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MBA-crosslinked Na-Alg/CMC as a smart full-polysaccharide superabsorbent hydrogels

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Abstract

A novel superabsorbent hydrogel composed of carboxymethylcellulose (CMC) and sodium alginate (Na-Alg) was prepared by using methylenebisacrylamide (MBA) as a crosslinking agent. Ammonium persulfate (APS) was used as an initiator. For investigation of the effect of reaction variables on water absorbency of the hydrogels, the synthetic conditions were systematically optimized through studying the influential factors, including temperature, Na-Alg/CMC weight ratio and concentration of MBA and APS. Increase in MBA and APS concentration results in the decrease in water absorbency of the hydrogels. The water absorbency of the hydrogels increased with increasing of reaction temperature and Na-Alg/CMC weight ratio up to 85 °C and 0.54, respectively. The hydrogel was identified using FT-IR spectroscopy and SEM pattern. These behaviors were discussed according to structural parameters. The influence of variables such as pH, particle size and MBA concentration on the swelling kinetics of the hydrogels was investigated. The water absorbency of these hydrogels in various salt solutions was studied. The tendency of the absorbency for these hydrogels in salt solutions is in the order $Na^+ > Ca^{2+} > Al^{3+}$ for NaCl, $CaCl_2$ and $AlCl_3$ aqueous salt solutions. The results showed that the water absorbency for the hydrogels in monovalent cations salt solutions is in order LiCl > NaCl > KCl. Crosslinked Na-Alg/CMC hydrogels exhibited a reasonable sensitivity to the pH.

Keywords: Sodium alginate; Carboxymethylcellulose; Hydrogel; Swelling kinetic; pH-responsive

1. Introduction

Superabsorbent hydrogels are crosslinked macromolecular network that swell in water or biological fluids. It has been reported that the presence of hydrophilic groups, high polymer chain flexibility, as well as the availability of large free volume between polymeric chains, enhances the swelling capacity of hydrogels (Buchholz & Graham, 1998). Crosslinked synthetic polymers such as polymethacrylates, polyacrylates and polyacrylamides have been reported to produce superabsorbent hydrogels (Chen & Zhao, 2000; Krul et al., 2000; Zhou, Yao, & Kurth, 1996). Hydrogels made from synthetic polymers exhibit excellent water absorbing properties. But toxicity and carcinogenicity of residual monomers in these hydrogels might pose problems with their use in drug delivery and consumer products, such as diapers.

Because of their exceptional properties, i.e., biocompatibility, biodegradability, renewability, and non-toxicity, polysaccharides form the main part of the natural-based superabsorbent hydrogels (Kurita, 2001). Water-soluble polysaccharides owe their solubility properties to the presence of functional groups (mainly OH, COOH, and NH_2), which can be used for the preparation of hydrogels. Crosslinking of polysaccharides is an efficient route to achieving new superabsorbent hydrogels. A great variety of methods to establish crosslinking have been used to prepare hydrogels (Hennink & van Nostrum, 2002).

Many structural factors (e.g., charge, concentration and pK_a of the ionizable groups, degree of ionization, and hydrophilicity) influence the degree of swelling of ionic

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polymers (Askadskii, 1990; Lee et al., 1999; Wu, Lin, Li, & Wei, 2001). In addition, properties of the swelling medium (e.g., pH, ionic strength and the counterion and its valency) affect the swelling characteristics (Gupta, Vermani, & Garg, 2002; Lio & Minoura, 1997). These responsive or smart hydrogels have become an important area of research and development in the field of medicine, pharmacy and biotechnology.

Carboxymethylcellulose (CMC) and sodium alginate are two important natural polymers and easy available. Sodium alginate is an anionic polysaccharide, which consists of α-L-guluronic acid and β-D-mannuronic acid substitutents. CMC is ionic ether of the cellulose and its major commercial derivative. These polysaccharides have hydrophilic carboxylate groups ($-COO^-$) in their backbones. Chemically modified CMC and sodium alginate with improved properties are gaining increasing in many fields not only because they are low in cost, but also mainly the polysaccharide portions of the products are biocompatible and biodegradable. Hydrogels from graft copolymerization of the hydrophilic monomers onto Na-Alg and CMC have been reported (Bajpai & Giri, 2003; El-Naggar, Abd Alla, & Said, 2006; Kim, Lee, Kim, & Lee, 2002; Kim, Yoon, Lee, Lee, & Kim, 2003). Also, alginate gels have been studied extensively for their ability to form gels in the presence of divalent cations (Favre, Leonard, Laurent, & Dellacherie, 2001).

The water absorbency of the superabsorbent made from polyacrylates and polysaccharides-*g*-poly(acrylates) in salt solutions is low (Mahdavinia, Pourjavadi, & Zohuriaan-Mehr, 2004; Omidian, Hashemi, Sammes, & Meldrum, 1999). In fact, the salt sensitivity of these hydrogels is high. The main factor affecting the swelling of the hydrogels in salt solution is the density of anionic groups. For this reason, we choose the CMC, an anionic polysaccharide, with low density of carboxylate groups (DS 0.52). But the gel strength of the crosslinked-CMC was low. So, we used the mixture of the CMC and Na-Alg to produce hydrogel. The influence of crosslinking agent (MBA) and APS concentrations as well as the Na-Alg/CMC weight ratio and reaction temperature on the swelling capacity of the hydrogels were investigated. The water absorbency and swelling behavior for these hydrogels in various salt solutions and different pHs were investigated. Also, the influence of variables such as pH, particle size and crosslinker concentration on the swelling kinetics of the hydrogels was investigated.

2. Experimental

2.1. Materials

Sodium alginate (mannuronate/guluronate ratio of the alginate = 1.56, $M_w = 270{,}000$) was purchased from Merck Chemical. Sodium salt of carboxymethylcellulose (DS = 0.52, $M_w = 100{,}000$) was obtained from Fluka Chemical. MBA (Merck) was used without any purification. Ammonium persulfate and buffer solutions (from 1 to 13) were purchased from Merck. All other materials are chemical grade.

2.2. Preparation of hydrogel

The reaction was carried out in a 2-liter reactor equipped with mechanical stirrer. CMC and sodium alginate in various weight ratios (Na-Alg/CMC = 0.14, 0.33, 0.54, 1.0, 1.86, and 3.0) were dissolved in 30 ml distilled water ($W_{\text{Na-Alg}} + W_{\text{CMC}} = 1g$). The reactor was placed in a water bath present at 70 °C. The mixture of CMC and Na-Alg was stirred for 30 min at 70 °C to achieve a homogeneous solution. Then, APS initiator was added to the mixture. The mixture was continuously stirred for 15 min. After adding APS, MBA was added to the solution. Gelatin was observed after ~10–15 min. The reaction product was allowed to cool to ambient temperature. Ethanol (200 ml) was added to the gelled product while stirring. After complete dewatering for 24 h, the product was filtered, washed with fresh ethanol and dried at 50 °C to constant weight.

2.3. Swelling measurements using tea bag method

Ultimate absorbency (equilibrium swelling) of the sol-free samples was determined using the tea bag method described elsewhere (Mahdavinia et al., 2004). Therefore, the equilibrium swelling values were reported as the weight of fluid absorbed at equilibrium per 1 g of dried sample (g/g). The maximum swelling was measured and calculated using the following equation:

$$\text{Swelling (g/g)} = (W_s - W_d)/W_d, \tag{1}$$

where W_s and W_d are the weights of swollen hydrogels and the dry samples, respectively.

2.4. Sol content determination

The sol content of the optimum samples (A1–A4) was determined as below: The weighted crude product particles (0.3 ± 0.0001 g) were dispersed in 500 mL distilled water to swell completely. The gel was filtered. A known weight of filtered water was heated in an oven at 70 °C to dryness. The dried extracted materials were weighed to give the total amount of solute extracted (Omidian, Hashemi, Sammes, & Meldrum, 1998a). The results are shown in Table 1.

2.5. Absorbency at various buffer solutions

To investigate the swelling behavior of Na-Alg/CMC hydrogels at various pHs, buffer solutions (ranging from 1 to 13) were used. The pH values were precisely checked by a pH-meter (Metrohm/620, accuracy ± 0.1). Then, 0.1 ± 0.0001 g of the dried hydrogel was used for the swelling measurements according to Eq. (1). To study the pH-reversibility of the crosslinked Na-Alg/CMC hydrogels, buffers with pH 3.0 and 8.0 were used.

Table 1
Percentage of solute portion for optimum samples in each series of optimizing

Sample	MBA (mol/L)	Na-Alg/CMC	APS (mol/L)	*T* (°C)	Sol%	ES (g/g)
A1	0.015	1	0.0104	70	84	70
A2	0.015	0.54	0.0104	70	72	89.1
A3	0.015	0.54	0.00486	70	49	153.5
A4	0.015	0.54	0.00486	80	41	194.2

2.6. FT-IR spectroscopy and SEM

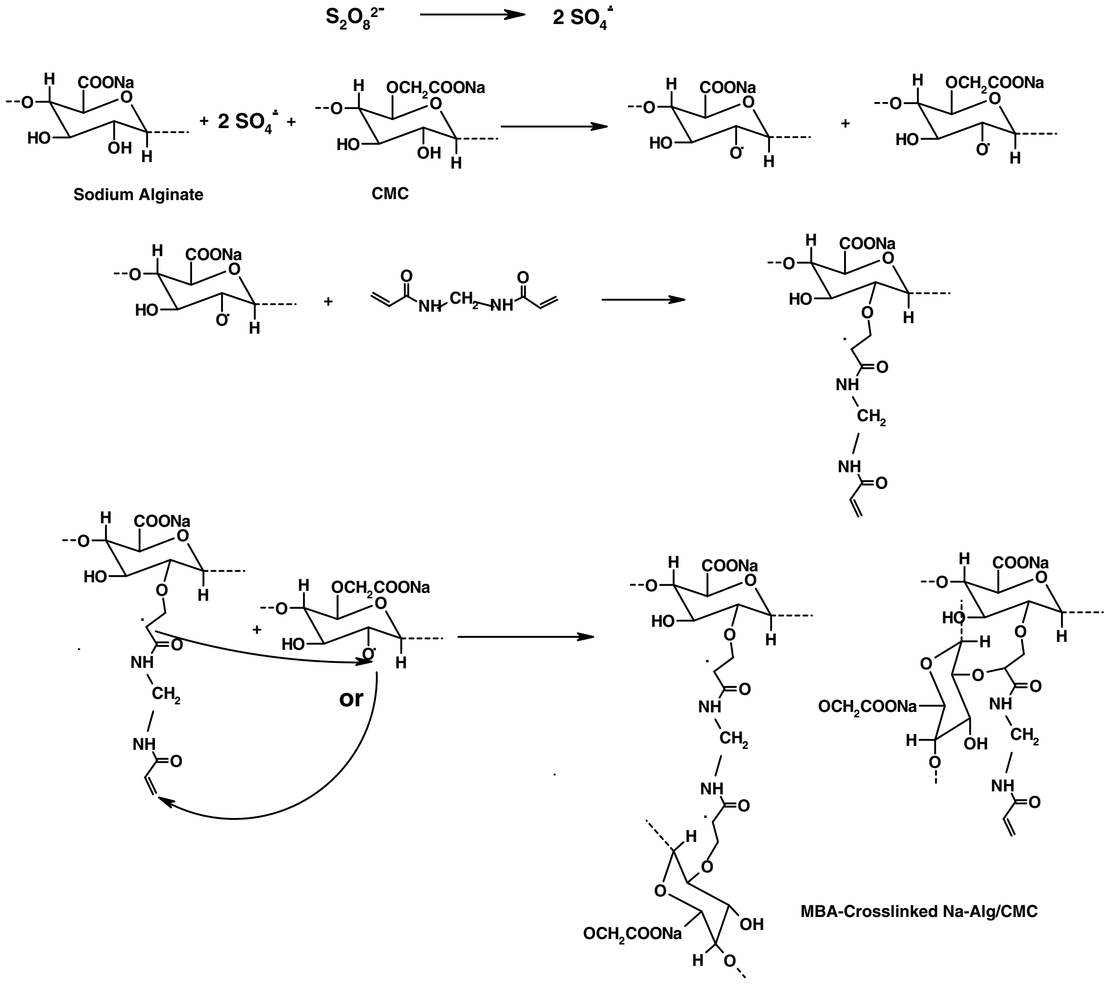
FT-IR spectra of samples were taken in KBr pellets using an ABB Bomem MB-100 FT-IR spectrophotometer. The hydrogel was analyzed by scanning electron microscopy (Philips, Model Stemi SV8).

3. Results and discussion

3.1. Synthesis and characterization

CMC and Na-Alg were simultaneously crosslinked in a homogeneous medium using APS as a free radical initiator and MBA as a crosslinking agent. Scheme 1 shows the mechanism of crosslinking of CMC and Na-Alg in the presence of MBA. The sulfate anion radical that produces from thermal decomposition of APS abstracts hydrogen from the hydroxyl groups of the polysaccharide substrate to form corresponding alkoxy radicals on the substrates. The hydrogel formation can be carried out in two ways: (a) the alkoxy radicals on the CMC and Na-Alg backbones result in active centers capable of initiating free radical reactions with MBA to form a hydrogel. (b) self-crosslinking of the free radicals onto polysaccharides results in crosslink points to produce hydrogel (Chen & Zhao, 2000).

For identification of the hydrogels, infrared spectroscopy was used. The FT-IR spectroscopy of CMC (Fig. 1(b)), Na-Alg (Fig. 1(d)), mixture of CMC and Na-Alg (Fig. 1(c)) and hydrogel (Fig. 1(a)) is shown in Fig. 1. In the spectra of CMC, Na-Alg and mixture of these polysaccharides, two strong peaks were observed at 1619 and 1420 $\mathrm{cm^{-1}}$ due to the asymmetrical and symmetrical stretching of $-\mathrm{COO^-}$ groups. Characteristic absorption peak of CMC and Na-Alg appeared at 3500 $\mathrm{cm^{-1}}$ for the hydroxyl group (Silverstein & Webster, 1998). In Fig. 1(a), a new and very



Scheme 1. General mechanism for the radical crosslinking of Na-Alg/CMC mixture in the presence of MBA.

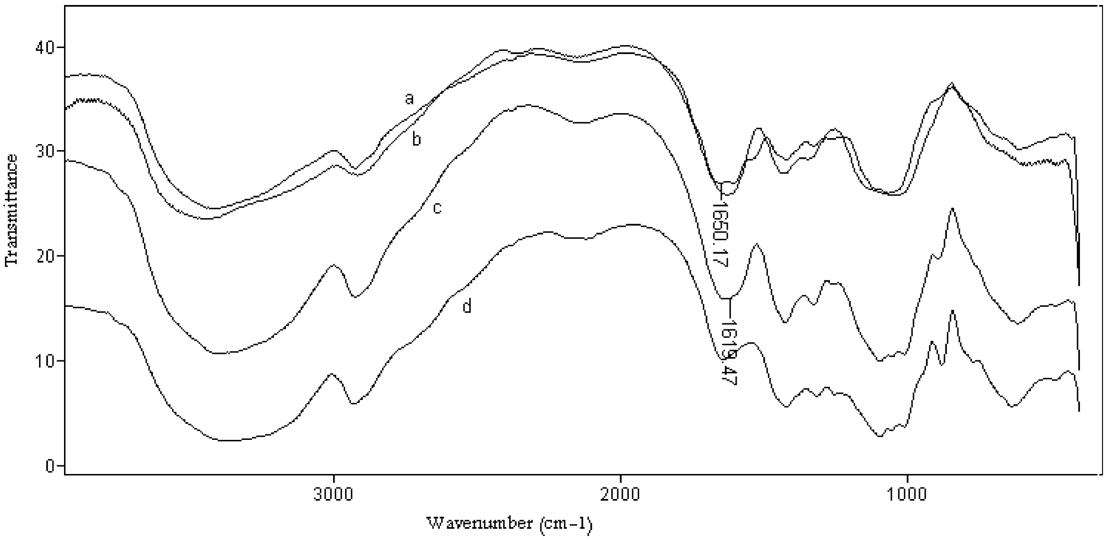


Fig. 1. FT-IR spectra of (a) hydrogel, (b) CMC, (c) mixture of CMC and Na-Alg and (d) Na-Alg. The Na-Alg/CMC weight ratio was 1 and MBA = 0.03 mol/L.

weak peak appeared at 1650 cm^{-1} that attributed to the presence of amide group of MBA in the hydrogel.

Scanning electron microscopy of the hydrogel is shown in Fig. 2. As shown in this figure, the SEM micrograph of the hydrogel revealed a porous internal structure. This porosity confirms the three-dimensional structure of the hydrogel.

3.2. Effect of crosslinker concentration

The water absorbency as a function of MBA concentration was investigated for crosslinked Na-Alg/CMC hydrogel. As shown in Fig. 3, the maximum absorbency is achieved at 0.015 mol/L of MBA. With varying MBA concentration from 0.005 to 0.01 mol/L, no gel was achieved. Slimly gel was formed at 0.015 mol/L of MBA concentration.

The relationship between the swelling ratio and network structure parameters given by Flory (1953) is usually used as the following equation:

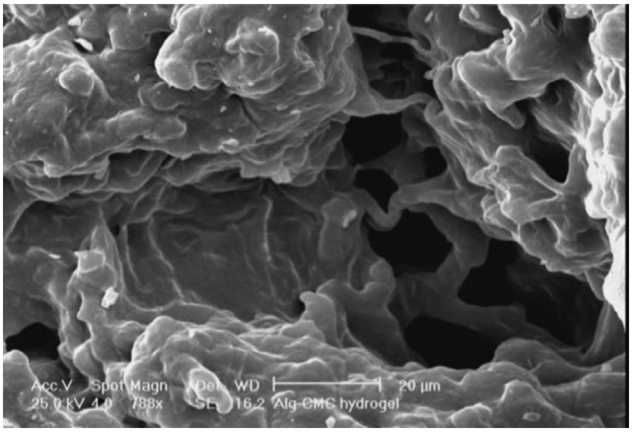


Fig. 2. SEM micrograph of MBA-crosslinked Na-Alg/CMC hydrogel.

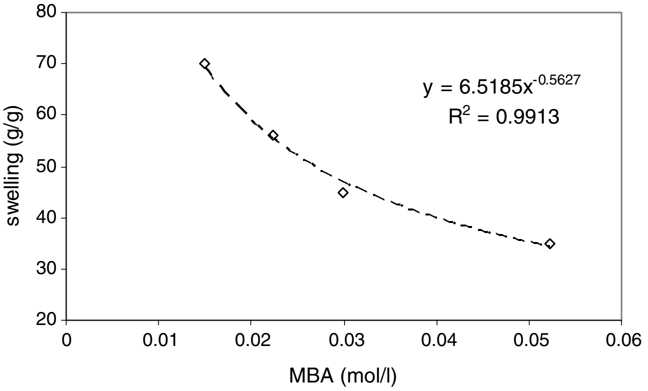


Fig. 3. Effect of crosslinker concentration on water absorbency of MBA-crosslinked Na-Alg/CMC hydrogel. APS 0.0104 mol/L, $T = 70\,°C$, and Na-Alg/CMC = 1.

$$q_m^{5/3} \cong \frac{(i/2v_u S^{*1/2}) + (1/2 - \chi_1)/v_1}{v_e/V_0}. \tag{2}$$

Here, $i/2v_u$ is the concentration of the fixed charges of the unswollen networks (i and v_u are the valence of ionic groups and the ionic hydrogel concentration, respectively), and S^{*} is ionic strength in the external solution; v_e/V_0 is the crosslink density which refers to the number of effectively crosslinked points between chains in unit volume (v_e and V_0 are the final volume of the swelled hydrogel and reference state volume dry hydrogel, respectively). The term $(1/2 - \chi_1)/v_1$ represents the interaction parameter, i.e., affinity of the hydrogel to water (χ_1 and v_1 are the solvent interaction parameter and molar volume of swelling liquid, respectively). The q_m term is swelling ratio of the hydrogel (Buchholz & Graham, 1998).

Increase in concentration of crosslinker results in the high crosslink points; that results in high crosslink density. So, according to Eq. (2), with increasing MBA concentration, the crosslink density is increased; that results in low swelling capacity (Fig. 3).

For crosslinked Na-Alg/CMC hydrogel the swelling was find to follow a power–law relationship with crosslinker concentration (C_c):

$$S = kC_c^{-n}, \tag{3}$$

where k and n are constant values for an individual hydrogel. Fig. 3 exhibits a power–law behavior of absorbency – C_c, with $k = 6.51$ and $n = 0.56$ which is obtained from the fitted curve. Similar observation has been reported by others (Pourjavadi, Harzandi, & Hosseinzadeh, 2004).

3.3. Effect of Na-Alg/CMC ratio

The swelling capacity in distilled water as a function of Na-Alg/CMC weight ratio was studied (Fig. 4). To investigate the Na-Alg/CMC ratio on swelling, the weight ratio of two polysaccharides was chosen from 0.14 to 3. The maximum water absorbency (89.1 g/g) was achieved in Na-Alg/CMC weight ratio of 0.54. After this amount, the swelling capacity was decreased. This can be attributed to the increased viscosity of the reaction mixture with increasing of Na-Alg amount in the mixture, which hinders the movement of the reactants (M_w of Na-Alg = 270,000 and M_w of CMC = 100,000). This reasoning was experimentally confirmed by the sol content values of the high alginate amount in hydrogel (i.e., Na-Alg/CMC = 1) compared with that of the 0.54 weight ratio sample (Table 1). The earlier contained higher sol content (84%) in comparison with the latter (sol content 72%).

3.4. Effect of initiator concentration

The effect of initiator concentration on swelling capacity of the hydrogels has been studied and is illustrated in Fig. 5. A power–law relationship was found for the dependency of the ultimate swelling to the initiator concentration as observed for the effect of MBA on swelling capacity. The power–law parameters are $n = 0.69$ and $k = 3.61$. According to this figure, the absorbency is decreased considerably with an increase in the amount of initiator. The maximum absorbency, 153.5 g/g, is obtained at APS 0.00486 mol/L. Increase in initiator concentration, results in large number of free radicals on substrates, which led to more crosslinking density in the network. Chen and Zhao (2000) refer to this phenomenon as "self-crosslinking".

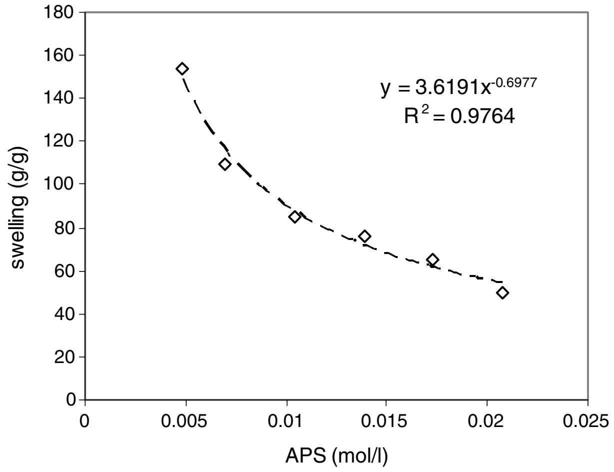


Fig. 5. Effect of APS initiator concentration on water absorbency of hydrogel. MBA 0.015 mol/L, $T = 70$ °C, and Na-Alg/CMC = 0.54 weight ratio.

3.5. Effect of reaction temperature

Fig. 6 demonstrates the effect of the reaction temperature on swelling of Na-Alg/CMC hydrogels. It has been observed that the water absorbency of the hydrogels increased initially on increasing the reaction temperature up to 85 °C, but decreased later as shown in Fig. 6. The swelling capacity for hydrogel is 194.2 g/g at 85 °C. APS

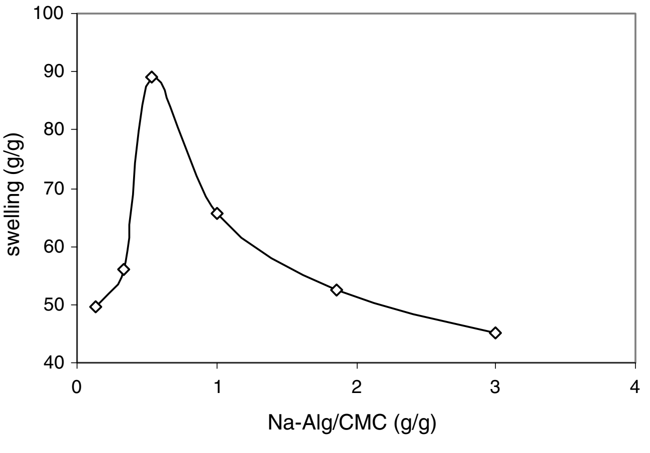


Fig. 4. Effect of polysaccharide weight ratios on water absorbency of hydrogel. MBA 0.015 mol/L, $T = 70$ °C, and APS 0.0104 mol/L.

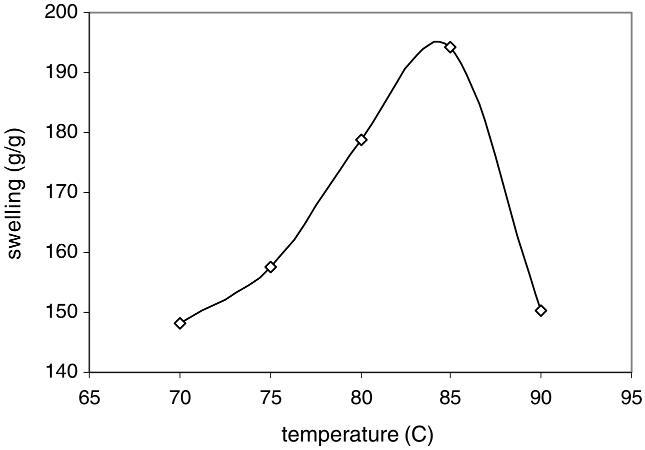


Fig. 6. Effect of temperature of reaction on water absorbency of hydrogel. MBA 0.015 mol/L, APS 0.00486 mol/L, and Na-Alg/CMC = 0.54 weight ratio.

is a thermal initiator, it is efficiently dissociated at the higher temperature than its dissociation temperature, i.e., about 70 °C (Brantrup & Immergut, 1989). The increase in temperature up to 85 °C favors the activation of backbone radicals, leading to an increase in gel content (Table 1). Beyond the optimum temperature, an increase in the temperature favors the increasing of radical centers, causing high crosslinking points in the hydrogel. So, the swelling capacity of the hydrogel is decreased.

3.6. Swelling kinetics

The following equation was used to investigate the swelling kinetic of crosslinked Na-Alg/CMC hydrogel:

$$\varepsilon(t) = \sigma_0/E[1 - \exp\{(t_o - t)/\tau_0\}], \tag{4}$$

where $\varepsilon(t)$ is the swelling at time t. The swelling $\varepsilon(t)$ at time t depends on two parameters, one, σ_0/E (power parameter), is both a measure of resistant to expansion of the polymer network and also the ultimate degree of absorption and the other, τ_0 (rate parameter), is a measure of the resistant to permeation.

Using this expression a better fit was obtained to the experimental data for all the samples (S1–S8) (Fig. 7). So, the experimental swelling data follow a typical exponential relationship which has two characteristics constant, i.e., σ_0/E and τ_0 (Omidian, Hashemi, Sammes, & Meldrum, 1998b). The quantitative value of the former can be estimated from the values of the steady-state swelling of the individual samples, since the water transport is diffusion-controlled. For the latter, the reciprocal value of the slope of the plot of $\mathrm{Ln}[1 - Wt/W\infty]$ gains time has been used ($W\infty$ is equilibrium or steady-state swelling). These characteristic parameters, i.e., steady-state swelling (g/g), τ_0(s) in our experiments and σ_0/E, and τ (for fitted curve) (S1–S8), are quoted in Table 2, i.e., σ_0/E and τ of fitted

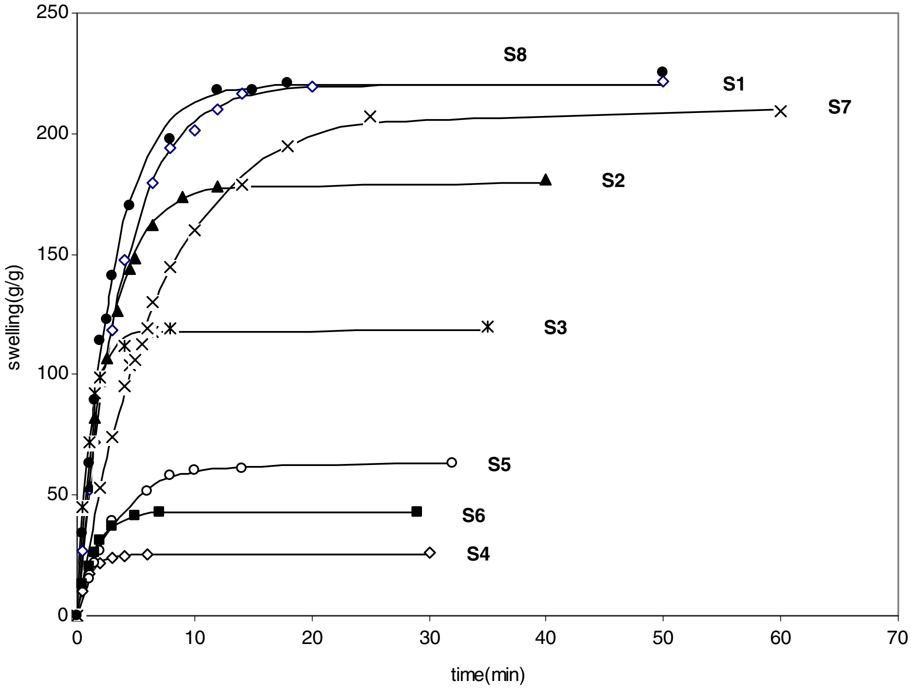


Fig. 7. Curves fitted to the experimental swelling values of the individual samples (S1–S8).

Table 2
Characteristic of samples (S1–S8), as well as parameters fitted to experimental swelling data (APS 0.00486 mol/L, polysaccharide ratio 0.54, $T = 85$ °C, D.W., distilled water; S.M., surrounding media)

Exp	MBA (mol/L)	S.M.	Average of particle size (μm)	Steady-state swelling (g/g)	Time to constant swelling (min)	Initial slope (g/min)	τ_0 (s)	σ_0/E (g/g)	τ (s)
S1	0.015	D.W.	335	221.3	50	38.04	227	220.4	227
S2	0.03	D.W.	335	181	40	43.71	156	179.6	163
S3	0.045	D.W.	335	120	35	73.45	62	118.1	63
S4	0.015	pH 2	335	26.3	30	17.33	65	25.41	57
S5	0.015	pH 6	335	63	32	12.13	212	63.16	204
S6	0.015	pH 10	335	43	29	18.07	95	43.07	93
S7	0.015	D.W.	377.5	209.6	60	19.91	400	210	414
S8	0.015	D.W.	292.5	225	50	48.66	178	220.4	177

curves, were used to obtain the value of initial slope, with this parameter, the slope of the line passed the point zero and the point of 60% fractional swelling was determined. The method for calculating these parameters was reported by Omidian et al. (1998b).

In these series of experimental, the swelling kinetic of the hydrogels as a function of MBA concentration, particle sizes and medium pH was investigated. Values of the parameters are given in Table 2 for samples at different levels of crosslinker and various particle sizes. For samples with similar particle size (S1, S2, and S3), the expansion parameter decreased as the level of crosslinker was raised. This is interpreted as evidence of increasing resistance to expansion caused by the additional crosslinks. Also, increase in crosslinker level causes the decrease in permeation resistance. The highest value for the permeation parameter was in S1, meaning that highest resistance to permeation occurred in these runs. The fall in resistance with increasing level of crosslinker is attributed to crosslinking preventing the collapsing as far when the polymer was dried (Omidian et al., 1999).

For samples with similar crosslinker levels (S1, S7, and S8), the expansion parameter changed little with increasing particle size. With decrease in particle size, the permeation parameter is decreased. This indicates that permeation resistance became smaller as the particle size becomes smaller, presumably as a result of the increase in surface area accessible to the water (Omidian et al., 1999).

The effect of pH on the swelling kinetic of hydrogel (S4, S5 and S6) was studied. At pH 6 (S5), the expansion and permeation parameters are higher than those of other pHs. This is attributed to the complete dissociation of the carboxylic groups to the carboxylate. Under acidic pHs (S4), most of the carboxylate anions are protonated, so the main anion–anion repulsive forces are eliminated and expansion parameter is decreased. At pH 10 (S6), the decrease of the expansion parameter is attributed to the charge screening effect of the additional cations causing a non-perfect anion–anion electrostatic repulsion.

3.7. Effect of salt solution on the water absorbency

Na-Alg/CMC superabsorbents are ionized hydrogels that their swelling behavior depends on both the characteristics of the chemical structure and the medium. The swelling of the absorbents in saline solutions was appreciably decreased compared to the values measured in deionized water. This well-known phenomenon (Castel & Audebert, 1990), commonly observed in the swelling of ionic hydrogels, is often attributed to a charge screening effect of the additional cations causing a non-perfect anion–anion electrostatic repulsion, led to a decreased osmotic pressure (ionic pressure) difference between the hydrogel network and the external solution. To study the effect of ionic strength, i.e., $S^{\cdot}$ factor on swelling, we have measured the swelling in various concentrations of NaCl solutions. The results included in Fig. 8 show that with an increase in ionic strength, a decrease in q_m is observed, suggesting agreement with the Flory theory.

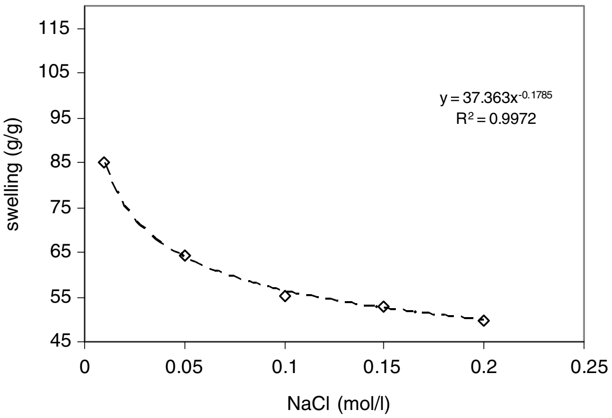


Fig. 8. Swelling of MBA-crosslinked hydrogel in different NaCl concentrations.

The equilibrium swelling data obtained from the chloride salt solutions of sodium, calcium and aluminum with same concentration are given in Fig. 9. The swelling capacity is decreased with an increase in charge of the metal cation ($Al^{3+} < Ca^{2+} < Na^{+}$). It may be explained by complexing ability arising from the coordination of the multivalent cations with carboxylate groups of the hydrogel. This ionic crosslinking mainly occurs at surface of particles and makes them rubbery and very hard when they swell in Ca^{2+} and Al^{3+} solutions.

To achieve a comparative measure of sensitivity of the hydrogels to the kind of aqueous fluid, a dimensionless swelling factor, *f*, is defined as follows:

$$f = 1 - (\text{absorption in given fluid})/ (\text{absorption in deionized water}). \quad (5)$$

The *f* values for the full-polysaccharide hydrogel and other hydrogels based on polysaccharides are given in Table 3. The low values of *f* factor show clearly that the Na-Alg/CMC hydrogel comprises low salt sensitivity. This low salt sensitivity is due to low charge screening effect, because there is low ionic group in the Na-Alg/CMC hydrogel structure (DS on CMC is 0.52).

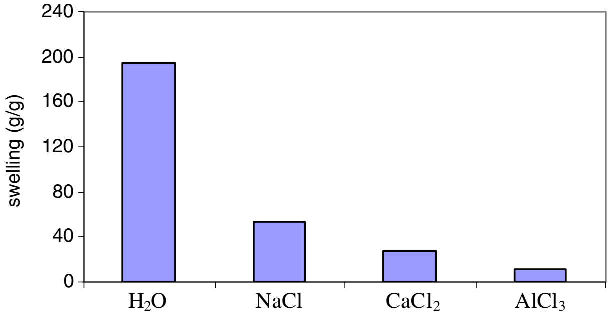


Fig. 9. Water absorbency for MBA-crosslinked full-polysaccharide hydrogels in different salt cation solutions (the NaCl, $CaCl_2$ and $AlCl_3$ concentrations were chosen 0.15 mol/L).

Table 3
Swelling data in water and saline solutions (0.15 mol/L) and salt sensitivity factor *f* for crosslinked carrageenan-*g*-PAA, full-synthetic superabsorbent based on 40% neutralized acrylic acid, and crosslinked Na-Alg/CMC hydrogel

Swelling medium	Crosslinked carrageenan-*g*-PAA (Pourjavadi et al., 2004)		Crosslinked PAA (Pourjavadi et al., 2004)		Crosslinked Na-Alg/CMC	
	ES (g/g)	*f*	ES (g/g)	*f*	ES (g/g)	*f*
H_2O	374	–	226	–	194	–
NaCl	37	0.89	18	0.92	53	0.72
$CaCl_2$	13	0.96	4	0.98	28	0.85
$AlCl_3$	4	0.99	1	0.99	11	0.94

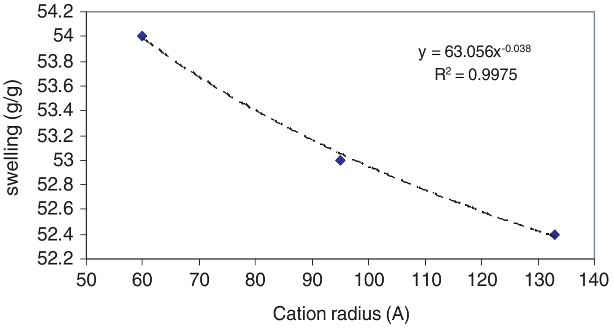


Fig. 10. Water absorbency for MBA-crosslinked hydrogels in different salt solutions with different cations ($\mathrm{Li}^+_{\mathrm{radius}} = 60$ pm, $\mathrm{Na}^+_{\mathrm{radius}} = 95$ pm, $\mathrm{K}^+_{\mathrm{radius}} = 133$ pm, 0.15 mol/L).

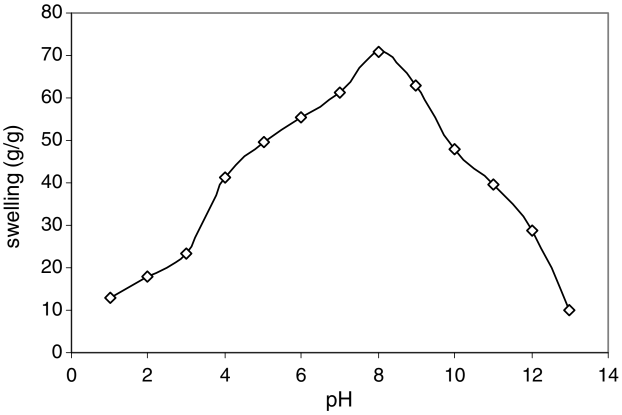


Fig. 11. Water-absorbency dependence of crosslinked Na-Alg/CMC hydrogel on pH.

The water absorbency for hydrogel in monovalent cations with a common anion (Cl^-) salt solution is shown in Fig. 10. The results show that the swelling for the hydrogel in monovalent cations salt solution is in order LiCl > NaCl > KCl. These results imply that the smaller the cation radius, the higher the water absorbency. This is because the smaller the cationic radius, the stronger the hydration ability of the cation, that is, the binding ability to the carboxylate group is weakened and leads to the water absorbency increase.

3.8. pH sensitivity and pulsatile behavior

In order to investigate the sensitivity of the hydrogel to pH, first the equilibrium swelling (ultimate absorbency) of the hydrogel was studied at various pHs ranging from 1.0 to 13.0. As shown in Fig. 11, the maximum swelling of the hydrogel (70.9 g/g) was achieved at pH 8. The crosslinked Na-Alg/CMC hydrogel comprises carboxylate groups (–COO^-). The pK_a value of the CMC, guluronic acid residue and mannuronic acid residue of alginate is 4.6, 3.2 and 4, respectively (Barbucci, Magnani, & Consumi, 2000; Kim et al., 2002). So, the carboxylic groups are ionized at pH >3, while at pH <3, they will be protonated. At higher pHs (above the pK_a of carboxylic groups), the carboxylic acid groups become ionized and the electrostatic repulsive force between the charged sites (COO^-) causes increasing in swelling. Under acidic pHs (pH <3), most of the carboxylate anions are protonated, so the main anion–anion repulsive forces are eliminated and consequently swelling values are decreased. At pH 8, the carboxylic acid groups become completely ionized and the electrostatic repulsive force between the charged sites (COO^-) causes an increase in swelling. However, at basic conditions (pH >8), a screening effect of the counter ions, i.e., Na^+, shields the charge of the carboxylate anions and prevents an efficient repulsion. As a result, a remarkable decrease in equilibrium swelling is observed (gel collapsing).

The pH-dependent swelling reversibility of the hydrogels was examined in buffered solutions (Fig. 12). The figure

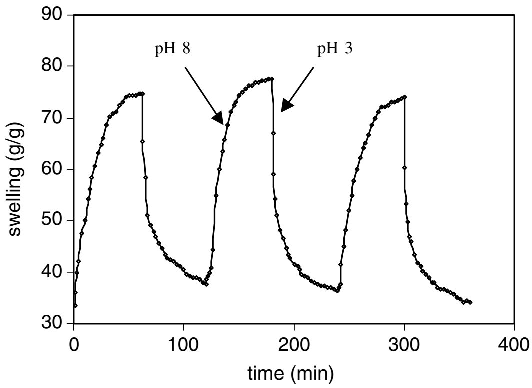
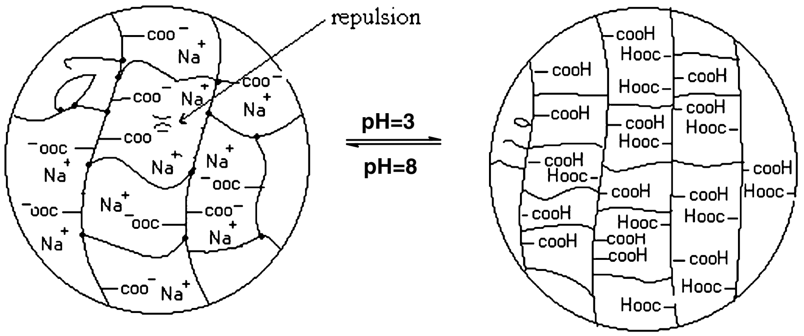


Fig. 12. On–off switching behavior as reversible swelling (pH 8.0) and deswelling (pH 3.0) of the pH-responsive crosslinked Na-Alg/CMC hydrogel.



Scheme 2. Effect of pH on the protonation and deprotonation of carboxylate groups that results in the swelling and deswelling of hydrogel.

demonstrates the hydrogel reversibility to absorb water upon changing the pH in acidic and basic region (pH 8 × 3). At pH 8, the hydrogel swells up to 75 g/g due to anion–anion repulsive electrostatic force, while at pH 3 it shrinks within a few minutes due to the protonation of carboxylate groups. This sudden and sharp swelling–deswelling behavior at different pH values makes the system highly pH-sensitive and suitable for tailoring pulsatile (on–off swelling) drug-delivery systems. Scheme 2 represents the behavior of carboxylate groups with changing the pH. Similar swelling-pH dependencies have been reported in the case of other hydrogel systems (Kim et al., 2002).

4. Conclusion

Hydrogels based on mixture of CMC and Na-Alg were prepared by the crosslinking method. Ammonium persulfate and MBA were used as initiator and crosslinker, respectively. The reaction variables that affect the swelling capacity of the hydrogels were optimized. The maximum water absorbency was achieved under the optimum conditions that found to be MBA 0.015 mol/L, APS 0.00486 mol/L, Na-Alg/CMC 0.54 weight ratio, and reaction temperature 85 °C. FT-IR spectroscopy and SEM pattern confirmed the structure of Na-Alg/CMC hydrogels. For the crosslinked Na-Alg/CMC in the presence of MBA as a crosslinking agent, the steady-state swelling was inversely proportional to the exponent of about 0.56 (n) of the concentration of crosslinker. This was close to the thermodynamically derived 0.6 power relationship obtained by Flory, for the non-ionic polymers.

The effect of MBA concentration, particle size and pH on the swelling kinetic of hydrogel was investigated. The results show that the expansion and permeation parameters are affected by the above factors. A good fit to the swelling data was obtained using Voigt model. The results show that with an increase in ionic strength, a decrease in water absorbency is observed, suggesting agreement with the Flory theory. Swelling capacity for these hydrogels in salt solutions with the same concentration is in order $NaCl > CaCl_2 > AlCl_3$. The results show that the swelling for the hydrogel in monovalent cations is in order $LiCl > NaCl > KCl$. This hydrogel network intelligently responding to pH may be considered as an excellent candidate to design novel drug-delivery systems.

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