MJEN

MANAS Journal of Engineering
ISSN 1694-7398 | e-ISSN 1694-7398

Volume 10, Issue 2, (2022) Pages 116-128
https://doi.org/10.51354/mjen.1194756

Eco-friendly and biodegradable dimethylacrylamide/starch hydrogels for controlled release of urea and its water retention

Tuba Ersen Dudu[1,2,]*, Duygu Alpaslan[1,2]

[1] Department of Chemical Engineering, Institute of Natural and Applied Science, Van Yuzuncu Yil University, Van, 65080, Turkey, tuba_ersen@hotmail.com, ORCID: 0000-0001-5564-2834

[2] Department of Mining Engineering, Faculty of Engineering, Van Yuzuncu Yil University, Van, 65080, Turkey

ABSTRACT

In this study, we focused on the synthesis of polymeric hydrogels that will support the sorption and controlled release of urea, which is a rich nitrogen source, from aqueous solutions and their usability in agricultural applications. N, N-Dimethylacrylamide (DMAAm) and Starch (St) were selected as monomers, and their superior properties, such as chemical stability, high sorption properties, biocompatibility, and the presence of modifiable groups, were utilized. A redox polymerization technique was used to create a poly(DMAAm-co-St)-based hydrogel that was then modified with acidic and basic agents to improve the properties of starch. The synthesized acid- and base-modified hydrogels were named DSt, DSt_1, and DSt_2, respectively. Swelling analyses were performed to examine the structural and morphological properties of DSt, DSt_1, and DSt_2 hydrogels, and Fourier-Transform Infrared Spectroscopy (FT-IR) and Thermogravimetric Analyzers (TGA) were used. Intense cross-linking, porosity, and the presence of hydrophilic groups were successfully detected by instrumental analysis and swelling results. The successful results of urea sorption by DSt, DSt_1, and DSt_2 hydrogels show that they can both minimize the harmful effects of urea in the environment and contain the nitrogen necessary for plants. At the same time, urea sorption behaviors were evaluated in terms of sorption isotherms and thermodynamic properties, and it was observed that urea sorption conformed to the Langmuir isotherm. The urea release results showed that DSt, DSt_1, and DSt_2 hydrogels exhibited different release properties in different pH solutions, and these results reached 94% at pH 6–8, 100% at pH 6, and 100% at pH 8–10, respectively. As a result of the gradual decrease in the water resources on the earth, the increase in the use of fertilizers in agricultural production, and the insufficient use of fertilizers, our study draws attention to the development and support of materials that absorb/store water, and forms of controlled release fertilizers and provides potential ease of application

ARTICLE INFO

Research article

Received: 26.10.2022
Accepted: 16.12.2022

Keywords:
controlled release hydrogel
nitrogen loss
starch
water retention

**Corresponding Author*

1. Introduction

Nitrogen, phosphorus, and potassium fertilizers are especially used to increase and improve productivity in agricultural areas [1–2]. If these fertilizers, also known as mineral fertilizers, are used in accordance with the plant's request, type, soil characteristics, and climatic conditions, significant problems do not occur in the soil. However, with the development of agricultural practices, various chemicals, fertilizers, various wastes, and residues applied to the soil and plants pollute the soil and water resources, making them uninhabitable for living creatures [3–4]. Some of these substances, which mix with precipitation and irrigation water in the lower layers of the soil and from there into the groundwater, deteriorate the quality of the waters and make them undrinkable. Thus, both unnecessary economic losses and important problems related to soil and water pollution arise [5-7]. Recently, various studies have been carried out on the capture and controlled release of nitrogen and phosphorus fertilizers, which play an important role in soil and water pollution, and attention has been drawn to various biocompatible polymeric materials for this purpose. Hydrogels, which are polymeric materials, provide advantages for use in agricultural applications due to their various properties, such as the presence of hydrophilic groups, cross-linked structures, and insolubleness in water [8–10]. Especially in the literature, the usability of hydrogels synthesized from many monomers, such as dimethylacrylamide, maleic acid, citric acid, acrylamide, cellulose, chitosan, alginate, and acrylic acid, in agricultural applications has been emphasized. The common point of all these studies is that the synthesized hydrogels have hydrophilic properties and superabsorbent properties [11–16].

As a non-ionic monomer that polymerizes easily, DMAA's characteristics, such as high reactivity, low initiation temperature, chemical stability, and high sorption capacity, make it suitable for copolymerization reactions [17–18]. Due to its various properties, such as being produced from various sources, being an annually renewable resource, being water sensitive, and being biodegradable, starch has been used in most fields, such as thickening, gelling, and encapsulating agents in food products; coating binders and adhesives in papermaking; and the development of textiles, cosmetics, plastics, and polymeric materials [19–20]. Therefore, in this study, DMAAm and starch were chosen as monomers due to their biodegradability, excellent biocompatibility, chemical stability, and high water retention, and the sorption and release studies of urea fertilizer were focused on. Polysaccharide-based DSt hydrogels were synthesized by the free radical addition polymerization technique, and modified with acid and base agents to improve the positive properties of starch and minimize its negative properties. The chemical structure and morphological properties of DSt, DSt_1, and DSt_2 hydrogels were investigated with FT-IR and TGA devices. At the same time, their water sorption capacity was examined in distilled water and solutions at different pH values. Urea sorption and release experiments with DSt, DSt_1, and DSt_2 hydrogels were also examined. Urea sorption experiments were carried out at different urea concentrations, different pHs, and different temperatures, and the release behavior of urea-sorbed hydrogels was investigated in different pH environments.

2. Experimental

2.1. Materials

N, N-Dimethylacrylamide (Sigma Aldrich, 100%, DMAAm), and starch (Merck, 100%, St) were starting materials for the hydrogel synthesis. The crosslinking agent, accelerator, and initiator used were N, N'-methylene bis acrylamide (Merck, 99%, MBA), N, N, N', N'-tetramethylethylenediamine (Merck, 99%, TEMED), and ammonium persulfate (Merck, 98%, APS), respectively. Urea (Merck, 100%) was used as sorbat. Sodium hydroxide (Merck, 100%, NaOH) and hydrochloric acid (Sigma Aldrich, 37.5%, HCl) were used as the modification agents. The deionized water (DI water) was obtained from 18.2 MΩ.cm (Millipore Direct-Q3 UV). The pH measurements were carried out with a Thermo Scientific pH meter (USA). Ultra-Viole spectroscopy (UV-Vis, Thermo Scientific GENESYS 10S, USA) was used to quantify the amount of urea during sorption and release studies.

2.2. Preparation of hydrogels

DMAAm and St monomers were used to synthesize hydrogels via the redox polymerization technique. Briefly, 1.5.10-3 g of MBA crosslinker was dissolved in 1 mL of DMAAm monomer, and 1 mL of deionized water was added to the mixture and thoroughly mixed (at 2500 rpm) for one minute. To this mixture, 2 mL of a St solution (1 g/10 mL) was added and thoroughly mixed. Then 5 μL of TEMED and 0.2 mL of APS solution were added sequentially. The reaction mixture was carefully mixed for approximately one minute and allowed to polymerize and crosslink to complete the reaction (at about six hours). Then, the hydrogel was removed from the polymerization medium, cut into 6 mm long cylinders, cleaned by placing it in DI water, and named p(DMAAm-co-St) (DSt) hydrogel. After the cleaning procedure, the hydrogel was dried in an oven at 40°C to a constant weight and kept in sealed containers for further studies [11–21]. In the hydrogel modification process, the method applied by Ersen Dudu et al. (2019) was used and named p(DMAAm-co-St)/HCl (DSt1) and p(DMAAm-co-St)/NaOH (DSt2) hydrogels [8].

2.3. Characterization of Hydrogels

The Fourier-Transform Infrared Spectroscopy (FT-IR) investigation was performed using an Attenuated Total Reflection (ATR) built-in instrument (Thermo, model Nicolet iS10 FT-IR Spectrometer, USA). After being ground into powder, the hydrogel was arranged on the ATR sample plate. 4 cm^{-1} of the resolution was used to examine the spectral range between 4000 and 650 cm^{-1}.

A Setaram Labsys Evo Gravimetric Analyzer (TGA/DSC 1600 model, France) was used to conduct TGA experiments on hydrogels. In ceramic crucibles, samples weighing 4–6 mg were put. Under an argon atmosphere, the samples were heated at a rate of 10°C/min from 50°C to 1000°C. A fixed 100 mL/min argon gas flow rate was used in the analyzer.

2.4. Swelling analysis

Swelling studies in water are a widely used technique for characterizing hydrogels. Both kinetic and balance swelling studies are based on the determination of the increase in mass or volume of a cross-linked gel held in a solvent. Swelling experiments were performed with the method specified in the literature, and swelling values (S%) were calculated using the equation given below.

$$S\% = \left(\frac{(M_t - M_0)}{M_0}\right).100 \qquad (1)$$

where M_0 is the beginning mass (g) of the hydrogel and is the mass of the hydrogel at the end of time t [22, 23]. The equilibrium swelling behavior of the synthesized hydrogels was also evaluated at different pH values. SR was also studied by adjusting the pH of the solutions with 0.1 M HCl and 0.1 M NaOH. Again, hydrogels were kept for 24 h in acidic and basic solutions to determine the effect of medium pH on the swelling ratios.

Swelling is a characteristic feature of polymeric networks. Depending on the amount of crosslinking and the presence of hydrophilic groups, polymeric networks can absorb very large amounts of liquid without dissolving. The most basic way to describe the swelling behavior is to apply the swelling data to the equation below by accepting the swelling kinetic curves created as a result of the dynamic swelling tests as quadratic [24].

$$\frac{\mathrm{dS}}{\mathrm{dt}} = \mathrm{k_s}.\,(S_{\mathrm{mak}} - \mathrm{S})^2 \tag{2}$$

where dS/dt is the swelling speed of hydrogels; S_{max} is the swelling value of hydrogel at equilibrium ($g_{water}/g_{hydrogel}$); S is the swelling value at time t ($g_{water}/g_{hydrogel}$); k_s represents swelling speed constant ($g_{hydrogel}/(g_{water}.min)$); r_0 is the initial swelling speed ($g_{water}/(g_{hydrogel}.min)$).

Modeling the swelling kinetics of hydrogels is important for understanding the type and rate of diffusion of water into the hydrogel, as well as the forces acting on the swelling of the hydrogel. The most commonly used relations for modeling the swelling kinetics of hydrogels are Fick's laws. The following equation is the version of Fick's law applied to reticulated, swellable polymers [25].

$$\mathrm{F} = \left(\frac{\mathrm{M_t}}{\mathrm{M_e}}\right) = \mathrm{k.\,t^n} \tag{3}$$

where M_e represents the mass of hydrogels that have reached equilibrium (g); k is a specific rate constant; n is a constant which shows diffusion exponent; t is time (min). The value of the diffusion exponent (n) is found from the slope of the graph between $\ln(M_t/M_e)$ and ln(t). The graph was drawn by applying it to data where the swelling has not yet reached equilibrium and the (M_t/M_e) ratio is less than 0.6.

2.5. *Sorption experiments*

Urea is a compound of physiological importance. It is both found in the bodies of mammals and excreted as waste, and it is also used in the production of fertilizer, animal feed, medicine, plastic, and paint. For this reason, it is in the class of pollutants that cause pollution of environmental waters and soil, and it is a fertilizer that has great importance in the development of plants. The sorption experiments were carried out in a temperature-controlled magnetic stirrer in triplicate. To examine the effect of initial urea concentrations, the urea concentration was kept in the range of 10 to 1000 mg/L, while the hydrogel concentration, time, temperature, and stirring speed were kept constant at 1 g/L, 48 hours, 298 K, and 150 rpm, respectively. To examine the effect of pH change on urea sorption, pH was changed between 2 and 12, and urea concentration, amount of hydrogel, temperature, stirring speed, and time were kept constant at 100 mg/L, 1 g/L, 298 K, 150 rpm, and 24 hours. The effect of temperature on urea sorption was investigated by changing the temperature between 283 and 323 K while keeping the urea concentration, hydrogel amount, ambient pH, mixing speed, and time constant at 100 mg/L, 1 g/L, 12, 150 rpm, and 24 hours. In all sorption studies, the amount of urea in the solution was determined by a UV-Vis spectroscopy device, and the amount of urea loaded per unit mass of hydrogels, q_e (mg/g), was calculated with the following equation [26].

$$\mathrm{q_e} = \frac{(\mathrm{C_o} - \mathrm{C_e}).\,\mathrm{V}}{\mathrm{M}} \tag{4}$$

where C_o represents the initial concentration of urea (mg/L); Ce is the equilibrium concentration of urea (mg/L); V represents the solution volume (L); and M is the hydrogel mass (g).

2.5.1. *Urea sorption isotherms and thermodynamic studies*

The urea sorption mechanism of hydrogels was evaluated using Langmuir (Eq. (5)) [27], Freundlich (Eq. (6)) [28], Temkin (Eq. (7)) [29], and Dubinin–Radushkevich (D–R) (Eq. (8)) [30] isotherm models (see Table 1a for equations).

In order to describe the thermodynamic behavior of urea sorption, thermodynamic parameters such as free energy change (ΔG°, J/mol), enthalpy change (ΔH°, J/mol), and entropy change (ΔS°, J/(mol.K)) were calculated using Equation 9 defined in the literature (see Table 1b for equations) [31–32].

Table 1. ***a)*** *Sorption isotherm models for urea sorption,* ***b)*** *Thermodynamic parameters of urea sorption, and* ***c)*** *Mathematical models for urea release*

a) Model	**Mathematical Equation**
Langmuir (Eq. 5)	$\frac{C_e}{q_e} = \left(\frac{C_e}{q_{max}}\right) + \left(\frac{1}{q_{max}.K_L}\right)$
Freundlich (Eq. 6)	$\log q_e = \log K_f + \left(\frac{1}{n}\right) \log C_e$
Temkin (Eq. 7)	$q_e = \frac{R.T}{b_T} \ln A_T + \left(\frac{R.T}{b_T}\right) \ln C_e$
Dubinin–Radushkevich (D–R) (Eq. 8)	$lnq_e = \ln q_s - \beta.\varepsilon^2$ $\varepsilon = R.T.\ln\left(1 + \frac{1}{C_e}\right)$ $E = \frac{1}{\sqrt{2.\beta}}$

b) Model	**Mathematical Equation**
Thermodynamic parameters (Eq. 9)	$\mathrm{K}^0 = \frac{\mathrm{C_t}}{\mathrm{C_e}}$ $\Delta\mathrm{G}^0 = \Delta\mathrm{H}^0 - \mathrm{T} \cdot \Delta\mathrm{S}^0$ $\mathrm{lnK}^0 = \frac{\Delta\mathrm{S}^0}{\mathrm{R}} - \frac{\Delta\mathrm{H}^0}{\mathrm{R} \cdot \mathrm{T}}$

c) Model	**Mathematical Equation**	**Release Mechanism**
Zero order kinetic model (Z-O) (Eq. 11)	$C_r = C_0 - k_0.t$	Diffusion Mechanism
First order kinetic model (F-O) (Eq. 12)	$lnC_r = lnC_0 - k_1.t$	Fick's first law, diffusion Mechanism
Higuchi Model (H) (Eq. 13)	$\frac{C_r}{C_\infty} = k_H.\sqrt{t}$	Diffusion medium based Mechanism in Fick's first law
Korsmeyer-Peppas Model (K-P) (Eq. 14)	$ln\frac{C_r}{C_\infty} = lnk_{KP} + n.lnt$	Semi empirical model, diffusion-based mechanism

q_{max} is the monolayer sorption capacity of urea (mg/g); K_L is the L sorption equilibrium constant (L/mg) which can be determined via the linearized L isotherm; K_f (mg/g) and n are the F constants related to sorption capacity and sorption intensity, respectively; R is universal gas constant (8.314 J/(mol.K)); T is temperature at 298 K; A_T and b_T are T isotherm equilibrium binding constant (L/g) and T isotherm constant, respectively; q_s is the D-R monolayer sorption capacity (mg/g); ε is the Polanyi potential based upon equilibrium concentration; β is a constant based upon sorption energy (mol^2/J^2); E is sorption energy (kJ/mol). C_r is concentration of urea release in time t (mg/L); C_0 is the initial concentration of urea in the solution (most times, $C_0 = 0$) (mg/L); k_0 is the Z-O release constant expressed in units of concentration/time (mg/(L.min)); t is time (min); k_1 is the F-O release constant (1/min); C_∞ is concentration of urea release in equilibrium (mg/L); k_H is H release rate constant ($1/\sqrt{\text{min}}$); k_{KP} is K-P release rate constant; n is release exponent which is indicative of the transport mechanism ($M_t/M_\infty < 0.6$ should only be used); K^0 represents sorption equilibrium constant; and Ct represents the sorbed urea concentration at time t (mg/L); ΔG° is Gibbs free energy change (J/mol), ΔH° is enthalpy change (J/mol) and ΔS° is entropy change (J/(mol.K)).

2.6. Urea release in an aqueous medium and mathematical modeling

In this study, we focused on both the sorption of urea and the controlled release behavior. Although the loss of urea in environmental waters causes pollution, its use as a controlled-release fertilizer is also of great importance. The usability of the DSt-based hydrogels we synthesized in the present study as a controlled urea release support material was also investigated and constituted the second pillar of this study. Urea release experiments were performed in triplicate in different aqueous buffer solutions ranging from 2 to 12. Ambient temperature, stirring speed, and amount of urea-loaded hydrogel were kept constant at 298 K, 150 rpm, and 0.05 g, respectively. Release experiments were performed until the equilibrium value was reached as a function of time. To determine the amount of urea released, approximately 2 mL of sample was withdrawn from the solution at regular intervals, and the amount of released urea was measured using a UV-visible spectrophotometer. The cumulative urea release percentage was calculated with the following equation [33];

$$\mathrm{Release\%} = \frac{Q_t}{Q_o}.100 \qquad (10)$$

where Q_o represents the urea amount sorbed by the hydrogel (mg/L) and Q_t is the urea amount released into the solution medium at time t (mg/L).

In order to examine the release kinetics of urea in DSt-based swellable polymeric hydrogels, the release data were obtained experimentally and applied to four different release equations: the zero-order kinetic model (Z-O model) (Eq. 11) [34], the first-order kinetic model (F-O model) (Eq. 12) [34], the Higuchi model (H model) (Eq. 13) [35], and the Korsmeyer-Peppas model (K-P model) (the power law) (Eq. 14) [36]. They were displayed in Table 1c as model equations.

3. Results and discussion

3.1. Characterization

Fourier transform infrared (FT-IR) spectroscopy is a method frequently used to identify bonds in the structure of molecules, such as the determination of intramolecular bonds, the determination of molecular structure, the examination of intramolecular functional groups, and the determination of unknown molecules by library scanning. Figure 1a shown the FT-IR spectra of all hydrogels. Figure 1a, when analyzed, represented the broad peak -OH band observed in the 3678 to 3035 cm^{-1} region. The peaks occurring around 3429 cm^{-1}, 3434 cm^{-1}, and 3459 cm^{-1} in the three FT-IR spectra were assigned to the N-H stresses caused by the crosslinker. The aliphatic -CH bending vibration of DMAAm, starch, and MBA occurred at about 2926 cm^{-1}. It was determined that the peaks observed at approximately 1619 cm^{-1} in the same spectra correspond to the C = O stresses of DMAAm and MBA. It was determined that the peak determined around 1498 cm^{-1} belonged to the C-N tension of acrylamide, and the intensity of this tension increased after the modification. When all spectra were examined, it was determined that the strength of the structural bonds changed and the strength of the hydrogen bonds increased with the modification.

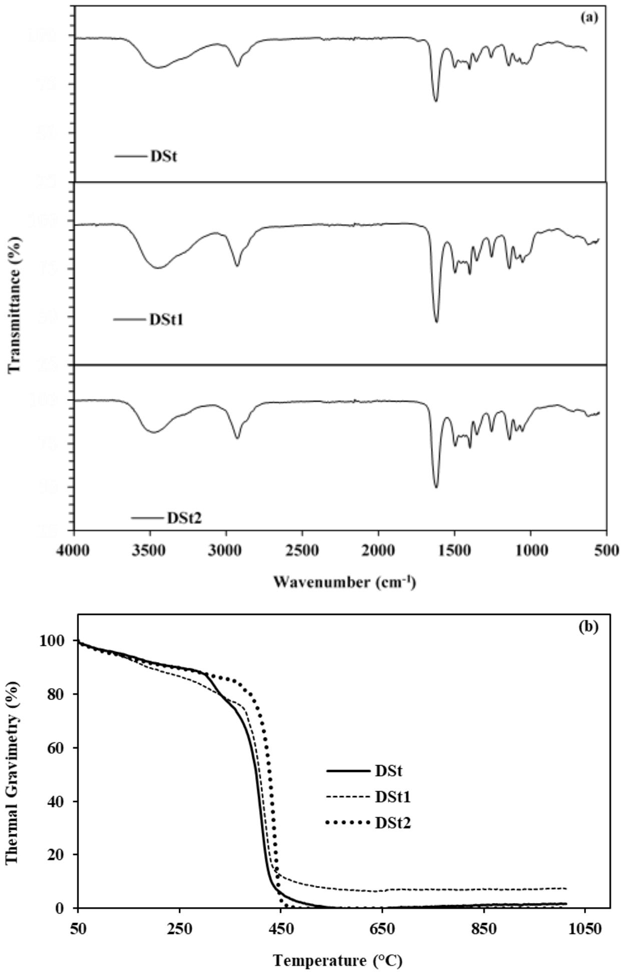


Figure 1. ***(a)*** *FT-IR Spectra of DSt, DSt$_1$, and DSt$_2$ hydrogels, and* ***(b)*** *The Thermogravimetric Analysis of DSt, DSt$_1$, and DSt$_2$ hydrogels.*

In the thermogravimetric analysis method, mass loss can be determined with temperature increases. For this reason, reactions such as oxidation, evaporation, sublimation, and desorption that may occur in the sample can be examined, and information about the degradation mechanism of the polymer can be provided. Thermogravimetric analysis results were presented in Figure 1b. In Figure 1b, it was seen that although DSt and DSt$_1$-based hydrogels degraded in four steps, the DSt$_2$-based hydrogel exhibited degradation behavior in two steps. When the temperature degradation curves were examined separately, it was determined that the DSt, DSt$_1$ and DSt$_2$ hydrogels had 100%, 6.4%, and 100% total mass loss, respectively, when temperatures of 597°C, 534°C, and 483°C were reached. Decomposition thermograms showed that after the modification of the DSt hydrogel with acid, its resistance to increasing temperature increased and its mass loss decreased. In addition, TGA thermograms showing the decomposition behavior with temperature explain that decompositions up to about 100–150 °C are caused by unbound water in the structure, losses between about 150–250 °C are caused by the removal of bound water and slightly volatile compounds, and decomposition steps above 250°C were caused by structural deterioration and bond breaks.

3.2. Swelling analysis

The swelling behavior of hydrogels in pure water and in buffer solutions with different pH values can be explained by the presence of intense cross-linking, porosity, and hydrophilic groups. With the diffusion of the solvent into the polymeric lattice, swelling begins, and after a while, the rate of solvent transfer to the gel and the rate of release from the gel become equal. In this case, the gel reaches the equilibrium swelling ratio (Smax) [37]. In order to examine the swelling behavior of the synthesized hydrogels in a deionized water environment, dynamic swelling experiments were carried out at 25°C with a 0.05 g hydrogel amount at certain time intervals, and the results are given in Figure 2a. According to the data obtained, it was found that the DSt, DSt1, and DSt_2 hydrogels reached the equilibrium swelling value after approximately 56 hours and were 1115%, 2364%, and 2629%, respectively. The equilibrium swelling values obtained indicate that the hydrophilicity of the DSt-based hydrogel increased after modification.

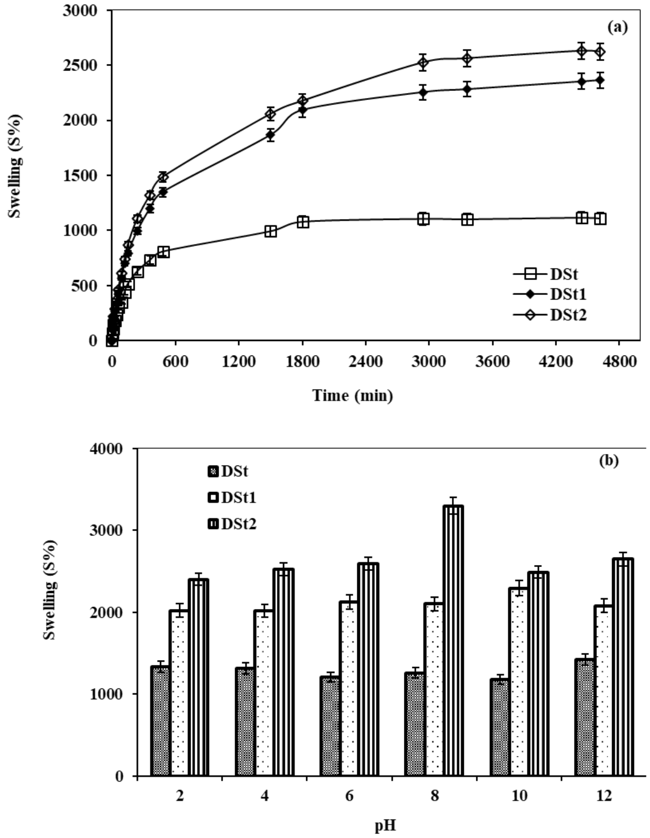


Figure 2. (a) *Percent swelling degree of the DSt, DSt_1, and DSt_2 hydrogels with time in deionized water, and* ***(b)*** *Swelling % of the DSt, DSt_1, and DSt_2 hydrogels as a function of pH (pH is adjusted by the addition of 0.1 M HCl, 0.1 M NaOH; time: 24 h).*

The water-holding capacity (swelling) of hydrogels containing anionic or cationic groups is significantly affected by pH change. The pH-dependent water holding capacities of DSt, DSt1, and DSt_2-based hydrogels synthesized within the scope of this study were examined at 25°C and 0.05 g hydrogel amount in the pH = 2–12 range, and the results were reported in Figure 2b. When Figure 2b was examined, it was concluded that the nonionic structure of the DMAAm monomer was dominant in the DSt-based hydrogel. At the same time, it was determined that the swelling behavior of the DSt-based hydrogel was not significantly affected by the pH change, and the equilibrium swelling value was 1421% at pH 12. When the graphs showing the swelling behavior of DSt_1 and DSt_2-based hydrogels were examined, it was determined that the swelling capacity was affected by the pH change and that they reached different swelling values. The maximum equilibrium swelling values of DSt_1 and DSt_2-based hydrogels were observed to be 2294% at pH 10 and 3302% at pH 8, respectively. The different swelling behavior of DSt_1 and DSt_2-based hydrogels at different pH values is due to the fact that the ions in the external environment they are placed in penetrate the hydrogel and come into contact with more ionic groups, and as a result, they reach different equilibrium swelling values at different pH values.

While calculating the diffusion exponent and constant by drawing the lnF-t graph using the data expressing the weight change over time obtained as a result of the dynamic swelling experiments, the theoretical swelling percentage, swelling velocity, and rate constant values were calculated by drawing the t/S-t curve. And then the results were summarized in Tables 2 and 3. When Table 2 was examined, the n values for DSt, DSt_1, and DSt_2 hydrogels were found to be 0.37, 0.45, and 0.45, respectively. These values comply with the $n \leq 0.45$ rule. In this case, it was concluded that the diffusion types of all three hydrogels fall into the Fickian type diffusion class. In this case, it can be said that swelling is controlled by the diffusion rate of water [38]. In addition, when Table 3 was examined, it was shown that the theoretical equilibrium swelling values (S_{max}) of the prepared cross-linked hydrogels were in harmony with the experimental equilibrium swelling values. This agreement in the swelling results was an indication that the swelling kinetics analysis was built on the right foundations. At the same time, it was observed that the initial swelling velocity (r_0) value and swelling capacity increased after the modification of the DSt hydrogel.

Table 2 *Results of the diffusion exponent (n), correlation coefficient (R^2), and the specific rate constant (k) for the swelling kinetics in deionized water of the hydrogels*

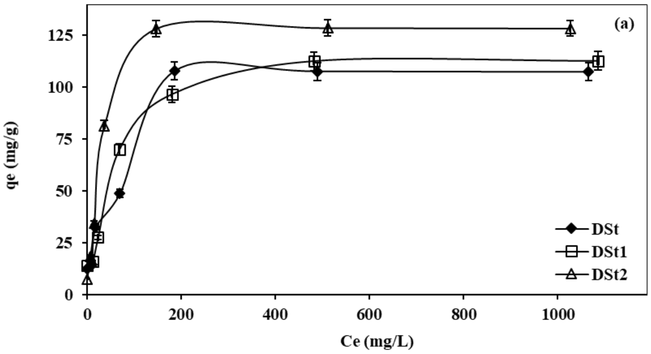
Water type	Hydrogels	Diffusion Exponent (n)	Specific Rate Constant (k)	Correlation Coefficient (R^2)
Deionized water	DSt	0.37	0.07	0.9873
	DSt_1	0.45	0.04	0.9904
	DSt_2	0.45	0.04	0.9906

Table 3 *Results belonging to the swelling value at time t (S), the swelling value at equilibrium (S_{max}), the initial swelling speed (r_0) and swelling speed constant (k_s) in deionized water of the hydrogels*

Water type	Hydrogels	S% ($g_{water}/g_{hydrogel}$)	S_{mak} ($g_{water}/g_{hydrogel}$)	r_0 $g_{water}/(g_{hydrogel}$•min)	k_s ($g_{hydrogel}/(g_{water}$•min))
Deionized water	DSt	1115	1111	7.58	$6.14*10^{-6}$
	DSt_1	2364	2500	9.24	$1.48*10^{-6}$
	DSt_2	2629	2500	9.83	$1.57*10^{-6}$

3.3. Sorption tests

In batch sorption studies, the effects of variables such as initial urea concentration, initial pH, and temperature on the sorption capacities of all sorbents were examined. The related graphics are given in Figure 3(a-c). The effect of initial urea concentration on urea sorption to dry DSt, DSt_1, and DSt_2 hydrogels was investigated at 48 hours, at 298 K, and in the range of 10–1000 mg/L urea. As seen in Figure 3a, it was determined that the sorption rate and capacity values increased as the initial urea concentration increased. It was determined that the urea sorption capacity of the DSt_2 hydrogel was higher than the other two hydrogels and was 128.5 mg/g. The results showed that the base modification made the hydrogel more sensitive to urea and increased its sorption capacity. At the same time, it was concluded that the hydrogel structure gave a remarkable attraction to urea in its modification with acid, and this value was 112.7 mg/g.



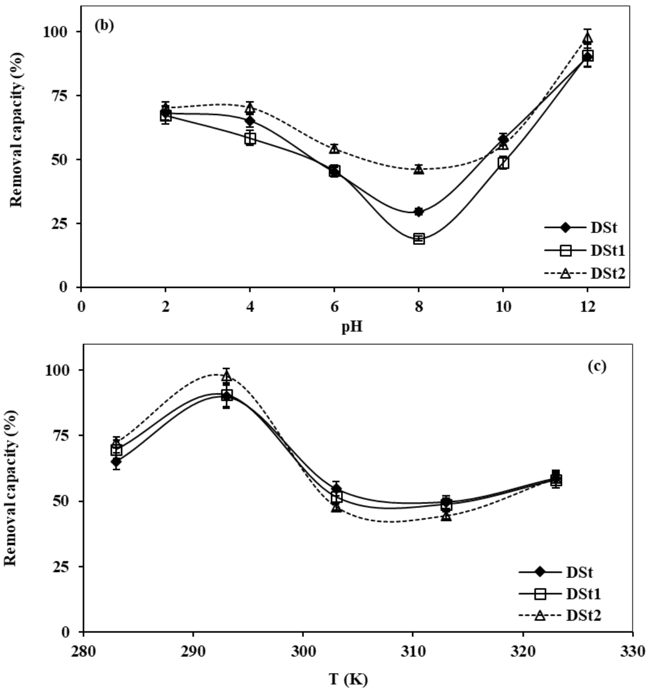


Figure 3. ***(a)*** *The q_e vs C_e graphs at different urea concentrations of the hydrogels (urea concentration: 10-1000 mg/L (50 mL), sorbent dosage: 1 g/L, time: 48 h, temperature: 25 °C),* ***(b)*** *Effect of pH on the percent uptake of urea onto the hydrogels (pH: 2-12, urea concentration: 100 mg/L (50 mL), sorbent dosage: 1 g/L, time: 24 h, temperature: 25 °C), and* ***(c)*** *Effect of temperature on the percent uptake of urea onto the hydrogels (temperature: 10-50 °C, urea concentration: 100 mg/L (50 mL), sorbent dosage: 1 g/L, pH: 12, time: 24 h).*

The urea removal potentials of dry DSt, DSt_1, and DSt_2 hydrogels from aqueous solutions were investigated in the pH 2–12 range for 24 hours at 298 K and 100 mg/L urea concentration. The amount of urea sorbed by all three sorbents was calculated as a percent, and the percent sorbed amounts against pH were shown in Figure 3b. It is seen from the graph that the sorption performances of each sorbent against urea are different from each other. Looking at Figure 3b, it was seen that the DSt_2-based hydrogel had a higher sorption ability against urea at different pHs than the other two hydrogels. DSt, DSt_1, and DSt_2 hydrogels reached the highest urea sorption capacity at pH 12; the results were 90%, 91%, and 98%, respectively. The fact that the surface functional groups of DSt_2 were higher than those of other sorbents caused an increase in sorption performance. In light of the sorption data obtained, it is concluded that the pH value is one of the most critical parameters affecting the sorption and that it significantly affects the sorption depending on the sorbate type and sorbent character of the solution.

In order to examine the effect of temperature on urea sorption from an aqueous solution on dry DSt, DSt_1, and DSt_2 hydrogels, sorption experiments between 283 and 323K were carried out. Initial urea concentration was chosen as

100 mg/L and pH 12, and sorption tests were applied under optimum conditions. Using the results obtained, the temperature–percent sorption graph was plotted in Figure 3c. When Figure 3c was examined in detail, as the temperature increased from 283 K to 293 K, the sorption efficiency increased from 65% to 89% for DSt, from 70% to 91 for DSt_1, and from 73% to 97% for DSt_2.It was seen that the sorption capacity for all hydrogels decreased with increasing the temperature from 293 K to 323 K. The positive effect of a temperature increase up to 293 K on sorption can be attributed to reasons such as increased sorbent-sorbate interaction with temperature, passive sites becoming more active, or intraparticle diffusion becoming more effective as a result of the enlargement of the pore structure of the sorbent. It was thought that the decrease after 293 K was due to the fact that the energy required for the sorption to take place was provided at 293 K and the increasing temperature affected the urea sorption negatively since the sorption exhibits exothermic properties after this temperature.

3.3.1. *Sorption isotherms and thermodynamics*

In order to explain the sorption behavior of DSt, DSt_1, and DSt_2 hydrogels against increasing initial urea concentrations, the four most known and applied sorption isotherms were examined, and the constants of the obtained sorption isotherms were given in Table 4. It was clear from Table 4 that the curves that best describe urea sorption by DSt, DSt_1, and DSt_2 hydrogels belong to the Langmuir isotherm, as confirmed by high R^2 values. In the Langmuir isotherm, the sorbent surface is considered to be similar in energy and is known to be used to explain monolayer homogeneous sorption. Thus, it is expected that these regions will form a monolayer by keeping the urea in equal numbers, irreversible adsorption, and high compatibility [39]. When the q_m values expressing the Langmuir sorption capacity were examined, it was observed that they were in good agreement with the experimental q_e values. The monolayer sorption capacities of urea for DSt, DSt1, and DSt_2 were calculated as 111 mg/g, 119 mg/g, and 132 mg/g, respectively. Table 4 showed that the Freundlich, Temkin, and D–R isotherms exhibited a lower correlation with experimental sorption data compared to the Langmuir model.

Table 4 *Isotherm results for sorption of urea by hydrogels*

Model		Hydrogels DSt	DSt_1	DSt_2
Langmuir Isotherm Constants	K_L (L/mg)	0.023	0.021	0.037
	q_m (mg/g)	111.1	119.1	131.6
	R^2	0.9930	0.9950	0.9981
Freundlich Isotherm Constants	K_f	10.3	10.9	13.2
	n	2.71	2.76	2.66
	R^2	0.8978	0.8746	0.8056
Temkin Isotherm Constants	b_T	145.9	142.3	103.8
	A_T (L/g)	0.7	0.71	0.46
	R^2	0.8456	0.8656	0.8758
D–R Isotherm Constants	E (kJ/mol)	0.13	0.11	0.16
	R^2	0.3343	0.3559	0.8171

Equation 9 was used to determine the thermodynamic parameters ΔG°, ΔS°, and ΔH°, and $\ln K_c$ – 1/T graphs were drawn. The values calculated from the graph were given in Table 5. When the ΔG° values in the table were examined, it was observed that the ΔG° values increased with increasing temperature. Negative ΔG° values indicated that urea sorption occurs spontaneously and in a suitable process, while positive ΔG° values indicated that increasing temperature negatively affects urea sorption. The results showed that urea sorption was possible at low temperatures. Negative ΔH° values indicated that urea sorption on the three hydrogels was an exothermic process. ΔH° can also be helpful in deciding whether sorption is chemical or physical. While the enthalpy value is generally less than 4.2 kJ/mol in physical sorption, it has a value greater than 21.0 kJ/mol in chemical sorption [40]. Looking at the ΔH° values in the able, it can be said that urea sorption on hydrogels proceeds chemically. The negative ΔS° values indicated that the randomness of the sorption equilibrium occurring at the solid-liquid interface during urea sorption decreased [41].

Table 5 *Thermodynamic parameters for sorption of urea by hydrogels*

Hydrogels	Thermodynamic Parameters			
	Temperature (K)	ΔG° (J/mol)	ΔH° (J/mol)	ΔS°(J/(mol.K)
DSt	283	-2028.5	-21756.1	-69.1
	293	-1331.4		
	303	-634.3		
	313	62.8		
	323	759.9		
DSt_1	283	-1979.7	-25060.1	-81.6
	293	-1164.1		
	303	-348.5		
	313	467.0		
	323	1282.6		
DSt_2	283	-1987.4	-28967.6	-95.3
	293	-1034		
	303	-80.6		
	313	872.7		
	323	1826.1		

3.4. *Cumulative urea release behavior*

In the study, the release of urea, which has fertilizer properties, was monitored from the synthesized and modified hydrogels. Urea release from DSt, DSt_1, and DSt_2 hydrogels was investigated at room temperature and a pH range of 2–12, and the graphs of urea release were shown in Figure 4. As seen in Figure 4, it was observed that the amount of urea released from the DSt-based hydrogels increased after the modification of the hydrogels. It was thought that the functional groups and porosity in the structure of the DSt-based hydrogel increased after the modification process, and at the same time, its tight structure loosened a little more. In addition, while the DSt-based hydrogel exhibited similar urea release behavior in the 4–8 pH range, this situation changed in the DSt_1 and DSt_2-based hydrogels. It was observed that the maximum amount of urea released from DSt, DSt_1, and DSt_2-based hydrogels reached 94% at pH 6–8, 100% at pH 6, and 100% at pH 8–10, respectively. If the amount of urea released was evaluated in terms of time, it was determined that all hydrogels reached the equilibrium release value after about 17 hours, and there was a rapid release in the first four hours. In the first 4 hours, urea that adheres to the surface and binds with weak interactions was released, while urea attached to the pores was released slowly in the next process.

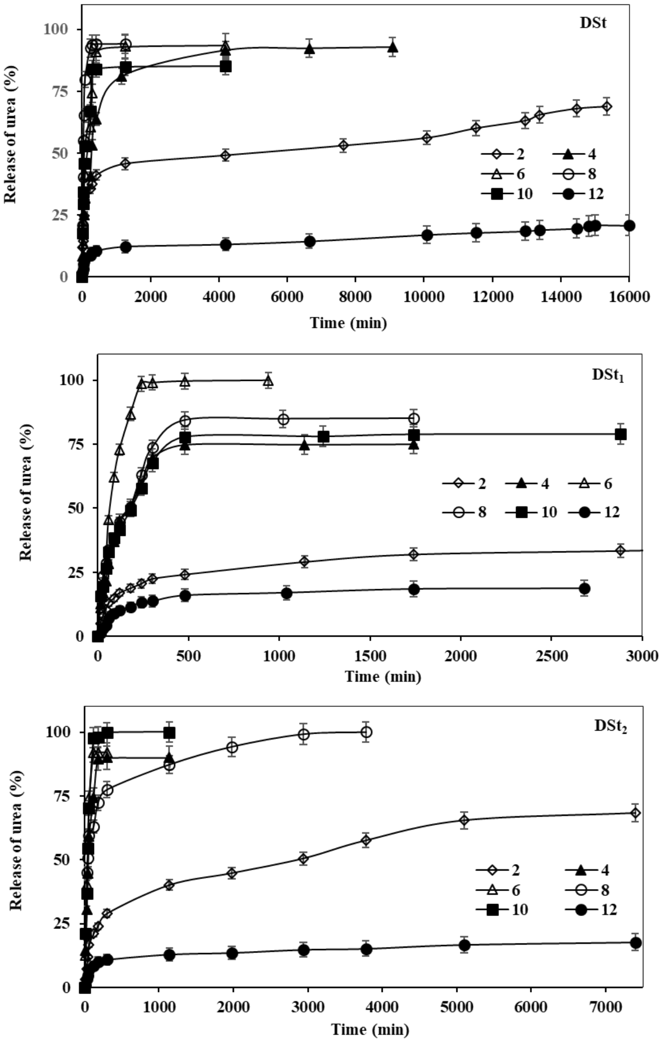


Figure 4. *Release behavior of urea in different pHs from DSt, DSt_1, and DSt_2 hydrogels.*

In the literature, various kinetic models have been proposed for drug release from the surface and pores of polymeric materials in the solution medium. Considering the slopes of the curves drawn according to the kinetic models, the model with the highest R^2 value is selected as the drug release kinetic model. In this study, the urea release mechanism from DSt, DSt_1, and DSt_2-based hydrogels was tried to be interpreted using Z-O model, the F-O model, the H model, and the K-P model, and the obtained kinetic model parameters were summarized in Table 6. Considering the R^2 values, it was seen that the best correlation for urea-loaded DSt, DSt_1, and DSt_2 hydrogels was obtained from the K-P model. When Table 6 was examined, it was observed that the diffusion exponent constants of DSt and DSt_1-based hydrogels at different pH values were both less than 0.45 and in the range of 0.45 to 0.89. In contrast to the DSt and DSt_1 hydrogels, the DSt_2 hydrogel was found to have diffusion exponent constants of less than 0.45 at all pH values. At n values less than 0.45, the release is diffusion-controlled and conforms to the Fickian diffusion type. At n values between

0.45 and 0.89, however, the release is affected by both the diffusion of water and the relaxation behavior of the hydrogel and conforms to the non-Fickian diffusion type [8, 42]. The release results supported the swelling analysis. One of the important parameters to be calculated while examining the release behavior of hydrogels is the diffusion coefficient. When the diffusion coefficient values were examined, it was observed that the urea release behavior from hydrogels was different at each pH value. The high diffusion coefficients in Table 6 suggest that urea diffusion into the solution medium was greater.

Table 6. *Release kinetic and mechanism of urea release*

Kinetic Models		**pH**					
DSt		**2**	**4**	**6**	**8**	**10**	**12**
Z-O	C_o	27.9	32.3	49.3	78.8	59.1	6.9
	k_o	-0.003	-0.012	-0.021	-0.020	-0.022	-0.001
	R^2	0.6895	0.7308	0.8923	0.7087	0.8436	0.5892
F-O	C_o	27.9	26.9	40.5	75.8	56.7	6.9
	k_1	-0.00009	-0.0002	-0.0002	-0.0001	-0.0002	-0.0001
	R^2	0.4057	0.4127	0.5658	0.4942	0.6231	0.4937
H	k_H	0.0054	0.0057	0.0074	0.007	0.0068	0.0057
	R^2	0.4785	0.8809	0.9786	0.8778	0.9723	0.8353
K-P	n	0.23	0.53	0.45	0.25	0.37	0.2
	K_{KP}	0.134	0.012	0.015	0.086	0.028	0.132
	D	$3.1*10^{-7}$	$1.2*10^{-5}$	$3.6*10^{-6}$	$2.2*10^{-7}$	$1.1*10^{-6}$	$2.6*10^{-8}$
	R^2	0.9383	0.9724	0.9776	0.9711	0.9688	0.9498
DSt_1		**2**	**4**	**6**	**8**	**10**	**12**
Z-O	C_o	11.9	45.7	71.8	56.3	45.2	8.3
	k_o	-0.023	-0.028	-0.035	-0.033	-0.03	-0.007
	R^2	0.6231	0.7493	0.6609	0.7715	0.8061	0.5316
F-O	C_o	16.4	42.6	54.8	33.5	44.5	7.4
	k_1	-0.0002	-0.0003	-0.0006	-0.0018	-0.0003	-0.0006
	R^2	0.4533	0.5354	0.3943	0.7635	0.6019	0.3108
H	k_H	0.0168	0.0108	0.0106	0.0154	0.0118	0.0182
	R^2	0.8892	0.9277	0.8582	0.9665	0.9621	0.7559
K-P	n	0.39	0.49	0.41	0.46	0.45	0.47
	K_{KP}	0.058	0.021	0.04	0.024	0.027	0.049
	D	$1.7*10^{-5}$	$2.1*10^{-5}$	$1.1*10^{-5}$	$1.2*10^{-5}$	$1.4*10^{-5}$	$6.3*10^{-5}$
	R^2	0.934	0.9775	0.9579	0.9914	0.9865	0.9406
DSt_2		**2**	**4**	**6**	**8**	**10**	**12**
Z-O	C_o	21.5	80.2	100.2	56.5	106.9	8.3
	k_o	-0.012	-0.031	-0.042	-0.035	-0.048	-0.003
	R^2	0.8083	0.7022	0.7319	0.7435	0.7365	0.6369
F-O	C_o	19.5	74.6	83.3	65.6	98.0	7.6
	k_1	-0.0003	-0.0002	-0.0003	-0.0003	-0.0003	-0.0002
	R^2	0.5176	0.4816	0.481	0.6383	0.5182	0.3772
H	k_H	0.011	0.011	0.011	0.012	0.0002	0.001
	R^2	0.9526	0.8944	0.9098	0.8732	0.8974	0.8265
K-P	n	0.35	0.31	0.3	0.17	0.39	0.24
	k_{KP}	0.050	0.073	0.077	0.122	0.041	0.124
	D	$3.6*10^{-6}$	$3*10^{-6}$	$1.5*10^{-6}$	$7.2*10^{-10}$	$5.1*10^{-6}$	$4.3*10^{-7}$
	R^2	0.9734	0.9424	0.9466	0.9527	0.9239	0.9261

4. Conclusions

Urea is a product that is naturally formed by the metabolism of proteins and can be excreted with feces. It is a physiologically important compound used both as fertilizer in crops and as animal feed in the agricultural sector. Therefore, the conscious and correct use of urea is of great importance for the environment and plants. The present study focused on both the synthesis of new and environmentally compatible hydrogels and the development and improvement of the urea absorption and release properties of these hydrogels. Dimethylacrylamide and starch-based hydrogels were synthesized by the free radical addition polymerization technique and separately modified with acid and base solutions. FT-IR, TGA, and swelling analyses were performed to determine whether hydrogel synthesis and modification took place. Intense cross-linking, porosity and the presence of hydrophilic groups were successfully detected by instrumental analysis and swelling results. In addition, urea sorption and release applications constituted the two important pillars of the presented study. The successful results of urea sorption by DSt, DSt_1 and DSt_2 hydrogels showed that they can both minimize the harmful effects of urea in the environment and contain the nitrogen necessary for plants. At the same time, the high swelling and urea sorption abilities of all hydrogels at different pH values give these hydrogels superior properties in terms of application area. When the urea release results were examined, it was determined that DSt, DSt_1, and DSt_2 hydrogels exhibited different release properties in different pH solutions, and these results reached 94% at pH 6–8, 100% at pH 6, and 100% at pH 8–10, respectively. The release results suggest that urea-loaded hydrogels in soils with different pH values will provide ease of application and positively affect plant growth. As a result, considering the synthesized hydrogels and their characterizations, urea sorption, and release results, it is predicted that the presented study will make important contributions to today's agriculture and that the damage that urea will cause in soil and environmental waters can be minimized.

Acknowledgements

This work is supported by the Van Yuzuncu Yıl University BAP with grant # FBA-2019-7912.

Conflict of interest

There is no conflict of interest.

References

[1]. Dawson C.J., Hilton J., “Fertiliser Availability in a Resource-Limited World: Production and Recycling of Nitrogen and Phosphorus”, Food Policy, 36, (2011), S14-S22.

[2]. Ghafoor I., Habib-ur-Rahman M., Ali M., Afzal M., Ahmed W., Gaiser T., Ghaffar A., “Slow-Release Nitrogen Fertilizers Enhance Growth, Yield, NUE In Wheat Crop and Reduce Nitrogen Losses Under an Arid Environment”, Environmental Science and Pollution Research, 28, (2021), 43528–43543.

[3]. Jarvis S.C., “Nitrogen Cycling and Losses from Dairy Farm”, Soil Use and Management, 9(3), (1993), 99-105.

[4]. Crusciol C.A.C., Almeida D.S., Alves C.J., Soratto R.P., Krebsky E.O., Spolidorio E.S., “Can Micronized Sulfur in Urea Reduce Ammoniacal Nitrogen Volatilization and Improve Maize Grain Yield?”, Journal of Soil Science and Plant Nutrition, 19, (2019), 701–711.

[5]. Rahman M.H., Ahmad I., Wang D. et al (2020) Influence of Semi-Arid Environment on Radiation Use Efficiency and Other Growth Attributes of Lentil Crop. Environ Sci Pollut Res 28:13697–13711. https://doi. org/10.1007/s11356-020-11376-w.

[6]. Rao E.P., Puttanna K., “Nitrates, Agriculture and Environment”, Current Science, 79(9), (2000), 1163-1168.

[7]. Bowles T.M., Atallah S.S., Campbell E.E., Gaudin A.C.M., Wieder W.R., Grandy A.S., “Addressing Agricultural Nitrogen Losses in a Changing Climate”, Nature Sustainability, 1, (2018), 399–408.

[8]. Ersen Dudu T., Alpaslan D., Aktas N., “Urea Uptake and Release by Novel Macrogels from Dimethylacrylamide”, Communications in Soil Science and Plant Analysis, 50(18), (2019), 2278–2293.

[9]. Neethu T.M., Dubey P.K., Kaswala A.R., “Prospects and Applications of Hydrogel Technology in Agriculture”, International Journal of Current Microbiology and Applied Sciences, 7(5), (2018), 3155-3162.

[10]. Das D., Prakash P., Rout P.K., Bhaladhare S., “Synthesis and Characterization of Superabsorbent Cellulose-Based Hydrogel for Agriculture Application”, Starch – Stärke, 73, (2021), 1900284.

[11]. Ersen Dudu T., Alpaslan D., Aktas N., “Superabsorbent Hydrogels Based on N,N-Dimethylacrylamide and Maleic Acid for Applications in Agriculture as Water Purifier and Nitrogen Carrier”, Polymer Bulletin, 79, (2022), 8551–8573.

[12]. Ersen Dudu T., Alpaslan D., Aktas N., “Development of Urea Uptake and Release Studies Using N, N-Dimethylacrylamide/Maleic Acid/Citric Acid Based Macrogel”, Journal of Polymers and the Environment, 29, (2021), 3636–3648.

[13]. Song B., Liang H., Sun R., Peng P., Jiang Y., She D., “Hydrogel Synthesis Based on Lignin/Sodium Alginate and Application in Agriculture”,

International Journal of Biological Macromolecules, 144, (2020), 219–230.

[14]. Cheng D., Liu Y., Yang G., Zhang A., "Water- and Fertilizer-Integrated Hydrogel Derived from the Polymerization of Acrylic Acid and Urea as a Slow-Release N Fertilizer and Water Retention in Agriculture", Journal of Agricultural and Food Chemistry, 66, (2018), 5762−5769.

[15]. Liu Y., Wang J., Chen H., Cheng D., "Environmentally Friendly Hydrogel: A review of Classification, Preparation and Application in Agriculture", Science of the Total Environment, 846, (2022) 157303.

[16]. Qu B., Luo Y., "Chitosan-Based Hydrogel Beads: Preparations, Modifications and Applications in Food and Agriculture Sectors – A Review", International Journal of Biological Macromolecules, 152, (2020), 437–448.

[17]. Akhmetzhan A., Myrzakhmetova N., Amangeldi N., Kuanyshova Z., Akimbayeva N., Dosmaganbetova S., Toktarbay Z., Longinos S.N., "A Short Review on the N,N-Dimethylacrylamide-Based Hydrogels", Gels, 7, (2021), 234.

[18]. Abdiyev K.Z., Toktarbay Z., Zhenissova A.Z., Zhursumbaeva M.B., Kainazarova R.N., Nuraje N., "The New Effective Flocculants Copolymers of N,N-Dimethyl-N,N-Diallyl-Ammonium Chloride and N,N-Dimethylacrylamide", Colloids Surf. A, 480, (2015), 228–235.

[19]. Soykeabkaew N., Thanomsilp C., Suwantong O., "A review: Starch-Based Composite Foams", Composites Part A: Applied Science and Manufacturing, 78, (2015), 246-263.

[20]. KaewtatipK., Tanrattanakul V., Phetrat W., "Preparation and Characterization of Kaolin/Starch Foam", Applied Clay Science, 80–81, (2013), 413-416.

[21]. Alpaslan D., Ersen Dudu T., Aktas N., "Synthesis of Smart Food Packaging from Poly(Gelatin-co-Dimethyl Acrylamide)/Citric Acid-Red Apple Peel Extract", Soft Materials, 19(1), (2021), 64–77.

[22]. Gupta N.V., Shivakumar H.G., "Investigation of Swelling Behavior and Mechanical Properties of a pH-Sensitive Superporous Hydrogel Composite", Iranian Journal of Pharmaceutical Research, 11 (2), (2012), 481-493.

[23]. Sievers J., Sperlich K., Stahnke T., Kreiner C., Eickner T., Martin H., Guthoff R.F., Schünemann M., Bohn S., Stachs O., "Determination of Hydrogel Swelling Factors by Two Established and a Novel Non-Contact Continuous Method", Journal of Applied Polymer Science 138, (2021), e50326.

[24]. Adnadjevic B., Jovanovic J., "Novel Approach in Investigation of the Poly(AcrylicAcid) Hydrogel Swelling Kinetics in Water", Journal of Applied Polymer Science, 107, (2008), 3579–3587.

[25]. Peppas N.A., Franson N.M. "The Swelling Interface Number as a Criterion for Prediction of Diffusional Solute Release Mechanism in Swellable Polymers", Journal of Polymer Science Polymer Physics Edition, 21, (1983), 983-997.

[26]. Alpaslan D., Ersen Dudu T., "Removal of As(V), Cr(VI) and Cr(III) Heavy Metal Ions from Environmental Waters Using Amidoxime and Quaternized Hydrogels", MANAS Journal of Engineering, 9(2), (2021), 104-114.

[27]. Langmuir I., "The Adsorption of Gases on Plane Surfaces of Glass, Mica and Platinum", Journal of the American Chemical Society, 40, (1918), 1361.

[28]. Freundlich H.M.F., "Uber Die Adsorption in Losungen", Zeitschrift für Physikalische Chemie, 57, (1906), 385-470.

[29]. Tempkin M.I., Pyzhev V., "Kinetics of Ammonia Synthesis on Promoted Iron Catalyst", Acta Physicochimica URSS, 12, (1940), 327-356.

[30]. Dubinin M.M., "The Potential Theory of Adsorption of Gases and Vapors for Adsorbents with Energetically Non-Uniform Surface", Chemical Reviews, 60, (1960), 235-266.

[31]. Al-Degs Y.S., El-Barghouthi M.I., El-Sheikh A.H., Walker G.M., "Effect of Solution pH, Ionic Strength, and Temperature on Adsorption Behavior of Reactive Dyes on Activated Carbon", Dyes and Pigments, 77, (2008), 16-23.

[32]. Çakmak M., Taşar Ş., Selen V., Özer D., Özer A., "Removal of Astrazon Golden Yellow 7GL from Colored Wastewater Using Chemically Modified Clay", Journal of Central South University, 24, (2017), 743−753.

[33]. Alpaslan D., Ersen Dudu T., Aktas N., "Development of Onion Oil-Based Organo-Hydrogel for Drug Delivery Material", Journal Of Dispersion Science And Technology, https://doi.org/10.1080/01932691.2021.1974869.

[34]. Varelas C.G., Dixon D.G, Steiner C., "Zero-Order Release from Biphasic Polymer Hydrogels", Journal of Controlled Release, 34, (1995), 185-192.

[35]. Higuchi T., "Mechanisms of Sustained Action Medication: Theoretical Analysis of the Rate of Release of Solid Drugs Dispersed in Solid Matrices", Journal of Pharmaceutical Sciences, 52, (1963), 1145-1149.

[36]. Korsmeyer R.W., Gurny R., Doelker E.M., Buri P., Peppas N.A., "Mechanism of Solute Release from Porous Hydrophilic Polymers", International Journal of Pharmaceutics, 15, (1983), 25-35.

[37]. Peppasv N.A., Bures P., Leobandung W., Ichikawa H., "Hydrogels in Pharmaceutical Formulations", European Journal of Pharmaceutics and Biopharmaceutics, 50, (2000), 27-46.

[38]. Khare A.R., Peppas N.A., "Swelling/Deswelling of Anionic Copolymer Gels", Biomaterials, 16, (1995), 559-567.

[39]. Swenson H., Stadie N.P., "Langmuir's Theory of Adsorption: A Centennial Review", Langmuir, 35(16), (2019), 5409–5426.

[40]. Zhou X., Yi H., Tang X., Deng H., Liu H., "Thermodynamics for the Adsorption of SO_2, NO and CO_2 from Flue Gas on Activated Carbon Fiber", Chemical Engineering Journal, 200–202, (2012), 399-404.

[41]. Edet U.A., Ifelebuegu A.O., "Kinetics, Isotherms, and Thermodynamic Modeling of the Adsorption of Phosphates from Model Wastewater Using Recycled Brick Waste", Processes, 8, (2020), 665. doi:10.3390/pr8060665.

[42]. Rezk A.I., Obiweluozor F.O., Choukrani G., Park C.H., Kim C.S., "Drug Release and Kinetic Models of Anticancer Drug (BTZ) from a pH-Responsive Alginate Polydopamine Hydrogel: Towards Cancer Chemotherapy", International Journal of Biological Macromolecules, 141, (2019), 388-400.