

# Synthesis, characterization and salt resistance swelling behavior of psy-g-poly(AA) hydrogel

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Received: 10 June 2010, Revised: 21 July 2010 and Accepted: 22 July 2010

## ABSTRACT

Psyllium, a medicinally important natural polymer was functionalized with acrylic acid using FAS-H<sub>2</sub>O<sub>2</sub> as redox initiator and glutaraldehyde as a crosslinker. Synthesized hydrogel was characterized with FTIR spectroscopy, SEM and TGA/DTA techniques to know their surface morphology and thermal stability. Salt resistant swelling behavior of synthesized hydrogel was studied in different salt solutions as a function of concentration of salt, temperature and pH. It was found that synthesized hydrogel showed maximum swelling (514.0 %) in NaCl solution followed by NH<sub>4</sub>Cl, MgCl<sub>2</sub>, CaCl<sub>2</sub> and BaCl<sub>2</sub> solution. Psy-g-poly(AA) hydrogel showed maximum swelling (863.49%) at 30 °C in distilled water. Copyright © 2010 VBRI press.

**Keywords:** Graft copolymers; hydrogel; swelling; thermogravimetric analysis.



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## Introduction

Polymeric hydrogels are water-swollen polymeric materials that maintain a distinct three-dimensional structure [1]. Their classification may be based on the source, nature of the crosslinking and networks, presence of pores and their fate in an organism. Hydrogels possess excellent biocompatibility due to their high water content. The amount of water in the equilibrium swollen state is a balance between the thermodynamic force of mixing (hydration) and the retractive force of the three-dimensional network. The mixing force depends mainly on the hydrophilicity of the polymer backbone and the retractive force on the number of crosslinks connecting polymer chains into a three-dimensional network [2, 3].

Pourjavadi et al [4] have synthesized acrylated starch based hydrogels by introducing acrylic groups onto starch backbone. Effect of salinity and pH of solutions on the swelling of hydrogels was investigated and it was found that acrylamide grafted hydrogels are less sensitive to these factors as compared to acrylic acid grafted hydrogels. Various researchers have studied the synthesis, characterization, swelling behavior and controlled drug delivery of the polymer hydrogels [5-7].

Kaith et al synthesized psyllium and acrylic acid based hydrogels under the influence of  $\gamma$ -radiations [8]. Swelling behavior of the synthesized hydrogel was investigated in distilled water as functions of time, temperature, and pH and hydrogel showed maximum swelling at 25 °C for 24 h. Hydrogel has been found to follow Non-Fickian type mechanism for the fungicide release. Singh et al have developed psyllium based hydrogels through graft copolymerization and characterized using SEMs, FTIR and swelling studies [9]. It was reported that the composition of the composite polymer matrix and nature of the swelling medium affect the swelling of the hydrogels. Swelling of hydrogels and release of tetracycline HCl from the drug loaded hydrogels have been observed more in pH 2.2 buffer as compared to the pH 7.4 buffer. They have reported that release of model antibiotic drug tetracycline HCl from the present drug delivery system may be used for the antibiotic therapy of peptic ulcer developed through *Helicobacter pylori*. The swelling and release of drug occurred through non-Fickian diffusion mechanism. Psyllium and *N*-hydroxymethylacrylamide based polymeric networks were prepared by Singh et al [10]. Synthesized hydrogels were characterized with scanning electron micrography, FTIR and thermogravimetric analysis techniques to study various structural aspects of the networks and swelling response of the polymeric networks were also studied as a function of time, temperature, pH and salt. Graft copolymerization of monomers onto natural polymers was reported by various researchers for synthesis of polymeric materials [11-13].

In present paper, a cross-linked three dimensional network of psyllium with acrylic acid has been synthesized using FAS-H<sub>2</sub>O<sub>2</sub> as an initiator [14] and glutaraldehyde as a crosslinker. The polymer formed was further studied for its salt-resistant behavior in different salt solutions such as NaCl, MgCl<sub>2</sub>, CaCl<sub>2</sub>, BaCl<sub>2</sub> and NH<sub>4</sub>Cl as a function of concentration, temperature and pH.

## Experimental

### Materials

*Plantago psyllium* (Sidhpur Sat-Isabgol Factory, India), acrylic acid (CDH), FAS: H<sub>2</sub>O<sub>2</sub> (SD fine) and glutaraldehyde (SD fine) were used as received. Weighing was done on electronic balance (LIBROR AEG-220 Shimadzu), FTIR spectra of the gels were recorded in KBr pellets using Perkin Elmer spectrophotometer, SEM of the samples were taken on Jeol Steroscan 150 Microscope and thermal studies were carried-out on Leinsis thermal analyzer at a heating rate of 10 °C/min in air.

### Synthesis of psy-g-poly(AA) hydrogel

Psyllium (0.5 g) was taken in a petri dish and a known volume of solvent (10 ml) was added. Known amount of initiator ratio (1:16.91) was added to the reaction mixture followed by the addition of known amount of acrylic acid (AA) with continuous stirring. The reaction was carried out at a definite temperature (60 °C), pH and for a particular time interval (60 min). Different reaction parameters such as reaction time, reaction temperature, initiator concentration, amount of solvent, and pH of the reaction medium were optimized, so as to get the optimized graft yield. The percent grafting ( $P_g$ ) was calculated as per the method reported in the literature. Homopolymer was removed by soxhlet extraction with acetone [15]. The graft copolymer obtained was dried at 45 °C till constant weight was obtained. The percent grafting ( $P_g$ ) was calculated as per the following equation (a) [13, 15]:

$$P_g = \frac{W_g - W_0}{W_0} \times 100 \text{ ----- (a)}$$

Where,  $W_g$  and  $W_0$  are the weights of grafted and ungrafted samples, respectively.

Graftcopolymer was further crosslinked using glutaraldehyde to give psy-g-poly(AA) product. Optimization of AA and glutaraldehyde was carried-out with respect to percent swelling ( $P_s$ ) in distilled water and  $P_s$  was calculated as per the following equation (b):

$$P_s = \frac{W_s - W_d}{W_d} \times 100 \text{ ----- (b)}$$

Where,  $W_s$  and  $W_d$  are the weights of swelled and dry samples, respectively.

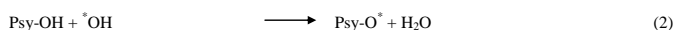
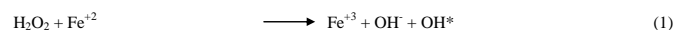
*Salt-resistant swelling behavior*

Psy-g-poly(AA) was studied for its salt resistant behavior by taking different salt solutions such as NaCl, MgCl<sub>2</sub>, CaCl<sub>2</sub>, BaCl<sub>2</sub> and NH<sub>4</sub>Cl of varying concentrations (0.5%, 1%, 5%, 10% and 15%). 0.1 g of psy-g-poly(AA) was immersed in each saline solution for 24 h at 25°C. The swollen samples were wiped, weighed and the percent swelling (P<sub>s</sub>) was calculated. Further, temperature dependent swelling of crosslinked sample was optimized by immersing 0.1 g of sample in optimum concentration of each salt solution for 24 h at 30, 40, 50, 60 and 70 °C. Similarly, pH dependent swelling was carried-out at optimum temperature in 0.5N HCl, distilled water and 0.5N NaOH.

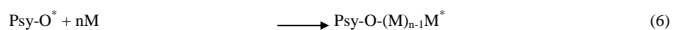
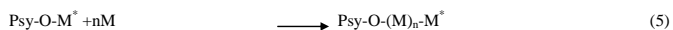
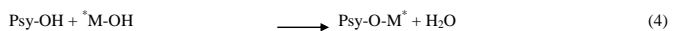
## Results and discussion

–OH groups present on the back bone polymer act as the active sites for the graft copolymerization of poly(AA) onto it and can explained through the following mechanism:

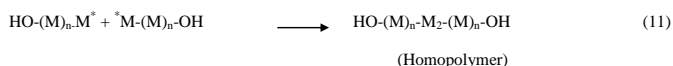
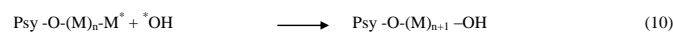
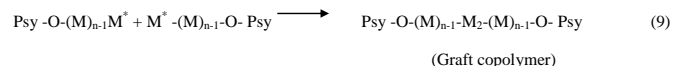
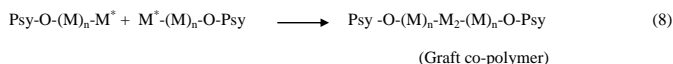
### Initiation



### Propagation



### Termination



M<sup>•</sup> = monomer free radical; Psy-O<sup>•</sup> = Backbone free radical

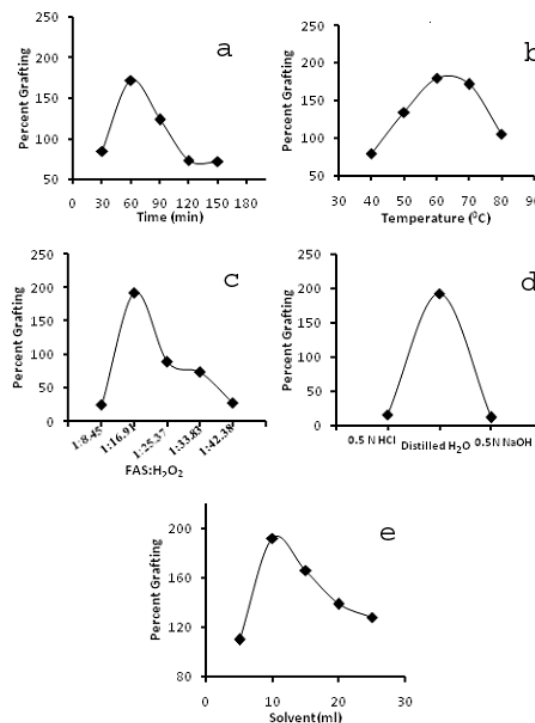
In the above discussed mechanism, reaction of FAS with H<sub>2</sub>O<sub>2</sub> has given <sup>•</sup>OH. Psyllium is attacked by <sup>•</sup>OH, thereby resulting in the formation of free radical site on the backbone and monomer, which further results in the formation of graft copolymer. However, the termination of the reaction takes place either by reaction between <sup>•</sup>OH and a free radical or the reaction between two activated chains. Multifunctional nature of glutaraldehyde leads to the formation of three dimensional networks between psyllium and poly(AA).

### Optimization of different reaction parameters

It is evident from **Fig. 1a**, P<sub>g</sub> increases with increase in reaction time and maximum P<sub>g</sub> was found to be (172.04 %) at 60 min. However, further increase in reaction time resulted in decrease of P<sub>g</sub>. The active sites on the backbone and monomer increases with increase in reaction time result in enhanced grafting of monomer on psyllium. Beyond the

optimum reaction time, the concentration of free radicals limits the length of polymeric chain by initiating numerous chains simultaneously, which results in decreased P<sub>g</sub> [16].

P<sub>g</sub> increases with increase in temperature and maximum P<sub>g</sub> was found to be (180.48 %) at 60 °C (**Fig. 1b**). However, further increase in temperature resulted in decrease of P<sub>g</sub>. This could be attributed to the fact that homo-polymerization predominates over graft copolymerization at higher temperature [17].



**Fig. 1.** Effect of reaction parameters onto percent grafting (P<sub>g</sub>) (a) reaction time (b) reaction temperature (c) initiator ratio (d) pH (e) amount of solvent.

It has been found that P<sub>g</sub> increases with increase in initiator concentration up to 1:16.91 and maximum grafting was found to be 192.48% and further increase in concentration of initiator ratio results in decrease of percent grafting (**Fig. 1c**). It is due to the fact that at higher initiator concentration, photopolymerization predominate graft copolymerization.

**Fig. 1d** showed the effect of pH on percent grafting. Graft copolymerization was carried out in acidic (0.5N HCl), neutral (distilled water) and basic (0.5N NaOH) medium and maximum grafting (192.48 %) was found in neutral medium, whereas acidic and basic medium results in negligible grafting. This is due to the reason that H<sup>+</sup> ion of the active -OH groups on the backbone chains got replaced with that of Na<sup>+</sup>, thereby, decreasing the number of active sites present on the backbone chain and leading to negligible P<sub>g</sub> [16].

Amount of solvent plays an important role in graft copolymerization (**Fig. 1e**). Maximum P<sub>g</sub> (192.48 %) was found with 10 ml of solvent and further increase in the amount of solvent results in decreased P<sub>g</sub>. This can be explained on the basis of <sup>•</sup>OH concentration, which is sufficient to propagate the polymerization reaction till optimum concentration is reached and further increase in

the amount of solvent resulted in termination of polymerization (Fig. 1e, eq. 10) [16].

Fig. 2a shows the effect on monomer concentration on percent swelling. It has been found that with increase in monomer concentration, the percent swelling first increases up to  $6.873 \times 10^{-1} \text{ molL}^{-1}$  and then it decreases with increase in monomer concentration. This can be explained on the basis that increases in monomer concentration beyond optimum level results in increased self crosslinking, which prevents the accessibility of more solvent into the polymeric matrix. Moreover, the viscosity of the reaction medium increases with increase in monomer concentration, thereby, hindering the free movement of free radicals and monomer molecules [18].

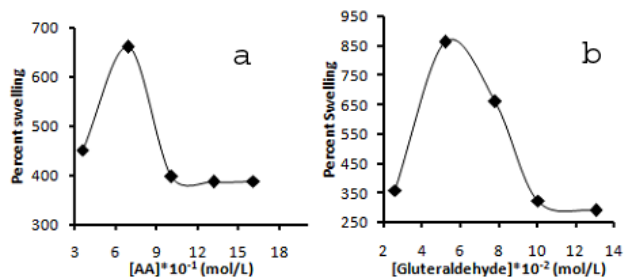


Fig. 2. Effect of (a) acrylic acid (b) glutaraldehyde onto percent swelling ( $P_s$ ).

Fig. 2b shows the effect of crosslinker on percent swelling. Percent swelling goes on increasing up to 863.49 % with the increase in crosslinker concentration, followed by a decrease in percent swelling. This is due to the reason that at higher crosslinker concentration, smaller pore size prevents solvent molecules to approach the matrix [18].

#### Characterization of psy-g-poly(AA)

FTIR spectra: FTIR spectra of psyllium (Fig. 3) and psyllium-g-poly(AA) (Fig. 4) has been studied. In case of psyllium, the absorption bands at  $3404.1 \text{ cm}^{-1}$  has been observed due to  $-\text{OH}$  stretching. In addition, absorption bands at  $2926.7 \text{ cm}^{-1}$  has been observed due to  $-\text{OH}$  and  $-\text{CH}$  stretching vibration. Absorption bands at  $1431.1 \text{ cm}^{-1}$  and  $1037.5 \text{ cm}^{-1}$  have been observed due to C-H deformation vibration and C-O stretching vibration, respectively. Whereas in case of psy-g-poly(AA), an addition peak appears at  $1726.0 \text{ cm}^{-1}$  has been observed due to the stretching of  $-\text{COOH}$  group of AA.

Morphological studies: Scanning electron micrographs were taken to differentiate the morphological differences on the surface of both psyllium and psy-g-poly(AA). Morphological changes in psyllium are quite evident after grafting and networking. Fig. 5b clearly showed that psy-g-poly(AA) has some crosslinked networks and porous structure, whereas psyllium has smooth and homogenous structure (Fig. 5a).

Thermal behavior of hydrogel: TGA/DTA studies of both the backbone and functionalized polymer were performed as a function of percent weight loss vs. temperature. In case of psyllium, three stage decompositions have been observed (Fig. 6). Primary decomposition reactions due to

dehydration were observed upto  $225 \text{ }^\circ\text{C}$  with 13.3 % weight loss. First stage decomposition has been observed from  $225 \text{ }^\circ\text{C} - 312 \text{ }^\circ\text{C}$  with 44.7 % weight loss. Second

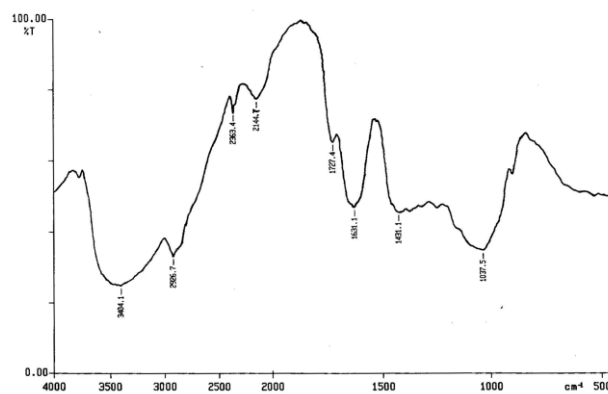


Fig. 3. FTIR spectra of psyllium.

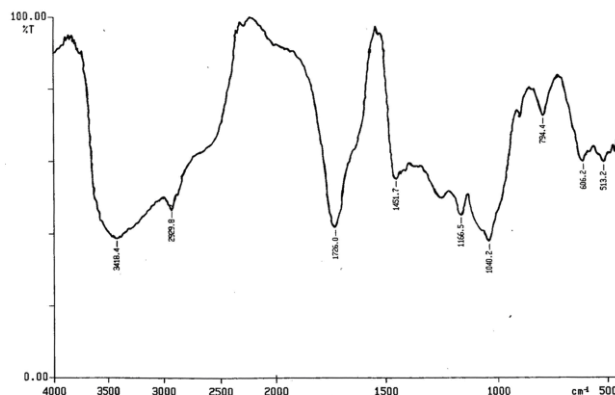


Fig. 4. FTIR spectra of psy-g-poly(AA).

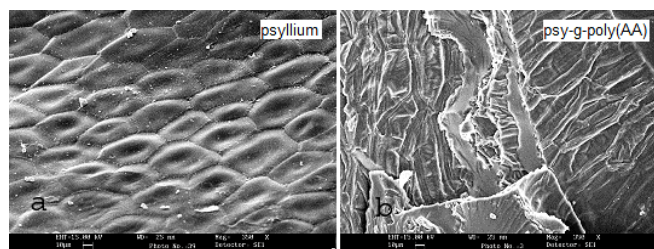


Fig. 5. SEM (a) psyllium (b) psy-g-poly(AA).

stage decomposition started at  $312 \text{ }^\circ\text{C}$  and continues upto  $432 \text{ }^\circ\text{C}$  with 17.2 % weight loss. Third stage decomposition started at  $432 \text{ }^\circ\text{C}$  and continues upto  $524 \text{ }^\circ\text{C}$  with 19.0 % weight loss. Psyllium showed initial decomposition temperature (IDT) at  $225 \text{ }^\circ\text{C}$  and final decomposition temperature (FDT) at  $524 \text{ }^\circ\text{C}$  while psy-g-poly(AA) showed initial decomposition temperature at  $149 \text{ }^\circ\text{C}$  and final decomposition temperature at  $528 \text{ }^\circ\text{C}$ . In case of psy-g-poly(AA), two stage decompositions has been observed (Fig. 7). Primary reaction takes place upto  $149 \text{ }^\circ\text{C}$  with 9.7 % weight loss. First stage decomposition started at  $149 \text{ }^\circ\text{C}$  and continues upto  $443 \text{ }^\circ\text{C}$  with

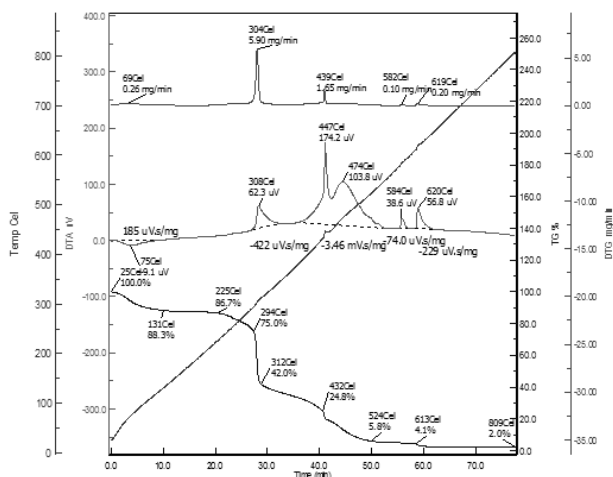


Fig. 6. TGA/DTA of psyllium.

maximum weight loss (61.0 %). Second stage decomposition started at 443 °C and continues upto 528 °C with 27.9 % weight loss. IDT of psy-g-poly(AA) is lower than that of psyllium because psy-g-poly(AA) underwent morphological changes during grafting which disturbed its crystalline structure whereas its FDT is slightly higher than that of psyllium which shows more thermal stability as compared to the raw back bone. Psyllium showed five exothermic peaks at 308 °C (62.3 $\mu$ V), 447 °C (174 $\mu$ V), 474 °C (103 $\mu$ V), 584 °C (38.6  $\mu$ V) and 620°C (56.8  $\mu$ V). On the other hand, psy-g-poly(AA) showed exothermic peaks at 485 °C (172  $\mu$ V).

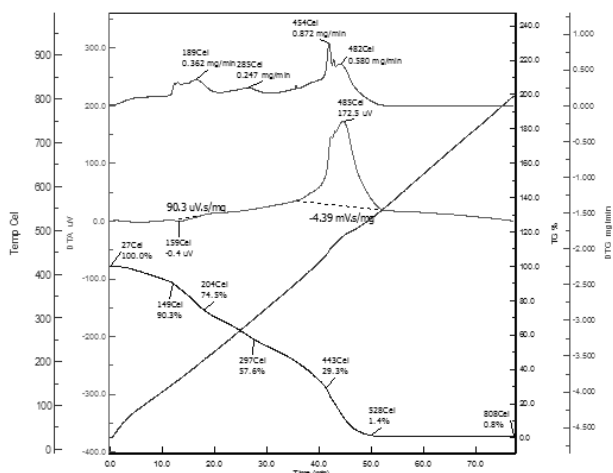


Fig. 7. TGA/DTA of psy-g-poly(AA).

*Salt resistant swelling behavior*

Effect of concentration of salt on  $P_s$ : The  $P_s$  of the hydrogel has been studied at different concentration (0.5, 1, 5, 10 and 15 %) of salt solution. It was found that  $P_s$  decreases with increase in concentration of salt solution. This is due to reverse osmosis process. Maximum swelling has been found at 0.5 % concentration in all the different salt solutions (Fig. 8).

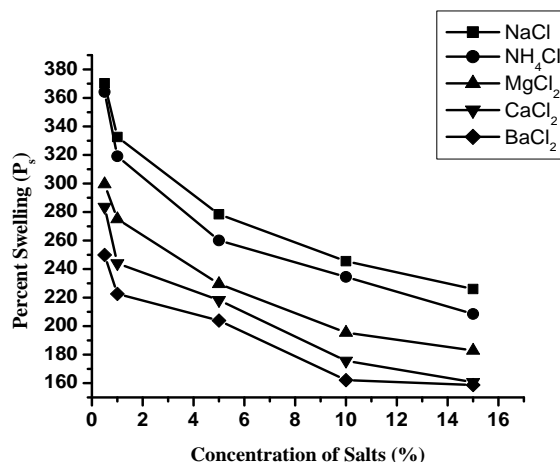


Fig. 8. Effect of concentration of salt onto percent swelling.

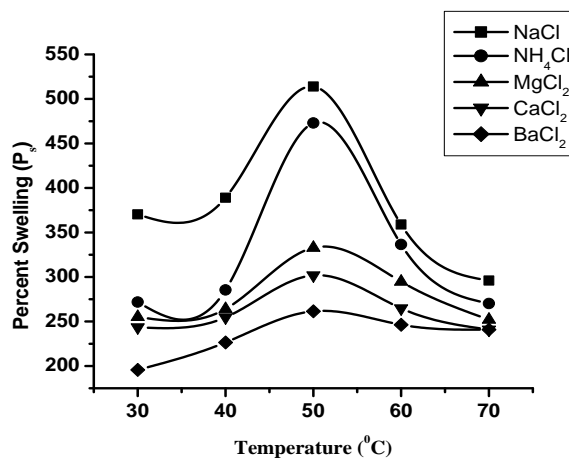


Fig. 9. Effect of temperature onto percent swelling.

Effect of temperature on  $P_s$ : Swelling temperature has been varied from 30-70 °C (Fig. 9). It was observed that  $P_s$  increases with increase in temperature and is maximum at 50 °C. However, further increase in temperature resulted in decreased  $P_s$ . This may be due to the reason that hydrogel tends to become more compact at higher temperature leading to desorption of solvent and resulted in decreased  $P_s$  [16].

Effect of pH on  $P_s$ : The water absorbing capacity of the polymer was investigated in different pH value (0.5N HCl for acidic medium, distilled water for neutral and 0.5N NaOH for basic medium). It was found that the hydrogel is pH sensitive and unstable in acidic and basic medium but showed appreciable swelling in distilled water (Fig. 10).

Effect of charge and size of cation on  $P_s$ : It was found that the swelling capacity of semi-IPN hydrogels appreciably decreased in saline solution as compared with the values measured in distilled water.

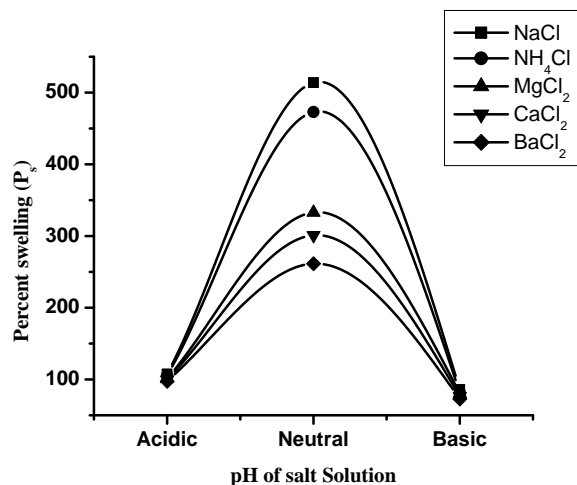
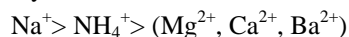


Fig. 10. Effect of pH of salt solution onto percent swelling.

The swelling capacity decreased with increasing charge of the cation of the salts. It is due to charge screening effect of additional cation causing non-perfect anion-anion electrostatic repulsion, leading to decreased osmotic pressure (ionic pressure) difference between the polymer network and the external solution [18]. Therefore, the swelling capacity would be in the order:



It was also found that among the same valent ions that lesser the size of cation, more is the swelling capacity and can be arranged in the following order:  $\text{Na}^+ > \text{NH}_4^+ > \text{Mg}^{2+} > \text{Ca}^{2+} > \text{Ba}^{2+}$ .

## Conclusion

The forgone study deals with the synthesis of hydrogel based on psyllium and AA through free radical graft copolymerization in the presence of FAS-H<sub>2</sub>O<sub>2</sub> initiator and glutaraldehyde cross-linker. It was found that hydrogel showed salt resistant swelling behavior in different saline solutions, which can be utilized in water treatment technology. Hydrogel was found to be pH as well as temperature sensitive, which widens its scope in medical sector as drug delivery devices.

## Acknowledgements

Ms. Anjna is highly thankful to the University Grant Commission, India for project fellowship and NIT, Hamirpur (H.P.) as this study was carried out under UGC- project in the Applied Chemistry Research Laboratory, NIT, Hamirpur (H.P.).

## References

1. Wichterle, O.; Lim, D. *Nature* **1960**, *185*, 117.
2. Dusek, K.; Prins, W. *Adv Polym Sci* **1969**, *6*, 1.
3. Kopec, J.; Yang, J. *J Polym Int* **2007**, *56*, 1078.
4. Pourjavadi, A.; Jahromi, P.E.; Seidi, F.; Salimi, H. *Carbohydrate Polymers* **2010**, *79*, 933.
5. Chen, L.Y.; Chen, J. *Carbohydrate Polymers* **2010**, *79*, 500.
6. Liu, T.; Lin, Y. *Acta Biomaterialia* **2010**, in press.
7. Wang, Q.; Zhang, J.; Wang, A. *Carbohydrate Polymers* **2009**, *78*, 731.
8. Kumar, K.; Kaith, B.S. *Fibers and Polymers* **2010**, *11*, 147.
9. Singh, B.; Sharma, V. *International Journal of Pharmaceutics* **2010**, doi:10.1016/j.ijpharm.2010.01.022.

10. Singh, B.; Chauhan, G.S.; Sharma, D.K.; Kant, A.; Gupta, I.; Chauhan, N. *International Journal of Pharmaceutics* **2006**, *325*, 15.
11. Sharma, A. K.; Mishra, A. K. *Advanced Materials Letters* **2010**, *1*, 59.
12. Singh, V.; Sharma, A.K.; Sanghi, R. *Journal of Hazardous Materials* **2009**, *166*, 327.
13. Kaith, B. S.; Kalia, S. *Int. J. Polym. Anal. Charact.* **2007**, *12*, 401.
14. Barros, J.A.G.; Fechine, G.J.M.; Alcantara, M.R.; Catalani, L.H. *Polymer* **2006**, *47*, 8414.
15. Kaith, B.S.; Kumar, K. *Express Polym. Lett.* **2007**, *1*, 474.
16. Kaith, B.S.; Kumar, K. *Bull. Mater. Sci.* **2007**, *30*, 387.
17. Kaith, B.S.; Kumar, K. *e-polymers* **2007**, 002.
18. Pourjavadi, A.; Mahdavinia, G.R. *Turk. J. Chem.* **2006**, *30*, 595.