The influence of biodegradable polymer coated fertilizers on the agrochemical parameters of the soil

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Abstract. This research paper is about the coating process with biopolymer (polyvinyl alcohol) as a coat of different fertilizer granules (Azafoska 16:16:16, potassium nitrate and magnesium nitrate as a core material) in presence of nitric acid. The biodegradable polymer layer provides uniform diffusion of minerals into the soil as the polyvinyl alcohol shell decays in the soil. Besides, Scanning Electron Microscope (SEM) and Energy – Dispersive X-ray spectroscopy (EDX - 3600) were carried out for the bio-modified fertilizers. The agrochemical changes of the soil in terms of macro – and microelements were also researched.

1. Introduction

By presenting the new innovative agricultural fertilizer systems, agrarians are strongly resorting to the use of controlled release fertilizers (CRF). According to Gabrys T., Fryczkowska B., the global market for polymer-modified fertilizers in the near future will reach around $ 20 billion. Besides, the average annual growth is up to 7%. High efficiency, ease of use and lowering costs for soil treatment allows to develop and maintain the biodegradable fertilizer market for long-term action. [1] The coating process (sulfur was used as a coat material) of the fertilizers was first developed in the United States in 1961, and commercial production began in 1978. Later in the USA, fertilizers were coated with sulfur potassium chloride and potassium sulfate. Later, the coating method was modified, where the surface of the fertilizer granules is coated with molten sulfur, and then, the defects on the surface of the sulfur coat are filled with molten paraffin wax. Paraffin by itself is not used as a coat material for fertilizers, as it causes sticking of the granules during transportation or packing process. To prevent from sticking of the fertilizer granules can be dusted with a diffused inorganic composite, for example: diatomaceous earth, clay and so on. The negative part of this type of fertilizer is that the nutrient core of the fertilizer (core) degradable faster, as the microorganisms in the soil rapidly destruct the wax wall (coat), resulting in an effect prolonged release action decreases in time. [2]

The other way of coating the fertilizer with a biodegradable polymer is to mix them in a right chosen solvent at certain temperature and substances of the coat to core material. One of the important aspects of receiving the wanted product is the mass ratio between starting materials. Biopolymer coated fertilizers are releases the macro – and micro-elements evenly, where membrane covering the granules is slowly decomposes within time. Such a coated fertilizer contains mineral elements – K, N, P, Mn in the quantity necessary for a particular plant. The importance of controlling the fertilizer release is due
to the nitrogen gas is slightly lighter than air and its volatilize to the atmosphere. Therefore, the main purpose of coating the fertilizer with a biodegradable polymer is to control the release of nutrient elements into the soil. NPK are known as macro-elements and most needed by plants. N (nitrogen) is necessary for new shoots and creation of a chlorophyll plant. P (Phosphoric acid) – promotes the ripening of flowers, fruits and develops the root system and K (potassium) does favourable affect on the process of photosynthesis and strengthens the immunity of plants, both against diseases and various pests.

NPK 16 :16 : 16, Mn(NO₃)₂ and K₂NO₃ are used complex granular fertilizers and mostly used until harvest period, except NPK 16 :16 : 16 which can be used for winter period for trees.

2. Methodology

The PVA was modified by starch biopolymer solution by a method reported in Key Engineering Materials, Volume 816. Polyvinyl alcohol was dissolved in water at 90 °C with continuous stirring for 40 min. In another tank, completely dissolved aqueous starch solution was added in PVA solution and the stirring process was continued for another 90 min at 90 °C. After set time the mixture was cooled down to room temperature 28 °C and followed by adding the aqueous citric acid solution. The mixing process was carried on for another 60 min, where the resultant Starch-polyvinyl alcohol evenly hydrogel was occurred. The received product was divided into 3 conical flasks at the same portions, where dissolved in water Azafoska 16:16:16, potassium nitrate and magnesium nitrate were added to the hydrogel at room temperature and magnetic stirrer mixing for 120 min. All 3 samples were left dry for another 48 hours at room temperature, where solid gel was received after water vaporization. The weight ratio of biopolymer to fertilizer was 5 %, in other words 1g of core material to 20g fertilizer. All 3 fertilizers coated with a modified PVA were applied to the soil and experimental areas were identified for each product.

After 3 month, from each experimental area, soil samples were collected before the modified product was applied into and after, therefore, further tests were carried out to determine the differences in a substrate.

The soil testing methods were: Determination of soil reaction (pH-water) according to GOST 26423-85; Determination of the electrical conductivity of the soil (EC) according to GOST 26423-85; Determination of the content of chloride ions (Cl⁻) and sodium ions (Na⁺) by potentiometric method in an aqueous extract; Determination of total humus content by the method of Tyurin; Determination of the content of mobile compounds of phosphorus and potassium according to the Machigin method in the modification of TsINAO according to GOST 26205-91; Determination of the content of metabolic calcium and metabolic magnesium by the trilonometric method in a 1.0 n extract of NaCl; Determination of the content of exchangeable sodium according to GOST 26950-86.

3. Results and discussion

3.1. Scanning Electron Microscope (SEM) (figure 1, 2 and 3) and Energy – Dispersive X-ray spectroscopy (EDX) (figure 4, 5 and 6) were carried out for the complex structures of coated Azofoska (NPK 16:16:16), Mn(NO₃)₂ and K₂NO₃ respectively

From the SEM images above (figure 1, 2 and 3) the presence of biopolymer can be illustrated and it’s uniformly distributed over fertilizer. Therefore, its reasonable to state that, at each time fertilizer (Azofoska (NPK 16:16:16), Mn(NO₃)₂ and K₂NO₃) was coated well. Additionally, for each obtained product, the chemical elementary analyses (by EDX-3600) were carried out to demonstrate the percentage of each component presented in the coated structure (figure 4, 5 and 6).
Figure 1. SEM image of biopolymer coated Azafoska (16:16:16).

Figure 2. SEM image of biopolymer coated Mn(NO$_3$)$_2$.

Figure 3. SEM image of biopolymer coated K$_2$NO$_3$. 
Figure 4. Elementary analysis of biopolymer coated Azafoska (16:16:16).

Figure 5. Elementary analysis of biopolymer coated Mn(NO$_3$)$_2$. 
By referring to the figures above (figure 4, 5 and 6) the presence of NPK and Mg found to be reasonable, hence, this illustration establishes the fact that, the structure of fertilizer wasn’t broken or changed. In the figure 4, where Azafoska 16:16:16 was coated with a polyvinyl alcohol modified with a starch, the presence of phosphorous is only 1.74%. Therefore, this could be to the area was detected in the sample or the coat material was incorrect portion in terms of NPK presence in the complex structure.

3.2 Soil tests
The soil samples were taken from the top layer of the soil (0 – 40 cm), then dried at room temperature and chopped with pester and mortar.

Table 1. Initial laboratory soil analysis results.

| Number of Sample | Soil layer, cm | pH water | Conductivity, µS/cm | Mass fraction of ions in the aqueous extract, mEq./100 g of soil | Humus, % | Cl⁻ | Na⁺ | P₂O₅, mg/kg | K₂O, mg/kg | Exchangeable cations, mEq/100 g. | Ca²⁺ | Mg²⁺ | Na⁺ |
|------------------|----------------|----------|---------------------|-------------------------------------------------------------|---------|-----|-----|------------|------------|-----------------------------------|-------|-------|-----|
| 1                | 0-40           | 8,11     | 0,103               | 0,068                                                       | 0,029   | 2,37| 62,6 | 206        | 18,14      | 7,04                              | 0,18  |       |     |
| 2                | 0-40           | 8,10     | 0,119               | 0,068                                                       | 0,029   | 2,77| 25,6 | 262        | 19,50      | 6,91                              | 0,20  |       |     |
From the table above (table 1), the soil analyses are given for the samples, where the coated fertilizer is not still applied. Therefore, in the tables bellow (table 2, 3 and 4), the laboratory analysis results are illustrated after coated fertilizers Azofoska (NPK 16:16:16), Mn(NO$_3$)$_2$ and K$_2$NO$_3$ were applied into the soil within 3 month.

**Table 2.** Laboratory soil analysis results where coated Azafoska 16:16:16 was enriched.

| Number of Sample | Soil layer, cm | pH water | P$_2$O$_5$, mg/kg | K$_2$O, mg/kg | Exchangeable cations, mEq / 100g. |
|------------------|----------------|----------|-------------------|---------------|----------------------------------|
|                  |                |          |                   |               | Machigin method                  |
|                  |                |          |                   |               | Ca$^{2+}$ Mg$^{2+}$ Na$^+$       |
| 1                | 0-40           | 8,01     | 71,1              | 349           | 18,09  6,53  0,20               |
| 2                | 0-40           | 8,00     | 49,8              | 402           | 19,59  6,29  0,19               |

From the table above (table 2), the fact can be stated, that the presence of nitrogen, phosphorous and potassium has increased in both samples, so, this tells that, macro-elements (NPK) are released evenly within time.

**Table 3.** Laboratory soil analysis results where coated Mn(NO$_3$)$_2$ was enriched.

| Number of Sample | Soil layer, cm | pH water | P$_2$O$_5$, mg/kg | K$_2$O, mg/kg | Exchangeable cations, mEq / 100g. |
|------------------|----------------|----------|-------------------|---------------|----------------------------------|
|                  |                |          |                   |               | Machigin method                  |
|                  |                |          |                   |               | Ca$^{2+}$ Mg$^{2+}$ Na$^+$       |
| 1                | 0-40           | 8,01     | 63,0              | 353           | 17,35  12,99  0,15              |
| 2                | 0-40           | 8,00     | 27,4              | 389           | 20,03  13,63  0,21              |

From the table above (table 3), the fact can be stated, that the presence of Mg$^{2+}$ has almost doubled, therefore, it states a good result of magnesium element release into the soil.

**Table 4.** Laboratory soil analysis results where coated K$_2$NO$_3$ was enriched.

| Number of Sample | Soil layer, cm | pH water | P$_2$O$_5$, mg/kg | K$_2$O, mg/kg | Exchangeable cations, mEq / 100g. |
|------------------|----------------|----------|-------------------|---------------|----------------------------------|
|                  |                |          |                   |               | Machigin method                  |
|                  |                |          |                   |               | Ca$^{2+}$ Mg$^{2+}$ Na$^+$       |
| 1                | 0-40           | 7.72     | 69,2              | 349           | 20,9   7,00  0,21               |


From the table above (table 4), the changes can be stated, as K\textsubscript{2}O, has almost doubled, hence, it represents well result of potassium release into the soil.

The other measurements are not changed too much, for example conductivity or pH water, they have just slightly changed within fertilizer application.

4. Conclusion
To sum up, the complex structure of starch modified polyvinyl alcohol with Azafoska 16:16:16, potassium nitrate and magnesium nitrate was obtained and tested in the results of fertilizer release into the soil. The product was enriched to the soil and showed very well results in terms of macro – and micro – elements availability during the time release (table 2, 3 and 4) for the plants in testing substrates. The SEM images (figure 1, 2 and 3) displays the allocation of biodegradable polymer in a mixture with Azofoska (NPK 16:16:16), Mn(NO\textsubscript{3})\textsubscript{2} and K\textsubscript{2}NO\textsubscript{3} respectively.

References
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