

A Novel Approach for the Removal of Fluoride from Water Using Active Hydrogels

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ABSTRACT

The principle of geochemical existence of F^- with Fe^{2+} and Al^{3+} has been used for its removal from water by using the metal ions loaded active hydrogels. Hydrogel based on the modified acrylic acid (AAc) has been prepared for use in fluoride removal from aqueous systems. AAc was reacted with dimethyl amine to obtain N, N-Dimethylacrylamide (DMAAm) that was subsequently polymerized using ammonium persulphate (APS) as initiator. The resulting poly(N, N-Dimethylacrylamide) (PDMAAm) was further copolymerized with AAc as the second component in the presence of N,N-methylenebisacrylamide (MBAAm) to get a crosslinked bifunctional hydrogel poly(N,N-DMAAm-co-AAc) [P(DMAAm-co-AAc) hydrogel] that has both amide and acid functional groups. For comparison, reference poly(acrylic acid) (PAAc hydrogel) was prepared by first polymerizing AAc with APS followed by crosslinking with MBAAm using AAc in equal weight, as the second component. The PDMAAm was characterized by nitrogen analysis, FTIR and NMR; while its hydrogel with AAc and reference PAAc hydrogel were characterized by nitrogen analysis, FTIR, SEM, and studying water uptake behavior, as a function of time, temperature, pH and in 5 % NaCl solution. The hydrogels were separately loaded with Fe^{2+} and Al^{3+} , and were used as adsorbent for the uptake of F^- as a function of external environmental factors such as temperature and pH.

Key words: active hydrogels; fluoride removal; geochemical principle; percent uptake; salt tolerance; swelling

INTRODUCTION

Polymeric gels are finding vast applications in environmental management technologies, especially in selective metal ion uptake from aqueous systems. Synthetic polymers have almost replaced inorganic adsorbents in the separation of heavy metal ions [1, 2] (Sugii, Ogawa and Hashizume 1993; Oren, Caykara, Kantoglu, and Guven 2000). Polymeric hydrogels have well-defined three-dimensional porous structures and stimuli responsive functional groups, which enable them to readily capture metal ions from wastewater and to release and clear these metal ions from the hydrogels upon changes in aqueous solution conditions (Zheng and Wang 2009). The hydrophilic character of hydrogels enable them to form a flexible network of polymer chains, that allows metal ions to quickly penetrate into the network and to form stable complexes with functional groups (Yetimoglu, Kahraman, Ercan, Akdemir, and Apohan 2007). The use profile of the reported polymeric supports is based on the selectivity for particular ions. Selectivity and efficiency in the ion uptake also depends on the crosslinking density of the polymers (Blasius, Janzen, Klein, Nguyen, Tien, Pfeiffer, Simon, Stockmayer, and Toussant 1980; Bicak, Scherrington, and Senkal 1999; Rivas, Pereria, and Reyes 1995). In general, the diffusion of ions into the polymer matrix becomes slower, as the crosslinking density increases and surface phenomenon becomes a dominant process. The polymeric supports designed as metal ions adsorbents usually have a polyelectrolyte character, hence a large number of sorption sites per macromolecule.

The presence of the ionizable carboxylic acid on the acrylic acid (AAc) based hydrogels makes these sensitive to pH and ionic strength (Ilavsky, Dusec, Jvacik, and Kopecek 1979). The use profile of poly(AAc) [PAAc] hydrogels in advanced technologies can be improved significantly by way of partial modification of the carboxylic groups by amidation and other polymer analogous reactions (Chauhan and Mahajan 2002; Chauhan, Singh, and Dhiman 2004). The copolymers of PAAc with poly(acrylamide) and poly(N,N-Dimethyl acrylamide) [P(DMAAm-co-AAc)] are reported to form chelated polymer complexes (Rivas and Morenovilloslanda 1998).

However, there are not many reports on these aspects of hydrogel synthesis. Iizawa *et al.* (Iizawa, Matsuura, Hashida, and Onohara 2003) have reported the synthesis of thermosensitive poly(N-Alkylacrylamide) gels by amidation of PAAc. Functional groups like amide those interact with water are essential for metal ion uptake (Devaky and Pillai 1993). Various methacrylamides have been synthesized in good yields directly from methacrylic acid using microwave irradiation in a solvent free environment (Goretzki, Krlej, Steffens, and Ritter 2004). There are many reports in literature on the use of hydrogels for the removal, enrichment and separation of metal ions from the aqueous solutions (Katime and Rodríguez 2001; Chauhan and Mahajan 2002; Inam, Caykara, and Kantoglu 2003; Chauhan, Chauhan, and Sen 2006; Tang, Sun, Li, Wu, and Lin 2009; Tang, Wu, Sun, Fan, Hu, and Lin 2009; Yildiz, Kemika, and Hazer 2010; Bekiari and Lianos 2010; Peng, Zhong, Ren, and Sun 2012; Wang and Liu 2013). However, to use these as anion exchangers, further functionalization is required to generate positive charge centre on the polymers, whose counter ion gets exchanged. Such derivatization reactions on polymers involve extra processes and the resultant anion adsorbents are cost-prohibitive.

In view of the above, in the present communication we report preparation and characterization of an active hydrogel for the removal of F^- as a function of different environmental factors like temperature and pH. Free F^- in water is a serious pollution hazard and it comes in water streams both due to the natural and man made processes. In geochemical formations, F^- exists with Fe^{2+} and Al^{3+} . Hence, we have used this principle of geochemistry of F^- to prepare a novel hydrogel as anion adsorbent. To prepare the hydrogel, N, N-Dimethylacrylamide (DMAAm) was prepared from AAc and dimethyl amine and the resultant amide was polymerized using ammonium persulphate (APS) as initiator. PDMAAm so obtained was further copolymerized with AAc in the presence of N,N-methylene bisacrylamide (MBAAm) to obtain a network. The network was separately loaded with Fe^{2+} and Al^{3+} to obtain active supports for F^- . The reference crosslinked poly(AAc) (PAAc hydrogel) was also studied for the F^- uptake. The method of preparation is simple, least time and energy intensive, and avoids the unnecessary derivatization reactions, as is the case with the preparation of the conventional anion exchangers. PDMAAm was characterized by nitrogen analysis, FTIR and NMR to obtain evidence of amidation reaction, while its

hydrogel was characterized by SEM, FTIR, nitrogen analysis; by water uptake studies as a function of time, temperature, pH, and in the presence of 5% NaCl. The reference PAAc hydrogel was characterized by FTIR, nitrogen analysis, SEM and water uptake studies as well.

EXPERIMENTAL

Materials

Acrylic acid, ammonium persulphate and dimethyl amine (S.D. Fine, Mumbai), N,N-methylene bisacrylamide, sodium chloride, Ferrous sulphate, aluminum sulphate, potassium fluoride, buffer tablets (pH 4.0, 7.0 and 9.2) (Merck, Schuchardt, Germany) and SPADNS reagent (M/s. Hach, US) were used as received.

Amidation reactions of acrylic acid

AAc (0.28 mol) was treated with equimolar amount of dimethyl amine at 25 °C. The resultant reaction system was treated with a solution of 0.5N NaHCO₃ and placed at low temperature till amide was separated from the solution. The amide formed was polymerized by initiation with ammonium persulfate (APS) [using 1% w/w of amide]. The reaction mixture was heated at 60 °C for 30 min in a controlled water bath to ensure complete polymerization. The reaction system was treated with minimum quantity of cold water and polymer was separated by filtration, which was followed by drying the resultant PDMAAm in vacuum oven at 40 °C.

Preparation of hydrogels

10.0 g. of dry fine powder of PDMAAm was mixed in 20.0 mL of water at 50 °C. It was followed by the addition of 10.0 g of AAc and MBAAm [2.5% by weight of the total weight of the PDMAAm and AAc] and APS (1% of the total weight of the reactants). The reaction system was heated to 60 °C for 30 min to ensure maximum crosslinking. The resulting semi-interpenetrating network (SIPN) was treated with water in a soxhlet (to extract any sol fraction), and dried at 30 °C in a vacuum oven. The extraction and drying cycles were repeated to obtain constant weight. SIPN was named as P(DMAAm-co-AAc) hydrogel, where -co- stands for the other monomer, not the copolymer. Reference hydrogel poly(AAc) [PAAc hydrogel] was prepared by following the similar procedure.

Characterization of polymers

FTIR spectra were recorded on Nicolette 5700 FTIR Spectrophotometer in KBr; NMR on Bruker AC-200 MHz using TMS as internal standard in CDCl₃. SEM was taken on Jeol JSM-6100 scanning electron microscope; and nitrogen analysis was carried on Carlo Erba EA-1108.

Water uptake studies

The known weight (0.1 g) of the hydrogel was immersed in water. Water uptake was measured gravimetrically at different time intervals from 30 min to 720 min over a temperature range from 25 °C - 45 °C in a temperature-controlled bath (accuracy ±0.1 °C). The swollen hydrogel was wiped off with a tissue paper to remove surface water and weighed immediately on Denver TR 203 (with minimum readability of 0.001 g). All the experiments were carried out in triplicate. The effect of pH on swelling was studied at optimum temperature, *i.e.*, 35 °C. The solutions of different pH were prepared by dissolving one tablet of standard buffer in 100 mL of double distilled water. Salt tolerance of the polymer was studied by using 5% NaCl solution in double distilled water as the swelling medium at 35 °C. Percent Swelling (P_s) of the hydrogels were calculated as follows:

$$P_s = \frac{\text{Weight of the swollen hydrogel} - \text{weight of the xerogel}}{\text{Weight of the xerogel}} \times 100$$

Fluoride uptake studies

The hydrogel was separately immersed for 4h at 35 °C in a known volume and concentration of metal ion solutions [FeSO₄ and Al₂(SO₄)₃], washed with water and dried. Dry sample (100 mg) of each metal ion loaded hydrogel was immersed in 50 mL of KF solution of known strengths at 35 °C and 7.0 pH. Percent uptake (P_u) of F⁻ was observed after 30 min, 60 min, 120 min and 240 min in each case using SPADNS reagent on DR 2010 spectrophotometer (M/s. Hach Co, US). The limit of [F⁻] that can be studied on this instrument is 0-2 mg/L of F⁻. The effect of time, temperature and pH on F⁻ uptake was studied only on the hydrogel loaded with Fe²⁺. P_u of the hydrogel has been calculated as per an earlier reported expression (Chauhan and Mahajan 2002).

$$\text{Percent uptake (P}_u\text{)} = \frac{\text{Total ions in the feed solution} - \text{amount of ions rejected}}{\text{Total ions in the feed solution}} \times 100$$

RESULTS AND DISCUSSION

Nitrogen analysis

The observed nitrogen (13.24%) in PDMAAm is only slightly less than the theoretically calculated value (14.14%), which provides evidence that almost complete amidation of the AAc has been achieved. Amine reacted and incorporated in amide was found to be 41.19% as compared to the theoretical value (44.44%). On the formation of P(DMAAm-co-AAc) hydrogel, % N in the sample was found to be very low (3.42%), corresponding to the lower incorporation of the amide in the network. These results also mean that as compared to the amide, poly(AAc) is incorporated more in the hydrogel.

FTIR spectroscopy

FTIR spectrum of PDMAAm has prominent peaks at 3405 cm⁻¹ (O-H and NH stretching), 1660 cm⁻¹ (C=O stretching of amide), 1122 cm⁻¹ (skeletal vibrations of N-gem dimethyl group). The spectrum of P(DMAAm-co-AAc) hydrogel has peaks at 3463 cm⁻¹ (O-H and NH stretching), 1722 cm⁻¹ (C=O stretching of -COOH), 1656 cm⁻¹ (C=O stretching of amide), and 1130 cm⁻¹ (skeletal vibrations of N-gem dimethyl group). These spectral studies provide evidence of amidation and network formation. The FTIR spectrum of PAAc hydrogel has peaks at 3471 cm⁻¹ (O-H stretching) and 1716 cm⁻¹ (C=O stretching of -COOH) (Fig. 1).

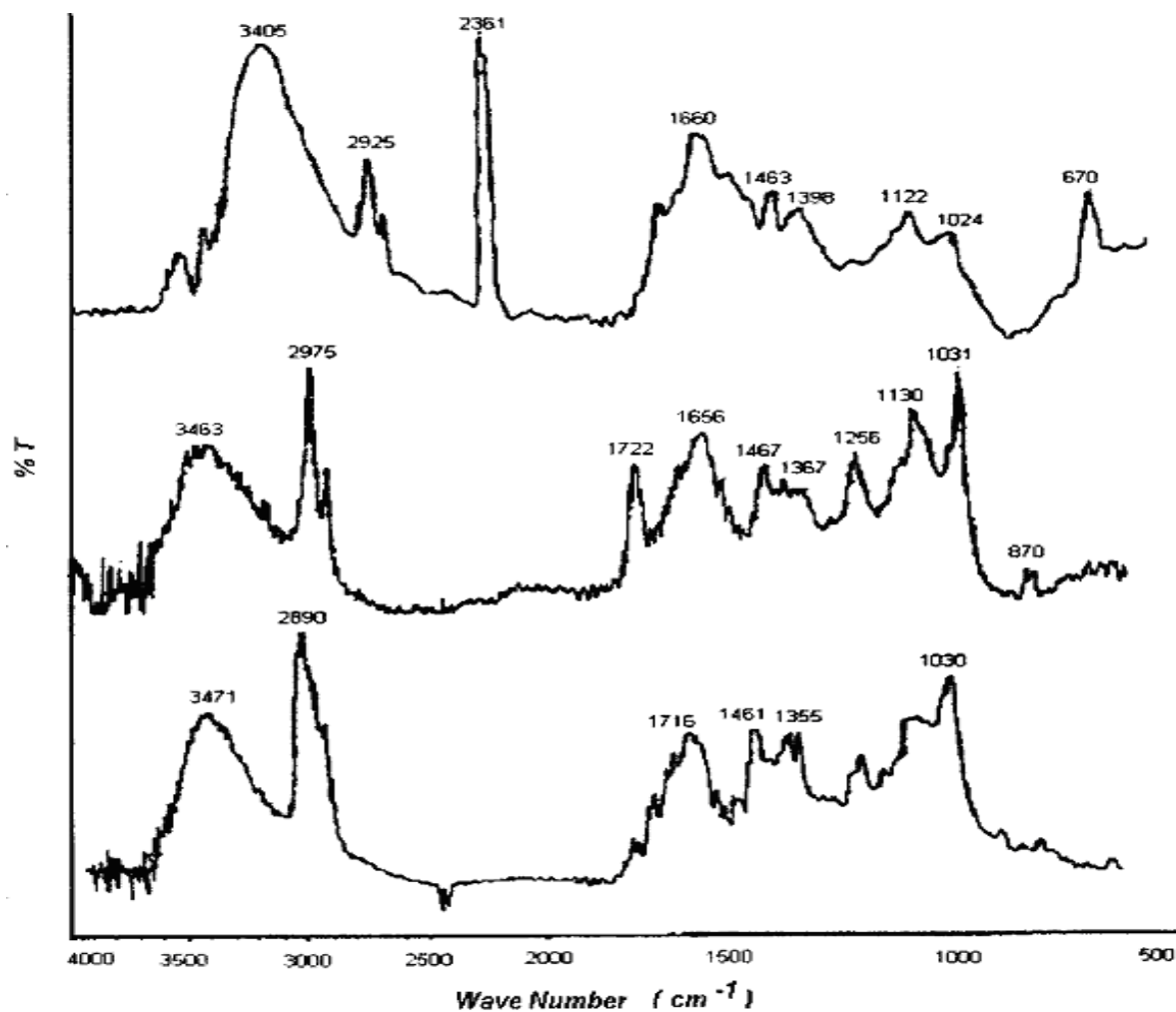
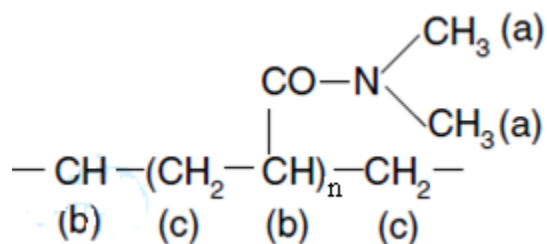


Fig. 1: FTIR spectra of PDMAAm, P(DMAAm- co-AAc) hydrogel and PAAc hydrogel

^1H NMR and ^{13}C MR spectroscopy

On the basis of NMR spectra, PDMAAm has been assigned the following structure having repeating unit - $[\text{CH}_2\text{-CH-CON}(\text{CH}_3)_2]_n$.



PDMAAm.

Evidence for the above structure are: (i) presence of substituents both from the precursor amines and monomers, (ii) absence of signal due to the expected absorption of the reacting groups and (iii) presence of new groups generated after amidation reaction. ^1H NMR spectrum has a singlet at 2.6δ , that is, equivalent to 6 H of two $-\text{CH}_3$ groups (assigned as a). A quintet at 2.9δ is equivalent to 1 H of two $-\text{CH}$ (assigned as b) (Fig. 2.1). A triplet at 1.75δ is equivalent to 2 H of two $-\text{CH}_2$ group (assigned as c). ^{13}C NMR spectrum has a quartet at 35 to 45 ppm equivalent to two $-\text{CH}_3$ groups (assigned as a), a doublet at 60-65 ppm due to $-\text{CH}$ (assigned as b), a triplet at 15 to 25 ppm due to $-\text{CH}_2$ (assigned as c) and a singlet at 180 ppm equivalent to carbon of N-alkylamide ($\text{CON}<$) (Fig. 2.2).

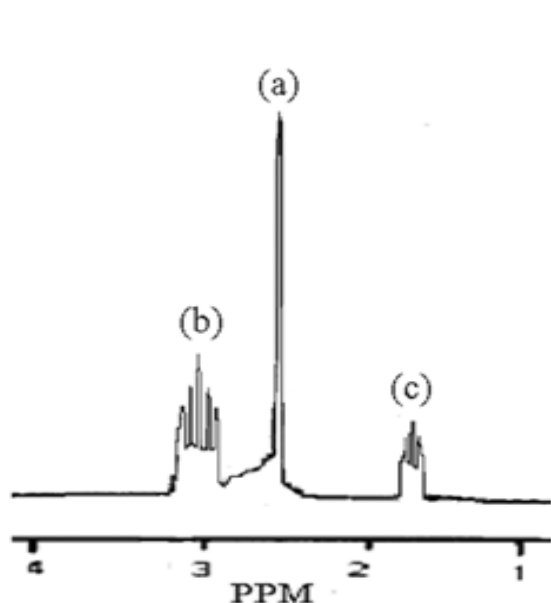


Fig. 2.1: ^1H NMR spectrum of PDMAAm

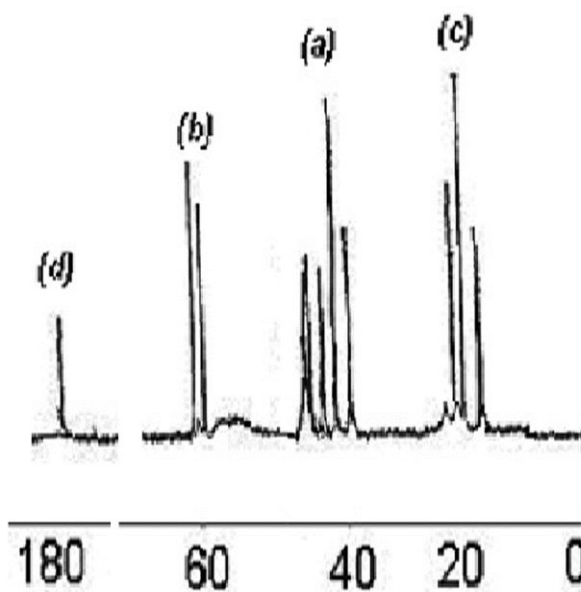
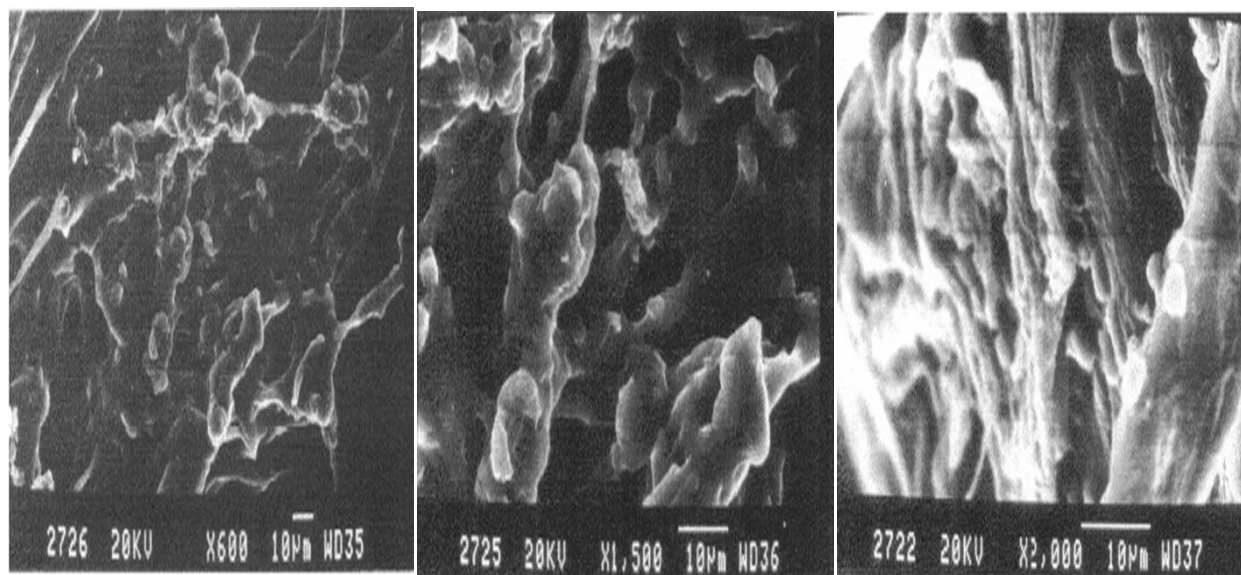


Fig. 2.2: ^{13}C NMR spectrum of PDMAAm

Scanning electron micrography

SEMs of hydrogels at different magnifications are shown in Figs. 3.1 (a) and (b). The surface morphology of the hydrogels reveals contrast in their structures. SEM of P(DMAAm-co-AAc) hydrogel shows less intense crosslinking, and pores of different sizes are visible. On the other hand, SEM of PAAc hydrogel has more intense crosslinking, and hence, smaller pores are formed [Fig. 3.1 (c)].



SEMs of (a) and (b) poly (DMAAm-*co*-AAc) hydrogel and (c) poly(AAc) hydrogel

Water uptake or swelling studies

Study of the water uptake behavior of the hydrogels is important to define its use profile in ion uptake technologies. Water transport through hydrogels is affected by a number of external factors including time, temperature and pH of the medium and many internal factors like, hydrogen bonding and polyelectrolyte character of the hydrogels. The hydrogels based on P(Acrylamide-*co*-AAc)-*cl*-MBAAm exhibit good dimensional stability and high yet reversible swelling at 60 °C (Begam, Nagpal, and Singhal 2004). In the present study, hydrogel contain both amide as well as carboxylic groups, hence, apart from the environmental factors; structural aspects are also expected to affect swelling or de-swelling of the hydrogel.

Swelling behavior as a function of time, temperature and pH

The effect of swelling time and temperature on swelling behavior of P(DMAAm-*co*-AAc) hydrogel is presented in Fig. 4.1. Swelling was studied at seven time intervals from 30 min - 720 min at five temperatures from 25 °C - 45 °C. The equilibrium swelling was observed to be temperature dependent, as it was attained at 480 min when temperature was varied from 25 °C to 30 °C, while at the higher temperatures it was attained at a shorter time interval of 240 min. P_s increased with the increase in temperature from 25 °C to 35 °C and varied only slightly from 35 °C to 40 °C. It is interesting to observe that modifications of AAc via amidation reaction

followed by network formation, increases P_s to a large extent (Chauhan 2005). The evidence of this fact has been obtained from the comparison of P_s of P(DMAAm-co-AAc) hydrogel with that of PAAc hydrogel. In case of P(DMAAm-co-AAc) hydrogel, maximum value of P_s is 8442 (at 40 °C and 480 minutes) while same for reference PAAc hydrogel is 734 (at 35 °C and 480 minutes) (Chauhan 2005). The effect of pH variation on P_s was studied at 35 °C and different time intervals. P_s increased in a sharp manner from 2347 to 3216 (30 min) and from 4904 to 8611 (480 min) with the increase in pH from 4.0 to 7.0. On the further increase in pH to alkaline range, it decreased to 2631 and 7912 (for 30 min and 480 min, respectively) (Fig. 4.2).

Swelling study (salt tolerance) of hydrogels in the presence of NaCl

A gel is said to be salt tolerant if it can retain considerable amount of water, and hence, resist deswelling in the presence of electrolytes. Hydrogels do not swell appreciably in the presence of electrolyte due to ex-osmosis, as even the swollen hydrogels loose water and shrink dramatically in the presence of salts. This property of hydrogels is significant from the technological viewpoint. The hydrogel shriveling results from the loss of hydrophilic-hydrophobic balance of the hydrogels in the presence of electrolyte salts. In the present study, the hydrogel show a small, yet significant swelling was observed (Fig.4.3). Hence, amidation reaction of AAc improves the salt tolerance of hydrogel (Chauhan 2005). The salt tolerance of P(DMAAm-co-AAc) hydrogel is almost two times higher than that of the reference PAAc hydrogel, as the maximum value of P_s obtained was 470 in the case of the former and 256 for the latter at 35 °C and 240 min. In the case of reference PAAc hydrogel, P_s increased from 612 to 734 with the increase in pH from 4 to 7, and thereafter it tends to remain constant, as the P_s value of 725 was observed at pH 9 (480 min) (Chauhan 2005). These trends in swelling behavior originate

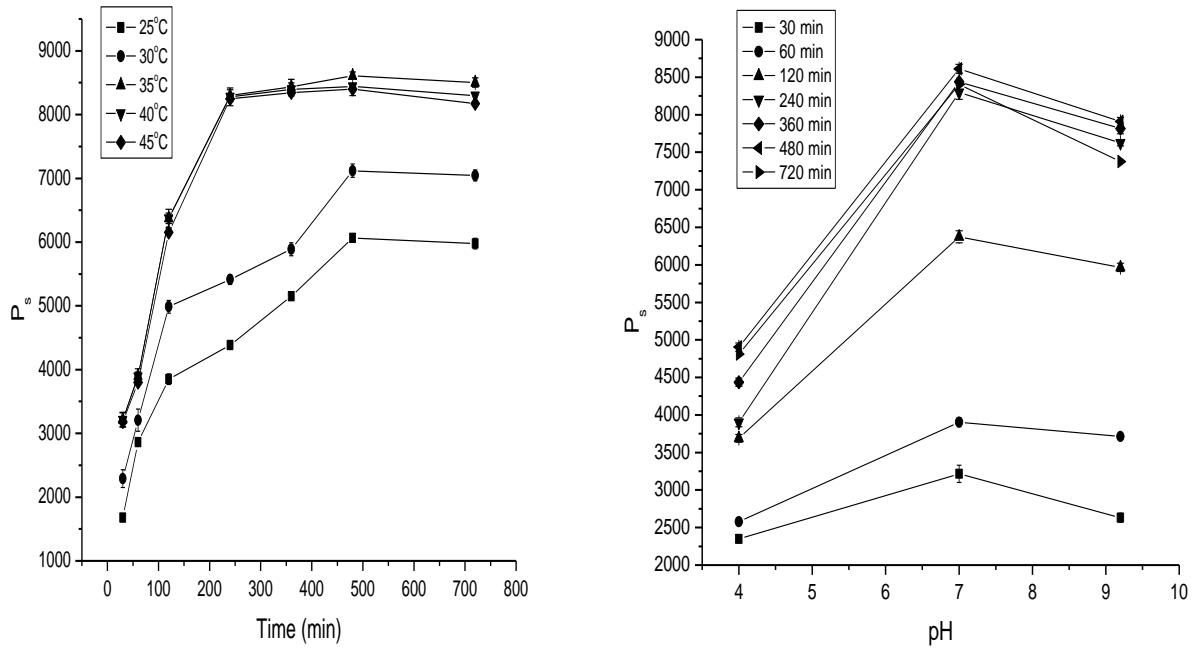


Fig. 4.1 & 4.2: P_s of poly (DMAAm- *co*-AAc) hydrogel as a function of time and pH at 35 °C

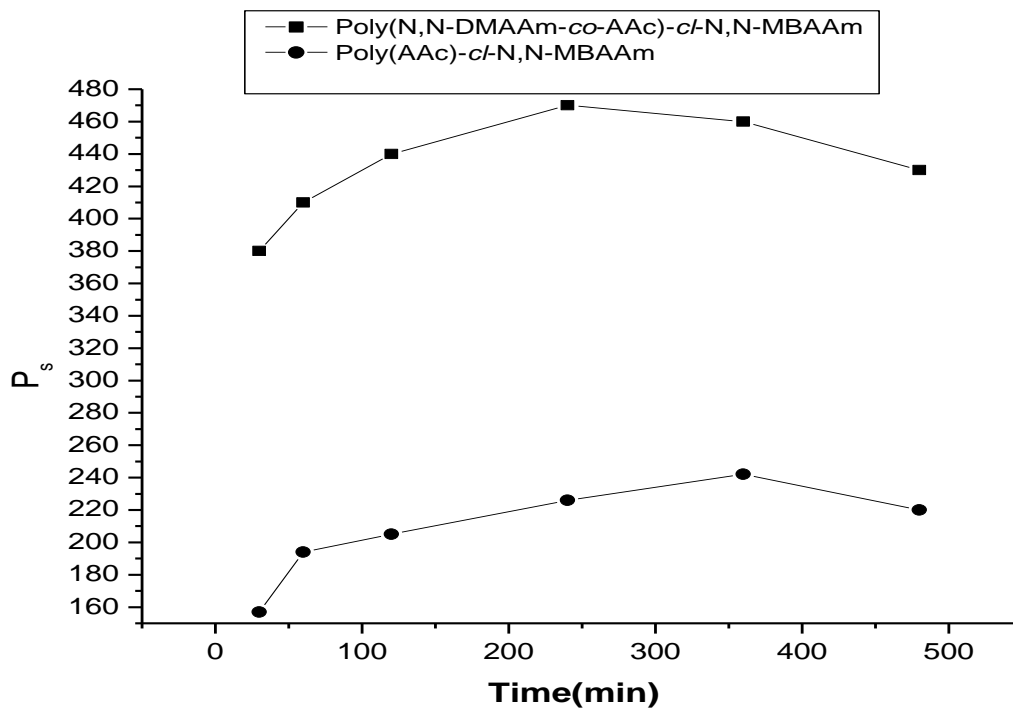


Fig. 4.3: Percent swelling of hydrogels in 5% NaCl solution as a function of time at 35°C

from the suppression of any ionized carboxylic groups at low pH and result in shriveling of the hydrogels, as strong hydrogen bonding interpolymer complexation between PAAc and PDMAAm side chains in semi dilute solution results in the formation of a transient hydrogel of the hydrogen bonded complex of PDMAAm/PAAc (Bossard, Sotiropoulou, and Staikos 2004). Such complex formation decreases the availability of the hydrogel pendant groups to form hydrogen bonds with water. In the alkaline pH (*i.e.*, 9.2 in the present case), these groups interact with the basic species of the medium again restricting the interaction of water molecules with those of the hydrogel. In other words, the expected dipole-dipole interactions of carboxylic groups and water are suppressed as the former shows preference for the basic moieties of the buffer.

Fluoride removal studies

Though the metal ion sorption has been widely reported using hydrogels, however, use of these supports, as anion exchanger is not investigated. In the present study, the hydrogel has been used for the sorption and removal of F^- ions as a function of different factors. F^- is a serious water contaminant and is often difficult to remove. Use of activated alumina and other inorganic materials are reported for its removal. However, in the present study, the basic principle of its geochemistry was used for its easy and effective removal from water. It is known that the F^- is present in the geological formations with Fe^{2+} and Al^{3+} and any disturbance of these geological formations results in leaching of F^- in the water streams. Hence, hydrogel was loaded with Fe^{2+} and Al^{3+} ions. Sorption of these ions can be in the bulk by way of partitioning; adsorption at the amide groups and possible exchange at $-CO_2H$, hence the general term sorption has been used to show the complex mechanism of metal ion uptake (Chauhan and Mahajan 2002). It is, thus, expected that the structural aspects of these polymers as crosslinking density and their water uptake behavior will affect the extent of sorption of these metal ions on polymers, which in turn will affect the F^- uptake along. Apart from these factors, the environmental factors like pH, time and temperature will also determine the quantum of F^- on the hydrogels. The SPADNS reagent method for fluoride determination involves the reaction of fluoride with a red zirconium-dye

solution. The fluoride combines with zirconium part of the dye to form a colorless complex, thus bleaching the red color in an amount proportional to the fluoride concentration.

Effect of hydrogel structure and loaded metal ions on F^- uptake: selection of the more suitable support

Hydrogels loaded with the same feed concentration of Fe^{2+} and Al^{3+} show selectivity for the F^- ions, as the extent of adsorption was different. For the hydrogels loaded with both Fe^{2+} and Al^{3+} , P_u was much higher for the P(DMAAm-co-AAc) hydrogel, as compared to the reference PAAc hydrogel. The hydrogel loaded with Fe^{2+} were observed to be more efficient adsorbents with the maximum value being 72 (Fig. 5.1), as compared 66 in the hydrogel loaded with Al^{3+} . The difference in these results is ascribed to the higher loading of Fe^{2+} on these hydrogels, hence resultant anchor sites are more in this case as compared to the other. Another reason ascribed to account for these results is more intense crosslinking of the hydrogel loaded with Al^{3+} and result is lower water uptake and lesser partitioning of the ions from the solution. P(DMAAm-co-AAc) hydrogel loaded with Fe^{2+} afforded the maximum P_u (72 % at 35 °C, 120 min and 7.0 pH), hence it was used for further studies to investigate the effect of time, temperature and pH on F^- uptake.

Effect of time on sorption of F^-

P_u of F^- on P(DMAAm-co-AAc) and PAAc hydrogels was studied at four different time intervals *i.e.* 30 min, 60 min, 120 min and 240 min. P_u increased from 30 min to 120 min and thereafter it showed a slow decrease with the further increase in the sorption time (Fig. 5.1). The results are good even at a contact time of 30 min. It is suggested that the tendency to attain equilibrium at the higher time is result of the saturation effects, as with the passage of time, the metal ion occupied sites are exhausted. In an almost similar study, Kamble *et al.* (Kamble, Jagtap, Labhsetwar, Thakare, Godfrey, Devotta, and Rayalu 2007) have reported rapid sorption of fluoride on 20% La^{3+} loaded chitosan with the attainment of the maximum uptake value just within twenty min. In another study, Zhou *et al.* (Zhou, Yu, and Shan 2004) reported the maximum uptake after a contact time of 40 min. However, in an early study we have reported the maximum uptake within the initial 10 min (Chauhan, Kumar, and Verma 2007) .

Effect of pH and temperature on sorption of F^-

P(DMAAm-co-AAc) hydrogel was used to study F^- uptake as a function of adsorption temperature and pH at four times (Fig. 5.2 for sorption time of 30 min.). At all the time intervals studied, the maximum uptake was observed at 7.0 pH. Initially, F^- uptake increased with

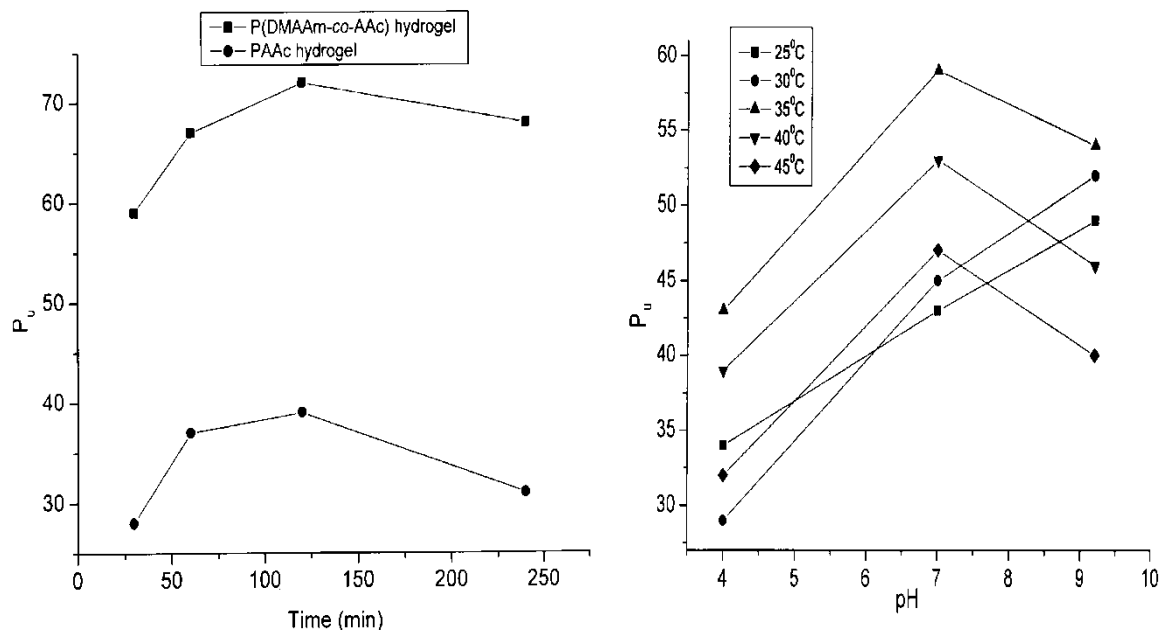


Fig. 5.1: Percent uptake of F^- ions on Fe^{2+} loaded hydrogels as a function of time (Temperature = 35°C [Fe^{2+}] = 50 mg/L) & Fig. 5.2: Percent uptake of F^- ions on Fe^{2+} loaded P(DMAAm-co-AAc) hydrogel as a function of pH (Time = 30 min, [Fe^{2+}] = 50 mg/L)

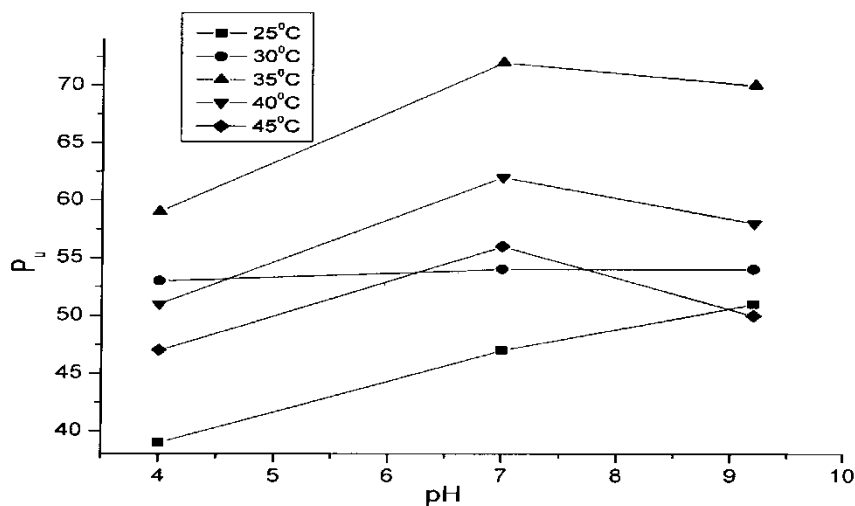


Fig. 5.3: Percent uptake of F⁻ ions on Fe²⁺ loaded P(DMAAm- co-AAc) hydrogel as a function of pH (Time = 120 min, [Fe²⁺] = 50 mg/L

temperature from 25 °C to 35 °C, and thereafter, a decrease was observed with the further increase in temperature at all pHs. This behavior can be explained on the basis of sorption-desorption equilibrium. When the temperature increased from 25 °C to 35 °C, the rate of sorption increases and maximum sorption was attained at 35 °C at all the pHs studied. Further increase in temperature accelerates the reverse process of desorption that results in the lower P_u. However, in an earlier study we have reported increasing trends with temperature up to 45 °C (Chauhan Kumar, and Verma 2007). The effect of pH variation was studied at five temperatures. At the lower temperatures (*i.e.* 25 °C and 30 °C) the adsorption showed a continuous increase with the increase in pH from 4.0 to 9.2. At the higher temperatures (*i.e.* 35 °C, 40 °C and 45 °C), however the trends were different, as P_u increased with pH from 4.0 to 7.0 and thereafter a slow decrease was observed. Similar trends in results have been reported in the earlier studies, where the maximum uptake was reported at pH 6.7 (Kamble, Jagtap, Labhsetwar, Thakare, Godfrey, Devotta, and Rayalu 2007) or 5-7pH (Zhou, Yu, and Shan 2004) with a sharp decrease followed thereafter. This shows that the hydrogel used in the present study is more stable and has a wider pH window as has afforded better results over a wider pH range. It is suggested that rather interacting with the partial ionic charges on the active hydrogels; F⁻ interacts more with the acidic moieties of the solution phase at the lower pH. The trends for the decrease in F⁻ at pH > 7 is explained by the presence of other anionic species in the medium those may compete for the active sites on the hydrogels. Further, the Fe²⁺ (anchorage for F⁻) sorption itself is an exothermic process, and these get desorbed at the higher temperature (Chauhan, Kumar, and Verma 2007).

Conclusions

A well characterized temperature and pH responsive hydrogel for use as adsorbent for fluoride removal has been reported. It follows from the forgone discussion that the hydrogel responds very quickly to small changes in its external environment and is thus a *smart or intelligent hydrogel*. The interaction of the hydrogel with water is affected by the environmental factors. Using the geochemical principle of natural occurrence of fluoride, functionalization of the hydrogel by metal ion loading makes this potential support for the removal of F⁻ from water.

The structure of the hydrogel as well as the environment of the F^- in the solution phase, both act as the determinants of F^- uptake. It can, thus, be concluded that a hydrogel support has been suitably tailored to effectively remove F^- from water by employing less energy and low time intensive clean processes. It can also be concluded that amidation and hydrogel formation results in the improvement of salt tolerance of these polymers though not significantly.

REFERENCES

1. Begam, T., A. K. Nagpal, and R. Singhal. A study on copolymeric hydrogels based on acrylamide-methacrylate and its modified vinyl-amine-containing derivative. *Designed Monomers and Polymers* 7: 311-330. 2004.
2. Bekiari, V., and P. Lianos. Poly (Sodium acrylate) hydrogels as potential pH-sensitive sorbents for the removal of model organic and inorganic pollutants from water. *Global Nest Journal*. 12: 262-269. 2010.
3. Bicak, N., D. C. Scherrington, and B. F. Senkal. Graft copolymer of acrylamide onto cellulose as mercury selective sorbent. *React Funct. Polym* 41: 69-76. 1999.
4. Blasius, E., K. P. Janzen, W. Klein, V. B. Nguyen, T. N. Tien, P. Pfeiffer, H. Simon, H. Stockmayer, and A. Toussant. Preparation, characterization and applications of ion exchangers with cyclic polyether anchor groups. *J Chromatogr* 201: 147-166. 1980.
5. Bossard, F., M. Sotiropoulou, and G. Stakes. Thickening effect in soluble hydrogen bonding interpolymer complexes. Influence of *pH* and molecular parameters. *Journal of Rheology* 48: 927-936. 2004.
6. Chauhan, G. S., S. Chauhan, K. Chauhan, and U. Sen. Synthesis and Characterization of Acrylamide and 2-Hydroxypropyl Methacrylate Hydrogels for Specialty Applications. *J Appl Polym Sci* 99: 3040-3049. 2006.
7. Chauhan, G. S., R. Kumar, and M. Verma. A study on the sorption of NO_3^- and F^- on the carboxymethylated starch-based hydrogels loaded with Fe^{2+} ions. 2007. *J Appl Polym Sci* 106, 1924-1931.
8. Chauhan, G. S., and S. Mahajan. Use of novel hydrogels based on modified celluloses and methacrylamides for separation of metal ions from water systems. *J Appl Polym Sci* 86: 667-671. 2002.

9. Chauhan, G. S., B. Singh, and S. K. Dhiman. Functionalization of poly(4-vinyl pyridine) grafted cellulose by quaternization reactions and a study on the properties of postquaternized copolymers. *J Appl Polym Sci* 91: 2454-2464. 2004.
10. Chauhan, S. Modification of acrylic acid and methacrylic acid via amidation and network formation for stimuli responsive hydrogels for specialty applications. Ph. D. Thesis, Department of Chemistry, Himachal Pradesh University, Shimla, India. 2005.
11. Devaky, K.S., and V.N.R. Pillai. Synthesis of amide and peptides using polymer-bound mixed carboxylic dithiocarbamic anhydrides. *Ind Acad Sci (Chem Sci)* 102, 521-533. 1993.
12. Goretzki, C., A. Krlej, C. Steffens, and H. Ritter. Green Polymer Chemistry: Microwave-Assisted Single-Step Synthesis of Various (Meth)acrylamides and Poly(meth)acrylamides Directly from (Meth)acrylic Acid and Amines. *Macromol Rapid Comm* 25, 513-516. 2004.
13. Ilavsky, M., K. Dusec, M. Jvacik, and J. Kopecek. Deformational, swelling, and potentiometric behavior of ionized gels of 2-hydroxyethyl methacrylate-methacrylic acid copolymers. *J Appl Polym Sci*, 23, 2073-2082. 1979
14. Inam, R., T. Caykara, and O. Kantoglu. Polarographic determination of uranyl adsorption onto poly(acrylamide-g-ethylenediaminetetraacetic acid) hydrogels in the presence of cadmium and lead. *Nucl Instrum Methods Phys Res Sect B* 208: 400-404. 2003.
15. Kamble, S. P., S. Jagtap, N. K. Labhsetwar, D. Thakare, S. Godfrey, S. Devotta, and S. S. Rayalu. Defluoridation of drinking water using chitin, chitosan and lanthanum-modified chitosan. *Chemical Engineering Journal* 129: 173-180. 2007.
16. Katime, I., and E. Rodriguez. Absorption of metal ions and swelling properties of poly(Acrylic acid-co-Itaconic acid) hydrogels. *Journal of Macromolecular Science, Part A: Pure and Applied Chemistry* 38: 543-558. 2001.
17. Iizawa, T., Y. Matsuura, K. Hashida, and Y. Onohara. Synthesis of Thermo-Sensitive Poly(*N*-alkylacrylamide) Gel by Amidation of Poly(acrylic acid) Gel. *Polymer Journal* 35: 815-818. 2003.

18. Oren, S., T. Caykara, O. Kantoglu, and O. Guven. Effect of pH, Ionic Strength, and Temperature on Uranyl Ion Adsorption by Poly(N-vinyl 2-pyrrolidone-g-tartaric Acid) Hydrogels. *J Appl Polym Sci.* 78: 2219–2226. 2000.
19. Peng, X.W., L.X. Zhong, J.L. Ren, and R.C. Sun. . Highly effective adsorption of heavy metal ions from aqueous solutions by macroporous xylan-rich hemicelluloses-based hydrogel. *J Agric Food Chem.* 60: 3909-3916. 2012
20. Rivas, B. L., H. A. Maturana, X. Ocampo, and I. M. Peric. Adsorption behavior of Cu^{2+} and UO_2^{2+} ions on crosslinked poly[2,2-bis(acrylamido) acetic acid]. *J Appl. Polym. Sci.* 58: 2201-2205. 1995.
21. Rivas, B. L., and I. Morenovilloslanda. Chelation properties of polymer complexes of poly(acrylic acid) with poly(acrylamide), and poly(acrylic acid) with poly(*N,N*-dimethylacrylamide). *Macromol Chem Phys* 199: 1153-1160. 1998.
22. Suggi,A., N. Ogawa, and H. Hashizume. Preparation and properties of macromolecular resins containing thiazole and thiazoline groups. *Talanta*, 27: 627-631. 1993.
23. Tang, Q., X. Sun, Q. Li, J. Wu, and J. Lin. Synthesis of polyacrylate/polyethylene glycol interpenetrating network hydrogel and its sorption of heavy-metal ions *Sci. Technol. Adv. Mater*, 10, 1-7. 2009.
24. Tang, Q., J. Wu, H.Sun, S.Fan, D. Hu, and J. Lin. Synthesis of polyacrylate/poly(ethylene glycol) hydrogel and its absorption properties for heavy metal ions and dye. *Polymer Composites*, 30,1183–1189. 2009.
25. Wang, J. J., and F. Liu. Enhanced adsorption of heavy metal ions onto simultaneous interpenetrating polymer network hydrogels synthesized by UV irradiation. *Polymer Bulletin.* 70: 1415-1430. 2013.
26. Yetimoglu, E. K., M. V. Kahraman, O. Ercan, Z.S. Akdemir, and N.K. Apohan. *React Funct Polym*, 67: 451–460. 2007.
27. Yildiz, U., O. F. Kemika, and B. Hazer. The removal of heavy metal ions from aqueous solutions by novel pH-sensitive hydrogels. *Journal of Hazardous Materials*, 183: 521–532. 2010.

28. Zheng, Y., and A. Wang. Evaluation of ammonium removal using a chitosan-g-poly (acrylic acid)/rectorite hydrogel composite. *J Hazard Mater*, 171: 671–677. 2009.
29. Zhou, Y., C. Yu, and Y. Shan. Adsorption of fluoride from aqueous solution on La³⁺-impregnated cross-linked gelatin. *Sep. Pur. Technol.* 36: 89-94. 2004.