IR SPECTROSCOPIC AND THERMAL INVESTIGATION OF ENCAPSULATED UREA WITH STABILIZED SOLUBILITY

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Annotatsiya Ushbu ishda poliakrilamid qo‘shimchasi bilan karbamid eritmasi asosida olingan kapsulalangan o‘g‘itlarning IK-spektroskopik va termogravimetrik tadqiqotlari amalga oshirildi. Tadqiqotlar shuni ko‘rsatdiki, kapsulalangan karbamid olish orqali uning tuproqdagi eruvchanligi va yo‘qotilishini kamaytirish hamda agroximik samaradorligini oshirish nafaqat eruvchanlikning pasayishiga, balki karbamidning xossalarining yaxshilanishiga ham olib keladi. Bu jarayon karbamid granulalarining yanada mustahkam va ixcham kristallik tuzilmasining shakllanishiga ijobiy ta’sir ko‘rsatadi.

Kalit so‘zlar: karbamid, poliakrilamid, azot, erish, yopishqoqlik, granula mustahkamligi, zichlik, erish tezligi

Аннотация В работе выполнен ИК-спектроскопические и термогравиметрическое исследования капсулированных удобрений полученных на основе плава карбамида с добавкой поли-акриламида. Выявлено что получения капсулированного карбамида для снижения растворимости и потери карбамида в почве и повышения агрохимический эффективности не только воздействует на снижения растворимости в почве, но и оказывает положительное влияние на свойства карбамида, происходит воздействие на формирование более устойчивой и компактной кристаллической структуры гранул карбамида

Ключевые слова: карбамид, полиакриламид, азот, растворения, вязкость, прочность гранула, плотность, скорость растворения**.**

Annotation. In this work, IR spectroscopic and thermogravimetric studies of encapsulated fertilizers obtained on the basis of molten urea with the addition of polyacrylamide were carried out. It was revealed that the production of encapsulated urea, aimed at reducing solubility and minimizing urea losses in the

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soil as well as increasing agrochemical efficiency, not only decreases its solubility in the soil, but also has a positive effect on the properties of urea. The encapsulation process promotes the formation of a more stable and compact crystalline structure of urea granules

Keywords: urea, polyacrylamide, nitrogen, dissolution, viscosity, granule strength, density, dissolution rate.

Introduction

Over the past two decades, the development and commercialization of slow-release and controlled-release fertilizers have advanced significantly, with the primary goal of reducing environmental problems associated with excessive fertilizer use. Various methodologies have been investigated and improved, including chemical and physical reactions, incorporation into carriers with porous and layered structures, as well as coating techniques.Global challenges such as drought and desertification highlight the need for controlled-release fertilizers that not only regulate nutrient release but also enhance soil moisture retention. Particular attention is given to the development and application of environmentally friendly starch-based hydrogels as fertilizer carriers and water-retaining agents for controlled-release systems, especially starch-based superabsorbent polymers obtained by graft polymerization with acrylamide.This review covers both scientific issues—including the microstructure of superabsorbent polymers and the mechanisms of nutrient release—and technical development aspects, such as polymerization technologies, multi-initiation processes, methods of fertilizer loading into hydrogels, and others. Starch, as a biodegradable and renewable carbohydrate polymer, offers advantages due to its high chemical stability and reactivity.Technologies for producing superabsorbent polymers have evolved from traditional batch polymerization in aqueous solutions to more efficient solvent-free reactive extrusion. The advantages of controlled-release systems based on superabsorbent polymers include improved soil aeration, prevention of soil degradation, minimization of water evaporation, environmental pollution control, reduction in plant mortality, and prolonged nutrient retention in soil [1].

Fertilizers with prolonged action are a promising and highly demanded agrochemical product, the development of which is aimed at solving a number of critical practical problems in agriculture—primarily reducing nutrient losses and, consequently, lowering the cost and energy intensity of transportation and application processes. The development of biosystems capable of providing slow nutrient release has become a central focus of many researchers.In the present study, a slow-release system was obtained by mixing molten poly(butylene succinate) filled with 30 wt% urea and 5 wt% montmorillonite clay. The optimal

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formulation increased the diameter of lettuce by 67%, whereas conventional urea application resulted in only a 48% increase in diameter [2,3].

A study presented in [4] describes the preparation of a new type of controlled-release fertilizer coated with polyurea. Granulated urea was first converted into liquid urea by heating, which served as the coating fluid. Through uniform spraying, the urea granules were coated with polyurea synthesized via the reaction of isocyanates with liquid urea. The influence of various modifiers on the nitrogen-release characteristics of polyurea-coated urea was investigated. The results showed that the new fertilizer reduced the nitrogen release rate and exhibited excellent controlled-release properties. The polyurea coating materials are capable of biodegrading in soil.

The historical inefficient use of nitrogen fertilizers due to N losses from the soil is a pressing issue in extensive agricultural systems. The present study tested the hypothesis that granulating synthetic nitrogen fertilizer with a natural organic carbon source, specifically brown coal, would reduce nitrogen losses from the soil system. After application to bare soils, the urea–brown coal granules reduced nitrous oxide emissions by up to 40%, decreased leaching of mineral nitrogen, and maintained higher N levels in the topsoil compared to the use of conventional urea alone. A reduction in gaseous N losses without compromising plant N uptake was also observed in sown soils treated with urea–brown coal granules [5].

Urea is the most widely used fertilizer in the world; however, it is lost to the environment through processes such as leaching, volatilization, and denitrification. As an alternative to prevent these losses, controlled-release and slow-release fertilizers have been proposed. Such systems allow plants to receive the necessary amount of nutrients for growth while simultaneously reducing environmental pollution. These systems can be manufactured from both synthetic and natural sources, such as wheat gluten proteins, polysaccharides, and composites (polymeric matrices, mixtures of wheat, gluten, and urea, etc.). This review presents an approach to sustainable agriculture through the application of controlled-release and slow-release fertilizers using inorganic and organic raw materials, with a particular focus on the use of wheat gluten proteins and urea in the development of these systems [6].

Nitrogen fertilizers play a vital role in increasing crop production and ensuring food security. The world's population, which is growing exponentially, has reached nearly 7.5 billion. Unbalanced use of nitrogen fertilizers can lead to N deficiency, affecting plant growth and development, while excess N has significant negative impacts on the environment and human well-being. These impacts include biodiversity loss, eutrophication, nitrate accumulation in water bodies, soil and water acidification, nitrous oxide emissions, and human health risks due to

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exposure to ozone and particulate matter.In agricultural systems, when fertilizers are applied to crops, they are primarily subject to losses through ammonia (NH_3) volatilization, nitrate (NO_3^-) leaching, and denitrification. Nitrogen loss in the forms of NH_3 and NO_3^- largely depends on factors such as temperature, soil pH, soil moisture, soil properties, plant characteristics, and seasonal fluctuations. A comprehensive approach is necessary to minimize nitrogen losses and improve crop yield.More broadly, strategies to reduce NH_3 volatilization and NO_3^- leaching involve management practices based on fertilizers, soil, and irrigation. Fertilizer management strategies, such as the 4R nutrient stewardship concept—using the right source of nutrients, at the right rate, at the right time, and in the right place—are critical. Soil management through conservation tillage practices combined with planned crop-based irrigation also contributes significantly. These integrated adjustments in nutrient, soil, and irrigation management provide a means to improve nutrient use efficiency, agricultural profitability, environmental safety, and sustainable ecosystems with fertilizers, particularly in developing countries [7].

Urea is the most widely used nitrogen-containing fertilizer in the world, with an annual production exceeding 170 million tons. In Uzbekistan, more than 650 thousand tons are produced annually. The quality requirements for granular urea are regulated and specified in GOST 2081-2010, while international standards (EU Regulation No. 2003/2003) impose even stricter requirements. Improving the quality characteristics of urea, particularly increasing the static strength of granules, helps reduce losses throughout the supply chain from production to application and has a positive impact on the soil–plant–fertilizer system [8–10].

It should also be noted that agricultural soils are a major source of nitrous oxide (N_2O) and nitric oxide (NO). Nitrous oxide is a greenhouse gas and also a precursor compound involved in the depletion of the stratospheric ozone layer. Due to the lack of precipitation in the upper layers of the atmosphere, the removal of nitrogen oxides occurs very slowly, contributing to their accumulation in this region and altering the spectral composition of solar radiation [11].

Based on the above, the processes of producing granular urea with stabilized solubility, incorporating polyacrylamide into molten urea, were investigated

In our previous study [12], the chemical composition of encapsulated fertilizers based on molten urea with the addition of polyacrylamide and ethylcellulose was determined. It was shown that with the addition of polyacrylamide at a mass ratio of $(NH_2)_2CO$: polyacrylamide = 100 : (0.1–3.0), the dissolution time of urea granules increased by 8–15 times. Moreover, at the studied ratios, the granule strength increased from the initial 2.52 to 5.10 MPa, the hygroscopic point rose from 58.4% to 72.3%, while the pH and porosity decreased from 9.18 to 7.06 and from 5.75 to 5.25, respectively. It was also found that at the

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studied polyacrylamide addition ratios in molten urea, the density and viscosity of the melt increased slightly. The addition of 0.5 g of polyacrylamide per 100 g of molten urea at 135 °C resulted in an increase in melt density and viscosity from the initial 1.20 to 1.21 g/cm³ and from 2.62 to 4.53 cP, respectively.

In the present study, IR spectroscopic and thermal investigations of granular urea with stabilized solubility were carried out.

Materials and Methods. To obtain granular urea with stabilized solubility, $(NH_2)_2CO$ grade A, containing 46.3% N, and polyacrylamide were used as the main components. The primary reactive site in the polyacrylamide molecule is the amide group (–$CONH_2$). In aqueous or alkaline media, it can partially hydrolyze to form –COONa groups, resulting in an anionic polyacrylamide. Cationic and amphoteric forms can also be synthesized. Polyacrylamide is capable of forming complex compounds with metal ions, which ensures its effectiveness in water treatment and flocculation processes. Under the action of crosslinking agents, it can form a three-dimensional network structure, producing a strong hydrogel.IR spectroscopic analysis clearly identifies the characteristic vibration bands of polyacrylamide: stretching vibrations of –NH_2 groups (3200–3400 cm^{-1}), C=O group vibrations (around 1650 cm^{-1}), and C–N bonds (in the region of 1450 cm^{-1}). Polyacrylamide is widely used in various fields, including agriculture to enhance soil water permeability and prevent erosion, in water treatment for pollutant removal and colloidal particle flocculation, and other applications [13,14].

The experiments were conducted as follows: urea was melted in a metal cup on an electric hotplate, and polyacrylamide powder was added to the melt at 135–140 °C at a mass ratio of $(NH_2)_2CO$: polyacrylamide = 100 : (0.1–3.0). The temperature was maintained constant by heating, and the melt was stirred continuously for 1–2 minutes after dosing to achieve a homogeneous state. It was then transferred into a granulator, consisting of a metal cup with a perforated bottom, where the hole diameter was 1.0 mm. Pressure was applied at the top of the cup using a pump, and the melt was sprayed from a height of 35 meters. This process produced urea granules containing ethylcellulose. Subsequently, the chemical composition and granule strength were determined. The chemical composition and rheological properties of the melts are presented in [12].

Samples for IR spectroscopy were prepared by pressing a sample portion (1.0 mg) with 250 mg of potassium bromide, as well as by immersing the specimens in vaseline oil. IR measurements were performed using Spekord 75-JR and FTJR Fourier-transform spectrometers. The spectra were recorded over the wavenumber range from 4000 cm^{-1} to 400 cm^{-1}.

In the IR spectrum (Fig. 1) of the initial urea, bands in the 3100–3500 cm^{-1} region were observed, corresponding to the symmetric and asymmetric stretching

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vibrations of the amide group (NH_2). The bands at 2166–2794 cm^{-1} belong to the NH_2^+ group, while the bands at 1653 cm^{-1} and 1593 cm^{-1} correspond to the stretching vibrations of C=O and NH_2 bending vibrations, respectively. The bands at 1149–1002 cm^{-1} represent the stretching vibrations of C–N bonds.Figure 2 presents the IR spectrum of encapsulated urea with polyacrylamide. In the 1650–1670 cm^{-1} range, C=O stretching corresponds to the amide groups of urea and polyacrylamide. The broadened N–H stretching at 3200–3400 cm^{-1} is due to hydrogen bonding with the polymer. The addition of polyacrylamide enhances the N–H hydrogen bonding, indicating a slower separation of urea molecules within the hydrogel structure [15,16].

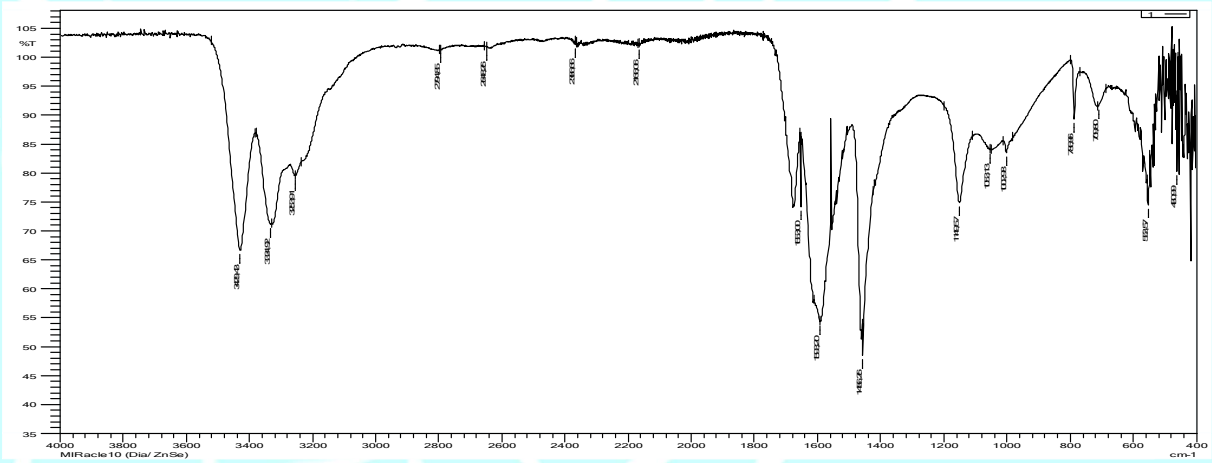


Fig. 1. IR spectrum of the original urea

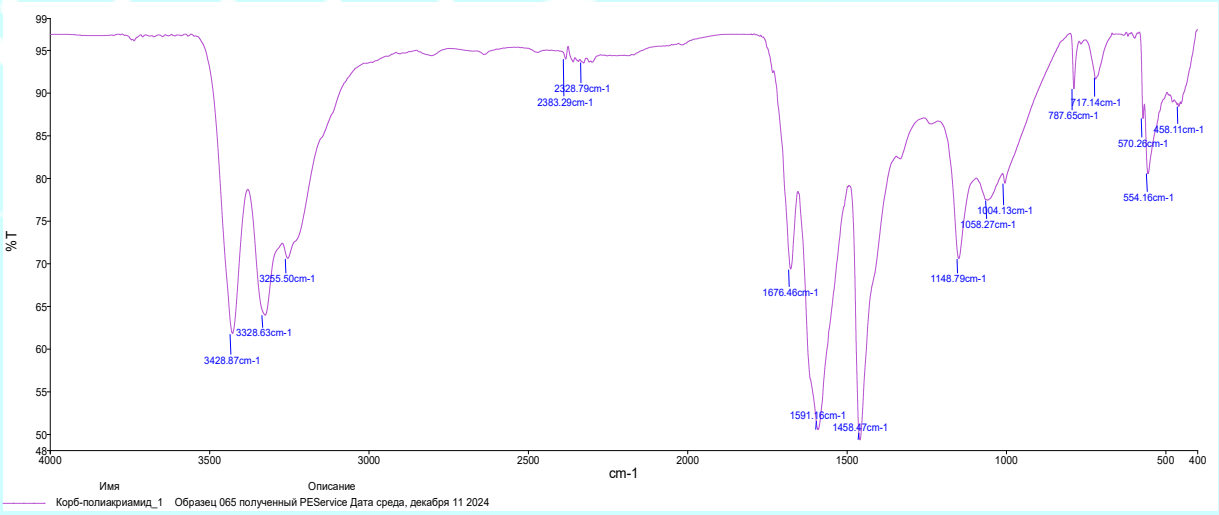


Fig. 2. IR spectrum of encapsulated urea with polyacrylamide

Figure 3 shows the DTA of the original urea, with the melting temperature recorded in the range of 132–135 °C. The melting process is endothermic, and no significant mass loss is observed at this stage. Above 150 °C, the main decomposition of urea occurs, producing ammonia and isocyanate.

$$CO(NH_2)_2 \rightarrow NH_3 + HNCO$$

HNCO molecules condense with each other, forming biuret, triuret, and cyanuric acid.

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$$2\ HNCO \rightarrow NH_2–CO–NH–CO–NH_2$$

During further decomposition and oxidation above 300 °C, gases such as CO_2, CO, and NH_3 are released. These processes define the practical limits of urea application. For example, when stored as a mineral fertilizer, stability at 150–200 °C is of great importance. In the experiment, the melting temperature of urea was determined to be 141 °C. The main mass loss occurred in the range of 200–270 °C (≈55%), with an endothermic peak recorded at 245 °C. In the subsequent stage (274–533 °C), a further 43% mass loss was observed, accompanied by an exothermic peak at 382 °C.

The results are fully consistent with the literature data. Urea is stable up to 150 °C, but above 200 °C, the main decomposition processes proceed intensively. This limits the thermal conditions for its practical application.

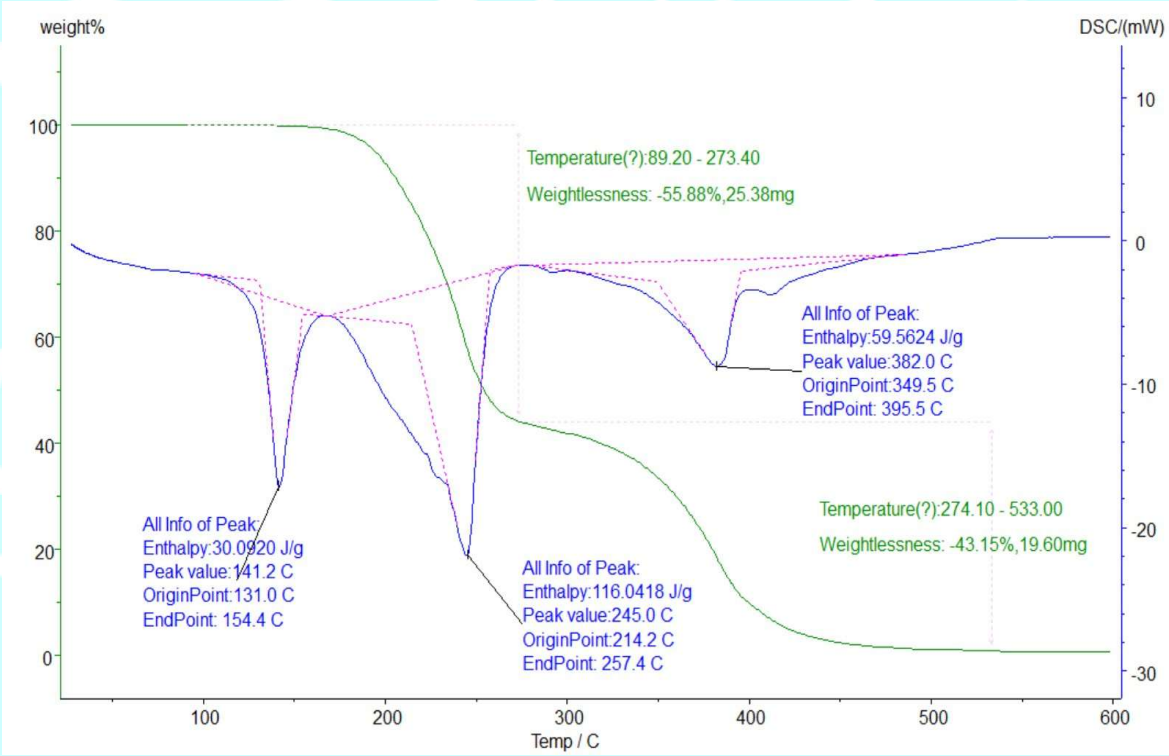


Fig. 3. DTA of the original urea.

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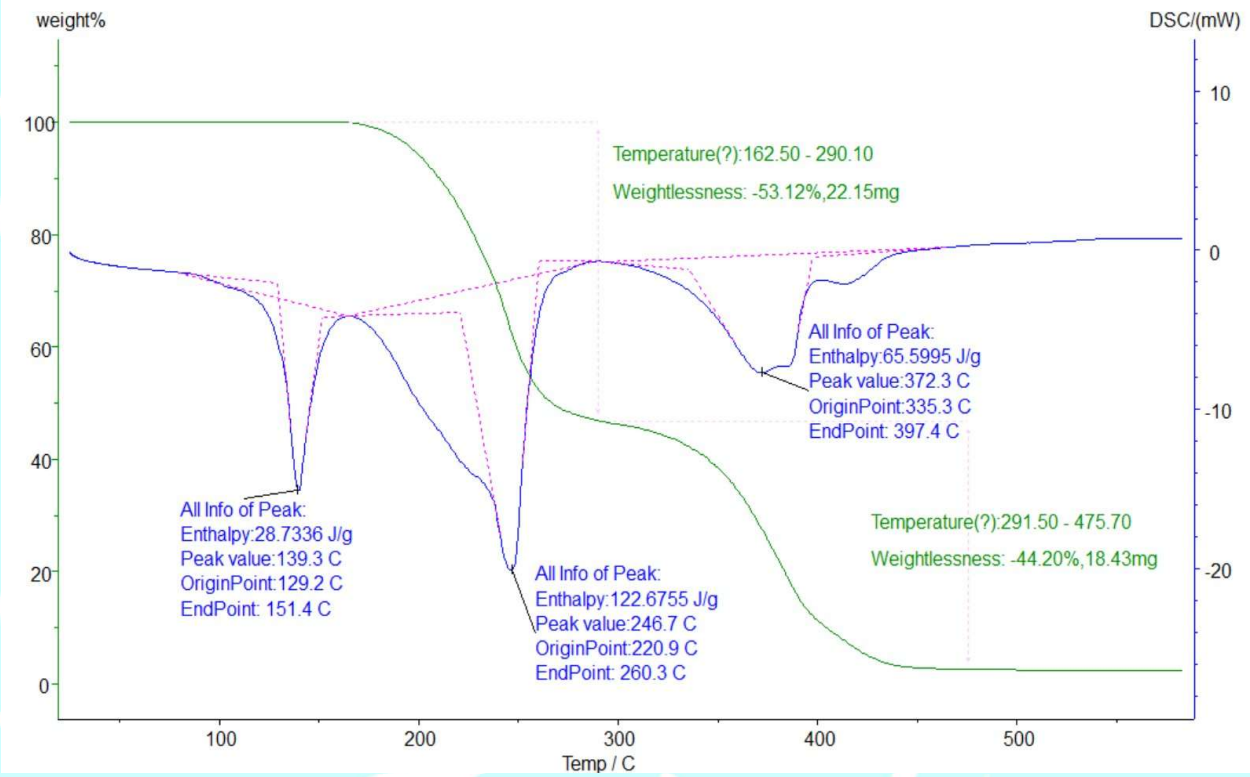


Fig. 4. DTA of encapsulated urea with polyacrylamide.

Figure 4 shows the DTA of encapsulated urea with polyacrylamide. The decomposition of polyacrylamide is mainly associated with deamidation processes in the range of 220–300 °C, accompanied by the release of ammonia and water: $–CH_2–CH(CONH_2)– \rightarrow –CH_2–CH(CN)– + H_2O$. At higher temperatures (>350 °C), chain scission occurs with the release of gaseous products. Such reactions lead to partial carbonization of the polymer chain, increasing the residual mass. The main mass loss was observed in the range of 162–290 °C (≈53%), with a strong endothermic peak recorded at 246 °C. In the subsequent stage, an exothermic peak was observed at 372 °C. These results are consistent with literature data.

Thus, the processes of producing granular encapsulated urea with stabilized solubility by adding polyacrylamide to molten urea were investigated to reduce solubility and urea losses in the soil and to enhance agrochemical efficiency. It was found that producing encapsulated urea with stabilized solubility using either ethylcellulose or polyacrylamide in molten urea not only decreases urea solubility in the soil but also positively affects the properties of urea. This is due to the formation of a more stable and compact crystalline structure of urea granules.

IR spectroscopic and thermogravimetric analyses of the obtained fertilizers were performed. Encapsulation of urea using polyacrylamide not only produces a homogeneous mass based on molten urea but also significantly improves the physicochemical and agrochemical properties of urea. The urea granules exhibit lower solubility compared to pure urea; that is, by reducing the dissolution rate of

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the fertilizer granules, they release nutrients gradually, thereby decreasing nitrogen losses in the soil. Ethylcellulose and polyacrylamide, by coating the granule surface, reduce solubility and irreversible losses in the soil, while also decreasing fertilizer consumption and enhancing agrochemical efficiency. This contributes to a substantial improvement in the agrochemical and agrophysical properties of the soil, thereby increasing its fertility.

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