



Synthesis of Pectin-poly(acrylonitrile) Superabsorbent Hydrogel with Salt and pH Responsiveness Properties

MOHAMMAD SADEGHI^{1,*}, MORTEZA NASROLAHI¹ and MOJGAN YARAHMADI²

¹Department of Chemistry, Science Faculty, Arak Branch, Islamic Azad University, Arak, Iran

²Department of English, Humanity Faculty, Arak Branch, Islamic Azad University, Arak, Iran

*Corresponding author: Fax: +98 861 3670017; Tel: +98 916 1613256; E-mail: m-sadeghi@iau-arak.ac.ir

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In the present paper, attention is paid to synthesis and investigates swelling behaviour of a superabsorbent hydrogel based on pectin (Pec) and polyacrylonitrile. The physical mixture of pectin and polyacrylonitrile was hydrolyzed by NaOH solution to yield pectin-poly(sodium acrylate-co-acrylamide) superabsorbent hydrogel. The nitrile groups of polyacrylonitrile were completely converted to a mixture of hydrophilic carboxamide and carboxylate groups during alkaline hydrolysis followed by *in situ* crosslinking of the polyacrylonitrile chains by the alkoxide ions of pectin. A proposed mechanism for hydrogel formation was suggested and the structure of the product was established using FTIR and SEM spectroscopies. Under the optimized conditions, maximum capacity of swelling in distilled water was found to be 523 g/g. The absorbency of the synthesized hydrogels was also measured in various salt solutions. Results indicated that the swelling ratios decreased with an increase in the ionic strength of the salt solutions. In addition, swelling capacity was conducted in solutions with pH ranged from 1 to 13. The pectin-poly(sodium acrylate-co-acrylamide) hydrogel exhibited a pH-responsiveness character so that a swelling-deswelling pulsatile behaviour was recorded at pHs 2 and 8.

Key Words: Pectin, Polyacrylonitrile, Hydrogel, Superabsorbent, Swelling behaviour.

INTRODUCTION

Pectin is a naturally occurring biopolymer that is finding increasing applications in the pharmaceutical and biotechnology industry. It has been used successfully for many years in the food and beverage industry as a thickening agent, a gelling agent and a colloidal stabilizer. Pectin also has several unique properties that have enabled it to be used as a matrix for the entrapment and/or delivery of a variety of drugs, proteins and cells.

The modification of natural polymers is a promising method for the preparation of new materials. Graft copolymerization of vinyl monomers onto natural polymers is an efficient approach to achieve these materials. Superabsorbing resins were first developed with a view to utilizing agricultural materials and are typed by the hydrolyzed starch-g-poly(acrylonitrile), H-SPAN¹. Since then, starches from different resources as well as other polysaccharides, for example, cellulose^{2,3}, hydroxyethyl cellulose^{4,5}, agar⁶, sodium alginate^{7,8} and guar gum⁹ were graft copolymerized to achieve water absorbing polymers. Polyacrylonitrile, polyacrylamide and poly(acrylic acid)¹⁰ have been frequently grafted, mostly onto starch, using different initiators especially the ceric-saccharide redox

system¹¹. Radical polymerization, however, has several disadvantages. The reproducibility of this method is poor and there is little control over the grafting process, so the molecular weight distribution is polydisperse. In addition, the necessity for inert gases (*e.g.*, argon) to prepare an oxygen-free atmosphere and the need for initiators, toxic and/or expensive monomers and crosslinkers are other disadvantages of free-radical polymerization reactions. These problems have been reviewed in detail¹². Fanta *et al*¹³ tried to synthesize H-SPAN superabsorbent hydrogel. They indicated by a solubility test that crosslinks were formed during graft copolymerization, by coupling of the two growing polyacrylonitrile radicals and during saponification, by the attack of pectin alkoxide ions on the nitrile groups as the initiation reaction of nitrile polymerization in the early stages of saponification. The nitrile groups of polyacrylonitrile were converted to a mixture of hydrophilic carboxamide and carboxylate groups during alkaline hydrolysis followed by *in situ* crosslinking of the grafted polyacrylonitrile chains. The initially formed oxygen-carbon bonds between the pectin hydroxyls and nitrile groups of the polyacrylonitrile chains remained crosslinking sites. Fanta and Doane¹⁴ attempted to extend this idea to the preparation of superabsorbent hydrogels by the saponification of polyacrylonitrile in the

presence of polyhydroxy polymers. Finally, Yamaguchi *et al.*¹⁵ reported the preparation of superabsorbing polymers from mixtures of polyacrylonitrile and various saccharides or alcohols. In this studies, we paid attention to the synthesis and investigation of a superabsorbent based on pectin and polyacrylonitrile. The effects of the hydrolysis reaction variables on the swelling properties as well as the salt and pH sensitivity of the hydrogels were also investigated.

EXPERIMENTAL

Pectin (chemical grade, MW 50000) was purchased from Merck Chemical Co. (Germany). Polyacrylonitrile was synthesized through a method mentioned in the literature¹³. Double distilled water was used for the hydrogel preparation and swelling measurements.

Hydrogel preparation: A facial one step preparative method was used for synthesis of pectin-poly(sodium acrylate-co-acrylamide) hydrogel and pectin-poly(NaAA-co-AAm), hydrogel. A general procedure for alkaline hydrolysis of pectin-polyacrylonitrile mixture was conducted as follows. Pectin (0.50-1.33 g) was added to a three-neck reactor equipped with a mechanical stirrer (Heidolph RZR 2021, three blade propeller type, 50-500 rpm), including 35 mL doubly distilled water. The reactor was immersed in a thermostated water bath. After complete dissolution of pectin to form a homogeneous solution, solution of sodium hydroxide (0/25-2/5N) was added to the pectin solution at desired temperature (alkalization temperature, 20-120 °C). The mixture was allowed to stir for certain times (alkalization times, 20-90 min). Various amount of polyacrylonitrile (0.50-4.50 g) was dispersed in the reaction mixture to saponify for certain times and temperatures (alkaline time and temperature). During the saponification NH₃ gas was evolved and a colour change from red to light yellow. This discolouration was an indication of the reaction completion. The pasty mixture was allowed to cool to room temperature and neutralized to pH 8 by addition of 10 wt % aqueous acetic acid solution. Then the gelled product was scissored to small pieces and poured in ethanol (200 mL) to dewater for 5 h. The hardened particles were filtered and dried in oven (50 °C, 10 h). After grinding, the powdered superabsorbent hydrogel was stored away from moisture, heat and light.

Swelling measurements using tea bag method: The tea bag (*i.e.* a 100 mesh nylon screen) containing an accurately weighed powdered sample (0.5 ± 0.001 g) with average particle sizes between 40-60 mesh (250-350 μ m) was immersed entirely in distilled water (200 mL) or desired salt solution (100 mL) and allowed to soak for 3 h at room temperature. The tea bag was hung up for 15 min in order to remove the excess fluid. The equilibrated swelling (ES) was measured twice using the following equation:

$$ES(g/g) = \frac{\text{Weight of swollen gel} - \text{Weight of dried gel}}{\text{Weight of dried gel}} \quad (1)$$

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 13) and HCl (pH 1) solutions to achieve pH = 6 and pH < 6, respectively. The pH values were precisely checked by a pH-

meter (Metrohm/620, accuracy ± 0.1). Then, 0.5 ± 0.001 g of the dried hydrogel was used for the swelling measurements according to eqn. 1.

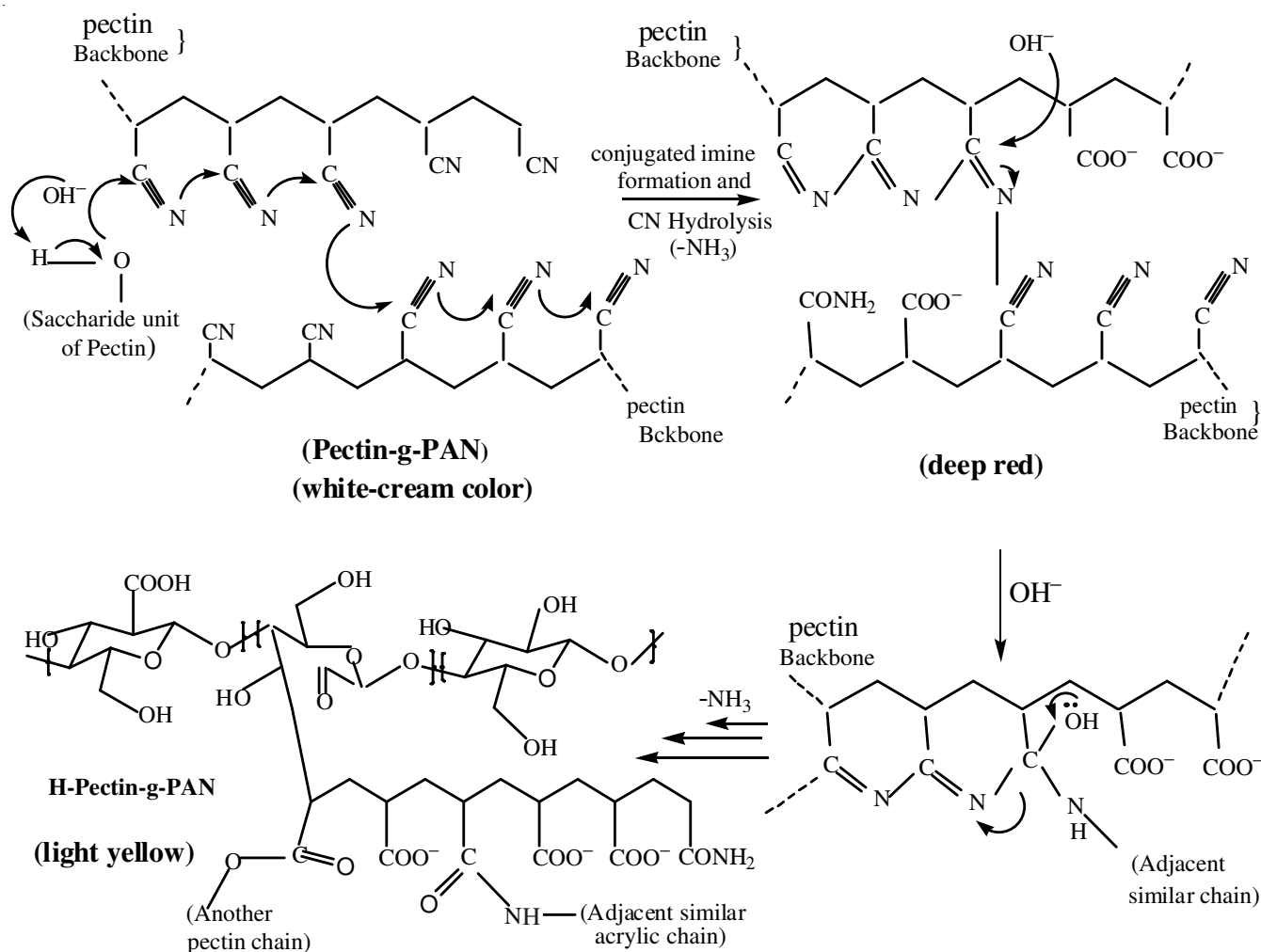
pH-sensitivity: pH-sensitivity of the hydrogel was investigated in terms of swelling and deswelling of the final product at two basic (pH 8) and acidic (pH 2) solutions, respectively. Swelling capacity of the hydrogels at each pH was measured according to eqn. 1 at consecutive time intervals (0.5 h).

RESULTS AND DISCUSSION

Mechanism of hydrogel formation: A general reaction mechanism for pectin-poly(acrylonitrile) hydrogel formation is shown in **Scheme-I**. At the first step, hydroxyl groups of pectin substrate was converted to corresponding alkoxide ions using sodium hydroxide solution (**Scheme-I**). Then, these macroalkoxides initiate crosslinking reaction between some adjacent polyacrylonitrile pendant chains. This reaction leads to intermediate formation of naphthyridine cyclic structures (including imine, -C=N-, conjugated bonds) with deep red colour. The intermediate was then hydrolyzed using residual sodium hydroxide aqueous solution to produce hydrophilic carboxamide and carboxylate groups (**Scheme-I**) with a resulting colour change from red to light yellow. This sharp colour change was used as an indication to halt the alkaline treatment. However, incompletely hydrolyzed structures may also give rise to a few crosslinking points result in a loosely crosslinked network. It has been reported, in the case of H-SPAN, a maximum conversion of 70 % of nitrile to carboxyl groups and the remaining 30 % are amide groups¹⁶. In fact, details of the chemical processes and mechanism involved in H-SPAN synthesis are not yet well understood. For instance, the incomplete hydrolysis is interpreted as being related to steric and polar factors¹⁷. Weaver *et al.*¹⁸ suggested that condensation might also occur between carboxyl and amide groups to form imide structures. Therefore, in the case of hydrogel, pectin-poly(NaAA-co-AAm), we realized that precise control of the ratio is practically impossible.

Fig. 1 shows the FTIR spectra of pectin-polyacrylonitrile physical mixture and the resulted hydrogel, pectin-poly(NaAA-co-AAm). The band observed at 2242 cm^{-1} can be attributed to stretching of -CN group of polyacrylonitrile (Fig. 1b). The hydrogel comprise an pectin backbone with side chains that carry carboxamide and carboxylate functional groups that are evidenced by three new peaks at 1407 , 1556 and 1675 cm^{-1} (Fig. 1c). These peaks attributed to C=O stretching in carboxamide functional groups and symmetric and asymmetric stretching modes of carboxylate groups, respectively¹⁹. The stretching band of -NH overlapped with the -OH stretching band of the pectin portion of the copolymer. As shown in Fig. 1c (**Scheme-I**), after alkaline hydrolysis, most of the nitrile groups are converted to carboxamide and carboxylate groups.

To obtain an additional evidence of *in situ* crosslinking during alkaline hydrolysis, a similar reaction was conducted in absence of the polysaccharide. Since the resulted product became soluble, the crosslinks really formed between the alkoxide ions of pectin and the nitrile groups of polyacrylonitrile. This fact practically proves that the starch hydroxyls are involved in the crosslinking.



Scheme-I Proposed mechanism for crosslinking during the hydrolysis of nitrile groups of the Pec-polyacrylonitrile mixture to produce the Pec-g-poly(acrylonitrile) hydrogel.

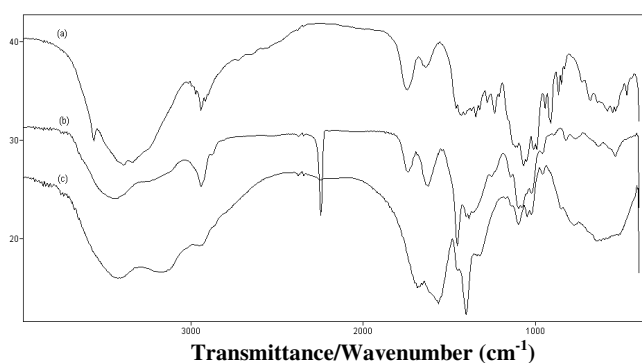


Fig. 1. FTIR spectra of Pectin (a), Pectin-g-polyacrylonitrile, and (c) H-Pectin-g-polyacrylonitrile

Scanning electron microscopy: 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. Fig. 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.

Optimization of the reaction conditions: All factors affecting on the saponification reaction of pectin-polyacrylonitrile mixture were systematically optimized to achieve superabsorbent with maximum water absorbency.

Effect of alkalization time: Fig. 3 depicts the effect of alkylation time on the swelling ratio. The alkalization time of the hydroxyl groups of pectin was varied from 20 to 95 min. The alkaline hydrolysis conditions were kept constant (1N NaOH, 85 °C). As shown in the figure, the absorbency is decreased with increasing the alkalization time. This swelling loss can be attributed to some sort of unwanted alkaline degradation of the polysaccharide. This disconnection decreases the main chain molecular weight. Since the swelling capacity is proportionally depended on the molecular weight of the chains in the networks of superabsorbent hydrogels²⁰, the unwanted disconnection results in the swelling-loss even though it is unextensive. Similar alkaline degradation behaviours were already reported in the case of other polysaccharides²¹. In addition, more -OH groups are converted to corresponding alkoxide anions at longer alkalization times (**Scheme-I**). Therefore, a higher crosslinked, rigid structure is formed. It is known that a higher degree of crosslinking results in a rigid network that can not hold a large quantity of fluid^{20,22,23}. Maximum water absorbency (523 g/g) was achieved at the time of 47 min. In

fact, with alkylation time lower than 47 min no gel is prepared, so that the swollen gel strength is not sufficient to be referred as a “real superabsorbent”.

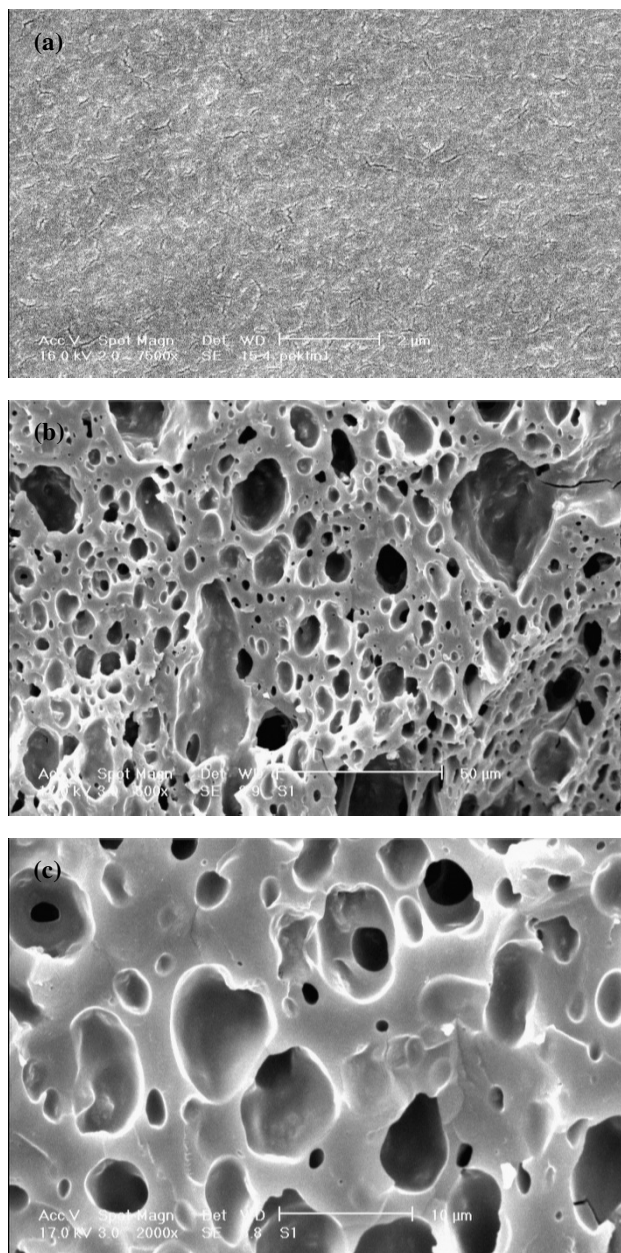


Fig. 2. SEM photograph of the pectin(a) and hydrogel surfaces with scale bar 10 and 50 μm (b,c)

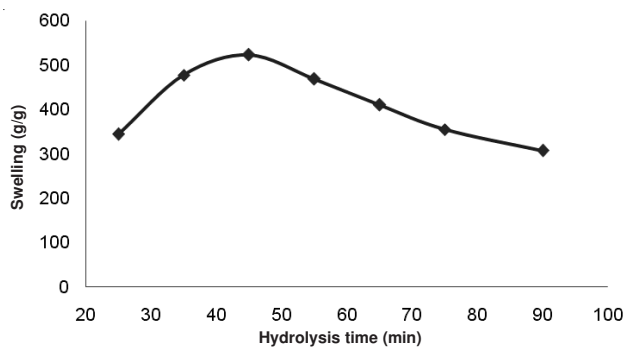


Fig. 3. Effect of alkylation time on swelling capacity of H-pectin-g-polyacrylonitrile hydrogel. Reaction conditions: NaOH 1N, alkaline hydrolysis temperature 85 $^{\circ}\text{C}$

Effect of alkalization temperature: Fig. 4 illustrates the effect of temperature of alkylation reaction on equilibrium swelling. The alkaline hydrolysis conditions were kept constant as mentioned above. As it is obvious from the figure, the temperature leading the hydrogel with highest absorbency (465 g/g) is around 85 $^{\circ}\text{C}$. The lower and higher temperatures than this optimum temperature resulted in reduced swelling capacity. This behaviour suggests the incomplete alkylation reaction at lower temperatures and alkaline degradation of the polysaccharide at higher temperatures.

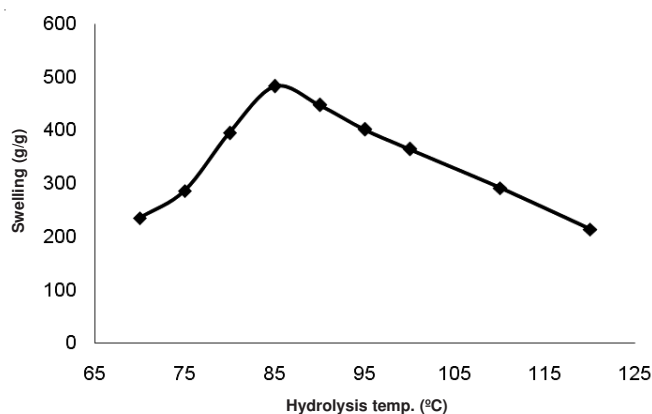


Fig. 4. Effect of hydrolysis temperature on the swelling capacity of H-pectin-g-polyacrylonitrile. Reaction conditions: alkylation time 1 h, NaOH1N, alkaline hydrolysis temperature 85 $^{\circ}\text{C}$.

Effect of NaOH concentration: Fig. 5 demonstrates the effect of NaOH concentration on swelling capacity of pectin-poly(NaAA-co-AAm) hydrogel. Alkaline hydrolysis reaction was carried out at 85 $^{\circ}\text{C}$ for 1 h. Maximum swelling capacity (450 g/g) was obtained at 1N NaOH. It is obvious that the higher the NaOH concentration leads to more carboxamide and carboxylate groups. The concentrations of NaOH higher than 1N, however, lead to low-swelling superabsorbents. This swelling-loss can be related to residual (excess) alkaline, which was not removed (*e.g.* neutralized), after completion of hydrolysis. The excess cations shield the carboxylate anions, so that the main anion-anion repulsive forces are eliminated and a less expanded networks of the hydrogel being able to uptake and retain lower quantities of the aqueous solution. This phenomenon is often referred to as charge screening effect²³. In addition, a higher crosslinked structure formed at higher OH-concentration. A similar observation has been reported by Castel *et al.*²⁴ in the case of the hydrolysis of starch-g-polyacrylonitrile. Furthermore, alkaline degradation of the polysaccharide part of network can be another reason of the swelling decrease in highly concentrated alkaline hydrolytic media.

Effect of salinity on swelling capacity: The swelling capacity of superabsorbent hydrogels could be significantly affected by various factors of the external solutions such as its valencies and salt concentration²³. The presence of ions in the swelling medium has a profound effect on the absorbency behaviour of the superabsorbent hydrogels. Many theories were reported in the case of swelling behaviour of ionic hydrogels in saline solutions. The simplest one of the theories is Donnan equilibrium theory. This theory attributes the electrostatic interactions (ion swelling pressure) to the difference

between the osmotic pressure of freely mobile ions in the gel and in the outer solutions. The osmotic pressure is the driving force for swelling of superabsorbents. Increasing the ionic mobile ion concentration difference between the polymer gel and external medium which, in turn, reduces the gel volume, *i.e.* the gel shrinks and swelling capacity decreases (charge screening effect). In addition, in case of salt solutions with multivalent cations, ionic crosslinking at surface of particles causing an appreciable decrease in swelling capacity. For example, Castel *et al.*²⁴ reported that calcium ion can drastically decrease the swelling capacity for a hydrolyzed starch-graft-polyacrylonitrile, due to the complexing ability of the carboxylate group to include the formation of intra- and inter-molecular complexes.

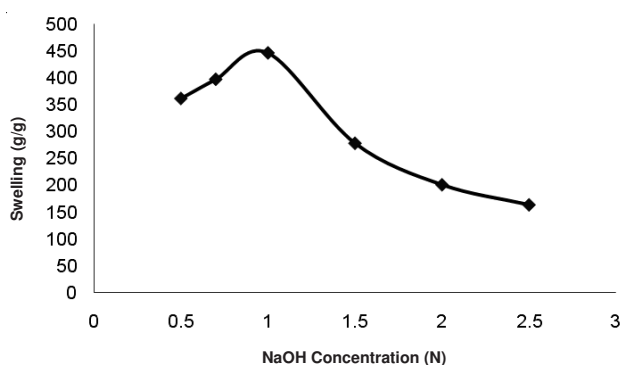


Fig. 5. Effect of NaOH concentration on the swelling capacity of H-pectin-g-polyacrylonitrile superabsorbent hydrogel. Reaction conditions: hydrolysis temperature 85 °C hydrolysis time 1 h

The effect of charge of cation on swelling can be concluded from Fig. 6. With increasing the charge of cation, degree of crosslinking is increased and swelling is consequently decreased. Therefore, the absorbency of the synthesized hydrogel is in the order of NaCl > CaCl₂ > AlCl₃. Fig. 6 also shows the swelling capacity of the hydrogel, [pectin-poly(acrylonitrile)], as a function of the salt concentration for NaCl, CaCl₂ and AlCl₃ solutions. The results reveal that the swelling ratio decreases as the salt concentration of the medium increases.

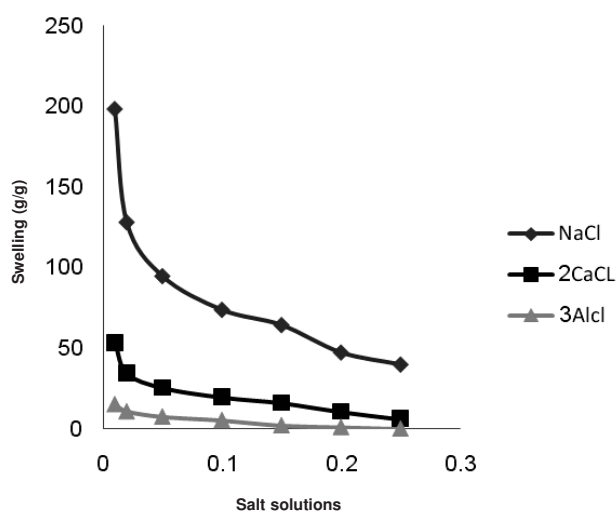


Fig. 6. Swelling capacity of the hydrogel (prepared from the pectin-g-polyacrylonitrile with optimum conditions) in chloride salt solutions with different size of cations

pH-depending swelling: Most ionic hydrogels are pH-sensitive and, therefore, the pH of the swelling medium has direct control over the degree of absorbency capacity of the network. So, the equilibrium swelling of pectin-poly(acrylonitrile) hydrogel was measured at solutions with various pH ranged from 1 to 13 (Fig. 7). Since the swelling capacity of all anionic hydrogels is appreciably decreased by addition of counter ions (cations) to the swelling medium, no buffer solutions were used. Therefore, stock NaOH (pH 13) and HCl (pH 1) solutions were diluted with distilled water to reach desired basic and acidic pHs, respectively. Maximum swelling (157 g/g) was obtained at pH 8. In the pH region from 1 to 3, most of carboxylate groups are in the form of -COOH and the low swelling values of hydrogels can be attributed to the presence of non-ionic hydrophilic COOH and -OH groups in the hydrogel network. The swelling ratio increased rapidly as the pH of solutions was increased from 4 to 8. At higher pHs (4-8), some of carboxylate groups are ionized and the electrostatic repulsion between COO⁻ groups causes an enhancement of the swelling capacity. The reason of the swelling-loss for the highly basic solutions (pHs > 8) is charge screening effect of excess Na⁺ in the swelling media which shield the carboxylate anions and prevent effective anion-anion repulsion. Similar swelling -pH dependencies have been reported in the case of other hydrogel systems²⁵⁻²⁸.

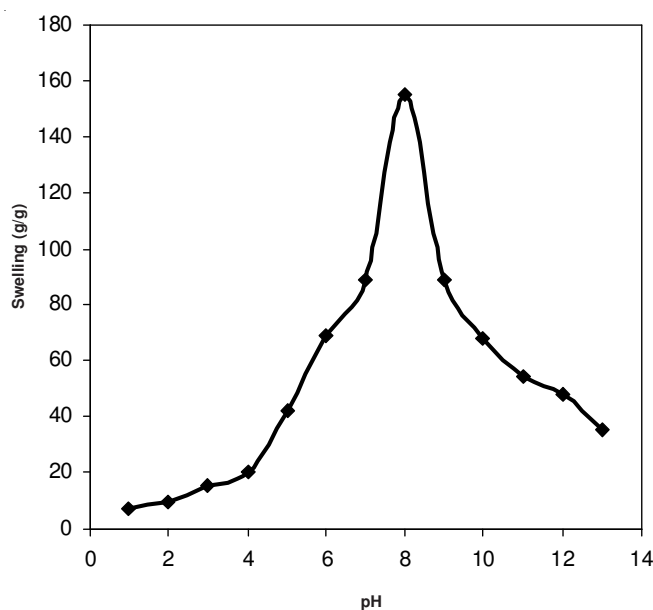


Fig. 7. Effect of buffered pH on swelling capacity of the H-pectin-g-polyacrylonitrile. Hydrogel prepared from pectin-g-polyacrylonitrile copolymer with optimum conditions

Conclusion

The superabsorbent hydrogel, pectin-poly(acrylonitrile), was synthesized through alkaline hydrolysis of pectin-polyacrylonitrile physical mixture. The reaction of pectin alkoxide anions with nitrile groups of polyacrylonitrile, forms cross-linking points and results in a three-dimensional network. Because a polymerization reaction is not involved, so there is no need to initiator, toxic and/or expensive monomer and crosslinker. Therefore, problems such as polymerization

control, conversion loss and residual monomer are eliminated. Indeed, since no toxic material is used for the synthesis, this practical approach may be preferred to as a relatively green process. In addition, this one-step preparative method conducted under normal atmospheric conditions in a short period of time. The dark red-yellow colour change provides a visual indication for recognizing the reaction completion. The reaction conditions were attempted to be optimized for obtaining hydrogels with higher swelling values. So, the maximum water absorbency (523 g/g) was achieved under the optimum conditions that found to be: alkalization time 1 h, alkalization temperature 85 °C, NaOH 1N, polyacrylonitrile, alkaline hydrolysis time 1 h. Swelling measurement of the synthesized hydrogels in different salt solutions showed appreciable swelling capacity, especially in NaCl solutions. However, swelling-loss in salt solutions, in comparison with distilled water, can be attributed to charge screening effect and ionic crosslinking for mono- and multi-valent cations, respectively. Also the superabsorbent hydrogels exhibited high sensitivity to pH, so that, several swelling changes of the hydrogel were observed in lieu of pH variations in a wide range (1-13).

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