

Synthesis, characterization, and swelling behaviors of a pH-responsive CMC-*g*-poly(AA-*co*-AMPS) superabsorbent hydrogel

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Abstract: New superabsorbent hydrogels were synthesized through free radical graft copolymerization of partially neutralized acrylic acid (AA) and 2-acrylamido-2-methylpropanesulfonic acid (AMPS) onto carboxymethyl cellulose (CMC) backbones. The structure and morphology of the synthesized superabsorbent hydrogels were characterized by Fourier transform infrared spectroscopy and scanning electron microscope. The effect of the molar ratio of AMPS to AA, the APS concentration, and the CMC content on swelling ratio was optimized. The swelling properties in various pH solutions and saline solutions as well as the swelling kinetics were also evaluated. Results showed that the introduction of AMPS enhanced the swelling capacity, swelling rate, and salt-resistance of the superabsorbent hydrogels. Moreover, the hydrogels exhibited smart swelling behavior in multivalent salt solutions and better reversible pH sensitivity in the pH 2.0 and 7.0 solutions, which makes the hydrogels available as a candidate for drug delivery systems.

Key words: Carboxymethyl cellulose, acrylic acid, 2-acrylamido-2-methylpropanesulfonic acid, superabsorbent hydrogel, pH-responsive

1. Introduction

Superabsorbent hydrogels (SAHs) are slightly crosslinked hydrophilic polymers with 3-dimensional network structure and excellent water-absorbing and retaining properties even under some pressure. Due to their unique advantages, SAHs are useful in various fields such as agriculture,^{1,2} pharmaceuticals,^{3,4} the food industry,⁵ hygienic products,⁶ and wastewater treatment.^{7,8} In recent years, the natural polysaccharide-based materials as potential substitutes for petroleum-based SAHs have received considerable interest because of their low costs, abundance, and eco-friendly properties.^{9,10} Many natural polysaccharides, including starch,^{11–13} salep,¹⁴ collagen,¹⁵ cellulose,¹⁶ sodium alginate,¹⁷ chitosan,¹⁸ and guar gum,^{19,20} have been focused on and used to prepare SAHs.

Carboxymethyl cellulose (CMC) is an anionic carboxymethyl ether of cellulose with tasteless, nontoxic, and water-soluble characteristics, which render it suitable for potential applications in industrial fields as a stabilizing, thickening, and bonding agent.²¹ The polar carboxyl groups give CMC chemically reactive and strongly hydrophilic characteristics, and so it shows promising application in superabsorbent fields. By virtue of the abundant reactive -OH groups on the CMC chains, CMC can be easily modified through its

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graft polymerization with hydrophilic vinyl monomers to derive new SAHs with improved properties.^{22,23} 2-Acrylamido-2-methylpropanesulfonic acid (AMPS) has received great attention in the last few years due to its strongly ionizable sulfonate group. As a good hydrophilic monomer, AMPS has usually been used to produce SAHs.^{24–27} In previous research work,²⁴ it was proven that the introduction of AMPS into the polymer networks could increase the swelling ratio, pH sensitivity, and salt resistance of SAHs. Thus, it is expected that the simultaneous introduction of CMC and AMPS can develop a new type of eco-friendly superabsorbent hydrogels with improved structure and performance.

Based on above description, an attempt has been made to synthesize the pH-sensitive superabsorbent hydrogel CMC-*g*-poly(AA-*co*-AMPS) by green aqueous solution polymerization. The effect of molar ratio of AMPS to AA on the swelling properties of the superabsorbent hydrogels was investigated to find the optimum synthesis conditions. The structure and morphologies of the superabsorbent hydrogels were characterized by Fourier transform infrared (FTIR) spectroscopy and scanning electron microscope (SEM). The swelling kinetics, pH, and saline-sensitive characteristics were also evaluated systematically.

2. Experimental

2.1. Materials

Sodium carboxymethyl cellulose (CMC, CP, 300–800 mPa · s (20 g/L, 20 °C)) was purchased from Sinopharm Chemical Reagent Co., Ltd, China. Acrylic acid (AA, chemically pure, Shanghai Shanpu Chemical Factory, Shanghai, China) was distilled under reduced pressure before use. 2-Acrylamido-2-methylpropanesulfonic acid (AMPS, chemically pure, Tokyo Chemical Industry Co., Ltd., Japan) was used as purchased. Ammonium persulfate (APS, analytical grade, Tianjin Chemical Reagent Co., Tianjin, China) and *N,N'*-methylenebisacrylamide (MBA, chemically pure, Shanghai Yuanfan Auxiliaries Co., Shanghai, China) were used as received. The other reagents used were all of analytical grade, and all solutions were prepared with deionized water.

2.2. Preparation of CMC-*g*-poly(AA-*co*-AMPS) superabsorbent hydrogel

CMC (1.17 g) was dispersed in 30 mL of distilled water in a 250-mL 4-necked flask equipped with a mechanical stirrer, a reflux condenser, a thermometer, and a nitrogen line. The reactor was immersed in an oil bath at 60 °C and kept for 1 h under continuous nitrogen purging to remove the oxygen dissolved from the system. APS (0.072 g, dissolved in 10 mL of distilled water) was then added to the slurry and the reaction mixture was stirred continuously (250 rpm) at 60 °C for 10 min. After 10 min, the reactants were cooled to 46 °C, and the desired amount of AA (preneutralized by NaOH solution), AMPS, and MBA was added. The total amounts of AA and AMPS were 0.1 mol and the AMPS/AA molar ratios were 0/1, 1/70, 1/50, 1/30, and 1/10 (mol/mol). Again, the oil bath was slowly heated to 70 °C and maintained for 3 h to complete the polymerization. Finally, the obtained gel products were dried in an oven at 70 °C for 72 h. All of the samples were passed through 40–80 mesh sieve (180–380 μm) after being ground.

2.3. Measurement of equilibrium swelling ratio

The xerogel (0.050 g) (m_1) was immersed in 250 mL of distilled water or 0.9 wt% NaCl solution at room temperature for 3 h to reach swelling equilibrium. The swollen gels (m_2) were separated from unabsorbed water by filtering through a 100-mesh screen and then drained for 10 min. After weighing the swollen gels (m_2), the swelling ratio of the superabsorbent hydrogel (Q_{eq} , g/g) was calculated using the following equation:

$$Q_{eq} = (m_2 - m_1)/m_1 \quad (1)$$

where m_1 and m_2 are the weights of the xerogel and the swollen gel, respectively. All procedures were carried out 3 times repeatedly and the averages were reported in this study.

The method of measuring the swelling ratio in various pH and saline solutions was similar to that used in distilled water.

2.4. Swelling kinetics measurement

Swelling kinetics of the superabsorbent hydrogels were measured in compliance with the following procedure: 0.05 g of xerogel was immersed in 250 mL of distilled water. At consecutive time intervals (1, 3, 5, 7, 10, 15, 20, 30, 60, and 120 min), the swollen gels were filtered out using a 100-mesh sieve and the swelling ratio of the superabsorbent hydrogels at a given time t was measured according to the method described above.

2.5. Evaluation of pH responsivity

The solutions with pH 2–13 were prepared by diluting HCl (pH 1.0) and NaOH (pH 13.0) solutions. The pH value of the solutions was determined by a pH meter (DELTA-320). The equilibrium swelling ratio in different pH solutions was measured by a method similar to that in distilled water. The pH reversibility of the superabsorbent hydrogel was investigated in terms of swelling and deswelling in 2 buffer solutions with pH 7.0 and 2.0, respectively. The consecutive time interval for each swelling–deswelling cycle was 40 min.

2.6. Characterization

FTIR spectra were determined with a Nicolet NEXUS FTIR spectrometer in the 4000–400 cm^{-1} wavelength region using KBr pellets. The surface morphologies of the xerogels were examined using a JSM-6701F field emission SEM (JEOL) after coating the xerogels with gold film.

3. Results and discussion

Crosslinking graft copolymerization of AA and AMPS onto CMC backbones was carried out using APS as a radical initiator and MBA as a crosslinker. The persulfate initiator was decomposed under heating to produce sulfate anion radicals, which extracted hydrogen from the hydroxyl groups of the CMC backbones to form macromolecular radicals on the substrates. The vinyl groups of AA and AMPS were then reacted with the active radicals to form covalent bonds and simultaneously generate the new radicals that can process the chain propagation. In the presence of the crosslinking agent MBA, the end vinyl groups of MBA participated in the polymerization and finally formed a 3-dimensional network of CMC-*g*-poly(AA-*co*-AMPS).

3.1. FTIR spectra analysis

The grafting polymerization was confirmed by comparing the FTIR spectra of CMC, CMC-*g*-PAA, and CMC-*g*-poly(AA-*co*-AMPS). As shown in Figure 1, the strong characteristic absorption band of CMC at 1049 cm^{-1} (-OH groups) was obviously weakened after the reaction. This indicates that CMC participated in the grafting copolymerization reaction through the -OH groups.²⁸ Meanwhile, the new bands at 1722 cm^{-1} (C=O stretching vibration of -COOH groups), 1627 cm^{-1} (COO asymmetrical stretching vibration of -COO⁻ groups), and 1455 and 1410 cm^{-1} (COO symmetrical stretching vibration of -COO⁻ groups) in the spectrum of CMC-*g*-PAA

reveal that AA monomers were grafted onto the CMC chains. In addition, 1632 cm^{-1} (C=O stretching vibration of -CONH groups) and 1192 cm^{-1} (stretching vibration of $-\text{SO}_3\text{H}$ groups) can be observed in the spectrum of CMC-*g*-poly(AA-*co*-AMPS), which strongly suggests the existence of AMPS. Consequently, it is concluded that the AA and AMPS monomers were successfully grafted onto the CMC backbones.

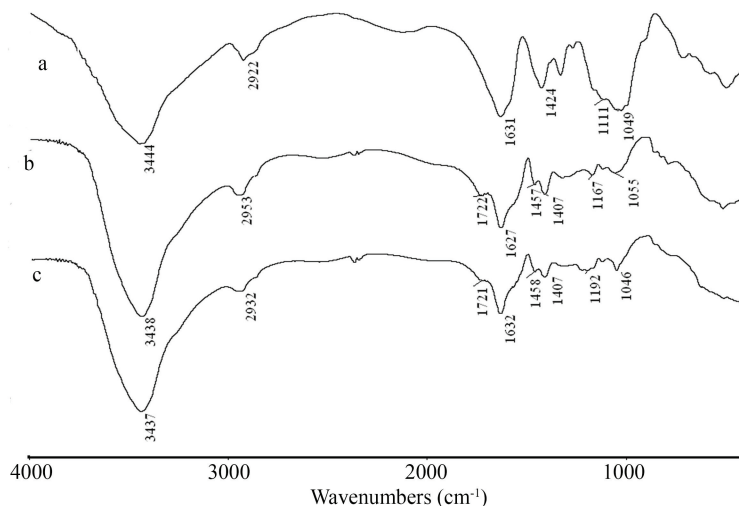


Figure 1. FTIR spectra of a) CMC, b) CMC-*g*-PAA, and c) CMC-*g*-poly(AA-*co*-AMPS) superabsorbent hydrogel.

3.2. Morphological analysis

Figure 2 shows the SEM images of CMC-*g*-PAA and CMC-*g*-poly(AA-*co*-AMPS) hydrogels with different molar ratios of AMPS to AA. It can be seen that the CMC-*g*-PAA hydrogel (Figure 2a) exhibits a smooth and tight surface whereas the CMC-*g*-poly(AA-*co*-AMPS) hydrogels (Figures 2b–2d) show an uneven and coarse surface, which can be beneficial to the swelling properties. This difference is related to the different molar ratio of AMPS to AA in the hydrogel, and the obvious coarse and microporous morphology can be observed in the image of the CMC-*g*-poly(AA-*co*-AMPS) ($n(\text{AMPS})/n(\text{AA}) = 1/50$) superabsorbent hydrogel (Figure 2c). The phenomenon can be explained by the fact that sulfonate groups can produce larger electrostatic repulsive forces than carboxylate groups, and thus the porosity was increased with the increasing of the AMPS/AA molar ratio. In addition, the alkyl group of AMPS is hydrophobic, which can form hydrophobic microdomains to decrease the hydrogen bonding interaction between hydrophilic polymeric chains.²⁹ It could expand the size of the network and the pores of the hydrogels are increased. However, excessive AMPS are not favorable to form good 3-dimensional network because the long chain of AMPS can easily intertwine with CMC macromolecules and increase the crosslinking of the hydrogels. Above all, the appropriate molar ratio of AA and AMPS could regulate the network structure and change the surface morphology, which is convenient for the penetration of water into the polymeric network.

3.3. Effect of APS concentration on the swelling ratio

Figure 3 illustrates the effect of APS concentration on the swelling ratio of the superabsorbent hydrogels in distilled water and 0.9 wt% NaCl solution. As can be seen, the swelling ratio increased with increasing APS concentration from 1.309 mmol/L to 6.545 mmol/L and then decreased considerably with a further increasing in the amount of APS. When the APS concentration was lower than the optimal value, the number of active radicals was increased with increasing APS concentration, which could efficiently improve the process of the

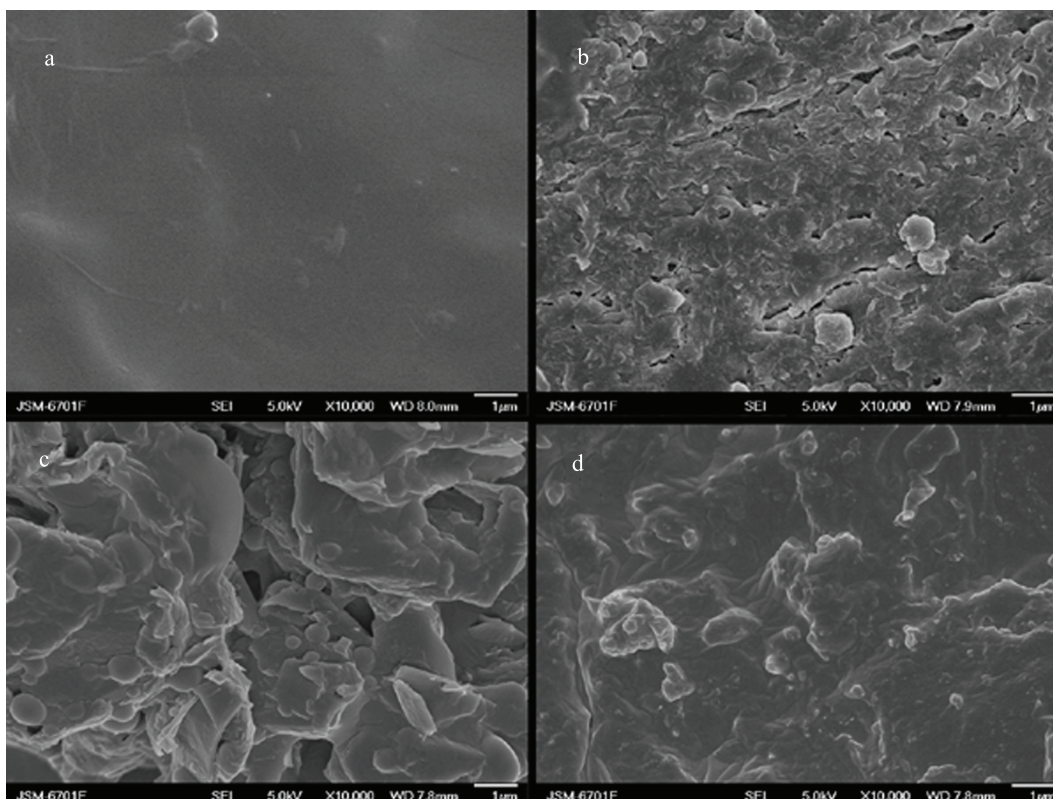


Figure 2. SEM images of a) CMC-*g*-PAA and b–d) CMC-*g*-poly(AA-*co*-AMPS) superabsorbent hydrogels with the molar ratio of AMPS to AA of 1:70, 1:50, and 1:10, respectively.

chain transfer reaction and affect the growth of grafting polymer chains to form a regular 3-dimensional network. Thus, the swelling ratio of the hydrogels was enhanced. However, when APS concentration was higher than the optimal value, many more active radicals could accelerate the terminating step reaction via bimolecular collision, which enhanced the crosslinking density. Thus, the swelling ratio of the hydrogel was decreased. The optimum APS concentration in this study is 6.545 mmol/L.

3.4. Effect of CMC content on the swelling ratio

The effect of CMC content on the swelling ratio was investigated and is shown in Figure 4. With increasing content of CMC, the swelling ratio of the hydrogel first increased and then decreased. The swelling ratio enhanced with increasing CMC content until a maximum absorption (540 g/g in distilled water and 78 g/g in 0.9 wt% NaCl solution) was achieved at 15.96 wt% of CMC. As the CMC dosage was increased from 9.54 wt% to 15.96 wt%, the macromolecular radicals that can be used to graft with monomers were increased and the grafting efficiency was enhanced. As a result, the swelling ratio increased with increasing CMC content. Beyond this content, the viscosity of the reaction system was increased and the chain transfer reaction was restricted, which decreases the molecular weight of the graft polymer chains. Thus, the swelling ratio was decreased.

3.5. Effect of molar ratio of AMPS to AA on the swelling ratio

The effect of AMPS/AA molar ratio on the swelling ratio of the superabsorbent hydrogels was studied by varying the AMPS/AA molar ratio from 0 to 0.1 ($n(\text{AA}) + n(\text{AMPS}) = 0.1 \text{ mol}$), as shown in Figure 5. The

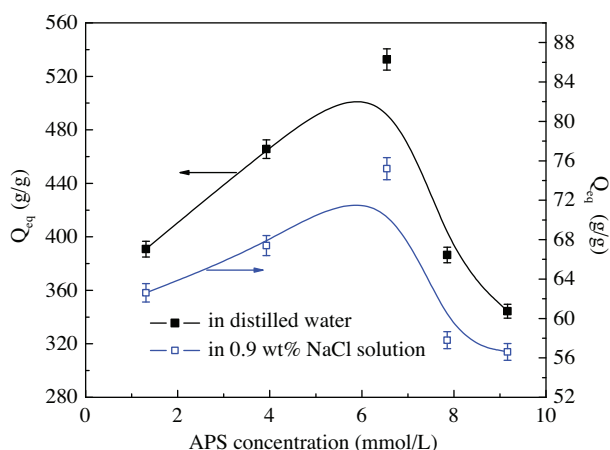


Figure 3. Effect of APS concentration on the swelling ratio of the superabsorbent hydrogels (CMC: 15.96 wt%, $n(\text{AMPS}):n(\text{AA}) = 1:50$).

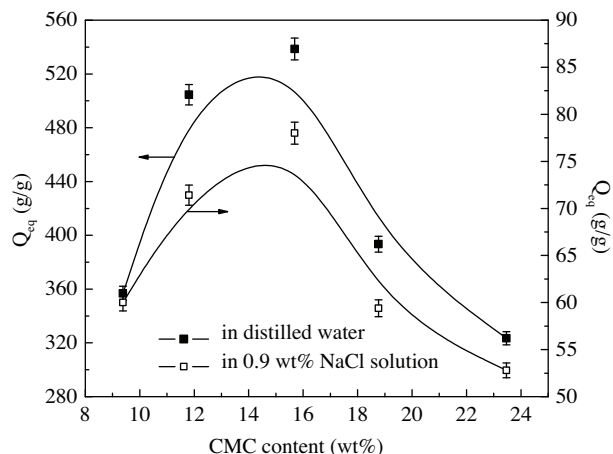


Figure 4. Effect of CMC content on the swelling ratio of the superabsorbent hydrogels ((APS: 6.545 mmol/L, $n(\text{AMPS}):n(\text{AA}) = 1:50$).

maximum swelling ratio (540 g/g in distilled water and 79 g/g in 0.9 wt% NaCl solution) was obtained at $n(\text{AMPS})/n(\text{AA}) = 0.02$. The increase in the swelling ratio with increasing molar ratio of AMPS/AA (from 0 to 0.02) can be attributed to the charge repulsion among sulfonate groups on the grafted poly(AMPS) chains, which have better hydrophilicity than carboxylate groups. The subsequent decrease in swelling ratio of the hydrogels can be ascribed to the low reactivity of the AMPS monomer.^{30–32} This indicates that the monomer grafting onto CMC chains decreases with increasing AMPS/AA molar ratio. In other words, the hydrophilic monomers in the polymer chains are reduced, which leads to a decrease of the swelling ratio.

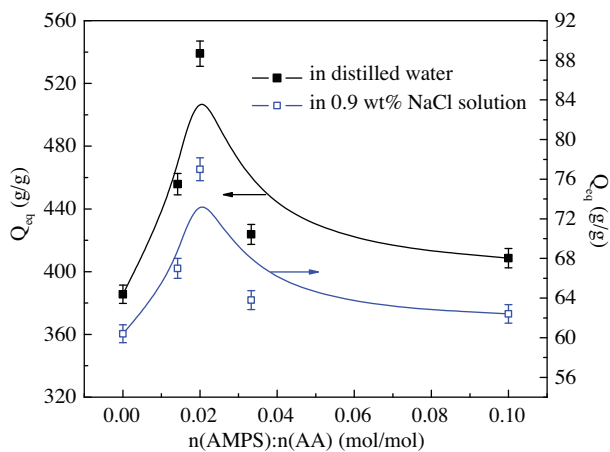


Figure 5. Effect of molar ratio of AMPS to AA on the swelling ratio (APS: 6.545 mmol/L, CMC: 15.96 wt%).

3.6. Swelling kinetics

To examine the influence of APS concentration and AMPS/AA molar ratio on the swelling kinetics, the profiles of the swelling ratio in distilled water as a function of swelling time for the hydrogels are presented in Figures 6 and 7, respectively. It can be seen in Figures 6a and 6b that the swelling ratio of the superabsorbent hydrogels was faster within 900 s. Later, the swelling ratio was reduced and the swelling curves became flatter. In this

section, the swelling kinetics can be described with Schott's second-order swelling kinetic model:³³

$$t/Q_t = A + Bt, \quad (2)$$

where Q_t is the swelling ratio at time t ; A is the reciprocal of the initial swelling rate, that is, $A = 1/K_{is}$; and $B = 1/Q_\infty$ (where Q_∞ represents the theoretical equilibrium swelling ratio). On the basis of the experimental data, t/Q_t is plotted against time t to give an excellent straight line (Figures 6b and 7b) with good linear correlation coefficient, indicating that the swelling of CMC-*g*-poly(AA-*co*-AMPS) follows the second-order swelling kinetics. From the slope and intercept of lines shown in Figure 6b and Figure 7b, the values of the initial swelling rate (K_{is}) and the linear correlation coefficient (R) can be calculated, and the results are listed in the Table.

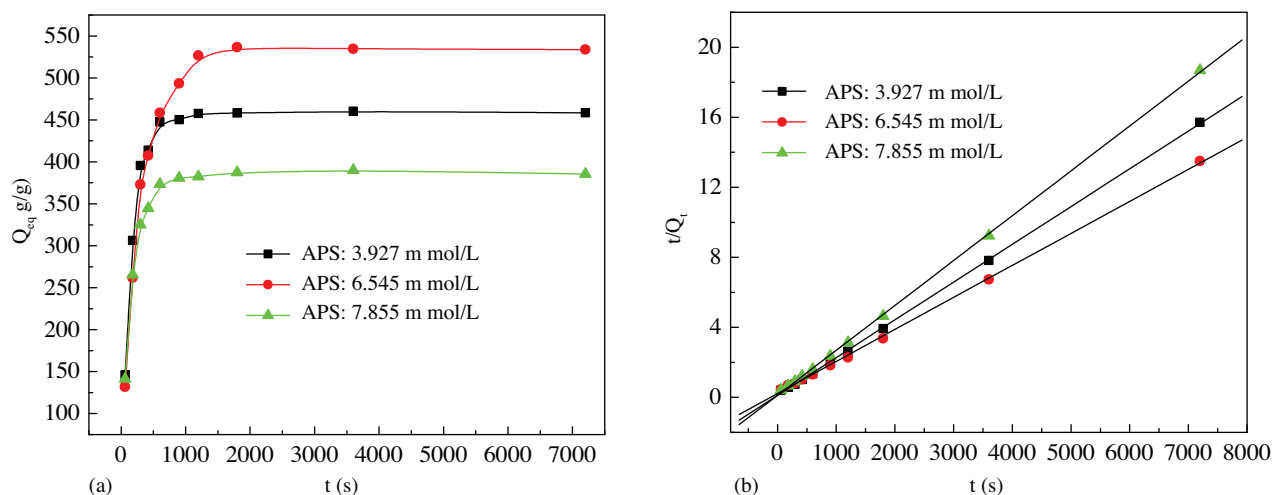


Figure 6. The a) swelling kinetic curves and b) swelling kinetic fitting curves of the superabsorbent hydrogels with different concentrations of APS.

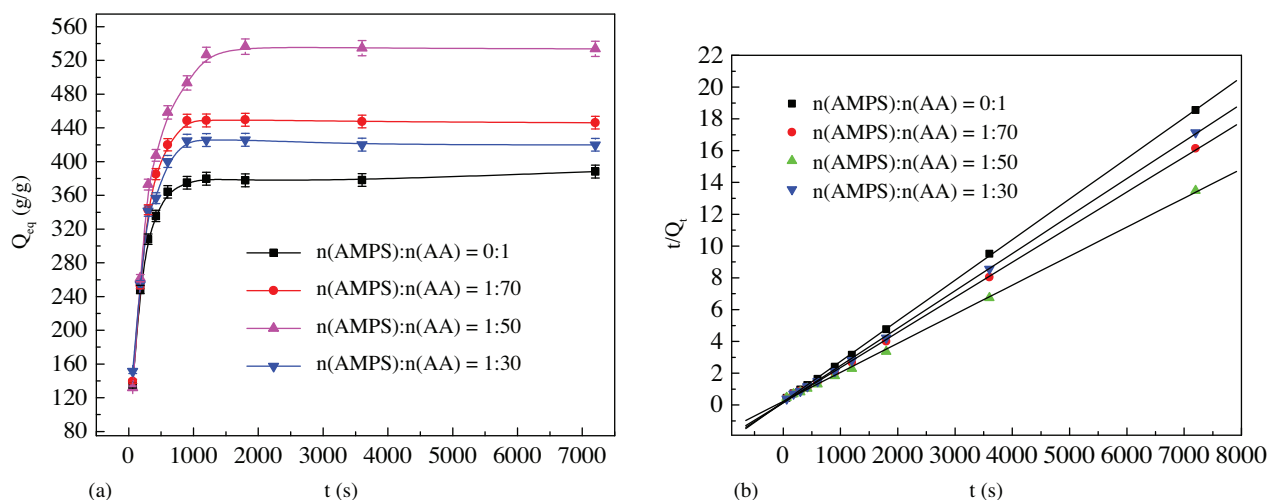


Figure 7. The a) swelling kinetic curves and b) swelling kinetic fitting curves of the superabsorbent hydrogels with different molar ratios of AMPS to AA.

Table. Swelling kinetics parameters for CMC-*g*-Poly(AA-*co*-AMPS) hydrogels.

Sample	Q_{eq} (g/g)	Q_{∞} (g/g)	K_{is} (g/g/s)	R
APS: 3.927 mmol/L, n(AMPS):n(AA) = 1:50	465.6	462.9	8.9333	0.9998
APS: 6.545 mmol/L, n(AMPS):n(AA) = 1:50	539.0	546.4	4.4812	0.9996
APS: 7.855 mmol/L, n(AMPS):n(AA) = 1:50	386.4	390.6	8.1913	0.9998
APS: 6.545 mmol/L, n(AMPS):n(AA) = 0:1	385.6	392.1	5.2306	0.9999
APS: 6.545 mmol/L, n(AMPS):n(AA) = 1:70	455.8	452.4	6.6786	0.9997
APS: 6.545 mmol/L, n(AMPS):n(AA) = 1:30	423.8	425.5	7.7501	0.9997

K_{is} : initial swelling rate constant (g/g/s); R : linear correlation coefficient.

As can be seen from the Table, the APS concentration and molar ratio of AMPS to AA have obvious influence on the swelling rate. For each sample, the initial swelling rate follows the order of: CMC-*g*-poly(AA-*co*-AMPS) (APS, 3.927 mmol/L; n(AMPS):n(AA) = 1:50) > CMC-*g*-poly(AA-*co*-AMPS) (APS, 7.855 mmol/L; n(AMPS):n(AA) = 1:50) > CMC-*g*-poly(AA-*co*-AMPS) (APS, 6.545 mmol/L; n(AMPS):n(AA) = 1:30) > CMC-*g*-poly(AA-*co*-AMPS) (APS, 6.545 mmol/L; n(AMPS):n(AA) = 1:50) > CMC-*g*-PAA (APS, 6.545 mmol/L). Compared with CMC-*g*-PAA, the introduction of AMPS may enhance the swelling rate. The significant enhancement of the swelling rate could be attributed to the simultaneous introduction of the appropriate amount of AA and AMPS. The results are in accordance with the SEM observations that the synergistic effect of AA and AMPS ameliorated the network and surface structure of superabsorbent hydrogels, which is favorable to increase the diffusion and capillary action, and thus enhance the swelling ratio and swelling rate.³⁴ In addition, the hydrophilicity of the superabsorbent was improved due to the polymerization of AMPS monomer, which could also benefit the swelling rate. Consequently, the introduction of an appropriate amount of AMPS contributes to improving the swelling properties of hydrogels compared with CMC-*g*-PAA hydrogel.

3.7. Effect of salt solution on the swelling behaviors

The effect of saline solution on the swelling behaviors of the optimized sample was measured in NaCl, MgCl₂, and AlCl₃ solutions with different concentrations and the swelling curves are shown in Figure 8. As can be seen, the swelling ratio of the hydrogels reduced with increased concentration of salt solutions. This swelling fall is often attributed to the decrease of osmotic pressure between the gel network and external solution and the enhancement of screening effect of counter ions.³⁵ The swelling ratio of the hydrogels in the saline solutions is in the order of: Na⁺ > Mg²⁺ > Al³⁺. Different from monovalent cations, multivalent cations may link with anionic hydrophilic groups to generate a strong surface ionic crosslinking, which can explain the sharper decreasing tendency of the hydrogels in MgCl₂ and AlCl₃ solution than in NaCl solution.

3.8. Effect of pH on the swelling behaviors and pH responsive characteristics

The external pH solutions have remarkable influence on the swelling ratio of the hydrogels. As shown in Figure 9, the swelling ratio of the CMC-*g*-poly(AA-*co*-AMPS) superabsorbent hydrogels increased sharply in the pH 2–5 range and then decreased in the pH 10–13 range. In acidic medium (pH < 5), the carboxylate and sulfonate groups on the polymeric chain can turn into carboxylic acid and sulfonic acid groups. As a result, the main anion–anion repulsive forces were eliminated, and the association among –COOH and –SO₃H groups was increased due to the hydrogen-bonding interaction. This increased the physical crosslinking degree and reduced the swelling ratio. When the pH values are in the range of 5–10, some of the carboxylate and sulfonate groups are ionized and the electrostatic repulsion between carboxylate and sulfonate groups causes an enhancement of

the swelling ratio. In basic medium with higher pH value (>10), a charge screening effect of the counter ions (Na^+) limits the swelling and leads to a decrease of the swelling ratio. Similar pH-dependent swelling behaviors have been reported in the case of other hydrogel systems.³⁶

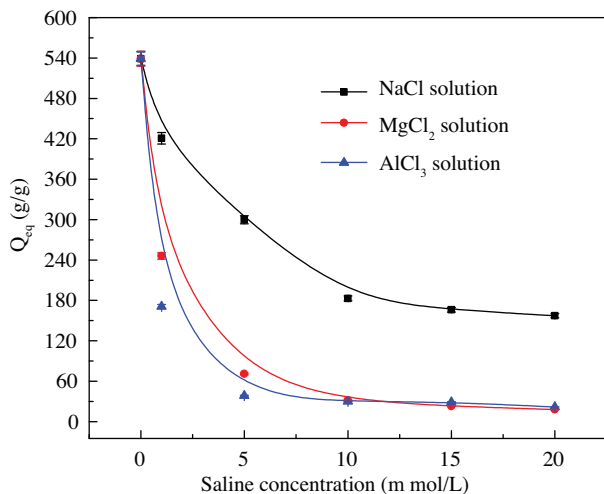


Figure 8. The equilibrium swelling of the optimized superabsorbent hydrogel in various concentrations of NaCl, MgCl₂, and AlCl₃ solutions.

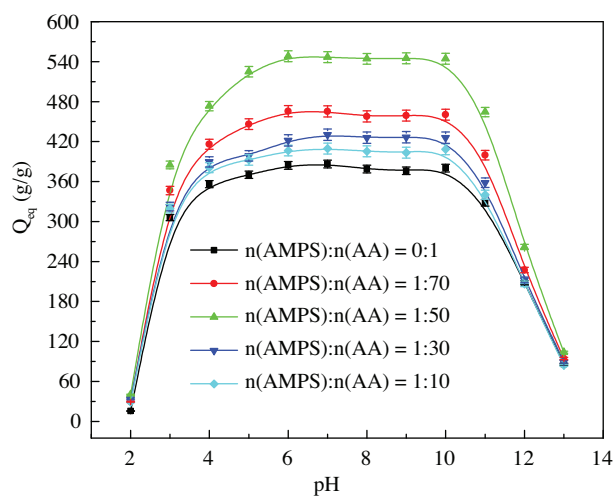


Figure 9. Effect of external pH levels on the swelling ratio of the superabsorbent hydrogels with different molar ratios of AMPS to AA.

Since the hydrogels showed different swelling behaviors in acidic and basic pH solutions from the results above, the reversible swelling–deswelling behavior of the optimized hydrogel was investigated in buffer solutions with pH 2.0 and 7.0. As shown in Figure 10, the hydrogel exhibited a higher swelling ratio at pH 7.0 due to the anion–anion repulsive electrostatic forces, whereas the swollen gel rapidly shrunk at pH 2.0 due to protonation of the carboxylate and sulfonate anions. After 4 on–off cycles, the hydrogel still exhibited good sensitivity, which renders the hydrogel promising for drug delivery application.³⁷

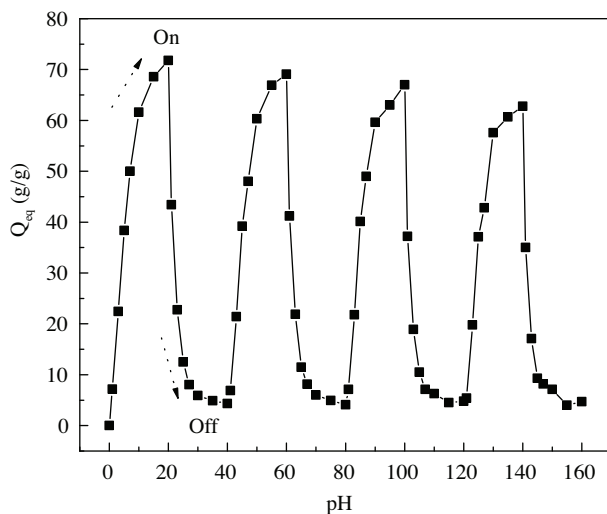


Figure 10. The pH responsivity for the optimized superabsorbent hydrogel.

4. Conclusions

For developing new types of eco-friendly superabsorbent hydrogel based on natural polysaccharides and reducing the excessive consumption of petroleum resources, the novel superabsorbent CMC-*g*-poly(AA-*co*-AMPS) hydrogels were prepared by free-radical solution graft copolymerization. The FTIR spectra demonstrated that the AA and AMPS monomers have been grafted onto CMC macromolecular backbones. SEM observations showed the morphological changes of the superabsorbents with different AMPS/AA molar ratios, which is in keeping with the swelling behaviors of the hydrogels. The effect of reaction parameters, such as AMPS/AA molar ratio, APS concentration, and CMC content, were investigated. The maximum swelling ratio was achieved under the optimum reaction conditions, which were found to be: AMPS/AA molar ratio = 1:50, APS = 6.545 mmol/L, and CMC = 15.96 wt%. The introduction of AMPS obviously improved the swelling ratio, swelling rate, and salt resistance of the hydrogels. Moreover, the hydrogels exhibited intriguing saline-responsive and pH-sensitive characteristics. The excellent on-off switching swelling behaviors were also observed in various pH buffer solutions between pH 2.0 and 7.0. Above all, the superabsorbent hydrogel, based on renewable and biodegradable natural CMC, showed improved swelling properties, salt-resistant properties, and smart pH responsivity, which means it can be used as a potential candidate for drug delivery systems.

Acknowledgments

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