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THERMODYNAMIC AND KINETIC PARAMETERS OF THE DEVELOPMENT OF TECHNOLOGY FOR PRODUCING COMPLEX MINERAL FERTILIZERS WITH AGROCHEMICAL PROPERTIES USING HYDROGEL

Abstract. This work is devoted in detail to elucidating the thermodynamic and kinetic considerations for the production of mineral fertilizers with a hydrogel consisting of hydrolyzed polyacrylonitrile (HIPAN) in the presence of a cross-linking agent – the product of the reaction of epichlorohydrin with a 33% aqueous ammonia solution (ECHA). Traditional qualitative analysis of individual factors based on kinetic and thermodynamic parameters does not sufficiently reveal the mechanism underlying the absorption of nutrients by hydrogel during the development of mineral fertilizers and the subsequent transfer of these nutrients and moisture into the soil. This study aimed to determine the influence of temperature, humidity and their interaction on kinetic and thermodynamic parameters, which revealed the key control mechanism underlying hydrogel nutrient uptake in mineral fertilizer development, modified the traditional Arrhenius model, and established a quantitative prediction model for cumulative nutrient uptake substances. Field experiments were carried out at different temperatures (T) (15°C, 20°C, 25°C and 35°C) and moisture content (θ) (60%, 80% and 100% of field capacity). The results showed that the influence of individual factors and their interaction on the values of reaction rate (KN), activation free energy (ΔG) and activation entropy (ΔS) followed the descending order T>θ>T·θ, while the enthalpy of activation (ΔH) and the degree of activation (logN) followed the descending order θ>T>T·θ. Results indicated an endothermic nutrient uptake reaction controlled by enthalpy, with a new model "A" (NH_4NO_3 (T, θ)) proving more accurate than traditional models, improving the accuracy of nutrient uptake prediction.

Keywords: mineral fertilizers, hydrogel, development of mineral fertilizers, kinetic parameters, thermodynamic parameters, soil moisture, soil fertilization, agriculture.

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Introduction. Fertilizer is one of the vital input materials for crop production. The fertilizer industry faces a major challenge in improving its products to improve fertilizer efficiency and minimize potential negative impacts on the environment. Using slow-release fertilizers, such as hydrogel mineral fertilizers, can help overcome the shortcomings of conventional fertilizers. Slow-release mineral fertilizers are designed to gradually release nutrients to plants at a rate that matches the plant's nutrient requirements while reducing the potential for nutrient loss [1-3]. Other advantages of hydrogel slow-release fertilizers over conventional fertilizers include reduced application frequency, minimizing the potential negative effects associated with overdosing. These types of fertilizers can be produced by coating conventional granular fertilizers with a membrane that serves as a diffusion barrier [3-5].

Hydrogels are cross-linked hydrophilic polymers that can absorb large amounts of water, fertilizers or other liquids. A hydrogel is an extremely voluminous hydrophilic polymer network with the ability to swell enormous amounts of water or many other liquids. The hydrogel network can consist of homo-polymers or copolymers [6-8]. Due to their unique three-dimensional network structure and various functional groups, hydrogels have found wide application in various fields such as agriculture. Recently, the use of hydrogels in agriculture as water management materials has attracted much attention. Thus, a hydrogel-coated soluble fertilizer would be an ideal formulation for increasing the growth and productivity of crops. Hydrogels based on acrylic polymers, obtained by graft polymerization in the presence of a cross-linking agent and subsequent drying of the formed hydrogel, where hydrolyzed polyacrylonitrile (HIPAN) is used as an acrylic polymer [9-11], and the product of the interaction of epichlorohydrin with an aqueous solution is used as a cross-linking agent ammonia 33%, widely used in agriculture. Recently, much attention has been paid to the preparation of hydrogel composites due to their relative low cost and good water retention capacity, as well as their significant sustained release properties. The hydrogel developed by our method not only has the ability to deliver and release fertilizers, but also has good water adsorption capacity, which can reduce fertilizer loss and improve water utilization in agriculture [12-13].

In the process of developing complex mineral fertilizers using hydrogel, there are two main stages: mixing the fertilizer composition with the hydrogel and increasing the crystallization of the finished fertilizer. These steps essentially control the size distribution of the fertilizer and its subsequent effect on the plants. Mass transfer of a solute from a supersaturated liquid solution to a pure crystalline solid and agitation can have a significant effect on product size distribution, purity and morphology. Saturation is defined as the excess of a dissolved fertilizer solution relative to the solubility curve. Thus, the overall efficiency of fertilizer application depends significantly on the interaction of thermodynamic, kinetic and transport processes (which in turn depend on the underlying hydrodynamics). Therefore, the ability to control and manipulate crystallizer performance requires a fundamental understanding of these aspects. In this work, we tried to give a brief and critical review of the available information on the thermodynamic, kinetic and hydrodynamic aspects of the development of complex mineral fertilizers using hydrogels [14].

The process of developing complex mineral fertilizers using hydrogel is based on the thermodynamic behavior of the system. These characteristics include hydrogel mixing, saturation, and metastable zone, which play a role in subsequent kinetics. Understanding the hydrogel mixing system is the starting point for fertilizer design, forming a key aspect for determining nutrient throughput and yield. In addition, it plays a decisive role in the fertilizer selection system as well as in the mixing mode. The next step, understanding metastable characteristics, relates to solutions that are saturated but not ready to spontaneously nucleate. These aspects are discussed in detail in the following sections.

Solubility is a dynamic equilibrium in which the rate of dissolution is balanced by the rate of crystallization. This is the maximum concentration that can exist at equilibrium under a given set of conditions and often increases with increasing solution temperature [14]. Therefore, it can be said that the temperature coefficient of solubility is an important factor that can determine the yield of the crystal; because if the coefficient is positive and increasing, it will mean that increasing temperature leads to greater solubility and therefore greater concentration of the solution. To dissolve a substance in a liquid, it must be able to destroy the structure of the solvent and ensure the binding of solvent molecules to the ions of the dissolved component. The forces that bind ions, atoms, or molecules together in a lattice oppose the tendency of a crystalline solid to enter solution. Thus, the solubility of a solid is determined by the resultant of these opposing effects [15].

The main point in managing the process of developing mineral fertilizers using hydrogel and system modeling of the process is the accurate measurement of the concentration of hydrogel in fertilizer suspensions. High precision is necessary because the kinetics is highly dependent on supersaturation, which is the difference between the actual solute concentration and the concentration of the saturated solution.

In general, experimental determination of the absorption of mineral fertilizers by hydrogel requires a large amount of dissolved substance and is usually a labor-intensive procedure. Absorbance prediction using thermodynamic models is the preferred choice. The thermodynamic properties of chemical systems liquid–vapor, liquid–liquid and solid liquid, found using various methods (for example, group contribution methods or regular solution theory), can be revealed by estimating the ideal absorption and activity coefficient of the absorbed substance in the hydrogel [16]. Prediction of uptake is a fundamental aspect in the development of any fertilizer because its prediction is necessary to calculate saturation, which in turn is used to determine solution concentration and other uptake phenomena.

To identify the best concentration of a mineral fertilizer solution, thermodynamic and kinetic aspects, one should refer to the entropy of mixing of the solution.

There are three contributions to the entropy of mixing: a) changes in vibrational entropy thermodynamics; b) thermodynamic changes in magnetic and electronic entropy; and c) configurational or statistical thermodynamics, which arises from mixing equivalent solutions of different chemical species [17]. The last one is the most important. It arises from statistical mechanics and is fundamentally related to the greater randomness in the solid solution compared to the pure finite element. This structural complexity must be reflected in the thermodynamics of the formation of the solid solution and its subsequent interaction with aqueous solutions.

The absorption of nutrients by hydrogel during fertilizer development and subsequent transfer to the soil is a complex process that is influenced by numerous factors such as soil moisture, temperature, soil pH, rainfall, wind speed and the amount of organic matter solution. However, soil moisture content and temperature are key factors affecting the nutrient absorption cycle of hydrogel during fertilizer development and subsequent transfer to soils and regulating mineral volatilization, since these two factors significantly influence soil aeration and soil enzymatic activity. Kinetics and thermodynamics are important techniques for analyzing the complex mechanism underlying the nutrient uptake reaction. Reaction rate (KN), temperature coefficient (Q10), enthalpy of activation (ΔH), free energy of activation (ΔG), entropy of activation (ΔS) and degree of activation (logN) are important indicators of the degree of complexity and rate of a chemical reaction [18]. From a kinetic point of view, it is known that the cumulative uptake of complex nutrients such as phosphorus and ammonium nitrate can be quantitatively described by the Elovich-1 model (Equation 1) [19]. The value of b in the Elovich-1 model indicates the curvature of the hydrogel's nutrient uptake curve, but these reports incorrectly consider b to be the reaction rate (KN). Therefore, these kinetic conclusions about reaction rates are questionable and should therefore be further studied.

$$Ct = a + b.\ln(t), \tag{1}$$

where: Ct – is the amount of nutrients (mg/kg) released at time t; a and b – are constants.

Previous studies have shown that at different temperatures, nutrients contain different amounts of moisture and, accordingly, different ability of the hydrogel to absorb nutrients. In these studies, the moisture content is 30% and the field capacity (θ) is 20%, or between 22% θ and 74% θ. Generally, plants need to be watered when the moisture content is less than 60%. After the hydrogel transfers the accumulated moisture along with nutrients into the soil, the moisture content approaches 100%. These previous studies, conducted in the laboratory of the Department of Chemical Technology of Inorganic Substances of SKSU named after. M. Auezov, cannot fully reflect real agricultural conditions and therefore require further study, which was carried out in this work. It is also possible to isolate the individual effects of moisture content and temperature on the temperature coefficient, enthalpy of activation, and free energy of activation, but the combined effect of these factors remains unknown. Several high-quality studies have been conducted on the thermodynamic and kinetic aspects of hydrogel uptake of nutrients from fertilizers, but both the individual and coupled effects of moisture content and temperature on activation entropy and degree of activation remain unclear. This study will help improve the understanding of the mechanism in the development of mineral fertilizers and the absorption of hydrogel nutrients during the development of fertilizers and the subsequent transfer of these nutrients to the soil.

The Elovich-1 model cannot provide a meaningful reaction rate parameter. Considering the shortcomings of the Elovich-1 model, the robust Elovich-2 model (Equation 2) was used in this study [18,19]. The KN value in equation 2 is the rate of reaction. The Elovich-2 model is rarely used in assessing the thermodynamic and kinetic aspects of mineral fertilizer development, which does not take into account the influence of temperature and humidity on the reaction rate. Therefore, Equation 2 must be further modified as Equation 3.

$$Ct = (1/m)\ln(KN.m) + (1/m)\ln(t) \tag{2}$$

$$Ct = (1/m)\ln(KN\ (\theta,T).m) + (1/m)\ln(t) \tag{3}$$

where: KN – is the reaction rate constant; KN (θ, T) – modifying function indicating the reaction rate when combining thermodynamic temperature (T) and humidity (θ); T – thermodynamic temperature; θ – humidity, mg/kg; m – is a constant [18,19].

The Arrhenius equation (Equation 4) is a classical theory in physical chemistry for describing the linear relationship between the logarithm of KN and the reciprocal of T. The Arrhenius equation can also be expressed in another form as Equation 5. The Arrhenius equation must be modified to establish the exact modification function KN (θ ,T) [20].

$$\ln(KN) = \ln(A) - \frac{Ea}{R \cdot T} \quad (4)$$

$$\ln(KN) = a + \frac{b}{T} \quad (5)$$

where: A – is the pre-exponential coefficient; Ea – energy differential, kJ/mol; R – gas constant (8.314 J/mol·k) [20].

This study aims to identify the key control mechanism underlying hydrogel uptake of nutrients during the development of mineral fertilizers and their subsequent transfer to the soil, determine the important degrees of influence of temperature, humidity and the interaction between them on kinetic and thermodynamic parameters, and establish an uptake prediction model hydrogel of nutrients under the coupled effects of humidity and temperature. This work is aimed at identifying key issues related to the development processes of hydrogel mineral fertilizers; the extent to which they focused on reviewing the current understanding of thermodynamic, kinetic and hydrodynamic aspects and identifying knowledge gaps that pose challenges to research as well as industrial requirements. The section is organized as follows: first, the practice of using hydrogel mineral fertilizers in agriculture is briefly reviewed and key issues are identified; secondly, an explanation is given of the thermodynamic and kinetic processes during the absorption of nutrients by the hydrogel during the development of mineral fertilizers and their subsequent transfer to the soil.

Materials and methods. The research was carried out on the Saidmurot Altyn-Dala farm (Termez district, Surkhandarya region) with the support of the Toshkent Research Institute of Chemical Technologies (TKTI) named after. J. Amirov, Termez State University (TerSU) and at Borsyksai LLP (Tyulkubas district, Zhaskeshu village). Soil samples were taken at the Saidmurot Altyn-Dala farm and at Borsyksai LLP. The soil type is sandy loam, and the pH is 8.84. The moisture content and field capacity are 21.63 g/kg and 217.79 g/kg, respectively. The content of mineral fertilizers and hydrogel is 4.1 mg/kg and 5.9 mg/kg, respectively. pH level, field capacitance and moisture content were measured using previous research methods. The content of mineral fertilizers and hydrogel was determined using a continuous flow analyzer. All chemicals used in the experiments were of an analytical class reagent and obtained from hydrolyzed polyacrylonitrile (HIPAN) in the presence of a cross-linking agent – the product of the interaction of epichlorohydrin with a 33% aqueous solution of ammonia (ECHA) and mineral potassium-phosphorus fertilizers.

Exactly 151 g of soil was added to a series of 500 ml glass beakers. Deionized water was added to the beakers to adjust the moisture content of the soil samples to θ60, θ80, and θ100 levels (60%, 80%, and 100% of field capacity, respectively). The remaining beakers were treated with three different levels of distilled water as a control. The beakers were incubated at different temperatures (15°C, 20°C, 25°C and 35°C) in incubators for 1 week. On odd-numbered days after the start of the experiment, nutrient uptake by the hydrogel was quantified using acid traps. Two sponges (2 cm thick, 8.5 cm in diameter) were moistened with 10 ml of phosphate-glycerol solution (40 ml of glycerol and 50 ml of phosphate were mixed and diluted in 1000 ml of deionized water). The lower sponge was placed 3 cm above the soil surface to capture fertilizer nutrients from the soil, and the top sponge was placed on the edge of the glass to capture fertilizer nutrients from the atmosphere. Soil water lost through evaporation was replaced with deionized water, and sponges were replaced every 2 days. A lower sponge and 100 ml of NH_4NO_3 (1 mol/L) solution were added to the flasks, which were then placed in a mechanical shaker and vibrated at a frequency of 50 Hz for 1 hour. The NH_4^+-N content in the pellucid filtrate was determined using a continuous flow analyzer.

Calculation of kinetic and thermodynamic parameters. Based on kinetic theory, the Elovich-2 model was used to describe the dynamic process of nutrient adsorption (Equation 2). To calculate model parameters based on experimental data, regression analysis was carried out. Thermodynamic parameters mainly include temperature coefficient (Q10), activation enthalpy (ΔH), activation free energy (ΔG), activation entropy (ΔS), activation degree (logN) and Ea. Ea can be calculated using equation 4. Other thermodynamic parameters can be calculated using the following equations:

$$Q_{10} = KT2 / KT1 \quad (6)$$

$$\log N = \log 10\,(Na.\exp(-Ea / (RT))) \quad (7)$$

$$\Delta H = Ea - RT \quad (8)$$

$$\Delta G = R \cdot T.\ln((RT) / (Na.h.KN)) \quad (9)$$

$$\Delta S = (\Delta H - \Delta G) / T \quad (10)$$

where: KT2 and KT1 – are the reaction rate constants at temperatures T2 and T1 (°C) (T2 = T1+10), respectively; Na – Avogadro's constant (6.022×10-23/mol); h – Planck's constant (6.626×10-34 J/s).

Data analysis and evaluation. All data were processed using Microsoft Excel 2013. Statistically significant analyzes were performed using one-way and two-way ANOVA. The creation of models was carried out using 1stOpt 7.0 software. Model accuracy was assessed using the coefficient of determination (R2) and mean absolute percentage error (MAPE), which were calculated as follows:

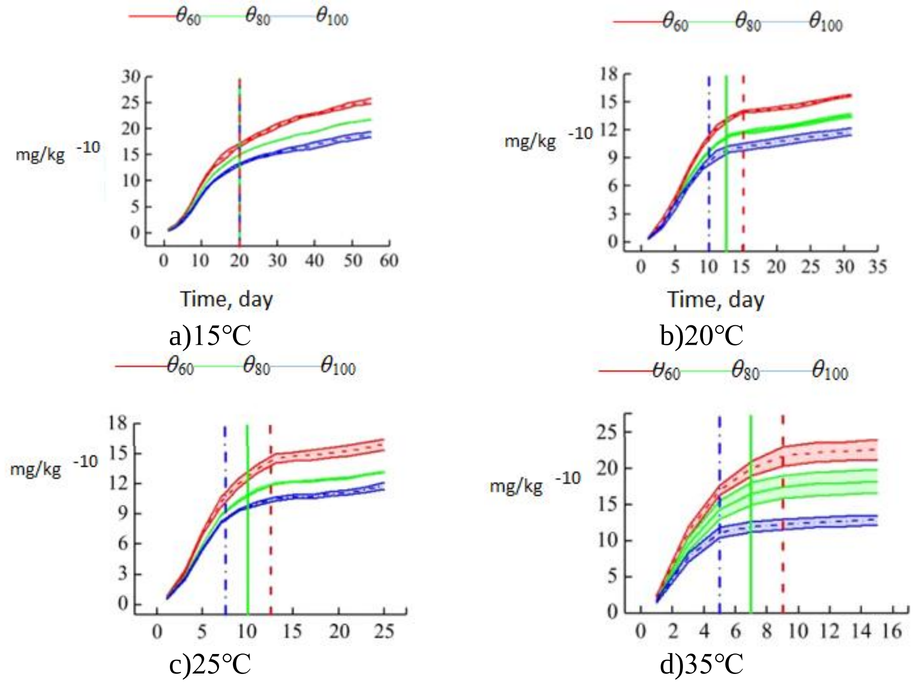
$$R^2 = \sum_{f=1}^{n}(C_i' - C^{-2}) / \sum_{f=1}^{n}(C_i - C^{-2}) \quad (11)$$

$$MAPE = \sum_{i-1}^{n}(|C_i - C_i'|/C_i)/n \times 100\% \quad (12)$$

where: Ci, C'i and C-2 – represent the measured, calculated and average amounts of mineral fertilizers (mg/kg) that were released at t, respectively; n – is the number of evaluated data points [9].

Research results. Characteristics of mineral fertilizers with hydrogel under various treatments. Figure 1 shows the values of mineral fertilizers with hydrogel at three different moisture contents. All three conditions, which were significantly increased initially and stabilized with increasing reaction time, followed the logarithmic function rule. The start and end times of the stage with different stages were almost the same at 15°C (Fig. 1a). Under other temperature conditions, high moisture content equates to a short rapidly increasing stage and a long stable stage (Fig. 1b-1c). The values of the amount of nutrients absorbed by the hydrogel in the three treatments followed the descending order of θ60>θ80>θ100 throughout the entire process. The result showed that θ100 is the best value to minimize nutrient volatilization with an average value of 13.10 mg/kg, which was only 86.9% and 75.3% of the θ80 and θ60 procedure, respectively, at 15°C. Similarly, the results for the two research methods were 87.8% and 75.5% at 20°C (Fig. 1b), 88.9% and 74.4% at 25°C (Fig. 1c), and 72.9 % and 59.4% at a temperature of 35°C (Fig. 1d). Extremely significant ($p<0.01$) difference at 15°C, 20°C, 25°C and 35°C and significant ($p<0.05$) difference at 35°C for three treatments (θ60, θ80 and θ100) were complied with.

Figure 1 also shows that the values of nutrients absorbed by the hydrogel at 15°C, 20°C and 25°C are similar, with the gap becoming increasingly smaller over time. As the temperature increased from 15°C to 35°C, the critical time of the two stages decreased from 20 to 5 at 100% field capacity (θ), from 20 to 7 at 80% field capacity, and from 20 to 9 at 60%, respectively. Additionally, high temperature equates to rapid absorption of nutrients and short release. The nutrients absorbed by the hydrogel in plant nutrition at 35°C were higher than in the other three cases. As shown in Figure 1, high temperature equates to steep absorbance growth curves and high initial velocity. The growth rates of nutrients absorbed by the hydrogel under different temperature treatments followed the descending order T35>T25>T20>T15 at the same moisture content.

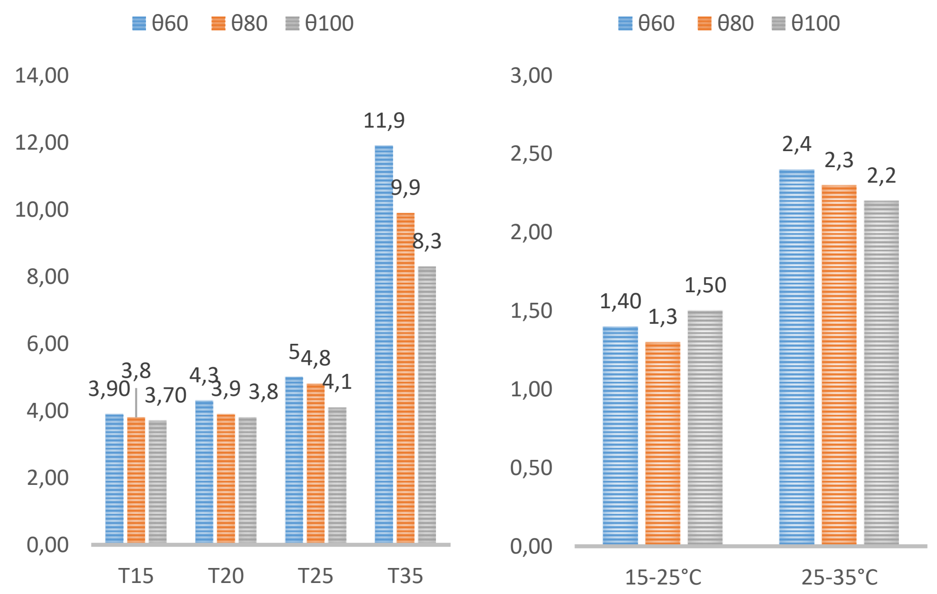


a)15°C b)20°C c)25°C d)35°C

Fig. 1. The values of mineral fertilizers with hydrogel at different moisture contents

Extremely significant (p<0.01) or significant (p<0.05) differences were observed between the four experimental conditions (T15, T20, T25 and T35), except when the 15°C and 20°C methods were compared and 15°C and 25°C methods. After 7 days, nutrients absorbed by the hydrogel at 35°C showed an almost stable trend. The reaction rate constant at 20°C and 25°C reached stability at the same level, and at 15°C it showed a steady increase and later exceeded those in the other three cases.

Effect of different types of nutrient absorption by hydrogel on kinetic parameters. The rate of accumulation of the reaction rate constant (KN) is a key parameter in chemical kinetics and indicates the degree of speed and complexity of a chemical reaction. The KN values at different temperatures and moisture contents are shown in Figure 2a. The KN values for different temperature treatments were arranged in the following order: T35>T25>T20>T15. The KN values at 35°C were 3.26, 3.09 at 15°C, and 2.98 at 60%, 80%, and 100% field capacity, respectively. Figure 2a shows that the KN value decreases with increasing moisture content. The KN values of the θ60 treatment were 1.30, 1.29, 1.28, and 1.42 higher than those of the θ100 treatment at 15°C, 20°C, 25°C, and 35°C, respectively. The maximum and minimum values of the constant were found in the regions of low humidity and high temperature, and high humidity and low temperature, respectively. When moisture content increased from 60% field capacity to 100%, the average KN was 1.304, 1.292, 1.283 and 1.424 at 15°C, 20°C, 25°C and 35°C, respectively. When the temperature increased from 15°C to 35°C, the average KN values were 0.401, 0.326 and 0.270 at 60%, 80% and 100% capacity, respectively. This finding indicated a significant difference between treatments at different temperatures and moisture contents and thus suggested an interaction between temperature and moisture content in the transfer of nutrients by the hydrogel to the soil.



a b

Fig. 2. Kinetic and thermodynamic parameters of nutrient accumulation by hydrogel during the development of mineral fertilizers at different temperatures and humidity

The result of two-way analysis of variance showed that the influence of individual factors and their interaction on the magnitude of the reaction rate followed in descending order T>θ>T×θ (Table 1). This discovery shows the extremely significant influence of humidity, temperature and their interaction on the magnitude of the reaction rate. Therefore, these factors should be taken into account when creating quantitative models in mineral fertilizers.

The influence of various types of processing on thermodynamic parameters

The parameters Ea, ΔH, ΔG, ΔS, Q10 and logN are key factors in thermodynamic theory. Different parameters play different roles in a chemical reaction. Activation energy (Ea) is the energy barrier at which a reactant molecule moves beyond the limits of a chemical reaction.

Table 1

Two-way analysis of thermodynamic parameters when combining humidity and temperature

Method	*ΔH*		lgN		*ΔG*		*ΔS*	
	F	Meaning	F	Meaning	F	Meaning	F	Meaning
T	3.194	0.042*	9.655	0.000**	16.437	0.000**	8.338	0.001**
θ	5.281	0.013*	13.742	0.000**	1.147	0.335	0.468	0.825
T×θ	0.310	0.925	1.009	0.443	1.137	0.371	0.079	0.925
Note: *, ** – shows the amplified value								

Enthalpy of activation (ΔH) is the thermal energy at which a reactant molecule is absorbed or released in a chemical process. Activation free energy (ΔG) is a measurement of the free energy required during the formation and decomposition of an activated complex. ΔS indicates the probability of reaching the transition state. Analysis of these parameters would make it possible to identify the mechanism of absorption of nutrients by the hydrogel and subsequent release into the soil at different temperatures and humidity.

Thermodynamic parameters for various treatments are shown in Figure 2a-2b. Q10 values in the high temperature zone (25°C-35°C) with average values of 2.322, 2.236 and 2.091 at 60%, 80% and 100% field capacity, respectively, were 1.47-1.66 times higher than in the low temperature zone (15°C-25°C) (Fig. 2b). This discovery showed that the KN reaction rate in the high-temperature zone was more sensitive to temperatures than in the low-temperature zone. Q10 at different moisture ratios and temperature zones was significant ($p<0.01$). The value of activation energy (Ea), which is the most important thermodynamic parameter, follows a descending order θ60<θ80<θ100 (Fig. 3). The difference in Ea at different moisture ratios was extremely significant.

As shown in Figure 2a, when the temperature increases from 15°C to 35°C or when the moisture content decreases from 100% throughput to 60%, the activation enthalpy (ΔH) decreases. This result showed that the absorption of nutrients by the hydrogel and subsequent release into the soil consumes a significant amount of energy. As the temperature increased, the activation free energy (ΔG) also increased, but the ΔG/T value decreased. This condition contributed to the development of the reaction. As moisture content increased, the rate of nutrient transfer decreased due to an increase in activation energy. The reagent molecules at 35°C were more easily activated than at other temperatures. In addition, when the temperature increases or the moisture content decreases, the activation entropy value |ΔS| and directionally arranged molecules increase in size.

This condition favored the acceleration of the reaction rate (Fig. 2a). The two-way ANOVA results presented in Table 1 reveal interaction effects.

In two-way analysis of variance, temperature significantly or extremely significantly affects the values of activation enthalpy ($p<0.05$), degree of activation ($p<0.01$), activation energy ($p<0.01$) and activation entropy ($p<0.01$)) (Table 1). A significant or extremely significant difference between water treatments was observed in the enthalpy of activation ($p<0.05$) and degree of activation ($p<0.01$) (Table 1). The interaction of temperature and humidity had no effect on the value of thermodynamic parameters during the absorption of nutrients by the hydrogel and subsequent transfer to the soil (Table 1). According to thermodynamic theory, the maximum value of activation enthalpy and minimum values of activation entropy and reaction rate constant occurred at T15 and θ100 treatments. Therefore, the absorption of nutrients by the hydrogel and subsequent transfer to the soil is an enthalpy-driven process.

Creation of a kinetic model for the development of mineral fertilizers using hydrogel. The Arrhenius model is a classical method for studying the kinetics of chemical reactions [10]. The R2 value of the Arrhenius model (KN(T)) is in the range of 0.932-0.949. Using this method to analyze the relationship between ln(KN) and 1/T by KN(T) was reasonable and feasible. However, the new KN(T)-2 model (Equation 13) (mean R2=0.999) can better describe the relationship between ln(KN) and 1/T than the traditional KN(T) model (mean R2=0.936).

$$\ln(KN) = a + b \cdot \exp\left(\frac{c}{T}\right) \quad (13)$$

where, C – is a constant value [21].

Moisture content had a significant effect on KN. However, the traditional Arrhenius model did not take into account the effect of moisture content on KN. The exponential function in Equation 14 describes the relationship between KN and moisture content well (average R2 =0.997). Considering the significant effect of the interaction of humidity and temperature on the value of KN, a multiplicative model was created in Equation 15 based on Equations 13 and 14. When Equation 15 was combined with Equation 3, a kinetic model of mineral fertilizer with hydrogel was obtained based on temperature (T) and humidity (θ) – model “A” (NH_4NO_3 (T, θ)), ammonium nitrate, hydrogel. Similarly, when Equation 4 was combined with Equation 2, a traditional kinetic model of mineral fertilizer with hydrogel based on temperature (T) – model “B” (NH_4NO_3 (T)) in ammonium nitrate hydrogel based on the Arrhenius equation was obtained.

A temperature and humidity based hydrogel mineral fertilizer model – Model “A” (NH_4NO_3 (T, θ)) – ammonium nitrate hydrogel was calibrated and validated using 80% and 20% of the data samples, respectively. The best parameters of model “A” are shown in Table 2. Figure 3 shows the linear relationship between the measured and predicted values and the simulation accuracy of these models. As shown in Figure 3a, the slope and R2 of model “A” were 1.021 and 0.989, respectively. The values of the average absolute percentage error of model “A” were 4.01% and 4.17% for calibration and prediction samples, respectively (Fig. 3b). The simulation accuracy of Model “A” was compared with that of the traditional Model “B” to show the effect of improving Model “A”. The values of the average absolute percentage error of model “B” were 6.49% and 7.11% for calibration and prediction samples, respectively (Fig. 3c). Model “A”, based on temperature and humidity, showed better accuracy than the traditional model "B", which is based only on temperature. Model "A" can be used to describe the process of nutrient absorption by hydrogel during fertilizer development and subsequent transfer to the soil through the interaction of humidity and temperature.

$$K_N = a . \exp(b . \theta) \quad (14)$$

$$K_N(T,\theta) = a . \exp(b + c . \exp(d / T) + e . \theta) \quad (15)$$

where, d and e – are constants [21-22].

Table 2

Installation parameters of model "A" (NH_4NO_3 (T, θ)) – mineral fertilizers with hydrogel

Model	a	b	c	d	e	m
A	0.227	4.063	624440.805	-462.642	-7.889E-3	0.171

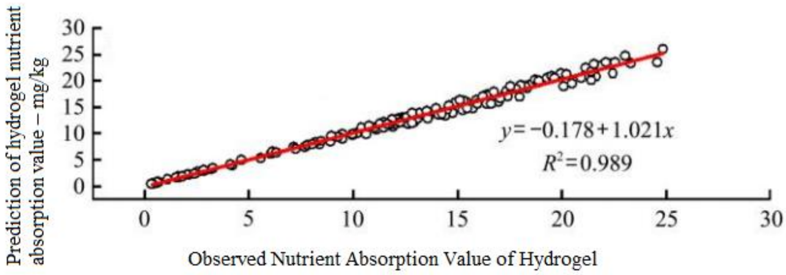


Fig. 3a. Linear relation

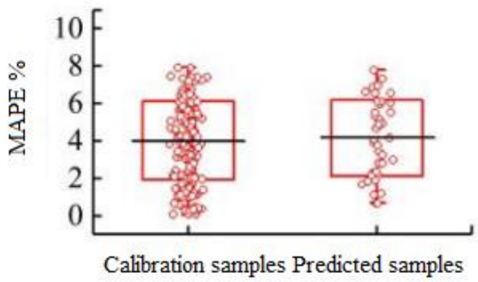


Fig. 3b. Modeling accuracy of model "A" (NH_4NO_3 (T, θ)) – mineral fertilizers with hydrogel

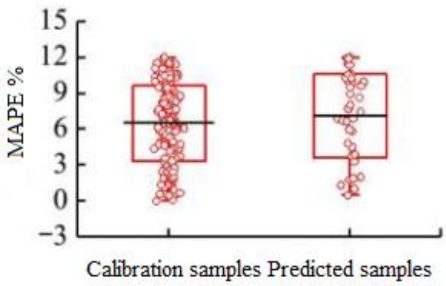


Fig. 3c. Modeling accuracy of model "B" (NH_4NO_3 (T))

Discussion. The influence of humidity and temperature on the absorption of nutrients by hydrogel during the development of fertilizers and subsequent transfer to the soil. Most previous studies have suggested that low temperature affects the hydrogel's absorption of fertilizer nutrients during development, and high soil moisture content is an important environmental factor that leads to high transfer rates of fertilizer nutrients from hydrogel in applied mineral fertilizers; this finding differs from the current work. In this study, when the moisture content increased from θ60 to θ100, the overall value of nutrient absorption process decreased by 25% to 43%. The difference may be caused by different experimental conditions.

In previous reports, development uptake was determined by the ammonium nitrate adsorption method and the soil surface was free. Under this condition, when soil moisture content increases, soil evaporation increases and causes loss of ammonia volatility. In this study, sponges were placed on the rim of a beaker to trap ammonia, thereby influencing the diffusion path of water vapor. The mechanism of the influence of moisture content on absorption in the previous study is not applicable in the present work.

The negative effect of moisture content on the nutrient absorption of the hydrogel during the development process was mainly due to two reasons. First, the ammonium nitrate used in this study is unsaturated, and the rate of hydrolysis depends on the substrate concentration. When the moisture content decreased from θ100 to θ60, the activity of ammonium nitrate decreased by 9-20%, which led to an increase in the NH_4^+-N content by 28-58%. This condition contributes to the loss of nutrients from the fertilizer and the hydrogel is less likely to absorb all the nutrients. Secondly, the pH of the θ60 treatment was between 8.32 and 9.16, which was higher than that of the θ100 treatment (between 8.19 and 9.07). The amount of OH in the θ60 treatment was between 10-5.68 mol/L and 10-4.84 mol/L, which was higher than that in the θ100 treatment (between 10-5.81 mol/L and 10-4.93 mol/l). Therefore, the reaction equilibrium in the θ60 treatment will shift more easily to the right side of Equation 16 than in the θ100 treatment [20-22].

$$N.H._4^{+}+OH^{-} = NH_3\uparrow + H_2O \qquad (16)$$

Previous studies have shown a significant positive correlation between nutrient evaporation rates and temperature. The results of the present study generally confirm this trend. The activity of ammonium nitrate increased by 33%-41% when the temperature increased from 10°C to 35°C. Consequently, fertilizer hydrolysis increased, resulting in increased NH_4^+ accumulation and solubility. The rate of diffusion of nutrients from the liquid phase to the vapor phase was also accelerated. In conclusion, high temperatures equate to a lot of evaporating nutrients.

Analysis of kinetic and thermodynamic mechanisms. In this work, a new kinetic model "A" (NH_4NO_3 (T, θ)) – ammonium nitrate, hydrogel – is established – the absorption of nutrients by the hydrogel during the development of fertilizers and the subsequent transfer of nutrients into the soil under the associated influence of humidity and temperature. Model "A" showed more accurate physical meaning, better prediction accuracy, and more general applicability than the traditional model "B". First, accurately obtaining the reaction rate (KN) is the basis for building a reliable model. The value of b in the Elovich-1 model indicates the curvature of the hydrogel nutrient absorption curve in fertilizer formulation, and some reports consider b as the reaction rate, which is inaccurate. In the present study, reaction rate (KN) was determined using the robust Elovich-2 model. Secondly, the Elovich-2 model and the "A"(NH_4NO_3 (T, θ)) model were adopted to quantify the nutrient uptake of the hydrogel for developing fertilizers suited to different processing regimes, respectively. In contrast, one model "A"(NH_4NO_3 (T, θ)) can satisfy all procedures. Model "A" is more applicable than other models. Third, model "B" (NH_4NO_3 (T)) and model "A" (NH_4NO_3 (T, θ)) were created based on the Arrhenius equation and the KN(T)-2 model, respectively. During the simulation, the traditional Arrhenius equation was revised as the KN(T)-2 model. The average R2 value of the new KN(T)-2 model was 0.999, which was better than that of the Arrhenius equation (R2 =0.936). This result helps improve the accuracy of the hydrogel nutrient uptake model for fertilizer formulation and subsequent transfer to the soil. Fourthly, the average absolute percentage error (MAPE) value of model "A" was 4.17%, which showed better forecasting accuracy than the traditional model "B" (MAPE = 7.11%).

In this study, the Q10 value was 1.38-1.43 in the low temperature zone (15°C-25°C) and 2.09-2.32 in the high temperature zone (25°C-35°C), in both cases the soil was fertilized with mineral fertilizer with hydrogel. The low temperature zone equates to a low Q10 value. The thermal stability of mineral fertilizers with hydrogel differed from the thermal stability of fertilizers without hydrogel. Secondly, the proportions of sand, silt and clay are 34.6%, 51.5% and 13.9% respectively. Third, the moisture content level is between 60%θ and 100%θ in the current study. Generally, plants need to be watered when the moisture content is less than 60% θ. The hydrogel, which accumulates liquid with nutrients, helps to gradually release moisture into the soil, thereby reducing the need for constant watering and saving water. After the hydrogel releases moisture into the soil, the moisture content approaches 100%.

Previous reports have shown that soil moisture loss shows a decreasing trend with increasing field capacity and decreasing temperature. At 15-25°C and 30-70% θ, the interaction between soil moisture and temperature is significant for moisture loss. Although the results of this study confirmed these trends, there was a slight limitation found in the previous study. Moisture content is typically between 60% θ and 100% θ in an agricultural system. As demonstrated by experimental methods, the current study reflects more realistic agricultural conditions than previous reports because it was conducted directly in the fields.

The average values of Ea, ΔH and ΔG were 47.6 kJ/mol, 45.1 kJ/mol and 104.1 kJ/mol with nitrophoska. The combined influence of temperature and moisture content factors on kinetic and thermodynamic parameters shows that the interaction between the two factors has a significant effect on the kinetic parameters and a minor effect on the thermodynamic parameters. The concentration of nitrophoska during treatment with θ100 was 1.42 mg/ml. The substrate concentration increased by 20% with increasing humidity to θ100. When the temperature increases from 15°C to 35°C, the lgN of solute molecules increases by 0.51 units. On the one hand, these two points help to increase the amount of nutrients in the hydrogel granule, thereby accelerating the correct movement of chemical equilibrium (Equation 16). On the other hand, these two points also help to increase the percentage of activated molecules and the collision efficiency, thereby increasing the likelihood of a chemical reaction and decreasing the reaction rate. In addition, the T35 and θ60 treatments had a minimum ΔH of 40.1 kJ/mol. At the same time |ΔS| and KN, not more than 97.7/mol and 11.6 mg/kg, respectively. Therefore, the absorption of nutrients by hydrogel in fertilizer formulation is an enthalpy-driven process according to thermodynamic theory. In conclusion, this study revealed the control mechanism of hydrogel nutrient uptake during fertilizer formulation and subsequent transfer to soil, and improved the prediction accuracy of hydrogel nutrient uptake during fertilizer formulation.

Conclusion. The influence of individual factors and their interaction on the reaction rate (KN), activation free energy (ΔG) and activation entropy (ΔS) followed the descending order T>θ>T·θ, while the enthalpy of activation (ΔH) and the degree of activation (logN) followed in descending order θ>T>T·θ. The interaction showed a significant effect on KN and a minor effect on all thermodynamic parameters. The role of water and temperature was mainly observed in the preparatory stage and the most critical stage of the transition state of a chemical reaction, respectively. These new discoveries have identified the key and specific role of these two factors in the process of nutrient absorption by hydrogel during the development of mineral fertilizers and their subsequent transfer to the soil.

Considering that the activation enthalpy and activation free energy are greater than zero, and the activation entropy is less than zero, the hydrogel's absorption of nutrients in fertilizer formulation is an enthalpy-controlled endothermic reaction. The findings represent an important step towards a good understanding of the key control mechanism.

The new model "A" (NH_4NO_3 (T, θ)), where KN(T)-2 with R2 0.999, was more accurate than the traditional Arrhenius model with R2 0.936. The new model "A" (NH_4NO_3 (T, θ)) with a mean absolute percentage error (MAPE) of 4.17% was more accurate than the traditional model "B" (NH_4NO_3 (T)) with a MAPE of 7.11%. The development of these two models represents an important step towards a good understanding of the relationship between reaction rate and temperature, as well as the relationship between reaction rate and environmental factors. Therefore, this study provides a valuable tool for predicting hydrogel nutrient uptake during fertilizer formulation and subsequent transfer to the soil.

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ГИДРОГЕЛЬДІ ПАЙДАЛАНА ОТЫРЫП АГРОХИМИЯЛЫҚ ҚАСИЕТТЕРІ БАР КЕШЕНДІ МИНЕРАЛДЫ ТЫҢАЙТҚЫШТАРДЫ АЛУ ТЕХНОЛОГИЯСЫН ӘЗІРЛЕУДІҢ ТЕРМОДИНАМИКАЛЫҚ ЖӘНЕ КИНЕТИКАЛЫҚ ПАРАМЕТРЛЕРІ

Аңдатпа. Бұл жұмыс эпихлоргидриннің 33% аммиак Сулы ерітіндісімен (ЭХГА) өзара әрекеттесу өнімі – айқаспалы агент қатысуымен гидролизденген полиакрилонитрилден (ГИПАН) тұратын гидрогельмен минералды тыңайтқыштарды өндіруге арналған термодинамикалық және кинетикалық ойларды егжей-тегжейлі түсіндіруге арналған. Кинетикалық және термодинамикалық параметрлер бойынша жеке факторлардың дәстүрлі сапалы талдауы минералды тыңайтқыштарды әзірлеу кезінде гидрогельдің қоректік заттарды сіңіруінің және кейіннен осы қоректік заттар мен ылғалдың топыраққа берілуінің механизмін жеткілікті түрде ашуға мүмкіндік бермейді. Бұл зерттеу температураның, ылғалдылықтың және олардың өзара әрекеттесуінің кинетикалық және термодинамикалық параметрлерге әсерін

анықтауға бағытталған, бұл минералды тыңайтқыштарды әзірлеу кезінде гидрогельдің қоректік заттарды сіңіруінің негізгі басқару механизмін анықтауға мүмкіндік берді, дәстүрлі Аррениус моделін өзгертті және қоректік заттардың кумулятивті сіңуін болжаудың сандық моделін белгіледі. Далалық тәжірибелер әртүрлі температурада (T) (15°C, 20°C, 25°C және 35°C) және ылғалдылықта (θ) (60%, 80% және 100% далалық сыйымдылық) жүргізілді. Нәтижелер жеке факторлардың әсері және олардың реакция жылдамдығының мәндеріне (KH), активтендірудің бос энергиясына (ΔG) және активтендіру энтропиясына (ΔS) өзара әрекеттесуі t>θ>T·θ төмендеу реті бойынша, ал активтендіру энтальпиясы (ΔH) және активтендіру дәрежесі (lgN) θ төмендеу реті бойынша жүретінін көрсетті>T > T·θ. Нәтижелер энтальпиямен басқарылатын қоректік заттардың эндотермиялық сіңіру реакциясын көрсетеді. Жаңа «A» моделі (NH_4NO_3 ((T, θ)) дәстүрлі модельдерге қарағанда дәлірек болып, қоректік заттардың сіңуін болжау дәлдігін жақсартады.

Тірек сөздер: минералды тыңайтқыштар, гидрогель, кинетикалық параметрлер, термодинамикалық параметрлер, ылғалдылық, тыңайтқыш.

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ТЕРМОДИНАМИЧЕСКИЕ И КИНЕТИЧЕСКИЕ ПАРАМЕТРЫ РАЗРАБОТКИ ТЕХНОЛОГИИ ПОЛУЧЕНИЯ КОМПЛЕКСНЫХ МИНЕРАЛЬНЫХ УДОБРЕНИЙ С АГРОХИМИЧЕСКИМИ СВОЙСТВАМИ С ИСПОЛЬЗОВАНИЕМ ГИДРОГЕЛЯ

Аннотация. Эта работа подробно посвящена выяснению термодинамических и кинетических соображений для производства минеральных удобрений с гидрогелем, состоящим изгидролизованного полиакрилонитрила(ГИПАН) в присутствии сшивающего агента – продукта взаимодействия эпихлоргидрина с 33% водным раствором аммиака (ЭХГА). Традиционный качественный анализ отдельных факторов по кинетическим и термодинамическим параметрам не позволяет в достаточной мере раскрыть механизм, лежащий в основе поглощения гидрогелем питательных веществ при разработке минеральных удобрений и последующей передачи этих питательных веществ и влаги в почву. Данное исследование было направлено на определение влияния температуры, влажности и их взаимодействия на кинетические и термодинамические параметры, что позволило выявить ключевой механизм управления, лежащий в основе поглощения гидрогелем питательных веществ при разработке минеральных удобрений, модифицировало традиционную модель Аррениуса и установило количественную модель прогнозирования кумулятивного поглощения питательных веществ. Полевые опыты проводились при различных температурах (*T*) (15°C, 20°C, 25°C и 35°C) и содержании влаги (ϑ) (60%, 80% и 100% полевой емкости). Результаты показали, что влияние отдельных факторов и их взаимодействие на значения скорости реакции (K_N), свободной энергии активации (ΔG) и энтропии активации (ΔS) следовали по нисходящему порядку $T>\vartheta>T{\cdot}\vartheta$, тогда как энтальпия активации (ΔH) и степень активации (lg$N$) следовали по нисходящему порядку $\vartheta>T>T{\cdot}\vartheta$. Результаты указывают на эндотермическую реакцию поглощения питательных веществ, контролируемую энтальпией, при этом новая модель «A» (NH_4NO_3(T, θ)) оказалась более точной, чем традиционные модели, улучшая точность прогнозирования поглощения питательных веществ.

Ключевые слова: минеральные удобрения, гидрогель, кинетические параметры, термодинамические параметры, влажность, удобрение.