

Optimization of Effective Parameters onto Synthesis and Swelling Behavior of Macromolecules Hydrogel based on Carboxymethylcellulose

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ABSTRACT

Novel biopolymer-based superabsorbent hydrogels were prepared by grafting with N-vinyl pyrrolidone and 2-acrylamido-2-methyl propan sulfonic acid monomers onto collagen backbones through a free radical polymerization method. The graft copolymerization reaction was carried out in a homogeneous medium and in the presence of Ceric ammonium Nitrate(CAN) as an initiator and N,N'-methylene bisacrylamide (MBA) as a crosslinker. A proposed mechanism for CMC-g-(PNVP-co-PAMPS) formation was suggested and the hydrogel structure was confirmed using FTIR spectroscopy. The morphology of the samples was examined by scanning electron microscopy (SEM). The CMC-based hydrogel exhibited a pH-responsiveness character so that a swelling-deswelling pulsatile behavior was recorded at pHs 2 and 8.

KEY WORDS: CMC; hydrogels; swelling; N-vinyl pyrrolidone; 2-acrylamido-2-methyl propan sulfonic acid.

INTRODUCTION

Superabsorbent can absorb tremendous amounts of water without dissolving in water because they contain considerable amounts of hydrophilic groups and have a three-dimensional structure. In fact, the network can swell in water and hold a large amount of water while maintaining the structure. Superabsorbent hydrogels are useful for many applications, such as disposable pads, sheets, and towels for surgery, adult incontinence, and female hygiene products, even though they were originally developed for agricultural applications to improve the water-holding capacity of soils to promote the germination of seeds and plant growth^[1].

Considerable interest has been focused on chemical modification by grafting synthetic polymers onto natural polymers such as CMC, chitosan, chitin, Na-Alginate, carrageenane and starch. Graft copolymerization with various vinyl monomers can be carried out with different initiator systems and by different mechanisms. CMC is an important derivative of cellulose and comprises carboxylate functional groups in its structure^[2,3]. This natural polymer is a hydrophilic polymer that dissolving of this polymer in water causes a viscose solution. Crosslinking of CMC backbones are an important route to preparation of CMC based hydrogels. An others efficient approach to modify swelling behaviour of CMC hydrogels is graft polymerization of vinylic monomers onto CMC. Graft copolymerization of vinyl monomers onto CMC to preparation of hydrogels have been reported. But, according to the literature survey based on Chemical Abstract Service, a few studies have been reported in the case of prepared CMC-based hydrogels with Simultaneously Grafting two monomers^[4,5]. Hence, the objective of the present paper is to describe the preparation and characterization of a CMC-g-poly(N-vinyl pyrrolidone-co-2-acrylamido-2-methylpropanesulfonic acid) hydrogel as a new natural-based polymer with pH-responsiveness properties. the reaction variables affected the swelling capacity of CMC-g-PNVP-co-AMPS Superabsorbent hydrogels was studied.

EXPERIMENTAL

Materials

The polysaccharide, Carboxymethylcellulose (CMC, degree of substitution 0.52, from Condinson Co., Denmark) was of analytical grade and was used as received. Ceric ammonium nitrate was purchased from Merck and was used without purification. It was employed as a freshly 0.1 mol/L acidic solution (2.74 g CAN in 50 mL of 1 N nitric acid), unless in the case of the initiator series of experiments. N-vinyl pyrrolidone, 2-acrylamido-2-methylpropanesulfonic acid (Merck, Darmstadt, Germany) were used after vacuum distillation. N,N'-methylene bisacrylamide was of analytical grade and used without further purification. Double distilled water was used. All other chemicals were of analytical grade.

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Preparation of hydrogel

CMC solution was prepared in a one-liter reactor equipped with mechanical stirrer and gas inlet. CMC was dissolved in degassed distilled water. In general, 1.00 g of CMC was dissolved in 30.00 mL of distilled degassed water. The reactor was placed in a water bath preset at 65 °C. After adding CMC, variable amounts of N-vinyl pyrrolidone and 2-acrylamido-2-methylpropanesulfonic acid monomers were simultaneously added to the reaction solution. MBA as a crosslinker (0.05 g in 2 mL water) was added to the reaction mixture after the addition of monomers and the mixture was continuously stirred for 15 min under argon. then a given volume of freshly prepared solution of CAN as an initiator was added and the graft copolymerization reaction was conducted for 1 h^[6]. The total volume of reaction was 40 mL. After 60 min., the reaction product was allowed to cool to ambient temperature and methanol (500 mL) was added to the gelled product. After complete dewatering for 24 h, the product was filtered, washed with fresh methanol (2×50 mL) and dried at 50 °C.

Infrared Analysis

The samples were crushed with KBr to make pellets. Spectra were taken on an ABB Bomem MB-100 FTIR spectrophotometer.

Swelling Measurements

A CMC-g-PNVP-co-AMPS sample (0.10 g) was put into a weighed teabag and immersed in 100 mL distilled water and allowed to soak for 2 h at room temperature. The equilibrated swollen gel was allowed to drain by removing the teabag from water and hanging until no drop drained (~30 min.). The bag was then weighed to determine the weight of the swollen gel. The absorbency (equilibrium swelling) was calculated using the following equation^[7]:

$$\text{Absorbency} = (W_s - W_d)/W_d \quad (1)$$

where W_s and W_d are the weights of the swollen gel and the dry sample, respectively. So, absorbency was calculated as grams of water per gram of resin (g/g). The accuracy of the measurements was $\pm 2\%$.

RESULTS AND DISCUSSION

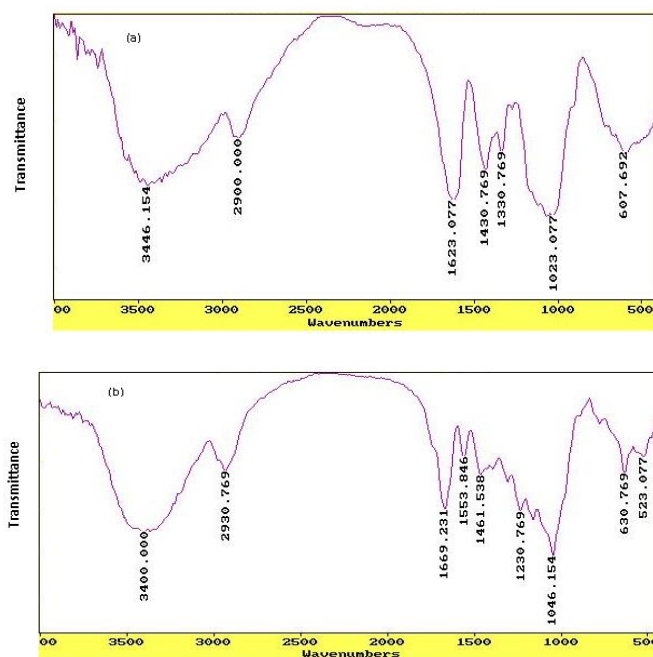
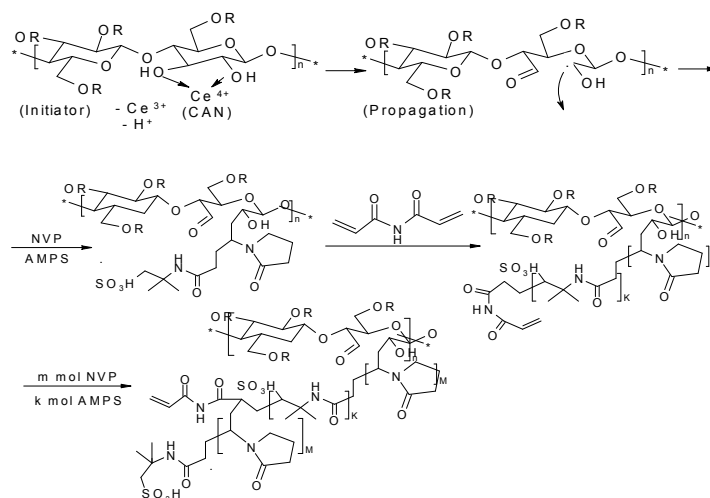


Figure 1. FTIR spectra of CMC (a) and crosslinked CMC-g-(PNVP-co-PAMPS) hydrogel (b).

Synthesis and Characterization

N-vinyl pyrrolidone, 2-acrylamido-2-methylpropanesulfonic acid monomers were simultaneously grafted onto CMC in a homogenous medium using CAN as a radical initiator and MBA as a crosslinking agent under an inert atmosphere. The crosslinker, initiator and the monomers concentration, as well as the reaction temperature four important variables affected on swelling capacity of hydrogel, were investigated. The mechanism of co polymerization of NVP and AMPS onto CMC in the presence of MBA is shown in Scheme 1. At the first step, a complex between the Ce^{4+} ion with the

oxygen atom at the C-3 position and the hydroxyl group at the C-2 position was formed. This Ceric-CMC complex is then abstracts hydrogen atom from polysaccharide substrate to form alkoxy radicals on the substrate. So, this Ceric-saccharide redox system is resulted in active centers on the substrate to radically initiate polymerization of NVP and AMPS led to a graft copolymer^[8-9]. Since a crosslinking agent, e.g. MBA, is presented in the system, the copolymer comprises a crosslinked structure.



Scheme 1. General reaction mechanism for graft copolymerization of N-vinyl pyrrolidone(NVP) and 2-acrylamido-2-methylpropanesulfonic acid (AMPS) onto CMC backbone in the presence of ceric (IV) ion.

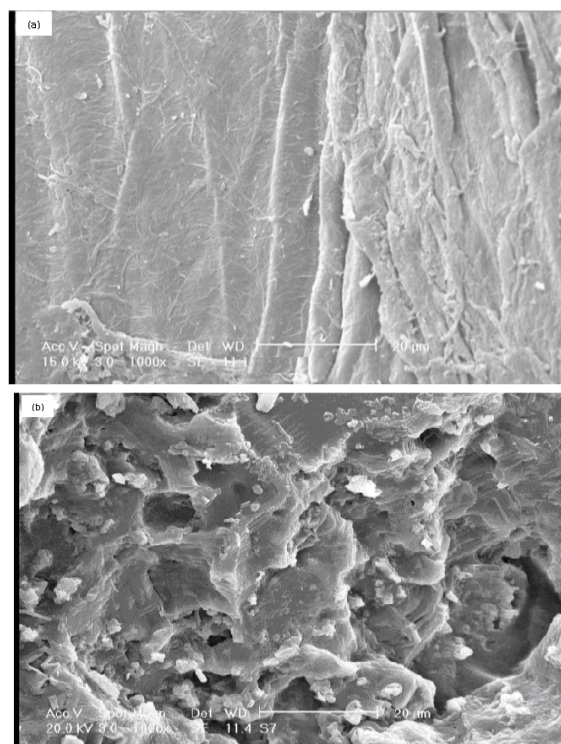


Figure 2. SEM photograph of the optimized superabsorbent hydrogel (a) Surface of pure carboxymethylcellulose; (b) Surface of porous hydrogel. The average pore diameter of the synthesized hydrogel was 16.7 nm.

FTIR spectroscopy was used for identification of the hydrogel. Figure 2 shows the IR spectra of the CMC and the resulted hydrogel. The band observed at 1623 cm^{-1} and can 1430 cm^{-1} be attributed to C=O stretching and bending in carboxylate(COO^-) functional groups of substrate backbone (Figure 2a). The broad band at $2500\text{-}3500\text{ cm}^{-1}$ is due to stretching of $-\text{OH}$ groups of the CMC. In the spectra of the hydrogel the characteristic bands at 1553 cm^{-1} , 1230 cm^{-1} and 1670 cm^{-1} were attributed to N-H, S=O (AMPS monomer) and C=O (vinyl pyrrolidone) stretching respectively^[17].

To obtain additional evidence of grafting, a similar polymerization was conducted in the absence of the crosslinker. After extracting the homopolymers (PNVP or PAMPS) and unreacted monomers using a cellophane membrane dialysis bag (D9402, Sigma–Aldrich), an appreciable amount of grafted CMC (83%) was observed. The graft copolymer spectrum was very similar to Figure 2b. Also according to preliminary measurements, the sol (soluble) content of the hydrogel networks was as little as 1.6 %. This fact practically proves that all NVP and AMPS are involved in the polymer network. So, the monomers percent in the network will be very similar to that of the initial feed of reaction.

Scanning electron microscopy

One of the most important properties that must be considered is hydrogel microstructure morphologies. Figure 2 shows the scanning electron microscope (SEM) photographs of the CMC surface (Fig. 2a) and surface of the hydrogel (Fig. 2b). These pictures verify that the synthesized polymer in this work have a porous structure, where the pores might be induced into the hydrogel by water evaporation resulting from reaction heat. It is supposed that these pores are the regions of water permeation and interaction sites of external stimuli with the hydrophilic groups of the graft copolymers.

Optimization of the grafting variables

In this work, the main factors affecting on the grafting conditions, i.e. concentration of MBA, NVP, AMPS, CAN, temperature and pH, media were systematically optimized to achieve superabsorbent with maximum water absorbency.

Effect of crosslinker concentration on the swelling capacity

Crosslinks have to be present in a hydrogel in order to prevent dissolution of the hydrophilic polymer chains in an aqueous environment. Efficiency of crosslinker incorporation controls the overall crosslink density in the final hydrogel. The effect of the extent of crosslinking on water absorbency of CMC-g-PNVP-co-AMPS hydrogel is shown in Figure 3. In this series reaction, the AAm concentration was constant. The results indicate power law behaviors of swelling-[MBA], so that the lower the crosslinking agent, the decreased water absorbency will be. Higher crosslinker concentration produce more crosslinked points in polymeric chains and increases the extent of crosslinking of the polymer network, which results in less swelling when it is brought into contact with solvent. Similar observations have been reported in the literature^[11,13]. The swelling capacity for hydrogel is 100 g/g, at a fixed MBA concentration of 0.0108 mol/L.

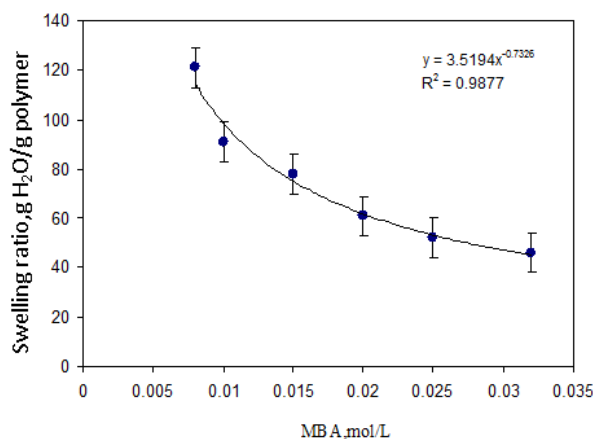


Figure 3. Effect of crosslinker concentration on swelling capacity.

Reaction conditions: CMC 1.0 g, NVP 0.5 mol/L, AMPS 0.8 mol/L, CAN 0.01 mol/L, 65 °C, 60 min.

Effect of NVP concentration on the swelling capacity

The substrate CMC was treated with different amounts of NVP (0.25-1.4 mol/L), while the rest of variables was unchanged. The maximum water absorbency (218.8 g/g) was obtained at NVP 0.40 mol/L (Fig. 4). The initial increase in water absorbency could be originated from the greater availability of monomer molecules in the vicinity of the chain propagating sites of CMC macroradicals. In addition, higher NVP content enhances the hydrophilicity of the hydrogel that, in turn, causes a stronger affinity for more absorption of water. A further increase of monomer concentration, however, results in decreased absorbency. It is probably due to (a) preferential homopolymerization over graft copolymerization, (b) increase in viscosity of the medium which hinders the movement of free radicals and monomer molecules, (c) the enhanced chance of chain transfer to monomer molecules, and (d) non grafted poly(NVP) chains. The latter reason is in close agreement with similar starch-based superabsorbents reported by Athawale *et al*^[2].

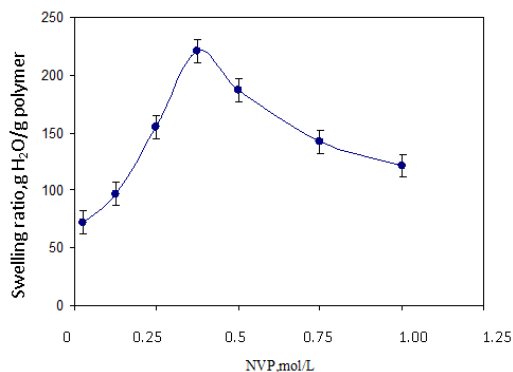


Figure 4. Effect of NVP monomer concentration on swelling capacity.

Reaction conditions: CMC 1.0 g, MBA 0.0108 mol/L, AMPS 0.8 mol/L, CAN 0.01 mol/L, 65 °C, 60 min

Effect of AMPS concentration on swelling capacity

The effect of monomer concentration on the swelling capacity of the hydrogel was studied by varying the AMPS concentration from 0.24 to 0.96 mol/L (Figure 5). As shown in this figure, with increasing of the AMPS, the water absorbency is increased up to 0.68. This phenomenon can be related to the increasing of anionic $-SO_3^-$ groups in the hydrogel^[15]. The high the concentration of ionic groups inside the hydrogel network results in a high osmotic pressure difference and the swelling is increased. In addition, higher AMPS content enhanced the hydrophilicity of the hydrogel, causing a higher absorption of water. The swelling-loss after the maximum may be originated from the increased chance of chain transfer to AMPS molecules and increase in viscosity of the reaction which restricts the movement of the reactants^[15-16].

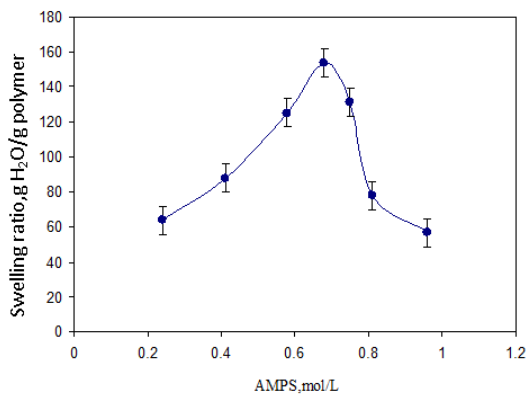


Figure 5. Effect of AMPS monomer concentration on swelling capacity.

Reaction conditions: CMC 1.0 g, MBA 0.0108 mol/L, NVP 0.4 mol/L, CAN 0.01 mol/L, 65 °C, 60 min.

Effect of bath temperature on swelling capacity

To study the influence of reaction temperature on water absorbency, the graft copolymerization of NVP and AMPS onto CMC was carried out at six temperatures ranging from 30 to 80 °C and the results are presented in Figure 6. Swelling capacity of the hydrogels is increased with increasing the temperature from 30 to 60 °C, and then decreased. At 60 °C, maximum swelling (315 g/g) was obtained.

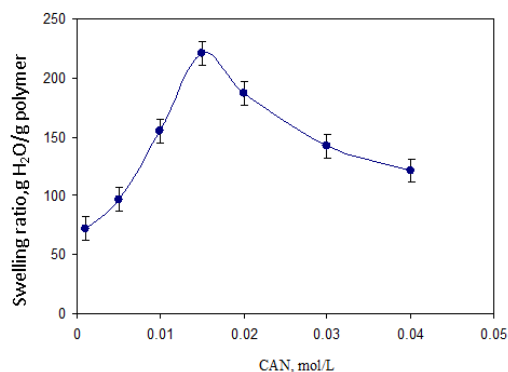


Figure 6. Effect of initiator concentration on swelling capacity.

Reaction conditions: CMC 1.0 g, MBA 0.0108 mol/L, NVP 0.4 mol/L, AMPS 0.68 mol/L, 65 °C, 60 min

Corresponding increase in water absorbency up to 60 °C could be attributed to the following factors: increased the number of free radicals formed on the CMC backbone, increased propagation of the graft copolymerization onto CMC, enhanced diffusion of monomers and initiator into and onto backbone structure, and increased in mobility of the monomers molecules and their higher collision probability with the backbone macroradicals^[18]. However, swelling capacity decreased as the bath temperature was raised beyond 60 °C. This can be accounted for in terms of chain radical termination at higher temperatures^[17].

Effect of initiator concentration on the swelling capacity

The effect of the CAN concentration on the swelling capacity of the hydrogels is given in Figure 7. The maximum swelling was obtained at initiator amount of 0.006 mol/L. the swelling of hydrogel increased initially on increasing the initiator concentration up to 0.015 mol/L. the increase of swelling may be ascribed to the increase of the active sites on the on the backbone of the CMC arising from the attack of Ce^{4+} , and so more hydrophilic AMPS/NVP ratio grafting takes place. The swelling decreased with the increase of the initiator concentration beyond the optimum condition. This behavior can be attributed to:

(a) oxidative degradation of CMC chains by excess Ce^{4+} ions, (b) an increase in the termination reaction of the chain radicals via bimolecular collision because of an increased population of macroradicals produced, and (c) enhancement in homopolymerization reaction. These observations are in agreement with similar observations reported by others^[18,19].

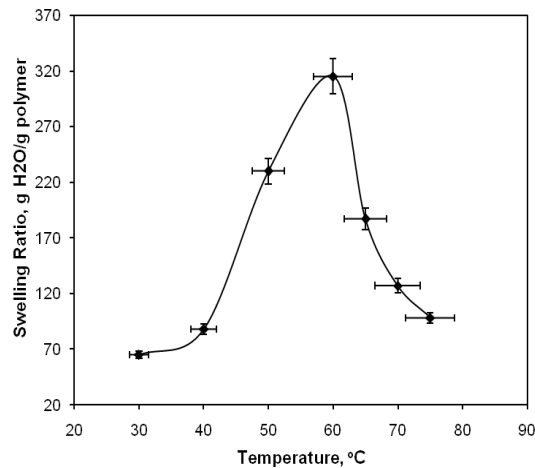


Figure 7. Effect of temperature on swelling capacity.

Reaction conditions: CMC 1.0 g, MBA 0.0108 mol/L, NVP 0.4 mol/L, AMPS 0.68mol/L, CAN 0.015 mol/L, 60 min

Effect of pH on the swelling capacity

In Figure 8 the equilibrium swelling of the hydrogel is presented as a function of pH (ranged from 1 to 12). No additional ions (through buffer solution) were added to medium for setting pH because absorbency of a superabsorbent is strongly affected by ionic strength. Therefore, stock NaOH (pH 13.0) and HCl (pH 1.0) solutions were diluted with distilled water to reach desired basic and acidic pHs, respectively.

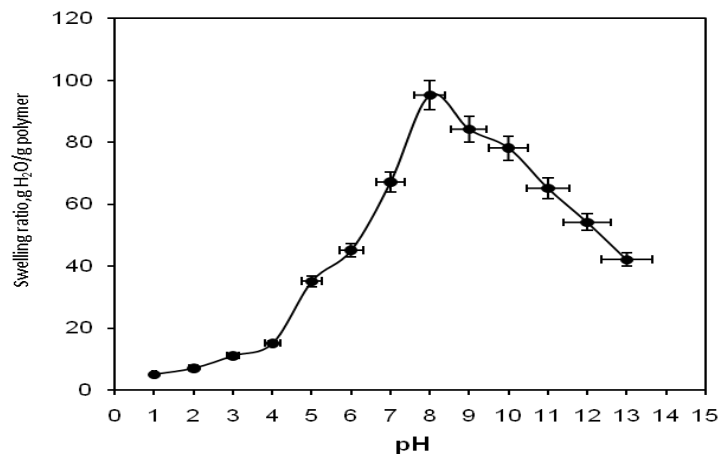


Figure 8. pH-dependent swelling of the superabsorbent hydrogel.

The hydrogel contained $-\text{SO}_3^-$ groups related to grafted poly(AMPS) monomers. These groups are very acidic and fast ionizable. As shown in Fig. 8, the swelling of the hydrogel is increased up to pH 8. Low swelling of the hydrogel in very acidic conditions may be attributed to the screening effect of the counter ions, i.e. Cl^- , shields the charge of the $-\text{SO}_3^-$ anions and prevents an efficient repulsion. As a result, a remarkable decreasing in equilibrium swelling is observed (gel collapsing). With increasing of the pH, the ionic strength of the solution (shielding effect of Cl^-) is decreased and the swelling increased. At pH 8, the high the anion-anion repulsive electrostatic forces of $-\text{SO}_3^-$ groups, the high swelling will be. Above pH 8 the swelling is decreased that it can be attributed to screening effect of the counter ions, i.e. Na^+ , shields the charge of the $-\text{SO}_3^-$ anions and prevents an efficient repulsion^[17-18].

pH-responsiveness behavior of CMC-g-PNVP-co-AMPS hydrogel

Since the present hydrogels show different swelling behaviors in acidic and basic pH solutions, we investigated the reversible swelling-deswelling behavior of these hydrogels in 0.01 M solutions at pH 2.0 and 8.0 (Figure 9). At pH 8.0, the hydrogel swells due to anion-anion repulsive electrostatic forces, while at pH 2.0, it shrinks within a few minutes due to protonation of the $-\text{SO}_3^-$ anions. This swelling-deswelling behavior of the hydrogels makes them as suitable candidate for designing drug delivery systems. Such on-off switching behavior as reversible swelling and deswelling has been reported for other ionic hydrogels^[18-19].

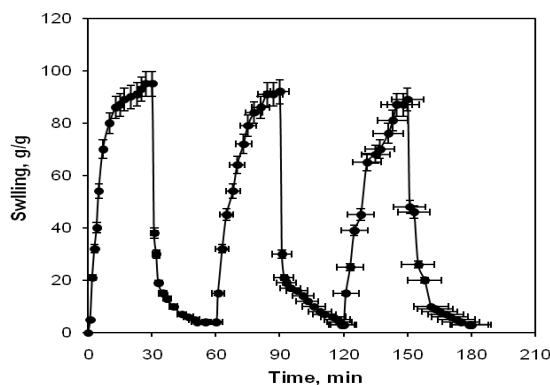


Figure 9. The pH-responsiveness behavior of CMC-g-(PNVP-co-PAMPS) superabsorbing hydrogel in solutions with pH 2.0 and 8.0.

Conclusion

The grafting of N-vinyl pyrrolidone(NVP) and 2-acrylamido-2-methylpropanesulfonic acid (AMPS) onto CMC was carried out using Ceric ammonium Nitrate(CAN) as an efficient initiator in the presence of methylenebisacrylamide (MBA) as a crosslinking agent. The optimum reaction conditions to obtain maximum water absorbency (315 g/g) were found to be: MBA 0.0108 mol/L, NVP 0.4 mol/L, AMPS 0.68 mol/L, CAN 0.015 mol/L and $T = 60^\circ\text{C}$. The characteristic absorbing peaks in the FTIR spectra have proven That CMC participates in graft copolymerization with NVP and AMPS monomers. The morphology of the samples was examined by scanning electron microscopy (SEM). In addition, the swelling of hydrogels in solutions with various pHs, exhibited high sensitivity to pH, so that the pH reversibility and on-off switching behavior makes the intelligent hydrogel as a good candidate for considering as potential carriers for bioactive agents, e.g. drugs.

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