^5 KSV/g).

PDP granulated with MC had fewer negative effects on soil bacteria. Wheat growth and fertilization did not decrease the number of any species of bacteria (Spore b., mineral nitrogen assimilating bacteria, and cellulose degrading bacteria) and there was a slight increase in the number of actinomycetes (from 8.5×10^5 to 2.9×10^6 KSV/g) and molds (from 3.0×10^4 to 1.4×10^5 KSV/g). This means that adding 5% MC had a positive influence on soil and not only maintained but also slightly increased the soil's microbiological activity. Our results are consistent with the scientists Mondejar et al. who stated that microorganisms decompose cellulose and hemicelluloses in soils, which makes them important players in the process of plant cultivation and making microflora and biomass in the soil adequate [52].

In summary, it can be stated that the method of production and granulation of PDP with the additive of MC developed and proposed by us allows to reduce the cost the production of KDP, increases its agro-efficiency, and does not adversely affect soil's microorganisms. In this way, it is possible to supply plants with macronutrients (potassium, phosphorus, and partly nitrogen) and to maintain the stability of the soil.

4 Conclusion

Crystalline PDP obtained via conversion reaction of potassium chloride and ammonium dihydrogen phosphate has similar physical properties to pure KH_2PO_4: pH of 10% solution is 3.8 and 4.5, and humidity is 3.3 and 1.3%,

Table 2: Bacteria and their content in the soil

No.	Soil sample	Ammonifying bacteria (KSV/g)			Mineral nitrogen assimilating bacteria (KSV/g)	Cellulose degrading bacteria, (KSV/g)	Molds, (KSV/g)
		Spore b.	Actinomy-cetes	Total number of bacteria			
1	Control (Sample 3)	$1.0 \times 10^5 \pm 0.03 \times 10^5$	$9.0 \times 10^5 \pm 0.25 \times 10^5$	$3.0 \times 10^6 \pm 0.38 \times 10^6$	$1.0 \times 10^5 \pm 0.19 \times 10^5$	$2.7 \times 10^6 \pm 0.12 \times 10^6$	$2.0 \times 10^4 \pm 0.31 \times 10^4$
2	Control (Sample 7)	$1.6 \times 10^5 \pm 0.03$	$8.0 \times 10^5 \pm 0.019 \times 10^5$	$2.5 \times 10^6 \pm 0.03 \times 10^6$	$1.4 \times 10^5 \pm 0.03 \times 10^5$	$1.0 \times 10^6 \pm 0.19 \times 10^6$	$4.0 \times 10^4 \pm 0.24 \times 10^4$
	Average value	1.3×10^5	8.5×10^5	2.8×10^6	1.2×10^5	1.9×10^6	3.0×10^4
3	Pure KH_2PO_4 (Sample 3)	$1.0 \times 10^4 \pm 0.19 \times 10^4$	$5.0 \times 10^5 \pm 0.25 \times 10^5$	$3.1 \times 10^5 \pm 0.12 \times 10^5$	$2.0 \times 10^4 \pm 0.28 \times 10^4$	$1.5 \times 10^5 \pm 0.25 \times 10^5$	$1.0 \times 10^5 \pm 0.02 \times 10^5$
4	Pure KH_2PO_4 (Sample 7)	$2.0 \times 10^4 \pm 0.19 \times 10^4$	$2.4 \times 10^5 \pm 0.05 \times 10^5$	$6.0 \times 10^5 \pm 0.19 \times 10^5$	$1.2 \times 10^4 \pm 0.04 \times 10^4$	$9.8 \times 10^4 \pm 0.19 \times 10^4$	$4.0 \times 10^5 \pm 0.17 \times 10^5$
	Average value	1.5×10^4	3.7×10^5	4.6×10^4	1.6×10^4	1.3×10^5	2.5×10^5
5	PDP with MC (Sample 3)	$1.6 \times 10^5 \pm 0.03 \times 10^5$	$3.0 \times 10^6 \pm 0.15 \times 10^6$	$7.0 \times 10^6 \pm 0.23 \times 10^6$	$3.4 \times 10^5 \pm 0.07 \times 10^5$	$4.2 \times 10^6 \pm 0.07 \times 10^6$	$1.0 \times 10^5 \pm 0.27 \times 10^5$
6	PDP with MC (Sample 7)	$3.0 \times 10^5 \pm 0.19 \times 10^5$	$2.8 \times 10^6 \pm 0.05 \times 10^6$	$6.4 \times 10^6 \pm 0.02 \times 10^6$	$5.0 \times 10^5 \pm 0.21 \times 10^5$	$2.4 \times 10^6 \pm 0.04 \times 10^6$	$1.8 \times 10^5 \pm 0.06 \times 10^5$
	Average value	2.3×10^5	2.9×10^6	6.7×10^6	4.2×10^5	3.3×10^6	1.4×10^5

respectively. The results of this study show that the PDP produced by the proposed method (which is enriched with 5% MC additive) has a positive effect on the growth of winter wheat during the active period and improves soil health. The effect of granulated PDP with MC on winter wheat was higher than that of pure KH_2PO_4 because wheat seedlings were longer (31.20 and 29.63 cm, respectively), leaf green mass was larger (0.763 and 0.471 g, respectively), and ash mass was greater (0.015 and 0.019 g, respectively). 5% MC additive had positive influence on soil and not only maintained but also slightly increased the soil's microbiological activity, because applying PDP with MC did not decrease the number of any species of bacteria (spore b., mineral nitrogen assimilating bacteria, and cellulose degrading bacteria) and slightly increased the number of actinomycetes (from 8.5×10^5 to 2.9×10^6 KSV/g) and molds (from 3.0×10^4 to 1.4×10^5 KSV/g). Since the breakage force of the obtained granulated product is sufficient – 3.2 N, the obtained fertilizer could be recommended for use on winter wheat, especially grown in soils with low potassium and phosphorus, thus maintaining soil health [53]. For a more detailed study, nitrogen could be added to fertilizer and additional research could be carried out.

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