Synthesis of a cellulose-based hydrogel network: Characterization and study of urea fertilizer slow release

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ABSTRACT: In the present study, we synthesized a low-cost biodegradable hydrogel based on cellulose in order to perform controlled release of fertilizer. For this purpose, the cellulose was modified and crosslinked with urea. Then the prepared hydrogel underwent loading with the fertilizer in order to study the controlled release. Characterization of the samples was carried out by Fourier Transform Infrared (FT-IR) spectroscopy, elemental analysis, thermal gravimetric analysis (TGA), and scanning electron microscopy (SEM). The hydrogel showed a good swelling behavior in distilled water, tap water, and 0.9% NaCl solution. Besides, water holding and water retention behavior of the hydrogel was investigated. Finally, the release of fertilizer from the loaded hydrogel was studied and showed excellent controlled release. According to the results, this hydrogel can be employed as a suitable moisture-holding additive in the soil for agricultural purposes. © 2015 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2016**, *133*, 42935.

INTRODUCTION

In recent years, industrial agriculture has been increasing with a rapid pace due to the fast growing of the population. Fertilizers—as a vital input material to supply nutrients—play an important role in increasing and sustaining an optimal crop yield for many years. The dramatic increase of chemical fertilizers, especially nitrogen, phosphorus, and potassium (N, P, and K) is forecasted to increase at a rate of 2.5 million metric tons per year in the last half of the 20th century. The urea fertilizer is an important source of nitrogen and about 43% of the present available commercial fertilizers can be found in the urea fertilizer. But in its intact state, this chemical compound has a low efficiency because of its high subtlety in water and a high degradation rate in the atmosphere and volatilization after using in the soil and planet.[1]

Whereas the application of fertilizers increased, the amount of nutrients recovered by crops was not kept at the same pace. In fact, the recovery of nutrients by crops has only been tripled over the same period as the nitrogen application increased 15 times over the 40-year period before 1990 signifying that much of the nutrients from fertilizers are not utilized by plants and is lost in the environment.[2]

There are many environmental problems and drawbacks associated with the use of conventional fertilizers, such as high waste and low use efficiency.[3–5] To ensure the proper use of fertilizers to both crop production and the environment, researchers have tried to achieve novel and efficient ways to minimize the environmental impacts.[6,7] Among these ways, the slow-release fertilizer has provided an effective means of overcoming these drawbacks.[8–10]

Hydrogels are defined as crosslinked hydrophilic polymers that can absorb water, saline solutions, or other liquids.[11] By advantages of the unique three-dimensional network structure and various functional groups, hydrogels have become one of the most attractive types of polymeric materials, which have assigned extensive applications in various fields such as drug delivery systems,[12–14] agriculture,[15,16] water and wastewater treatment,[17] biosensors,[18] and other applications.[19] In some application fields such as agricultural uses, the water absorbency and water retention properties of the hydrogels are essential to be determined.[19] From the application point of view, the use of hydrogels in slow-release fertilizers has attracted a lot of attention due to the increase of the fertilizer use efficiency and preventing environmental pollution.[20,21]

Most of the hydrogels are made from synthetic hydrophilic polymers such as poly (acrylic acid) or its copolymer with poly (acrylamide),[22,23] but due to their biodegradability and low cost, the demand for using natural hydrogels such as starch, cellulose,[24,25] chitosan,[26] and alginate[8] as fertilizer carriers is continuously increasing. Cellulose is a natural renewable and biodegradable polymer which has gained great attention in agriculture and is used as a fertilizer carrier. Cellulose is the most abundant natural polymer and a very promising raw material with low cost for the preparation of its various derivatives.[27,28]

In this study, we developed an eco-friendly hydrogel system based on the cellulose for the controlled fertilizer release (CFR) systems. For this purpose, first the cellulose was bromoacetylated and then the bromoacetylated cellulose was crosslinked with urea to form the required hydrogel. The loading and slow release of urea fertilizer investigation was carried out in the final step.

EXPERIMENTAL

Equipment

IR spectra were recorded with a Fourier transform infrared spectrometer (Nexus 670, Thermo Nicolet, USA). The thermal gravimetric analysis (TGA) of the prepared samples was determined using the LENSESSTAPT-1000 calorimeter (Germany) by scanning from room temperature up to 600°C with the heating rate of 10°C min^{-1} under nitrogen atmosphere. The morphology of the hydrogels was studied by scanning electron microscopy (SEM) images which were obtained using a SEM-3200 scanning electron microscope. The elemental analysis of the prepared hydrogels was performed by Perkin-Elmer C H N S Analyzer 2400 series 2 (USA).

Materials

Cellulose microcrystals, bromoacetyl bromide (BAB) (>99%), N,N-dimethylacetamide (DMA), triethylamine (TEA), and urea (>99%) were purchased from Merck and used without further purifications. Urea fertilizer was kindly donated from Shiraz Petrochemical.

Synthesis of Bromoacetylated Cellulose (BA-Cell)

The BA-cell was prepared by a dry grinding method. Cellulose powder (0.5 g, 9.259 mmol OH) was poured in a porcelain mortar and then BAB (1.86 g, 9.259 mmol) was added dropwise with continuous grinding for 2.5 h. The reaction mixture was washed successively with tetrahydrofuran (THF) and dried under vacuum for 5 h.

Synthesis of Urea-modified BA-Cell Hydrogel (CBA-Cell)

The BA-cell (1 g) and urea (0.17 g, 2.8 mmol) was placed in a 100-mL round-bottom flask. Then DMA (30 mL) and TEA (0.58 g, 5.7 mmol) were added to the flask and the reaction mixture was stirred at 85°C for 48 h. The precipitate was immersed in methanol, filtered and dried in vacuum oven at 60°C.

Swelling Degree and Water Absorption Behavior

Three desired amounts of dry hydrogel were placed in separate tea bags and each one was immersed in three discrete media [distilled water (500 mL), tap water (500 mL), and saline solution (0.9 wt % NaCl, 500 mL)] at room temperature. In certain time intervals, the tea bags were lifted from solutions and weighed. The swelling ratio (SR) was calculated from the equation below[29,30]:

$$SR = \frac{(W_t - W_1 - W_0)}{W_1}$$

where the W_t shows the weight of swollen hydrogel and wet tea bag in a certain time, W_1 represents the weight of dry hydrogel and W_0 relates to the weight of wet tea bag.

The equilibrium swelling ratio (ESR), which was attributed to the amount of water absorbed by the hydrogel in equilibrium condition, was also calculated by the same equation, but W_{eq} was placed instead of W_t which referred to the weight of hydrogel in equilibrium condition (no changes in weight over time).

$$ESR = \frac{(W_{eq} - W_1 - W_0)}{W_1}$$

Loading of Fertilizer on CBA-Cell

For this purpose, a concentrated aqueous solution of the urea fertilizer was prepared. Then a certain weight of the hydrogel was immersed in the above mentioned solution and slowly shook for 72 h at room temperature until completing uptake of the urea aqua solution. The loaded hydrogel was filtered and washed by distilled water to remove any surface adhered urea and dried at 40°C.

To calculate the loading capacity, a certain weight of the dry hydrogel (0.462 g) was carefully weighed. After loading and complete drying, the loaded hydrogel was weighed again (0.675 g). Therefore, the net weight of the fertilizer was obtained 0.213 g. The loading capacity (LC %) was calculated from the following equation:

$$Loading\ Capacity\ (LC) = \frac{W}{W'} \times 100$$

where the W is the weight of the net fertilizer and W' is the weight of the dry hydrogel before loading. From the equation above, the LC was obtained 46.1%.

Determination of the Acyl Content and the Degree of Substitution (DS)

The acyl content and DS were determined according to the literature method.[31] Briefly, a certain weight of the BA-cell was taken into a 150-mL flask and then ethanol (75%, 25 mL) was added. The mixture was stirred at 50°C for 30 min and allowed to cool down slowly to room temperature. After that the KOH solution (20 mL, 0.5M) was added to the above mixture and stirred for 72 h at room temperature to complete hydrolysis of the BA-cell. The mixture was then back-titrated with HCl (0.5M) in the presence of phenolphthalein as an indicator for determination of excess KOH in the reaction medium. The same procedure was repeated for the cellulose as blank. The DS and the acyl content were calculated using the following equations:

$$\%\ acyl\ content = \frac{[(V_s - V_b) \times molarity\ of\ HCl \times M_{acyl} \times 10^{-3}]}{sample\ weight\ (gr)} \times 100$$

Table I. Mathematical Models Used to Evaluate the Experimentally Determined Release Kinetics

Model	Mathematical equation	Y axis	X axis	Slope	y intercept
Zero order	$Q_t - Q_0 = k_0 t$	Q_t	t	K_0	Q_0
First order	$\log Q_t - \log Q_0 = k_0 t/2.303$	$\log Q_t$	$t/2.303$	$K_0/2.303$	$\log Q_0$
Korsmeyer–Peppas	$M_t/M_\infty = kt^n$	$\log(M_t/M_\infty)$	$\log t$	n	$n \log k$
Baker–Lonsdale	$3/2[1-(1-F_t)^{2/3}]-F_t = kt$	$3/2[1-(1-F_t)^{2/3}]-F_t$	t	k	0
Higuchi	$Q_t = k_H t^{1/2}$	Q_t	$t^{1/2}$	k_H	0
Hixson–Crowell	$(1-F_t)^{1/3} = 1-kt$	$(1-F_t)^{1/3}$	t	$-k$	1
Ritger–Peppas	$\ln F_t = \ln k + n \ln t$	$\ln F_t$	$\ln t$	n	$\ln k$

$$DS = \frac{(162 \times \% \text{ acyl content})}{M_{acyl} \times 100 - ((M_{acyl}-1) \times \% \text{ acyl content})}$$

where the V_b and V_s refer to the volume of the HCl that is used for titration of blank and sample, respectively, M_{acyl} is the molecular weight of bromoacetyl group, which is 121.94 g mol^{-1}, and the molecular weight of each anhydroglucose unit is 162 in cellulose structure.

Water-holding Capacity (WH) and Water-retention Ratio (WR) of the Hydrogel

The WH and WR study for the hydrogel is to show the efficiency of the prepared hydrogel to hold water in soil.[29,30,32] In this experiment, the soil was collected from the apple garden of the Urmia University (mesh < 30). For the WH study, certain weights of the soil (4 × 10.00 g) were prepared. Three separate weights of the hydrogel (0.05, 0.1, and 0.2 g) were mixed with each of the soil samples to obtain 0.5, 1, and 2% (w/w) samples. One of the soil samples was kept blank (no hydrogel). Each sample was then placed in a 1 cm diameter plastic pipe. The bottom of each pipe was sealed by filter paper and weighed. After that, water was slowly poured from the top until the first drop was seeped from the bottom of the pipe. The pipe was weighed again and the WH % was calculated using the following equation:

$$\% WH = \frac{(W_2 - W_1)}{W_0} \times 100$$

where W_0 is the weight of pure soil, W_1 is the weight of each sample without water and W_2 is the weight of each sample after first drop seeping.

The obtained wet samples from WH study were used for WR study. The samples were kept at room temperature for 1 month and weighed every other day. From the equation below, WR % was determined:

$$\% WR = \frac{(W_t - W_1)}{(W_2 - W_1)} \times 100$$

where the W_1 and W_2 are the same as the WH equation, and the W_t refers to the weight of sample after specified time intervals (every other day here).

Urea Fertilizer Release Study

According to the recent study by Teodorescu et al.,[33] the release of fertilizer is calculated by determining the weight of the fertilizer in a certain volume of aqua solution during a specific time.

Hence, 1 g of the loaded hydrogel was kept in 100 mL distilled water without stirring at room temperature. In certain time intervals, a 2 mL amount of the solution from the liquid surface was transferred to a preweighed watch glass and kept in oven at 60°C. After complete drying, the watch glass was reweighed and the absolute weight of the fertilizer was determined. The fertilizer release percentage (FR %) was calculated by the following equation:

$$\% \ FR = \frac{\left(\Delta W_n \times \frac{(100-(n-1)\times 2)}{2}\right) + \sum_{i=1}^{n} \Delta W}{W_0} \times 100$$

Where Δw is the weight of the released fertilizer in 2 mL of the solution and W_0 is the initial fertilizer weight in the loaded hydrogel, which was determined by subtraction of the dry loaded hydrogel weight from the initial weight of the hydrogel before loading.

Kinetic Parameters of Swelling Behavior

This study is to determine the diffusion content (k) and the diffusion exponent (n) from the equation below[34]:

$$\frac{M_t}{M_{eq}} = kt^n$$

The t, k, and n represent time, diffusion content, and diffusion exponent, respectively. The factor "k" depends on the hydrogel type and the swelling medium. The factor "n" supplies information on the type of transport mechanism that impels the sorption of a given solute. M_t and M_{eq} are masses of hydrogel at swelling time and equilibrium state, respectively.

This equation can be applied from the initial stages until ~60% of the swelling, because at that stage, the increase of the swelling degree over time is an ascending straight line. For the calculation of "n" and "k," ln (M/M_{eq}) vs. ln (t) graphs were made for each assay. Parameters "n" and "k" were obtained from the angular and the linear coefficients, respectively.

Kinetic Parameters of Fertilizer Release

The release of urea fertilizer from the hydrogel was analyzed for fitness with mathematical models of release kinetics which was described in Table I.[35–37] The correlation coefficient (R^2) was used to find the best kinetic model for characterization of release mechanism.

According to Table I, Q_t and Q_0 are the amounts of released material, "t" is the release time and k_0 is the zero-order rate
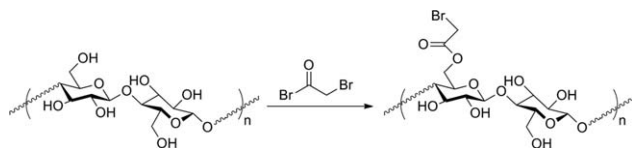
Scheme 1. Bromoacetylation reaction of cellulose.

constant at $t = 0$. The term "k" is the first-order rate constant, k_H is the Higuchi dissolution constant and F_t is the fraction of released material at time "t." In the Korsmeyer–Peppas model, (M_t/M_1) is the fraction of material released at time "t," "k" is the release rate constant, "n" is the diffusion type or index of release exponent, and "t" is the release time.

RESULTS AND DISCUSSION

Synthesis and Preparation of BA-Cell and Hydrogel Network

The hydrogel was synthesized in two steps. In the first step, BA-cell was prepared by grinding process (Scheme 1). In this reaction, cellulose was bromoacetylated by nucleophilic attack of cellulose hydroxyl groups to bromoacetyl bromide. During grinding, BAB was added dropwise to the mortar while the mortar was kept in ice bath to control the heat of the reaction. The advantages of this method, compared to solvent dispersion

method, are solvent nonuse and it needs a shorter reaction time.[31,38–40] In the next step, urea was used as crosslinking agent to synthesize the CBA-cell hydrogel. This reaction was carried out in DMF in the presence of TEA, to neutralize generated HBr (Scheme 2).

Structural Characterization

The FT-IR spectrum of BA-cell is shown in Figure 1(B). The sharp peak at 1740 cm^{-1} is related to the esteric carbonyl groups and the 780 cm^{-1} absorption bond is attributed to C-Br bonds. For comparison, the FT-IR spectrum of pure cellulose is added to the figure [Figure 1(A)]. Figure 1(C) shows the FT-IR spectrum of CBA-Cell. In this figure, the absorption bond at 1636 cm^{-1} is attributed to the amidic carbonyl groups and the C—N stretching vibration is appeared at 1395 cm^{-1}. Also the absorption bond at 1650 cm^{-1} is related to the N—H deformation. Moreover, the C—Br peak has been weakened and the N-H absorption bond has overlapped with the cellulose OH stretching vibrations.

Acyl Content and DS

The acyl content and DS was determined by hydrolysis of BA-Cell and pure cellulose as blank to indicate the efficiency of esterification reaction. The DS is variable between 0 and 3, meaning the number of substituted hydroxyl groups placed on
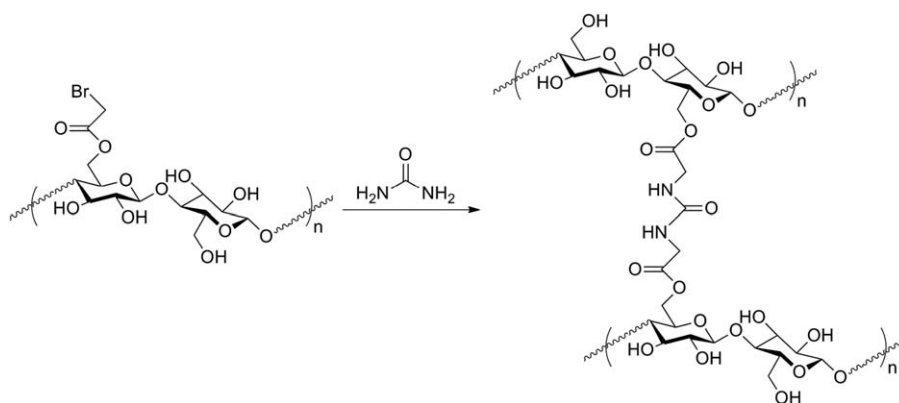
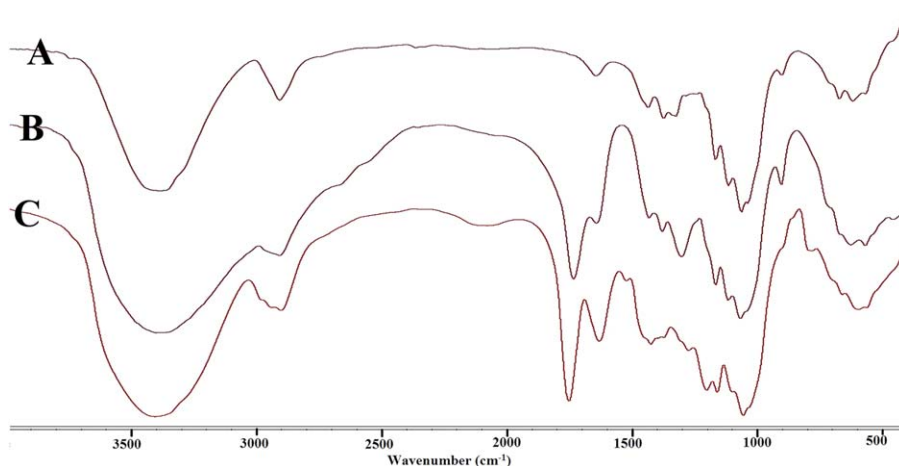**Scheme 2.** Crosslinking of BA-cell with urea.

Figure 1. FT-IR spectrum of (A) Cellulose, (B) BA-Cell, and (C) CBA-Cell. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
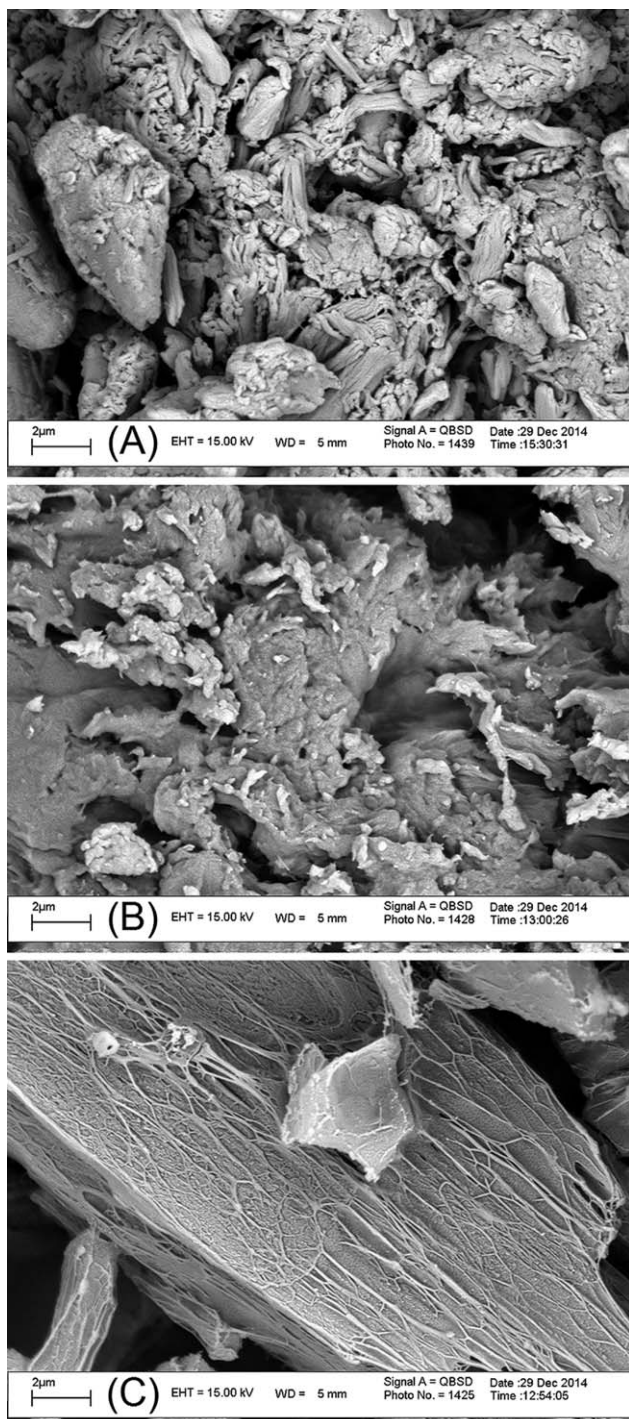
Figure 2. SEM image of (A) BA-Cell, (B) CBA-Cell, and (C) The loaded hydrogel.

Figure 3. TGA thermograms of (A) Cellulose, (B) BA-Cell, and (C) CBA-Cell.

each anhydroglucose unit in the cellulose structure. By the presented method, the acyl content and DS for BA-cell were obtained 39.84 and 0.87%, respectively.

Elemental Analysis

The results from elemental analysis show 43.69% carbon, 6.15% hydrogen, and 2.59% nitrogen present in CBA-cell. The consid-
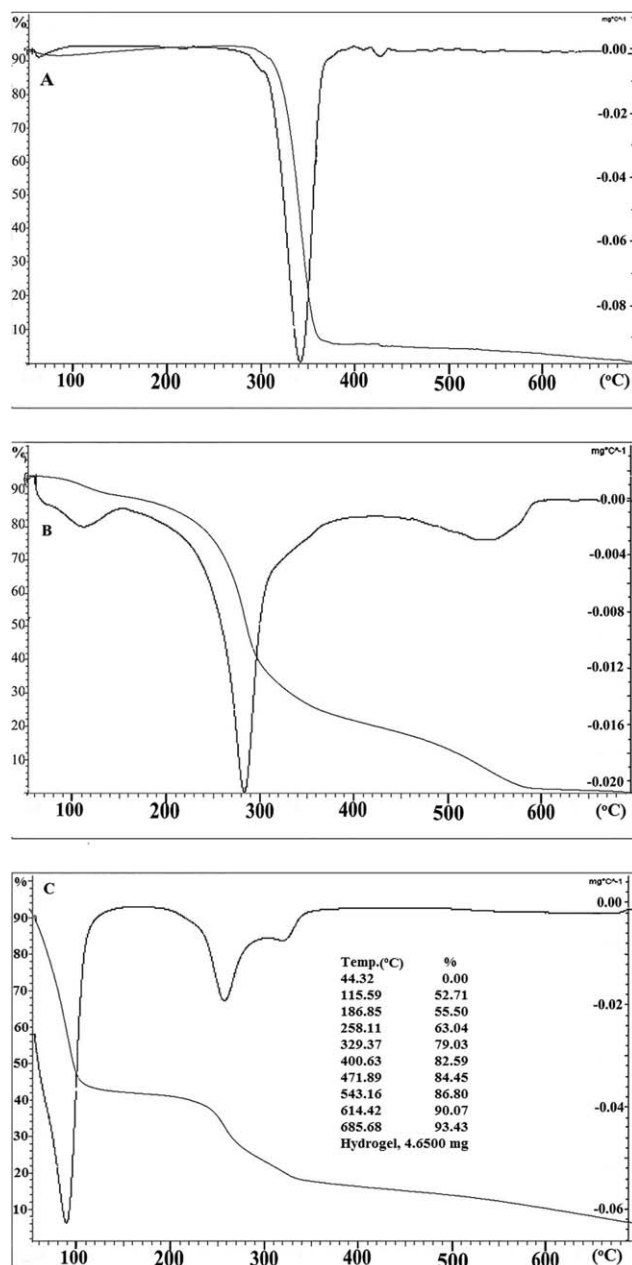
erable amount of nitrogen atom is the key evidence that the crosslinking reaction is carried out and the hydrogel has been prepared. Also, by calculating results and comparing the elemental analysis with that of the acyl content and DS, it is found that ~50% of bromoacetyl active sites have undergone reacting with urea.

Investigation of Surface Morphology

Figure 2 shows the SEM images of the samples. In Figure 2(A), which is related to the BA-Cell, the rough surface and cavities are clearly observable. By crosslinking the BA-Cell with urea, as Figure 2(B) shows, the surface became smoother, as the chains are arranged in order, but the porous' structure is still
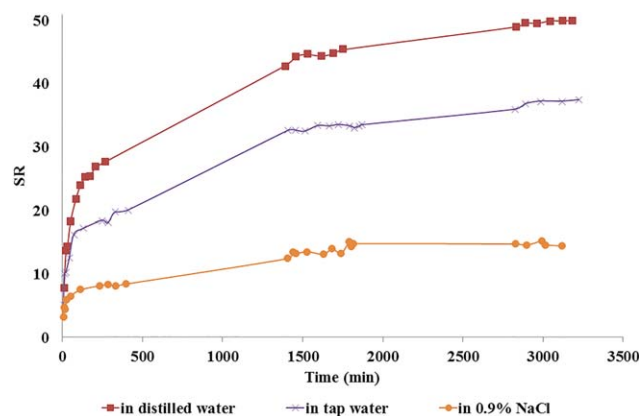
Figure 4. Swelling behavior of CBA-Cell in (A) Distilled water, (B) Tap water, and (C) Saline solution (% 0.9 W/W NaCl). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 5. ESR in different pH values. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

observable. After loading the hydrogel with the urea fertilizer [Figure 2(C)], the surface turns to a uniform structure, as the pores fill with the fertilizer.

Thermogravimetric Analysis

Figure 3 shows the TGA thermograms of the samples. For the pure cellulose [Figure 3(A)] a single and sharp degradation range is shown at about 340°C, demonstrating the degradation of cellulose chains. In the case of BA-Cell, a moisture evaporation step is shown between 70 and 120°C [Figure 3(B)] due to the functionalization of cellulose and enhancement of its hydrophilicity. The second step has begun from 230°C with continuous degradation up to 580°C, demonstrating degradation of the bromoacetyl functional groups continued by degradation of the cellulose backbone. Figure 3(C) shows the TGA thermogram of the final hydrogel. The first weight loss peak between 60 and 115°C is attributed to the disjunction and degradation of the crosslinker, which generates CO and NH_3. It is notable to say that the vacuum drying process was the same for all samples. The next step, 240 to 270°C, is almost similar to that of the BA-Cell [Figure 3(B)], related to the degradation remaining functional groups. Degradation of the backbone continues with a gentle slope after 330°C. A tangible change in the thermal pattern of the prepared hydrogel respects to BA-Cell and the pure cellulose confirms the successful synthesis of hydrogel network.

Swelling Behavior of the Hydrogel Network

The water absorption behavior of the hydrogel was studied in distilled water, tap water, and 0.9% NaCl solution as seen in Figure 4. Moreover, the ESR was also studied at different pH values and results are shown in Figure 5. The data for both figures are summarized in Table II. It was found that the swelling behavior depends on the kind, charge, and concentration of ions in solution and it depends on the ionic strength of solu-
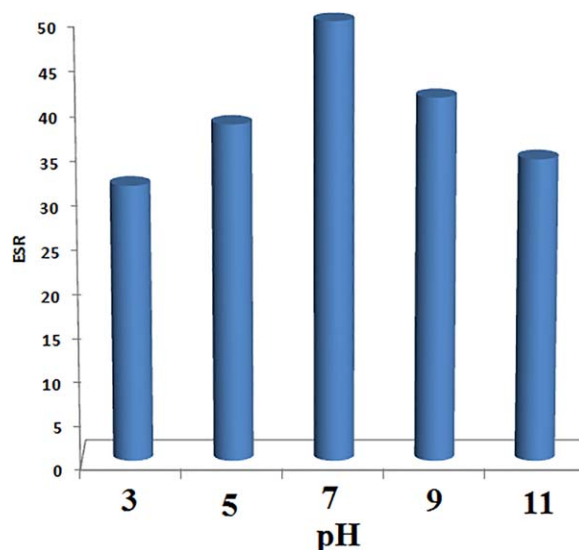
tion, overall. Also the pore size of hydrogel is related to the density, type, rigidity of crosslinking agent and the hydrogel nature. In our study, because of low DS for the BA-cell and consequently low crosslinking agent present, the hydrogel has a large pore size. It is notable that the urea crosslinker has a rigid structure. Based on the Flory's network theory,[1] the density of crosslinker plays an important role in determining the SR. According to this, the water absorption and SR can be taken into account as a function of crosslinker density.

As it is shown in Figure 4, because of high hydrophilic nature of the hydrogel, the initial swelling of the hydrogel is very fast and reaches to the maximum value during 3 days.

Also Figure 4 shows that the SR in tap water has a significant reduction, compared to that of distilled water. This can be attributed to the kind and amount of different ions present in tap water, including ions that cause water hardness. These ions can play the role of crosslinking agents and enmesh the polar functional groups present in the hydrogel. So the reduction of SR in tap water to SR in distilled water is according to the Flory's network theory. In the saline solution, due to the single-valence ions present, the osmotic pressure increases and leads to desorption of water from the hydrogel.[41-43] Therefore, the lowest SR was observed in this medium.

The effect of pH on the SR was also investigated (Figure 5). It was found that by increasing the acidity and basicity, the SR decreased. It can be attributed to the presence of H^+ and OH^- in acidic and basic media respectively. Their effect can be explained as the effect of single-valence ions which is discussed above. Also in acidic media, the amide moieties undergo protonation. This protonation increases hydrogen bonds with the

Table II. ESR Values in Different Media

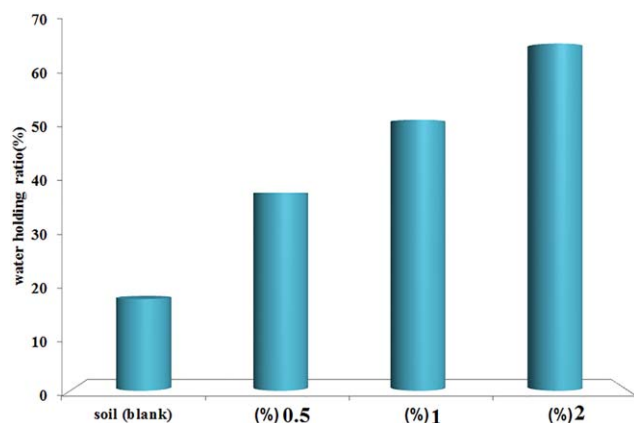| Medium	Distilled water	Tap water	Sailing solution	pH = 3	pH = 5	pH = 9	pH = 11
ESR	49.80	27.94	11.04	31.53	38.47	41.46	34.52

Figure 6. Water holding ratios with different hydrogel contents in soil. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

hydroxyl groups of cellulose, thus it enhances the rigidity of the hydrogel and reduces the SR more, compared with basic media.

Water-holding (WH) and Water-retention (WR) Capacity of Hydrogel-containing Soil
In this part, two important characters were investigated: water holding and water retention capacities of soil containing different amounts of the hydrogel. Figure 6 shows the WH capacity of soil with 0, 0.5, 1, and 2% (w/w) of the hydrogel. As seen in Figure 6, the WH capacity increases by increasing the content of the hydrogel in soil. Therefore, the addition of the hydrogel to the soil has significantly enhanced the WH factor of the soil.

Figure 7 shows the WR capacity of each sample from the WH experiment. As shown in this figure, the WR capacity of soil also increases by increasing hydrogel content. As an example, the WR capacities after 15 days were as follows: 7.85% for the pure soil and 16.85, 19.98, and 32.75% for 0.5, 1, and 2% samples, respectively. The pure soil sample rapidly lost water during 21 days, but other samples still had 1.85, 15.47, and 22.39% water for 0.5, 1, and 2% samples, respectively. Therefore, agri-
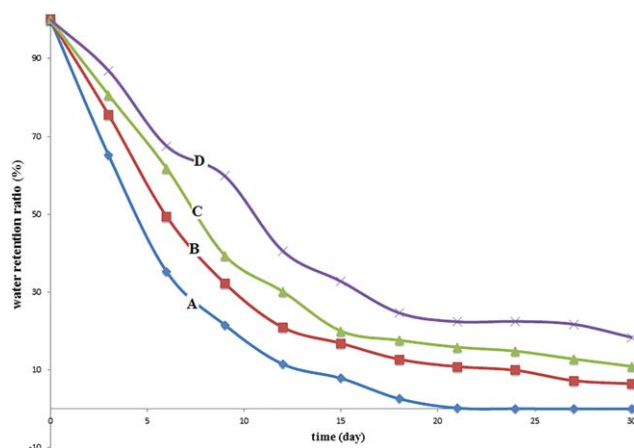

Figure 7. Water retention capacity of soil with different hydrogel content: (A) Pure soil, (B) 0.5%, (C) 1%, and (D) 2% (w/w). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
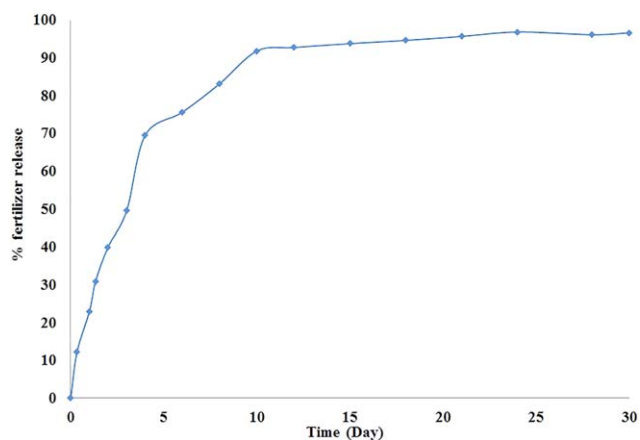

Figure 8. The fertilizer release diagram. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table III. Kinetic Parameters of Swelling Behavior with the Korsmeyer–Peppas Model

Swelling medium	Distilled water	Tap water	%0.9 NaCl solution
R^2	0.9635	0.9534	0.9631
n	0.498	0.452	0.601
$k(min^{-1})$	6.124×10^{-4}	3.02×10^{-4}	2.69×10^{-4}

cultural lands with moisture-holding additives in their soil can hold much more water during irrigation or raining periods and slowly release water in drought times. Furthermore, these hydrogels can also be used in areas in which water is insufficient. It is noteworthy to say that in soil, each hydrogel particle is surrounded by soil particles under limiting pressure from the soil. Therefore, the swelling degree of the hydrogel reduces in soil rather than distilled water.

Fertilizer Release Study
The urea fertilizer release was studied in an aqua solution at room temperature and results are shown in Figure 8. In this figure, the fertilizer release is reported based on the fertilizer concentrations as a function of time. Because of high solubility of urea fertilizer in water, it can be considered that in the absence of any carrier, almost 100% of the urea releases in water within a few minutes.[30,34,44]

Table IV. Kinetic Parameters of Release

Kinetic model	R^2	k (min^{-1})	n
Zero order	0.6497	0.1121	–
First order	0.9035	0.1796	–
Korsmeyer–Peppas	0.9899	0.9033	1.4476
Hixson–Crowell	0.9683	7.9431	–
Ritger–Peppas	0.9899	0.2296	1.4476

R^2, k, and n are correlation coefficient, rate constant related to mathematical models and diffusional exponent, respectively.

The release of the urea fertilizer after 1, 3, 6, 10, and 21 days were 22.9, 49.5, 75.6, 91.3, and 95.71%, respectively. The initial release of the fertilizer at the first 5 days was so-called "burst release," which is attributed to the initial high concentration gradient of loaded urea on the hydrogel matrix and also release of urea molecules near the surface. Liu et al.,[2] Lü et al.,[43] Lü et al.,[45] Liang et al.,[46] and Aouada et al.[34] also provided similar results. After 5 days, the release continues with gentle slope up to 30 days, in which almost 97% of the fertilizer was released.

Kinetic Parameter of Swelling Behavior. Table III presents the results of mathematical kinetic parameters of the hydrogel swelling in different solutions based on the Korsmeyer–Peppas model represented by Ribeiro et al.[34] In this model, the diffusion exponent parameter "n" is defined as follows: if $n \geq 0.45$. It shows a Fickian diffusion mechanism, if $0.45 < n < 0.89$, and also it shows a non-Fickian transport, if $n = 0.89$, then it is a Case II (relaxational) transport, and if $n > 0.89$, it relates to a Super case II transport.

Table III shows n and R^2 values obtained for the hydrogel in different environments. As the table shows, the R^2 values are above 0.95, which can be considered as an acceptable value to confirm that the swelling behavior follows the Korsmeyer–Peppas model. Also the "n" values are near 0.45, which corresponds to Fickian diffusion mechanism.

From the "k" values, it was concluded that the prepared hydrogel is not fast-swelling, but on the other hand this can be a positive point of view, since the release rate is also not fast, and causes the hydrogel to release its fertilizer content in a longer time period.

Kinetic Parameters of Fertilizer Release. Table IV shows the results of release kinetic parameters obtained from different mathematical models that were presented in Table I. To find the best proportionality between the fertilizer release and the mathematical models, the correlation coefficients (R^2) were used. It should be mentioned that the Zero order, First order, and Hixson-Crowell models have been ignored because they show poor proportion with urea fertilizer release. For Korsmeyer–Peppas and Ritger–Peppas models, the correlation coefficients should be calculated below % 60 releases until they are given the highest linearity. Because the two models have the same formula, two identical results are obtained. Moreover, according to the previous section, the "n" value (0.89) shows a Super case II transport type diffusion. A reason for this kind of diffusion may be due to the high solubility of urea in water, which leads to higher rates of urea release.

CONCLUSION

In this work, a low-cost biodegradable hydrogel based on cellulose was prepared and employed as a fertilizer carrier. Different parameters such as thermal behavior, water storage capability, swelling, and release rate were studied. Also, kinetic parameters were investigated for swelling and releasing. Results showed remarkable ability for the hydrogel to be used as a fertilizer carrier and a moisture-holding additive in soil for agricultural and husbandry purposes.

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