

A Study on the Sorption of NO_3^- and F^- on the Carboxymethylated Starch-Based Hydrogels Loaded with Fe^{2+} Ions

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ABSTRACT: Using the principle of geochemistry of fluoride, green and cost effective anion adsorbents were developed for the removal of F^- from water systems. The scheme was further applied for the removal of NO_3^- also. Carboxymethylated starch functionalized through network formation with acrylamide was used as adsorbent, and the resultant hydrogels were loaded with Fe^{2+} ions to generate anchorage for the anions. Sorption of Fe^{2+} was studied as a function of different factors such as time, temperature, pH, and ion strength. The network having the highest Fe^{2+} uptake was loaded with the Fe^{2+} ions under optimum con-

ditions and used for the sorption of F^- and NO_3^- . High efficiency has been observed for F^- , as even up to 100% uptake has been observed within just 10 minutes. The support shows high selectivity for NO_3^- , which was used as anion reference. Thermodynamics of sorption confirms low order and low energy processes. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 106: 1924–1931, 2007

Key words: anion remediation; carboxymethylation; geochemistry of fluoride; green products and green processes; polymeric support

INTRODUCTION

Recent developments in the field of ion-specific resins have been reported for the heavy metal ion removal.^{1–5} Complexation behavior of these resins is influenced by their characteristic features.^{6–9} Polymeric supports possessing amide, carboxylic, or ammonium groups have been widely used in this area.^{10–13} On the other hand, utilization of natural resources in developing ion-binding supports is increasing because of their cost-effective, eco-friendly, and renewable nature. Many workers have reported the use of natural wastes to develop ion adsorbents.^{14–18} In our earlier studies, we have utilized pine needles as a source of cellulose to develop metal ion adsorbents.^{19–21} Amylopectin, corn starch, waxy corn starch, and potato starch have also been used in complexing various metal ions.²² Polymers based upon acrylamide (AAM) have also been widely reported as effective ion sorbents primarily because they are highly water solubilizing monomers, are efficient adsorbents, and offer tremendous ease of modification by polymer analogous reactions like partial hydrolysis, alkylation, and other reactions.^{23–26} Polysaccharides are a rich reservoir of structurally and functionally different chemical moieties and possess additional advantage of under-

going simple chemical modifications. Being biodegradable and hydrophilic, these polymers are important materials in the areas of separation, enrichment, and water management. Modification of polysaccharides via carboxymethylation is the commonest of all the polymer analogous reactions that enhances water interaction of polymer and also contributes to cation exchange property of these polymers. Further modification of these polymers through grafting and crosslinking reactions affords tailor-made products with desirable and targeted features. In view of the above, the present communication reports an attempt to develop green products and green processes using starch-based cost effective polymeric supports for the removal of F^- from water. Apart from arsenic, F^- is the major anionic hazard in the water systems in many parts of India and many other countries. Apart from the natural occurrence, fluoride enters water stream from the discharges of effluents of industries like steel and aluminum, electroplating, pesticides, fertilizers, glass manufacturing, groundwater, and the semiconductor industries. Geochemistry of fluoride reveals that F^- is present along with Al^{3+} or Fe^{2+} in the natural systems. In our earlier studies, we have reported that poly(AAM) and natural polymer based hydrogels have greater affinity for Fe^{2+} ions that are not only adsorbed at the surface, but are also held in the bulk by interaction with the pendant polar groups. Thus, assuming the nontoxic nature of Fe^{2+} and geo-chemical affinity of Fe^{2+} and F^- ions; Fe^{2+} loaded matrix can thus be easily prepared to be

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used as F⁻ adsorbent. Using the same assumption, NO₃⁻ ions were also sorbed as reference anions on the Fe²⁺ loaded supports to evaluate the selectivity of these supports to different anionic species. Carboxymethylated starch and its hydrogels with AAm were prepared in the presence of ammonium persulphate (APS) and tetramethylethylene diamine (TEMED) as initiator–accelerator system, and *N,N*-methylene bisacrylamide (*N,N*-MBAAm) and ethylene glycol dimethacrylate (DEGMA) as two different crosslinkers. Water uptake, FTIR, and SEM were used to characterize these hydrogels.

EXPERIMENTAL

Materials and methods

Starch (Nice, Kochi, India), AAm, *N,N*-MBAAm, and TEMED (S.D. Fine, Mumbai), DEGMA (Merck, Schuchardt, Germany), APS (analytical grade, Glaxo, Mumbai, India), and monochloroacetic acid (BDH, India) were used as received.

Functionalization of starch by carboxymethylation

Starch was carboxymethylated using an improvised technique. Ten grams of the polymer was stirred with 18% NaOH for 1 h. It was followed by the addition of 2-propanol to the reaction mixture and was kept at 70°C for 45 min. After that a solution of 14 g of chloroacetic acid dissolved in 2-propanol was added slowly (over a period of 20–30 min) to the contents and kept undisturbed for heating at 70°C for 2.5 h. The reaction mixture was cooled, neutralized with acetic acid, and then extracted with methanol. The water soluble carboxymethyl starch product was labeled as CMS. Degree of substitution (DS) was calculated by volumetric method.²⁷

Functionalization of CMS by network formation

CMS was crosslinked with AAm using a set of optimum conditions of initiator and accelerator concentration (CMS = 2.0 g, APS = 0.44 mM, TEMED = 0.33 mM).²⁸ Crosslinker concentration was varied over a range of 1–6% of the AAm concentration. All the reactions were carried out at 50°C for 30 min. The self-insolubilized product was separated from the reaction mixture and stirred with water for 1 h to remove any soluble fraction. The hydrogels were dried in air oven at 40°C and represented as CMS-*cl*-poly(AAm)-*cl*-*N,N*-MBAAm and CMS-*cl*-poly(AAm)-*cl*-DEGMA, where *cl* stands for crosslinked. The process was repeated to obtain constant weight and polymer yield was noted. Percent polymer yield (%*P*) was calculated as²⁹:

$$\%P = \frac{\text{Weight of crosslinked polymer}}{\text{Weight of all the reacting mass}} \times 100$$

Characterization of hydrogels

Evidence of crosslinking has been provided by FTIR and SEM. FTIR spectra of CMS and the different crosslinked hydrogels were recorded on Perkin Elmer spectrophotometer in KBr pellets. SEMs were taken on Jeol JSM-6100 scanning electron microscope. Water uptake of the hydrogels was studied in distilled water by immersion of the polymers in water at different time intervals from 10, 30, 60, 120, 240, and 480 min to observe equilibrium swelling. The effect of temperature was studied at five different temperature conditions, as well as under alkaline and acidic pH to evaluate the water uptake potential of the polymers under variable parameters. Swelling ratio (*S_r*) was calculated as shown:

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

Ion sorption studies

Around 0.1 g of the hydrogel was immersed in the solution of known concentration of FeSO₄·7H₂O (20 mL), and ion uptake (Fe²⁺) for solution was studied on candidate polymers as a function of time, temperature, pH, and ionic strengths of the feed solution. The hydrogels were removed from the ion solution by filtration, whereas in case of starch and carboxymethyl starch, after the completion of sorption time, the solutions were subjected to centrifugation (at 3000 rpm) for 5 min and then allowed to stand to ensure complete separation of the soluble polymer phase. All the residual solutions thus obtained were analyzed for the concentration of rejected ions on DR 2010 spectrophotometer (Hach Co., US) by using its pillow reagents. The hydrogel that showed the best Fe²⁺ uptake was used for the sorption of anions. It was loaded with Fe²⁺ under optimum conditions of time, temperature, pH, and ionic strength. Known weight of the Fe²⁺ loaded hydrogel was immersed separately in a known volume and strength of KF and KNO₃. The maximum readability of the spectrophotometer is 0–3.0, 0–2.0, 0–30.0 mg/L for Fe²⁺, F⁻, and NO₃⁻, respectively. Ion uptake was expressed by the following relationships:

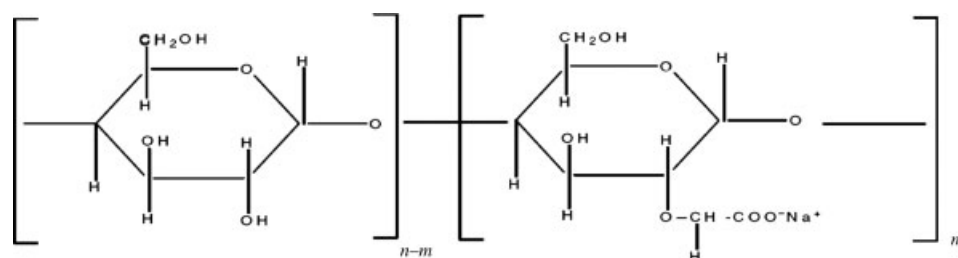
$$\text{Percent uptake } (P_u) = \frac{\text{Amount of metal ions sorbed}}{\text{Total ions in the feed solution}} \times 100$$

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

Maximum retention capacity (MRC) was calculated from the milligram of metal ion retained per gram of the polymer.³⁰

$$\text{MRC} = \frac{(C_m \times V)}{m}$$

where C_o and C_t denote the concentrations of ions, respectively, in the feed and after time t in the solution, m is the weight of dry polymer (g), C_m is the metal ion concentration sorbed by the polymer, and V is the total volume of the solution (L).



where n is degree of polymerization and DS is represented by m and the later was found to be 0.49. Crosslinking reactions take place via free radical mechanism, as hydrogen atoms from C-2, C-3, and C-6 positions of anhydroglucose units of the polysaccharides are abstracted by the free radicals resulted from the initiator system. Crosslinker concentration corresponding to 5% by weight of the [AAm] provided the maximum crosslinking efficiency as was observed from the %P values (Fig. 1). The modified starch has been characterized by FTIR and SEM to obtain evidence of crosslinking and poly(AAm) incorporation.

FTIR spectroscopy

FTIR spectra of CMS and the corresponding hydrogels with AAm have been shown in Figure 2. Pres-

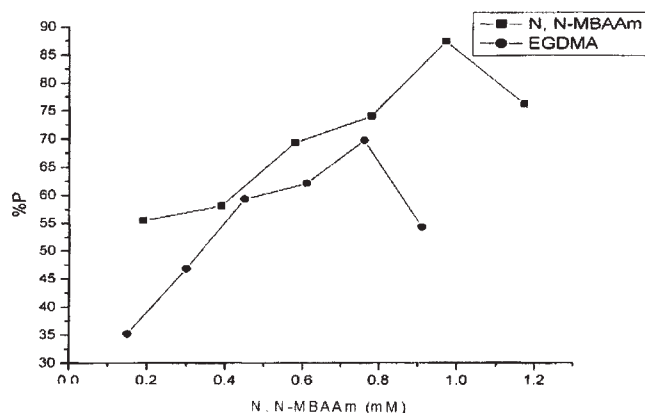
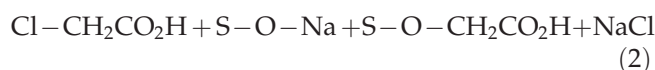


Figure 1 %P values as function of crosslinker concentrations.

RESULTS AND DISCUSSION

Carboxymethylation is an etherification reaction that proceeds as follows:



Sodium salt of CMS can be represented as shown ahead:

ence of peaks characteristic of C=O and C—N stretching of amide group and those because of the functionalities of the crosslinkers in the hydrogels, besides the peaks characteristic of the backbone, confirm the incorporation of the monomer onto the polymer. CMS absorbs at 3412.9 cm^{-1} . (O—H stretching because of the 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) [Fig. 2(a)]. CMS-cl-poly(AAm)-cl-N,N-MBAAm shows prominent peaks at 1670.5 cm^{-1} (C=O stretching of amide group) and 1454.1 cm^{-1} (C—N stretching) besides the above listed peaks [Fig. 2(b)]. Spectrum of the network crosslinked with DEGMA also possesses peaks ascribed to the grafted poly-(AAm) [Fig. 2(c)].

Scanning electron micrography

Considerable morphological changes in the hydrogels have been observed compared with the continuous surface of the native starch. These provide strong evidence that starch backbone has been functionalized (Fig. 3).

Water uptake behavior

Water uptake was studied on the crosslinked hydrogels corresponding to the lowest and the highest %P as a function of time, temperature, and pH. The equilibrium swelling of the hydrogels was observed after 240 min, as water uptake remains constant

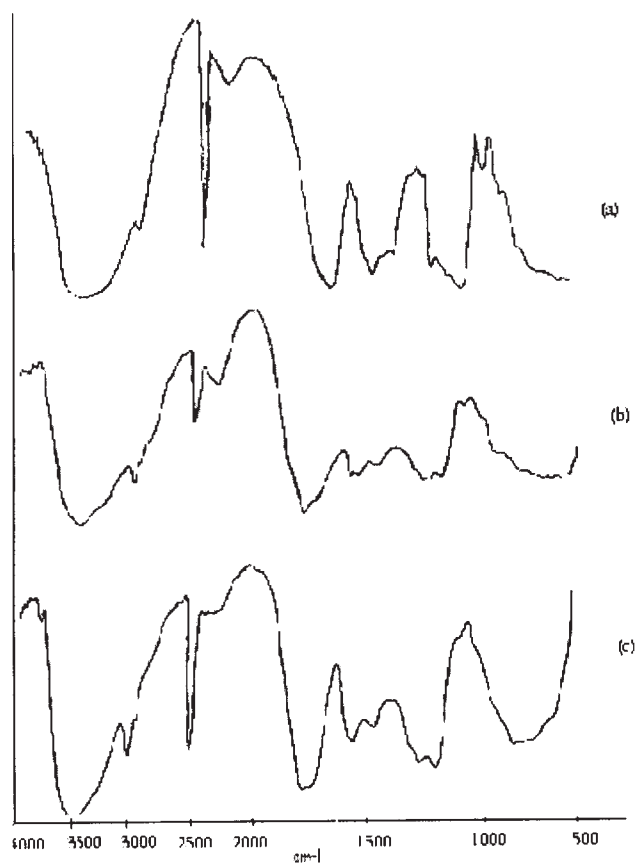


Figure 2 FTIR spectra of different hydrogels (a) CMS, (b) CMS-co-poly(AAm)-cl-N,N-BAAm, and (c) CMS-co-poly(AAm)-cl-EGDMA.

thereafter (Table I). Increase in the swelling temperature lowered the swellability of the polymers, whereas pH affected the uptake potential in the order: 7.0 > 9.2 > 4.0.

Fe²⁺ sorption: Selection of the most efficient support

Apart from —OH, —CONH₂, —CO₂H, and —SO₃H, glycolic functions of the anhydroglucose units of the polysaccharides also afford coordination of linkage for metal ions. In case of the hydrogels, ion sorption is a combination of ion exchange by —COO—, adsorption on adsorbent groups like —CONH₂, and sorption in bulk by water absorption as a result of the partitioning of metal ions between solution and gel phase. The results from the present study for the Fe²⁺ sorption have been presented in Table I. For the sake of comparison, the results of sorption of Fe²⁺ by starch and CMS are presented in Table I. Metal ion uptake is increased on carboxymethylation of starch, but not significantly. Starch and CMS are not very efficient metal ion sorbents compared with the crosslinked networks. The later not only contain metal ion active amide groups, but they also are

good absorbents of water, and hence also partition metal ions from the solution phase. In case of the crosslinked networks, after 240 min, the network crosslinked with *N,N*-MBAAm has higher P_u of 90.93% compared with 85.78% in case of the DEGMA crosslinked network. An increase in temperature adversely affected both water uptake and ion sorption. Hence, Fe²⁺ sorption as a function of pH and ionic strength of the feed solution was studied at 240 min and 25°C. The nature of the medium affects P_u in the order: 9.2 > 7.0 > 4.0. The highest value of 91.64% was observed in *N,N*-MBAAm crosslinked polymer in medium of pH 9.2. On increasing the Fe²⁺ strength, P_u increased up to 10.0 mg Fe²⁺ per liter (equilibrium concentration) and remained almost same on further increase of the ion strength. Water uptake by the hydrogels investigated in ionic solutions was observed to be lesser than in case of pure water. The presence of Fe²⁺ ions in the hydrogel results in new crosslink formation, and thus, a reduction in water uptake is observed. This also explains the equilibrium ion uptake after certain ion strength. CMS-cl-poly(AAm) crosslinked with *N,N*-MBAAm was investigated further for evaluating its MRC for Fe²⁺ ion uptake by using total three feeds of the ion solution.

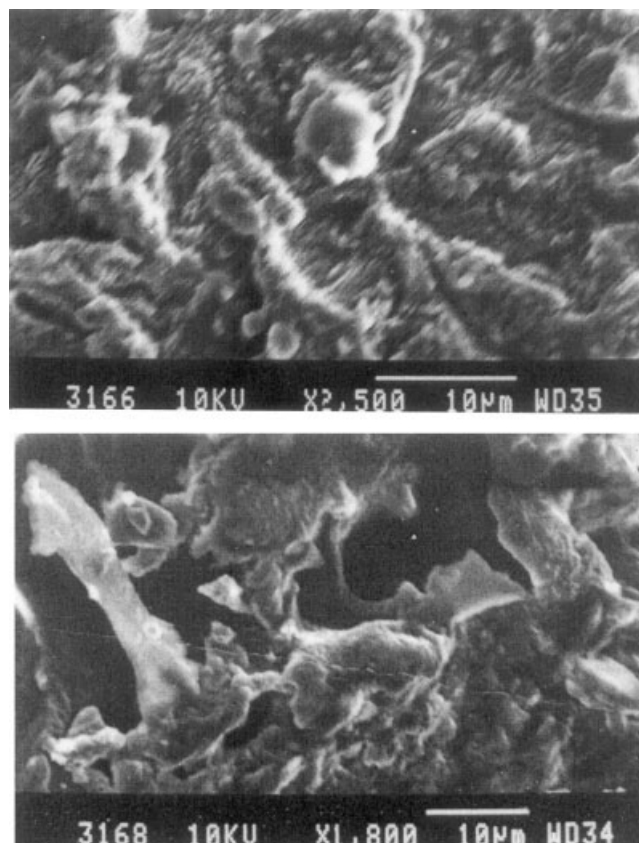


Figure 3 SEMs (from top): CMS and CMS-co-poly(AAm)-cl-N,N-MBAAm.

TABLE I
 S_r , P_u , and MRC Values of Fe^{2+} Sorption

Polymers	Variation of time at 25°C ^a									
	10 min		30 min		60 min		120 min		240 min	
	P_u	S_r	P_u	S_r	P_u	S_r	P_u	S_r	P_u	S_r
Starch	2.79	–	10.92	–	13.81	–	18.37	–	20.54	–
CMS	3.31	–	13.34	–	21.50	–	29.23	–	30.21	–
CMS- <i>cl</i> -poly(AAm) ^b	16.09	19.3	30.4	32.7	50.2	40.2	73.93	56.4	90.93	60.2
CMS- <i>cl</i> -poly(AAm) ^c	11.4	12.3	27.0	17.7	44.3	28.3	80.12	48.3	85.78	51.9

Polymers	Variation of temperature at 240 min ^a									
	25°C		30°C		35°C		40°C		45°C	
	P_u	S_r	P_u	S_r	P_u	S_r	P_u	S_r	P_u	S_r
CMS- <i>cl</i> -poly(AAm) ^b	90.93	60.2	77.4	56.4	51.2	40.3	30.6	32.7	23.6	19.6
CMS- <i>cl</i> -poly(AAm) ^c	85.78	51.9	69.2	43.7	41.7	36.4	19.2	21.2	17.2	11.2

Polymers	Variation of ionic strength at 240 min and 25°C									
	7 mg Fe^{2+} /L		8.5 mg Fe^{2+} /L		10 mg Fe^{2+} /L		11.5 mg Fe^{2+} /L		13 mg Fe^{2+} /L	
	P_u	S_r	P_u	S_r	P_u	S_r	P_u	S_r	P_u	S_r
CMS- <i>cl</i> -poly(AAm) ^b	17.44	48.2	20.0	45.9	90.93	60.2	88.85	35.6	87.44	23.6
CMS- <i>cl</i> -poly(AAm) ^c	21.01	10.2	18.82	10.6	85.78	51.9	85.32	11.5	83.76	9.2

Polymers	Variation of pH at 240 min and 25°C ^a					
	4.0		7.0		9.2	
	P_u	S_r	P_u	S_r	P_u	S_r
CMS- <i>cl</i> -poly(AAm) ^b	25.91	7.8	90.93	60.2	91.64	18.7
CMS- <i>cl</i> -poly(AAm) ^c	23.83	4.9	85.78	51.9	85.68	7.9

Polymers	Evaluation of MRC at 240 min and 25°C ^a								
	First feed of feed solution			Second feed of feed solution			Third feed of feed solution		
	P_u	S_r	MRC	P_u	S_r	MRC	P_u	S_r	MRC
CMS- <i>cl</i> -poly(AAm) ^b	88.35	35.6	3.918	93.51	53.9	4.146	94.21	65.4	4.176

^a FeSO_4 solution = 20 mL and hydrogel's weight = 0.1 g.

^b Crosslinked with *N,N*-MBAAm.

^c EGDMA.

Thermodynamic behavior of Fe^{2+} ion sorption

Temperature variation significantly affects ion sorption behavior of the polymeric matrices. Thermodynamic approach can thus be utilized for further simplification and understanding of the sorption behavior in terms of thermodynamic properties. Adsorption capacity (Q) was evaluated for the hydrogels under different temperature conditions and $\log Q/C_e$ was plotted against $1/T$. Slope of the graph provided the enthalpy change (ΔH^0) for the sorption process and entropy change (ΔS^0) was calculated using Van't Hoff equation.³¹

$$\log \frac{Q}{C_e} = \frac{\Delta H^0}{2.303RT} + \frac{\Delta S^0}{2.303R}$$

where C_e is the equilibrium concentration of the ion solution, that is, affording maximum P_u . Gibb's free

energy change (ΔG^0) was calculated from equation given below:

$$\Delta G^0 = \Delta H^0 - T\Delta S^0$$

These observations are presented in Table II. It can be deduced from the negative values of ΔH^0 and ΔG^0 that cation sorption processes were exothermic and spontaneous in nature. Positive entropy values manifest lower order of the processes at all the temperatures.

Adsorption of F^- and NO_3^- on Fe^{2+} loaded hydrogel

Since the highest P_u was observed in CMS-*cl*-poly(AAm)-*cl*-*N,N*-MBAAm for Fe^{2+} , it was loaded with Fe^{2+} under the optimum conditions of sorption, as

TABLE II
Thermodynamic Values of Fe²⁺ Sorption

CMS- <i>cl</i> -poly(AAm) ^a			
Temperature (K)	ΔH^0 (J/mol)	ΔG^0 (KJ/mol)	ΔS^0 (J/mol/K)
298	-22.59	-1.53	5.05
303		-1.96	6.39
308		-3.05	9.84
313		-4.47	14.2
318		-5.22	16.34
CMS- <i>cl</i> -poly(AAm) ^b			
Temperature (K)	ΔH^0 (J/mol)	ΔG^0 (KJ/mol)	ΔS^0 (J/mol/K)
298	-18.57	-1.69	5.61
303		-2.24	7.34
308		-3.58	11.55
313		-5.67	18.06
318		-6.00	18.82

^a Crosslinked with *N,N*-MBAAm.

^b EGDMA.

evaluated above to study uptake of two anionic species, viz., NO₃⁻ and F⁻ as a function of time, temperature, pH, and ionic strength. The results for F⁻ uptake reveal that P_u decreases with time as the highest uptake of 50% was observed just within 10 min under neutral pH (Fig. 4) at lower temperatures (25–35°C), but it was observed to increase to 100% at the higher temperatures (40 and 45°C) (Fig. 5). In the acidic medium P_u observed was lower than observed in the neutral pH. On increasing the pH to alkaline range, 100% increase was observed (Fig. 6). P_u was also studied at five different concentrations of KF (Fig. 7). Up to 100% sorption was observed in the solutions of 0.5 mg and 0.75 mg F⁻ per liter at 40°C. Further increase in the [KF] beyond 1.0 mg/L resulted in the decrease of P_u to 48.38% in 10 min at

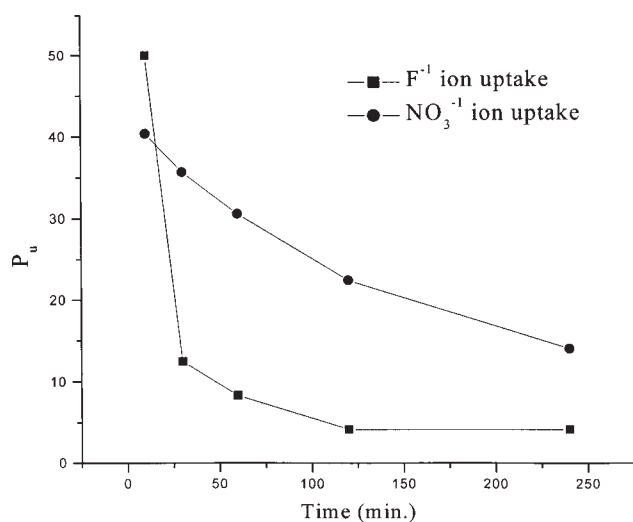


Figure 4 Sorption of F⁻ and NO₃⁻ on Fe²⁺ loaded *N,N*-MBAAM crosslinked hydrogel as function of time ([KF] = 1.0 mg/L, [KNO₃] = 20 mg/L at 25°C).

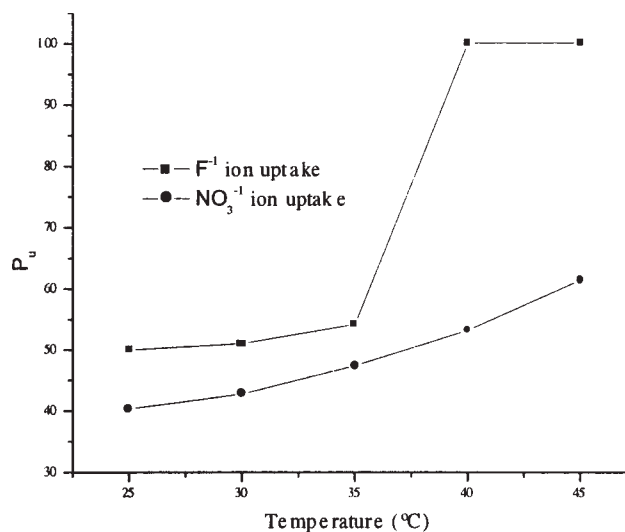


Figure 5 Sorption of F⁻ and NO₃⁻ on Fe²⁺ loaded *N,N*-MBAAM crosslinked hydrogel function of temperature ([KF] = 1.0 mg/L, [KNO₃] = 20 mg/L at 10 min).

the highest [KF] studied. Fe²⁺ loaded polymer has been observed to be less selective to the adsorption of NO₃⁻, as a maximum P_u of just 40.38% was observed in 10 min at 25°C under the neutral conditions, whereas it increased appreciably to 61.35% on increase in temperature to 45°C. P_u variation in different media followed the same order as in case of Fe²⁺, that is, 9.2 > 7.0 > 4.0. The variation of ionic strength of KNO₃ solution was also observed to affect the sorption capacity of the hydrogel. Results for the NO₃⁻ sorption as a function of anionic strength are presented in Figure 8. The high uptake of the anionic species within short time is explained by the fact that most of the sites created by the Fe²⁺ adsorption on the polymer create positive charge on

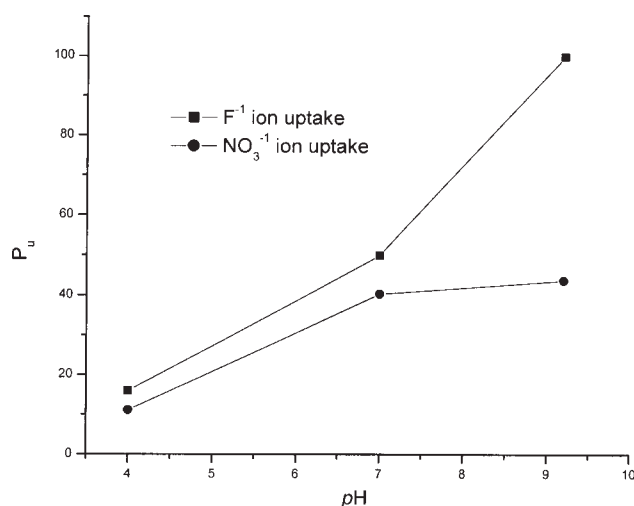


Figure 6 Sorption of F⁻ and NO₃⁻ on Fe²⁺ loaded *N,N*-MBAAM crosslinked hydrogel function of pH ([KF] = 1.0 mg/L, [KNO₃] = 20 mg/L at 25°C and 10 min).

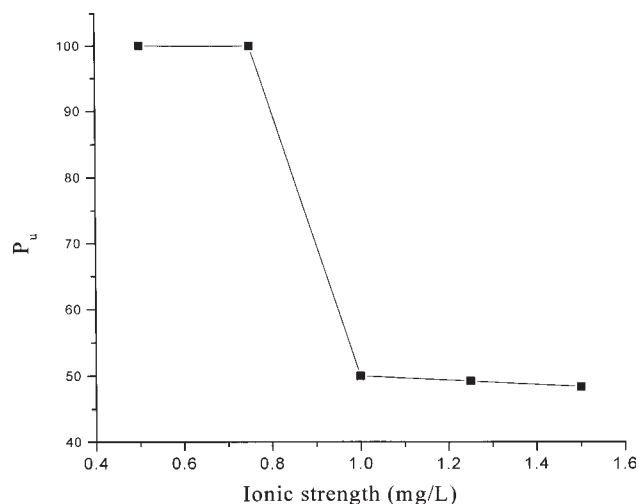


Figure 7 Sorption of F^- on Fe^{2+} loaded N,N -MBAAm crosslinked hydrogel as a function of anion strength (25°C and 10 min).

the hydrogel, which immediately partitions the anion from the solution. Same explanation holds for the effect observed on the increase of ionic strength. In case of the variation of pH, it is proposed that at low pH, the presence of acidic species suppresses the solubility of the salts and such interactions in the solution phase restrict the partitioning of anionic species to the hydrogel phase. The preferential F^- uptake by the Fe^{2+} loaded hydrogel is explained by the fact that being a smaller anion with strong negative field, F^- can approach Fe^{2+} even in bulk compared to NO_3^- . Further the strength of NO_3^- in solution is far more than the F^- . This means that the polymer has very high preference for the later anion.

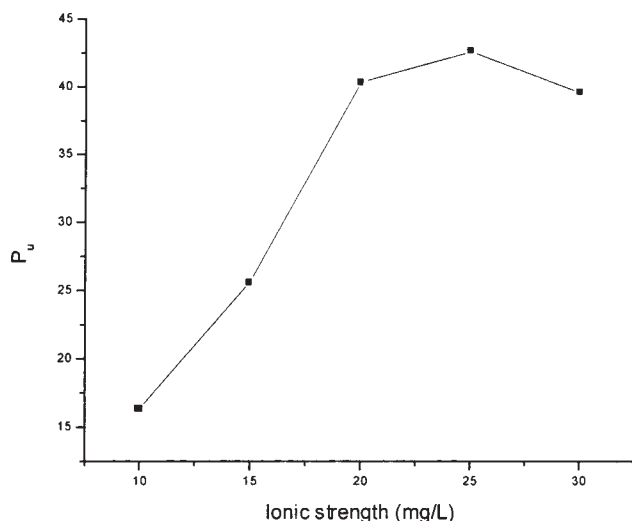


Figure 8 Sorption of NO_3^- on Fe^{2+} loaded N,N -MBAAm crosslinked hydrogel as a function of anion strength (10 min).

The Fe^{2+} ions are linked to the pendant polar groups of the polymer; hence the charge density on Fe^{2+} is significantly reduced. This makes the anchored Fe^{2+} weak acid. Hence, it has more preference for F^- compared with its own counter anion (SO_4^{2-}) and NO_3^- and the later anions will prefer to remain in aqueous solution.

CONCLUSIONS

Employing a novel approach hydrogels based on starch functionalized by simple chemical modification was used for the removal of NO_3^- and F^- ions from the aqueous systems. Using the principle of the geochemistry of F^- , the hydrogels loaded with Fe^{2+} were used as novel polymeric supports. The sorption behavior of the hydrogels is dependent both on the structural attributes of the supports as nature of the crosslinker, and also of the external environmental factors such as like time, temperature, pH and ionic strength. The functionalization of the hydrogel with Fe^{2+} changes even the mechanism of the sorption processes as evident from the behavior of the effect of temperature variation. Fe^{2+} sorption processes are exothermic, spontaneous in nature, and have positive entropy values that manifests lower order of the processes. Hydrogels sorb maximum amount of anionic species within minimum time of 10 min. The high sorption of F^- ions within short time by the Fe^{2+} -loaded network is an important result of the study. From the foregone discussion, it is clear that these polymers are cost effective green supports prepared by least energy intensive processes that can operate at eco-friendly conditions to afford very high performance. These are, thus, excellent host molecules for both cations and anions and can be effectively utilized in water treatment and ion enrichment technologies.

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