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Post functionalization of carboxymethylated starch and acrylonitrile based networks through amidoximation for use as ion sorbents

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Abstract

Carboxymethylation of starch provided carboxymethyl starch (CMS) and the modification was followed by grafting CMS with acrylonitrile (AN) using ammonium per sulphate-*N*,*N*,*N*,*N*-tetramethylethylene diamine as initiator–accelerator system. Crosslinked networks of CMS and AN were obtained using two crosslinkers, viz., *N*,*N*-methylenebisacrylamide and ethyleneglycoldimethacrylate. The networks were further reacted with hydroxylamine to generate metal ion active amidoxime groups. The synthesized hydrogels were characterized by FTIR, SEM, nitrogen analysis and swelling studies to evaluate water uptake and the candidate polymers were used as matrices for the sorption of Fe^{2+} ions, as a model metal ion, as a function of time, temperature, pH and ionic strength. An attempt was made to investigate the thermodynamics of its sorption behaviour.

Keywords: Carboxymethylation; Acrylonitrile; Amidoxime and ion sorption

1. Introduction

Biopolymers afford eco-friendly and cost-effective materials with diverse properties for use in a wide spectrum of applications. Hydrogels based upon biopolymers like starch, cellulose, gums and chitosan are finding extensive use in various fields including enrichment and separation technologies. Heavy metal ions constitute a major part of the pollutants in the environment (Molina, Gomez-Anton, Rivas, Maturana, & Pierola, 2001; Rivas, Maturana, Peric, & Villegas, 1999). Many conventional techniques are used for the removal of toxic metal ions (Rivas, Pooley, Maturana, & Villegas, 2001). Natural renewable polysaccharides have been reported to be efficient metal ion sorbents as their main chain units contain hydroxyl groups which act as binding sites for metal ions (Chauhan, Guleria, & Sharma, 2005; Muzzarelli, 1973). The hydrophilicity of these polymers contributes to amorphous structure in water and hence improves their metal ion sorption properties (Tokura et al., 1984). Modification of these polymers via simple derivatization, grafting or network formation improves these properties further, hence end-use spectrum of these polymers is widened. Carboxymethylation is one such derivatization reaction of the polysaccharides that enhances their water interaction property along with imparting cation exchange properties due to the carboxyl group. This results in strong metal ion partitioning between the gel and the solution phase.

Functionalized biopolymers based supports have been found to be excellent host molecules for metal ion sorption (Chauhan & Mahajan, 2002). Cellulose graft polymers have been used for the competitive removal of Pb^{2+}, Cu^{2+} and Cd^{2+} ions from aqueous solutions (Guclu, Gurdag, & Ozgumus, 2003). Amaranthus starch has been complexed with metal cations and the –OH groups of the polymer are found to be the co-ordination sites (Ciesielski & Tomasik, 2003). Another report reveals the complexation behaviour of

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starch with Cr^{6+} ions (Xu, Zhang, Lu, Yang, & Cui, 2003). Crosslinked poly(acrylonitrile) and amidoximated networks obtained from the post functionalization of acrylonitrile (AN) based polymers are also useful in metal ion remediation (Badawy, 2003; Choi, Choi, Park, Lee, & Kang, 2003). A chelating resin is prepared with hydroxamic and amidoxime groups and the retention property of the resin for Pb^{2+}, Cd^{2+}, Cu^{2+}, Ni^{2+}, Zn^{2+}, Mn^{2+} and Fe^{3+} ions has been studied (Neagu, Bunia, Plesca, & Popa, 2003). Another study reveals the removal of cadmium from the scallop waste. A fabric adsorbent having amidoxime moiety has been used for the purpose (Shiraishi, Tamada, Saito, & Sugo, 2003). Amylopectin, corn starch, waxy corn starch and potato starch have been complexed with Co^{2+}, Cr^{2+}, Cu^{2+}, Mn^{2+} and Fe^{3+} ions and the ion binding is found to involve lone pairs of polysaccharide –OH groups (Ciesielski, Lii, Yen, & Tomasik, 2003).

The present article discusses the utilization of natural renewable resources for developing polymeric materials by using low energy processes and a minimum amount of auxiliary chemicals and solvents for the realization of some fundamental objectives of *green chemistry*. Starch is a natural plant product and it has been modified to the carboxymethylated form (CMS). The effect of the degree of substitution by carboxymethylation and saponification on the water interaction properties of poly(acrylonitrile) [PAN] grafted sodium salt of amylose and sodium salt of CMS has been well correlated (Shah, Patel, Patel, & Trivedi, 1992; Sinha, Patel, & Trivedi, 1993). Many other workers have also reported fundamental aspects of the carboxymethylation of starch and grafting of PAN onto it. However, there is not much information on the use of functionalized starches in specialty applications including water technologies. In the present article an active and easily amenable functional groups like nitrile and amidoxime have been incorporated onto the modified polymer through grafting and crosslinking reactions with acrylonitrile (AN) and further modification through polymer analogous reaction. Ammonium persulphate (APS) and *N*,*N*,*N*,*N*-tetramethylethylene diamine (TEMED) were used as initiator–accelerator system and crosslinking has been performed with two different crosslinkers viz. *N*,*N*-methylenebisacrylamide (*N*,*N*-MBAAm) and ethyleneglycoldimethacrylate (DEGMA). Networks of CMS and AN have been amidoximated to investigate the effect of conversion of hydrophobic nitrile function to hydrophilic amidoxime moiety. A range of polymers is obtained for use as supports for the sorption of Fe^{2+} ions. Fe^{2+} ion sorption on polymeric supports is a serious concern in the enrichment of actinides like uranium and in the drinking water technology as it is a common pollutant in the natural sources and industrial wastewater. However, after loading on the suitable polymers, it can also be utilized further as a catalyst in organic synthesis and also as supports for the anion adsorption (Chauhan et al., 2005). The main objective of the present study combines almost all these concerns. Thermodynamics of the metal ion has been investigated to understand the behaviour of these matrices as ion sorbents.

2. Materials and methods

2.1. Materials

Starch (Nice, Kochi, India), acrylonitrile, tetramethylethylene diamine (S. D. Fine Chemicals, Mumbai, India), *N*,*N*-Methylene bisacrylamide (CDH, New Delhi, India), ethyleneglycol dimethacrylate (Merck, Schuchardt, Germany), ammonium persulphate (analytical grade, Glaxo, Mumbai, India), monochloroacetic acid (BDH, Mumbai, India), hydrochloric acid, hydroxylamine and methanol (Ranbaxy, New Delhi) were used as received.

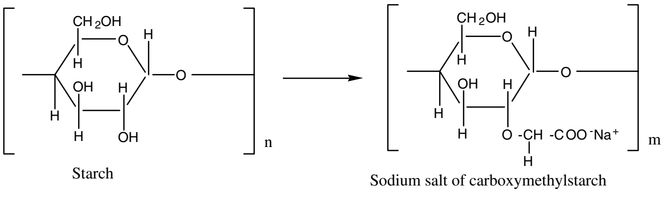
2.2. Derivatization of starch to CMS

An improvised technique was employed for the derivatization of starch via carboxymethylation. 10 g of the polymer was stirred with 18% NaOH for 1 h and 2-propanol was then added to the contents. Reaction mixture was kept for a period of 45 min at 70 °C. A solution of 14 g of chloroacetic acid in 2-propanol was then added to the contents over a period of 20–30 min and kept undisturbed for heating at 70 °C for another 2.5 h. Cooling of the reaction mixture, neutralization with acetic acid and then extraction with methanol afforded water-soluble carboxymethylated product, i.e., carboxymethyl starch (CMS). Carboxymethylation of starch (S) occurs in two steps given below:

$$\text{S–OH} + 18\%\ \text{NaOH} \rightarrow \text{S–O}^-\text{Na}^+ + \text{H}_2\text{O} \tag{1}$$

$$\text{Cl–CH}_2\text{CO}_2\text{H} + \text{S–O}^-\text{Na}^+ \rightarrow \text{S–O–CH}_2\text{CO}_2\text{H} + \text{NaCl} \tag{2}$$

Sodium salt of CMS is shown here.



Volumetric method was used to evaluate the degree of substitution (DS) in the products, which is symbolized by *m* and found to be 0.49 for CMS.

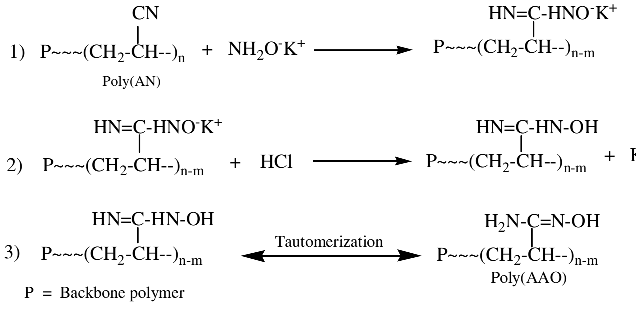
2.3. Functionalization of CMS

Further functionalization of CMS through grafting and crosslinking reactions with AN was affected through chemical initiation using the APS–TEMED system and crosslinkers. C_2, C_3 and C_6 positions of anhydroglucose units of the polysaccharide are attacked by the free radicals formed from the initiator system resulting in polymeric radicals that react further with the monomer to give graft polymers. Three dimensional crosslinked networks are formed in the presence of crosslinkers. A set of reactions was carried out keeping all the parameters constant excluding one and optimum reaction conditions with respect to initiator–accelerator, monomer and crosslinker concentration were evaluated. Hence, 0.44 mM of APS and 3.33 mM of TEMED were evaluated as optimum [APS–TEMED] and all the reactions were carried out at 50 °C for 30 min. Homopolymer of AN was separated from the reaction mixture by using DMF as the non-solvent and graft copolymer was recovered by fractional precipitation. The polymers were dried in an oven at 40 °C and finally weighed. Crosslinking reactions using 18.87–47.17 mM of AN in the presence of 0.32 and 0.81 mM of *N*,*N*-MBAAm and 0.25 and 0.63 mM of DEGMA, separately, were found to afford networks with the lowest and the highest network yield expressed in terms of $P_{\text{add-on}}$, where:

$$P_{\text{add-on}} = \frac{\text{Weight of the network}}{\text{Weight of the CMS}} \times 100$$

2.4. Amidoximation

CMS-*co*-poly(AN) corresponding to the lowest and the highest $P_{\text{add-on}}$ synthesized with both the crosslinkers were further treated with hydroxylamine for the conversion of $-C{\equiv}N$ function to $-CH{=}NOH$ moiety. 1.0 g of the each of the polymers was taken with 50.0 mL of the distilled methanol. 20.0 mL of 20% $NH_2O^-K^+$ was added to the mixture followed by refluxing at 60–70 °C for 6 h with occasional shaking. The resulting product was filtered, washed with methanol and then with distilled water to remove traces of untreated $NH_2O^-K^+$. 0.5 N HCl was used to replace K^+ ions by H^+. The product was dried in oven at 50 °C, characterized and was labeled as CMS-*co*-poly(AAO). The mechanism of the reaction follows:



$$1)\ P\sim\sim\sim(CH_2\text{-}\overset{CN}{C}H\text{--})_n + NH_2O^-K^+ \longrightarrow P\sim\sim\sim(CH_2\text{-}\overset{HN=C\text{-}HNO^-K^+}{C}H\text{--})_{n-m}$$

Poly(AN)

$$2)\ P\sim\sim\sim(CH_2\text{-}\overset{HN=C\text{-}HNO^-K^+}{C}H\text{--})_{n-m} + HCl \longrightarrow P\sim\sim\sim(CH_2\text{-}\overset{HN=C\text{-}HN\text{-}OH}{C}H\text{--})_{n-m} + KCl$$

$$3)\ P\sim\sim\sim(CH_2\text{-}\overset{HN=C\text{-}HN\text{-}OH}{C}H\text{--})_{n-m} \xleftrightarrow{\text{Tautomerization}} P\sim\sim\sim(CH_2\text{-}\overset{H_2N\text{-}C=N\text{-}OH}{C}H\text{--})_{n-m}$$

P = Backbone polymer

Poly(AAO)

A net weight gain in the resultant amidoximes confirms the occurrence of the post reaction as is evident from Table 1.

Table 1
Percent Weight Change after Amidoximation

Network	$P_{\text{add-on}}$	Percent weight gain
CMS-*co*-poly(AAO)-*cl*-N,N-MBAAm	41.65	26.7
CMS-*co*-poly(AAO)-*cl*-N,N-MBAAm	68.15	59.4
CMS-*co*-poly(AAO)-*cl*-DEGMA	16.05	24.8
CMS-*co*-poly(AAO)-*cl*-DEGMA	33.07	25.3

2.5. Characterization

2.5.1. FTIR spectra

FTIR spectra of the CMS and its crosslinked networks were recorded on Perkin Elmer spectrophotometer in KBr pellets. Fig. 1a reveals the spectrum of CMS which exhibited prominent peaks at 3412.9 cm^{-1} (O—H stretching due to polymeric association), 2933.8 cm^{-1} (C—H stretching), 1156.6 cm^{-1} (C—O—C stretching) and at 1601.9 cm^{-1} (COO^- stretching). Network crosslinked through DEGMA shows peaks characteristic of AN function as revealed in Fig. 1b. CMS-*co*-poly(AN)-*cl*-*N*,*N*-MBAAm (-*cl*- stands for crosslinked) absorbs at 2245.0 cm^{-1} ($C{\equiv}N$ stretching) besides the usual peaks observed for CMS (Fig. 1c).

CMS-*co*-poly(AAO)-*cl*-*N*,*N*-MBAAm with bands at 3432.9 cm^{-1} (–OH stretching), 1669.8 cm^{-1} (C=N stretching) and 1023.8 cm^{-1} (N—O stretching) had residual $-C{\equiv}N$ peak with 16.8% decrease in absorbance that was observed at 2361.6 cm^{-1} (Fig. 2a). Fig. 2b reveals the spectrum of CMS-*co*-poly(AAO)-*cl*-DEGMA. Peaks corresponding to 3417.3, 1659.7, 1019.5 and 2363.2 cm^{-1} were observed due to the –OH stretching, C=N stretching, N—O stretching in oxime and residual $-C{\equiv}N$ moiety, respectively. The later was observed with 8.07% lowered absorbance, thus confirming the post reaction in the precursors.

2.5.2. SEM

SEMs of different polymers were taken on Jeol JSM-6100 scanning electron microscope. Surface morphology of polymeric structures as revealed from the SEMs clearly indicates the morphological changes brought about by different chemical reactions. Crosslinking of the backbone chains with monomer and crosslinker in the networks is evident as pore formations and crosslinks are visible as compared to the continuous surface of the backbone. Post reaction also affects the surface morphology in a significant manner as the pores got well defined after amidoximation (Fig. 3).

2.5.3. Nitrogen analysis

Carlo Erba EA-1108 was used to estimate the amount of nitrogen in various networks. Nitrogen contents in all the networks show much higher nitrogen. An increase in the amount of nitrogen is observed in all the amidoximes in comparison to their precursors, thus supporting the functionalization by post reaction. On amidoximation, nitrogen

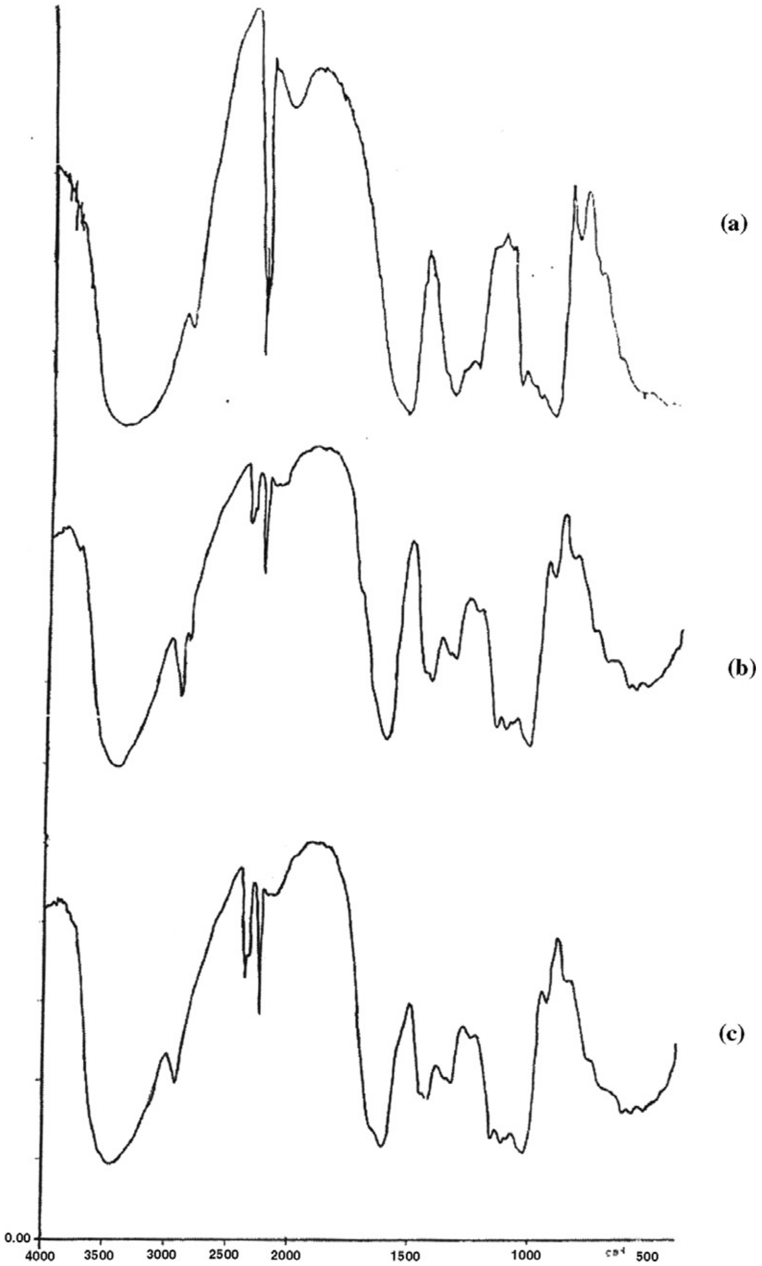


Fig. 1. FTIR spectra of (a) CMS (b) CMS-*co*-poly(AN)-*cl*-DEGMA (c) CMS-*co*-poly(AN)-*cl*-N,N-MBAAm.

contents increase by 2.43% in case of CMS-*co*-poly(AN)-*cl*-*N*,*N*-MBAAm, while an increase of 4.37% was observed in the network crosslinked with DEGMA. The results of nitrogen analysis are presented in Table 2.

2.5.4. Water uptake studies

Water uptake potential of various networks corresponding to the lowest and the highest $P_{\text{add-on}}$ was analyzed in distilled water. Polymers were immersed in water for different time intervals of 10, 30, 60, 120, 240 and 480 min at 25 °C. Swellability was evaluated in terms of S_r calculated as:

$$S_r = \frac{\text{Weight of swollen network}}{\text{Weight of xerogel}}$$

Water uptake was also studied as a function of temperature (30, 35, 40 and 45 °C) and pH. All the networks swell to the maximum in 240 min followed by constant S_r thereafter. Hence 240 min were taken as equilibrium swelling time. Temperature variation affects swellability in an adverse manner as polymers shrink on increase in temperature. The networks corresponding to the lowest $P_{\text{add-on}}$ exhibited higher S_r as compared to others. This may be attributed to the lower degree of crosslinking in these polymers with the result of more solvent diffusion into the polymeric structure and thus a higher S_r. The order of swellability in the medium of different pH was observed to be $7.0 > 9.2 > 4.0$. Functionalization of —CN groups to amidoxime groups are also supported from the observation that the later

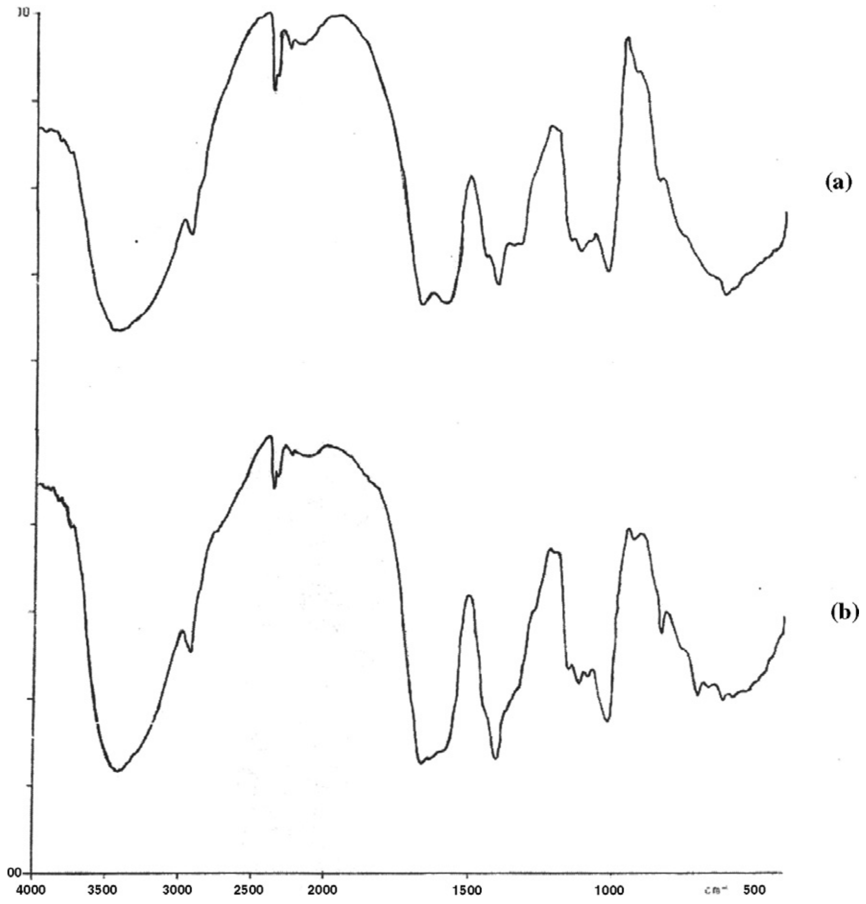


Fig. 2. FTIR spectra of (a) CMS-*co*-poly(AAO)-*cl*-N,N-MBAAm (b) CMS-*co*-poly(AAO)-*cl*-DEGMA.

shows higher water uptake than the hydrophobic precursor (Fig. 4).

2.6. Fe^{2+} sorption

The hydrogels were used as supports for the sorption of Fe^{2+} ions from the $FeSO_4 \cdot 7H_2O$ solution. Fe^{2+} ion uptake was studied as a function of different environmental factors like time, temperature, pH and ionic strength of the solution to evaluate the best conditions for its uptake. Known weight of the polymers was immersed separately in a known volume and strength of the ion solution. The residual solutions were analyzed for the concentration of rejected ions on DR 2010 spectrophotometer (Hach Co., US) by using the standard pillow reagents. The ion uptake was analyzed using the following relationships:

$$\text{Percent uptake } (P_u) = \frac{\text{Amount of metal ions sorbed}}{\text{Total ions in the feed solution}} \times 100$$

$$\text{Adsorption capacity } (Q) \text{ (mg/g)} = \frac{(C_o - C_t)V}{m}$$

where C_o and C_t denote the concentrations of ions, respectively, in the *feed* and after time t in the solution, V is the total volume and m is the weight of dry polymer (g).

3. Results and discussion

Anhydroglucose units of the polysaccharides possess active glycolic functionalities those can act as active sites to co-ordinate with the metal ions. The incorporation of metal ion active functional groups such as $-NH_2$, $-CO_2H$ and $-CH{=}NOH$ improves performance of the polymeric supports in enrichment and separation technology. Depending upon the structure of the supports and the nature of the active groups, mechanism of ion uptake is generally a combination of different processes like ion exchange, chelation and simple adsorption on the polymer surface as well as in the bulk. Hence, the general term sorption has been used to account for all the possible processes. As in the present study supports have active groups like $-CO_2H$ on CMS (exchange), $-CH{=}NOH$ (co-ordination) and the water uptake level of these supports counts for the partitioning of the metal ions between the solution and polymer phase.

3.1. Fe^{2+} sorption

Polymeric supports prepared after functionalization of starch by different post polymer reactions were used as supports for the uptake of Fe^{2+} from its aqueous solution. Ion

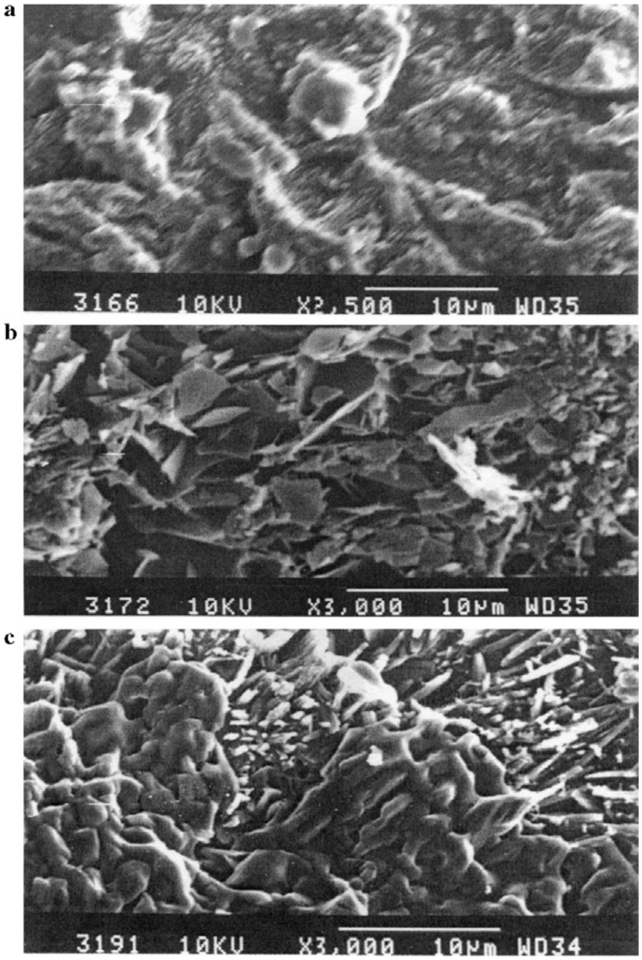


Fig. 3. Scanning Electron Micrographs of (a) CMS (b) CMS-*co*-poly(AN)-*cl*-N,N-MBAAm (c) CMS-*co*-poly(AAO)-*cl*-N,N-MBAAm.

uptake was thus studied as a function of the structural aspects of the polymeric supports as well as a function of different external environmental variable like time, temperature, pH and ionic strength.

3.1.1. *Effect of pH*

pH is an important determinant in the use of polymers as supports in the metal ion separation and enrichment technologies. In the present study it has been observed that Fe^{2+} uptake on the hydrogels is pH dependent. On variation of pH in the range from 4.0 to 9.2, the ion uptake decrease in the order $9.2 > 7.0 > 4.0$ for all the hydrogels. CMS-*co*-poly(AN)-*cl*-*N*,*N*-MBAAm sorbed a maximum of 75.32% of the Fe^{2+} ion under alkaline condition while the corresponding amidoxime showed some higher uptake of 77.14% of the ion under similar conditions. In both the series of hydrogels, comparatively the higher ion uptake was observed on the amidoxime under acidic conditions (Fig. 4a). This implies that with the change in the pH, there is not only change in the amount of ion uptake, but there is also change in the mechanism of the sorption from the preferred co-ordination at the lower pH to adsorption at the higher and alkaline pH.

The effect of the nature of the crosslinker is evident. In the case of CMS-*co*-poly(AN)-*cl*-DEGMA, a maximum P_u of 90.34% was observed in the alkaline medium. Increase in the ion uptake at the higher pH is due to the higher partitioning of the metal ions from the solution phase as compared to rather deswelling at the lower pH where cationic species form the buffer also compete for the active sites on the polymer phase. At the lower pH, amidoximes synthesized from both the crosslinkers showed the higher P_u than the precursors. At the higher pH, DEGMA based hydrogels are more efficient. Hence for further studies only the DEGMA based hydrogels were used.

3.1.2. *Effect of time*

The high water absorbing tendency of the polymers enable these to partition ionic species from the solution phase to the polymer phase. Within just 10 min 32% ion uptake has been observed and that too at the ambient temperature. The ion uptake increases with time, up to 240 min and neutral pH, as is evident from Fig. 4b. Thereafter it tends to become independent of the time as P_u was almost constant on further increase in sorption time to 480 min. Hence, 240 min was taken as equilibrium sorption time. A maximum P_u of 41.45% was observed after 240 min at 25 °C in case of CMS-*co*-poly(AN)-*cl*-DEGMA, that is more than the value observed for corresponding amidoxime. It, thus, implies that the mechanism of sorption is more by adsorption rather than by co-ordination on the pendant groups.

3.1.3. *Effect of temperature*

The effect of variation of temperature is evident from Fig. 4c. Increase in temperature beyond 30 °C adversely affects sorption behaviour of the polymeric supports. However, there is more selectivity as the temperature increases to 40 °C. These results are of technical interest as at low temperature these hydrogels exhibits the higher efficiency.

Table 2
Nitrogen Analysis

Network	$P_{add\text{-}on}$	Weight of polymer (mg)	Percent Nitrogen	Weight of Nitrogen (mg)
CMS	—	2.016	0.0	0.0
CMS-*co*-poly(AN)-*cl*-N,N-MBAAm	68.15	2.134	7.08	0.151
CMS-*co*-poly(AN)-*cl*-DEGMA	33.07	1.844	7.24	0.133
CMS-*co*-poly(AAO)-*cl*-N,N-MBAAm	68.15	1.872	9.52	0.166
CMS-*co*-poly(AAO)-*cl*-DEGMA	33.07	2.305	11.61	0.187

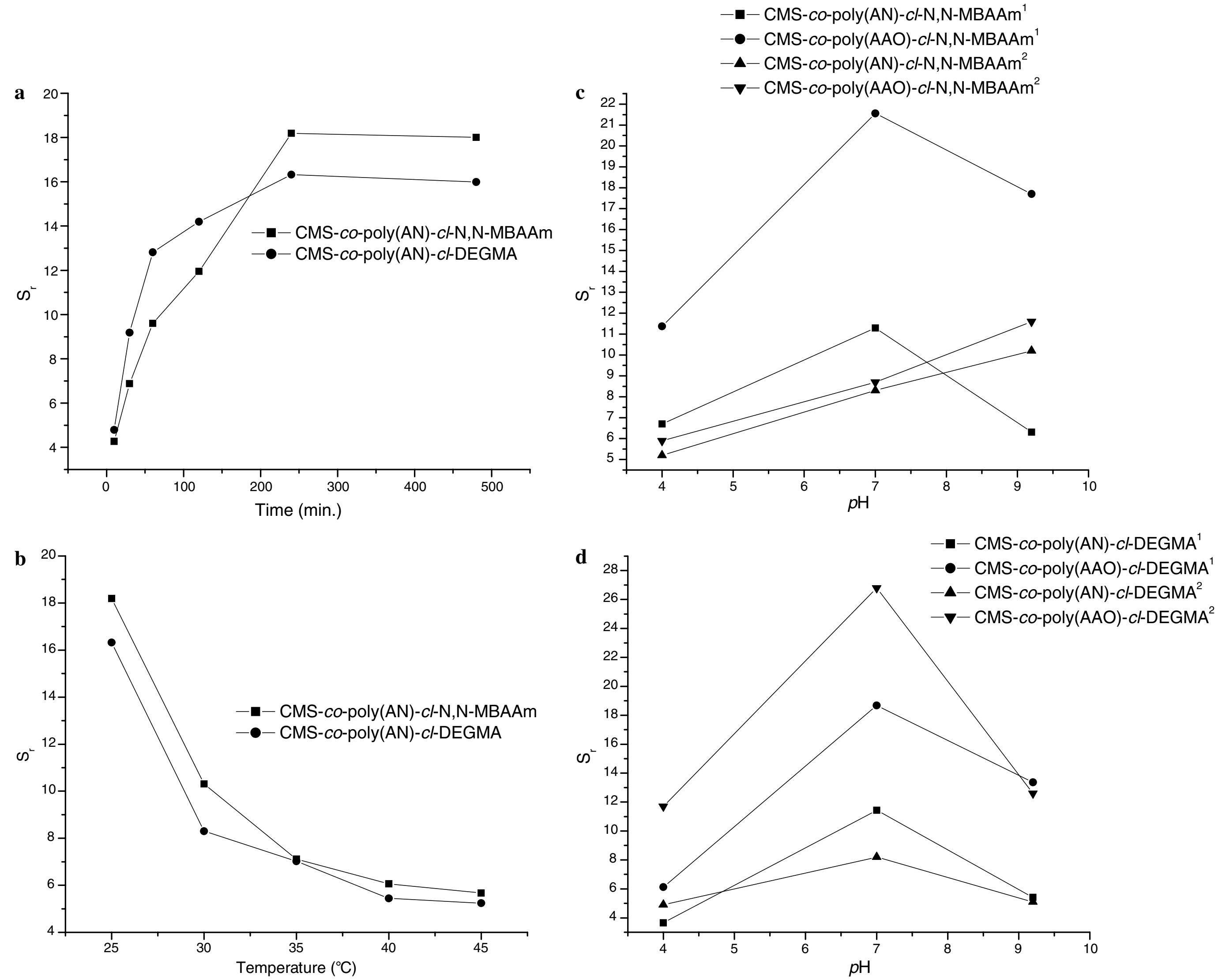


Fig. 4. (a) Fe^{2+} ion uptake potential of the polymers as a function of time. $FeSO_4.7H_2O$ sol. = 10 mg Fe^{2+}/L, temp. = 25 °C, weight of the polymer = 0.1g. (b) Fe^{2+} ion uptake potential of the polymers as a function of temperature. $FeSO_4.7H_2O$ sol. = 10 mg Fe^{2+}/L, time = 240 min., weight of the polymer = 0.1 g. (c) Fe^{2+} ion uptake potential of the polymers as a function of *p*H. $FeSO_4.7H_2O$ sol. = 10 mg Fe^{2+}/L, time = 240 min., temp. = 25 °C, weight of the polymer = 0.1 g. (d) Fe^{2+} ion uptake potential of the polymers as a function of ionic strength. Feed Sol. = $FeSO_4.7H_2O$, time = 240 min, temp. = 25 °C, weight of the polymer = 0.1g.

The observed results for the structural aspects of the hydrogels are similar to those discussed when considering the effect of time. Functionalization of nitrile groups to amidoxime does not increase ion uptake.

3.1.4. Effect of ionic strength

The effect of the Fe^{2+} ion strength on P_u was also studied (Fig. 4d). An initial increase in P_u was observed up to an intermediate concentration (10 mg Fe^{2+}/L), which tends to be constant thereafter till 11.5 mg Fe^{2+}/L followed by steep decrease. Thus, 10 mg Fe^{2+}/L was taken as the equilibrium concentration. At the higher concentrations of the ion solution, the tendency of the hydrogels to partition metal ions is decreased. The reason for the observed behaviour is correlated and is discussed under the water uptake behaviour of the hydrogels.

3.1.5. Water uptake in ion solution

A comparison of the water uptake capacity of the hydrogels in water and in Fe^{2+} ion solution reveals that under all the conditions of time, temperature and pH, all the hydrogels showed lesser water uptake in the ion solution than in the pure water (Fig. 5c and 5d). It is implied there from that metal ions are sorbed into the bulk of the hydrogels, where these crosslink with the pendant groups of the polymer as well as with the pendant groups of the backbones and other active sites including those of the corresponding crosslinkers. The resultant increase in the crosslinking density reduces the surface area of the bulk of the polymer, hence lower water uptake. Lowering of water uptake on metal ions loading also implies reduced biodegradability of the polymers and enhanced dimensional and mechanical stability of the metal ion loaded polymer.

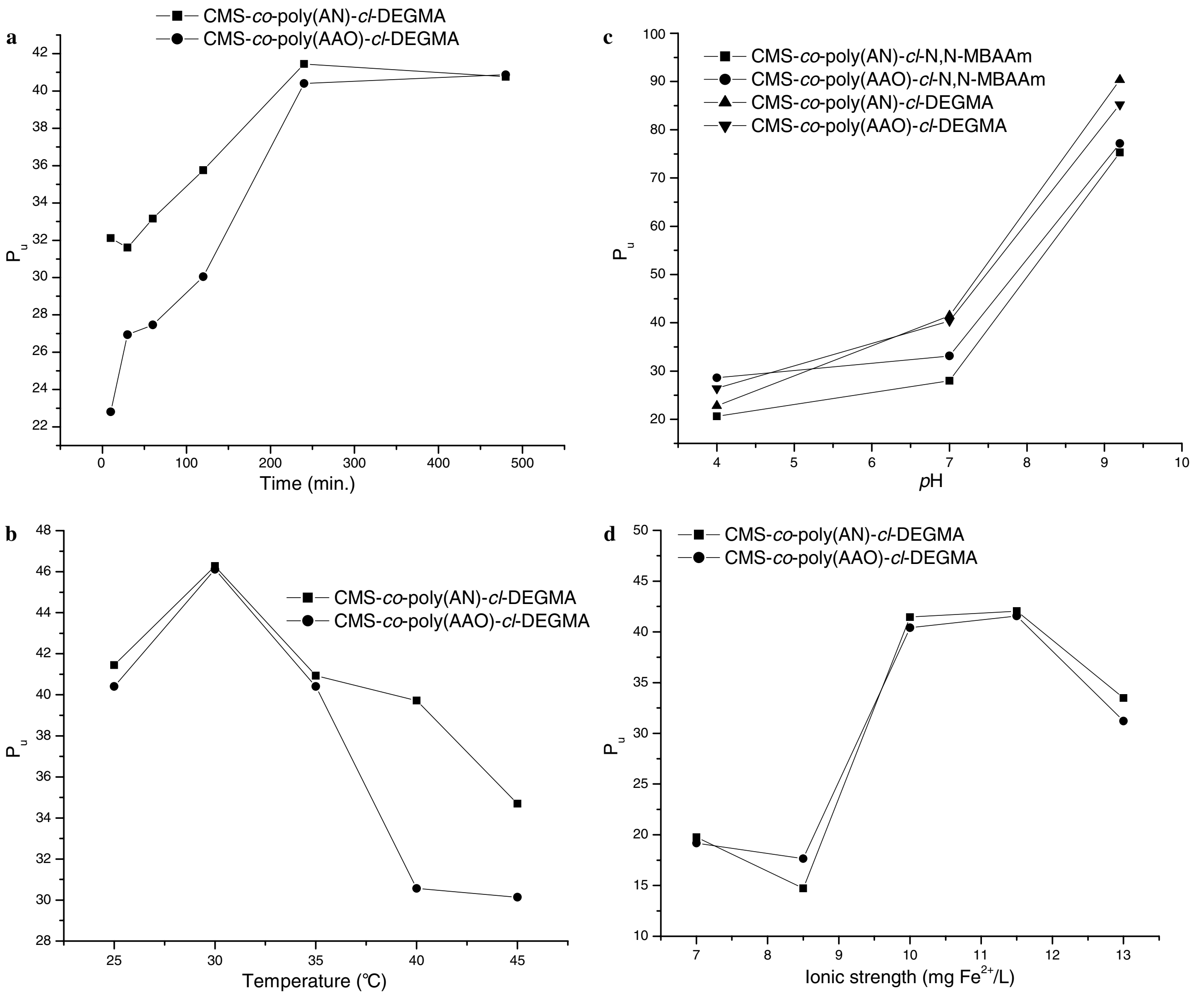


Fig. 5. (a) Water uptake of CMS-*co*-poly(AN) as a function of time. Temperature = 25 °C. (b) Water uptake of CMS-*co*-poly(AN) as a function of temperature. Time = 240 min. (c) Water uptake of various networks as a function of *p*H. Time = 240 min., temperature = 25 °C, $^{1} = H_2O$, $^{2} = FeSO_4.7H_2O$. (d) Water uptake of various networks as a function of *p*H. Time 4h, temperature = 25 °C, $^{1} = H_2O$ $^{2} = FeSO_4.7H_2O$.

3.1.6. Thermodynamics of the adsorption process

Temperature of the medium significantly affects adsorption characteristics of these polymer supports. Simplification and understanding of the adsorption processes in terms of the mechanism of the metal ion uptake is understood by using thermodynamic approach. Adsorption capacity (Q) was calculated for all the observations at different temperatures and log Q/C_e was plotted versus $1/T$. Enthalpy change (ΔH°) for the adsorption process was obtained from the slope of the graph and entropy change (ΔS°) was calculated using Van't Hoff equation.

$$\log\frac{Q}{C_e}=\frac{\Delta H^\circ}{2.303RT}+\frac{\Delta S^\circ}{2.303R}$$

where C_e was the equilibrium concentration of the ion solution. Gibbs free energy change (ΔG°) was calculated from equation given below:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

The values of different parameters are presented in Table 3 and it can be deduced from the negative values of ΔH° and ΔG° that these adsorption processes are exothermic and spontaneous in nature. The high efficiency of the metal sorption at lower temperatures is a significant observation that should be useful to develop least energy intensive supports for the metal ion enrichment and remediation technologies. Further, the positive entropy values manifest a lower order for the processes.

4. Conclusion

From the forgoing discussion it can be concluded that the Fe^{2+} ion uptake is dependent both on the structural aspects of the polymers as well as on the environmental

Table 3
Evaluation of Thermodynamic Parameters for Fe^{2+} Ion Sorption

Temperature (°K)	Δ H° (J mol^{-1})	Δ G° (KJ mol^{-1})	Δ S° (J $mol^{-1}K^{-1}$)
CMS-*co*-poly(AN)-*cl*-DEGMA			
298	−11.26	−13.69	45.89
303		−13.85	45.66
308		−14.06	45.62
313		−14.26	45.53
318		−14.14	44.42
CMS-*co*-poly(AAO)-*cl*-DEGMA			
298	−7.66	−13.62	45.69
303		−13.76	45.40
308		−13.72	44.52
313		−13.57	43.33
318		−13.76	43.26

Feed solution = Fe^{2+} (10mg iron/L).

factors. The effect of the nature of the crosslinker is an important observation as the higher ion uptake has been observed with hydrogels crosslinked with ethyleneglycol dimethacrylate. The effect of the functionalization of polymers by polymer analogous reactions like amidoximation did not result in the improvement of the ion uptake efficiency, especially at the higher pH. The observed ion uptake behaviour is both temperature and pH dependent. These results are important from the technological viewpoint as the pH and temperature sensitivity of these polymers towards ion uptake can be used to desorb the metal ions for reusability of the polymers. The adsorption processes are exothermic and spontaneous in nature. Positive entropy values manifest lower order of the processes at all the temperatures. The operation of ion sorption provides energy economy as the best results were obtained at ambient temperatures.

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