

SYNTHESIS OF CELLULOSE-BASED HYDROGEL FOR REGULATING THE RELEASE OF NITROGEN FERTILIZER

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Received August 1, 2022

This study aimed to synthesize a cellulose-based hydrogel as a new green fertilizer with slow-release properties. The cellulose-based hydrogel was prepared by reacting carboxymethyl cellulose solution with cellulose and was cross-linked with citric acid. The structure of the hydrogel was confirmed by FT-IR. The nitrogen fertilizers KNO_3 and $(\text{NH}_4)_2\text{SO}_4$ were loaded during the preparation. The swelling behavior of the hydrogel in deionized water was studied, in addition to the effects of pH, salinity, and drought on swelling behavior. Finally, the fertilizer release behavior in deionized water and a soil mix was investigated, in addition to the soil water content. The optimum hydrogel formulation (HG) showed good absorbance capacity – of 450%, and good durability for one month in deionized water. The swelling-deswelling studies revealed its sensitivity to different solutions. The HG loaded with nitrogen fertilizers showed slow, sustained release rates in deionized water and the soil mix; the cumulative release rates approached 70%, 65%, 60%, and 65%, respectively. Moreover, soil moisture was improved by the addition of the hydrogel by 100% on day 20 and reached 12% on day 30. The results were in accordance with the Committee of European Normalization standards. In conclusion, this new green hydrogel could be used in agricultural applications.

Keywords: citric acid, slow-release fertilizer, potassium nitrate, ammonium sulfate, soil-water retention, CMC-Na

INTRODUCTION

The growing demand for high-quality and abundant food necessitates an efficient and environmentally friendly use of fertilizers, including nitrogen fertilizers. Crops need nitrogen for growth and development.¹ Plants can significantly absorb two nitrogen forms: ammonium (NH_4^+) and nitrate (NO_3^-).² The application of nitrogen fertilizers at high rates leads to a reduction in the quality of crops, mainly leafy crops, because nitrate tends to accumulate in the leaves,^{3,4} nitrogen losses to groundwater and/or volatilization to the atmosphere, contributing to global warming and climate change.⁵ However, the nitrate content of the plant depends on many factors, including the form of nitrogen fertilizer. The high nitrate content of the product has adverse effects on human health, such as NO_3^- reduction to NO_2^- , causing

methemoglobinemia or reduction to other N-nitroso compounds in the human stomach, which causes gastric cancer.⁶ Besides, nitrate is considered toxic to leafy vegetables,⁷ since it increases their vulnerability to fungal infections.⁸ Thus, optimizing the rate of applied fertilizer, especially nitrogen, is necessary. Slow-release nitrogen fertilizers, such as composites of nitrogen fertilizers/hydrogels, have been developed and reported to increase nitrogen use efficiency and reduce nitrogen loss due to ammonia gas (NH_3^+) volatilization and NO_3^- leaching to the soil.¹

A hydrogel, a three-dimensional network polymer enriched with hydrophilic groups, has the ability to imbibe, retain, and discharge water and other physiological fluids.^{9,10} The synthesis and uses of hydrogels attracted attention early in the past century.¹¹ Hydrogels have been used in

medical applications as drug delivery systems,¹⁰ but also in agricultural practices,¹¹ to avoid water deficiency during drought and decrease irrigation frequency,¹² to purify water from dyes and industrial wastes,¹³⁻¹⁵ and as a slow-release fertilizer carrier. An NPK fertilizer (SRF) composite of PAM hydrogel, nanohydroxyapatite, and soluble NPK was synthesized; this composite decreased the nitrogen release rate significantly compared to the conventional fertilizer.¹⁶ Similar results were obtained for the PAM-hydrogel-urea composite, demonstrating an acceptable nitrogen release rate (80%).¹⁷

Hydrogels are classified into three types: homopolymers, copolymers, and interpenetrating polymers,¹⁸ and they are either natural or synthetic.¹⁹ Hydrogels are cross-linked either by physical reversible interactions, such as van der Waals forces, hydrogen bonds, and ionic interactions; or chemical irreversible interactions by covalent bonds formed between polymers.¹⁰ Even though natural-based hydrogels are environmentally friendly, they are not preferred because of their low water-holding capacity and short durability.⁹ Also, most hydrogels are polyacrylamide (PAM)-based hydrogels,^{12,16,17} and are well known to be carcinogenic and non-biodegradable.¹⁰

Natural polymers, such as cellulose, are nontoxic, cost-effective, renewable, and biodegradable, compared to synthetic polymers.²⁰ Cellulose is composed of long chains of glucose monomers linked by β -1,4-glycosidic bonds and is a component of all plant tissues.¹¹ Cellulose is rich in hydrophilic groups (OH-, COO-) and has high mechanical strength, is biodegradable and biocompatible; is responsive to pH, time, and temperature; has high water absorption capacity; is environmentally friendly and a promising alternative to synthetic suspicious polyacrylamide-based superabsorbent gels.⁹

Besides, the synthesis of cellulose-based hydrogels is very simple and can be made in two steps: dissolving cellulose in an aqueous solution and then carrying out the cross-linking reaction between the polymers.²¹ On the other hand, harmful synthetic materials, such as the cross-linking agent epichlorohydrin (ECH), is often used to synthesize natural cellulose-based hydrogels.²²⁻²⁶ Recently, a cellulose-based hydrogel loaded with chlorhexidine, with slow-release properties, was synthesized using the cross-linker epichlorohydrin used to treat periodontitis.²⁷ However, ECH is considered toxic

to animals' and humans' respiratory systems and skin.²⁸

Demitri *et al.* created a biodegradable, non-toxic cellulose-based hydrogel that was cross-linked with various concentrations (1.75, 2.75, 3.75%) of citric acid (CA),²⁹ which extended soil-water content at the field capacity for 22 days,³⁰ Montesano *et al.* reported that amending sandy soil with 2% of this hydrogel improved the soil-water content by 400% and enhanced the growth and quality of cucumber and sweet basil in soilless media.³¹ Durpekova *et al.* modified this hydrogel by adding acid whey to increase its water absorption capacity.³² Recently, another green superabsorbent hydrogel was created, employing the cellulose derivative carboxymethyl cellulose-sodium salt (CMC-Na) and glycol as a cross-linking agent.³³ Its durability has not, however, been thoroughly investigated or put to the test in agricultural applications.

This work aimed at the synthesis of a green cellulose-based hydrogel, cross-linked with citric acid, loaded with two forms of nitrogen fertilizers, to investigate the effects of deionized water, salinity, pH, and drought on the swelling capacity of the hydrogel; the release behavior of nitrate and sulfate in deionized water and the soil mix of peat moss and sand (weight ratio 1:1); as well as the effect of amending the soil mix with this hydrogel on the soil-water content.

EXPERIMENTAL

Carboxymethyl cellulose sodium salt (CMC-Na) (medium viscosity) and microcrystalline cellulose (MCC) were purchased from Sigma Aldrich, Germany, with purity ≥ 99 . The citric acid (CA) was purchased from CBH Lab Chemicals, Nottingham, UK, with a purity ≥ 99 .

A first experiment was made to synthesize the cellulose-based hydrogel using three concentrations of cross-linking agent CA (3.75%, 2.75%, and 1.75%).²⁹ The cellulose-based hydrogel was prepared by mixing 1 g of MCC in deionized water; at this stage, cellulose absorbs water and becomes saturated, then 3 g of CMC-Na is added and mixed until the mixture is homogenized. After that, CA was added dropwise to the mixture in three concentrations (3.75%, 2.75%, and 1.75%) under continuous stirring using an overhead stirrer (OSD-20, BOECO, Germany) for 1 hour. Finally, the gel mixtures were left in a water bath at 30 °C for 24 hours, and excess water was decanted. The next day, the temperature was increased to 80 °C for 24 hours to complete the cross-linking reaction, which allowed cellulose to dissolve and cross-link with CMC-Na. These mixtures were frozen at -80 °C, and

they were dried in a freeze-drying chamber (Operon F-5, Gimpo Gold Valley, Korea) for 72 hours.

In the second experiment, the cellulose-based hydrogel was prepared using the previous procedure by lowering the cross-linking agent CA concentrations to 1.5, 1.25, 1.0, 0.75, and 0.5%, and the samples were dried using two different methods: first, in a freeze-drying chamber (Operon F-5, Gimpo Gold Valley, Korea) for 72 hours, second, in an oven at 40 °C for 72 hours. All the hydrogels were kept in a dry condition for further investigations.

The cross-linking of CMC-Na with citric acid was carried out as reported by Demitri *et al.*²⁹ The mechanism of cross-linking is shown in Scheme 1.

The characterization of HG was carried out using Fourier transform infrared spectroscopy (FT-IR) spectra (4000 to 400 cm⁻¹, 4 cm⁻¹ spectral resolution, KBr pellets), which were measured using a Thermo Nicolet NEXUS 670 FT-IR spectrometer.

For studying the water absorbance and durability of the synthesized hydrogels with different concentrations of CA, dried samples were weighed (W_D), and then soaked in deionized water for a period of one day, and 1, 4, 8, 12, and 16 weeks. The gel samples were reweighed after removing excess water with filter paper (W_S). The swelling ratio percentages (SR %) were calculated according to Equation (1) and expressed as percentages (%):²⁹

$$SR\% = \frac{(W_S - W_D)}{W_D} \times 100\% \quad (1)$$

The hydrogel (HG) made using 0.75% of CA and oven dried, which showed good durability and appropriate swelling ratio, was selected for further investigations.

To investigate the effect of salinity on the water absorbance of HG, the dried samples were weighed and soaked in distilled water and 0.1 M solution of NaCl for 24 hours. Then, the HG samples were weighed after removing excess water using filter paper.

Dried HG samples were soaked in 0.1 M solution of NaOH (pH = 8) or 0.1 M solution of HCl (pH 2) to study the effect of pH on the HG swelling ratio. The samples were weighed after the removal of excess liquid with filter paper. W_S and SR% were measured and calculated.

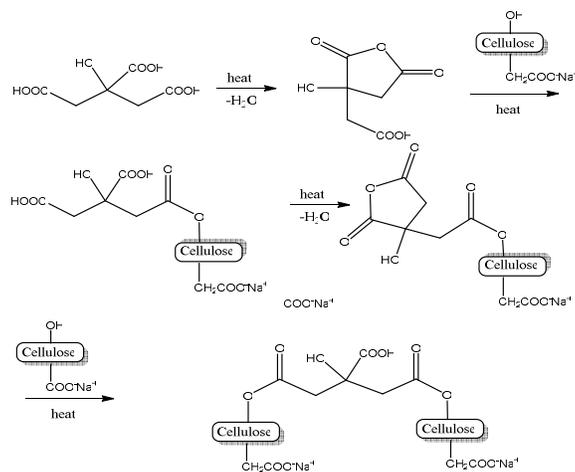
The HG samples were also subjected to soaking cycles with distilled water and drying in the oven. W_S and SR% were measured and calculated.

The durability of the HG was checked by leaving samples in distilled water and measuring their W_S and SR% as a function of time.

For the formulation of HG/N fertilizers, nitrogen fertilizers were loaded by incorporation during synthesis, and a predetermined amount of nitrogen fertilizer was added to the hydrogel mixture during the hydrogel preparation.¹²

Fertilizer release behavior was observed by measuring NO₃⁻ and SO₄⁻ concentrations using a UV spectrophotometer (Genesys, 10UV Scanning). Samples of HG/N fertilizer were soaked in plastic cups with 100 mL of deionized water. A 10 mL sample of HG/N fertilizer was taken daily to measure NO₃⁻ and SO₄⁻ concentration, and 10 mL of distilled water was added to keep the volume constant. Concentrations were achieved daily, according to the WE Federation and APH Association (2012).²⁸

To study the fertilizer release rate in soil, a soil mix of peat moss and sand (weight ratio 1:1) was amended with HG/N fertilizers and then filled in a glass-centered column equipped with a valve, to which 80 mL distilled water was added and left at room temperature. For the control group, identical columns were filled with the same soil mix amended with a similar amount of commercial fertilizers. A 10 mL sample was taken to measure electric conductivity (μs/cm) using a TDS and EC meter (hold) model A1. Ten mL of distilled water was added to keep the volume constant.



Scheme 1: Possible mechanism of cross-linking reaction between CMC-Na and cellulose by citric acid

To study the effect of the hydrogel on soil water content, a soil mix of peat moss and sand (weight ratio 1:1) was amended with 1% hydrogel (HG), then placed in plastic cups and weighed (W0), then irrigated to field capacity and weighed (W1) again; for the control group, plastic cups were filled with the soil mix without HG. Cups were left at room temperature and weighed daily (W2). Soil water content (SW %) was calculated according to Equation (2) and expressed as a percentage (%):¹²

$$SW\% = \frac{W2 - W0}{W1 - W0} \times 100\% \quad (2)$$

All experiments were repeated three times. Graphs, means, and standard deviation were generated using Microsoft Excel version 10.

RESULTS AND DISCUSSION

According to the findings in Figure 1 (a), 1.75% of CA hydrogel had the highest swelling ratio, which corroborates the conclusion of Demitri *et al.*²⁹ This is because the higher the cross-linker content, the more the hydrogel becomes rigid and loses elasticity, and the swelling ratio decreases. However, the swelling ratio increased after 12 weeks. All the samples showed good durability for all the periods from one day to 12 months. In the second experiment, a comparison was made between the two drying methods. Figure 1 (b and c) presents the swelling

ratios of freeze-dried and oven-dried hydrogels with the CA concentrations (0.5, 0.75, 1, 1.25, and 1.5%). Freeze-dried specimens showed a higher swelling ratio than oven-dried ones; the highest swelling ratios were recorded for 0.5% and 0.75% CA hydrogels on day one – 3000% and 2200%. Whereas in oven-dried ones, the swelling ratio was reduced to 300% and 200%, respectively, and they reached their maximum swelling ratio on week 2 (1300%) and (500%) on week 4. This may be because the freeze-drying method keeps the size of the pores intact and increases the internal surface area. At the same time, drying in the oven leads to shrinking pores and decreases pore size and absorption capacity. Oven-dried samples showed better durability, in which water uptake was slower over a prolonged time; 0.5% of CA hydrogels degraded in two weeks, and 0.75% of CA hydrogels remained for more than 12 weeks. In contrast, freeze-dried specimens of 0.5% of CA hydrogels reached the maximum swelling ratio and degraded in two weeks. Due to its good durability and appropriate swelling ratio, the hydrogel made using 0.75% of CA, and oven-dried was selected for future experiments and was termed “HG”.

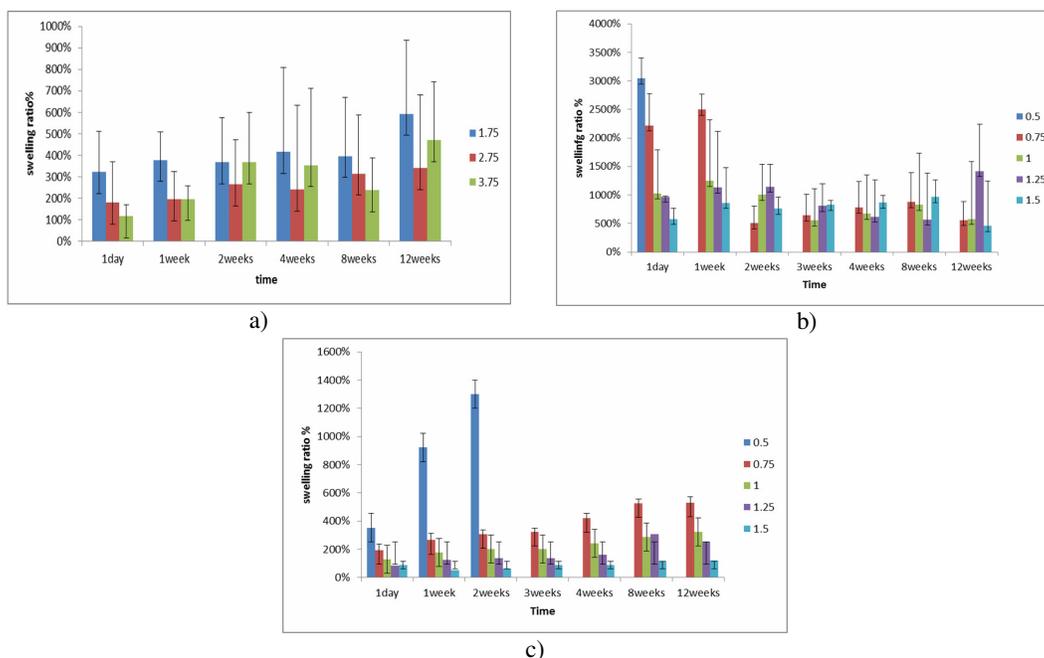


Figure 1: Swelling ratios of freeze-dried hydrogels prepared using CA concentrations of (a) 1.75, 2.75, and 3.75%; (b) 0.5, 0.75, 1, 1.25 and 1.5%, in deionized water, and (c) of oven-dried hydrogels prepared using CA concentrations of 0.5, 0.75, 1, 1.25 and 1.5% in deionized water

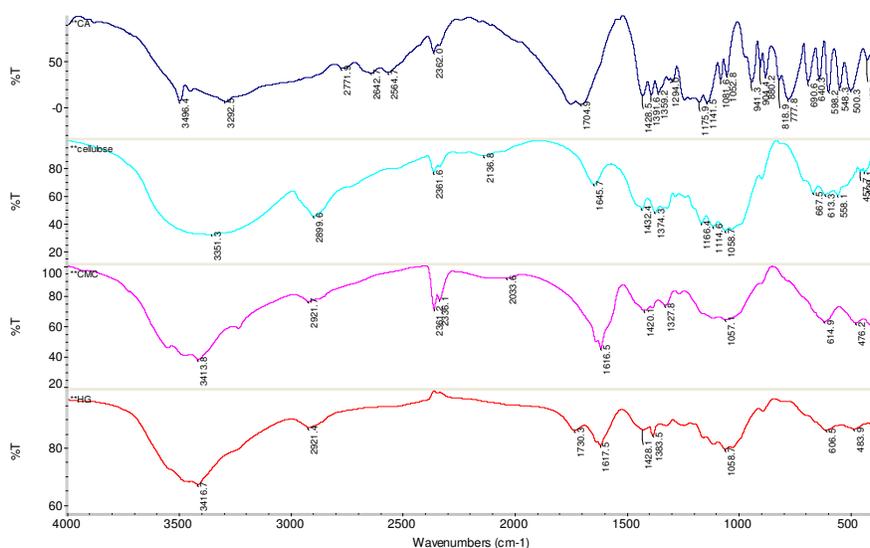


Figure 2: FTIR spectra of CA, cellulose, CMC and HG

The FTIR spectra of CA, cellulose, CMC-Na, and HG are presented in Figure 2. The characteristic bands of CA at 3292.5 cm^{-1} , 1704 cm^{-1} , 1081.6 cm^{-1} , and 777.6 cm^{-1} are related to OH and C=O stretching vibrations, and C-OH and CH₂ stretching vibrations, respectively.³⁵ The FTIR spectrum of cellulose showed the bands at 3351.3 cm^{-1} , 2899.8 cm^{-1} , 1645.7 cm^{-1} , 1432.4 cm^{-1} , 1166.4 cm^{-1} , and 1058.7 cm^{-1} , which are related to the OH and CH stretching vibration, H₂O and CH bending vibrations, CO stretching ester bond and C-O alcohol 1° and 2°, respectively.³⁶ The FTIR spectrum of CMC-Na showed the bands at 3413.6 cm^{-1} , 2921.7 cm^{-1} , 1616.5 cm^{-1} , 1420.1 cm^{-1} , and 1327.8 cm^{-1} related to OH and COO⁻ stretching, COO⁻ stretching and C-O-C stretching vibrations, respectively. CH₂ bands at 1600 cm^{-1} , 1429 cm^{-1} , 1159 cm^{-1} , and 1059 cm^{-1} are related to water bending vibrations, CH stretching vibrations, and CO stretching vibrations, respectively.³⁶ The FTIR spectra of HG confirmed cross-linking formation by showing the absorption band for cross-linking carboxylic ester groups at 1730 cm^{-1} . Moreover, an absorption band for the sodium carboxymethyl group appeared at 1617 cm^{-1} (Fig. 2). The results are in good agreement with what is reported for similar systems.²⁹

Swelling studies

Figure 3 presents the HG's swelling percentage and durability, which showed a steady, sustained increase in water absorption, approaching 450% on day 30.

The effect of a low concentration of NaCl on the swelling capacity of HG was investigated for 7 consecutive cycles of soaking hydrogels with 0.1 M NaCl and distilled water for 24 hours alternately. The water absorption capacity was decreased by the monovalent cation Na⁺, which might increase network density due to the complex formation between COO⁻ and Na⁺. The absorption capacity was recovered after soaking with distilled water by about 15%. A slight increase in the swelling was noticed after the fourth cycle and remained unchanged until the seventh cycle (Fig. 4). The results agree with Zhang *et al.*¹⁷

At low pH, nearly all carboxylate groups in CMC-Na are protonated (COO⁻ is converted to COOH), removing repulsive forces and decreasing expansion. In contrast, at high pH, the carboxyl groups are deprotonated (COOH is converted to COO⁻), and there are repulsive forces between COO⁻ that enhance water absorption.^{30,38} HG showed an increase in SR% of about 50% when soaked in a slightly basic solution (pH = 8); the highest swelling ratio was observed in the third cycle (Fig. 5). The results are in accordance with the results of Georgieva *et al.*, and Demitri *et al.*^{30,37}

The swelling capacity of HG exhibited cycles of slightly increasing and decreasing in weight after each drying cycle, which is due to the breaking up of the outer layer of the HG when it reaches its extreme expansion, allowing the inner layers to be exposed to the water until the complete degradation of the HG. The highest

swelling ratio was recorded in the first cycle,

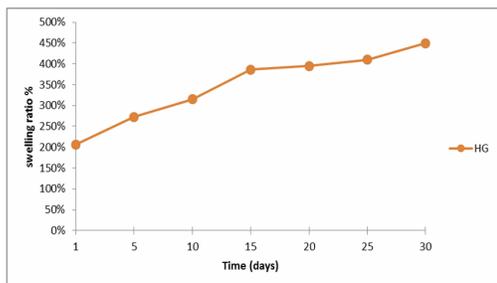


Figure 3: Swelling ratio of HG in deionized water for 30 days

followed by the seventh cycle (Fig. 6).

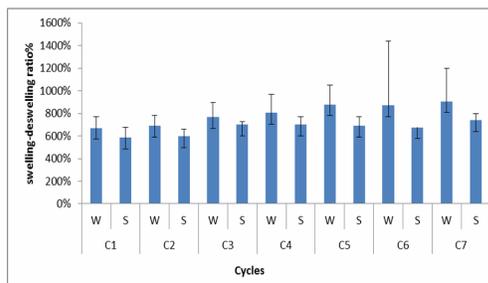


Figure 4: Swelling-deswelling behavior of HG; swelling (W) in deionized water and deswelling (S) in NaCl (0.1M)

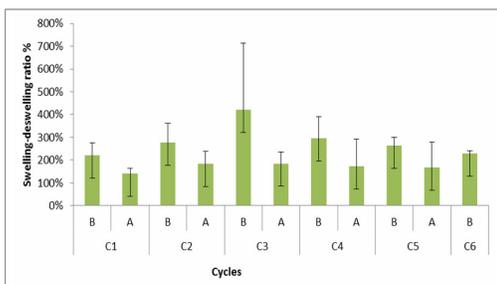


Figure 5: Swelling-deswelling behavior of HG, swelling at pH 8 and deswelling at pH 2

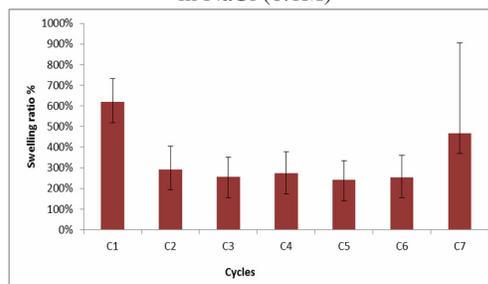


Figure 6: Swelling-deswelling behavior of HG, swelling in deionized water and deswelling by oven-drying

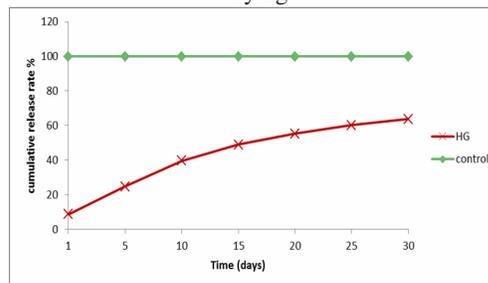
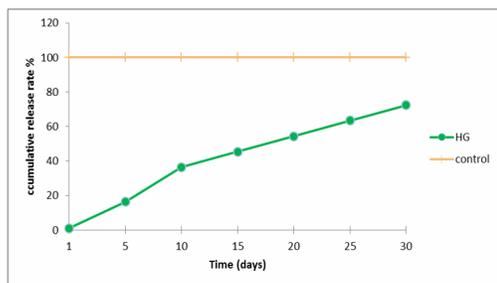


Figure 7: (a) Nitrate release rate of KNO₃ and HG/KNO₃, and (b) sulfate release rate of (NH₄)₂SO₄, and HG/(NH₄)₂SO₄, in deionized water

Release behavior in deionized water

Figure 7 (a and b) depicts the nitrate and sulfate release behavior trends in deionized water, which showed a slow initial release of 1% and 10% on the first day and a constant, sustained increase in the cumulative release rate over the course of 30 days. The cumulative release rate reached 70% and 63% on day 30, respectively.

Release behavior in soil

Figures 8 (a and b) shows the fertilizer release rates of (NH₄)₂SO₄ /HG and KNO₃/HG in a soil mix of peat moss and sand (weight ratio 1:1). In both experiments, the results showed that HG/N fertilizers released at a slower rate than the

control groups. Potassium nitrate and ammonium sulfate reached 60% and 65% on day 30. The results of the cumulative release rate in deionized water and soil mix were in parallel with the definition set by the Committee of European Normalization (CEN) for slow-release standards.³⁸ Similar results were obtained by Olad *et al.*¹²

Soil-water content

Figure 9 presents the soil water content of a soil mix of peat moss, and sand (weight ratio 1:1) amended with 1% of HG. The water content of the soil mix amended with HG was improved and reached 15% on day 30. In contrast, the soil mix

without hydrogel in the control group showed a sharp drop in water content after the seventh day, reached 15% on the fifteenth day, and completely disappeared on day 20. In general, the water content of the soil mix was improved by 100% on days 15 and 20 due to the addition of the

hydrogel, which was similar to the results obtained by Montesano *et al.*³¹ Therefore, it could be practically used in agriculture to decrease the frequency of irrigation and improve plant performance during drought periods.^{32,17}

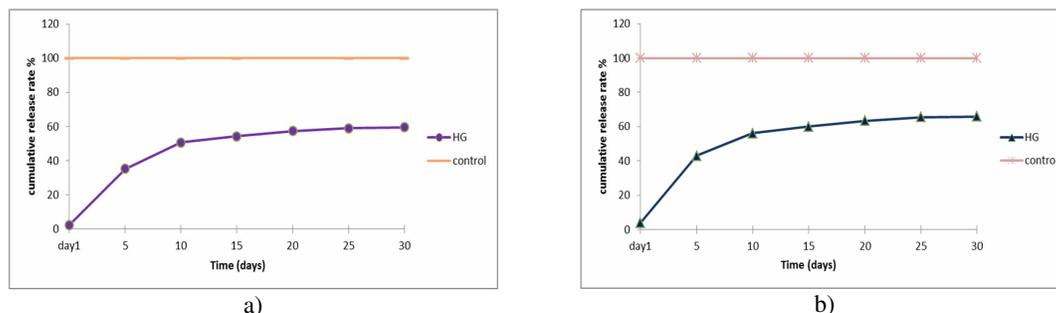


Figure 8: Release rate of (a) KNO₃ and HG/KNO₃, and (b) (NH₄)₂SO₄ and HG/(NH₄)₂SO₄, in a soil mix of peat moss and sand (weight ratio 1:1)

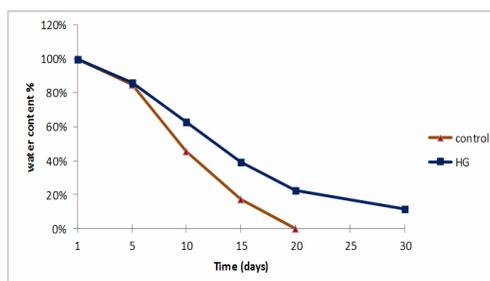


Figure 9: Moisture content of the soil mix of peat moss and sand (weight ratio 1:1), without (control) and with the addition of HG

CONCLUSION

A cost-effective, slow-release green nitrogen fertilizer hydrogel was synthesized using the CMC-Na backbone and the natural polymer cellulose and cross-linked with CA. In addition, the nitrogen fertilizers KNO₃ and (NH₄)₂SO₄ were loaded successfully. The hydrogel (HG) showed sensitivity to pH and salt, in addition to a good SR% and durability, compared to other synthetic polyacrylamide-based hydrogels. Moreover, the HG/N fertilizers showed slow-release behavior, which agrees with the CEN. This new formula could be practically applied in agriculture to improve soil-water content, improve the plant use efficiency of nitrogen fertilizers, and decrease the footprint of nitrogen fertilizers on the environment.

ACKNOWLEDGMENT: The authors thank the Scientific Research Deanship at the University of Jordan for funding this work.

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