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OBTAINING ENVIRONMENTALLY FRIENDLY ENCAPSULATED MINERAL FERTILIZERS USING ENCAPSULATED MODIFIED PET

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Abstract. The article deals with the study of the prospects for the use of mineral fertilizers encapsulated in PET for bioremediation. This increases efficiency, prevents environmental pollution from undigested plants with plant nutrients, and minimizes the number of application operations. In addition, it disposes of a significant portion of PET waste, the uncontrolled accumulation of which poses a threat to the environment. The basic technological schemes of preparation of a film-forming composition and encapsulation of fertilizers are offered. The kinetic parameters of the process of release of batteries of granulated ammonium nitrate encapsulated with a film based on modified PET are determined.

Keywords: encapsulated mineral fertilizers, PET, nutrients, environmental hazards, release of nutrients.

1. Introduction

In modern times, the problem of synthesis of mineral fertilizers, the release rate of which should be regulated, is becoming increasingly important. In this case, the loss of soluble plant nutrients in the environment is reduced, the efficiency of their assimilation by plants is increased, the shelf life of fertilizers is extended, and thus the number of applications is minimized. This is important for agricultural crop production technologies but is especially relevant for biological reclamation technologies. This is because biological reclamation needs to ensure assimilation of the new land by the plants used for reclamation, the highest possible efficiency of fertilizer use, and the minimum number of application operations.

An important aspect is to increase the efficiency of fertilizer use and thus reduce the environmental impact of undigested nutrients. The root system of crops absorbs only a part of fertilizers, namely: Nitrogen compounds 50–60 %, potassium 50–60 %, phosphorus 10–25 % (Hrekov et al., 2008). This leads to the emergence of environmental problems: Salinization of soils, contamination of surface water, groundwater and groundwater by particles of fertilizers. Most mineral fertilizers are salts that dissolve quickly in water during periods of heavy rainfall and tend to migrate into the soil, especially during their application and during the growing season (Miliutenko et al., 2014).

Pollution of the environment occurs through dissolved fertilizers that are washed out of the soil

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environment during precipitation. Nitrate concentration in surface and ground waters increases and the process of eutrophication of water bodies intensifies, resulting in water blooms. With a large amount of nitrogen, phosphorus and potassium compounds dissolved in water, lakes, ponds, engineered water bodies, rivers and reservoirs are susceptible to eutrophication. Populations of blue-green cyanobacteria, which produce toxins as they grow and develop, are increasing. These toxins are highly toxic natural compounds that alter the metabolism of proteins and carbohydrates and have negative effects on the central nervous system (Tomaszewska et al., 2006). Reduced productivity of water bodies is due to the increase in nitrite and nitrate concentrations associated with fertilizer use. Highly carcinogenic nitrosamines are formed by the interaction of nitrites and nitrates with biologically active amines or nitrogenous substances in water bodies and are formed by the decomposition of algae at the end of their life cycle (Global..., 2013).

Exceeding the amount of fertilizer will result in a decrease in the fertilizer utilization rate and loss of nutrients. Each soil type requires a different amount of fertilizer. Increasing the rate of chemicalization must be adjusted to the specifics of fertilizer behaviour in the soil and the balance in the soil-fertilizer-plant system. Fertilizer application provides nutrients to the root system of rotational crops, but it is necessary to ensure that crop nutrient needs are met by applying the amount necessary to maintain soil fertility at a reasonable cost (Ihnatenko et al., 2005). This prevents contamination of water by fertilizer residues.

A promising method of releasing nutrients from the fertilizer particles into the soil solution is to encapsulate the mineral fertilizer particles with capsules (encapsulated mineral fertilizers). The capsules that encase the fertilizer granules are permeable to aqueous solutions and water. They slow the release of nutrients into the soil environment. This slowdown is mainly determined by the thickness and composition of the capsule. If the capsules are impermeable but can biodegrade in the soil environment, the granule contents are released into the soil environment as part of this biodegradation. In this release variant, it is not the intensity of dissolution of the mineral fertilizer granules that is regulated, but the onset of biodegradation of the capsule (Zaharenko, 2000; Hospodarenko, 2002).

Despite a large number of developed film-forming materials (Ovchinnikov et al., 2011), the production of encapsulated mineral fertilizers is small, mainly nitrogen fertilizers, accounting for only 0.4–0.5 % of the world production (Wielgosz et al., 1996). Such a low production volume of encapsulated mineral fertilizers is associated with a significant increase in their cost compared to conventional granular fertilizers, mainly due to the cost of film-forming compositions. One of the impediments to the mass use of encapsulated fertilizers is their higher cost compared to conventional granular fertilizers, despite their agronomic and environmental attractiveness. A promising way to increase the availability of encapsulated mineral fertilizers for mass agricultural use is to use polymer wastes and improve coating technology (Malovanyy et al., 2016, Synelnikov et al., 2019). Polymer waste of industrial origin is usually processed directly in enterprises. At the same time, polymer waste from households ends up almost entirely in landfills. The use of the capsule as a material for encapsulation of mineral polymer waste will, on the one hand, provide a competitive price and wider use of encapsulated fertilizers, and, on the other hand, solve the problem of plastic waste, the uncontrolled accumulation of which in the environment poses significant environmental hazards (Malovanyy et al., 2020). The possibility of using plastic waste for encapsulation of mineral fertilizers arises from the considerable amount of this type of waste suitable for use as a capsule material (Vashchuk et al., 2010). The use of different types of plastics to produce a capsule with prolonged action on the granules of mineral fertilizers is a promising way to dispose of it. In the soil environment, this capsule is biodegradable under the influence of the environment and releases the target component (Nagurskyy et al., 2022).

The main parameter that determines the duration of the release of mineral nutrients by the diffusion mechanism is the permeability of the envelope. This value depends on the coefficient of internal diffusion of the shell material and its thickness. The polymer shell of the encapsulated fertilizer is not a nutrient carrier and is considered ballast. In this case, it is logical to apply a shell with a minimum thickness. The minimum thickness of the shell that can fulfil its functional purpose is determined by the physicochemical properties of the film former and the parameters of the device. Thus, according to data (Nagurskyy, 2012), the minimum thickness of the polymer shell (polystyrene-based) of encapsulated artificial fertilizers, where the kinetics of release of elements from the encapsulated particle was predicted, was 10–50 μm. In the case of encapsulated fertilizers for bioremediation, the requirements for the period of biodegradation of the capsule are not as stringent from the standpoint of environmental safety of the soils. Finally, the remediated soils will not be used for agricultural technologies, they will not be subjected to further agrotechnical operations, and the presence of self-decomposed plastic will not cause additional environmental hazards.

2. Results and Discussion

For the research, the options for using polymers that are part of household waste (Nagurskyy, 2012) were considered: polyethylene, polypropylene, polyvinyl chloride, polyethylene terephthalate. Granular synthetic mineral fertilizer – ammonium nitrate – was used as a base fertilizer.

Polymeric materials used as a basis for film-forming compositions must meet the following basic conditions:

– ensure the appropriate intensity of the release of components of the mineral nutrient;

– be safe for the environment - after the release of fertilizer components, the casing material must be neutralized in some way to avoid contamination of the soil environment with polymers.

– must have an organized collection system to ensure continuity of raw materials for the production of encapsulated fertilizers.

Polyethylene terephthalate (PET) could meet these conditions, provided it is soluble, which plays a crucial role in the production of a film-forming composition and encapsulation of mineral fertilizer granules. Finally, for PET, the system of separate collection (used PET bottles) and recycling (secondary raw materials for fibre production, PET bottles, films for thermoforming, binding tape, etc.) is widely developed in Ukraine and other countries. Therefore, we decided that the best option is to use PET, either in the melt or modified, to ensure solubility in civil organic solvents.

The shell on the surface of the encapsulated fertilizer granules contains various functional additives besides the polymer. Mixing of the components of the shell, as well as their application on the surface of the mineral fertilizer granules, is best done in a liquid state. This problem can be solved in two ways:

1) dissolving the necessary components with the help of solvents;

2) mixing the components of the composition in the PET melt.

The use of melts as shell formers requires proper equipment to maintain the correct temperature from the storage tank to the spray nozzle. Since the melting point of PET is 280 °C, the use of melts will result in additional heat consumption. It is also not recommended to heat nitrogen granular fertilizer above 70 °C, as this may lead to its thermal decomposition. The method of application of solutions is free from these disadvantages, but in this case increases the cost of materials, evaporation and purification of liquefied exhaust air from solvent vapours. From the point of view of environmental protection and minimal material costs, the use of aqueous solutions would be the most acceptable. PET, however, is insoluble in water and in many organic solvents. It dissolves only at a temperature of 40–150 °C in phenols and their alkyl and chlorine-substituted, aniline, benzyl alcohol, chloroform, pyridine, dichloroacetic and chlorosulfonic acids, cyclohexanone and so on. In our opinion, the use of acids or aromatic solvents to dissolve PET acids to obtain film-forming compositions is not appropriate due to the aggressiveness and high toxicity of these substances. This leads to excessive material and energy costs in the extraction of coated fertilizers and, consequently, to lower availability for mass agricultural production.

Modification of PET wastes allows for improving their solubility, which plays a crucial role in preparing a film-forming composition and coating of mineral fertilizer granules. We proposed to use a well-known modification method for encapsulation, namely the reaction of alcoholism with diethylene glycol (Gak et al., 2005).

The modification of PET with diethylene glycol (DEG) was carried out in the laboratory setup shown in Fig. 1. Reactor 1 was loaded with PET waste in the form of flakes that had been primarily processed in a specialized plant and diethylene glycol in a molar ratio of PET: DEG 1: 0.5. The contents of the reactor were heated to a temperature of 493 K. The reactor was then heated to the required temperature. Two hours after reaching the required temperature, the vacuum pump 5 was turned on and the ethylene glycol was distilled off from the reactor at a residual pressure of 20 kPa. The ethylene glycol condensate obtained in refrigerator 3 was collected in collection 4. The total process time was 3.5 hours. As a result of the interaction, ethylene glycol is displaced by diethylene glycol to give a product soluble in ethyl acetate.

The particles were coated with a solution of the film-forming agent in the apparatus of the fluidized state with periodic action, the schematic diagram of which is shown in Fig. 2.

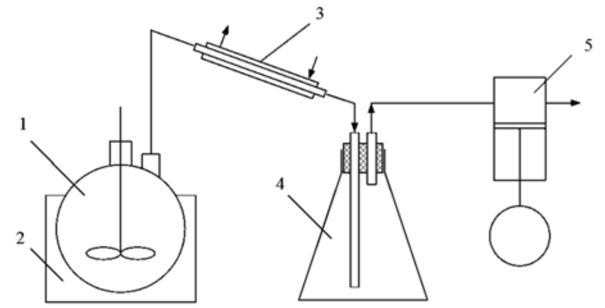

Fig. 1. Installation of the modification of PET waste with diethylene glycol: 1 – reactor; 2 – thermostat; 3 – refrigerator; 4 – condensate collector; 5 – vacuum pump

The device consists of a working cylinder with constant cross-section (1), in which a gas distribution grid 3 and a pneumatic nozzle (2) are mounted. The liquefied air is heated to the desired temperature in the heater 6 and blown through the device by a fan 16. The temperature in the unit is controlled and regulated by an electronic control unit (9). The flow of liquefied air is controlled by an inclined differential pressure gauge (14) connected to the Pitot tube (13). The film-forming solution from meter (5) is fed to the pneumatic nozzle (2) via the metering pump (6), which is supplied by compressor (5).

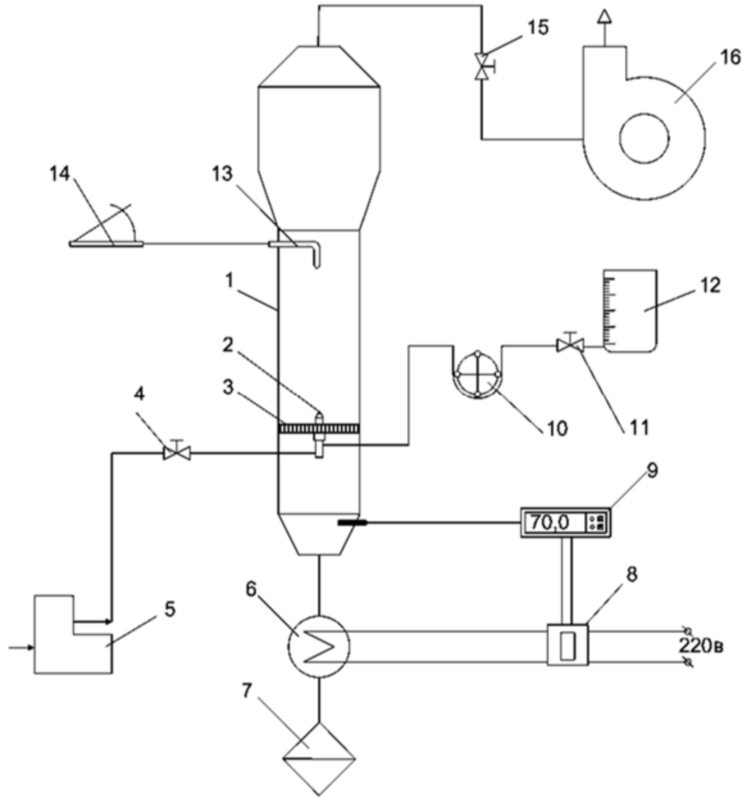

Fig. 2. Scheme of the experimental equipment for applying film coatings to solid particles: 1 – product tank; 2 – nozzle; 3 – gas distribution grid; 5 – compressor; 6 – heater; 7 – air filter; 8 – relay; 9 – regulator meter RT -0102; 10 – metering pump; 12 – meter; 13 – Pitot tube; 14 – differential pressure gage; 16 – fan; 4, 11, 15 – control valve

Encapsulation of solid particles with a water-insoluble film of different thicknesses was carried out using modified PET, dissolved in ethyl acetate. The process was carried out at an operating temperature of 70 °C and a fluidization number of 1.5–2.0. The working chamber of the device was loaded with particles with a total mass of 0.25 kg, the air was supplied at the required rate, the required temperature was set, and the film-forming solution was introduced into the spray nozzle through a metering pump. The encapsulation process was continued until an envelope of the desired thickness was obtained.

The most important parameter that determines the duration of the release of mineral substances by the diffusion mechanism is the permeability of the coating. This value depends on the coefficient of internal diffusion of the shell material and its thickness. The diffusion of ammonium nitrate solution through a polymer film of different thicknesses was studied in a conductometric apparatus using a method based on the measurement of the electrical conductivity of solutions (Fig. 3).

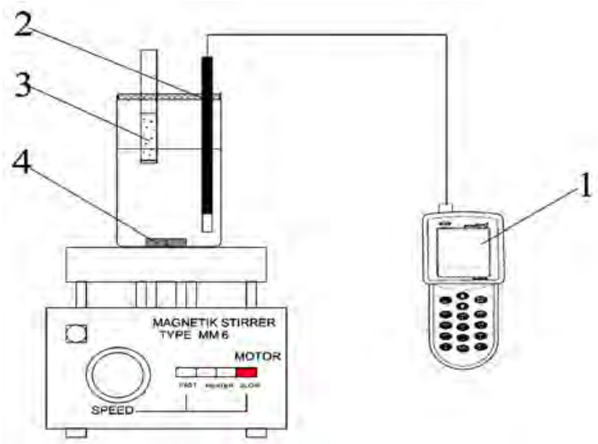

Fig. 3. Scheme of conductivity installation for measuring the specific conductivity of electrolyte solutions:
1 – *Sension* 5 portable conductivity sensor; 2 – measuring electrode; 3 – glass cylinder; 4 – magnetic stirrer

The instrument consists of a *Sension 5* portable conductivity sensor (1) and a measuring cell. The measuring cell consists of a measuring electrode (2) and a glass cylinder (3). The cylinder is filled with a saturated solution of ammonium nitrate. The opening of the cylinder, which is immersed in the measuring cell, is hermetically sealed with a polymer film of the material under investigation of a certain thickness. Mass transfer from the cylinder into the volumetric flask occurs by diffusion through the polymer film and by mass transfer from its external surface into the medium of distilled water. To eliminate the external diffusion resistance for the mass transfer process, the water in the flask was intensively mixed with a magnetic stirrer (4).

The results of the experimental studies are presented graphically in the form of dependences of the concentration of ammonium nitrate C_1 (kg/m^3), which passed through a polymer film of different thicknesses in distilled water with a volume of 400 ml, on the time τ (h) (Fig. 4).

The diffusion coefficient D was determined using the equation (Hiroko Akiyama et al., 2000):

$$\frac{dM}{d\tau} = \frac{D}{\delta} F(C_s - \bar{C}) \,, \qquad (1)$$

Where δ is the thickness of the polymer film, m; F is the area of the polymer film through which the salt solution diffuses, m^2; Cs is the saturation concentration of ammonium nitrate, kg/m^3; $\bar{C}$ is the average concentration of ammonium nitrate in water during the study, kg/m^3; τ is the time of the process, p.

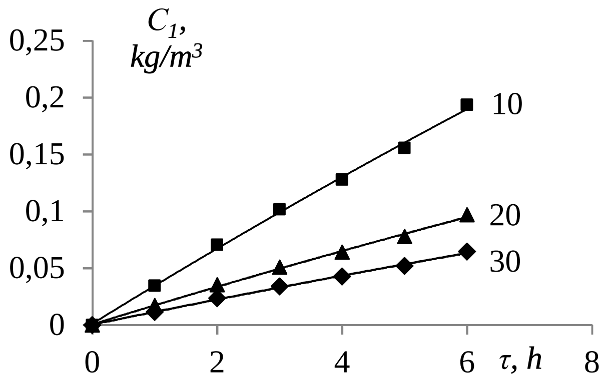

Fig. 4. The results of experimental studies on the diffusion of ammonium nitrate solution through a polymer film of different thickness δ (μm)

Studies have shown that the average value of the diffusion coefficient of ammonium nitrate through the PET film is 7.4·10–12 m^2/s. The analysis of the obtained result shows that PET can be used as a basis for a film-forming composition for the preparation of encapsulated granular mineral fertilizers with a thickness of δ≈10–50 μm and a release period of the base fertilizer of 3 months.

The basic technological scheme of preparation of a film-forming composition for encapsulation of granular mineral fertilizers is offered (Fig. 5). PET Waste in the form of flakes and diethylene glycol are loaded into the reactor (1), where the process of alcoholism is carried out. The ethylene glycol released during the reaction is distilled off from the reactor, condensed in the condenser (2) and fed to the collector (3). After the reaction, the product is loaded into the crusher (4), where it is ground to a size of < 0.5 mm.

The crushed modified PET is fed to the mixer (5), where the solvent and (if necessary) compound additives are also loaded. Ethyl acetate was used as the solvent. The solution of a film-forming composition obtained according to this scheme was used for encapsulation of granulated ammonium nitrate.

An important indicator of the coating quality is the uniformity of the shell thickness. This allows you to predict the intensity of the release of components into the soil environment and accordingly produce encapsulated fertilizers with the required shelf life. To study the coating quality in the cylindrical fluidized bed apparatus, which operated in a periodic mode, encapsulation of granulated ammonium nitrate was carried out.

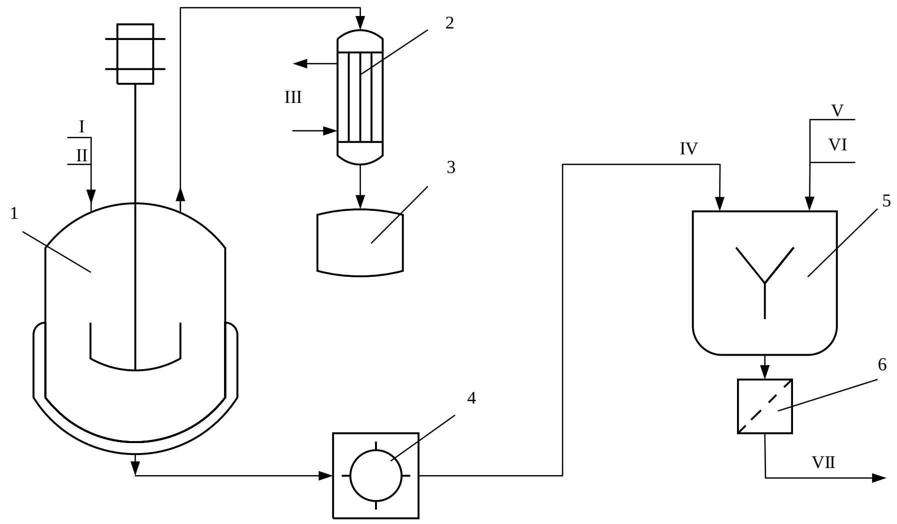

Fig. 5. Technological scheme of film-forming composition preparation:
1 – reactor; 2 – ethylene glycol condenser; 3 – ethylene glycol collector; 4 – crusher; 5 – mixer; 6 – sieve; I – PET; II – diethylene glycol; III – coolant; IV – modified PET; V – solvent; VI – compound additives; VII – film-forming composition

The amount of coating was 10 % and 20 % by weight of fertilizers, corresponding to an average film thickness on the surface of ammonium nitrate particles of 5.74 10^{-5} m and 11.48 10^{-5} m, respectively. The solubility of the obtained fertilizers was tested experimentally by the conductometric method. European standard EN 13266: 2001 (DSTU EN 13266: 2017, 2017). The quality control of encapsulation was monitored by the type of release curve.

The results of the study are graphically shown in Fig. 6.

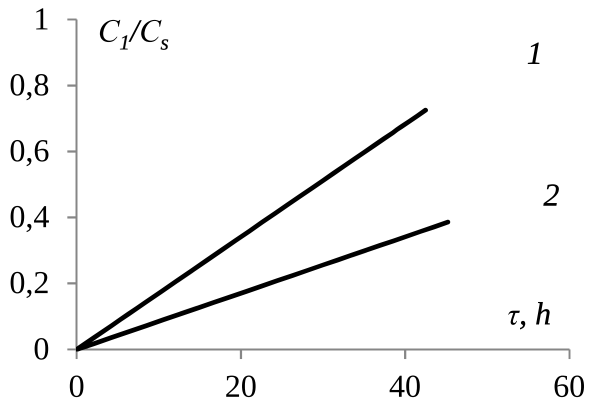

Fig. 6. Dissolution kinetics of encapsulated ammonium nitrate coated based on modified PET with different thickness (wt%): 1 – 10, 2 – 20.

The obtained results (Fig. 6) show that the kinetic curves of dissolution are predictable, and the process is uniform without sharp decreases or increases. This is the evidence of a uniform, high-quality coating which allows obtaining long-acting mineral fertilizers with the required release time.

3. Conclusion

1. The research results confirm the prospects for the use of encapsulated fertilizers for biological reclamation, encapsulated PET, which provides greater efficiency, prevents environmental pollution by undigested plant nutrients, minimizes the number of application operations and allows additional disposal of a significant part of PET – uncontrolled waste.

2. The basic technological schemes for the preparation of a film-forming composition for encapsulation of granular mineral fertilizers by modification of PET waste with diethylene glycol and the technological scheme of encapsulation using fluidized bed apparatus are offered.

3. Based on experimental studies, the kinetic parameters of the process of release of batteries of granulated ammonium nitrate encapsulated in a film based on modified PET were determined.

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