

Full Length Research Paper

Synthesis and characterization of superabsorbent hydrogel based on chitosan-g-poly (acrylic acid-co-acrylonitrile)

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In this work, acrylonitrile (AN) and acrylic acid (AA) monomers were directly grafted onto chitosan using ammonium persulfate (APS) as an initiator and methylenebisacrylamide (MBA) as a crosslinking agent under an inert atmosphere. The hydrogels structure was characterized by Fourier transform infrared (FTIR) spectroscopy, scanning electron microscopy (SEM) and thermogravimetric analysis (TGA). The effect of grafting variables, that is, AA/AN weight ratio and concentration of MBA and APS, was systematically optimized to achieve a hydrogel with swelling capacity as high as possible. The water absorbency increased with increasing the AA amount in the monomer feed due to formation of polyelectrolyte. The swelling of the hydrogel samples in saline solution (0.15 mol/l NaCl, CaCl₂ and AlCl₃) was examined. The results indicate that the swelling capacity decreased with an increase in the ionic strength of the swelling medium. This behavior can be attributed to charge screening effect for monovalent cations, as well as ionic crosslinking for multivalent cations. Furthermore, the swelling of superabsorbing hydrogels was examined in solutions with pH values ranging between 1 and 13.

Key words: Hydrogel, chitosan, superabsorbent, acrylonitrile, acrylic acid.

INTRODUCTION

Highly swelling polymers, which is, superabsorbent hydrogels are hydrophilic three dimensional networks that can absorb water in the amount from 10% up to thousands of times their dry weight Po (1994). They are widely used in various applications such as drug delivery, hygienic, foods, cosmetics and agriculture (Zhou et al., 2011; Huixia et al., 2010; Raghavendra et al., 2010; Hoffman, 2002; Peppas and Harland, 1990; Kost, 1995). This accounts for increase in the worldwide production of superabsorbent polymers (SAPs) from 6000 tons in 1983 to 450000 tons in 1996. Nowadays, the worldwide production of SAPs is more than one million tons in

year. Hence, synthesis and characterization of superabsorbent hydrogels is the main goal of the several research groups in the world (Hua and Wang, 2009; Wang et al., 2009; Zheng and Wang, 2009; Chen et al., 2009; Wang and Wang, 2010; Pourjavadi et al., 2009; Wang and Wang, 2010; Zohuriaan-Mehr et al., 2009; Ebru et al., 2008).

Because of their exceptional properties, that is, biocompatibility, biodegradability, renewability and non-toxicity, polysaccharides are the main part of the natural-based superabsorbent hydrogels. Graft copolymerization of vinyl monomers onto polysaccharides is an efficient rout to preparation of hydrogels. Vinyl graft copolymerization onto polysaccharides and proteins is a well-known method for synthesis of natural-based superabsorbent hydrogels. The first industrial superabsorbent hydrogel, hydrolyzed starch-graft-polyacrylonitrile, was synthesized using this method Fanta (1996). The hydrogel forming ability through graft copolymerization of vinyl monomers onto polysaccharides such as starch, chitosan, sodium alginate, carrageenan and cellulose

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Abbreviations: AN, Acrylonitrile; AA, acrylic acid; APS, ammonium persulfate; SEM, scanning electron microscopy; TGA, thermogravimetric analysis; MBA, methylenebisacrylamide; FTIR, fourier transform infrare

has been well documented, (Sokker et al., 2001; Yu et al., 2006; Lin et al., 2010). Because of the presence of certain functional groups along the polymer chains, hydrogels are often sensitive to the conditions of the surrounding environment, which are referred to as "intelligent materials" or "smart materials". For example, the water uptake of these materials may be sensitive to temperature, pH or ionic strength of the swelling solutions or even to the presence of a magnetic field or ultraviolet light. These smart hydrogels are of general interest for biomedical applications, such as artificial muscles or switches, biomedical separation systems and controlled release systems.

Chitosan is a linear natural polysaccharide composed of a partially deacetylated material of chitin, (Roberts, 1992). It is a basic polymer, having amine side groups. Due to its excellent biocompatibility and biodegradability, chitosan and its derivatives were widely applied to fabrication of biomedical materials, enzyme and cell immobilization, especially for drug delivery. Since chitosan is easily soluble in acidic solutions, crosslinking of chitosan to form a network is the only way to prepare chitosan hydrogels Zhang et al. (2007). When anionic monomer such as acrylic acid in present acrylonitrile monomer is grafted onto chitosan (in the presence of a divinyl crosslinking agent monomer), an ampholytic hydrogel containing both cationic and anionic charges is prepared. So, by introducing anionic charges ($-\text{COO}^-$) onto chitosan, a hydrogel with swelling ability at various pH is prepared. In this study, we evaluate the synthesis and characterization of chitosan-g-poly(acrylic acid-co-acrylonitrile) hydrogel as a new natural-based polymer with pH-responsiveness properties. In this hydrogel, AN is as a co-monomer (as seen from the title of the paper) and used mainly for increasing the hydrophilicity and improving the swelling rate of the resulted network.

MATERIALS AND METHODS

Chitosan (from Fluka, with MW=22742 and degree of deacetylation of 0.7) was used as received. Acrylic acid (AA, Merck) and acrylonitrile (AN, Merck) were used after vacuum distillation. Ammonium persulfate (APS, Merck) was used without purification. Methylenebisacrylamide (MBA, Fluka) was used as received. All other chemicals, that is, NaCl, CaCl_2 , AlCl_3 , HCl, NaOH and methanol, were of analytical grade and purchased from Fluka chemical company.

Synthesis of hydrogels

A general procedure for chemically crosslinking graft copolymerization of AA and AN onto chitosan backbones was conducted as follows. Chitosan was dissolved in degassed, distilled water containing 2 wt% of acetic acid. In general, (0.15 to 1.2 g) of chitosan was dissolved in 35.0 ml of the acetic acid solution. The reactor was placed in a water bath preset at 60°C. Then, APS (0.03 to 0.13 g in 5 ml H_2O) was added to the chitosan solution and stirred for 10 min at 60°C. Following this, AA (2.0 to 4.5 ml) and AN (0.5 to 3.0 ml) were added to the chitosan solution. MBA (0.01 to

0.13 g in 5 ml H_2O) as a crosslinker was added to the reaction mixture after the addition of monomer and the mixture was continuously stirred for 60 min under argon atmosphere. After 60 min, the reaction product was allowed to be cooled to ambient temperature. The resulting hydrogel was neutralized to pH 8 by addition of 1 N NaOH solution. Then, methanol (500 ml) was added to the gel product, while stirring. After complete dewatering for 24 h, the product was filtered, washed with fresh methanol (2×50 ml) and dried at 50°C.

Infrared analysis

Fourier transform infrared (FTIR) spectroscopy absorption spectra of samples were taken in KBr pellets, using an ABB Bomem MB-100 FTIR spectrophotometer (Quebec, Canada), at room temperature, with an average of 64 scans at 4 cm^{-1} resolution. The sample/KBr ratio was 0.5% and the IR peak signal-to-noise ratio was typically 30,000: 1 for 1 min scan time. The surface morphology of the gel was examined using scanning electron microscopy (SEM). Dried superabsorbent powder were coated with a thin layer of palladium gold alloy and imaged in a SEM instrument (Leo, 1455 VP). Thermogravimetric analyses (TGA) were performed on a Universal V4.1D TA Instruments (SDT Q600) with 8 to 10 mg samples on a platinum pan under nitrogen atmosphere. Experiments were performed at a heating rate of 20°C/min until 600°C.

Swelling measurements

Chitosan-g-poly(acrylic acid-co-acrylonitrile) sample (0.10 g) with average particle sizes between 40 to 60 mesh (250 to 350 μm) was put into a weighed teabag and immersed in 100 ml distilled water and allowed to soak for 2 h at room temperature (Zohuriaan-Mehr and Pourjavadi, 2003). The equilibrated swollen gel was allowed to drain by removing the teabag from water (~20 min). The bag was then weighed to determine the weight of the swollen gel. The absorbency (equilibrium swelling) was calculated using the following equation:

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

Where, W_s and W_d are the weights of the samples swollen in water and in dry state, respectively. So, absorbency was calculated as grams of water per gram of resin (g/g). The accuracy of the measurements was $\pm 3\%$.

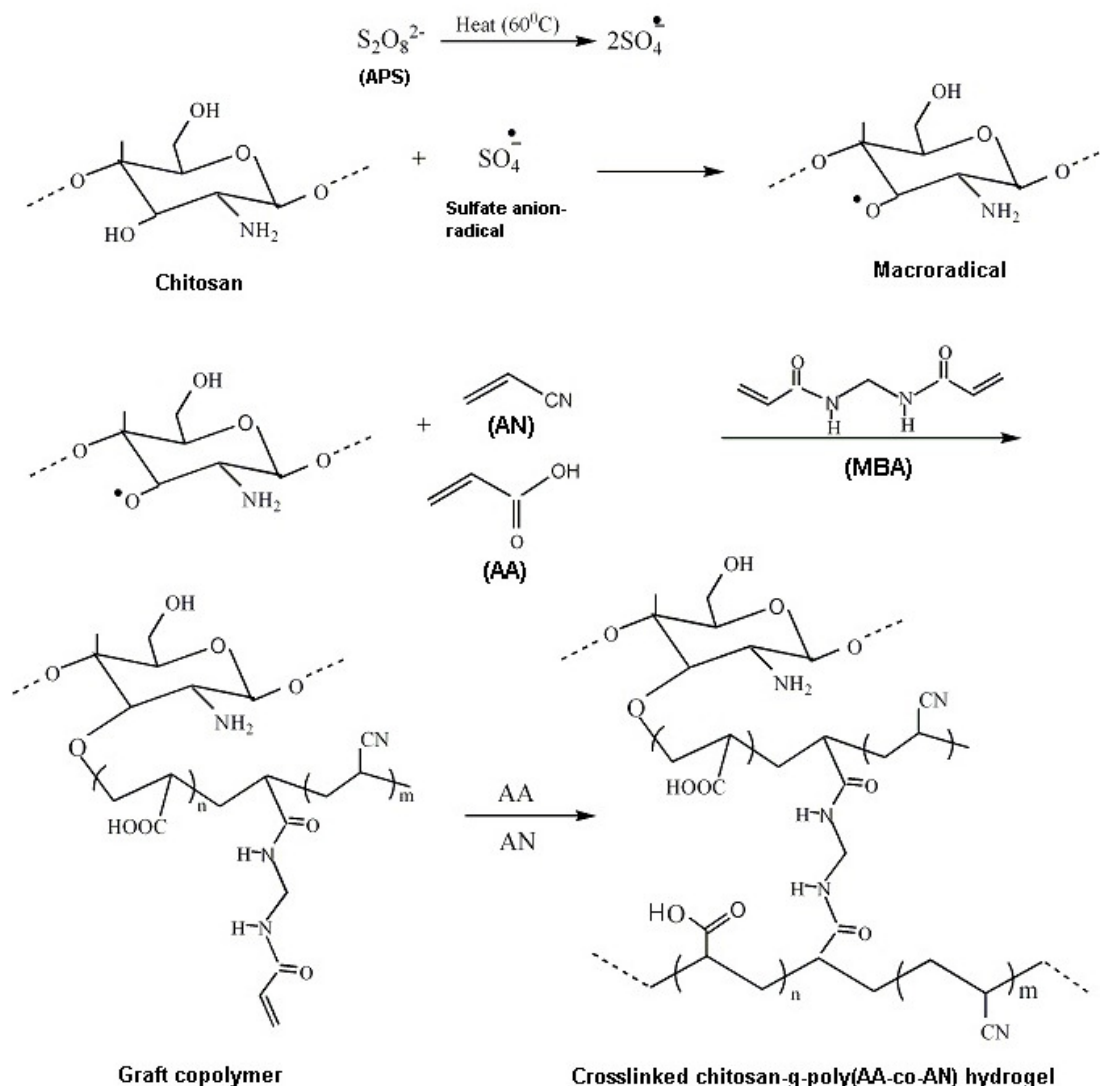
Absorbency at various pHs

Individual solutions with acidic and basic pHs were prepared by dilution of NaOH (pH 10.0) and HCl (pH 1.0) solutions to achieve pH ≥ 6.0 and < 6.0 , respectively. The pH values were precisely checked by a pH-meter (Metrohm/620, accuracy ± 0.1). Then, 0.5 g (± 0.001 g) of the dried hydrogel was used for the swelling measurements according to Equation 1. To study the pH-reversibility of the hydrogels, solutions with pH 2.0 and 8.0 were used. Swelling capacity of the hydrogels at each pH was measured according to Equation 1.

RESULTS AND DISCUSSION

Synthesis and spectral characterization

Superabsorbent hydrogels were prepared by graft



Scheme 1. General mechanism for APS-initiated graft copolymerization of acrylic acid and acrylonitrile onto chitosan in the presence of MBA.

copolymerization of acrylic acid and acrylonitrile onto chitosan in the presence of MBA as a crosslinking agent. Ammonium persulfate was used as an initiator. The persulfate is decomposed under heating and produced sulfate anion-radicals that remove hydrogen from -OH groups of chitosan backbones. So, this persulfate-saccharide redox system results in active centers capable to radically initiate polymerization of AA and AN leading to graft copolymer. Since the crosslinking agent, MBA, is presented in the system, the copolymer comprises a crosslink structure. A possible mechanism of the polymerization of acrylic acid and acrylonitrile onto chitosan in the presence of MBA are shown in Scheme 1.

For identification of the hydrogel, infrared spectroscopy and SEM were used. The FTIR spectra of pure chitosan and superabsorbent hydrogel based on chitosan, chitosan-g-poly(acrylic acid-co-acrylonitrile) are shown in

Figure 1. In Figure 1a, a broad band at 3418 cm^{-1} corresponds to the associated -OH stretching vibrations of the hydroxyl groups and the peak at 1611 cm^{-1} corresponds to the N-H deformation bending of chitosan. The superabsorbent hydrogel product comprises a chitosan backbone with side chains that carry sodium carboxylate and cyanide functional groups that are evidenced by new peaks at 1576 and 2246 cm^{-1} , respectively. The very intense characteristic band at 1576 cm^{-1} is due to C=O asymmetric stretching in carboxylate anion that is reconfirmed by another sharp peak at 1448 cm^{-1} which is related to the symmetric stretching mode of the carboxylate anion. To obtain an additional evidence of grafting, a similar polymerization was conducted in absence of the crosslinker. After extracting the homopoly(AA) and homopoly(AN) (3.5%), appreciable amount of grafted chitosan was concluded. The graft

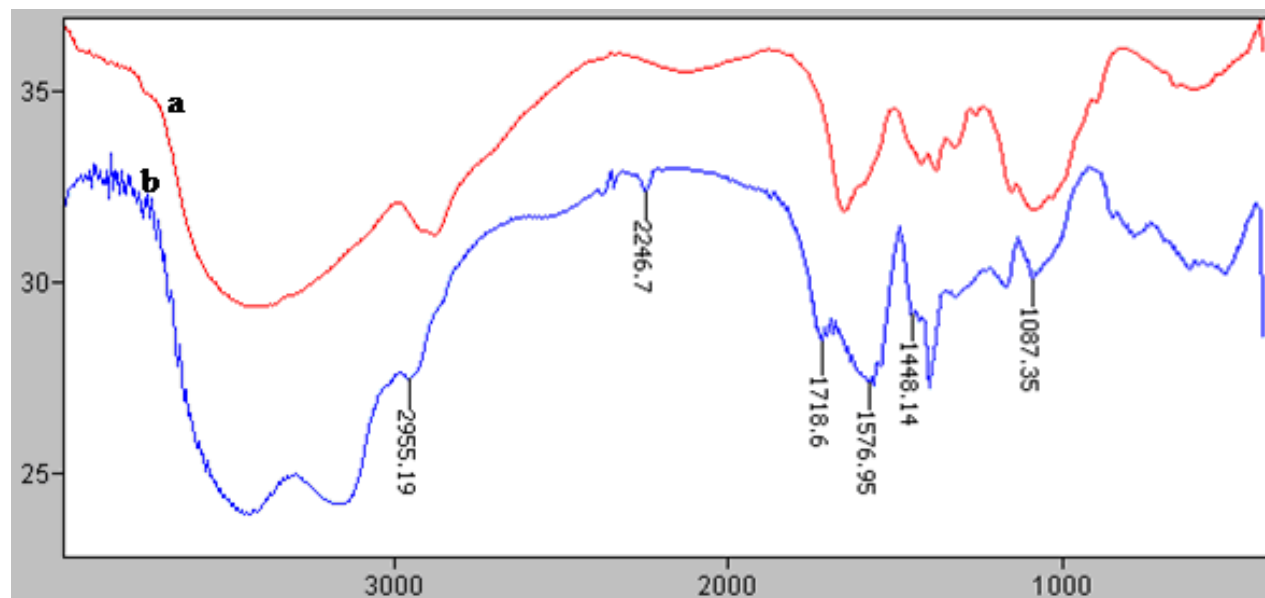


Figure 1. FTIR spectra of (a) chitosan and (b) chitosan-g-poly(NaAA-co-AN) hydrogels.

copolymer spectrum was very similar to Figure 1b.

One of the most important properties that must be considered is hydrogel microstructure morphologies. The surface morphology of the samples was investigated by scanning electron microscopy. Figure 2 shows an SEM micrograph of the polymeric hydrogels obtained from the fracture surface. The hydrogel has a porous structure. 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.

Thermogravimetric analysis

TGA of chitosan (Figure 3a) showed a weight loss in two distinct stages. The first stage ranges between 168 and 300°C and showed about 42% loss in weight. This may correspond to the loss of adsorbed and bound water. No such inflexion was observed in the TGA curve of chitosan-g-poly(AA-co-AN). This indicated that the grafted copolymers were resistant to moisture absorption. The second stage of weight loss starts at 353°C and continues up to 450°C during which there was 28% weight loss due to the degradation of chitosan. Grafted samples, however, showed almost different behavior of weight loss between 97 and 602°C (Figure 3b). The first stage of weight loss starts at 97°C and continues up to 341°C due to the degradation of chitosan. The second stage from 402 to 602°C may contribute to the decomposition of different structure of the graft copolymer. The appearance of these stages indicates the structure of chitosan chains has been changed, which might be due to the grafting of PAA and PAN chains. In general, the copolymer had lower weight loss than

chitosan. This means that the grafting of chitosan increases the thermal stability of chitosan in some extent.

Effect of crosslinker concentration on swelling capacity

Crosslinks have to be present in a hydrogel in order to prevent dissolution of the hydrophilic polymer chains in an aqueous environment. The crosslinked nature of hydrogels makes them insoluble in water. Efficiency of the incorporated crosslinker controls the overall crosslink density in the final hydrogel. Figure 4 shows the influence of the crosslinker concentration (C_c) on the swelling capacity of chitosan-g-poly(NaAA-co-AN) hydrogel. In this reaction series, the AA/AN ratio in monomer feed was chosen to be 1. As indicated in Figure 4, the maximum absorbency is achieved at 0.013 mol/l of crosslinker MBA. Higher values of absorbency is obtained using lower C_c , however, the hydrogels prepared do not possess good dimensional stability, so that the swollen gel strength is not sufficient to be referred to as a real superabsorbent. Higher crosslinker concentration decreases the space between the copolymer chains and consequently, the resulted highly crosslinked rigid structure cannot be expanded and hold a low quantity of water.

Effect of monomer ratio on swelling capacity

The swelling capacity of the hydrogels prepared with various ratios of monomers is shown in Figure 5. Since pH of the polymerization mixture was adjusted at 8.0 after

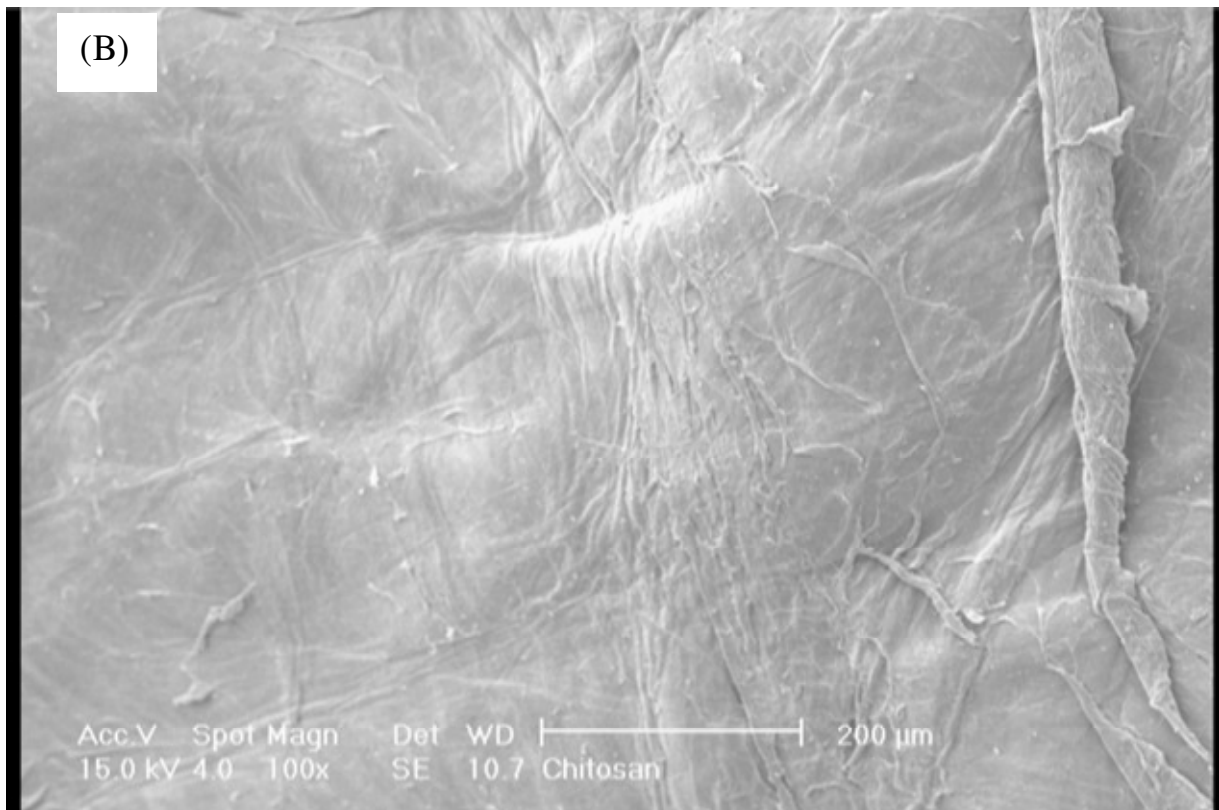
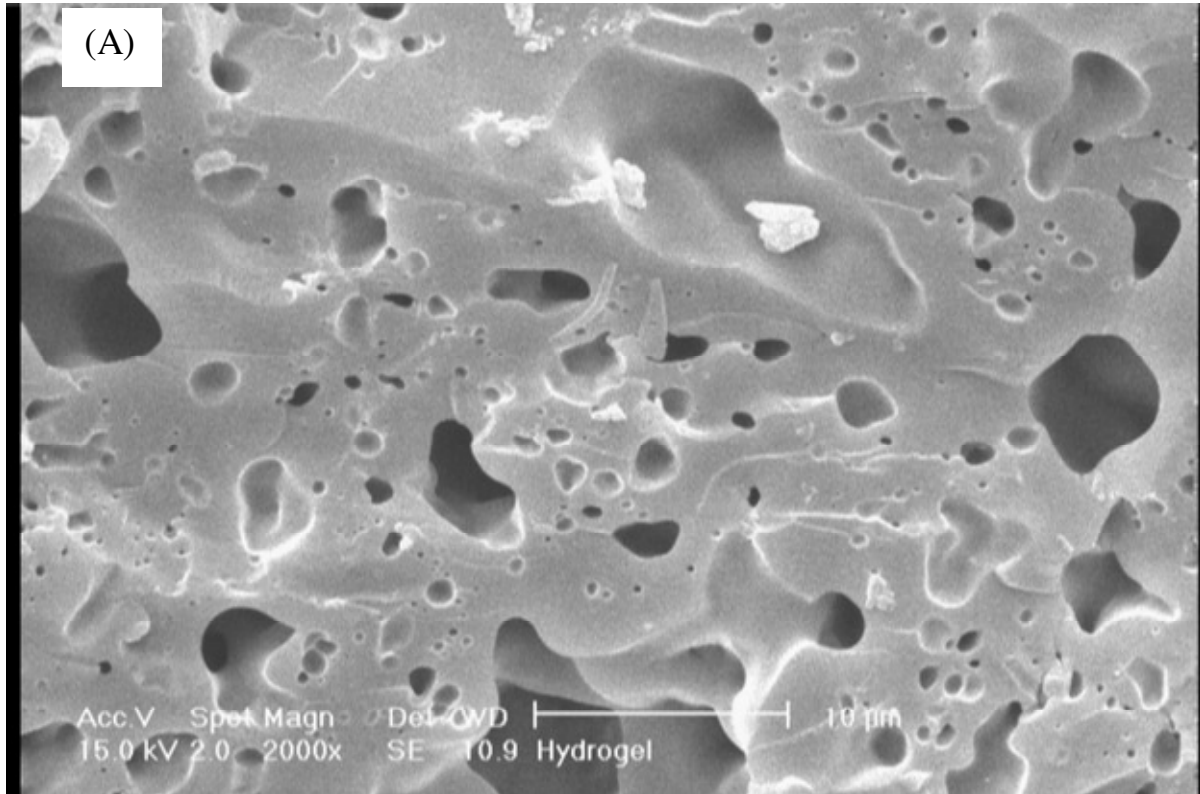


Figure 2. SEM photograph of the optimized superabsorbent hydrogel. (A) Surface of porous hydrogel; (B) cross-sectional area of porous hydrogel. The average pore diameter of the synthesized hydrogel was 16.7 nm.

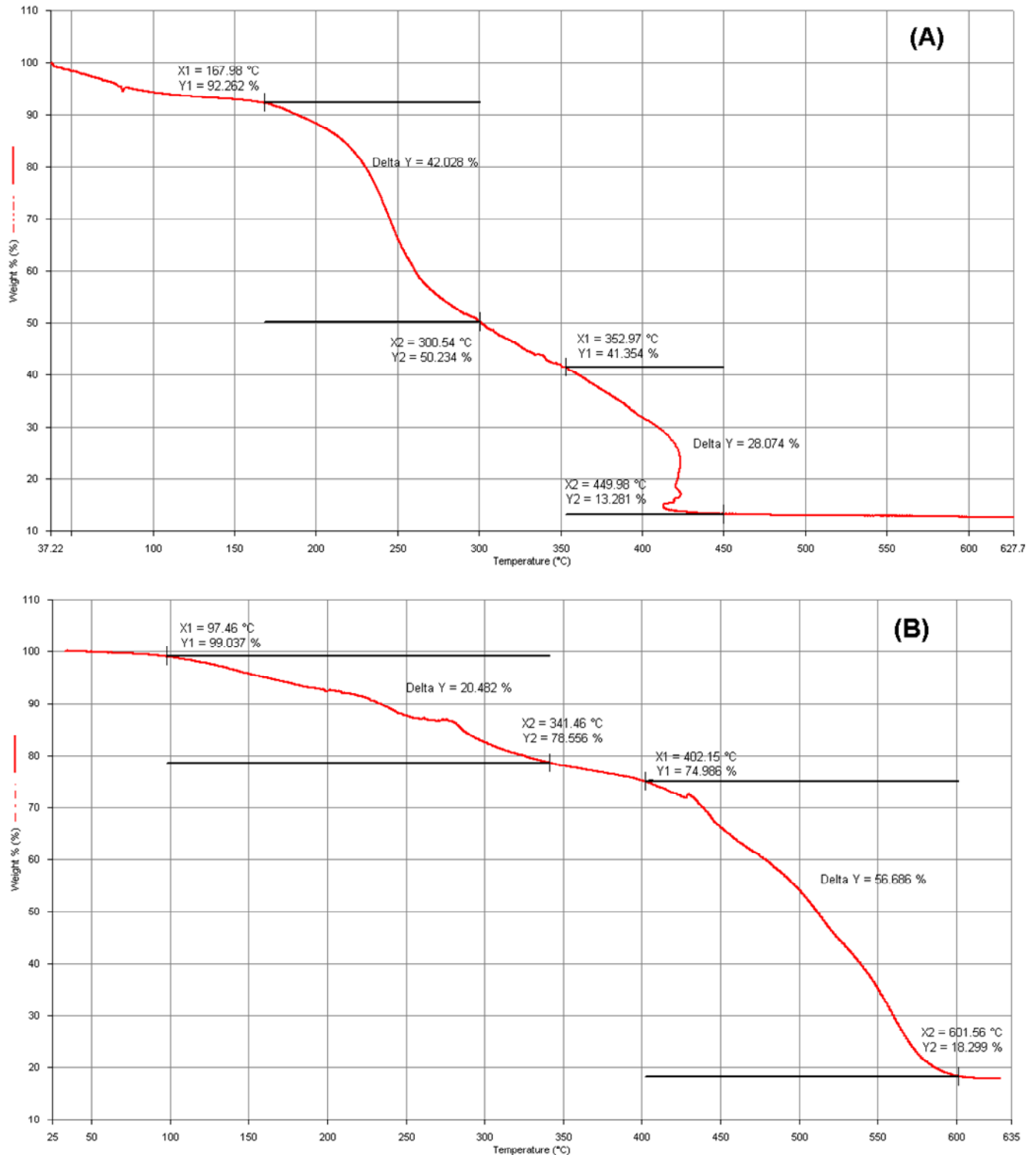


Figure 3. TGA thermograms of (A) chitosan and (B) chitosan-*g*-poly(AA-co-AN) superabsorbent. Heating rate 20 °C/min, under N₂.

the reaction, the superabsorbency of chitosan-*g*-poly (NaAA-co-AN) hydrogel is due to both functional groups of ionic carboxylate (from neutralized AA) and non-ionic

cyanide (from AN). The presence of the ionic groups in polymer chains results in increasing of swelling, because the ions are more strongly solvated rather than non-ionic

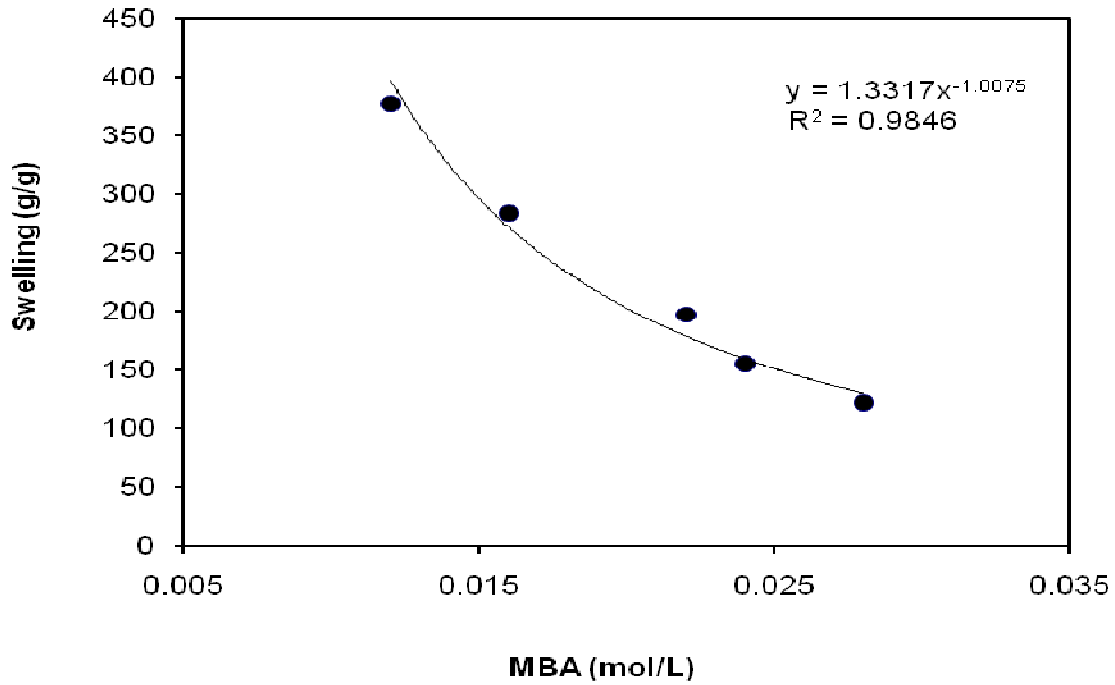


Figure 4. Effect of MBA concentration on the swelling capacity of chitosan-g-Poly(NaAA-co-AN).

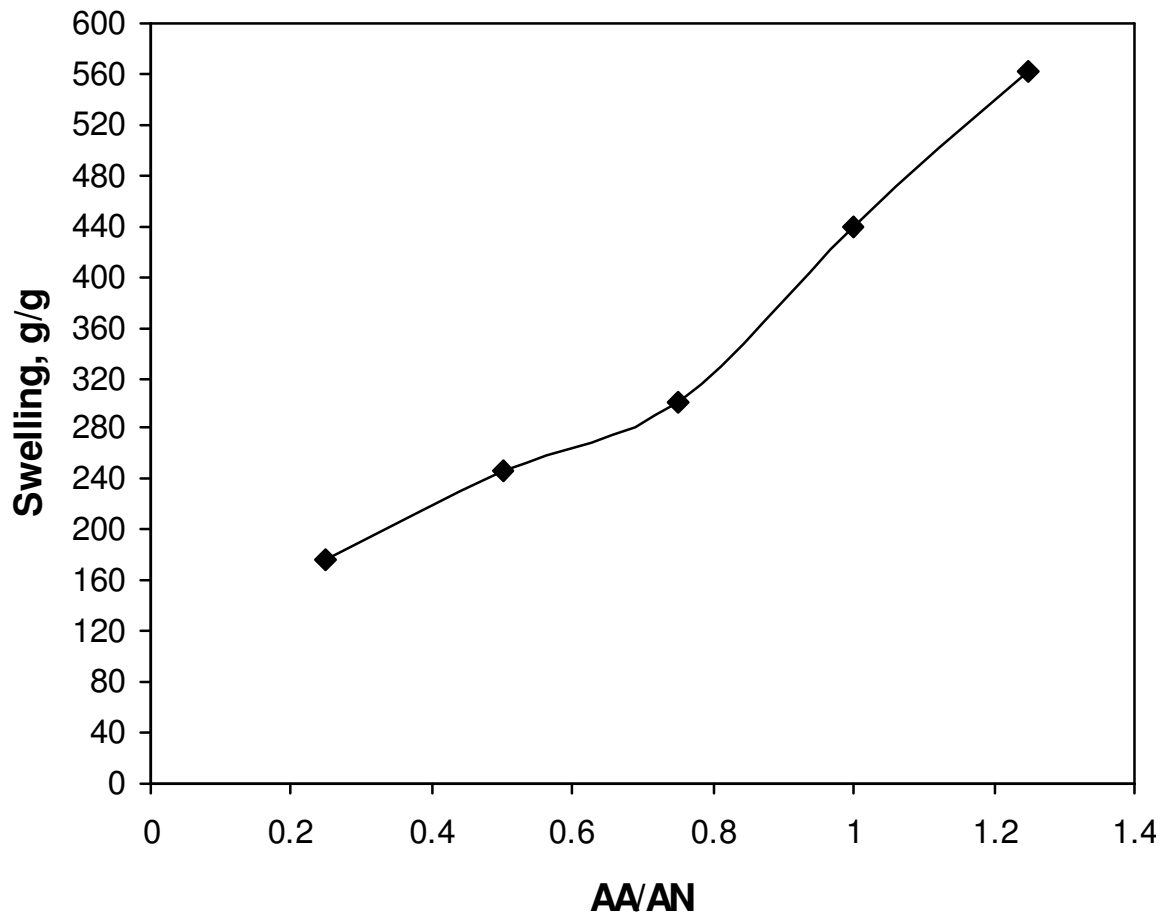


Figure 5. Effect of monomer ratio on swelling capacity of the chitosan-based hydrogels.

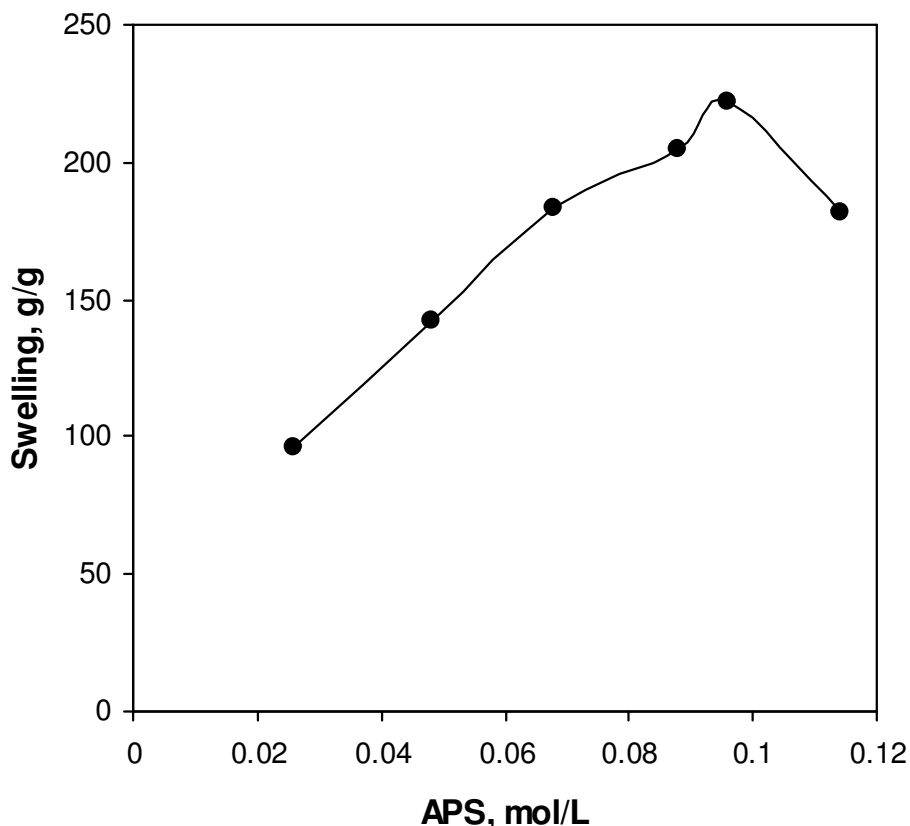


Figure 6. Effect of initiator concentration on water absorbency of the superabsorbent composite.

groups in the aqueous medium. Higher swelling capacities are obtained from employing higher initial ratios of AA/AN. Therefore, the swelling enhancement versus higher AA/AN ratio can be attributed to the formation of high carboxylate groups in the synthesized samples.

Effect of initiator concentration on swelling capacity

The swelling ratio as a function of initiator concentration, for chitosan-g-poly(NaAA-co-AN) hydrogel was investigated (Figure 6). The absorbency is increased versus increasing the APS concentration from 0.026 up to 0.114 mol/l and then, it is decreased considerably with a further increase in the amount of APS. The maximum absorbency (223 g/g) is obtained at APS 0.114 mol/l. The number of active free radicals on the hydrogel backbone is increased in terms of the initiator levels lower than 0.114 mol/l. This accounts for the initial increment in swelling up to a certain amount of APS. The swelling decrease after the maximum may be attributed to increased number of produced radicals led to terminating step via bimolecular collision resulting in enhanced crosslink density. An additional reason for decreasing the absorbency can be related to decreasing molecular

weight (MW) of the grafted monomers at high levels of APS concentration. On the other hand, free radical degradation of chitosan substrate is also possible at high APS levels (Hsu et al., 2002).

Swelling in salt solutions

The swelling behavior of hydrogel in aqueous solutions of NaCl, CaCl₂ and AlCl₃ with various concentrations is shown in Figure 7. The swelling of the absorbents in saline solutions was appreciably decreased comparing to the values measured in distilled water. This well-known phenomenon, commonly observed in the swelling of ionic hydrogels is often attributed to a screening effect of the additional cations causing a non-perfect anion-anion electrostatic repulsion, leading to a decreased osmotic pressure (ionic pressure) difference between the hydrogel network and the external solution. The swelling capacity increases with a decrease in charge of the metal cation (Al³⁺ < Ca²⁺ < Na⁺). This may be explained by complexing ability arising from the coordination of the multivalent cations with carboxylate groups present in hydrogel. This ionic crosslinking mainly occurs at the surface of particles and makes them rubbery and very

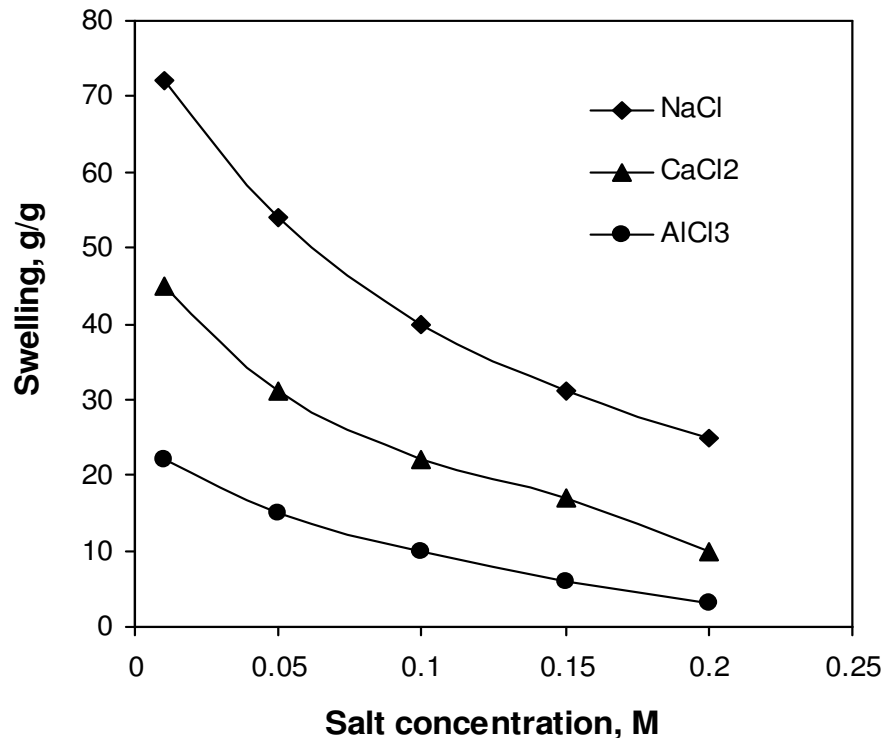


Figure 7. Swelling capacity of hydrogels in salt solutions (0.15 mol/L).

hard when they swell in Ca^{2+} or Al^{3+} solution.

Effect of pH on equilibrium swelling

Figure 8 represents pH dependence of the equilibrium swelling for chitosan-g-poly(NaAA-co-AN) hydrogels at ambient temperature (25°C). The equilibrium swelling (ultimate absorbency) of the hydrogels were studied at various pHs ranged from 1.0 to 13.0. No additional ions (through buffer solution) were added to medium for setting pH because absorbency of a superabsorbent is strongly affected by ionic strength. In addition, it has been reported that the swelling properties of polybasic gels are influenced by buffer composition (composition and pK_a). 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.

The effective pK_a for chitosan is 6.5 and that for carboxylic acid groups is ~ 4.7 . In Figure 8, the dependence of the equilibrium swelling of the chitosan-g-poly(NaAA-co-AN) hydrogel is characterized by a curve with two maximum at pHs 3 and 8. The remarkable swelling changes are due to the presence of different interacting species depending on pH of the swelling medium. It can be assumed that chitosan-g-poly(NaAA-co-AN) hydrogel includes chitosan, poly(acrylic acid) and poly(acrylonitrile) structures. The structure of chitosan and PAA are ionizable. Therefore, based upon pK_a of PAA (~ 4.7) and pK_a

of chitosan (6.5), the involving species are NH_3^+ and COOH (at pHs 1-3), NH_2 and COO^- (at pHs 7-13) and NH_3^+ and COO^- or NH_2 and COOH (at pHs 4-7). Under acidic conditions, the swelling is controlled mainly by amino group (NH_2) on the C-2 carbon of the chitosan component. It is a weak base with an intrinsic pK_a of about 6.5, so it gets protonated and the increased charge density on the polymer should enhance the osmotic pressure inside the gel particles because of the NH_3^+ - NH_3^+ electrostatic repulsion. This osmotic pressure difference between the internal and external solution of the network is balanced by the swelling of the gel. However, under a very acidic condition (pH <3), a screening effect of the counter ion, that is, Cl^- , shields the charge of the ammonium cations and prevents an efficient repulsion. As a result, a remarkable decreasing in equilibrium swelling is observed (gel collapsing). At pH >4.7, the carboxylic acid component comes into action as well. Since the pK_a of the weak polyacid is about ~ 4.7 , its ionization occurring above this value, may favor enhancing absorbency. But under pH 6.4 or in a certain pH range 4 to 7, the majority of the base and acid groups are as NH_3^+ and COO^- or NH_2 and COOH forms and therefore, ionic interaction of NH_3^+ and COO^- species (ionic crosslinking) or hydrogen bonding between amine and carboxylic acid (and probably carboxamide groups) may lead to a kind of crosslinking followed by decreased swelling. At pH 8, the carboxylic acid groups become ionized and the electrostatic repulsive force between the charged sites (COO^-) causes increasing in swelling.

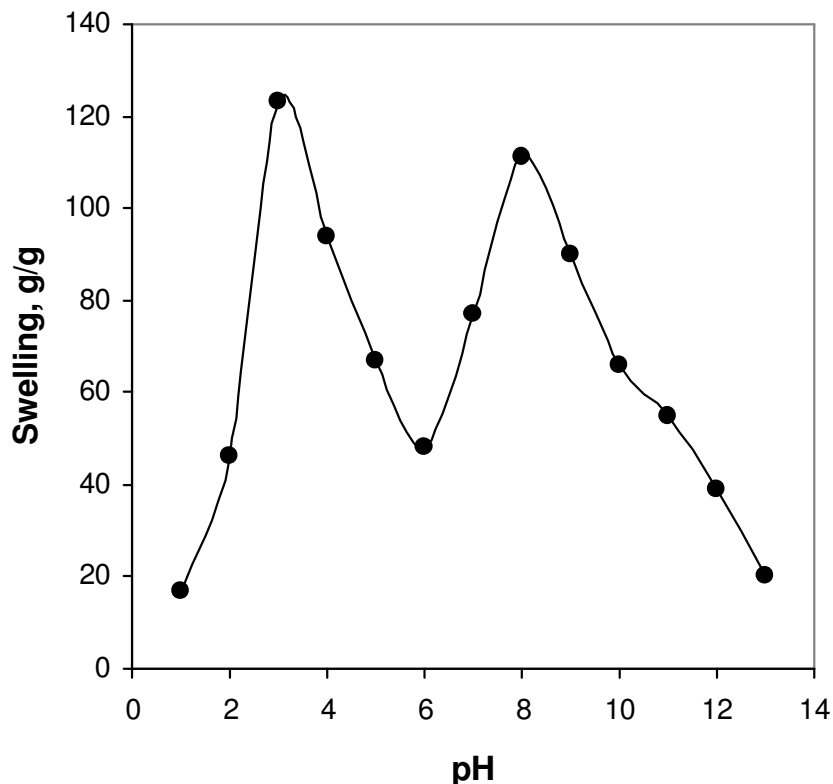


Figure 8. Swelling dependency of chitosan-g-poly(AA-co-AN) superabsorbent on pH.

Again, a screening effect of the counter ions (Na^+) limits the swelling at pHs 9 to 13.

Conclusion

Superabsorbent hydrogels, chitosan-g-poly(NaAA-co-AN) hydrogel, were synthesized through grafting of AA and AN monomers onto chitosan using ammonium persulfate (APS) as an initiator and methylene bis acrylamide (MBA) as a crosslinking agent under an inert atmosphere. Swelling capacity of the hydrogels was found to affect by monomers and crosslinker concentrations. The swelling of the hydrogels exhibited a high sensitivity to pH in 3 and 8. Net effect of H^+/OH^- concentration was examined at various pHs in absence of any buffer solution. One sharp and large volume change was observed for chitosan-g-poly(NaAA-co-AN) versus small pH variations in. Ionic repulsion of protonated groups in acidic solutions causes volume change. Ionic repulsion between charged groups incorporated in the gel matrix by an external pH modulation could be assumed as the main driving force responsible for such abrupt swelling changes. It also exhibited ampholytic nature of pH-responsiveness in swelling behavior. We investigated their swelling in different salt solutions and in media with a wide range of pHs. This hydrogel polyampholytic network intelligently

responding to pH may be considered as an excellent candidate to design novel drug delivery systems.

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