

RESEARCH ARTICLE

Synthesis and Application of Biodegradable Cellulose Hydrogels From Sunflower Husks as a Water-Retaining Material in Agriculture

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ABSTRACT

The water shortage is currently a major problem for agriculture around the world, and this, in turn, can negatively impact food safety. Therefore, in this article, acrylamide monomer (AAM) was bound by the cross-linking agent N, N'-methylene-bis-acrylamide (MBA) in amounts of 10, 15, and 20 mg along with microcrystalline cellulose (MCC) obtained from sunflower seed husk (SFH) and a biodegradable hydrogel in the soil layer with high sorption capacity was synthesized. As a result of the study, the AAM monomer found to be attached to the MCC matrix via intermolecular hydrogen bonds. The kinetics of swelling of the obtained hydrogels in aqueous, electrolytic and water-ethanol, water-acetone binary solutions at various amounts of cross-linking agent were comparatively studied, and it was found that the water sorption potential of the natural polymer—MCC-based hydrogel (MCC hydrogel)—is high at pH = 6.5 and corresponds to the pH of the soil environment. The study showed that the synthesized hydrogel is optimal when using 10 mg of a cross-linking agent, has mechanical strength, withstands pressure up to 27 MPa, completely decomposes at 796°C, and has good thermal stability. It has been established that the pore sizes of hydrogel with 10 mg of cross-linking agent lie within the range of 313.9 nm–den 3.41 μ m and belong to mesoporous materials, where the degree of swelling is 1176%. The MCC hydrogel was saturated with water from the soil within 5 days and collapsed within 35 days, releasing the absorbed water back into the soil, losing 66% of its mass and undergoing biological decomposition. These properties of MCC hydrogel allow it to be used as a “water-retaining material” in agriculture.

1 | Introduction

It is known that the growth and productivity of agricultural crops depend on climate changes and external factors. The global warming and drought, one of the pressing world problems of the 21st century, brings the solution to the problem of growing crops regardless of this factor [1]. In addition, the

growth of human population on earth, and the corresponding increase in food consumption and production of agricultural raw materials, have influenced agricultural patterns throughout the world [2]. These problems are present in many countries where the main production activity is concentrated on the development of agricultural land, which includes the Republic of Kazakhstan. The share of irrigated fields of lands

used in agriculture of Kazakhstan is only 0.7% [3]. This confronts the scientific community with solutions to the problems of developing rain-fed crops, where, as a result of many years of using monocultures, the moisture-accumulating capacity is reduced. In addition, land use in conditions of drought and soil erosion is relevant.

The results of research in recent decades have shown that the use of polymer-based hydrogels has great potential in mitigating desertification and erosion of soil, while also improving its physicochemical properties [4].

Research has been carried out on improving soil quality through the usage of superabsorbents obtained from synthetic polymers [5, 6]. The composite hydrogels had a sorption capacity ranging from 400 to 800 g/g, and exhibited fertilizing properties with the potential to enhance productivity by up to 30%. However, synthetic monomers, such as acrylic acid, polyacrylamide, acrylamide, polyvinyl alcohol, polyvinylpyrrolidone, N-isopropylacrylamide, and diallyldimethylammonium chloride, used in the production of superabsorbents, leads to changes in soil composition, destabilization of pH, soil salinization, soil hardening, and air infiltration into the soil while also having a negative effect on the maturation of plant roots and the supply of nutrients to the soil microflora [7, 8].

Therefore, intensive research has begun on using biodegradable composite hydrogels based on natural polymers. In particular, scientists are greatly interested in utilizing cellulose and its derivatives to produce biodegradable composites [9]. Cellulose is an inexpensive, easily biodegradable material obtained from wood, various annual plants, and agricultural residues [10]. A key feature is that the hydroxyl groups in the molecule are very convenient for modification [11, 12]. Furthermore, hydrogels obtained using cellulose are intensively studied as drug carriers [13], wound healing agents [14], sorbents for the removal of heavy metals from industrial wastewater [15], packaging materials for the food industry [16], and, in agriculture, as seed additives, seed coatings, root dips, growth regulators, protective agents, and controlled release agents [17, 18]. Several research endeavors have investigated the potential of synthesizing hydrogels through cross-linking cellulose with various substances, including polyacrylamide [19, 20], acrylic acid [21], starch [22, 23], alginate [24], and glycerol [25, 26], with the aim of applying them in agriculture. Synthesis of hydrogels by combining synthetic monomers with cellulose ensures biodegradability, in addition to having a positive effect on sorption and mechanical properties [27, 28].

The authors of the present study previously synthesized hydrogels by combining hydroxyethylcellulose and acrylamide with glutaraldehyde, varied in a range of 0.5%–1.5% [29]. As a result, the degree of swelling of the hydrogels at a low concentration of cross-linking agent was significant. However, the desorption time of sorbed water was found to be short and was not subject to degradation, either through biological or standard means. In another study, a hydrogel was synthesized from cellulose and acrylamide nanocrystals in the presence of N, N-methyl bisacrylate and was placed into soil with a humidity of 45% [30]. The hydrogel absorbed moisture from the soil over the first 10 days, then desorbed water into the soil for a further 35 days.

Therefore, fast moisture sorption time and maximum water absorption properties of hydrogels are important. Also, the slow release of moisture absorbed by the hydrogel makes it possible to ensure stability in the amount of moisture in the soil and, accordingly, good plant growth. Therefore, it is important to synthesize environment-friendly superabsorbents with high sorption capacity and biodegradability based on natural polymers obtained from agricultural waste and use them in agriculture.

Sunflower cultivation is the leading branch of agriculture in Kazakhstan, and the area under oilseed crops is steadily growing and has already exceeded one million hectares, which is about 5% of all the cultivated areas of the country. Accordingly, the processing of sunflower seeds increases, which ultimately leads to an increase in waste from the oil processing plant, the disposal of which in large volumes is expensive and difficult. Since the oil extraction method produces approximately 14–25 kg of husk from every 100 kg of sunflower seeds [31] The use of SFH in its pure form as animal feed is unacceptable due to its high content (about 50%) of fiber, as it is poorly digested by the stomach of animals. Therefore, it is important to solve the problem of processing large quantities of SFH, which are simply used by local residents as fuel. The cellulose content in SFH reaches from 47.8 up to 50.7% by weight [32, 33]. This indicates that the potential for using SFH as a source of cellulose raw materials is very high.

In this regard, the main objective of this research work is to use as a reinforcing matrix microcrystalline cellulose (MCC), a natural polymer obtained from sunflower seed husk (SFH), which is agricultural waste, and acrylamide monomer (AAm) bound to it by varying amounts of a cross-linking agent MBA, synthesize MCC hydrogel with biodegradable and superabsorbent properties, to study its physical, chemical properties, soil moisture retention, and determination its biodegradation period.

2 | Experimental Section

2.1 | Materials

Hydrogen peroxide ($\geq 15\%$, H_2O_2), acetic acid ($\geq 55\%$, CH_3COOH), sulfuric acid ($\geq 98\%$, H_2SO_4), acrylamide ($\geq 99\%$, $\text{CH}_2=\text{CHCONH}_2$), N, N'-methylenebis(acrylamide) ($\geq 99\%$, $(\text{H}_2\text{C}=\text{CHCONH})_2\text{CH}_2$), ammonium persulfate ($\geq 98\%$, $(\text{NH}_4)_2\text{S}_2\text{O}_8$), sodium hydrogen phosphate ($\geq 99\%$, Na_2HPO_4), sodium chloride ($\geq 99\%$, NaCl), ethanol ($\geq 96\%$, $\text{C}_2\text{H}_5\text{OH}$), and acetone ($\geq 99.5\%$, CH_3COCH_3) were obtained from Sigma-Aldrich (Bangalore, India). All reagents were of analytical grade and were used without additional purification.

2.2 | Methods

2.2.1 | Preparation of the MCC Hydrogel

The natural monomer, MCC, used in the preparation of the hydrogels, was obtained from sunflower seed husk (SFH) in accordance with the method described by [33]. To synthesize the hydrogel, 1 g of MCC mass was continuously mixed with 40 mL of deionized water at a temperature of $35^\circ\text{C} \pm 2^\circ\text{C}$ using

a magnetic stirrer (MS LabSol China) at a speed of 500rpm for 8h, until a homogeneous thick suspension was formed. A volume of 5 mL of the suspension was poured into a cylindrical plastic test tube, and then 0.125 g of the functional monomer, acrylamide (AAM), was added, followed by 10, 15 or 20 mg of the cross-linking agent, N, N-methylenebisacrylamide (MBA), initiator—ammonium persulfate (AMPS) (10 mg) was added. The reaction mixture was continuously stirred with a glass stick until complete homogeneity was achieved. In order to remove oxygen dissolved in the solution, purging with argon was performed for 2–3 min. Next, the solution was placed in a DC-80 vacuum cabinet (Grodorgmash, Belarus) at a temperature of $60^{\circ}\text{C} \pm 2^{\circ}\text{C}$ for 1 h (Figure 1). The hydrogels were then washed with deionized water for 1 week to remove unreacted radicals.

For the study, MCC hydrogel variants were assigned designations based on the amount of MBA that was added: 10 mg of MCCHG₁₀, 15 mg of MCCHG₁₅, and 20 mg of MCCHG₂₀.

2.2.2 | Swelling Properties of the MCC-Based Hydrogels

2.2.2.1 | Swelling Kinetics in Water. The degree of swelling of the MCC hydrogels in water was determined using the gravimetric method, by which a sample of each hydrogel was dried in a DC-80 vacuum cabinet (Grodorgmash, Belarus) at a temperature of 70°C , until a constant mass was achieved, which was measured on an LV 210-A analytical scale (Sartogasm, Russia) with an accuracy of 0.0001 g. The samples were then immersed in deionized water until equilibrium mass was reached. The mass of the swollen gel was measured on the same analytical scale. The swelling degree were determined based on the formula:

$$\alpha (\%) = (m - m_0) / m_0 \times 100\% \quad (1)$$

where α is the degree of swelling, m is the mass of gel swollen in water (g), and m_0 is the initial mass of dried gel (g).

The kinetics of swelling of the samples were determined by the formula:

$$kt^n = M_t / M_{\infty} \quad (2)$$

where k is the characteristic constant of the hydrogel, t is the time, n is the characteristic exponent describing the mechanism of liquid diffusion into the gel volume, M_t is the mass of liquid sorbed during time t , and M_{∞} is the mass of liquid sorbed in the equilibrium-swollen state (i.e., at $t \rightarrow \infty$). The constant k is determined by the point at which the curve of $\ln (M_t / M_{\infty})$ intersects with $\ln (t)$ on the ordinate axis [34].

2.2.2.2 | Sensitivity to pH. To determine the sensitivity of the MCC hydrogels to pH, a sample of each gel was divided into disk-shaped pieces and placed into one of 12 buffer solutions that ranged from pH = 3.5–9.0 for a period of 24 h, after which the change in mass was evaluated. Then, the pH sensitivity of the gel was calculated using the following formula:

$$\alpha (\%) = m_{\text{pH}} / m_{\text{w.s.}} \times 100\% \quad (3)$$

where α is the degree of swelling, m_{pH} is the mass of the gel in a pH solution (g), and $m_{\text{w.s.}}$ is the mass of the gel swollen in water (g).

2.2.2.3 | The Effect of Ionic Strength. To determine the effect of ionic strength on the volume-phase properties of the MCC hydrogels, a sample of each gel was divided into disk-shaped portions and placed into one of NaCl solutions that ranged in the concentration of 0.001–1.0 N for a period of 24 h, and then mass changes were measured on an LV 210-A analytical scale (Sartogasm, Russia) with an accuracy of 0.0001 g. The effect of low molecular weight ions on the hydrogel was calculated using the following formula:

$$\alpha (\%) = m_{\text{i.s.}} / m_{\text{w.s.}} \times 100\% \quad (4)$$

where α is the degree of swelling, $m_{\text{i.s.}}$ is the mass of the gel in a saline solution (g), and $m_{\text{w.s.}}$ is the mass of the gel swollen in water (g).

2.2.2.4 | The Effect of Organic Solvents. The resistance of the MCC hydrogels to organic solvents was determined using water/ethanol and water/acetone solutions, with volume ratios (mL/mL) of 10/0, 8/2, 6/4, 5/5, 4/6, 2/8, and 0/10. Weight changes were recorded over a period of 24 h, then the gel swelling-collapse kinetics were determined using the following formula:

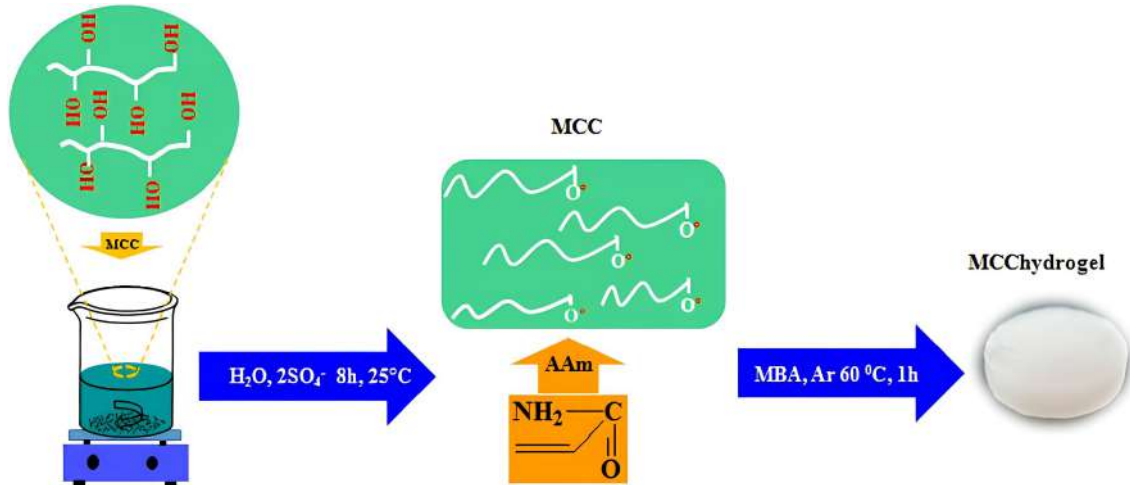


FIGURE 1 | Synthesis of MCC hydrogels.

$$\alpha (\%) = m_{\text{org}} / m_{\text{w.s.}} \times 100\% \quad (5)$$

where α is the degree of swelling, m_{org} is the mass of the gel in an organic solvent (g), and $m_{\text{w.s.}}$ is the mass of the gel swollen in water (g).

2.2.2.5 | Scanning Electron Microscopy (SEM). The surface morphologies of the microcrystalline MCC hydrogels were examined using a Quanta 200i 3D SEM (FEI, The Netherlands). Measurements were carried out in high vacuum mode using a secondary electron detector at an accelerating voltage of 15 kV. The surface of the MCC hydrogels was coated with gold nanoparticles to improve the transfer of electrons, and the specimens were mounted onto aluminum pins with carbon tape.

2.2.2.6 | Mechanical Characterization. The mechanical characteristics of the MCC hydrogels were studied using a WDW-5 tensile testing machine (Time Group Inc., China), with a measured load range of 0.01–5 kN and a loading speed range of 0.0005–500 mm/min. Data recording was performed automatically. While testing the samples under a load of 0.01 kN, the movement speed was 2 mm/min. The samples were tested until the maximum tensile force was reached or after the sample became deformed.

2.2.2.7 | Fourier-Transform Infrared Spectroscopy (FTIR). FTIR analysis of the MCC hydrogels was performed on an FT-801 FTIR spectrometer (Simex, Russia), with a resolution of 1 cm^{-1} and a wavelength $4500\text{--}4700\text{ cm}^{-1}$, at a temperature of 25°C and a scan rate of 100.

2.2.2.8 | Thermogravimetric Analysis (TGA). The thermal characteristics of the MCC hydrogels were studied using a LabSysevo differential TGA (Setaram, France), in an argon atmosphere. The temperature range was $30^\circ\text{C} \pm 5^\circ\text{C}$ – $700^\circ\text{C} \pm 5^\circ\text{C}$, with a heating rate of $10^\circ\text{C} \pm 1^\circ\text{C}/\text{min}$. The mass of the samples was found to be approximately $25 \pm 2\text{ mg}$.

2.2.2.9 | Biodegradability of the MCC Hydrogel. To test the water retention and biodegradability of the MCC hydrogels under agricultural conditions, solid, gel-like samples were placed at a depth of 15 cm in soil, at a humidity level of $60\% \pm 10\%$ and a temperature of $25^\circ\text{C} \pm 2^\circ\text{C}$. Later, the change in mass was determined using the gravimetric method over a period of time. First, the ability of the hydrogel samples to absorb water while in situ was determined, and then the time necessary for the samples to biologically decompose was measured.

3 | Results and Discussion

3.1 | Swelling Kinetics of the MCC Hydrogels

3.1.1 | Swelling Kinetics of the MCC-Based Hydrogels in Water

Figure 2 shows the degree of swelling of the MCC hydrogels in water, designated according to the amount of cross-linking agent, MBA. When the gels swell, water molecules easily diffuse into the samples, which results in a high swelling coefficient. MCCHG₁₀

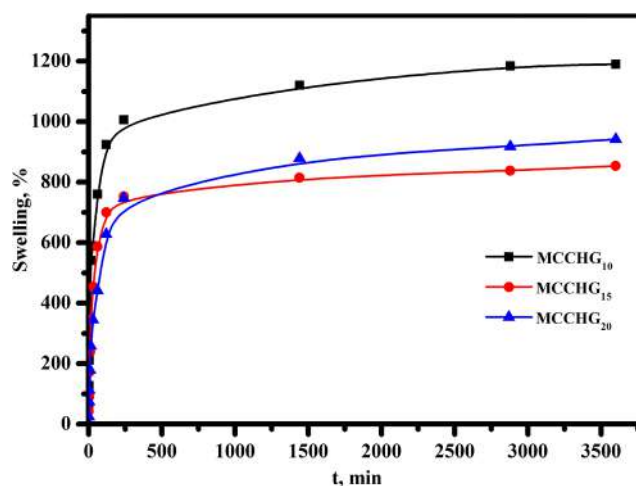


FIGURE 2 | Water swelling kinetics of MCC hydrogels.

TABLE 1 | The values n and k of hydrogel MCC-AAm = 1:1 (mass.) during sorption.

Samples	M_∞	n	k
MCCHG ₁₀	1191.09	1.3	$2.9 \cdot 10^{-1}$
MCCHG ₁₅	852.65	0.58	$2.6 \cdot 10^{-1}$
MCCHG ₂₀	942.29	0.89	$3.4 \cdot 10^{-1}$

had an initial 2-h swelling rate of 920%, and a 2-day swelling rate of 1176%. MCCHG₁₅ had an initial 2-h swelling rate of 699%, and a 2-day swelling rate of 916%. Finally, MCCHG₂₀ had an initial 2-h swelling rate of 622%, and a 2-day swelling rate of 833%. This indicates that the water absorption efficiency of MCCHG₁₀ hydrogel is evident in the first 2h, making its full use in agriculture during this period particularly effective. The swelling degree in the first 2h for the MCCHG₁₀ sample was found to be 1.3 and 1.5 times higher than the masses of the MCCHG₁₅ and MCCHG₂₀ samples, respectively, and after 2 days, they were 1.28 and 1.4 times higher, respectively. Additionally, MCCHG₁₀ hydrogel absorbed up to 200% more water than the MCCHG₁₅ and MCCHG₂₀ hydrogels. This result shows that the lower the amount of cross-linking agent, the greater the degree of water swelling. This indicates that the lower the concentration of the binding agent, the larger the pore size of the hydrogel and the higher the sorption capacity [35]. The superior effectiveness of the lower MBA gel is likely due to increased cross-linking caused by the MBA, which in turn results in the folding of the polymeric chains, and the subsequent attainment of reticulation points, thus reducing the aqueous absorption capacity [36]. Similar results were obtained when studying the water sorption properties of other hydrogels [37, 38].

Table 1 includes the values of diffusion indicators of water into the MCC hydrogels, and Figure 3 is a dependence graph. The diffusion constant, k , for MCCHG₁₀ is $2.9 \cdot 10^{-1}$ and Fickian diffusion, n , is 1.3, for MCCHG₁₅ is $k 2.6 \cdot 10^{-1}$ and Fickian is 0.58, and for MCCHG₂₀ is $3.4 \cdot 10^{-1}$ and Fickian is 0.89. At a Fickian diffusion value of $n > 0.5$, the rate of water penetration into the hydrogel and the relaxation rate are close, which means that the processes of sorption and desorption are more readily controlled [39, 40]. Conversely, if the Fickian diffusion

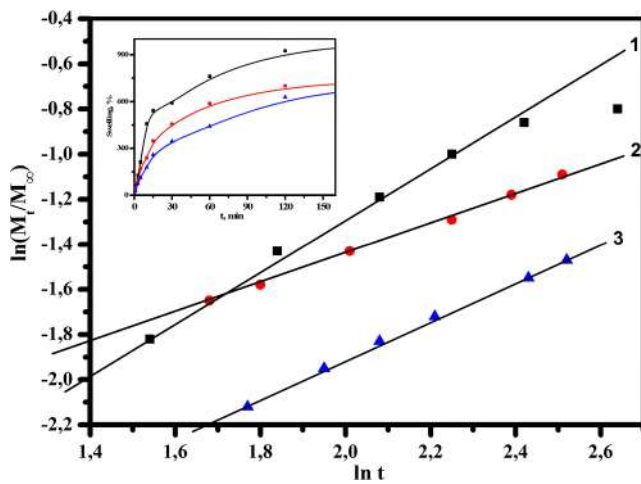


FIGURE 3 | Logarithmic dependence of MCC hydrogel swelling. MBA amount: 1 is MCCHG₁₀; 2 is MCCHG₁₅; 3 is MCCHG₂₀.

value is $n < 0.5$, the relaxation rate becomes high, thus water quickly leaves the hydrogel [41]. Finally, when the Fickian diffusion value is $n \geq 1$, the largest amount of water can be absorbed, as the rate of penetration and relaxation is greatest [42]. According to the results, because the Fickian diffusion value of MCCHG₁₀ was $n \geq 1$, this sample was seen to be the most effective composition for production of a superabsorbent that would best allow regulation of water absorption, depending on external environmental factors.

3.1.2 | Swelling Kinetics of the MCC Hydrogels in Buffer Solutions With Different pH Environments

Because the pH of soil found in agriculture is in the range of 3–9 [43], the swelling kinetics of hydrogels was studied in 12 model pH environments corresponding to this range. Figure 4 shows the swelling kinetics curves of MCCHG₁₀, MCCHG₁₅, and MCCHG₂₀ hydrogels in the dependence of pH. The swelling degree of MCCHG₁₀, MCCHG₁₅, and MCCHG₂₀ hydrogels decreased, and the collapse process was observed in the pH range of 3.5–4.5. Moreover, in the pH range of 4.5–6.5, the swelling degree increases, and at pH=6.5, it has the highest degree of water absorption. The swelling degree was 111% for MCCHG₁₀, 104% for MCCHG₁₅, and 102% for MCCHG₂₀. It was also found that the most effective water sorption mode for MCC hydrogel is observed in a neutral environment (pH=6.5). It was found that the synthesized hydrogel MCCHG₁₀ reaches the maximum degree of swelling at pH=6.5 and is an effective water-retaining material.

The pH value of the medium increases, approaching an alkaline environment, the degree of sorption of the hydrogels decreases, and a process of collapse is observed. At pH=9, the degree of swelling of hydrogels was found to decrease to a minimum and approach the initial value. The sensitivity of MCC hydrogel to the pH of the environment is explained by the electrostatic interaction of H⁺ and OH⁻ ions in solutions of amine and hydroxyl groups of various pH values, contained in the MCC and AAm monomers in the hydrogel. The obtained data are in good agreement with previously conducted studies [44].

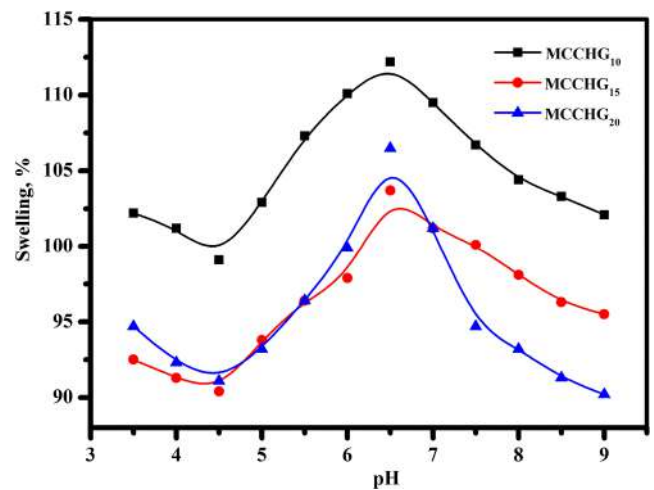


FIGURE 4 | Effect of pH on the swelling of the MCC hydrogels.

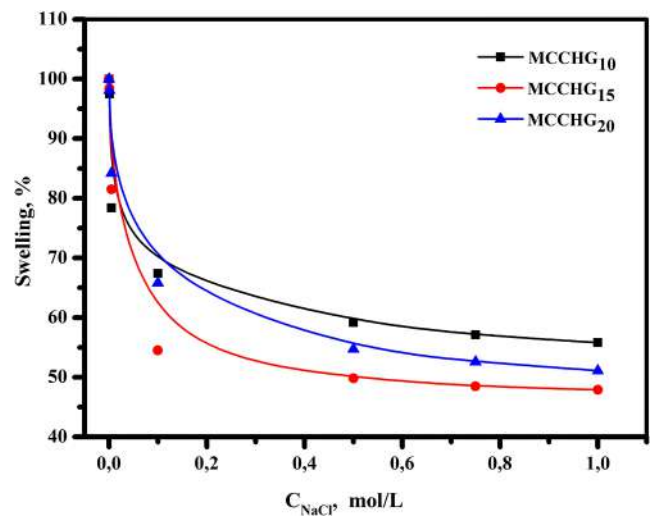


FIGURE 5 | The effect of NaCl concentration on the swelling ratio of the MCC hydrogels.

It has been established that the pH value of the soil in the crop fields of Kazakhstan is within 5–7, which corresponds to the maximum sorption capacity of the synthesized MCC hydrogel. Thus, it has been established that the obtained MCC hydrogel effectively works in the agricultural fields of Kazakhstan.

3.1.3 | The Effect of Ionic Strength on the Swelling of the MCC Hydrogels

Figure 5 shows the swelling kinetics of the MCC hydrogels in sodium chloride solutions of various concentrations (0.001–1.0 mol/L). As the concentration of NaCl in the solution increases, the degree of swelling of the hydrogels is seen to decrease. At NaCl concentrations from 0.001 to 0.2 mol/L, the hydrogels were found to quickly collapse, with the degree of swelling decreasing to approximately 66% for MCCHG₁₀ and MCCHG₂₀, whereas the level dropped to 55% for MCCHG₁₅. The collapse of the hydrogels in solutions with increasingly higher amounts of NaCl results in a decrease in the amount of water in the gels. This transition likely occurs as the ionic

activity of the saline solution becomes competitive with the functional groups of the polymer chains. The swelling degree of the hydrogels does not change significantly after the electrolyte concentration reaches 0.2 mol/L, at which point an equilibrium is established, with swelling remaining relatively constant until 1.0 mol/L. On the whole, MCCHG₁₀ collapses less than those gels with a greater amount of MBA at all electrolyte concentrations. Such collapses may result from reverse osmosis occurring in the electrolytic solution of salts entering the hydrogels, disrupting the hydrophilic-hydrophobic balance in the chains, which undergo immediate contraction [45, 46]. Other studies have found that biodegradable hydrogels containing AAm collapse in an electrolytic environment [47, 48]. Therefore, the results of this study are consistent with previous research.

3.1.4 | Kinetics of Swelling of the MCC Hydrogels in Organic Solvents

The effect of binary solutions of water-ethanol and water-acetone on the swelling kinetics of the MCC hydrogels is shown in Figure 6. When the proportion of ethanol in the water-ethanol mixture reaches 60%, the collapse of the hydrogels was rapid, and the swelling rate was reduced by 85% in MCCHG₁₀, 88% in MCCHG₁₅, and 91% in MCCHG₂₀. There was little observed change in the swelling ratio afterward, despite the greater ethanol concentration. A similar result was obtained in the water-acetone mixture. At 60%, the degree of swelling was found to be reduced by 81% in MCCHG₁₀, 88% in MCCHG₁₅, and 90% in MCCHG₂₀. Similar results are seen in other studies, which note the interaction of highly polar solvents with the carboxyl and hydroxyl groups in the monomer molecules that make up the hydrogels [49, 50].

3.2 | Mechanical Properties of the MCC Hydrogels

The results of testing the mechanical strength of the MCC hydrogels at different MBA concentrations are presented in Figure 7, which demonstrate that the concentration of the cross-linking

agent has a significant effect on the mechanical properties of the MCC hydrogels. From compression testing, MCCHG₁₀ was found to withstand pressures of up to 27 MPa, whereas MCCHG₁₅ was shown to handle only up to 15.9 MPa, whereas MCCHG₂₀ reached 7.7 MPa. Based on this, a determination was made that the lower the concentration of the cross-linking agent, the higher the mechanical strength of the MCC hydrogel. That is, MCC hydrogel with low cross-linking agent content can better distribute water between polymer chains, which improves elasticity and mechanical strength [51]. Moreover, as the amount of cross-linking agent in a hydrogel is increased, frequent cross-linking of monomers reduces the kinetics of swelling in water, electrolytic solution, and aqueous-organic solutions, as well as making the hydrogel more fragile.

3.3 | Morphology of MCCHG₁₀

From the SEM analysis, the morphology of the synthesized MCCHG₁₀ hydrogel was found to be generally uniform and mesoporous (Figure 8a). The pore sizes of the sorbent vary from 313.9 nm down to 3.41 μ m (Figure 8b). The space in the hydrogel

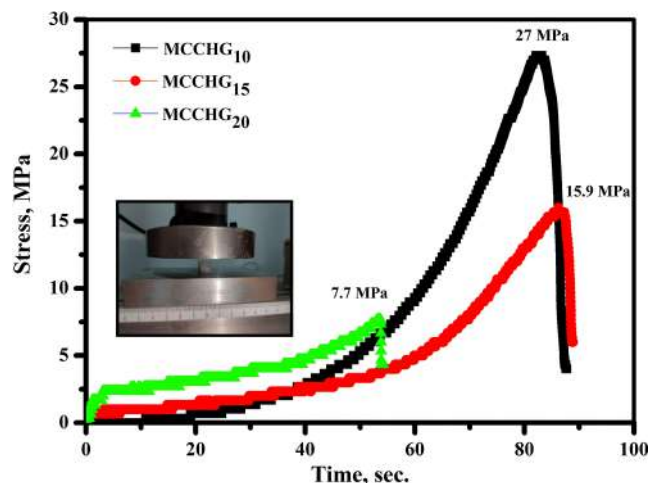


FIGURE 7 | Mechanical properties of MCC hydrogels.

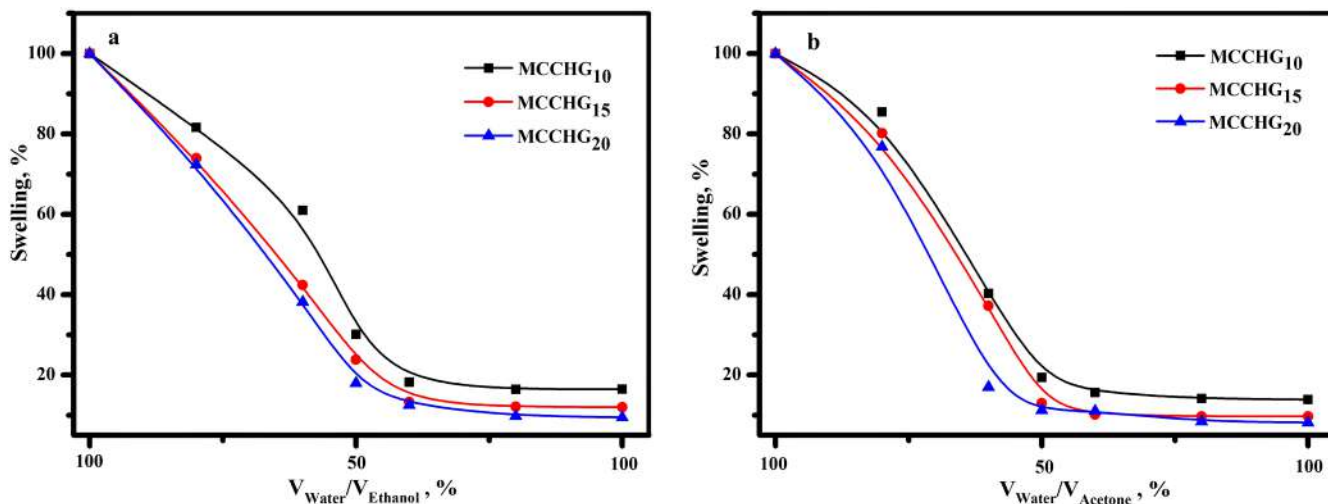


FIGURE 6 | Swelling kinetics of MCC hydrogels in (a) ethanol and (b) acetone solutions.

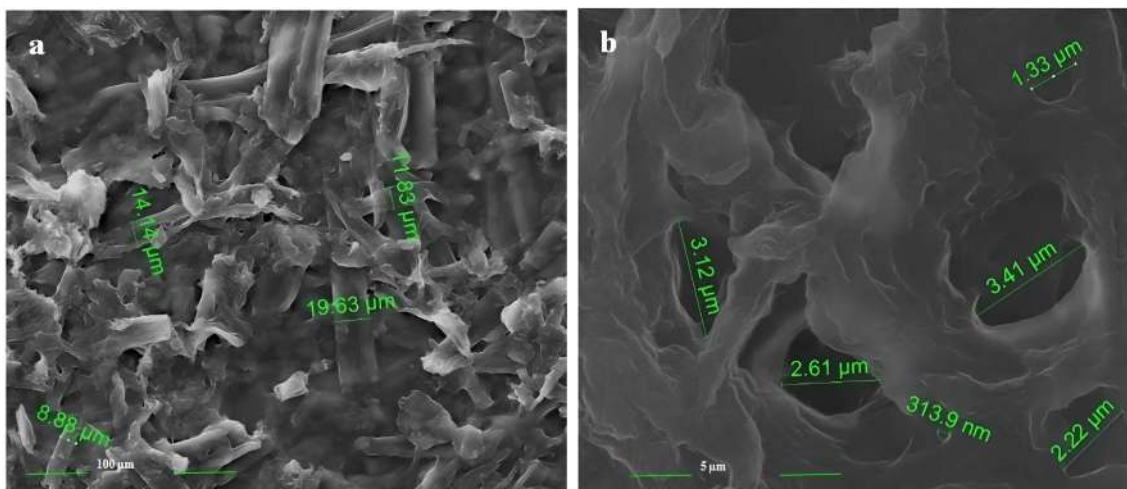


FIGURE 8 | SEM images of MCCHG₁₀.

networks increases due to electrostatic repulsions caused by the ionic nature of hydroxyl and carboxylate anions in the monomer molecules [45]. As a result, water molecules easily diffuse into the hydrogel, which leads to an increase in the swelling coefficient. This was shown in the determination of the swelling degree of MCCHG₁₀ (Figure 2). The pore sizes of hydrogels were also found to decrease when raising the concentration of the cross-linking agent, thus limiting the free penetration of water molecules into the hydrogels [45, 52]. The swelling degree of MCCHG₁₀ in water was found to be 1176%, which is 1.28 and 1.4 times higher than MCCHG₁₅ and MCCHG₂₀, respectively. These are in good agreement with the SEM results. Other researchers have also found that the surface morphology of MCC-based hydrogels had a mesoporous structure, so the SEM results obtained in this study show that the present hydrogel has a typical surface morphology [53].

3.4 | FTIR Spectroscopy of MCCHG₁₀

The chemical structure of MCCHG₁₀ was studied using FTIR, and compared with those of the initial MCC and AAm (Figure 9).

Figure 9a shows the absorption regions of the MCC spectra: 655.9 cm⁻¹, at the C—OH bond, due to out-of-plane bending; 891 cm⁻¹ and 1153.6 cm⁻¹ β- (1, 4), caused by the glycoside C—O—C, an amorphous region; 1014.7 cm⁻¹ and 1153.6 cm⁻¹, high-intensity signals from C—O and C—C bonds in the aromatic ring and C—O in the pyranose ring; 1053.3 cm⁻¹, showing chronic oscillations of the C bond; 1253.9 cm⁻¹, 1307.9 cm⁻¹, and 1365.8 cm⁻¹, due to the C—H bond; 1412.1 cm⁻¹, from the C—H₂ groups; 1635.9 cm⁻¹, caused by the O—H in the water molecule sorbed from the air; and, 2889.8 cm⁻¹ and 3337.8 cm⁻¹, due to the CH and OH groups. The data fit well with previous studies [32, 33, 54]. In the FTIR spectra of AAm in Figure 9b, the wave number values are as follows: 3100–3200 cm⁻¹ is CO—NH; 2824 cm⁻¹ is C—H; 1672 cm⁻¹ is C=O; 1660 cm⁻¹ is CO—NH₂; 1615 cm⁻¹ is C=C; 1140–1440 cm⁻¹ is C—H; and, 685–995 cm⁻¹ is in the range of HC=CH [55].

In the IR spectrum of the MCCHG10 hydrogel (Figure 9c), the AAm monomer used in the synthesis, 685–995 cm⁻¹ characteristic of HC=CH, 1140–1440 cm⁻¹ characteristic of C—H, and

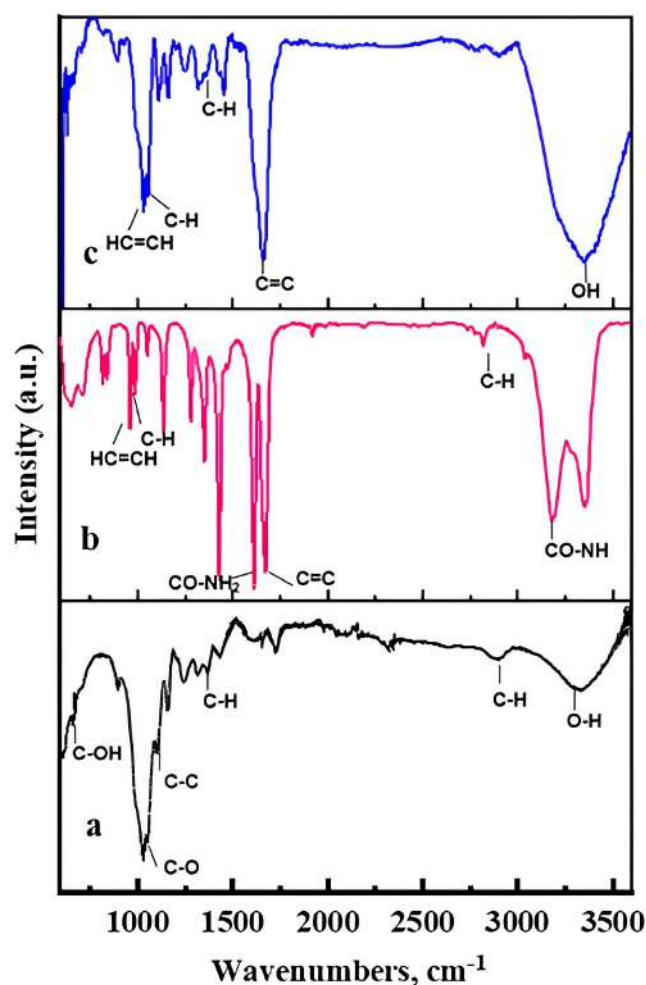


FIGURE 9 | FTIR spectra of: (a) MCC, (b) AAm, and (c) MCCHG₁₀.

1615 cm⁻¹ corresponding to C=C weakening, was observed [55]. In addition, in the spectrum of the resulting product, an intense signal at 1770 cm⁻¹, indicating the presence of an intermolecular hydrogen bond between the hydroxyl groups of the MCC molecule and the NH-amino groups of AAm, determines the formation of a new bond. This connection indicates that the MCC molecule is a complete and homogeneous

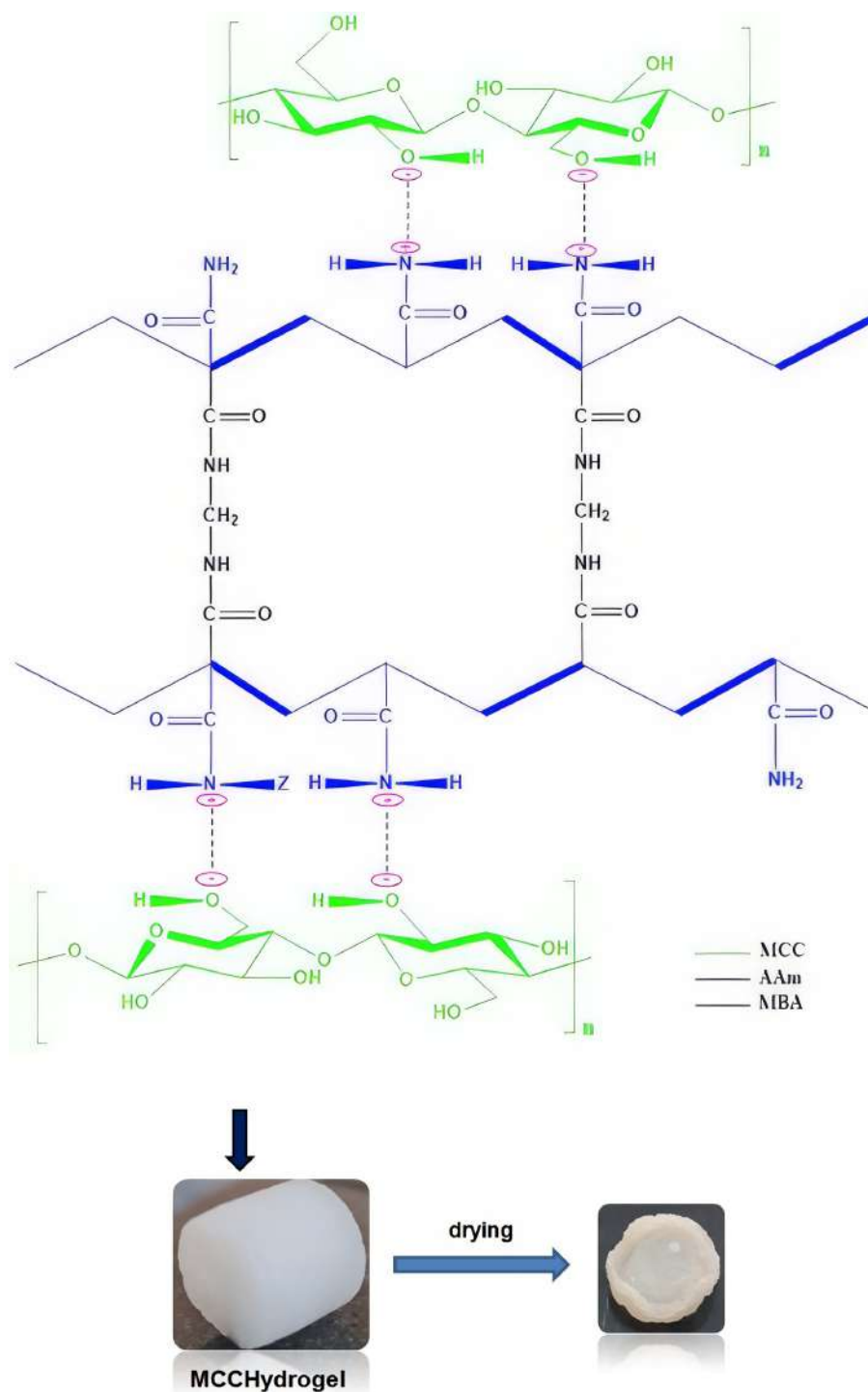


FIGURE 10 | The reaction scheme for synthesis of MCC hydrogels.

polymer mixture in the hydrogel [29]. The obtained FTIR result corresponds to the structural formula in Figure 10.

3.5 | Thermogravimetric Analysis of MCCHG₁₀

Figure 11 shows comparative thermograms of MCC and MCCHG₁₀. The reduction in MCC mass can be divided into two stages. The first stage is the evaporation of water molecules. The evaporation of free water molecules sorbed from the air for MCC occurs in the range of 75°C–255°C and loses 7% of its mass, and for

MCCHG₁₀, in the temperature range of 96°C–226°C and loses 5% of its mass. At the second stage, a large loss of MCC mass occurs in the range of 255°C–376°C. In this temperature range, cellulose undergoes strong depolymerization to form volatile gases of CO, CO₂, and CH₄, so MCC loses 90% of its initial mass (Figure 11a). The obtained result corresponds to the study in [33].

At the same time, in MCCHG₁₀, the loss of mass of the hydrogel occurs in the temperature range of 255°C–700°C, while the hydrogel loses 95% of its initial mass (Figure 11b). This is explained by an increase in the thermal stability of the macromolecule

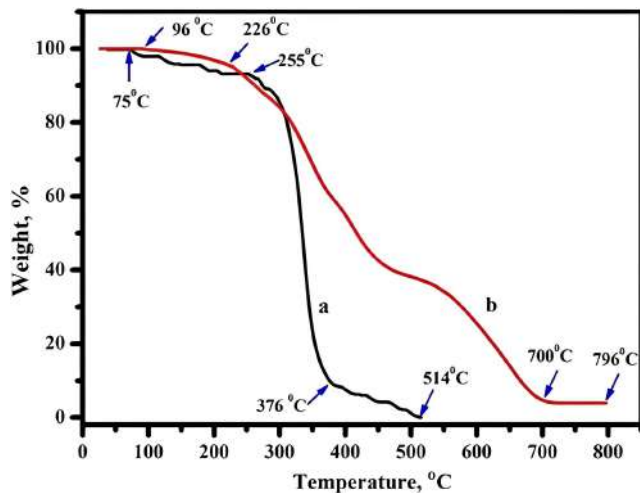


FIGURE 11 | TGA curves of (a) MCC and (b) MCCHG₁₀.

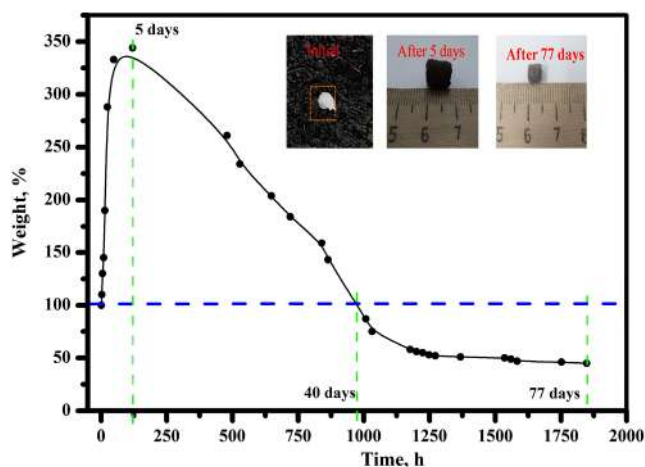


FIGURE 12 | Biodegradation of MCCHG₁₀.

obtained as a result of the intermolecular formation of hydrogen bonds with monomers. The results obtained are in good agreement with previous studies [53]. Thermal destruction of MCCHG₁₀ occurs with the formation of CO, CO₂, CH₄, and solid resins similar to MCC [56, 57]. The thermal decomposition of levoglucosan, coke, and volatile intermediate products such as hydrogen, ethylene, and ethane in MCC occurs in the temperature range of 376°C–514°C, and in MCCHG₁₀ in the temperature range of 700°C–796°C [33, 56].

3.6 | Biodegradation of MCCHG₁₀ in Soil

Figure 12 shows the biodegradation results of MCCHG₁₀ in a soil layer. The period of biological degradation of the MCCHG₁₀ hydrogel can be divided into three stages. In the first stage, MCCHG₁₀, which had been dried to a constant weight, was placed in soil, where it absorbed moisture over the first 5 days, resulting in a 342% increase in weight (Figure 12). Furthermore, in the second stage, saturated MCCHG₁₀ returned water to the soil over a period of 5–40 days. On average, 9.8% of moisture could be transferred to the soil each day. Finally, in the third stage, within a period of 40–77 days, MCCHG₁₀ underwent

TABLE 2 | Water retention and biodegradation of MCC hydrogel in soil.

MCCHG ₁₀	WA	WD	BD
m, g	0.41	0.12	0.08
Day intervals	0–5	5–40	40–77

Abbreviations: BD, biodegradation; WA, water absorption; WD, water desorption.

biological decomposition, resulting in a 66% loss of its initial mass (Table 2). On average, 2% ± 0.1 of the mass of the hydrogel was lost to biodegradation each day. The biodegradation of MCC hydrogel is caused by the destruction of hydrogen bonds in cellulose molecules under the influence of soil microorganisms and ultraviolet radiation [58]. This means that the biodegradation period of MCCHG₁₀ corresponds to the vegetation period in Kazakhstan, which is 60–77 days [30]. The remaining 34% of the hydrogel mass was mixed with soil particles, its weight could not be accurately measured. Other studies have shown that biodegradation of cellulose-based hydrogels is caused by soil microorganisms, resulting in a mass loss of around 60%, which is consistent with the data obtained in the present research [59–61].

4 | Conclusions

In conclusion, by linking different amounts (10, 15, and 20 mg) of the cross-linking agent methylene bis-acrylamide with AAm monomer to the MCC matrix obtained from sunflower seed husks, a biodegradable, water-absorbing and self-storing hydrogel was synthesized. The result of FTIR analysis proved the formation of mutual intermolecular hydrogen bonds between the hydroxyl groups in the MCC molecule and the amino groups in the acrylamide molecule.

A comparison of the MCCHG₁₀ variant, which was determined to have been the best, with MCCHG₁₅ and MCCHG₂₀ shows that the degree swelling after 2 days was 1176%, as the result of absorbing up to 200% more water. It was found that MCCHG₁₀ hydrogel reaches its maximum swelling degree at pH = 6.5 and has great potential for use as an effective water-retaining material in the soil of cultivated fields in Kazakhstan. The MCC hydrogel to be found collapsed with increasing concentration of the electrolyte, binary solutions of water-ethanol and water-acetone. In a study of the mechanical strength of MCC hydrogel, it was found that MCCHG₁₀ has low fragility compared to other gels, that is, the mechanical strength was 27 MPa. It was found that the optimal hydrogel MCCHG₁₀ has a mesoporous structure with pore sizes from 313.9 nm to 3.41 μm and thermal stability up to 226°C.

The moisture retention and biological degradation of the MCCHG₁₀ hydrogel in the soil were studied, and as a result, the hard gel mass absorbed the moisture in the soil for 5 days, gradually releasing the amount of water in the saturated gel mass to the soil during 35 days, and in 37 days, the gel lost 66% of its initial mass and also underwent biological degradation. Based on the obtained results, it is evident that MCCHG₁₀ hydrogel, which has high sorption potential, mechanical strength, and temperature stability, and is also prone to biodegradation, can be widely used as a “water-retaining material” in agriculture.

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Ethics Statement

The authors have nothing to report.

Conflicts of Interest

The authors declare no conflicts of interest.

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