Pectin and Acrylamide Based Hydrogels for Environment Management Technologies: Synthesis, Characterization, and Metal Ions Sorption

Ghanshyam S. Chauhan, Anita Kumari, Rakesh Sharma

Department of Chemistry, Himachal Pradesh University, Shimla 171 005, India

ABSTRACT: The present article describes various aspects of preparation and characterization of hydrogels based on pectin and three different amide monomers viz: acrylamide (AAm), *N*-isopropyl acrylamide (*N*-i-PAAm), and 2-acrylamido-2-methyl-1-propane sulfonic acid (AAmPSA). Hydrogels have been prepared by graft copolymerization as well as in the presence of crosslinker *N*,*N*-Methylene bisacrylamide ((*N*,*N*-MBAAm) and initiated by redox system comprising of ammonium peroxysulphate–ferrous ammonium sulfate (APS: FAS) at two temperatures. Hydrogels thus synthesized have been characterized by SEM, FTIR, and water uptake studies. The later has been carried as a function of time, temperature, pH, crosslinker concentration,

and temperature at which the hydrogels were prepared. Candidate hydrogels have been used for the sorption of some common metal ions pollutants found in soil, industrial, and mining water bodies. Biodegradability studies have been carried by soil burial method to investigate the effect of chemical modification on biodegradability of pectin and to understand the possibility of eco-friendly nature and to explore the scope of reusability of the hydrogels and waste minimization. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 106: 2158–2168, 2007

Key words: acrylamides; crosslinking; grafting; hydrogels; metal ion sorption; pectin; water uptake

INTRODUCTION

There are many reports on the use of hydrogels as supports for metal ion uptake.[1–6] Pectin, being the major constituent of some agro-wastes, can be used to develop cost-effective and eco-friendly supports for metal ion separation and enrichment technologies. The reported selectivity of pectin in metal binding can be used to develop effective detoxificant as it forms insoluble salts with heavy metal ions. Pectin interacts with the heavy metal ions under mild conditions. However, poor compact ability and low resistance to chemical and microbial attack limit industrial applications of pectin. Its modification by grafting, crosslinking by polymer analogous reactions, and simply by interactions with metal ions can improve some of these limitations. Pectin has —CO_2H groups those interact with metal ions by ion exchange. There are some reports on the use of pectin modified with metal ions like calcium and zinc in biomedical applications like lowering of blood cholesterol[7] and colon targeted drug delivery systems.[8–11] Apart from its uses as drug release device, pectin interactions with heavy metal ions,[12] complexation of nitrolignin-pectin with copper ions,[13] and iron (III) ions[14] have been

reported. Kaley et al.[15] have reported gel beads of sugar beet pectin for the removal of cadmium from aqueous solution. Dronnet and coworker[16] have reported selectivity in the binding of divalent metal ions by citrus and sugar beat pectin. Grafting and crosslinking reactions of pectin are not much investigated. Use of pectin, as component of hydrogels with poly(AAm) and its derivatives is not reported. Apart from their biodegradable and eco-friendly nature, use of biopolymers such as pectin as reinforcing components of the hydrogels afford better mechanical properties to the resulting hydrogels.

The present article reports development of eco-friendly and low cost polymeric materials for metal remediation, enrichment and separation technologies and as possible metal ion detoxificant by using pectin as the major component. In our earlier communications, we have reported alternate polymeric materials based on biopolymers for use in environment management studies.[17–21] In the present article, we report modification of pectin by grafting and crosslinking reactions. Modification of pectin by grafting and crosslinking reactions with a series of closely related monomers, but at the same time offering a wide spectrum of properties like thermo sensitivity of *N*-isopropyl acrylamide (*N*-i-PAAm) and ion exchange and self-ionization of —SO_3H group of 2-acrylamido-2-methyl-1-propane sulfonic acid (AAmPSA) is expected to afford a wide range of useful hydrogels. Three common water effluent metal ions, i.e., Fe^{2+},

Correspondence to: G. S. Chauhan. (ghanshyam_in2000@yahoo.com, ghanshyamschauhan@gmail.com)

Cu^{2+}, and Cr^{6+} has been explored as model ions to explore the structure-property relationship of these hydrogels for end-uses in metal ion removal and enrichment processes. Possible use of hydrogels can also be explored as detoxificant agents and also in the loading of some metal ions of medicinal importance.

EXPERIMENTAL

Materials

Acrylamide (S.D. Fines, Mumbai, India), 2-acryla-mido-2-methtyl-1-propanesulphonic acid (Aldrich Chemical, Milwaukee, WI), N-isopropyl acrylamide (Aldrich Chemical, Milwaukee, WI), N,N-methylene bisacrylamide (CDH, Mumbai, India), pectin (Loba Chemie, Mumbai India), ammonium persulphate (Glaxo, Mumbai, India), and ferrous ammonium sulfate (Sarabhai M. Chemicals, Vadodara, India) have been used as received.

Preparation of hydrogels by graft copolymerization

Hydrogels were prepared by changing reaction parameters one at a time. In a model reaction scheme pectin (2.0 g) was taken in distilled water (20.0 mL) along with known concentration of initiator ammonium persulphate (APS): ferrous ammonium persulphate (2.185 mM: 0.255 mM) and AAm (28.137 mM). The reaction system was allowed to react for 0.5 h at 25°C. The procedure was repeated at 70°C. Grafting on pectin with AAmPSA and N-i-PAAm was also carried at 25 and 70°C. Homopolymer was separated from the reaction mixture by fractional precipitation using acetone. Graft copolymer being of higher molecular weight as compared with the homopolymer is precipitated out first. The graft copolymers were dried under vacuum. In repeated cycles, the graft copolymers were solubilized in water and then precipitated with acetone and dried in vacuum oven at 40°C. The process was repeated till constant weight of graft copolymer was obtained. Incorporation of monomer on pectin backbone has been defined as percent grafting (P_g) which was calculated as:

$$P_g = \frac{\text{Weight of graft copolymer} - \text{weight of pectin}}{\text{weight of pectin}} \times 100$$

Preparation of hydrogels by crosslinking reactions

The crosslinked hydrogels with all the three monomers were prepared separately using four different concentrations of crosslinker (N,N-methylene bisacryl-amide). In the presence of known concentrations of crosslinker, 2.0 g pectin in 20.0 mL of distilled water

was taken along with 2.185 mM: 0.255 mM of APS-FAS, 28.137 mM AAm. The reaction system was allowed to react for 30 min. The synthesis was carried at two different temperatures (25 and 70°C). The insolubilized product/network formed was separated by filtration, and then without drying, was repeatedly extracted separately with water and methanol to remove any sol fraction. The gels were then treated with acetone to remove the absorbed water and dried under vacuum. The amount of the monomer and crosslinker incorporated on pectin was expressed as:[20]

$$P_{\text{add-on}} = \frac{\text{Weight of graft copolymer} - \text{weight of pectin}}{\text{weight of pectin}} \times 100$$

Elemental analysis, FTIR, and water uptake studies

SEMs of the networks were recorded on Joel JSM 6100 and FTIR spectra were recorded in KBr on Perkin–Elmer RX-1. The graft copolymers and networks synthesized and reported above were subjected to water uptake studies. Polymer (0.1 g) was immersed in distilled water at 25°C in a controlled water bath. After defined time intervals (2, 4, 6, 8, and 24 h) the samples were taken out and surface water was removed by pressing the swollen hydrogel between the fold of soft tissue paper. The swollen polymers were immediately weighed.[20] The above process was repeated to study the effect of temperature and pH (4.0 and 9.2). The effect of partial hydrolysis on swelling was studied by using hydrogels pretreated with 0.5N NaOH at 50°C for 48 h. Percent water uptake (P_s) was calculated from the following relationship:[20]

$$\% \text{ Water uptake } (P_s) = \frac{(W_w - W_d)}{W_d} \times 100$$

W_w and W_d are the weights of swollen hydrogels and dried polymers (xerogels), respectively.

Metal ion sorption studies

Two networks from each monomer series prepared with the lowest and the highest crosslinker concentrations and prepared at 25°C were selected due to the better swellability as compared with the other series prepared at 70°C. Copper sulfate, ferrous sulfate and chromium oxide were used as received, for making solutions of particular concentrations of respective metal ions in water. Sorption studies were carried as reported earlier.[19] Hydrogels were immersed for 24 h in 20.00 mL solutions of known strength. Filtrates of the solutions were analyzed for concentration of rejected ions on DR 2010 Spectrophotometer (M/s.

Hach) by using its standard pillow reagents. Using this method maximum limit of ion strength that can be studied on this instrument is, 5.0, 3.0, and 0.6 mg/L of solution, respectively, of Cu^{2+}, Fe^{2+}, and Cr^{6+}. Selected polymeric matrices, which showed compara- tively better results in the metal ion sorption studies, were subjected to partial hydrolysis as foresaid, and then, metal ions were sorbed on the hydrolyzed mat- rices. Amount of the metal ion sorbed was calculated as:[19]

$$\text{Percent uptake } (P_u) = \frac{\text{Initial concentration of the metal ions} - \text{rejected concentration of the metal ions}}{\text{Initial concentration of the metal ions}} \times 100$$

Biodegradation studies

Biodegradation of the polymeric networks was stud- ied by soil burial method on the precharacterized gar- den soil (pH = 6.63). To the known amounts of the soil taken in open petri dishes, known weights of the polymeric networks were mixed with soil and the mixture was then mixed with known weights of water. The petri dishes were incubated at 40°C and weight of the total system was monitored weekly. The cumulative weight loss was recorded after four weeks to account for any biodegradation of the poly- mers.

RESULTS AND DISCUSSION

Preparation of hydrogels by graft copolymerization

Grafting on polysaccharide are usually of the anhy- droglucose units, where H is abstracted by the radical generated by the redox initiator system. In the present case $SO_4^{-\bullet}$ is generated by the $S_2O_8^{-2}$ of the initiator.[22] The monomer growing macroradical attaches at these sites to give graft copolymers. Grafting reactions of AAm with pectin in the absence of crosslinker were studied at the fixed reaction parameters those include initiator and monomer concentrations, reaction time and amount of water. The hydrogels were synthe- sized at two different temperatures to study the effect of homogenization of reaction mixtures and energy requirements of the grafting reactions. P_g varied from 82.95 at 25°C to 97.55 as the temperature was increased to 70°C. Grafting of other monomers at 25 and 70°C, in case of AAmPSA afforded P_g of 195.9 and 208.50 at 25°C and at 70°C, respectively, while in the case of N-i-PAAm very low P_g (2.0 and 11.20) was obtained at the same temperatures. The lower reactiv- ity of N-i-PAAm as compared with the AAm and AAmPSA is explained on the basis of its hydrophobic nature and resultant lesser interactions with the water-soluble backbone. Thus, the reactivity trends in grafting reactions for different monomers follow the order AAmPSA > AAm > N-i-PAAm. The results for grafting at the optimum conditions for all the three monomers have been incorporated with those ob- tained for the crosslinking reactions.
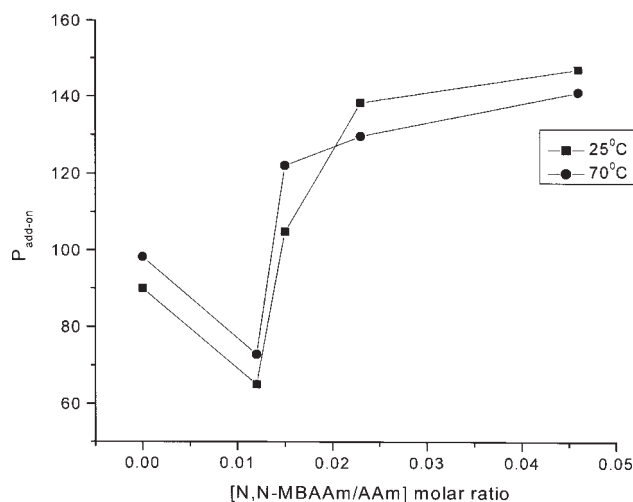

Figure 1 $P_{\text{add-on}}$ as a function of molar ratio of crosslinker to acrylamide.
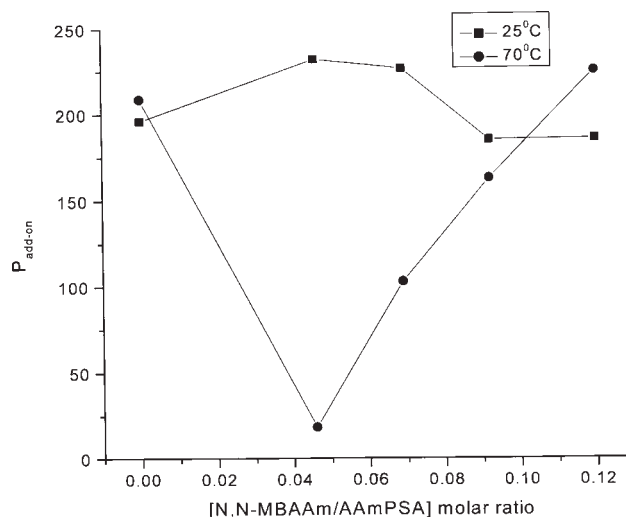

Figure 2 $P_{\text{add-on}}$ as a function of molar ratio of crosslinker to AAmPSA.
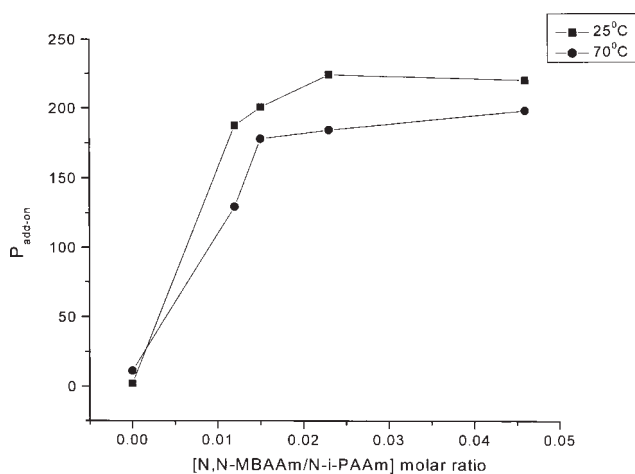
Figure 3 P_{add-on} as a function of molar ratio of crosslinker to N-i-PAAm.

Preparation of hydrogels by crosslinking reactions

Keeping other reaction conditions same as used for the grafting reaction, networks were prepared by variation of the crosslinker concentration ([N,N-MBAAm]) from 0.324 to 1.297 mM and P_{add-on} varied from 65.05, 104.85, 138.30, and 147.0, and 72.85, 122.1,

129.65, and 141.0 at 25 and 70°C, respectively, (Fig. 1). In case of AAmPSA, the [N,N-MBAAm] varied from 1.297 to 3.243 mM. At the lower concentration, it did not afford network, i.e., no insolubilized product was obtained at the conditions employed for the preparation of AAm based networks. At 25°C, P_{add-on} decreased from 232.00, 226.40, 185.00, and 185.50 with the increase of [N,N-MBAAm] (Fig. 2). P_{add-on} increased progressively from 18.30, 102.80, 162.80 to 225.00 with [N,N-MBAAm] at 70°C. In case of N-i-PAAm based networks, P_{add-on} varied from 187.50, 200.60, 224.2, and 220.20 and 129.30, 177.90, 184.20, 198.20, at 25 and 70°C, respectively, (Fig. 3). The P_{add-on} values were observed to increase with the increase of at [N,N-MBAAm] at both the temperatures.

Characterization of hydrogels

Scanning electron microscopy

The nature of monomers and grafting conditions has significant effect on the morphology of the crosslinked polymers. Scanning electron micrographs (SEMs) of pectin and different graft copolymers are presented in Figure 4(a–f). The comparison of the SEMs of the pure

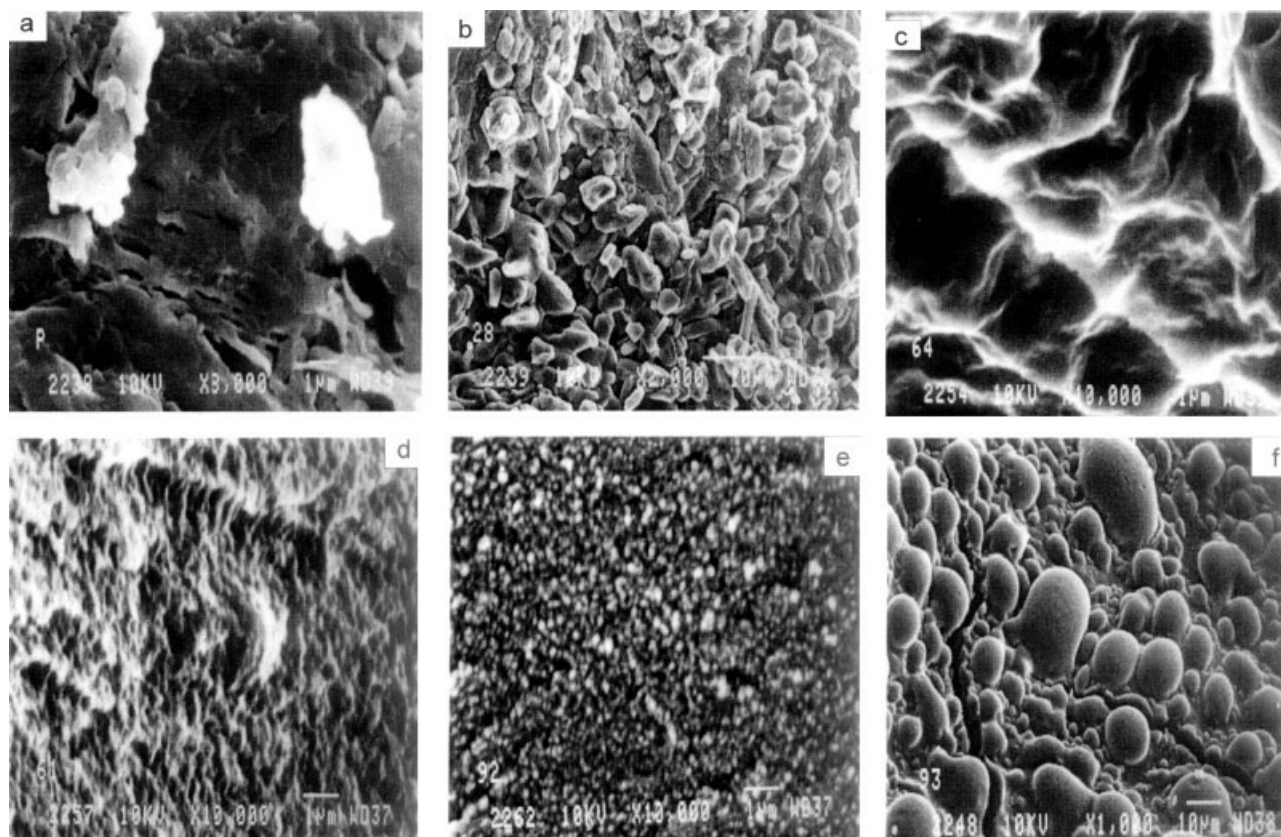**Figure 4** SEM images of: (a) Pectin, (b) Pectin-*cl*-poly(AAm), [crosslinker/AAm] = 0.046, prepared at 25°C]; (c) Pectin-*cl*-poly(AAmPSA) [crosslinker/AAmPSA] = 0.12, prepared at 70°C]. (d) Pectin-*cl*-poly(AAmPSA) [crosslinker/AAmPSA] = 0.046, prepared at 25°C], (e) Pectin-*cl*-poly(*N*-i-PAAm) [crosslinker/*N*-i-PAAm = 0.046, prepared at 25°C]; (f) Pectin-*cl*-poly(*N*-i-PAAm) [crosslinker = 0.012, prepared at 25°C].

TABLE I
Analysis of FTIR Spectra of Networks of Pectin and Acrylamides

Polymer	[Crosslinker]/[monomer]	Synth.temp. (°C)	Characteristic peaks cm^{-1}	% absorbance	Remarks
Pectin			2939.0	53.84	C—H str.
			1749.0	43.94	C=O str. of COOR
			1052.1	84.20	COC str.
Pectin-*cl*-poly(AAm)	0.012	25	1740.1	58.49	C=O str. of acid and ester
			1664.3	81.32	C=O str. of CONH$_2$
Pectin-*cl*-poly(AAm)	0.012	70	1745.3	61.23	C=O str. of acid and ester
			1654.5	88.16	C=O str. of CONH$_2$
Pectin-*cl*-poly(N-i-PAAm)	0.023	25	3265.4	83.60	—NH str.
			1660.1	78.15	C=O str. of CONH$_2$
			1394.7	71.77	(CH$_3$)$_2$ bending
			1018.6	64.02	COC str.
Pectin-*cl*-poly(N-i-PAAm)	0.023	70	3261.0	85.10	—NH str.
			2974.6	79.58	C—H str.
			1657.1	86.16	C=O str. of CONH$_2$
			1387.3	70.01	(CH$_3$)$_2$ bending
			1119.0	72.08	COC str.
			1018.6	64.69	COC str.
Pectin-*cl*-poly(AAmPSA)	0.046	25	2934.2	68.81	C—H str.
			1655.9	75.68	C=O str. of subst. amide
			1301.7	55.75	S=O str.
			1130.1	84.86	COC str.
Pectin-*cl*-poly(AAmPSA)	0.046	70	2950.0	61.25	C—H str.
			1649.9	75.72	C=O str. of subst. amide
			1288.0	55.32	S=O str.
			1100.9	63.12	COC str.

pectin [Fig. 4(a)] and that of its network with poly (AAm) prepared with 0.046M ratio of the crosslinker to the monomer reveals contrasting morphologies due to the crosslink formation and presence of numerous particles of smaller size in the SEM of the later. The crosslinked polymer has pore of smaller size and higher crosslinking density [Fig. 4(b)]. The effect of [N,N-MAAm] on surface morphology is shown in the SEMs of poly(AAmPSA) based networks synthesized at 0.046 and 0.12 of molar ratio of the crosslinker to the monomer. These micrographs also reveal morphological features where the pore formation in the networks is better defined [Fig. 4(c,d)]. The effect on surface morphology of the temperature at which the networks were prepared is also clearly visible from these SEMs of poly (AAmPSA) based networks synthesized at 25 and 70°C [Fig. 4(c,d)]. The structural differences in these two networks as can be made out from their surface morphologies is revealed in the occurrence of more uniform and homogenous nature of reactions at the higher temperature that affect crosslinking density and pore size distribution in a significant way. The SEM of poly(N-i-PAAm) based network synthesized at 25°C with the 0.012 and 0.046M ratio of crosslinker to monomer is also presented in Figure 4(e,f).

FTIR spectroscopic study

Prominent peaks with wave numbers and % absorbance from the FTIR spectra of pectin and its graft copolymers and networks with poly(AAm) have been presented in Table I and Figure 5(a). In the spectrum of pectin, peaks at 3390.6 cm^{-1} (89.46), 2939.0 cm^{-1} (53.84), 1749.0 cm^{-1} (43.94), and 1052.1 cm^{-1} (84.20), corresponding, respectively, for —OH, —CH, C=O of ester, and —COC— stretching. Its networks with AAm shows extra peaks at 1664.3 cm^{-1} (81.32) and 1654.5 cm^{-1} (88.16) due to the stretching of C=O of AAm for networks synthesized at 25 and 70°C as shown in Table I and Figure 5(b). Data of FTIR spectra of pectin with poly(AAmPSA) has been given in Table I and Figure 5(c). It shows absorption peak due to the S=O stretching at 1301.7 cm^{-1} (55.75) apart form the other important peaks due to the C=O stretching at 1655.9 cm^{-1}. FTIR spectrum of pectin-*cl*-poly(N-i-PAAm) networks show characteristic peaks at 1109.0 cm^{-1} (72.08) and 1657.1 cm^{-1} (86.16) and 1130.1cm^{-1} (84.86) and 1660.1 cm^{-1} (78.15), respectively, for networks synthesized at 70°C and 25°C, [Table I and Fig. 5(d)].

Water uptake behavior of hydrogels

All the hydrogels prepared in the absence of crosslinker at the optimum reaction conditions for grafting and also by the variation of four different ([N,N-MBAAm] were swollen in water as a function of time, temperature and pH and partial hydrolysis with 0.5N NaOH.
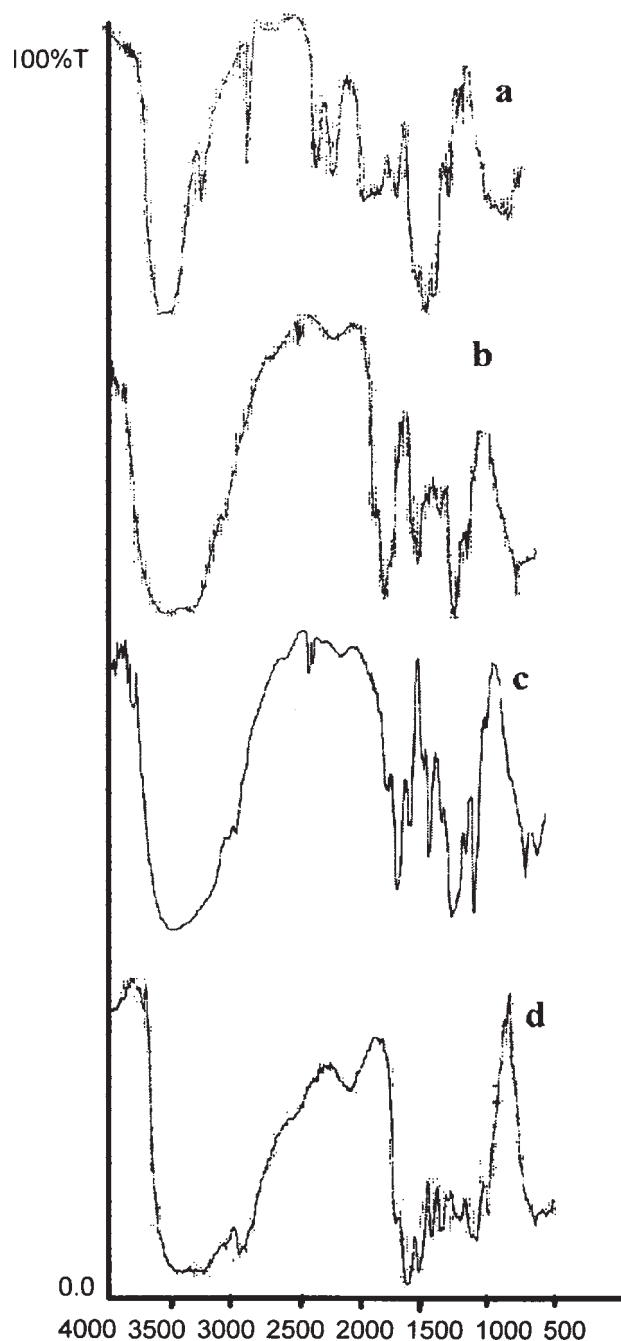
Figure 5 FTIR spectra of: (a) Pectin, (b) Pectin-cl-poly (AAm) [crosslinker/AAm]- = 0.12, prepared at 25°C]; (c) Pectin-cl-poly(AAmPSA), [crosslinker/AAmPSA] = 0.18, prepared at 70°C]. (d) Pectin-cl-poly(N-i-PAAm) [crosslinker = 0.12, prepared at 70°C].

Effect of time

In case of pectin-g-poly(AAm) it was observed that P_s increases progressively in from 444.0 to 656.4 in the hydrogel prepared at 25°C. It increases with time from 630.0 to 689.6 in the hydrogel prepared at 70°C. In case of pectin-cl-poly(AAm) P_s decreases with the increase in the [N,N-MAAm] in the hydrogels prepared at 25°C. However, it increases in hydrogels pre-

pared at 70°C [Fig. 6(a,b)]. Though there is no relationship between the $P_{\text{add-on}}$ and water uptake, yet the effect of synthetic temperature is significant. P_s in case of pectin-g-poly(AAmPSA) prepared at 25°C was 486.7 within 2 h. However, it decreased to 285.1 as the time was increased to 24 h. The decrease in P_s is due to the slow change of hydrogel into sol form at the higher time intervals. Similar behavior has been observed for the hydrogels prepared at the higher temperature. This hydrogel takes up water at a much faster rate, but it also changes to sol within 24 h. In case of pectin-cl-poly(AAmPSA), P_s increases with the swelling time for a particular hydrogel. It decreases with the increase in the [N,N-MBAAm] in all the hydrogels. Apart from the hydrogel prepared with 1.297 mM of crosslinker to the monomer, all other hydrogels synthesized at 70°C swell more at the same swelling time, as compared with those prepared at 25°C [Fig. 7(a,b)]. In case of pectin-g-poly(N-i-PAAm), the hydrogel prepared at 25°C (P_g = 2.0) swells to a maximum of 486.7. There after it starts deswelling and changes into sol though complete transition was not observed up to 24 h (P_s = 285.1). Pectin-g-poly(N-i-PAAm), prepared at 70°C (P_g = 11.20) swells from 782.9 to 1223.8 with increase of time. P_s of pectin-cl-

Figure 6 Effect of crosslinker concentration on P_s with respect to time at pH 7 on poly(AAm) based hydrogels, from top (a) prepared at 25°C (b) prepared at 70°C.
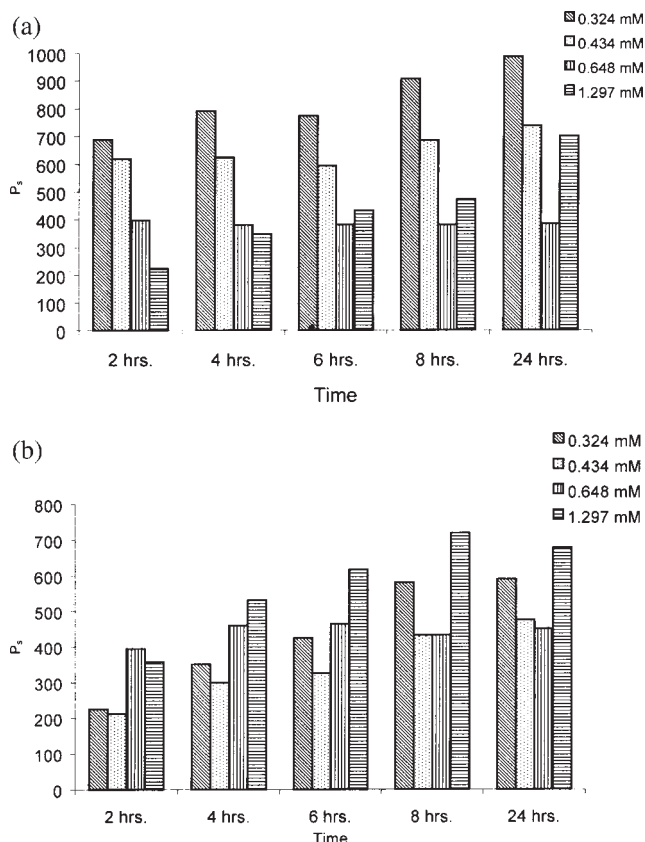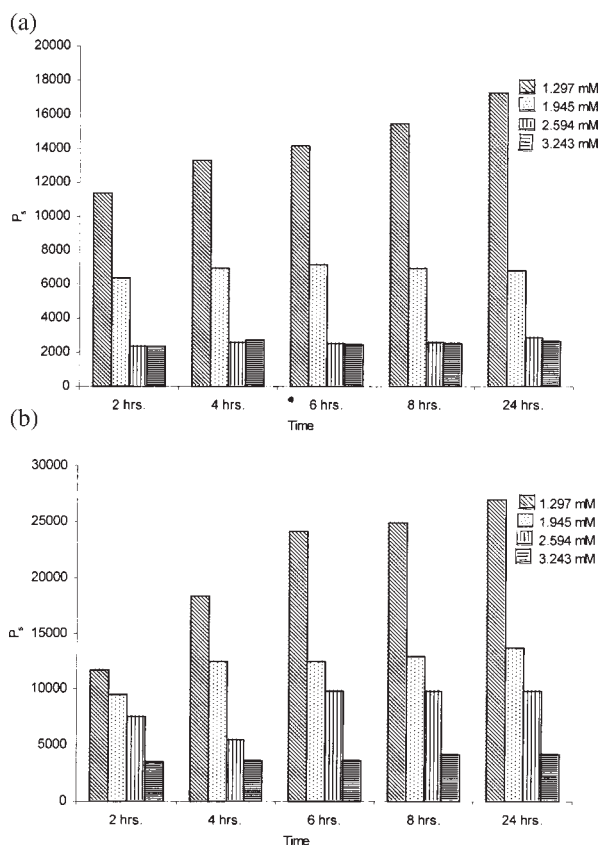
(a)

(b)

Figure 7 Effect of crosslinker concentration on P_s with respect to time at pH 7 on poly(AAmPSA) based hydrogels, from top (a) prepared at 25°C (b) prepared at 70°C.

poly(N-i-PAAm) prepared at 25°C increases with swelling time. P_s decreases with the increase in the [N,N-MBAAm] for every swelling time. However, hydrogels prepared at 70°C show different swelling behavior [Fig. 8(a,b)]. In this case, the effect of the reaction temperature on the structural aspects of the networks is evident.

Effect of temperature

The effect of the swelling temperature was studied for 24 h. In case of pectin-cl-poly(AAm), P_s decreases with the increase in swelling temperature. And it does so in a sharp manner when temperature was increased beyond 37°C. Thus, these hydrogels exhibit a pronounced sensitivity towards changes in their thermal environment [Fig. 9(a,b)]. Poly(AAmPSA) behaves as polyelectrolyte due to the self-ionization of —SO$_3$H groups. It was, thus, expected that changes in its thermal environment should affect swelling behavior in a marked manner [Fig. 10(a,b)]. The high water uptake has been observed for these hydrogels and P_s increases with the rise in swelling temperature in a linear fashion. It decreases with the increase of

molar ratio of the crosslinker to the monomer. Poly(N-i-PAAm) is a thermoresponsive polymer and it undergoes sharp volume transition with temperature above 32.5°C its lower critical solution temperature (LCST). In this case hydrogels prepared at both the temperatures deswell with the rise in swelling temperature. However, deswelling is not very sharp and the hydrogels do not show the highest deswelling at 32.5°C. Similar behavior has been observed when water uptake was studied with the increase in [N,N-MBAAm]. Such behavior is attributed to the structural features of pectin. The large number of hydrophilic groups on it trap large amount of water that prevents sudden collapse of the gel [Fig. 11(a,b)].

Effect of pH and partial hydrolysis

pH of the swelling medium has significant effect on the swelling behavior of the hydrogels. Similarly, partial hydrolysis leads to the generation of new water interaction centers on the polymer chains. Hence, new ion-dipole interactions result in significant changes in water uptake on partial saponification with 0.5N NaOH. Some of the —CONH$_2$ changes to —CO$_2^-$Na$^+$ groups. The water uptake behavior of pectin-cl-poly(AAm) as a function of pH change and partial hydrolysis is given in Table II. The hydrogels
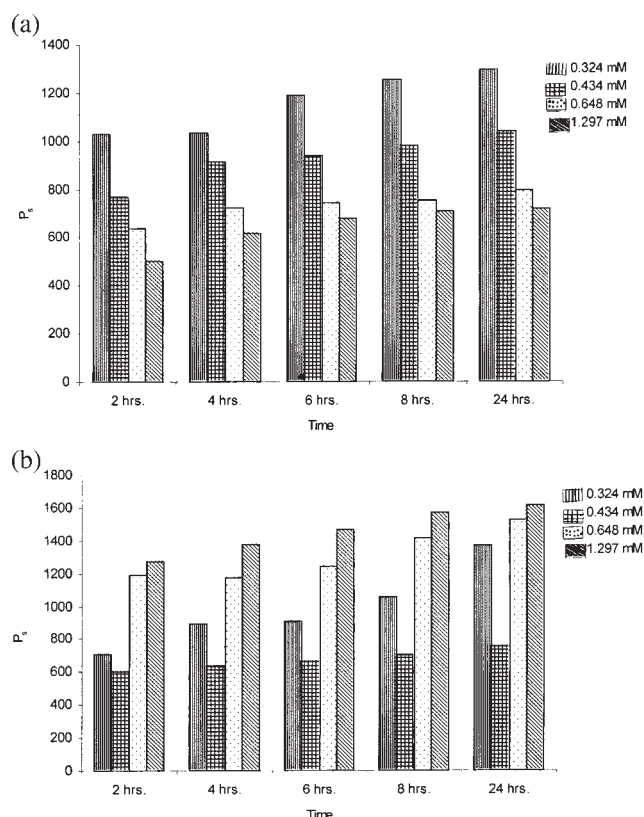
(a)

(b)

Figure 8 Effect of crosslinker concentration on P_s with respect to time at pH 7 on poly(N-i-PAAm) based hydrogels, from top (a) prepared at 25°C (b) prepared at 70°C.
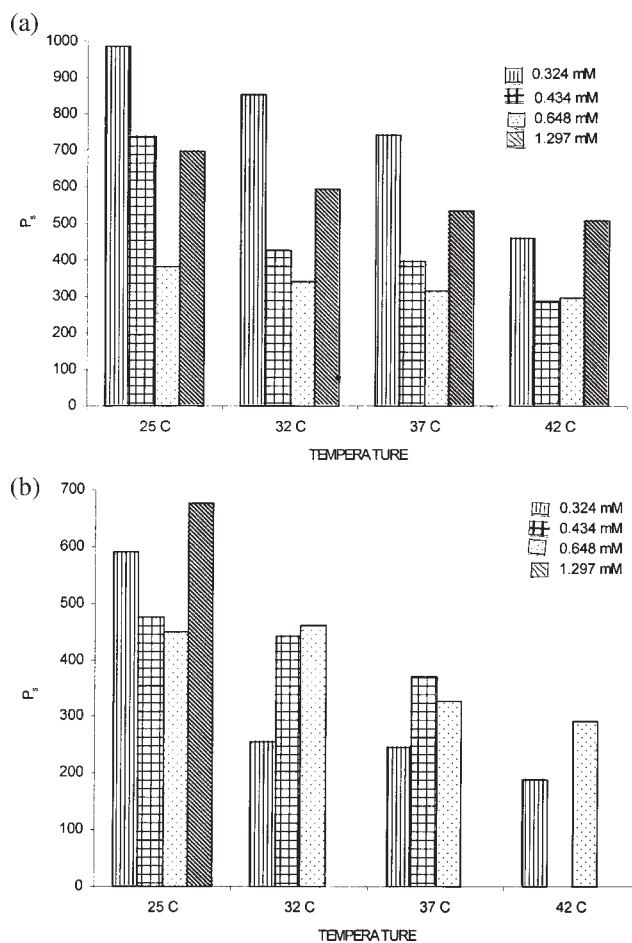
Figure 9 Effect of crosslinker concentration on P_s with respect to temperature at pH 7 on poly(AAm) based hydrogels, from top (a) prepared at 25°C (b) prepared at 70°C.

deswell at pH 4.0, but absorb more water at pH 9.0 and also on partial hydrolysis.[6] The hydrogels of poly (AAmPSA) prepared at both the temperatures are very good absorbents of water, however, change of pH considerably deswell the hydrogels. P_s decreases from 17,196.0 at pH 7.0 to 5170.0 at pH 4.0 in the hydrogels synthesized at 25°C with 0.046 [N,N-MBAAm] (Table II). In case of poly(N-i-PAAm) based hydrogels almost similar behavior has been observed.

In the present study partial hydrolysis has not been found to improve water retention by the gels. Poly (AAmPSA) is itself a polyelectrolyte, hence, partial hydrolysis does not make any impact on the structural changes of the hydrogels. In case of poly(N-i-PAAm) partial hydrolysis is not effective due to the inherent structural factors of the secondary amido groups, as it is not easily amenable to hydrolysis. It is also understandable that when these polymers were subjected to saponification, the alkali preferentially reacts with —CO_2H groups of the backbone and partial hydrolysis of the grafted amido groups is not affected to a larger extent (Table II).

Sorption of metal ions on hydrogels

Metal ions uptake is affected by the hydrophilic–hydrophobic balance, nature of monomer and extent of the crosslinking of macromolecular supports as major factors apart from the complexation ability of the ligands present on polymers. Apart from the metal ion active —CO_2H on pectin, amido group is common to all monomers incorporated onto these hydrogels. As aforesaid, the [C/M] and the temperature at which the hydrogels have been prepared, affect the structure of the hydrogel, which in turn affects the swellability of the hydrogel. The later affects the partitioning of the metal ions between the polymer and solution phase. To account for the effect of [N,N-MBAAm] on the metal ion sorption, two networks of each series prepared with the highest and the lowest [N,N-MBAAm] have been used. All the results from metal ions sorption are presented in Table III. Pectin-cl-poly(AAm) sorbs considerable amount of Cr6+ as compared with two other series of hydrogels. The hydrogels prepared with the lowest
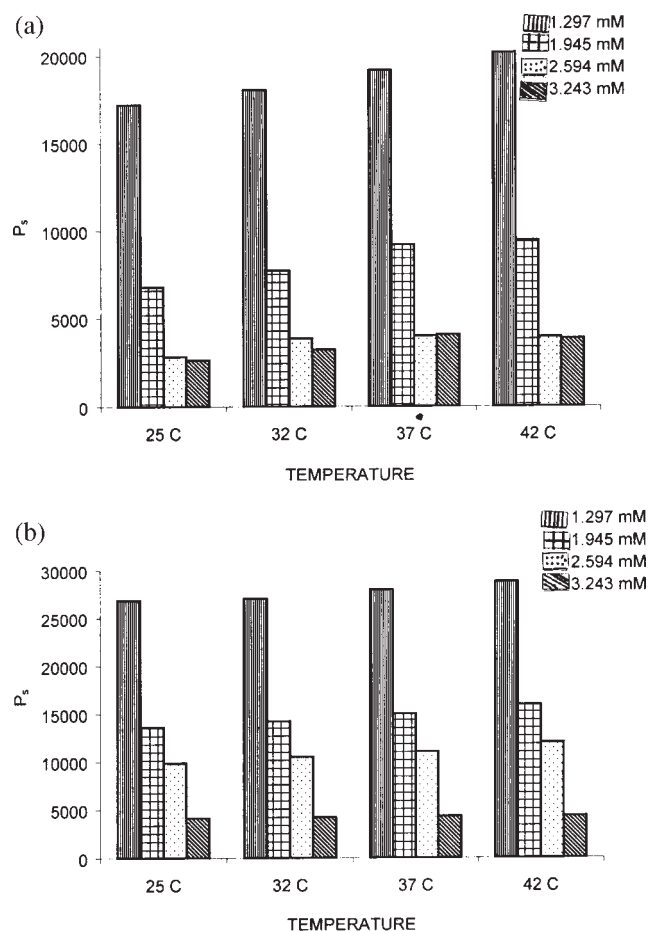

Figure 10 Effect of crosslinker concentration on P_s with respect to temperature at pH 7 on poly(AAmPSA) based hydrogels, from top (a) prepared at 25°C (b) prepared at 70°C.
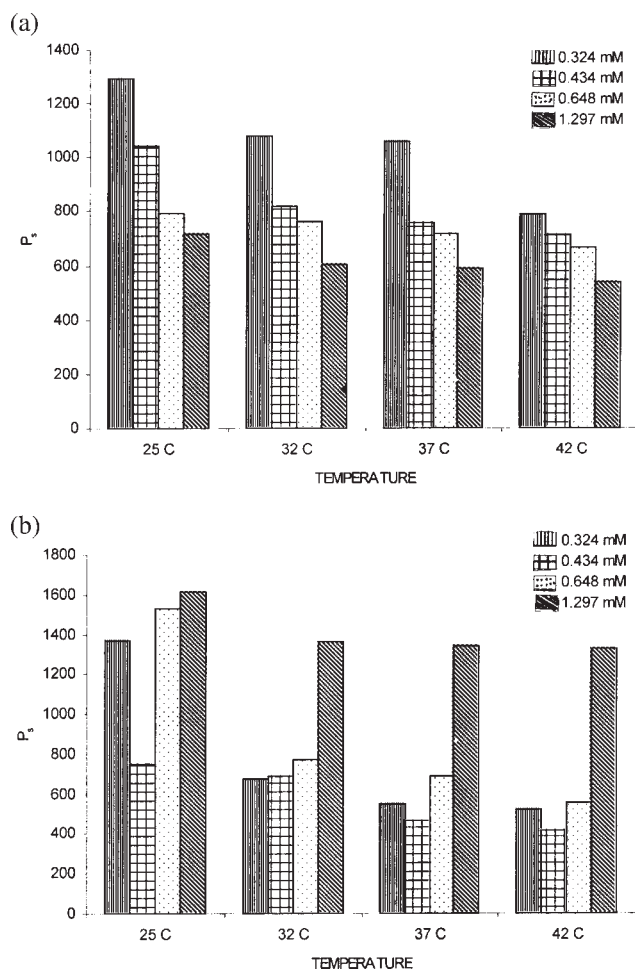
(a)

(b)

Figure 11 Effect of crosslinker concentration on P_s with respect to temperature at pH 7 on poly(N-i-PAAm) based hydrogels, from top (a) prepared at 25°C (b) prepared at 70°C.

[N,N-MBAAm] sorb higher amount of ions than those prepared with the highest [N,N-MBAAm] (Table IIIa). Somewhat similar trends have been observed with poly(N-i-PAAm) hydrogels. In case of poly(AAmPSA) based hydrogels, no ion uptake was observed with the network prepared at the highest [N,N-MBAAm]. For the same series of polymers, higher Cu^{2+} was sorbed as compared with that of Cr^{6+} (Table IIIa). Poly(AAmPSA) based hydrogels sorb very high Cu^{2+} (even >90% in some cases). Further, in this case the ion uptake is higher in those hydrogels those were prepared at the highest [N,N-MBAAm] as compared with other monomers based hydrogels. The hydrogels based on poly(N-i-PAAm) are the least efficient sorbent of Cu^{2+}. Sorption of Fe^{2+} is higher than observed for Cu^{2+} and Cr^{6+}. The order for different monomer based series for Fe^{2+} and Cu^{2+} can be put as: poly(AAmPSA) > poly (AAm) > poly(N-i-PAAm) while for Cr^{6+} the trend can be put as: poly(AAm) > -(N-i-PAAm) > poly (AAmPSA). Polymeric matrices, those were observed

to sorb appreciably higher amount of metal ions, were subjected to partial hydrolysis with 0.5N NaOH. The partially hydrolyzed hydrogels were used for metal ions sorption. Partial hydrolysis should enhance metal ion uptake, as it increases polymer-metal ion and polymer-water interactions.[19] From Table IIIb it is understandable that most of the hydrolyzed samples do not absorb any Cr^{6+} ions while it is lower than the unhydrolyzed in case of Cu^{2+}. In hydrogels loaded with Cr^{6+} breakdown of the networks was observed due to oxidation of the pectin chains. In case of Fe^{2+} ions, an appreciable increase in the metal ion uptake was observed, as compared with the unhydrolyzed hydrogels. The results for Fe^{2+} and Cr^{6+} corroborate well with our earlier reported studies on poly(AAm) and hydroxypropyl cellulose based networks.[19] Further, the effect of partial hydrolysis on the sorption levels of these two ions is evident in case of poly(AAm) based hydrogels as compared with those based on poly(N-i-PAAm) due to the ease of comparative hydrolysis of the former than the later.

Biodegradation studies

The weight loss after four weeks in soil burial method[23] is significant in some hydrogels, while it is not so in others (Table IV). It appears that poly (AAmPSA) based hydrogels due to very high water uptake interact in a more facile manner with the soil microorganisms to facilitate enzyme action on the polymers.[24] Further, higher [N,N-MBAAm] also facilitates biodegradation due to the fact that more biocompatible amide groups are available in good measure. Thus, higher incorporation of more amide groups on the hydrogel help in more positive interactions of polymer and microorganisms. The ease of biodegradation follows the order: poly(AAmPSA) > poly(N-i-PAAm) > poly(AAm).

CONCLUSIONS

In lieu of the conclusion it can be stated that the properties of the hydrogels are determined by the monomer nature, crosslinker concentration, and by the temperature at which the hydrogels are prepared. The preparation of hydrogels at higher temperature involves more uniform reactions. The hydrogels show sensitivity to the thermal and pH changes made in their swelling environment. Poly(AAmPSA) based hydrogels are of special interest due to high water absorption as well as lesser resistance to the biodegradability. Metal ion sorption is dependent on the structural aspects of the hydrogels, as selectivity in metal ion sorption results from the molar ratio of crosslinker to monomer as well as after subjecting these hydrogels to partial hydrolysis. Hence, to suit the technological requirements of the removal of the

TABLE II
Effect of pH on Water Uptake Behavior of Networks at 25°C

Sr. no.	[Crosslinker]/[monomer]	P_{add-on}	P_s pH 7.0	pH 4.0	pH 9.0	Partially hydrolyzed hydrogels
Pectin-*cl*-poly(AAm) prepared at 25°C						
1.	0.012	65.05	984.0	446.0	749.0	1371.0
2.	0.015	104.85	736.0	1108.0	1093.0	1205.0
3.	0.023	112.3	383.0	766.0	1018.0	1457.0
4.	0.046	147.0	698.0	453.0	787.0	938.0
Pectin-*cl*-poly(AAm) prepared at 70°C						
1.	0.012	72.85	590.0	606.0	876.0	1046.0
2.	0.015	122.1	475.0	583.0	593.0	755.0
3.	0.023	89.65	450.0	1075.0	1328.0	1510.0
4.	0.046	142.0	677.0	666.0	749.0	1067.0
Pectin-*cl*-poly(AAmPSA) prepared at 25°C						
1.	0.046	232.0	17196.0	5170.0	4055.0	3569.0
2.	0.069	226.0	6773.0	3205.0	3203.0	28780
3.	0.092	185.0	2829.0	2603.0	1921.0	1805.0
4.	0.12	192.5	2623.0	2567.0	2130.0	1912.0
Pectin-*cl*-poly(AAmPSA) prepared at 70°C						
1.	0.046	−18.3	26891.0	6473.0	5853.0	5129.0
2.	0.069	102.8	13589.9	4987.0	4212.0	3843.0
3.	0.92	162.8	9841.6	3775.0	3487.0	2969.0
4.	0.12	225.0	4103.0	2683.0	2237.0	1983.0
Pectin-*cl*-poly(N-i-PAAm) prepared at 25°C						
1.	0.012	187.5	1294.0	1246.0	1220.0	489.0
2.	0.015	200.6	1040.0	1102.0	933.0	370.0
3.	0.023	242.2	792.0	766.0	877.0	377.0
4.	0.046	220.2	716.0	830.0	927.0	527.0
Pectin-*cl*-poly(N-i-PAAm) prepared at 70°C						
1.	0.012	129.3	1370.0	830.0	1080.0	574.0
2.	0.015	144.2	753.0	921.0	1055.0	509.0
3.	0.023	171.9	1528.0	918.0	1051.0	610.0
4.	0.046	198.2	1613.0	636.0	625.0	430.0

TABLE IIIa
Sorption Studies of Metal Ion on Hydrogels

Polymer	[Crosslinker]/[monomer]	P_u
Cr^{6+} ions sorption		
Pectin-*cl*-poly(AAm)	0.012	53.57
Pectin-*cl*-poly(AAm)	0.046	40.68
Pectin-*cl*-poly(N-i-PAAm)	0.012	46.42
Pectin-*cl*-poly(N-i-PAAm)	0.046	16.07
Pectin-*cl*-poly(AAmPSA)	0.046	20.23
Pectin-*cl*-poly(AAmPSA)	0.12	0.0
Cu^{2+} ions sorption		
Pectin-*cl*-poly(AAm)	0.012	54.28
Pectin-*cl*-poly(AAm)	0.046	38.57
Pectin-*cl*-poly(N-i-PAAm)	0.012	43.57
Pectin-*cl*-poly(N-i-PAAm)	0.046	37.85
Pectin-*cl*-poly(AAmPSA)	0.046	67.14
Pectin-*cl*-poly(AAmPSA)	0.12	72.85
Fe^{2+} ions sorption		
Pectin-*cl*-poly(AAm)	0.012	27.65
Pectin-*cl*-poly(AAm)	0.046	11.06
Pectin-*cl*-poly(N-i-PAAm)	0.012	15.31
Pectin-*cl*-poly(N-i-PAAm)	0.046	20.00
Pectin-*cl*-poly(AAmPSA)	0.046	48.08
Pectin-*cl*-poly(AAmPSA)	0.12	92.34

TABLE IIIb
Comparison of Metal Ion Sorption on Hydrolyzed and Unhydrolyzed Networks

Sr. no.	Polymer	[Crosslinker]/ [monomer]	P_u Unhydrolyzed	Hydrolyzed
Cr^{6+} ions uptake				
1.	Pectin-*cl*-poly(AAm)	0.012	53.57	13.95
2.	Pectin-*cl*-poly(N-i-PAAm)	0.012	46.42	22.86
3.	Pectin-*cl*-poly(AAmPSA)	0.046	20.09	0.0
Cu^{2+} ions uptake				
1.	Pectin-*cl*-poly(AAm)	0.012	54.28	28.64
2.	Pectin-*cl*-poly(N-i-PAAm)	0.012	43.57	31.35
3.	Pectin-*cl*-poly(AAmPSA)	0.12	72.85	0.0
Fe^{2+} ions uptake				
1.	Pectin-*cl*-poly(AAm)	0.012	27.65	89.54
2.	Pectin-*cl*-poly(N-i-PAAm)	0.012	15.31	44.87
3.	Pectin-*cl*-poly(AAmPSA)	0.12	92.34	73.65

TABLE IV
Biodegradation of networks (initial weight of the polymer = 0.3 g)

Sr. no.	Polymer	[Crosslinker]/ [monomer]	Weight of polymer left after 4 weeks (g)	Cumulative weight loss after 4 weeks (g)	Total weight loss (%)
1.	Pectin-*cl*-poly(AAm)	0.012	0.184	0.116	38.66
2.	Pectin-*cl*-poly(AAm)	0.046	0.107	0.193	64.33
3.	Pectin-*cl*-poly(AAmPSA)	0.012	0.076	0.224	74.66
4.	Pectin-*cl*-poly(AAmPSA)	0.046	0.020	0.28	93.33
5.	Pectin-*cl*-poly(N-i-PAAm)	0.046	0.103	0.197	65.66
6.	Pectin-*cl*-poly(N-i-PAAm)	0.12	0.083	0.217	72.33

metal ions, selectivity and high efficiency can be induced in the networks by choosing reaction conditions to tailor the structural aspects of polymers. The results from biodegradation studies are useful from the technological viewpoint. The facile biodegradability of these hydrogels means that after use in metal ion separation and enrichment technologies, these hydrogels will not generate waste as after repeated uses these hydrogels can be subjected to biodegradation for recovery of the sorbed metal ions.

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