Investigation of Effective Parameters onto Swelling Behaviour of Superabsorbent Hydrogels

Fatemeh Soleimani[1,*], Hossein Sadeghi[2], Hadis Shahsavari[2], Arezou Soleimani[1] and Fatemeh Sadeghi[2]

[1]Young Researcher Club, Khorramabad Branch, Islamic Azad University, Khorramabad, Iran
[2]Department of Chemistry, Science Faculty, Khorramabad Branch, Islamic Azad University, Khorramabad, Iran

*Corresponding author: Fax: +98 861 3670017; Tel: +98 9161613256; E-mail: fatisoleymani@yahoo.com

In this work, we investigated swelling behaviours of a novel superabsorbent hydrogel based on carboxymethylcellulose. A mechanism for the superabsorbent hydrogel formation was also suggested. The effect of methylenebisacrylamide, ammonium persulfate, carboxymethyl-cellulose concentration and MAAm/NIPAAm weight ratio on the water absorbency capacity has been investigated. The swelling variations of hydrogels were explained according to swelling theory based on the hydrogel chemical structure. The temperature-sensitivity properties of the hydrogels also make the intelligent polymers as good candidates for considering as potential carriers for bioactive agents, *e.g.*, drugs.

Key Words: Carboxymethyl cellulose, Superabsorbent, Hydrogel, N-Isopropylacrylamide, Methacrylamide.

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[1-3].

Considerable interest has been focused on chemical modi-fication by grafting synthetic polymers onto natural polymers such as carboxymethylcellulose, 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[4]. Carboxymethylcellulose is an important derivative of cellulose and comprises carboxylate functional groups in its structure. This natural polymer is a hydrophilic polymer that dissolving of this polymer in water causes a viscose solution. Crosslinking of carboxymethyl-cellulose backbones are an important route to preparation of carboxymethylcellulose based hydrogels[5,6]. Anothers efficient approach to modify swelling behaviour of carboxymethyl-cellulose hydrogels is graft polymerization of vinylic monomers onto carboxymethylcellulose[7]. Graft copolymerization of vinyl monomers onto carboxymethylcellulose to preparation of

hydrogels have been reported. The present work reveals simultaneously graft copolymerization of methacrylamide (MAAm) and N-isopropylacrylamide (NIPAm) monomers onto carboxymethylcellulose in the presence of methylenebis-acrylamide as a crosslinking agent. The reaction variables affected the swelling capacity of CMC-g-PMAAm-co-PNIPAm superabsorbent hydrogels was studied.

EXPERIMENTAL

The polysaccharide, carboxymethylcellulose (CMC, degree of substitution 0.52, from Condinson Co., Denmark) was of analytical grade and was used as received. N-Isopropyl-acrylamide (NIPAm, Merck) and methacrylamide (MAAm, Merck) were used after recrystalization. Amounium persulfate (APS, Merck) was used without purification. Methylenebis-acrylamide (MBA, Fluka), was used as recieved. All other chemicals were of analytical grade. Double distilled water was used for the hydrogel preparation and swelling measurements.

Preparation of hydrogel: Carboxymethylcellulose solution was prepared in a one-liter reactor equipped with mechanical stirrer and gas inlet. Carboxymethylcellulose was dissolved in degassed distilled water. In general, 0.50 g of carboxymethylcellulose was dissolved in 30 mL of distillated degassed water. The reactor was placed in a water bath preset at 60 ℃. Then 0.10 g of APS (dissolved in 5 mL water) as an initiator was added to carboxymethylcellulose solution and was allowed to stir for 10 min at 60 ℃. After adding initiature, variable amounts of MAAm and NIPAAm were added to the carboxymethylcellulose solution. Methylenebisacrylamide as

a crosslinker (0.050 g in 5 mL water) was added to the reaction mixture after the addition of monomer and the mixture was continuously stirred for 1 h under argon. The total volume of reaction was 40 mL. After 1 h, 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 mL × 50 mL) and dried at 50 ℃[8,9].

Swelling measurements: A CMC-g-PMAAm-co-PNIPAAm sample (0.10 g) was put into a weighed teabag and immersed in 100 mL distilled water or salinity solution (0.9 % wt NaCl) 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 (*ca.* 0.5 h). The bag was then weighed to determine the weight of the swollen gel. The absorbency (equilibrium swelling) was calculated using the following equation, Flory[4]:

$$\text{Absorbency} = \frac{(W_s - W_d)}{W_d} \qquad (1)$$

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 copolymer (g/g). The accuracy of the measurements was ± 3 %.

RESULTS AND DISCUSSION

Effect of crosslinker concentration on the swelling capacity: The effect of crosslinker concentration (C_c) on swelling capacity of crosslinked CMC-g-(PMAAm-co-PNIPAm) was investigated. In this series reaction, the weight ratio of monomers was constant. As shown in Fig. 1, more values of absorbency are obtained by lower C_c. Such a well-known behaviour reported by pioneering scientists[10,11]. The results indicate power law behaviours 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[6,12]. The swelling capacity for hydrogel is 210 g/g, at a fixed methylenebisacrylamide concentration of 0.002 mol/L.
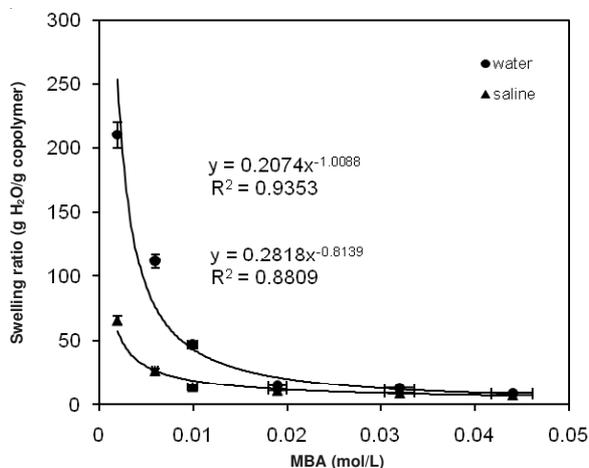
Fig. 1. Effect of crosslinker concentration on swelling capacity of the CMC-based hydrogels. Reaction conditions: CMC 1.0 g, MAAm 1.2 mol/L, NIPAAm 0.8 mol/L, APS 0.005 mol/L, 55 ℃, 90 min

In fact, higher C_c decrease the free space between the copolymer chains and consequently the resulted highly cross-linked rigid structure can not be expanded and hold a large quantity of water[13]. This power law behaviour between swelling capacity and MBA concentration (eqn. 2) was conducted from Fig. 1.

$$\text{Swelling capacity} \approx k[MBA]^{-n} \qquad (2)$$

The k and n in eqn. 3 are constant values for an individual superabsorbent. The n value represents the extent of the sensitivity of the hydrogel to the crosslinker content, while the k value gives an amount useful for comparing the extent of swelling *versus* fixed crosslinker content. The k = 0.207 and n = 1.008 is obtained from the curve fitted with eqn. 2.

Effect of initiator concentration: The influence of initiator concentration on final swelling capacity of the hydrogel has been studied by varying the ammonium persulfate concentration from 0.001 to 0.008 mol/L (Fig. 2). Maximum swelling (188 g/g) was obtained at 0.0025 mol/L of initiator concentration. More or less than this concentration gives hydrogel with decreased swelling capacity. The number of active free radicals on the carboxymethylcellulose backbone is decreased at lower concentrations than 0.0025 mol/L which, in turn, resulting in lower graft polymerization extent and consequently lower final water absorbency. Subsequent swelling loss can be explained on the basis of (a) an increase in terminating step reaction *via* bimolecular collision, which is referred to as 'self-crosslinking' by Chen *et al.*[14] and (b) the decrease in molecular weight (MW) of grafted PMAm + PNIPAAm of the hydrogel causes to decrease swelling value. The latter reason is due to the inverse relationship between molecular weight and initiator concentration. Also, the free radical degradation of carboxymethyl-cellulose backbones by sulfate radical-anions is an additional reason for swelling-loss at higher ammonium persulfate concentration. The proposed mechanism for this possibility is reported in the previous work[12].
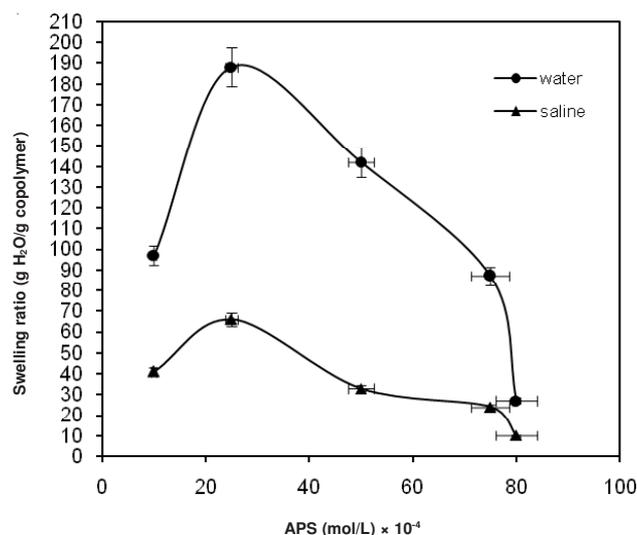
Fig. 2. Effect of monomers ratio on swelling capacity of the CMC-based hydrogels. Reaction conditions: CMC 1.0 g, MAAm 1.2 mol/L, NIPAAm 0.8 mol/L, MBA 0.002 mol/L, 55 ℃, 90 min

A similar observation is recently reported by Hsu and Wang[6], in the case of degradation of chitosan with potassium

1. Thermal dissociation of APS

$$(NH_4)_2S_2O_8 \xrightarrow{70\,^\circ C} 2\ \overset{\cdot}{S}O_4^- + 2\ \overset{+}{N}H_4$$
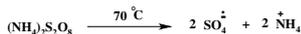
2. Hydrogen abstraction by sulfate anion-radical

(R= -CH₂COOH)
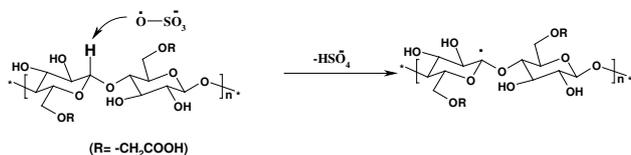
3. Degradation of Carboxymethylcellulose macroradical

Scheme-I: A proposed mechanism for degradation of carboxymethyl-cellulose substrate by the persulfate initiator

persulfate. According to **Scheme-I**, the sulfate radical-anion produced from thermal dissociation of APS (step 1) abstracts a hydrogen atom from the acetal carbon of the κC backbone (step 2). The resulting free radical intermediate is disconnected and lead to chain scissoring (step 3).

Effect of MAAm/NIPAAm weight ratio on the swelling capacity: The substrate carboxymethylcellulose was treated with different weight ratio of MAAm/NIPAAm, (with optimum PC % = 83.5) is illustrated in Fig. 3. In this series reaction, the rest of variables was unchanged. 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 carboxymethylcellulose macroradicals. In addition, higher MAAm/NIPAAm weight ratio 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. The latter reason is in close agreement with similar starch-based superabsorbents reported by Athawale *et al.*[2].
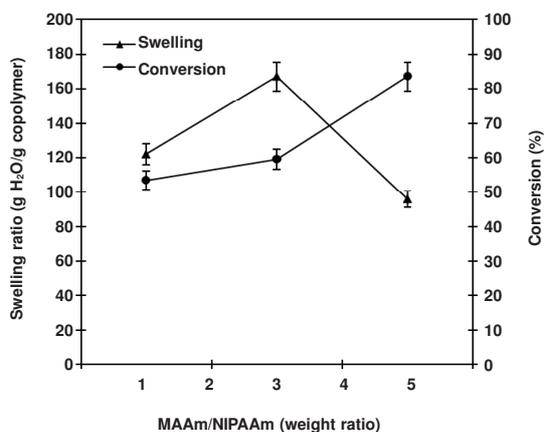
Fig. 3. Effect of monomers ratio on swelling capacity of the CMC-based hydrogels. Reaction conditions: CMC 1.0 g, APS 0.0025 mol/L, MBA 0.002 mol/L, 55 °C, 90 min

Effect of reaction temperature: The swelling capacity of the hydrogels prepared with various reaction temperatures, is shown in Fig. 4. Higher temperatures favour the rate of diffusion of monomers to the carboxymethylcellulose macroradicals as well as increase the kinetic energy of radical centers. In addition, higher temperatures increase the rate of decomposition of the thermally dissociating initiator, APS[15,16].
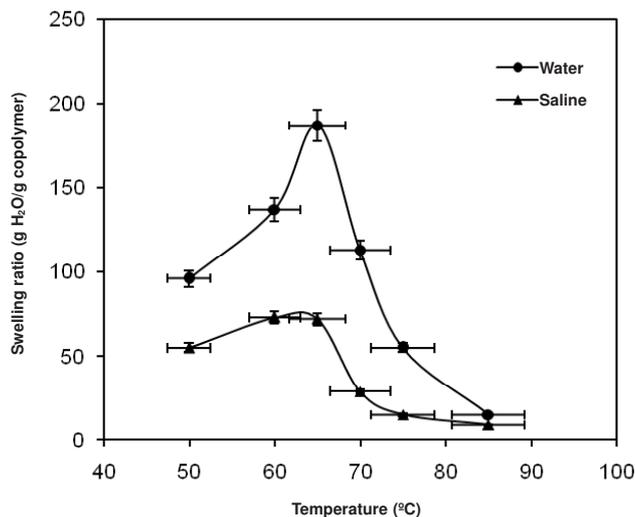
Fig. 4. Effect of reaction temperature on swelling capacity of the CMC-based hydrogels. Reaction conditions: CMC 1.0 g, APS 0.0025 mol/L, MBA 0.002 mol/L, MAAm/NIPAAm = 3, 90 min

The temperatures higher than the optimum value (65 °C), however, lead to low-swelling superabsorbents. This swelling-loss may be attributed to (a) oxidative degradation of carboxymethylcellulose chains by sulfate radical-anions, (b) increasing the rate of termination and chain transfer reactions and (c) decomposition of ammonium persulfate to give O_2 (a radical scavenger), which reacts with primary free radicals (eqns. 3 and 4)[8,17], resulting in decreased molecular weight and decreased swelling (the sulfate radical anions may react with water to produce hydroxyl radicals (eqn. 3) and finally oxygen (eqn. 4)).

$$\overset{\cdot}{S}O_4^- + H_2O \longrightarrow HSO_4^- + H\overset{\cdot}{O} \tag{3}$$

$$2\,H\overset{\cdot}{O} \longrightarrow H_2O_2 \longrightarrow H_2O + 1/2\,O_2 \tag{4}$$
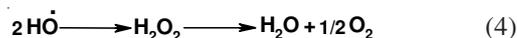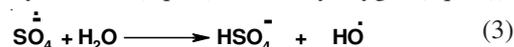
The rate of graft copolymerization (R_p) was calculated simply using the following empirical formula[14], for four initial points of Fig. 6:

$$R_p(\text{mol L}^{-1}\,\text{s}^{-1}) = \frac{1000 m_H}{MTV} \tag{5}$$

where m_H (g) stands for the weight of produced dry hydrogel, M (g mol⁻¹) denotes the molecular weight of monomers, T and V are the reaction time (sec) and total volume (L) of the reaction mixture, respectively. The overall activation energy (E_a) for the graft polymerization reaction was calculated *via* the slope of the plot ln R_p *versus* 1/T (Fig. 5) based on Arrhenius relationship [$k_p = A \exp(-E_a/RT)$]. Therefore, E_a for the graft copolymerization of monomers onto polysaccharide backbones was found to be 78.3 kJ/mol.

Effect of carboxymethylcellulose concentration: The effect of carboxymethylcellulose weight on hydrogel swelling is shown in Fig. 6. Maximum swelling (116 g/g) has been

y = -100x + 8.1
R² = 1
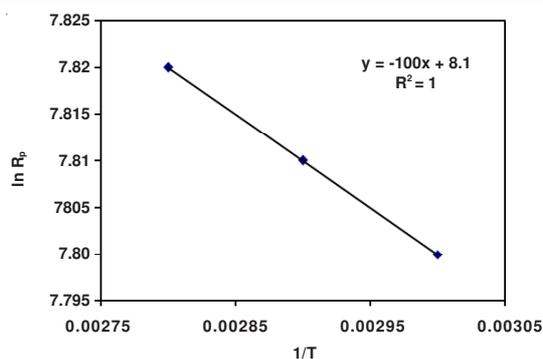
Fig. 5. Plot of ln R$_p$ *versus* 1/T
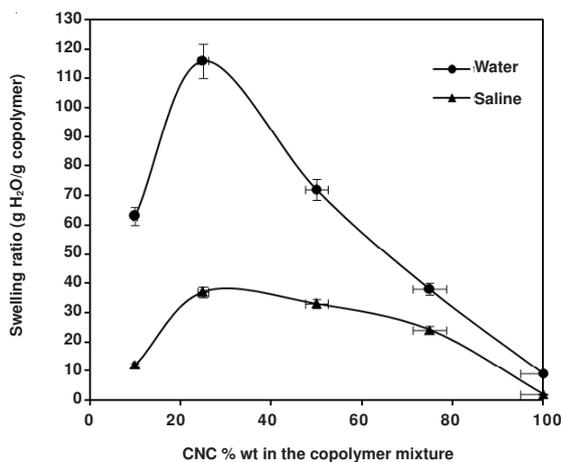
Fig. 6. Effect of polysaccharide concentration on swelling capacity of the CMC-based hydrogels. Reaction conditions: APS 0.0025 mol/L, MBA 0.002 mol/L, MAAm/NIPAAm = 3, 65 ℃, 90 min

viscosity of the medium and a decrease in the diffusion of monomers to active sites to produce crosslinked hydrogels[18].

Conclusion

In the present study, we investigated independent on swelling behaviours of novel superabsorbent hydrogel based on carboxymethylcellulose backbone. The optimum reaction conditions to obtain maximum water absorbency (210 g/g) were found to be: MBA 0.002 mol/L, weight ratio of MAAm/NIPAAm = 3, APS 0.0025 mol/L, carboxymethylcellulose 25 wt % and reaction temperature 65 ℃. swelling-loss in salt solution (0.9 % wt NaCl) in comparison with distilled water, can also be attributed to charge screening effect and ionic crosslinking for Na⁺ cations.

observed at 25 wt % of carboxymethylcellulose in the co-polymer mixture, while other factors including monomer, initiator and methylenebisacrylamide concentration were kept constant. Swelling capacity increased by increasing the carboxymethyl-cellulose wt % from 10.0-25.0 wt %. As the carboxymethyl-cellulose weight was increased in the polymerization feed, the active sites can react easily with monomers. Increasing carboxy-methylcellulose content more than 25 wt %, results in a high

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